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Use of the Pitzer Equations to Examine the Dissociation of TRIS in NaCl Solutions†

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The TRIS buffer system is frequently used to calibrate electrodes and indicators that are used to determine the pH of natural waters. Most of the potentiometric and spectrophotometric systems used to measure the pH are calibrated with TRIS buffers. Since most natural waters contain high concentrations of NaCl, it is useful to be able to determine the pK of TRIS using ionic interaction models. In this paper, the dissociation constants of TRIS in NaCl solutions from (0 to 100) °C and (0 to 5) mol·kg^{-1} have been fitted to Pitzer equations. This allows one to estimate the values of the pH for TRIS buffers for natural brines over a wide range of conditions.

Introduction

The pH of natural waters is determined by potentiometric and spectrophotometric techniques.[1,2] The electrodes[3,4] and indicators[5−9] used to measure the pH are calibrated using buffers. The TRIS buffer is frequently used to calibrate these systems since it has a pH around 8 that is similar in most natural waters. In this paper, the dissociation constants of TRISH, tris(hydroxymethyl)methylamine hydrogen chloride, in NaCl solutions[10] from (0 to 100) °C and (0 to 5) mol·kg^{-1}, have been modeled using the Pitzer[11] equations. These results will be useful in determining the pH of NaCl brines in natural waters over a wide range of conditions.

Pitzer Equations for Dissociation of TRISH$^+$ in NaCl Solutions. The dissociation of TRISH$^+$, tris(hydroxymethyl)methylamine hydrogen chloride, is given by

$$\mathrm{TRISH}^+ = \mathrm{H}^+ + \mathrm{TRIS} \qquad (1)$$

The thermodynamic equilibrium constant (K_{mTRISH}) is related to the stoichiometric constant (K^*_{TRISH}) and activity coefficients $\gamma(i)$ by

$$K_{\mathrm{mTRISH}} = K_m{}^*{}_{\mathrm{TRISH}}\{\gamma_{\mathrm{m}}(\mathrm{H}^+)\gamma_{\mathrm{m}}(\mathrm{TRIS})/\gamma_{\mathrm{m}}(\mathrm{TRISH}^+)\} \qquad (2)$$

The measured stoichiometric constants $K_{\mathrm{m}}{}^*(i)$ are related to the total concentration (mol·kg^{-1}) of the acid−basic species by

$$K_{\mathrm{m}}{}^*{}_{\mathrm{TRISH}} = [\mathrm{H}^+][\mathrm{TRIS}]/[\mathrm{TRISH}^+] \qquad (3)$$

The Pitzer[11] model can be used to examine the effect of ionic strength (I_{m}) and temperature on the activity coefficients of H$^+$, TRISH$^+$, and TRIS.[12] The activity coefficients of these species using the Pitzer[11] model are given where m_{Na} or m_{Cl} is the molality in mol·kg^{-1}

$$\ln \gamma_{\mathrm{m}}(\mathrm{H}^+) = f^{\gamma} + 2m_{\mathrm{Cl}}(B_{\mathrm{HCl}} + m_{\mathrm{Cl}}C_{\mathrm{HCl}}) + R + S + m_{\mathrm{Na}}(2\Theta_{\mathrm{HNa}} + m_{\mathrm{Cl}}\psi_{\mathrm{HNaCl}}) \qquad (4)$$

$$\ln \gamma_{\mathrm{m}}(\mathrm{TRISH}^+) = f^{\gamma} + 2m_{\mathrm{Cl}}(B_{\mathrm{TRISHCl}} + EC_{\mathrm{TRISHCl}}) + R + S \qquad (5)$$

$$\ln \gamma_{\mathrm{m}}(\mathrm{TRIS}) = 2m_{\mathrm{Na}}\lambda_{\mathrm{TRIS\text{-}Na}} + 2m_{\mathrm{Cl}}\lambda_{\mathrm{TRIS\text{-}Cl}} + m_{\mathrm{Na}}m_{\mathrm{Cl}}\xi_{\mathrm{TRIS\text{-}Na\text{-}Cl}} \qquad (6)$$

The Debye−Hückel limiting law f^{γ} is defined by

$$f^{\gamma} = -A^{\phi}[I_{\mathrm{m}}{}^{1/2}/(1 + 1.2I_{\mathrm{m}}{}^{0.5}) + (2/1.2)\ln(1 + 1.2I_{\mathrm{m}}{}^{0.5})] \qquad (7)$$

The values of limiting slope A^{ϕ} from (0 to 100) °C can be estimated from the equation[13] ($\sigma = 0.00005$)

$$A^{\phi} = 0.37674 + 5.040\ 10^{-04}(T/\mathrm{K} - 273.15) + 3.30 \cdot 10^{-06}(T/\mathrm{K} - 273.15)^2 \qquad (8)$$

The parameters B_{MX} and C_{MX} account for the interactions of the cations (H$^+$ and TRISH$^+$) with Cl$^-$. They are related to the Pitzer parameters $\beta^{(0)}{}_{\mathrm{MX}}$, $\beta^{(1)}{}_{\mathrm{MX}}$, and $C^{\phi}{}_{\mathrm{MX}}$ by

$$B_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \beta^{(1)}_{\mathrm{MX}}f_1 \qquad (9)$$

$$C_{\mathrm{MX}} = C_{\mathrm{MX}}{}^{\phi}/2 \qquad (10)$$

The terms R and S in eqs 4 and 5 are related to the media affects (NaCl) and are given by[14]

$$R = m_{\mathrm{Na}}m_{\mathrm{Cl}}\beta'_{\mathrm{NaCl}} = m_{\mathrm{Na}}m_{\mathrm{Cl}}(\beta^{(1)}_{\mathrm{NaCl}}f_2) \qquad (11)$$

$$S = m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}} = m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}}{}^{(\phi)}/2 \qquad (12)$$

The values of f_1 and f_2 are functions of the ionic strength ($I_{\mathrm{m}} = m_{\mathrm{NaCl}}$)

$$f_1 = [1 - (1 + 2I_{\mathrm{m}}{}^{0.5})\exp(-2I_{\mathrm{m}}{}^{0.5})]/2I_{\mathrm{m}} \qquad (13)$$

$$f_2 = [-1 + (1 + 2I_{\mathrm{m}}{}^{0.5} + 2I_{\mathrm{m}})\exp(-2I_{\mathrm{m}}{}^{0.5})]/2I_{\mathrm{m}}{}^2 \qquad (14)$$

The parameters Θ_{HNa} and Ψ_{HNaCl} account for the common ion interactions between H$^+$ and Na$^+$ and triplet interactions of H$^+$ with Na$^+$ and Cl$^-$. The parameters $\lambda_{\mathrm{TRIS\text{-}Na}}$ and $\lambda_{\mathrm{TRIS\text{-}Cl}}$ account for the interactions of TRIS individually with Na$^+$ and Cl$^-$, while the parameter $\zeta_{\mathrm{TRIS-Na\text{-}Cl}}$ accounts for interactions with NaCl. All the Pitzer parameters $\beta^{(0)}{}_{\mathrm{MX}}$, $\beta^{(1)}{}_{\mathrm{MX}}$, $C^{\phi}{}_{\mathrm{MX}}$, Θ_{HNa}, and Ψ_{HNaCl} for HCl, NaCl, TRISHCl, and $\lambda_{\mathrm{TRIS\text{-}Na}}$ for TRIS at 25 °C are given in Table 1. Since the values of $\lambda_{\mathrm{TRIS\text{-}Na}}$ +

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Table 1. Pitzer Coefficients for the NaCl, HCl, and TrisHCl Systems at 25 °C

species	$\beta^{(0)}_{MX}$	$\beta^{(1)}_{MX}$	C^{ϕ}_{MX}	ref
HCl	0.1775	0.2945	0.00080	Pitzer[11]
NaCl	0.0765	0.2664	0.00127	Pitzer[11]
TrisHCl	0.03950	0.20978	−0.00236	Bates and Macaskill[17]

i	j	k	Θ_{ij}	Ψ_{ijk}	ref
H	Na	Cl	0.0289	0.0002	Campbell et al.[16]

$\lambda_{\text{TRIS-Na}}$	$\lambda_{\text{TRIS-Cl}}$	$\zeta_{\text{TRIS-Na-Cl}}$	ref
0.0239	0	0	Millero et al.[4]

$\lambda_{\text{TRIS-Cl}}$ which are related to the salting coefficient ($k = (2\lambda_{\text{TRIS-Na}} + 2\lambda_{\text{TRIS-Cl}})$ cannot be separated, the value of $\lambda_{\text{TRIS-Cl}}$ is taken to be zero.

The Pitzer[11] parameters for NaCl[13,15] from (0 to 250) °C can be determined from

$$\beta^{(0)}_{\text{NaCl}} = 14.3783204 + 0.00560767406T/\text{K} - 422.185236(\text{K}/T) - 2.51226677\ln(T/\text{K}) - 0.00000261718135(T/\text{K})^2 + 4.43854508/(680 - T/\text{K}) - 1.70502337/(T/\text{K} - 227) \quad (15)$$

$$\beta^{(1)}_{\text{NaCl}} = -0.483060685 + 1.40677479\cdot10^{-3}T/\text{K} + 119.311989/(T/\text{K}) - 4.23433299/(T/\text{K} - 227) \quad (16)$$

$$C^{\phi}_{\text{NaCl}} = -0.100588714 - 1.80529413\cdot10^{-5}(T/\text{K}) + 8.61185543(\text{K}/T) + 0.012488095\ln(T/\text{K}) + 3.41172108\cdot10^{-9}(T/\text{K})^2 + 6.83040995\cdot10^{-2}/(680 - T/\text{K}) + 0.293922611/(T/\text{K} - 227) \quad (17)$$

The Pitzer parameters for HCl[16] from (0 to 100) °C can be determined from

$$\beta^{(0)}_{\text{HCl}} = 1.2859 - .0021197(T/\text{K}) - 142.5877(\text{K}/T) \quad (18)$$

$$\beta^{(1)}_{\text{HCl}} = -4.4474 + 8.425698\cdot10^{-3}(T/\text{K}) + 665.7882(\text{K}/T) \quad (19)$$

$$C^{\phi}_{\text{HCl}} = -0.305156 + 0.000516(T/\text{K}) + 45.52154(\text{K}/T) \quad (20)$$

Calculation of Pitzer Parameters from (0 to 100) °C for TRIS. The Pitzer parameters for TRISHCl[17] and TRIS[4] are only known at 25 °C. Values at higher temperatures can be determined from the measurements of the dissociation of TRISH$^+$ in NaCl solutions.[10] Since the values of $\gamma_m(\text{TRISH}^+)$ at 25 °C[17] are more reliable than the values of $\gamma_m(\text{TRIS})$, we have redetermined the values of $\gamma_m(\text{TRIS})$ and $\text{p}K_m{}^0{}_{\text{TRIS}}$ from the tabulated $\text{p}K_{m\text{TRIS}}$ values of Foti et al.[10] The rearrangement of eq 2 and solving for $\ln\gamma_m(\text{TRIS}) - \ln K_m{}^0{}_{\text{TRISH}}$ gives

$$Y = \ln\gamma_m(\text{TRIS}) - \ln K_m{}^0{}_{\text{TRISH}} = -\ln K_m{}^*{}_{\text{TRISH}} - \ln\gamma_m(\text{H}^+) + \ln\gamma_m(\text{TRISH}^+) \quad (21)$$

The values of Y calculated from eq 21 are shown as a function of molality of NaCl in Figure 1. The Y values are a smooth function of molality over the entire temperature range. The extrapolated values of Y to $m_{\text{NaCl}} = 0$ yield values of $-\ln K^0_{\text{TRISH}}$ that are plotted as a function of K/T in Figure 2. The values of $\ln\gamma_m(\text{TRIS})$ have been determined from $Y - \ln K^0_{\text{TRISH}}$ shown in Figure 3. The values of $\ln\gamma_m(\text{TRIS})$ are smooth functions of molality and temperature.

The values of Y have been fitted to the equation ($\sigma = 0.005$) where m is the molality in mol·kg^{-1}

$$Y = -175.8077 + 11250.18(\text{K}/T) + 29.41326\ln(T/\text{K}) + 1.6757m - 0.0108m^2 - 0.002732m^3 - 118.564m(\text{K}/T) - 0.22038m\ln(T/\text{K}) + 8.103m^2(\text{K}/T) \quad (22)$$

The first three terms of this equation represent $-\ln K_m{}^0{}_{\text{TRISH}}$, and the latter terms are for $\ln\gamma_m(\text{TRIS})$

$$\ln K_m{}^0{}_{\text{TRISH}} = -175.808 + 11250.187(\text{K}/T) + 29.413\ln(T/\text{K}) \quad (22a)$$

$$\ln\gamma_m(\text{TRIS}) = 0.04721m + 0.000474m(T/\text{K} - 273.15) - 0.002190m^2 - 0.0000799m^2(T - 273.15) \quad (22b)$$

The values of $\text{p}K_m{}^0{}_{\text{TRISH}}$ and $\ln\gamma_m(\text{TRIS})$ together with the $\ln\gamma_m(\text{H}^+)$ and $\ln\gamma_m(\text{TRISH})$ from eqs 4 and 5 have been used to determine the values of $\text{p}K_{m\text{TRISH}}$. The differences between the measured and calculated values of Y as a function of molality and temperature are shown in Figure 4. The larger deviations at higher temperature are similar to the uncertainties of the values of $\text{p}K_{m\text{TRISH}}$ tabulated by Foti et al.[10] Most of the measurements from (0 to 60) °C are within the overall standard deviation of 0.005.

The values of $\ln K_m{}^*{}_{\text{TRISH}}$ can be calculated from the calculated value of $\ln K_m{}^0{}_{\text{TRISH}}$ and activity coefficients using

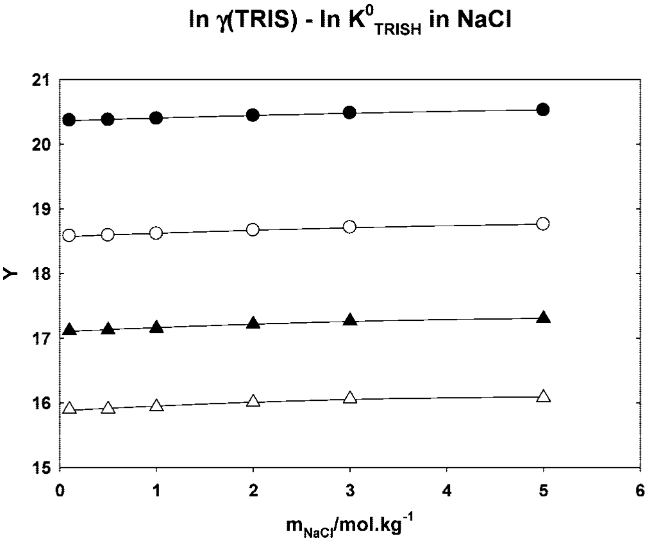

Figure 1. Effect of molality on the values of Y in NaCl solutions at different temperatures. The symbols are: solid circle, 0 °C; open circle, 25 °C; solid triangle, 50 °C; and open triangle, 75 °C.

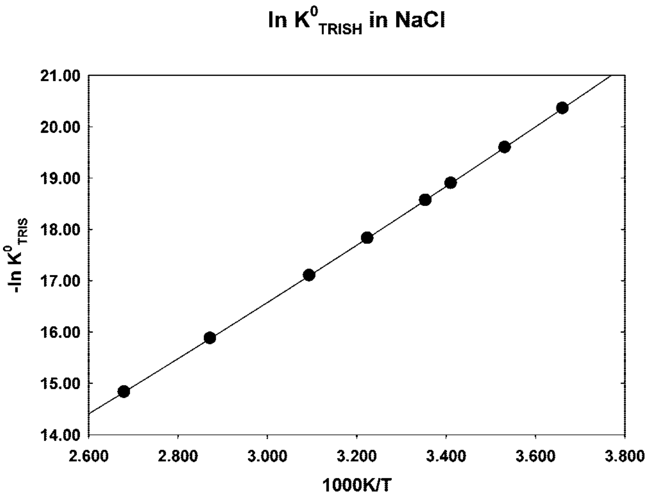

Figure 2. Effect of temperature on the values of $\ln K_m{}^0{}_{\text{TRISH}}$ in NaCl solutions.

$$\ln K_{\mathrm{m}}{}^{*}{}_{\mathrm{TRISH}} = \ln K_{\mathrm{m}}{}^{0}{}_{\mathrm{TRISH}} - \ln \gamma_{\mathrm{m}}(\mathrm{H}^{+}) - \ln \gamma_{\mathrm{m}}(\mathrm{TRIS}) + \ln \gamma_{\mathrm{m}}(\mathrm{TRISH}^{+}) \quad (23)$$

The calculated values ln $K_{\mathrm{m}}{}^{*}{}_{\mathrm{TRISH}}$ agree with the measured values with a standard error of 0.005 similar to the fits for Y discussed above. These results should be useful in calibrating pH electrodes and indicators in natural brines made up mostly of NaCl.

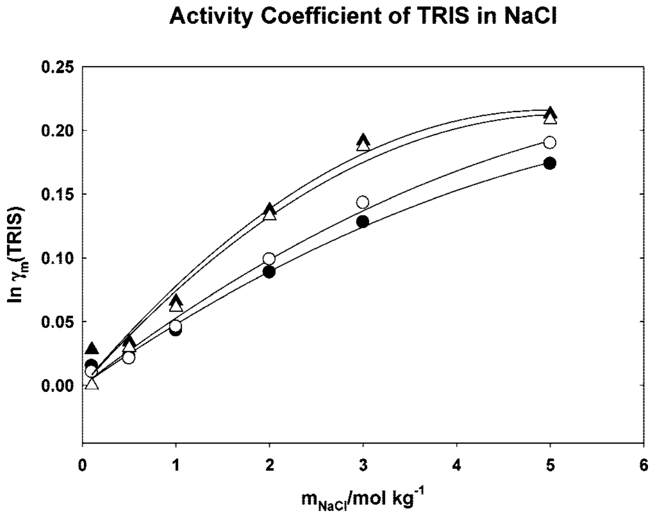

Figure 3. Effect of molality on the values of ln gm(TRIS) at different temperatures. The symbols are: solid circle, 0 °C; open circle, 25 °C; solid triangle, 50 °C; and open triangle, 75 °C.

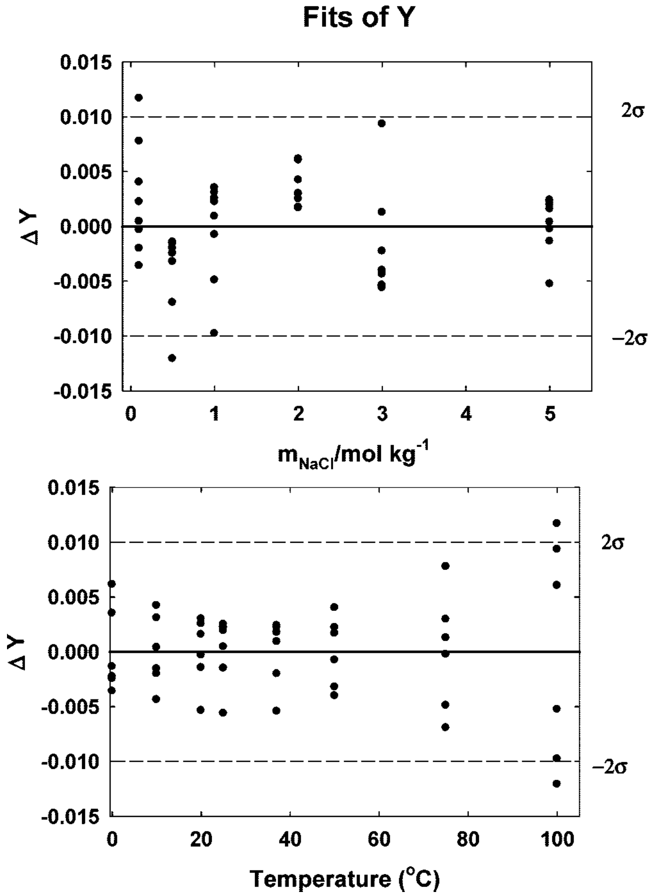

Figure 4. Differences between the measured and calculated values of Y for the dissociation of TRISH in NaCl as a function of molality and temperature (°C).

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The author wishes to acknowledge the contributions of Roger Stokes to solution chemistry. Before graduate school, I had a job working at the National Bureau of Standards (now National Institute for Standards and Technology) with the Roger Bates group. While there I met Robbie Robinson, and he introduced me to the book “Electrolyte Solutions” by Robinson and Stokes. While in graduate school at Carnegie Mellon, my major professor Loren Hepler went on a sabbatical leave with R. Stokes. Loren made measurements on molar volume measurements of electrolytes in dilute solutions which led to my early studies on the density of electrolytes. The book still sits on my desk with scotch tape holding it together, and I frequently pick it up to get an activity coefficient.

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