The Partial Molal Volume and Compressibility of TRIS and TRIS-HCl in water and 0.725m NaCl as a function of temperature

Carmen Rodriguez*, Fen Huang and Frank J. Millero

Rosenstiel School of Marine and Atmospheric Chemistry

University of Miami

4600 Rickenbacker Causeway

Miami, FL 33149

***Corresponding author email address: crodriguez@rsmas.miami.edu.**

Abstract

The apparent molal volumes and compressibilities of TRIS and TRIS-HCl have been determined in water (5 to 45^{o}C) and 0.725m NaCl (5 to 25^{o}C). The changes in the volume (ΔV) and compressibility ($\Delta\kappa$) for the dissociation of TRIS-H^+

$$\text{TRIS-H}^+ = \text{TRIS} + \text{H}^+$$

as functions of temperature in water and 0.725m NaCl have been determined from these measurements. The values of ΔV and $\Delta\kappa$ have been used to determine the effect of pressure on the dissociation constant for TRIS-H^+ (K^P/K^0).

$$\ln(K^P/K^0) = -\Delta V/(RT)\,P + 0.5\,\Delta\kappa/(RT)\,P^2$$

These results will be useful in the calibration of pH systems making *in-situ* measurements at high pressure in seawater. In 0.725m NaCl at 5^{o}C and a pressure of 2000 bar, the dissociation constant is reduced by 29%.

KEYWORDS: Seawater pH; TRIS buffer; high pressure; dissociation constant; partial molal volume; compressibility.

1. Introduction

The absorption of atmospheric CO_2 by the world's oceans and has led to a measurable change in oceanic pH, often referred to as *ocean acidification*. To understand the change in ocean chemistry from the surface to the deep ocean, traditional methods have relied on depth-discrete seawater samples collected onboard ships, with subsequent analysis performed in laboratories at atmospheric pressure. In recent years, autonomous sensors have been developed to analyze the *in-situ* chemistry of the ocean, including measuring the pH directly (Martz et al., 2010; Bresnahan et al., 2014). The sensor technologies to vertically-profile the pH of a water-column *in-situ* are still emerging. Nevertheless, these pH sensors should contribute to our understanding of the state of oceanic pH and overall trends in *ocean acidification*. As the measurements obtained from the sensors reflect the physical conditions of the surrounding waters, their influences should be accounted for when making calculations of chemical equilibrium systems.

TRIS buffers have proved useful in calibrating pH electrodes and indicators for natural waters (Ramette et al., 1977; Dickson, 1993; Millero et. al., 1993; Clayton and Byrne, 1993; Pratt, 2014). The buffer system is typically composed of an equimolal ratio of the neutral species, TRIS, and the protonated species, TRIS-H^+, which may come in the form of a TRIS-HCl salt. The dissociation of TRIS-H^+ is maintained by equilibrium between the two species

$$\text{TRIS-H}^+ = \text{TRIS} + \text{H}^+ \qquad (1)$$

For an equimolal buffer solution, the pH can be calculated directly from the p*K* via the Henderson-Hasselbalch relationship: pH = p*K* = - log(*K*), where (*K*) is the dissociation constant for the reaction above. The temperature- and salinity-dependence of (*K*) for TRIS-H^+

dissociation in natural waters at 1 atm pressure have been characterized previously, with a precision on the order of ± 0.0004 pK units (Datta et al., 1963; Ramette et al., 1977; Dickson, 1993; DelValls and Dickson, 1998; Foti et al., 1999 reformulated by Millero, 2009, and Millero et al., 2009). The effect of pressure (P) on TRIS-H^+ dissociation has not been thoroughly examined; however it can influence a reaction through changes in the volume (V) and compressibility ($\kappa = - \partial V/\partial P$). It is possible to estimate the effect of pressure on the dissociation constant (K) of a weak acid with

$$\ln(K^P/K^0) = - \Delta V/(RT)\, P + 0.5\, \Delta\kappa/(RT)\, P^2 \qquad (2)$$

where the superscript on the dissociation constant indicates the gauge pressure (P = 0 at 1atm or 1.013 bar). T is the absolute temperature (in Kelvin), and R is the universal gas constant (83.1441 cm^3 bar mol^{-1} K^{-1}). The change in the volume (ΔV) and compressibility ($\Delta\kappa$) for the dissociation (**equation 1**) are determined by differencing the values of the products and reactants

$$\Delta V = \overline{V}^{\,0}(\mathrm{TRIS}) + \overline{V}^{\,0}(\mathrm{H^+}) - \overline{V}^{\,0}(\mathrm{TRIS\text{-}H^+}) \qquad (3)$$

$$\Delta\kappa = \overline{\kappa}^{\,0}(\mathrm{TRIS}) + \overline{\kappa}^{\,0}(\mathrm{H^+}) - \overline{\kappa}^{\,0}(\mathrm{TRIS\text{-}H^+}) \qquad (4)$$

The bar denotes the partial molal property ($\overline{V}(i) = \partial V/\partial n_i$ and $\overline{\kappa}(i) = \partial \kappa/\partial n_i$, where V and κ are the solution volume and compressibility, respectively, and n_i is a mole of species (i)). The superscript (0) indicates reference conditions of infinite dilution concentration and atmospheric pressure (1.1013 bar).

Previous studies have demonstrated the success of this method for estimating the influence of pressure on the dissociation of weak acids such as phosphoric and boric acids (Millero et al., 2010, 2012). The values of ΔV and $\Delta\kappa$ can also be determined from direct measurements of the effect of pressure on a dissociation constant. For example, Hopkins et al. (2000) directly measured the effect of pressure on the dissociation of thymol blue indicator (a reagent used in pH measurements) and derived the associated change in volume and compressibility.

There is limited data available for the change in volume (ΔV) for TRIS-H^+ dissociation in water (Neuman et al., 1973; Kitamura and Itoh, 1987; Ford et al., 2000); however, the change in volume due to pressure, or the compressibility ($\kappa = - \partial V/\partial P$), has not been determined. In this paper, we have made measurements of the density and sound speed of TRIS and TRIS-HCl to determine the infinite dilution partial molal volumes ($\bar{V}^0$) and compressibilities ($\bar{\kappa}^0$) as a function of temperature in water (5 to 45^{o}C) and in 0.725m NaCl (5 to 25^{o}C). The results have been used to estimate the effect of pressures up to 2000 bar on the dissociation of TRIS-H^+ in water and 0.725m NaCl solutions. The results found for 0.725 m NaCl solutions can be used to examine the TRIS buffer equilibrium prepared in artificial seawater (Owen and Brinkley, 1941), thus allowing for the *in situ* calibration of pH sensors in seawater at high pressure.

2. Experimental

2.1. Density

All solutes used in this study were reagent grade (>99% purity), and used without further purification. The TRIS and NaCl were from Sigma-Aldrich and the TRIS-HCl salt was from MP Biomedicals. The densities of the solutions (ρ) have been measured on an Anton Paar 5000 vibrating tube densimeter. The temperatures were maintained to ± 0.002^{o}C and measured with a Platinum thermometer embedded in the system. The densimeter was calibrated at 25^{o}C with deionized water (Millipore Super Q) and dry air and the measurements were made with a precision of ± 9 ppm. The values for the density of water (ρ_0) are taken from Kell (1975) adjusted to the 1990 temperature scale (Millero and Huang, 2009) and are embedded in the densimeter. The densities of water and 0.725m NaCl agree with the published values of Millero and Huang (2009) and Connaughton et al. (1986) to ± 7 ppm and ± 13 ppm, respectively.

Separate stock solutions of TRIS and TRIS-HCl were prepared in water and 0.725m NaCl with molalities (mol kg-H_2O^{-1}) starting near 1 molal and diluted by weight. Measurements in seawater were inhibited by the low solubilities of TRIS, which is likely a product of precipitation with calcium or magnesium. As suggested by Owen and Brinkley (1941), solutions of 0.725m NaCl can be used to represent average seawater at the same ionic strength. The densities ($\Delta\rho = \rho - \rho_0$) were examined by subtracting the density of the solvent (ρ_0 for water, or ρ_2 for 0.725m NaCl) from the solution (ρ). They were measured as a function of temperature from 5 to 45^{o}C in water, and from 5 to 25^{o}C in 0.725m NaCl. The results for $10^3\ \Delta\rho$ (g cm^{-3}) in water are given in **TABLE 1** and the results in 0.725m NaCl are given in **TABLE 2**.

2.2. Sound Speeds

Separate stock solutions of TRIS and TRIS-HCl were prepared in water and 0.725m NaCl and the sound speeds were measured as a function of temperature (5 to 45^{o}C in water; 5 to 25^{o}C in 0.725m NaCl). The sound speeds have been measured with a sing-around sound velocimeter at 2 MHz (Nusonic, Inc.) in a 250 cm^3 water-jacketed cell. The temperatures were controlled to ± 0.002^{o}C with a Thermo Scientific bath and measured with a Guildline digital Pt resistance thermometer. The velocimeter has two transducers (a sender and a receiver). The pulse repetition frequency (f, s^{-1}) was measured with a BK Precision Frequency counter. The sound speed (U, m s^{-1}) is related to the measured frequency by (Millero and Kubinski, 1975)

$$1/f = \ell/U + \tau \qquad (5)$$

where ℓ is the effective path length between the transducers and τ is the electronic delay time. The system was calibrated at each temperature with 18 MΩ ion exchange water (Millipore Super Q) using the equation for the sound speed of pure water (U_0) of Del Grosso and Mader (1972). The values of ℓ = 0.011849 ± 0.000002 m and τ = 3.465 ± 0.03E-7 s were determined at 25°C using U_0 = 1496.67 m s^{-1}. The values for the sound speeds ($\Delta U = U - U_0$) were calculated from (Millero and Kubinski, 1975)

$$U - U_0 = \ell\,(f - f_0) / [(1 - f\,\tau)\,(1 - f_0\,\tau)] \qquad (6)$$

where the pure solvent is demarcated with the subscript (U_0, f_0 for water; U_2, f_2 for 0.725m NaCl), and U is the sound speed of solution. The sound speed of 0.725m NaCl at 25°C had a value of U_2 = 1540.83 m s^{-1} which is in agreement (± 0.01 m s^{-1}) with the literature values (Millero, et al, 1987). The average precision of the sound speed measurements was ± 0.07 m s^{-1}. Results of ΔU measured in water and 0.725m NaCl are given in **TABLE 3** and **TABLE 4**, respectively. They have been used to calculate the adiabatic compressibility (β_S) of the solution

$$\beta_S = 1/(\rho\,U^2) \qquad (7)$$

It should be noted that the adiabatic compressibility (β_S) is not exactly equal to the isothermal compressibility (β_T) which requires accurate values for the expansibility ($\alpha = -\,\partial\rho/\partial T$) and heat capacity ($C_P$) that are often unavailable.

$$\beta_T = \beta_S + \alpha^2\,T/\rho\,Cp \qquad (8)$$

Ultimately, values of β_T or β_S will be used to determine the partial molal compressibilities at infinite dilution ($\overline{\kappa}^0$). Desnoyers and Phillips (1971) have derived a relationship to convert between the isothermal ($\overline{\kappa}_T$) and adiabatic ($\overline{\kappa}_S$) partial molal compressibilities at 25°C

$$10^4\ \overline{\kappa}_T^{\,0} = 10^4\ \overline{\kappa}_S^{\,0} + 36.79\ \overline{E}^{\,0} - (1.135 \times 10^{-3})\ \overline{C_P}^{\,0} \qquad (9)$$

where $\overline{E}^{\,0}$ is the partial molal expansibility ($\overline{E}(i) = \partial\alpha/\partial n_i$) at infinite dilution. The difference between the values of $\overline{\kappa}_T$ and $\overline{\kappa}_S$ for various solutes in water has been shown to be on the order of 10% or less (Desnoyers and Phillips, 1971; Mathieson and Conway, 1974; Millero and Huang, 2011). Since reliable values for the expansibility (α) and heat capacity (Cp) of TRIS and TRIS-HCl are not available, we have assumed equivalency between β_S and β_T, and hereafter leave off the subscript (s). The adiabatic compressibility at 25°C for water (β_0) was measured as 44.775 x 10^{-6} bar^{-1} and the value for 0.725m NaCl was measured as β_2 = 41.061 x 10^{-6} bar^{-1}. These are within ± 0.001 and 0.002 x 10^{-6} bar^{-1}, respectively, of the literature values (Kell, 1975; Millero et al., 1980).

3. Results

The apparent molal volumes (${}^{\phi}V$) and apparent molal adiabatic compressibilities (${}^{\phi}\kappa$) of TRIS and TRIS-HCl in water have been determined from the density (ρ) and compressibility (β) measurements

$${}^{\phi}V(i) = 1000(\rho_0 - \rho)/(\rho\,\rho_0\, m_i) + M_i/\rho \qquad (10)$$

$${}^{\phi}\kappa(i) = 1000(\beta\,\rho_0 - \beta_0\,\rho)/(\rho\,\rho_0\, m_i) + \beta\, M_i/\rho \qquad (11)$$

The m_i is the molality and M_i the molecular weight of solute (i) (M_i = 121.14 g mol^{-1} for TRIS and M_i = 157.6 g mol^{-1} for TRIS-HCl) and the other terms have been defined previously. Since we are interested in measurements relative to pure water, the apparent molal volumes and compressibilities in 0.725m NaCl have been determined from

$$^{\phi}V(i) = 1000(\rho_2 - \rho)/(\rho\,\rho_2\,m_3) + M_3/\rho + m_2\,M_2/m_3\,(1/\rho - 1/\rho_2) \qquad (12)$$

$$^{\phi}\kappa(i) = 1000(\beta\,\rho_2 - \beta_2\,\rho)/(\rho\,\rho_2\,m_3) + \beta\,M_3/\rho + m_2\,M_2/m_3\,(\beta/\rho - \beta_2/\rho_2) \qquad (13)$$

Where ρ and β are the density and (adiabatic) compressibility, respectively, of the mixture; the subscript (2) denotes the solvent (0.725m NaCl); and the subscript (3) denotes the solute (TRIS or TRIS-HCl). For 0.725m NaCl, m_2 = 0.725 mol kg-H_2O^{-1} and M_2 = 54.882 g mol^{-1}. The apparent molal volumes and compressibilities were measured with an average precision of ± 0.01 cm^3 mol^{-1} and ± 0.19 x 10^{-4} cm^3 mol^{-1} bar^{-1}, respectively.

The results for $^{\phi}V(i)$ and $^{\phi}\kappa(i)$ x 10^4 calculated in water and 0.725m NaCl are given in **TABLES 1-4**. The apparent molal compressibilities of TRIS and TRIS-HCl in water are shown as a function of molality and temperature in **FIGURE 1.** In general, the apparent molal properties are positively-correlated with temperature and concentration. The results of $^{\phi}V(i)$ and $^{\phi}\kappa(i)$ measured at 25^{o}C are shown as a function of molality in **FIGURE 2**. The poorer fits as $m \rightarrow 0$ mol kg-H_2O^{-1} are likely due to the greater uncertainty in the measurements of the densities and sound speeds relative to pure water in dilute solutions. At a given temperature, the apparent molal volumes display stronger concentration-dependence in 0.725m NaCl solutions than in H_2O: at high solute concentration, values of $^{\phi}V(i)$ in 0.725m NaCl are higher than in water; in dilute solutions, values of $^{\phi}V(i)$ approach lower values in 0.725m NaCl than in pure water. The apparent molal compressibilities for both salts are offset to more positive values in 0.725m NaCl versus water.

4. Data Treatment

4.1. Fitting Equations

Values for the apparent molal volume and compressibility of TRIS-HCl in water have been fitted to the Pitzer model. The Pitzer equations (1991) are ideal for representing the properties of electrolytes in solutions because they can account for the potential contributions of various ionic interactions. When the solution involves a single electrolyte dissolved in water, the model takes a simplified form

$$^{\phi}X_{MY} = \overline{X}^{0}_{MY} + \nu|Z_M Z_Y|\, A_X/(2b) \ln(1 + bI^{1/2}) + 2RTm\, \nu_M \nu_Y [\beta_{MY}^{(0)X} + \beta_{MY}^{(1)X} g(\alpha) + m C_{MY}^{X}] \quad (14)$$

Where, $X = V$ or κ. The bar represents the partial molal property, the superscript zero denotes the infinite dilution value in water (note, $\overline{V}^{0} = {}^{\phi}V^{0}$), and $\beta^{(0)X}$, $\beta^{(1)X}$, and C^{X} are adjustable Pitzer ionic interaction parameters. The values of $\nu = \nu_M + \nu_Y$ are the number of ions M or Y with charge Z_M and Z_Y (M = TRIS-H^+; Y = Cl^-), b is a parameter set to 1.2 kg$^{1/2}$ mol$^{-1/2}$, and I is the ionic strength. The value of $g(\alpha)$ is given by

$$g(\alpha) = 2/\alpha^2 [1 - (1 + \alpha) \exp(-\alpha)] \quad (15)$$

where $\alpha = 2\, I^{1/2}$.

Values for the Debye-Huckel limiting slopes, A_V and $A_{\kappa,S}$, are taken from the equations of Pierrot and Millero (2000) and Rodriguez and Millero (2013), respectively, as a function of temperature (t, ^{o}C)

$$A_V\ (\mathrm{cm}^3\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-3/2}) = 1.50619 + 0.0130073\ t + 4.8307\mathrm{E}{-5}\ t^2 + 8.95087\mathrm{E}{-7}\ t^3 - 3.7279\mathrm{E}{-9}\ t^4 + 2.3942\mathrm{E}{-11}\ t^5 \quad (16)$$

$$10^4\ A_{\kappa,s}\ (\mathrm{cm}^3\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-3/2}\ \mathrm{bar}^{-1}) = -\ 2.187 - 0.105314\ t + 1.46994\mathrm{E}{-03}\ t^2 - 7.82165\mathrm{E}{-05}\ t^3 + 1.70244\mathrm{E}{-06}\ t^4 - 2.253236\mathrm{E}{-08}\ t^5 + 1.51313\mathrm{E}{-10}\ t^6 - 4.1478\mathrm{E}{-13}\ t^7 \quad (17)$$

Each adjustable parameter, $Y^X = \overline{X}^{\,0}$, $\beta^{(0)X}$, $\beta^{(1)X}$, and C^X, for TRIS-HCl in water has been fitted to a polynomial function of absolute temperature (T, in Kelvins) with

$$Y^X = \sum_j a_j\ (T - T_R)^j \quad (18)$$

Where j is an integer (j = 0, 1, 2, 3), $X = V$ or κ; and T_R = 298.15K is the reference temperature. The coefficients and standard errors of the fits are given in **TABLE 5**.

Values for the apparent molal volumes and compressibilities of TRIS-HCl in 0.725m NaCl, TRIS in water, and TRIS in 0.725m NaCl have been fitted to functions of the molality with

TRIS-HCl in 0.725m NaCl: $$^{\phi}X(i) = \overline{X}^{\,0}(i) + A_j\, m_i^{1/2} + B_j\, m_i \quad (19)$$

TRIS in water and 0.725m NaCl: $$^{\phi}X(i) = \overline{X}^{\,0}(i) + B_j\, m_i + C_j\, m_i^2 \quad (20)$$

where $X(i) = V(i)$ or $\kappa(i)$, the bar represents the partial molal property, and the superscript zero denotes the infinite dilution value in water or 0.725m NaCl. The values of $Y^X = \overline{X}^{\,0}$, A_j, B_j, or C_j

have been fitted to polynomial functions of absolute temperature as in **equation 18**. The standard errors and coefficients for the fits of TRIS-HCl in 0.725m NaCl are given in **TABLE 6**, and those for TRIS in water and 0.725m NaCl are given in **TABLE 7**.

4.2. Infinite Dilution Values

The infinite dilution partial molal volumes ($\bar{V}^0$) and compressibilities ($\bar{\kappa}^0$) have been determined by extrapolating **equations 14**, **19**, and **20** to m_i = 0 mol kg-H_2O^{-1}. The results for the values of $\bar{V}^0$ and $\bar{\kappa}^0$ are given as a function of temperature in **TABLE 8**. The values of $\bar{V}^0$ are lower in 0.725m NaCl solutions than in pure water, whereas the values of $\bar{\kappa}^0$ are more positive in 0.725m NaCl solutions than in water. The partial molal volumes and compressibilities increase with temperature, which suggests greater dehydration as temperature is increased (Ward and Millero, 1974).

5. Effect of Pressure on Acid Dissociation

Values for the infinite dilution partial molal volumes ($\bar{V}^0$) and adiabatic compressibilities ($\bar{\kappa}^0$) of TRIS and TRIS-HCl have been used to determine the change in the volume (ΔV) and compressibility ($\Delta\kappa$) from the dissociation of TRIS-H^+ using **equations 3 & 4**. The partial molal property for the protonated species, $\bar{X}^0$(TRIS-H^+), where $\bar{X}^0 = \bar{V}^0$ or $\bar{\kappa}^0$, was determined by subtracting the value for chloride (Cl^-) from the value for TRIS-HCl

$$\bar{X}^0(\text{TRIS-H}^+) = \bar{X}^0(\text{TRIS-HCl}) - \bar{X}^0(\text{Cl}^-) \qquad (21)$$

Values for $\bar{X}^0(Cl^-)$ in water were calculated from the equations of Hershey et al. (1984); and values for $\bar{X}^0(Cl^-)$ in 0.725m NaCl were calculated from the equations of Millero (1983).

It has been suggested that the change in volume for a reaction (ΔV) is correlated with the charge on the reactant (Kitamura and Itoh, 1987). As the TRIS buffer reaction involves a single proton exchange, the value of ΔV should be minimal. Gayána et al. (2013) recently compiled literature values of ΔV for the dissociation of TRIS-H^+ in water at 25°C. Our result of $\Delta V = 4.38$ $cm^3\ mol^{-1}$ at 25°C is in agreement with the average literature value of $\Delta V \sim 4\ cm^3\ mol^{-1}$. The results for ΔV and $\Delta\kappa$ in water and 0.725m NaCl at each temperature have been tabulated in **TABLE 9**. They have been fitted to functions of temperature (t, °C)

$$\Delta V\ (cm^3\ mol^{-1};\ \text{in water}) = 4.074 - 8.066E\text{-}02\ t + 5.474E\text{-}03\ t^2 - 7.04E\text{-}05\ t^3 \quad (22)$$

$$\Delta\kappa\ (cm^3\ mol^{-1}\ bar^{-1};\ \text{in water}) = 17.66 - 2.98E\text{-}01\ t + 1.257E\text{-}02\ t^2 - 1.037E\text{-}04\ t^3 \quad (23)$$

$$\Delta V\ (cm^3\ mol^{-1};\ \text{in 0.725m NaCl}) = 4.872 + 0.033\ t - 1.6E\text{-}04\ t^2 \quad (24)$$

$$\Delta\kappa\ (cm^3\ mol^{-1}\ bar^{-1};\ \text{in 0.725m NaCl}) = 9.24 + 0.547\ t - 0.0026\ t^2 \quad (25)$$

The effect of pressure on the dissociation constant (K^P) in water and 0.725m NaCl has been estimated to 2000 bar from the values of ΔV and $\Delta\kappa$ using **equation 2**. Because ΔV is positive, pressure acts to reverse the dissociation and the value of K^P is reduced. The results for the estimation of K^P/K^0 in water and 0.725m NaCl as a function of temperature are given in **TABLE 10**. The percent reduction in the dissociation constant has been calculated (% reduction $= 100 \times [1 - K^P/K^0]$) and is shown as a function of pressure at 5 and 25°C in **FIGURE 3**. Pressure is estimated to reduce the dissociation reaction by up to 29% in 0.725m NaCl at 5°C and 2000 bar. This is equivalent to an increase of + 0.15 in the pK for TRIS-H^+ dissociation ($pK = -\log K$), and is significant in terms of the precision of the reference equations based on temperature and molality alone (Ramette et al., 1977; DelValls and Dickson, 1998; Foti et al., 1999; Millero et al., 2009).

When measurements of the sound speeds are unavailable, the effect of pressure on the dissociation constant may be estimated with the relationship given in **equation 2** and the values for ΔV only. In **FIGURE 4**, the estimated reduction in K^P by either including or omitting the compressibility values in 0.725m NaCl at 25°C has been plotted and shows that the change in compressibility becomes significant starting at pressures ~ 600 bar. At high pressures, neglecting the compressibility change leads to an overestimation of the effect of pressure on the dissociation constant.

6. Conclusions

Buffers such as TRIS/TRIS-HCl are often selected in biochemical and chemical studies because they are expected to resist the influence of pressure. In this study, the changes in volume and compressibility from the dissociation of TRIS-H^+ at atmospheric pressure have been measured to estimate the effect of pressure on the equilibrium state. The results show that high pressures can significantly reduce the dissociation equilibrium (29% reduction in K determined at 2000 bar in 0.725m NaCl). These measurements are relevant to the conditions of the upper 2 km of the ocean in which *in-situ* pH sensors can be deployed. New equations have been derived to account for the influence of pressure on the dissociation constant and should be used in conjunction with the existing equations valid at atmospheric pressure to better constrain the equilibrium of the TRIS buffer system. These equations will aid in the direct calibration of *in-situ* pH sensors at high pressures in natural waters. Direct pressure measurements on the dissociation constant of TRIS-H^+ in water and 0.725m NaCl would be useful in validating these estimations.

Acknowledgement. The authors wish to thank the oceanographic section of the National Science Foundation and the National Oceanic and Atmospheric Administration for supporting our Marine Physical Chemical Studies. In addition the authors would like to thank two anonymous reviewers for their helpful comments.

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Table 1. The density ($\Delta\rho = \rho - \rho_0$) and apparent molal volumes ($^{\phi}V$) of TRIS and TRIS-HCl in water.

TRIS				TRIS-HCl			
Temp. (^{o}C)	m (mol kg^{-1})	10^3 $\Delta\rho^a$ (g cm^{-3})	$^{\phi}V$ (cm^3 mol^{-1})	Temp. (^{o}C)	m (mol kg^{-1})	10^3 $\Delta\rho^b$ (g cm^{-3})	$^{\phi}V$ (cm^3 mol^{-1})
5	0.0459	1.449	89.42	5	0.0270	1.499	101.89
5	0.1340	4.165	89.68	5	0.0997	5.335	103.55
5	0.2875	8.799	89.75	5	0.1501	7.940	103.87
5	0.3898	11.796	89.82	5	0.2542	13.190	104.33
5	0.5741	17.000	90.00	5	0.4108	20.727	104.97
5	0.6504	19.093	90.06	5	0.5981	29.377	105.39
5	0.9253	26.470	90.15	5	0.6942	33.668	105.55
5	1.1282	31.714	90.17	5	0.7889	37.838	105.64
5	1.2012	33.587	90.15	5	1.0076	47.094	105.87
5	1.4945	40.965	90.04	5	1.1411	52.588	105.94
15	0.0459	1.419	90.13	15	0.0270	1.466	103.16
15	0.1340	4.101	90.22	15	0.0997	5.230	104.65
15	0.2875	8.595	90.52	15	0.1501	7.783	104.98
15	0.3898	11.492	90.67	15	0.2542	12.925	105.43
15	0.5741	16.652	90.68	15	0.4108	20.371	105.91
15	0.6504	18.704	90.74	15	0.5981	28.932	106.20
15	0.9253	25.953	90.79	15	0.6942	33.144	106.38
15	1.1282	31.104	90.80	15	0.7889	37.239	106.48
15	1.2012	32.941	90.78	15	1.0076	46.384	106.67
15	1.4945	40.141	90.70	15	1.1411	51.774	106.76
25	0.0318	0.976	90.53	25	0.0270	1.457	103.59
25	0.0459	1.405	90.56	25	0.0484	2.564	104.45
25	0.0598	1.828	90.58	25	0.0827	4.347	104.74
25	0.0982	2.984	90.67	25	0.0997	5.209	104.97
25	0.1340	4.048	90.74	25	0.1267	6.579	105.13
25	0.1543	4.650	90.77	25	0.1501	7.752	105.29
25	0.2451	7.297	90.89	25	0.2034	10.391	105.58
25	0.2875	8.514	90.94	25	0.2542	12.875	105.74
25	0.3297	9.710	90.99	25	0.3342	16.698	106.03
25	0.3898	11.404	91.03	25	0.4108	20.293	106.22
25	0.4397	12.791	91.07	25	0.4590	22.502	106.35
25	0.5741	16.458	91.16	25	0.5981	28.763	106.61
25	0.5884	16.840	91.17	25	0.6482	30.943	106.73
25	0.6504	18.500	91.19	25	0.6942	32.967	106.77
25	0.8300	23.202	91.26	25	0.7889	37.021	106.89

25	0.9253	25.654	91.26	25	0.9007	41.652	107.07
25	1.1282	30.757	91.26	25	1.0076	46.093	107.10
25	1.1338	30.883	91.27	25	1.0977	49.643	107.23
25	1.2012	32.561	91.25	25	1.1411	51.458	107.17
25	1.4945	39.665	91.17	35	0.0270	1.448	104.09
35	0.0445	1.336	91.34	35	0.0997	5.200	105.22
35	0.0859	2.565	91.40	35	0.1501	7.758	105.41
35	0.1246	3.705	91.42	35	0.2542	12.923	105.71
35	0.2280	6.702	91.50	35	0.4108	20.383	106.16
35	0.3764	10.867	91.65	35	0.5981	28.890	106.56
35	0.4620	13.215	91.70	35	0.6942	33.185	106.61
35	0.6292	17.674	91.81	35	0.7889	37.249	106.76
35	0.8056	22.247	91.87	35	1.0076	46.543	106.80
35	0.9881	26.843	91.90	35	1.1411	52.136	106.71
35	1.1294	30.307	91.91	45	0.0270	1.450	104.20
45	0.0445	1.327	91.78	45	0.0997	5.197	105.46
45	0.0859	2.546	91.86	45	0.1501	7.728	105.82
45	0.1246	3.673	91.93	45	0.2542	12.866	106.15
45	0.2280	6.631	92.06	45	0.4108	20.273	106.65
45	0.3764	10.763	92.18	45	0.5981	28.820	106.90
45	0.4620	13.101	92.20	45	0.6942	33.092	106.97
45	0.6292	17.482	92.38	45	0.7889	37.155	107.11
45	0.8056	22.059	92.36	45	1.0076	46.434	107.14
45	0.9881	26.628	92.37	45	1.1411	52.014	107.05
45	1.1294	30.206	92.25				

a. Measured values of ρ_0 at each temperature: 5°C: ρ_0 = 0.999984 g cm^{-3}; 15°C: ρ_0 = 0.999100 g cm^{-3}; 25°C: ρ_0 = 0.997036 g cm^{-3}; 35°C: ρ_0 = 0.993997 g cm^{-3}; 45°C: ρ_0 = 0.990151 g cm^{-3}.

b. Measured values of ρ_0 at each temperature: 5°C: ρ_0 = 0.999994 g cm^{-3}; 15°C: ρ_0 = 0.999114 g cm^{-3}; 25°C: ρ_0 = 0.997045 g cm^{-3}; 35°C: ρ_0 = 0.994003 g cm^{-3}; 45°C: ρ_0 = 0.990159 g cm^{-3}.

Table 2. The density ($\Delta\rho = \rho - \rho_2$) and apparent molal volumes ($^{\phi}V$) of TRIS and TRIS-HCl in 0.725m NaCl.

TRIS				TRIS-HCl			
Temp.	*m*	$10^3\ \Delta\rho^a$	$^{\phi}V$	Temp.	*m*	$10^3\ \Delta\rho^b$	$^{\phi}V$
(°C)	(mol kg^{-1})	(g cm^{-3})	(cm^3 mol^{-1})	(°C)	(mol kg^{-1})	(g cm^{-3})	(cm^3 mol^{-1})
5	0.0820	2.404	88.60	5	0.0533	2.693	103.11
5	0.1209	3.515	88.75	5	0.1177	5.831	103.78
5	0.1901	5.464	88.91	5	0.1570	7.689	104.11
5	0.3443	9.622	89.33	5	0.2091	10.107	104.51
5	0.4564	12.484	89.66	5	0.3939	18.181	105.81
5	0.5709	15.302	89.95	5	0.5877	26.132	106.63
5	0.7147	18.655	90.34	5	0.6455	28.389	106.87
5	0.9103	23.116	90.64	5	0.8265	35.198	107.51
5	1.1747	28.800	90.99	15	0.0533	2.636	104.24
15	0.0820	2.363	89.18	15	0.1177	5.731	104.70
15	0.1209	3.455	89.33	15	0.1570	7.559	105.01
15	0.1901	5.349	89.60	15	0.2091	9.956	105.31
15	0.3443	9.388	90.10	15	0.3939	18.022	106.30
15	0.4564	12.191	90.40	15	0.5877	25.913	107.10
15	0.5709	14.965	90.65	15	0.6455	28.185	107.28
15	0.7147	18.317	90.92	15	0.8265	35.003	107.84
15	0.9103	22.683	91.23	25	0.0428	2.124	104.23
15	1.1747	28.284	91.55	25	0.0533	2.633	104.43
25	0.0473	1.372	89.24	25	0.0736	3.614	104.62
25	0.0814	2.340	89.41	25	0.1177	5.712	105.00
25	0.0820	2.353	89.45	25	0.1284	6.208	105.10
25	0.1209	3.440	89.60	25	0.1570	7.540	105.28
25	0.1442	4.076	89.72	25	0.1845	8.807	105.45
25	0.1901	5.328	89.87	25	0.2091	9.924	105.61
25	0.2377	6.584	90.07	25	0.2695	12.619	105.95
25	0.3443	9.349	90.37	25	0.3439	15.848	106.34
25	0.3718	10.042	90.44	25	0.3939	17.964	106.60
25	0.4564	12.137	90.67	25	0.4752	21.369	106.87
25	0.5549	14.529	90.86	25	0.5760	25.420	107.26
25	0.5709	14.887	90.94	25	0.5877	25.825	107.41
25	0.7147	18.214	91.23	25	0.6455	28.071	107.61
25	0.7207	18.405	91.15	25	0.8073	34.277	107.97
25	0.9103	22.553	91.54	25	0.8265	34.859	108.18
25	0.9645	23.806	91.51	25	1.1828	47.605	108.72
25	1.1747	28.136	91.85				

25	1.2242	29.293	91.76
25	1.4833	34.567	91.90

a. Measured values of ρ_2 at each temperature: 5°C: ρ_2 = 1.029811 g cm^{-3}; 15°C: ρ_2 = 1.028331 g cm^{-3}; 25°C: ρ_2 = 1.025828 g cm^{-3}.

b. Measured values of ρ_2 at each temperature: 5°C: ρ_2 = 1.029798 g cm^{-3}; 15°C: ρ_2 = 1.028319 g cm^{-3}; 25°C: ρ_2 = 1.025802 g cm^{-3}.

Table 3. The sound speed ($\Delta U = U\text{-}U_0$) and apparent molal compressibilities ($^{\phi}\kappa$) of TRIS and TRIS-HCl in water.[a]

TRIS				TRIS-HCl			
Temp. (°C)	***m*** (mol kg^{-1})	**ΔU** (m s^{-1})	**$10^4\,{}^{\phi}\kappa$** (cm^3 mol^{-1} bar^{-1})	**Temp.** (°C)	***m*** (mol kg^{-1})	**ΔU** (m s^{-1})	**$10^4\,{}^{\phi}\kappa$** (cm^3 mol^{-1} bar^{-1})
5	0.0410	1.35	-12.25	5	0.0244	2.35	-44.31
5	0.0703	2.42	-12.02	5	0.0403	3.90	-43.39
5	0.1193	4.13	-11.72	5	0.0683	6.57	-42.09
5	0.1979	6.97	-11.68	5	0.1144	10.88	-40.60
5	0.3254	11.59	-11.23	5	0.2003	19.11	-39.89
5	0.5144	18.94	-10.99	5	0.3592	33.72	-37.67
5	0.7740	29.95	-10.31	5	0.5732	52.62	-35.05
5	0.9999	44.58	-9.93	5	0.8447	75.70	-32.42
5	1.3019	57.24	-9.42	5	1.0732	94.48	-30.64
15	0.0658	3.54	-6.77	15	0.0343	3.03	-33.27
15	0.1203	6.47	-6.53	15	0.0592	5.22	-32.31
15	0.1986	10.65	-6.26	15	0.1003	8.96	-32.39
15	0.3418	18.08	-5.66	15	0.1735	15.11	-30.34
15	0.5459	28.63	-5.25	15	0.2661	22.93	-29.19
15	0.7859	40.66	-4.70	15	0.3961	33.72	-27.89
15	1.1240	57.18	-4.13	15	0.5837	48.79	-26.17
15	1.4952	74.69	-3.64	15	0.8046	66.07	-24.53
25	0.0924	4.36	-0.94	15	1.1502	92.02	-22.43
25	0.1484	7.00	-1.02	25	0.0262	2.09	-26.10
25	0.2419	11.40	-1.04	25	0.0454	3.64	-25.47
25	0.3510	16.58	-1.09	25	0.0771	6.21	-25.08
25	0.5700	26.64	-0.73	25	0.2231	17.87	-23.70
25	0.8791	40.57	-0.35	25	0.3470	27.49	-22.56
25	1.1711	53.29	0.00	25	0.5213	40.67	-21.17
25	1.5074	68.52	-0.09	25	0.7083	54.82	-20.19
35	0.0607	2.66	1.21	25	0.9516	72.97	-19.16
35	0.1717	7.47	1.50	25	1.2594	93.28	-17.20
35	0.2818	12.10	1.90	35	0.0590	4.59	-22.42
35	0.4638	19.75	2.21	35	0.0961	7.43	-21.90
35	0.6852	28.82	2.57	35	0.1724	13.15	-20.80
35	0.9662	40.04	2.94	35	0.2954	22.20	-19.57
35	1.2570	51.48	3.15	35	0.4484	33.28	-18.45
45	0.0513	2.08	3.45	35	0.6091	44.43	-17.25
45	0.0828	3.38	3.31	35	0.7716	56.00	-16.65
45	0.1444	5.90	3.30	35	1.0428	73.26	-15.01
45	0.2358	9.38	3.98	45	0.0440	3.30	-20.55
45	0.3723	14.47	4.60	45	0.0733	5.49	-19.99
45	0.5246	20.39	4.68	45	0.1206	8.91	-18.97
45	0.8216	31.77	4.82	45	0.2042	15.10	-18.55
45	1.0342	39.03	5.24	45	0.3417	24.40	-16.59
45	1.3265	49.22	5.31	45	0.5243	36.59	-15.14

45	0.7134	48.90	-14.04
45	0.9159	61.60	-13.03
45	1.1963	78.50	-11.97

a. Values of U_0 calculated from equation of Del Grosso and Mader (1972). 5^{o}C: U_0 = 1426.16 m s^{-1}; 15^{o}C: U_0 = 1465.92 m s^{-1}; 25^{o}C: U_0 = 1496.67 m s^{-1}; 35^{o}C: U_0 = 1519.79 m s^{-1}; 45^{o}C: U_0 = 1536.39 m s^{-1}.

Table 4. The sound speed ($\Delta U = U$-U_2) and apparent molal compressibilities ($^{\phi}\kappa$) of TRIS and TRIS-HCl in 0.725m NaCl.

TRIS				TRIS-HCl			
Temp.	***m***	ΔU^{a}	$10^4\,{}^{\phi}\kappa$	**Temp.**	***m***	ΔU^{b}	$10^4\,{}^{\phi}\kappa$
(°C)	**(mol kg^{-1})**	**(m s^{-1})**	**(cm^3 mol^{-1} bar^{-1})**	**(°C)**	**(mol kg^{-1})**	**(m s^{-1})**	**(cm^3 mol^{-1} bar^{-1})**
5	0.0638	3.50	-6.80	5	0.0388	3.28	-24.16
5	0.1057	5.90	-7.35	5	0.0648	5.61	-24.68
5	0.1686	9.43	-7.31	5	0.1048	9.15	-24.42
5	0.2490	13.94	-7.09	5	0.1811	15.88	-23.91
5	0.3727	20.85	-6.73	5	0.3060	26.60	-22.58
5	0.5283	29.30	-6.06	5	0.4259	36.56	-21.27
5	0.7176	39.26	-5.23	5	0.5413	46.00	-20.21
5	1.1232	59.39	-3.65	5	0.7430	61.86	-18.44
15	0.0812	4.07	-2.86	5	1.0469	85.04	-16.49
15	0.1431	7.33	-3.16	15	0.0326	2.68	-21.94
15	0.2502	12.67	-2.52	15	0.0566	4.67	-20.88
15	0.4286	21.39	-1.72	15	0.1002	8.18	-20.88
15	0.6899	33.62	-0.65	15	0.1813	14.64	-18.86
15	0.9596	45.75	0.24	15	0.2910	23.35	-18.86
15	1.2847	59.78	1.06	15	0.4399	34.85	-17.55
25	0.0981	4.25	1.57	15	0.6481	50.18	-15.74
25	0.1702	7.47	1.49	15	0.8789	66.42	-14.05
25	0.2995	13.26	1.62	15	1.2284	89.46	-12.03
25	0.4312	19.01	1.98	25	0.0361	2.67	-17.65
25	0.5681	24.81	2.42	25	0.0596	4.43	-17.44
25	0.7452	32.50	2.69	25	0.1037	7.83	-17.65
25	1.0181	43.22	3.55	25	0.1852	13.96	-16.99
25	1.3754	56.73	4.29	25	0.3166	23.50	-15.63
				25	0.4963	36.06	-13.94
				25	0.7246	51.32	-12.12
				25	0.9553	65.96	-10.58
				25	1.1341	77.02	-9.68

a. Measured values of U_2(NaCl) at each temperature: 5°C: U_2 = 1478.91 m s^{-1}; 15°C: U_2 = 1513.81 m s^{-1}; 25°C: U_2 = 1541.02 m s^{-1}.

b. Measured values of U_2(NaCl) at each temperature: 5°C: U_2 = 1478.87 m s^{-1}; 15°C: U_2 = 1513.88 m s^{-1}; 25°C: U_2 = 1540.83 m s^{-1}.

Table 5. Coefficients for the fits[a] of $^{\phi}V$ and $^{\phi}\kappa$ for TRIS-HCl in water.

	Coeff.	$^{\phi}V$ ($cm^3\ mol^{-1}$)	$10^4\ ^{\phi}\kappa$ ($cm^3\ mol^{-1}\ bar^{-1}$)
$\overline{X}^{0}$	**Constant**	104.0859	-27.271
	$(T- T_R)$	0.02203	0.49055
	$(T- T_R)^2$	-1.542E-03	-0.016525
	$(T- T_R)^3$	8.28E-05	2.071E-04
$\beta^{(0)X}$	**Constant**	3.673E-06	-3.686E-05
	$(T- T_R)$	1.802E-06	-1.98E-06
	$(T- T_R)^2$	-3.077E-08	6.201E-08
$\beta^{(1)X}$	**Constant**	1.31826E-04	-2.36E-04
	$(T- T_R)$	-6.254E-06	1.682E-05
	$(T- T_R)^2$	1.3205E-07	-7.745E-07
$C^{(0)X}$	**Constant**	-1.0042E-05	-7.42E-06
	$(T- T_R)$	-7.74E-07	1.261E-06
	Std.Err.Fit	**0.08**	**0.21**

a. Coefficients fit to **equation 18** where T_R = 298.15K is the reference temperature.

Table 6. Coefficients for the fits[a] of $^{\phi}V$ and $^{\phi}\kappa$ for TRIS-HCl in 0.725m NaCl.

	Coeff.	$^{\phi}V$ (cm^3 mol^{-1})	10^4 $^{\phi}\kappa$ (cm^3 mol^{-1} bar^{-1})
$\overline{X}^{0}$	**Constant**	103.203	-19.7306
	$(T - T_R)$	0.02403	0.534
	$(T - T_R)^2$	-0.002753	-0.000195
$m^{1/2}$	**Constant**	5.1124	5.041
	$(T - T_R)$	-0.1116	-0.5261
	$(T - T_R)^2$	-0.002817	-0.03005
m	**Constant**	0.437	4.307
	$(T - T_R)$	0.1405	0.3506
	$(T - T_R)^2$	0.006775	0.0244
	Std.Err.Fit	**0.03**	**0.20**

a. Coefficients to **equation 19**, where T_R = 298.15K is the reference temperature.

Table 7. Coefficients for the fits[a] of $^{\phi}V$ and $^{\phi}\kappa$ for TRIS in water and 0.725m NaCl.

		Water		NaCl	
		$^{\phi}V$	$10^4\,^{\phi}\kappa$	$^{\phi}V$	$10^4\,^{\phi}\kappa$
	Coeff.	**(cm^3 mol^{-1})**	**(cm^3 mol^{-1} bar^{-1})**	**(cm^3 mol^{-1})**	**(cm^3 mol^{-1} bar^{-1})**
$\overline{X}^{0}$	**Constant**	90.6331	-1.916	89.1617	1.135
	$T - T_R$	0.05859	0.3823	0.01039	0.4106
	$(T - T_R)^2$	-1.38E-04	-6.68E-03	-1.5976E-03	-2.78E-03
	$(T - T_R)^3$	3.94E-06	4.75E-06	-	-
m	**Constant**	1.4016	2.616	3.9397	1.993
	$(T - T_R)$	-0.00477	0.0206	-	-0.1348
	$(T - T_R)^2$	-	1.233E-03	-1.237E-03	-
m^2	**Constant**	-0.696	-0.856	-1.437	0.2784
	$(T - T_R)$	-	-0.029	-	-
	$(T - T_R)^2$	-	-	1.127E-03	-2.24E-03
	Std.Err.Fit	**0.05**	**0.27**	**0.03**	**0.21**

a. Coefficients for **equation 20**, where T_R = 298.15K is the reference temperature.

Table 8. The infinite dilution partial molal volume ($\overline{V}^{0}$, cm^3 mol^{-1}) and compressibility ($\overline{\kappa}^{0}$, cm^3 mol^{-1} bar^{-1}) of TRIS and TRIS-HCl as a function of temperature in water and 0.725m NaCl.

		Volume ($\overline{V}^{0}$)		**Compressibility ($\overline{\kappa}^{0}$)**	
	t°C	**TRIS**	**TRIS-HCl**	**TRIS**	**TRIS-HCl**
Water	5	89.37	102.37	-12.27	-45.35
	15	90.03	103.63	-6.41	-34.04
	25	90.63	104.09	-1.92	-27.27
	35	91.21	104.23	1.24	-23.81
	45	91.78	104.57	3.10	-22.41
0.725m NaCl	5	88.31	102.25	-8.19	-30.24
	15	88.90	103.41	-3.25	-23.79
	25	89.16	103.65	1.14	-18.55

417

Table 9. The change in partial molal volume (ΔV, cm^3 mol^{-1}) and compressibility ($\Delta\kappa$; cm^3 mol^{-1} bar^{-1}) from the deprotonization of TRIS-H^+ calculated with equations 2 and 3.

	t^oC	ΔV	10^4 $\Delta\kappa$
Water	5	3.80	16.47
	15	3.86	15.67
	25	4.38	16.44
	35	4.94	18.18
	45	5.12	20.26
0.725m NaCl	5	4.40	11.66
	15	4.60	15.56
	25	5.15	20.12

Table 10. Effect of pressure on the dissociation constant (K^P/K^0) of TRIS-H$^+$ in water and 0.725m NaCl as a function of temperature.

K^P/K^0 in water[a]

P **(bar)**	**0**	**200**	**400**	**600**	**800**	**1000**	**1200**	**1400**	**1600**	**1800**	**2000**
45°C	1.000	0.964	0.931	0.903	0.878	0.856	0.838	0.822	0.809	0.799	0.792
35°C	1.000	0.964	0.931	0.902	0.877	0.854	0.835	0.818	0.804	0.793	0.784
25°C	1.000	0.967	0.937	0.910	0.887	0.866	0.849	0.833	0.821	0.810	0.802
15°C	1.000	0.970	0.943	0.919	0.898	0.880	0.864	0.851	0.840	0.832	0.826
5°C	1.000	0.969	0.942	0.918	0.897	0.879	0.864	0.852	0.842	0.835	0.830

K^P/K^0 in 0.725m NaCl[b]

P **(bar)**	**0**	**200**	**400**	**600**	**800**	**1000**	**1200**	**1400**	**1600**	**1800**	**2000**
25°C	1.000	0.957	0.920	0.887	0.858	0.833	0.811	0.793	0.778	0.766	0.756
15°C	1.000	0.958	0.920	0.886	0.856	0.829	0.805	0.785	0.767	0.751	0.738
5°C	1.000	0.958	0.920	0.885	0.853	0.823	0.796	0.772	0.749	0.729	0.710

a. Uncertainty in K^P/K^0 estimation due to 2 x uncertainty in $^{\phi}V$ and $^{\phi}\kappa$: ± 0.0008 (or ± 0.1%).

b. Uncertainty in K^P/K^0 estimation due to 2 x uncertainty in $^{\phi}V$ and $^{\phi}\kappa$: ± 0.012 (or ± 1.2%).

Figure 1: Apparent Molal Compressibilities ($^{\phi}\kappa$) of a) TRIS and b) TRIS-HCl in water as a function of concentration and temperature. Symbols: direct measurements. Lines: fitted values (Tables 5 & 7).

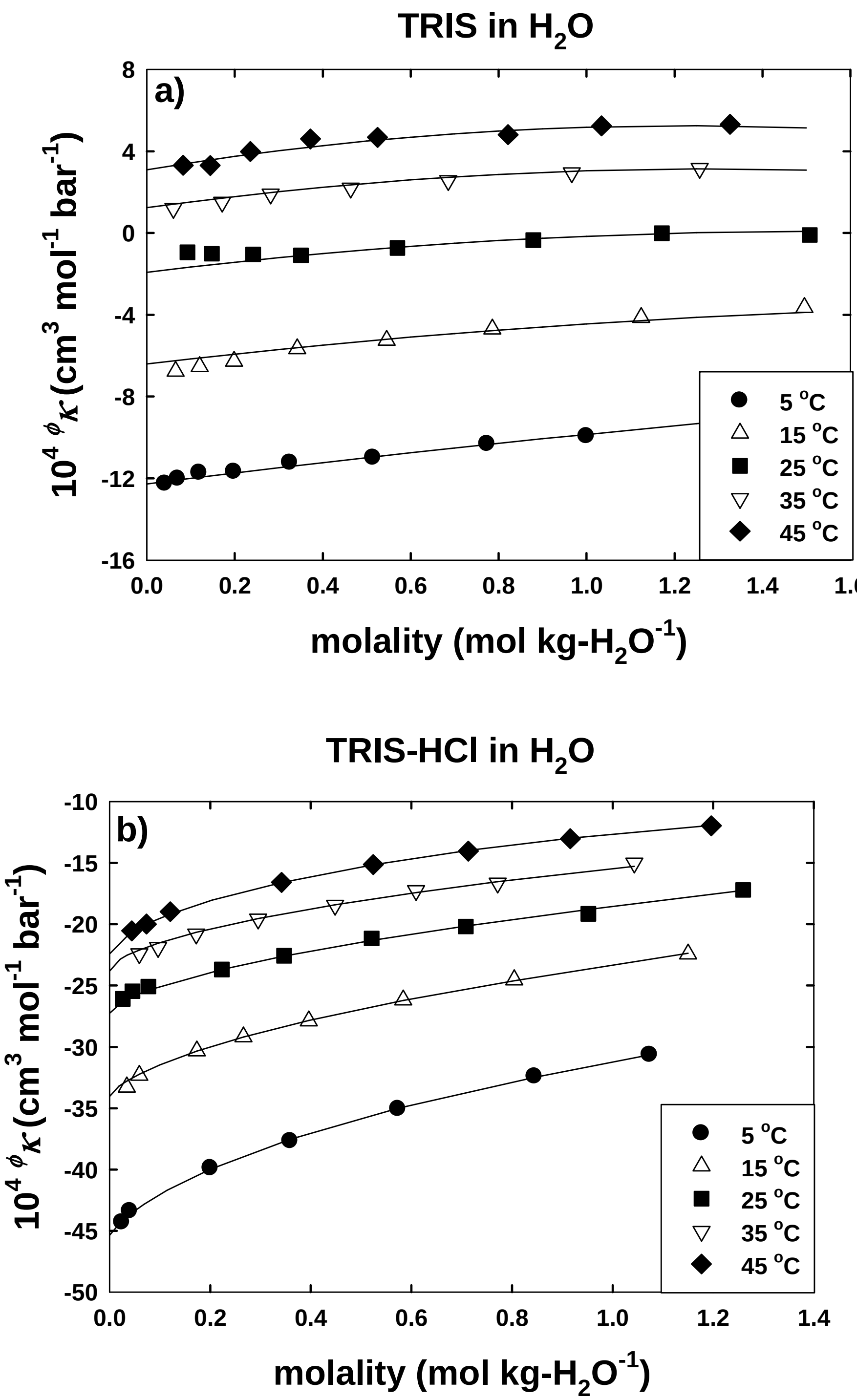


Figure 2: a) Apparent molal volumes ($^{\phi}V$) and b) Apparent molal compressibilities ($^{\phi}\kappa$) at 25°C. Black Circles: measurements in water. White Circles: measurements in 0.725m NaCl. Lines: fitted values.

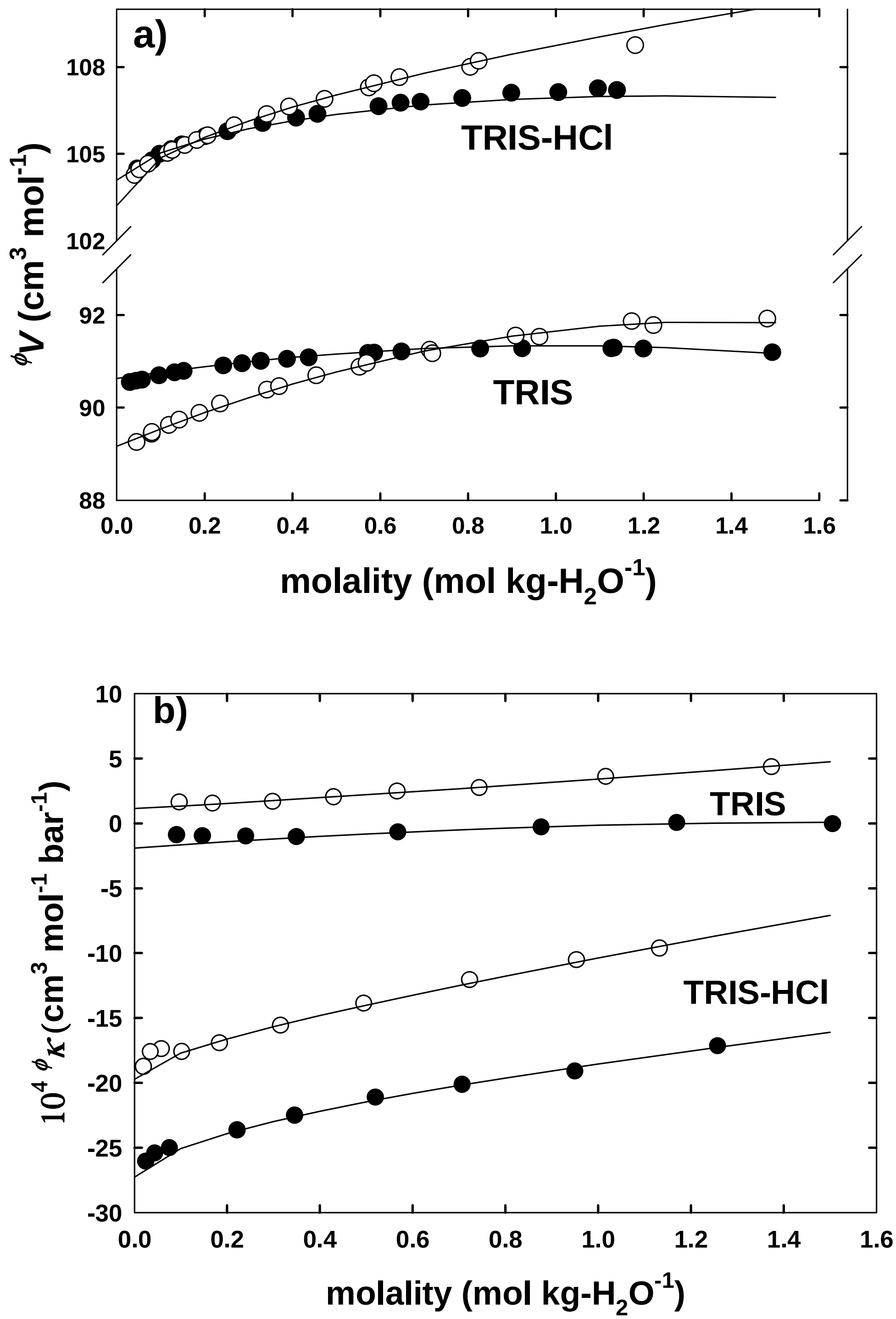


Figure 3: Percent reduction in dissociation constant for TRIS-H^+ (K) as a function of pressure and temperature.

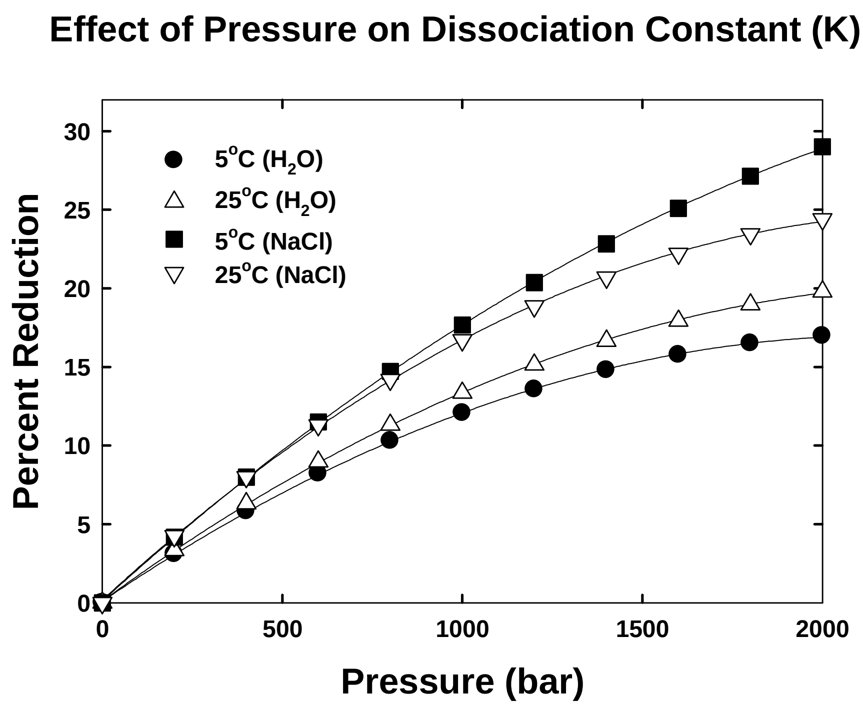
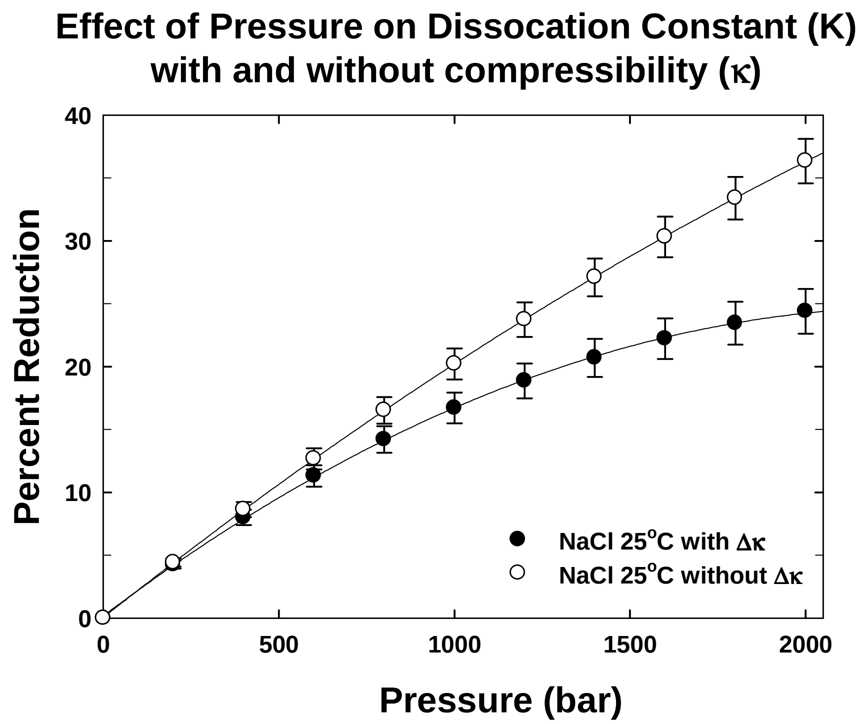


Figure 4: Percent reduction in dissociation constant (*K*) as a function of pressure with and without compressibility (*κ*) values. Vertical bars are the uncertainties due to experimental error.



Graphical Abstract