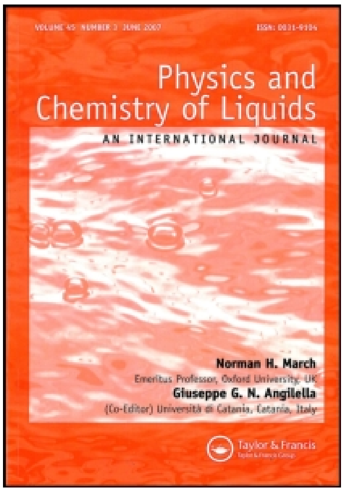

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# Standard Potentials of Silver, Silver Chloride Electrode and Protonation of Tris (Hydroxy Methyl) Amino Methane in Water-Pyridine Mixtures

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# STANDARD POTENTIALS OF SILVER, SILVER CHLORIDE ELECTRODE AND PROTONATION OF TRIS (HYDROXY METHYL) AMINO METHANE IN WATER–PYRIDINE MIXTURES

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The protonation behaviour of Tris(hydroxy methyl)amino methane was investigated in water–pyridine mixtures up to 30 wt% pyridine using the cell

$$\text{Pt, } H_2(\text{g, 1 atm})\ \text{Tris HCl}(m_1)\text{Tris}(m_2)\text{AgCl}(s)\text{Ag} \\ \text{in solvent mixture}$$

at 30°C. The $pK_{BH^+}$ of Tris $H^+$ decreases gradually with increasing composition of pyridine and this variation has been rationalised in terms of solute–solvent interactions in these mixtures through the relation

$$\Delta pK = pK_{BH^+(s)} - pK_{BH^+(w)} = \Delta G^0_{t(\text{salt})}$$
$$= \Delta G^0_{t(B)} + \Delta G^0_{t(H^+)} - \Delta G^0_{t(BH^+)}$$

where the subscripts *s* and *w* represent the solvent mixture and water respectively and $\Delta G_t^0$'s represent the Gibbs energies of transfer of the various species from water to water–pyridine mixtures.

KEY WORDS: Tris(hydroxymethyl)amino methane, protonation, water–pyridine mixtures.

An understanding of the phenomena of solution chemistry will be possible only when solute–solute, solute–solvent and solvent–solvent interactions are completely elucidated. Theoretical treatment[1,2] of these processes is hampered by incomplete knowledge of the electrostatic forces in the immediate vicinity of solvated ions and by an inadequate model of the hydrogen bonded solvents[3]. However, experimental approaches which depend on evaluating the effect of changing solvent composition on acid–base dissociation equilibria involving acids of different charge type can offer some guidance[4,5]. Especially, the effect of solvent on dissociation equilibria of cationic acids like $BH^+$

$$BH^+ \rightleftharpoons B + H^+ \tag{1}$$

will provide valuable information on specific solute–solvent interactions in mixed solvents because the effect due to the differences in dielectric constant of the solvent mixtures may be expected to be small. As part of a program of work dealing with the selective solvation of silver(I), Cu(II) salts in water–pyridine mixtures by various electrochemical methods[7,8], the protonation behaviour of Tris was studied as a probe to elicit the nature of ion–solvent and solvent–solvent interactions in these mixtures.

## EXPERIMENTAL AND RESULTS

### a) *Materials*

Pyridine (GR, BDH) was purified following the procedure of Vogel[9]. It was kept over KOH pellets for 24 hours, decanted and refluxed over the same for 12 hours and distilled. The middle fraction boiling at 115°C, was collected and stored over fresh KOH pellets.

Fresh double distilled water was distilled in presence of a few $KMnO_4$ crystals and NaOH pellets in an all glass apparatus and stored out of contact with air.

Tris (AR, BDH) having a purity greater than 99.8%, was dried at 105°C and preserved under vacuum over anhydrous $CaCl_2$ until use.

### b) *Methods*

The method of generation of HCl, its dissolution and standardisation, the preparation of hydrogen[10] and silver–silver chloride electrodes[11] has been described previously.

A K5 potentiometer (Leeds and Northrup, USA) capable of measuring the EMF to within ±0.01 mV was used in all EMF measurements. A Kiethley solid state electrometer (Model 620) was used as null detector in all EMF measurements.

To evaluate the Gibbs transfer energy of the salt, the solubility of Tris in various compositions of water–pyridine mixtures was determined at 30°C and the saturated solutions of the salt for this purpose were prepared as described earlier[12]. After saturation, the solution is centrifuged and a known amount of the clear, supernatant liquid was taken in a porcelain crucible and evaporated carefully to dryness at 120°C in an air oven. It was then cooled to room temperature and weighed. This procedure was repeated until the residue attained a constant weight.

### c) *Procedure for determination E° of Ag–AgCl electrodes in water-pyridine mixtures*

To calculate the $pK_{BH^+}$ of Tris $H^+$, the standard electrode potential of Ag–AgCl electrode in water–pyridine mixtures is necessary for which the data is not available in literature. The following cell

$$\begin{array}{l|l|l}\text{Pt, } H_2(\text{g, 1 atm}) & \text{HCl}(m_1) & \text{AgCl, Ag} \\ & \text{in the given} & \\ & \text{solvent mixture} & \end{array} \qquad \text{(I)}$$

was set up and its EMF is given by

$$E = E_m^0 - 2k \log m \pm -2k \log \gamma_\pm \qquad (2)$$

**Table 1** Physical constants and other data of water–pyridine mixtures at 30°C.

| *Wt% Py* | *D* | *A* | $B \times 10^{-8}$ | $d_0$ | $M_{xy}$ |
|---|---|---|---|---|---|
| 5 | 76.0 | 0.5219 | 0.3313 | 0.9965 | 18.7 |
| 10 | 73.5 | 0.5487 | 0.3369 | 0.9975 | 19.5 |
| 20 | 69.5 | 0.5968 | 0.3465 | 0.9988 | 21.3 |
| 30 | 64.0 | 0.6753 | 0.3610 | 1.0000 | 23.4 |

$D$ = Dielectric constant.
$A$ and $B$ = Debye–Hückel constants (molal scale).
$d_0$ = density of the solvent mixture (g cm$^{-3}$).
$M_{xy}$ = mean molecular weight of the solvent, calculated from

$$M_{xy} = \frac{100}{[(x/M_x) \pm (y/M_y)]}$$

where $x$ and $M_x$, $y$ and $M_y$ are the weight percent compositions and the molecular weights of pyridine and water respectively.

where $k = 2.303\ \mathrm{RT/F}$, $m_\pm$ and $\gamma_\pm$ are the mean molality and activity coefficient of the acid. Substituting Huckel's equation for $\gamma_\pm$ (molal scale) in Eq. (2), we get

$$E^0_m = E + 2k \log m - [2kAm^{1/2}d_0^{1/2}/(1 + aBm^{1/2}d_0^{1/2})] \\ - 2k \log(1 + 0.002\, m\, M_{xy}) + 2k\, \beta m \quad (3)$$

Representing the first four terms on the R.H.S. of Eq. (3) as $E^{0'}_m$, we get

$$E^{0'}_m = E^0_m - 2k\, \beta m = E^0_m + f(m) \quad (4)$$

In Eq. (3), $A$ and $B$ are Debye–Hückel constants on molal scale, $d_0$ is the density of the solvent mixture, $a$ is the ion size parameter, $\beta$ is an empirical constant and $M_{xy}$ is the mean molecular weight of the solvent mixture. All these constants are recorded in Table 1. The EMF data of cell I at various concentrations of the acid are given in Table 2. The function $E^{0'}_m$ was calculated at different molalities of acid and a plot

**Table 2** EMF data of cell I in water–Py mixtures at various molalities of HCl at 30°C.

| $m_{HCl}$/*mol kg*$^{-1}$ | *EMF/V* *Wt% Py* | | | |
|---|---|---|---|---|
| | *5* | *10* | *20* | *30* |
| 0.008 | 0.76303 | 0.76657 | 0.75561 | 0.73259 |
| 0.010 | 0.75193 | 0.75535 | 0.74341 | 0.72177 |
| 0.012 | 0.74241 | 0.74828 | 0.73977 | 0.71549 |
| 0.015 | 0.73372 | 0.73636 | 0.73065 | 0.70605 |
| 0.018 | 0.72474 | 0.72684 | 0.72378 | 0.70109 |
| 0.025 | 0.70642 | 0.71245 | 0.71114 | 0.69454 |

EMF values are accurate to within ±0.05 mV.

**Table 3** Standard electrode potentials, ${}_sE^0_m$ of silver–silver chloride electrode and the standard Gibbs transfer energies of HCl (molal scale) in water–Py mixtures at 30°C.

| *Wt% Py* | ${}_sE^0_m/V$ | $\Delta G^0_t(HCl)/kJ\ mol^{-1}$ [a] |
|---|---|---|
| 0 | 0.2190 | 0.0 |
| 5 | 0.5059 | −27.7 |
| 10 | 0.5085 | −27.9 |
| 20 | 0.4916 | −26.3 |
| 30 | 0.4667 | −23.9 |

[a] $\Delta G^0_t(\mathrm{HCl}) = -F({}_sE^0_m - {}_wE^0_m)$.

**Table 4** EMF data of cell (II) for the determination of dissociation constant ($pK_{BH^+}$) of Tris H$^+$ in water–Py mixtures at 30°C.

| *Concn. of Tris HCl/mol kg$^{-1}$* | *Concn. of Tris/ mol kg$^{-1}$* | *E/V* | $pK'_{BH^+}$ | $pK_{BH^+}$ |
|---|---|---|---|---|
| | | *5 Wt% Py* | | |
| 0.008 | 0.008 | 0.81853 | 3.01 | 2.99 |
| 0.010 | 0.010 | 0.81239 | 2.99 | |
| 0.012 | 0.012 | 0.81017 | 3.02 | |
| 0.015 | 0.015 | 0.80190 | 2.97 | |
| 0.018 | 0.018 | 0.80028 | 3.01 | |
| 0.025 | 0.025 | 0.79395 | 3.02 | |
| | | *10 Wt% Py* | | |
| 0.008 | 0.008 | 0.81427 | 2.89 | 2.88 |
| 0.010 | 0.010 | 0.80857 | 2.88 | |
| 0.012 | 0.012 | 0.80580 | 2.90 | |
| 0.015 | 0.015 | 0.80209 | 2.92 | |
| 0.018 | 0.018 | 0.79690 | 2.90 | |
| 0.025 | 0.025 | 0.78929 | 2.91 | |
| | | *20 Wt% Py* | | |
| 0.008 | 0.008 | 0.78535 | 2.68 | 2.62 |
| 0.010 | 0.010 | 0.78438 | 2.75 | |
| 0.012 | 0.012 | 0.78252 | 2.79 | |
| 0.015 | 0.015 | 0.78066 | 2.84 | |
| 0.018 | 0.018 | 0.77766 | 2.85 | |
| 0.025 | 0.025 | 0.77444 | 2.99 | |
| | | *30 Wt% Py* | | |
| 0.008 | 0.008 | 0.76645 | 2.77 | 2.60 |
| 0.010 | 0.010 | 0.76048 | 2.75 | |
| 0.012 | 0.012 | 0.75833 | 2.78 | |
| 0.015 | 0.015 | 0.75768 | 2.85 | |
| 0.018 | 0.018 | 0.75617 | 2.89 | |
| 0.025 | 0.025 | 0.75520 | 2.98 | |

of $E_m^{0'}$ against $m$ of the acid was made in various compositions of solvent mixtures. The plots are found to be linear and on extrapolation to zero molality of acid gave $E_m^0$ in different compositions. The ion size parameter $a = 5A°$ for HCl was used in these calculations and the density data was taken from literature. The standard potentials and Gibbs energies of transfer of the acid from water to water–pyridine mixtures are given in Table 3.

d) *EMF measurements for determination of* $pK_{BH^+}$

The following cell was set up for this purpose.

$$\begin{array}{l|l|l}
\text{Pt, } H_2(\text{g, 1 atm}) & BH^+Cl^-(m_1)B(m_2) & \text{AgCl, Ag} \\
 & \text{in the given} & \\
 & \text{solvent mixture} &
\end{array} \qquad \text{(II)}$$

where BHCl and B represent Tris HCl and Tris respectively.

A stock solution of Tris ($\approx 0.1$ m) was prepared in the desired solvent mixture and its strength was determined by titration against the standard aqueous HCl using methyl red as indicator. A stock solution of Tris HCl was prepared by weight by adding a solution of Tris of known strength to a solution of HCl in the same solvent mixture such that the ratio of Tris $H^+$ and Tris is exactly 1:1. Experimental solutions of known ionic strengths were prepared by dilution of stock solution of Tris and Tris HCl by weight with solvent mixture of the same composition. The details of the experimental cell and the procedure adopted for EMF measurements are reported earlier[13].

No EMF measurements were possible beyond 30 wt% Py due to the deterioration of the coating of platinum black on the hydrogen electrode and the consequent drift of EMF with time.

The EMF data of cell II at various molalities of Tris and Tris HCl in different solvent mixtures are given in Table 4. The ionic strength was varied from 0.08 to 0.025. The EMF of the cell $B$ is given by

$$E = {}_sE_m^0\text{, AgCl, Ag} + 2.303\ RT|F[pK_{BH^+} - \log(m_1/m_2) - \log m_3 + 2A\mu^{1/2} - \beta\mu] \qquad (5)$$

where ${}_sE_m^0$, AgCl, Ag is the standard potential of Ag, AgCl electrode in the given composition of solvent mixture (molal scale), $m_1$, $m_2$ and $m_3$ are molalities of Tris $H^+$, Tris and $Cl^-$ ions, $\mu$ is the ionic strength and $A$ is the Debye–Hückel constant of the equation for activity coefficient, and $\beta$ is a constant. In the present case, $m_1 = m_2 = m_3$ and on rearranging, we get

$$pK'_{BH^+} = \frac{E - {}_sE_m^0\text{, AgCl, Ag}}{2.303\ RT/F} + \log m_3 + \log(m_1/m_2) - 2\ A\mu^{1/2}$$

$$= pK_{BH^+} - \beta\mu \qquad (6)$$

**Table 5** Solubility ($S$) and Gibbs transfer energy (kJ mol$^{-1}$) data (molal scale) of Tris ($B$) in water–Py mixtures at 30°C.

| *Wt % Py* | *S/mol kg$^{-1}$* | $\Delta G_t^0(B)/kJ\ mol^{-1}$ |
|---|---|---|
| 0 | 6.682 | 0.00 |
| 5 | 6.610 | 0.03 |
| 10 | 6.534 | 0.06 |
| 20 | 6.211 | 0.18 |
| 30 | 5.479 | 0.50 |
| 40 | 4.501 | 1.0 |
| 50 | 3.590 | 1.6 |
| 70 | 1.679 | 3.5 |
| 90 | 0.435 | 6.9 |
| 100 | 0.079 | 11.2 |

Solubility values are accurate to ±0.2%. $\Delta G_t^0$ values are accurate to ±0.05 kJ mol$^{-1}$.

Plots of $pK'_{BH^+}$ against $\mu$ were made in all compositions and are found to be linear which on extrapolation to $\mu = 0$ gave $pK_{BH^+}$. The $pK'_{BH^+}$ and $pK_{BH^+}$ data are also given in Table 4.

The solubility and the standard Gibbs energy of transfer of Tris (from water to water-pyridine mixtures) calculated from

$$\Delta G_t^0(B) = 2.303\ \mathrm{RT} \log \frac{S_B(W)}{S_B(S)} \tag{7}$$

[$S_B(W)$ = solubility in water; $S_B(S)$ = Solubility in mixed solvent] are recorded in Table 5.

## DISCUSSION

It is seen that the $pK_{BH^+}$ values of Tris H$^+$ are positive throughout and decrease continuously with the addition of Py up to 30 wt% Py. Similar variation is noted for Tris H$^+$ in water–methanol[14], water–propionamide[15], water–propylene glycol[16] and water-DMF mixtures[17]:

Considering the difference ΔpK, we can write

$$\Delta pK = pK_{BH^+}(s) - pK_{BH^+}(w) = \frac{1}{2.303\ \mathrm{RT}} [\Delta G_t^0(\mathrm{H}^+) + \Delta G_t^0(\mathrm{B}) - \Delta G_t^0(\mathrm{BH}^+)] \tag{8}$$

$$= \frac{1}{2.303\ \mathrm{RT}} [\Delta G_t^0(\mathrm{HCl}) + \Delta G_t^0(\mathrm{B}) - \Delta G_t^0(\mathrm{BHCl})] \tag{9}$$

**Table 6** Standard Gibbs transfer energies (kJ mol$^{-1}$) of various species involving Tris from water to water–Py mixtures at 30°C (molal scale).

| *Wt% Py* | $\Delta G^0_{t(\mathrm{diss})}$ | $\Delta G^0_{t(B)}$ | $\Delta G^0_{t(\mathrm{HCl})}$[a] | $\Delta G^0_{t(\mathrm{H^+})}$[b] | $\Delta G^0_{t(\mathrm{Cl^-})}$[c] | $\Delta G^0_{t(\mathrm{BH^+})}$[d] | $\Delta G^0_{t(\mathrm{BHCl})}$ | $\Delta G^0_{t(B)} - \Delta G^0_{t(\mathrm{BHCl})}$ |
|---|---|---|---|---|---|---|---|---|
| 0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5 | −28.7 | 0.03 | −27.7 | −25.5(−29.0) | −2.2 | 3.23 | 1.0 | −0.97 |
| 10 | −29.3 | 0.06 | −27.9 | −28.1(−32.2) | 0.2 | 1.26 | 1.5 | −1.4 |
| 20 | −30.8 | 0.18 | −26.3 | −28.2(−35.4) | 1.9 | 2.78 | 4.7 | −4.5 |
| 30 | −30.9 | 0.50 | −23.9 | −29.3(−38.0) | 5.4 | 2.10 | 7.5 | −7.0 |

[a] by EMF method from the present work.

[b] by nLJP method from Ref. 18. Values in parentheses are those based on Foc-Fic$^+$ method.

[c] $\Delta G^0_{t(\mathrm{Cl^-})} = \Delta G^0_{t(\mathrm{HCl})} - \Delta G^0_{t(\mathrm{H^+})}$.

[d] $\Delta G^0_{t(\mathrm{BH^+})} = \Delta G^0_{t(B)} + \Delta G^0_{t(\mathrm{H^+})} - \Delta G^0_{t(\mathrm{diss})}$.

$\Delta G^0_t$ values are accurate to ±0.05 kJ mol$^{-1}$.

where $\Delta G^0_t(i) = G^0_i(s) - G^0_i(w)$ and represents the standard Gibbs energy of transfer of $i$ from water to water–Py mixture. $\Delta G^0_t(\mathrm{BHCl})$ and $\Delta G^0_t(\mathrm{BH^+})$ were evaluated from Eqs. (9) and (8) using $\Delta G^0_t(\mathrm{HCl})$ from Table 3 and $\Delta G^0_t(\mathrm{H^+})$ from the work of Brisset[18] based on nLJP method. All these data are given in Table 6.

It is seen that $\Delta G^0_t(\mathrm{diss})$ is negative and decreases continuously with the addition of Py. This indicates that equilibrium (1) is more favoured to the right in water + Py mixtures than in water. The variation of $\Delta G^0_t(\mathrm{diss})$, which is a composite function of $\Delta G^0_t(\mathrm{HCl})$ and $\Delta G^0_t(\mathrm{B}) - \Delta G^0_t(\mathrm{BHCl})$ is governed by the relative magnitudes of the two quantities, the dominant factor being $\Delta G^0_t$ (HCl) in view of the small values of $\Delta G^0_t(\mathrm{B}) - \Delta G^0_t(\mathrm{BHCl})$.

The $\Delta G^0_t(\mathrm{B})$ of Tris is positive and increases with the addition of Py indicating that the transfer of Tris from water to the mixed solvent is not favourable. This can be rationalized as follows. Addition of Py to water breaks the three dimensional network of water and intercomponent H-bonded complexes between Py and $H_2O$ of the type Py.n$H_2O$ are formed[19]. These H-bonded complexes are more basic than water because the lone pair of electrons on N atom in Py enhances the negative charge density on the oxygen of water molecule. Also, pure Py is known to be more basic than water[20]. Tris is most presumably solvated through the N-atom of $-NH_2$ group and the hydrogen bridge forming H atoms supplied by the solvent molecules and the strength of the H-bonding is largely guided by the relative charge densities on the oxygen and hydrogen charge centers of isolated dipoles.

The protonic character of H-atom in water is more than that in Py (i.e. ${}_w\partial^+ > {}_{Py}\partial^+$) or Py.n$H_2O$ complexes since the solvation of Tris through H-bond formation between the lone pair of electrons of $-NH_2$ group and the H-atom of solvent dipoles having the stronger protonic character i.e. with the H-atoms of water dipoles is favoured, its solubility will be expected to decrease with the addition of Py. Thus the small positive $\Delta G^0_t(\mathrm{B})$ values arise due to decreasing H-bond availability for Tris because of formation of Py.n$H_2O$ complexes. Although the participation of the three terminal $-OH$ groups of Tris in H-bond formation with the H-atoms or water molecules is possible, this effect will be less important as the proportion of Py in mixed solvent increases.

The $\Delta G_t^0(H^+)$ of proton is negative throughout and decreases continuously indicating that it is in a lower free energy state in mixed solvent than in water. This is due to the increased basicity of water–Py mixtures than water as mentioned earlier.

The $\Delta G_t^0(BH^+)$ is positive, passes through a maximum around 5 wt% Py, decreases up to 10 wt% Py and then remains constant with a slight increase at 20 wt% Py. However, the protonated base is better stabilized in water than in the mixed solvent. Tris H$^+$ undergoes solvation through (i) the terminal $-OH$ groups with water and (ii) the H-atom attached to the positively charged N-atom ($-\overset{+}{N}H_3$) with more negatively charged oxygen center of the Py.n$H_2O$ complex. It appears that at higher compositions of water, the first type of interaction predominates while second type interaction is dominant beyond 20 wt% Py.

The $\Delta G_t^0(BHCl)$ values are positive and increase with increasing proportion of Py which shows that Tris HCl is better stabilised in water than in water–Py mixtures. The cumulative effect of the different variations of $\Delta G_t^0(Cl^-)$ and $\Delta G_t^0(BH^+)$ leads to the observed change in $\Delta G_t^0(BHCl)$ in which the large $\Delta G_t^0(Cl^-)$ beyond 10 wt% Py contributes significantly. The large positive values of $\Delta G_t^0(Cl^-)$ arise due to its destabilisation from decreasing hydrogen bond availability from water molecules as Py competes with Cl$^-$ ions for forming H-bonds with water.

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