PITZER AND THERMODYNAMIC PARAMETERS OF TRIETHANOLAMINE AND GLYCINE IN AQUEOUS SALINE SOLUTIONS

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On the basis of the ionic strength dependence of the equilibrium constant (pK^*) of triethanolamine (TEA) and glycine, the ionic interaction parameters of the species involved in the equilibria $TEAH^+ \Leftrightarrow TEA + H^+$ (for TEA), $AH_2^+ \Leftrightarrow AH + H^+$ and $AH \Leftrightarrow A^- + H^+$ (for glycine) in aqueous solutions of KCl and KNO_3, respectively, were determined using the Pitzer equations. Values of pK^* were expressed on both the molarity and the molality scale at various temperatures and values of thermodynamic quantities ΔG^0, ΔH^0 and ΔS^0 ascertained, for TEA.

It is well known that acid-base equilibrium constants depend on the ionic strength; the type of dependence employed is normally based in some model for the activity coefficients of the species present in the medium.

In the seventies, Pitzer[1] developed a semiempirical model for the activity coefficients of the chemical species in saline media of different composition which has been and is still applied relatively frequently in determining the dependence of osmotic and activity coefficients on the ionic strength, particularly in concentrated aqueous solutions of strong electrolytes[2]; however, weak electrolytes have scarcely been dealt with in this respect and particularly such a formalism has been seldom used to interpret the ionic strength dependence of acid-base or complex stability constants, which are most often determined potentiometrically by using commercially available H^+ ion sensitive glass electrodes, although some work had been previously carried out by Millero et al.[3].

In this work, the Pitzer equations are used to account for the influence of the ionic strength on the pK^* (K^* being the stoichiometric equilibrium constant) of the weak electrolytes triethanolamine (TEA) and glycine on both the molality and molarity scale, in KCl and KNO_3 aqueous solutions, respectively.

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We also considered the possibility of calculating ΔH^0 and ΔS^0 for the equilibrium $TEAH^+ \Leftrightarrow TEA + H^+$ at a non-zero ionic strength from pK^* vs $f(T)$ data, where $f(T)$ denotes functions typically employed in temperature fits.

EXPERIMENTAL

We used a titration cell furnished with inlets for a Radiometer GK2401C electrode, a Crison microBur 2031 autoburette, a temperature probe and a nitrogen stream that was bubbled through the solution in order to effect stirring and provide an inert atmosphere. Standardized solutions of 0.1 M HCl and 0.01 M triethanolamine (TEA) and glycine were prepared by dilution and by dissolution of an appropriate amount of commercially available product, respectively, the ionic strength of the solutions being adjusted with KCl and KNO_3 in each case. All reagents used were Merck p.a. chemicals and deionized water (Millipore Milli-Q) was used throughout.

The titration system was operated in automatic fashion under the control of a Tandon DataPack computer running the programme ALIA (ref.[4]), which regulated and commanded addition of titrant from the burette, acquired pH-meter readouts and generated a data file to be subsequently processed by the programme MINIQUAD (ref.[5]), in order to obtain the sought reaction constants. The pK^* values thus obtained were fitted to the ionic strength functions of the Pitzer model by using the statistical package SOLO (ref.[6]), which provided ionic interaction parameters. As noted earlier, this model requires the ionic strength to be expressed as a molality, so pK^* and I values must be previously converted by using the following equation

$$m = 6.3359 \,.\, 10^{-4} + 0.99778\, c + 0.032831\, c^2 \quad (\mathrm{KCl}) \tag{1}$$

$$m = 7.1923 \,.\, 10^{-4} + 0.99627\, c + 0.046610\, c^2 \quad (\mathrm{KNO_3}) \tag{2}$$

($c < 1.7$ mol dm^{-3}), where m denotes molality and c molarity. The data used to derive this equation were reported elsewhere[7]. From Eqs (*1*) and (*2*) it is straightforward to convert pK^* values on either molarity or molality scale according to the relationship

$$\mathrm{p}K_m^* = \mathrm{p}K_c^* + \log(c/m)\,, \tag{3}$$

where pK_m^* and pK_c are the stoichiometric pK's in the molality and molarity scale, respectively, c is the concentration in mol dm^{-3} and m the concentration in mol (kg water)$^{-1}$.

Prior to each titration, a calibration graph was constructed in order to check that the electrode obeyed the equation $E = E^{\mathrm{ref}} - s \log [H^+]$ and thus calculate E^{ref}. Following literature recommendations, calibrations were done in the acid region[8] (pH 2.3 – 2.9). In order to minimize the potential effect of systematic errors in the titrant concentration[9], E vs $\log [H^+]$ plots were obtained by adding HCl over the supporting electrolytes (KCl and KNO_3) solutions and measuring the potential on each addition. The reference potentials and slopes obtained in the calibrations are listed in Tables I and II.

RESULTS AND DISCUSSION

Ionic Interaction Parameters

Let us consider the disociation equilibrium of the protonated form of TEA, $TEAH^+ \Leftrightarrow TEA + H^+$, the thermodynamic constant of which is given by

$$K^{T} = \frac{[\mathrm{TEA}][\mathrm{H}^+]}{[\mathrm{TEAH}^+]}\,\frac{\gamma_{\mathrm{TEA}}\,\gamma_{\mathrm{H}^+}}{\gamma_{\mathrm{TEAH}^+}} = K^{*} K^{\gamma}\,, \qquad (4)$$

where γ_i denotes the activity coefficients of the species involved in the equilibrium. The Pitzer equations corresponding to such coefficients are as follows[1,3]:

$$\ln \gamma_{\mathrm{TEAH}} = f^{\gamma} + 2\sum_{a} m_a\,[B_{\mathrm{TEAHa}} + E C_{\mathrm{TEAHa}}] + \sum_{c}\sum_{a} m_c\, m_a\,[B'_{ca} + C_{ca}] \qquad (5)$$

$$\ln \gamma_{\mathrm{H}} = f^{\gamma} + 2\sum_{a} m_a\,[B_{\mathrm{Ha}} + E C_{\mathrm{Ha}}] + 2\sum_{c} m_c\,\theta_{\mathrm{Hc}} + \sum_{c}\sum_{a} m_c\, m_a\,[B'_{ca} + C_{ca} + \psi_{\mathrm{Hca}}] \qquad (6)$$

$$\ln \gamma_{\mathrm{TEA}} = 2\,\lambda\, m\,, \qquad (7)$$

where m is the molality, and

$$E = \sum_{c} m_c\, z_c = \sum_{a} m_a\,|z_a| \qquad (8)$$

is the equivalent molality (subscripts a and c denote the anions and cations present in the solution), B and C are the second and third virial coefficients which are functions of ionic strength.

$$B_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \frac{\beta^{(1)}_{\mathrm{MX}}}{2I}\,[1 - (1 + 2\,I^{1/2})\exp(-2\,I^{1/2})] \qquad (9)$$

$$B'_{\mathrm{MX}} = \frac{\partial B_{\mathrm{MX}}}{\partial I} = \frac{\beta^{(1)}_{\mathrm{MX}}}{2\,I^2}\,[-1 + (1 + 2\,I^{1/2} + 2\,I)\exp(-2\,I^{1/2})] \qquad (10)$$

TABLE I

Standard potentials measured in an acid medium at different ionic strengths for TEA. pK^* values obtained at various ionic strengths and residual values obtained with and without C^{ϕ} on the molality scale

I	E^0	$-s$	pK^*_m/pK^*_c	With C^{ϕ}	Without C^{ϕ}
0.10	568.07	58.939	7.747/7.750(±0.059)	−0.025	−0.024
0.25	561.80	58.492	7.808/7.811(±0.006)	0.006	0.007
0.50	565.58	59.756	7.930/7.937(±0.004)	0.062	0.063
0.75	564.10	58.705	7.853/7.863(±0.007)	−0.092	−0.093
1.00	571.90	59.392	8.062/8.075(±0.006)	0.031	0.030
1.25	577.19	60.079	8.144/8.161(±0.032)	0.022	0.021
1.50	577.66	60.194	8.207/8.227(±0.013)	−0.013	−0.012

TABLE II

Standard potentials measured in an acid medium at different ionic strengths for glycine. pK^* values obtained at various ionic strengths and residual values obtained with and without C^{Φ} on the molality scale

I	E^0	s	p$K^*_{1,m}$/p$K^*_{1,C}$	With C^{Φ}	Without C^{Φ}	p$K^*_{2,m}$/p$K^*_{2,C}$	With C^{Φ}	Without C^{Φ}
0.30	374.24	59.45	2.422/2.428(±0.017)	-0.005	0.010	9.595/9.600(±0.008)	-0.001	0.002
0.51	374.91	59.41	2.428/2.437(±0.006)	-0.002	0.004	9.597/9.606(±0.003)	0.006	0.007
0.72	376.15	59.61	2.426/2.439(±0.009)	0.001	-0.003	9.574/9.587(±0.017)	-0.013	-0.014
0.93	377.56	59.52	2.434/2.451(±0.003)	0.015	0.005	9.591/9.608(±0.016)	0.009	0.007
1.15	578.59	59.74	2.419/2.440(±0.019)	0.004	-0.007	9.584/9.604(±0.023)	0.007	0.004
1.37	579.46	59.61	2.389/2.413(±0.039)	-0.029	-0.032	9.560/9.584(±0.014)	-0.012	-0.013
1.60	580.79	59.86	2.442/2.470(±0.011)	0.014	0.028	9.571/9.599(±0.012)	0.004	0.007

$$C_{\mathrm{MX}} = \frac{C^{\phi}_{\mathrm{MX}}}{2\,|z_{\mathrm{M}}\,z_{\mathrm{X}}|^{1/2}} \tag{11}$$

(MX being the supporting electrolyte)

$$f^{\gamma} = -0.392\left[\frac{I^{1/2}}{1 + 1.2\,I^{1/2}} + \frac{2}{1.2}\ln\left(1 + 1.2\,I^{1/2}\right)\right] \tag{12}$$

θ and ψ are related to double interactions between ions of the same sign and triple interactions, respectively. As usual, the logarithms of the activity coefficients of the neutral species are assumed to be proportional to the solution ionic strength[10].

Taking logarithms in Eq. (*4*) and substituting Eqs (*5*) – (*7*) into it yields

$$F_{\mathrm{TEA}}(I) = \ln K + (\beta^{(0)} - \lambda)\,f^{(1)} + \beta^{(1)} f^{(2)} + C^{\phi} f^{(3)} \tag{13}$$

$$F_{1,\mathrm{GLY}}(I) = \ln K_1 + (\beta^{(0)}_{\mathrm{AH_2NO_3}} - \lambda)\,f^{(1)} + \beta^{(1)}_{\mathrm{AH_2NO_3}} f^{(2)} + C^{\phi}_{\mathrm{AH_2NO_3}} f^{(3)} \tag{14}$$

$$F_{2,\mathrm{GLY}}(I) = \ln K_2 - (\beta^{(0)}_{\mathrm{AK}} - \lambda)\,f^{(1)} - \beta^{(1)}_{\mathrm{AK}} f^{(2)} - C^{\phi}_{\mathrm{AK}} f^{(3)}, \tag{15}$$

where $f^{(1)} = 2\,I$, $f^{(2)} = 1 - (1 + 2\,I^{1/2})\exp(-2I^{1/2})$, $f^{(3)} = I^2$ and $F(I)$ function groups all the ionic strength terms of known coefficients.

$$F_{\mathrm{TEA}}(I) = \ln K^{*} + (\beta^{(0)}_{\mathrm{HCl}} + \theta_{\mathrm{HK}})\,f^{(1)} + \beta^{(1)}_{\mathrm{HCl}} f^{(2)} + (C^{\phi}_{\mathrm{HCl}} + \psi_{\mathrm{HKCl}})\,f^{(3)} \tag{16}$$

$$F_{1,\mathrm{GLY}}(I) = \ln K_1^{*} + (\beta^{(0)}_{\mathrm{HNO_3}} + \theta_{\mathrm{HK}})\,f^{(1)} + \beta^{(1)}_{\mathrm{HNO_3}} f^{(2)} + (C^{\phi}_{\mathrm{HNO_3}} + \psi_{\mathrm{HKNO_3}}) \tag{17}$$

$$\begin{aligned} F_{2,\mathrm{GLY}}(I) = {} & \ln K_2^{*} + (\beta^{(0)}_{\mathrm{HNO_3}} + \theta_{\mathrm{HK}})\,f^{(1)} + \beta^{(1)}_{\mathrm{HNO_3}} f^{(2)} + (C^{\phi}_{\mathrm{HNO_3}} + C^{\phi}_{\mathrm{KNO_3}})\,f^{(3)} + {} \\ & + 2\,f^{(4)} + \beta^{(1)}_{\mathrm{KNO_3}} f^{(5)} \end{aligned} \tag{18}$$

with $f^{(4)} = f^{\gamma}$, $f^{(5)} = -1 + (1 + 2\,I^{1/2} + 2\,I)\exp(-2\,I^{1/2})$ and $\beta^{(0)}_{\mathrm{HCl}} = 0.1775$, $\beta^{(1)}_{\mathrm{HCl}} = 0.2945$, $C^{\phi}_{\mathrm{HCl}} = 0.00080$, $\theta_{\mathrm{HK}} = 0.005$, $\psi_{\mathrm{HKCl}} = -0.007$, $\beta^{(0)}_{\mathrm{HNO_3}} = 0.1119$, $\beta^{(1)}_{\mathrm{HNO_3}} = 0.3206$, $\beta^{(1)}_{\mathrm{KNO_3}} = 0.0494$, $C^{\phi}_{\mathrm{HNO_3}} = 0.001$, $C^{\phi}_{\mathrm{KNO_3}} = 0.0066$ and $\ln K = -17.891$, $\ln K_1 = -5.434$, $\ln K_2 = -22.519$ (refs[2,11]).

A linear fit of Eqs (*13*) – (*15*) allows calculation of the ionic interaction parameters $\beta^{(0)} - \lambda$, $\beta^{(1)}$ and C^{ϕ}, which represent different interactions between species $\mathrm{TEAH^+}$, $\mathrm{AH_2^+}$ and $\mathrm{A^-}$ and the electrolytes anions and cations (see Table III). In this way, the dependence of $\mathrm{p}K^{*}$ on the ionic strength is found to be of the form

$$\mathrm{p}K^{*}_{\mathrm{TEA}} = 7.761 + 0.1823f^{(1)} - 0.1943f^{(2)} + 0.0100f^{(3)} \tag{19}$$

$$\mathrm{p}K^{*}_{1,\,\mathrm{GLY}} = 2.358 - 0.225f^{(1)} + 0.640f^{(2)} + 0.128f^{(3)} \tag{20}$$

$$\mathrm{p}K^{*}_{2,\,\mathrm{GLY}} = 9.779 + 0.092f^{(1)} + 0.094f^{(2)} - 0.052f^{(3)} + 0.868f^{(4)} + 0.0214f^{(5)}\,. \tag{21}$$

TABLE III
Pitzer parameters obtained with pK^* in the molality (m) and the molarity (c) scale with C^{ϕ} included (σ = 0.06 and 0.02) and excluded (σ = 0.05 and 0.02) for TEA and glycine, respectively in both cases

Equation No.	$\beta^{(0)} - \lambda$		$\beta^{(1)}$		$C\phi$	
	m	c	m	c	m	c
			Triethanolamine (TEA)			
19	-0.2372	-0.2414	0.7419	0.7201	-0.02918	-0.0360
22	-0.2707	-0.2899	0.8158	0.8160	–	–
			Glycine			
20	0.635	0.646	-1.153	-1.325	-0.294	-0.326
23	0.200	0.186	-0.202	-0.230	–	–
21	0.095	0.093	-0.104	-0.058	-0.127	-0.111
24	-0.082	-0.059	0.280	0.276	–	–

TABLE IV
pK^* values of TEA obtained at various temperatures

T, K	pK^*
289	8.109 ± 0.002
293	8.024 ± 0.001
298	7.937 ± 0.005
303	7.796 ± 0.002
308	7.680 ± 0.003
313	7.563 ± 0.002
317	7.447 ± 0.003

On the other hand, inasmuch as the working ionic strength range was less than 2 *m*, we fitted Eqs (*13*) and (*15*) similarly but neglecting C^{Φ} (ref.[2]). The results thus obtained (Table III) gave rise to the following equation:

$$\mathrm{p}K^{*}_{\mathrm{TEA}} = 7.762 + 0.1968 f^{(1)} - 0.2264 f^{(2)} \qquad (22)$$

$$\mathrm{p}K^{*}_{1,\,\mathrm{GLY}} = 2.365 - 0.036 f^{(1)} + 0.227 f^{(2)} \qquad (23)$$

$$\mathrm{p}K^{*}_{2,\,\mathrm{GLY}} = 9.776 + 0.015 f^{(1)} + 0.261 f^{(2)} + 0.868 f^{(4)} + 0.0214 f^{(5)}, \qquad (24)$$

which features a slightly smaller fitting error, σ. However, both equations provides quite reasonable values of the $\mathrm{p}K_{\mathrm{exp}} - \mathrm{p}K_{\mathrm{cal}}$ residuals (Tables I and II) that are within the experimental error commonly accepted for this type of measurement[12]. Therefore, from the results obtained follows that the Pitzer equations predict pK^* values within the accepted experimental error (Figs 1, 2).

As noted earlier, the above calculations were done by using ionic strengths and pK^* values on the molality scale that were subsequently applied a conversion equation (Eqs (*1*), (*2*)) since the constants were determined on the molarity scale. However, we also believed it of interest to recalculate parameters without scale conversion. The results thus obtained for both TEA and glycine are given in Table III. As can be seen, avoiding the scale conversion resulted in no significant differences in the interaction parameters; in fact, such differences were smaller than those arising from inclusion of a new variable in the fitting, as is the case when the term accounting for triple interactions is considered or left out.

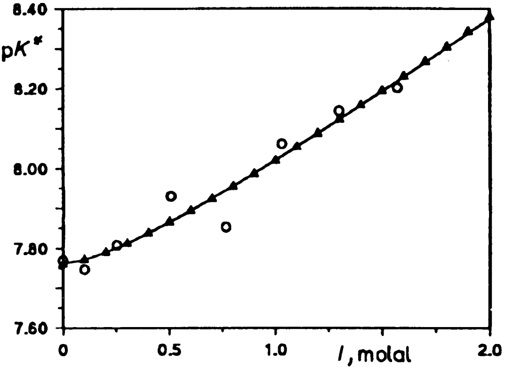

FIG. 1
pK^* of TEA versus I plot at 25 °C. ○ Experimental points, ▲ pK^* calculated from Eq. (*19*), —— pK^* calculated from Eq. (*22*)

pK^* as a Function of Temperature

The stoichiometric equilibrium constant was determined at five different temperatures between 16 and 44 °C and an ionic strength of 0.5 mol dm^{-3} (see Table IV). TEA was found to conform accurately to the Perrin equation[13] for the protonation of organic bases

$$-\frac{\mathrm{d}(\mathrm{p}K_\mathrm{a})}{\mathrm{d}T} = \frac{(\mathrm{p}K_\mathrm{a} - 0.9)}{T}\,. \tag{25}$$

In fact, the value of the constant obtained from the previous equation, 0.023, is quite consistent with the reported value for temperatures above 25 °C (0.024).

Also, pK^* values were fitted to the following two temperature functions that were developed by Harned and Owen[14]

$$\text{Model 1} \qquad -\log K = A/T + B + CT \tag{26}$$

$$\text{Model 2} \qquad -\log K = A/T + B + D\log T\,. \tag{27}$$

The values of parameters A, B, C and D for each model are given in Table V, together with the fitting error, according to which both models are acceptable for calculating the pK^* values over the stated temperature range.

The above equations were used to derive expressions for the standard free energy, enthalpy and entropy changes as a function of temperature:

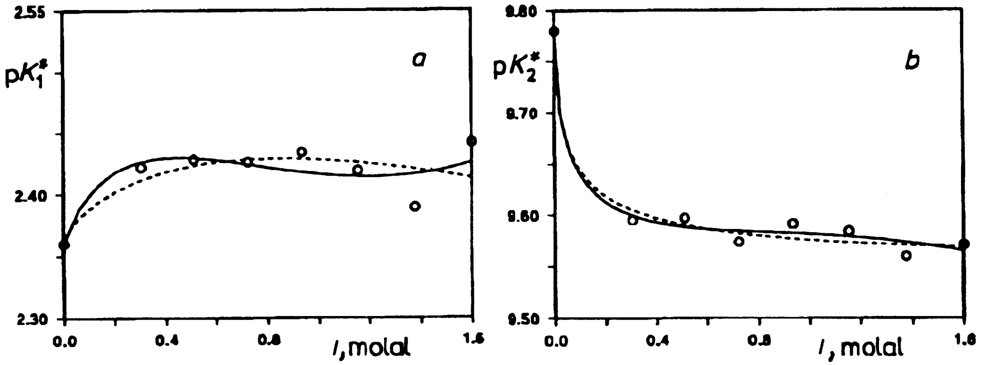

FIG. 2

pK_1^* (*a*) and pK_2^* (*b*) of glycine versus I at 25 °C. O Experimental points, —— pK^* calculated from Eqs (*20*), (*23*), – – – pK^* calculated from Eqs (*21*), (*24*)

Model 1

$$\Delta G = -75\,728.2 + 786.4561\,T - 1.2782\,T^2 \tag{28}$$

$$\Delta H = -75\,728.2 + 1.2782\,T^2 \tag{29}$$

$$\Delta S = -786.5 + 2.5564\,T \tag{30}$$

Model 2

$$\Delta G = -193\,193.8 + 5\,215.376\,T - 1\,784.605\,T \log T \tag{31}$$

$$\Delta H = -193\,193.8 + 775.0442\,T \tag{32}$$

$$\Delta S = -4\,440.331 + 1\,784.605 \log T\,. \tag{33}$$

The values of these quantities at 25 °C are listed in Table V. As expected, they were somewhat different from those reported for a zero ionic strength, viz. $\Delta H^0 = 34$ kJ mol^{-1} and $\Delta S^0 = -35$ J mol^{-1} K^{-1} (ref.[15]).

TABLE V

Numerical values of the constants of Eqs (*26*) and (*27*) obtained over the temperature range 16 – 44 °C and thermodynamic constants of TEA in 0.5 mol dm^{-3} KCl at 25 °C

Model No.	A	B	C	D	$\Delta G^{0\,a}$	$\Delta H^{0\,a}$	$\Delta S^{0\,b}$
1	-3 957.682	41.102	-0.0668	–	45.13	37.78	-24.7
2	-10 096.63	272.564	–	-93.266	45.17	37.77	-24.8

^{a} kJ mol^{-1}; ^{b} J mol^{-1} K^{-1}.

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