SOLVENT EFFECTS ON THE PROTONATION OF TRIS — (HYDROXY METHYL) AMINO METHANE IN WATER PROPYLENE GLYCOL MIXTURES FROM E.M.F. MEASUREMENTS

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The protonation behaviour of Tris in water-propylene glycol (P.G) has been investigated as 25° C by an EMF method involving a cell without liquid junction. The free energy of transfer of different species from water to water-PG mixed solvents are computed.

Tris is widely used as a buffer in the pH range 7.3 to 8.7 which is very important in the study of physiological processes <1,2>. Acid base equilibria involving Tris are, therefore, of considerable importance. Although some equilibria have been investigated to understand solute-solvent interactions in water - PG mixtures, no work involving Tris has yet been reported. The results of such study are reported here.

EXPERIMENTAL

Tris (B.D.H., A.R) was dried at 105° C and stored in vacuum desciccator before use. Propylene glycol and water, used for making solvent mixtures, were purified as described previously <3>. Solutions of HCl in the desired solvent mixtures, Silver - Silver chloride and Hydrogen electrodes were prepared by the procedure given earlier <3>. All EMF measurements were made at 25 ± 0.1° C by circulating water from an ultracryostat (Messgerate Work Lauda, West Germany). An EMF method (employing a Leeds and Northyup K 3 potentiometer) was adopted and measurements were made on the cell

$$Pt, H_2(g)/BH^+\ Cl^-(m_1), B(m_2)/AgCl, Ag \quad \ldots (1)$$

(1 atmos) in the given solution.

to study the dissociation equilibrium of Tris H^+ in water - PG mixtures. BHCl and B in the above cell represent Tris HCl & Tris respectively.

A stock solution of Tris was prepared in the solvent mixture and was standardised in the usual way. Solutions were prepared by weight, mixing HCl and Tris such that their ratio is 1:1 i.e. neutralisation is complete. The experimental solutions of suitable ionic strength (μ) were then prepared, by diluting and mixing stock solutions of Tris and Tris HCl by weight with the solvent mixtures of same composition. The procedure for EMF measurements is the same as described already <3>. Saturation solubility of Tris in different solvent mixtures was determined at 25 ± 0.1° C, by the usual procedure and the solubility vlaues were found to be accurate to within ± 1%.

RESULTS

The EMf data of cell (1) at various molalities of Tris and Tris HCl on a series of water - PG mixtures are recorded in Table 1. The ionic strength was maintained between 0.005 to 0.1. Assuming that Tris HCl is completely dissociated and that correction due to solvolysis of Tris is negligible, the pK values in all the solvent mixtures at 25° C, were obtained by plotting the function pK'_{BH^+} defined by the equation (2).

$$pK'_{BH^+} = \frac{E - (\delta E^\circ)}{2.303\ RT/F} + \log m_3 + \log \frac{m_1}{m_2} - ZA\mu^{1/2}$$

$$= pK_{BH^+} - B\mu \quad \ldots\ldots\ldots (2)$$

against μ and extrapolating to $\mu = 0$. In equation (2), δE°_m is the standard potential of Ag-AgCl in the given solvent. m_1 m_2 and m_3 are the molalities of Tris H^+, Tris and Cl^- respectively. 'A' the Debye-Huckel constant and β is a constant.

The plots of L.H.S. of equation (2) against 'μ' in various solvent mixtures (Fig.1) are fairly linear in all solvent compositions and the intercepts at μ=0, gave the corresponding pK^{BH^+} values. The $pK^m_{BH^+}$ values obtained above have been converted to $pK^N_{BH^+}$ using the relation <4>.

TABLE 1

E.M.F DATA OF CELL (1) FOR THE DETERMINATION OF pK OF TRIS H^+ IN WATER - PG MIXTURES AT 25 C (B = Tris ; X = wt. % PG)

Conc. in moles/Kg Tris HCl	Tris	E.M.F. of cell(2) E/V	pk'_{BH^+}
	X = 20		
0.00595	0.00465	0.81175	8.01
0.01036	0.01022	0.80697	8.04
0.01970	0.02155	0.79769	8.07
0.03005	0.02962	0.78537	8.05
0.04126	0.03918	0.77853	8.05
0.05054	0.05000	0.77520	8.04
0.05996	0.05807	0.76998	8.02
0.08239	0.07929	0.76365	8.00
	Average value		8.05
	X = 40		
0.00538	0.00579	0.80540	7.96
0.01048	0.01036	0.79087	8.00
0.01988	0.02005	0.78092	8.04
0.02965	0.03024	0.77214	8.01
0.03880	0.04145	0.76764	8.00
0.04969	0.05070	0.76205	8.00
0.05969	0.06118	0.75798	7.97
0.07912	0.08104	0.75257	7.95
	Average value		8.01
	X = 75		
0.00780	0.00903	0.75894	7.89
0.00978	0.01005	0.75350	7.93
0.01905	0.02106	0.74967	8.02
0.02980	0.02964	0.74188	8.04
0.04037	0.03842	0.73596	8.02
0.05027	0.04887	0.73302	8.00
0.07913	0.08104	0.72715	7.93
0.08959	0.08983	0.72598	7.93
	Average value		7.98
	X = 90		
0.00579	0.00597	0.73440	8.28
0.00803	0.00815	0.73338	8.37
0.00986	0.01005	0.73264	8.41
0.01930	0.01937	0.72376	8.42
0.02356	0.02141	0.71694	8.38
0.02954	0.02887	0.71668	8.38
0.03869	0.03595	0.71668	8.34
0.04963	0.04790	0.71141	8.35
0.06953	0.06917	0.70948	8.27
0.07550	0.08013	0.70889	8.27
	Average value		8.39

*pK data accurate to with in ± 0.02 units.

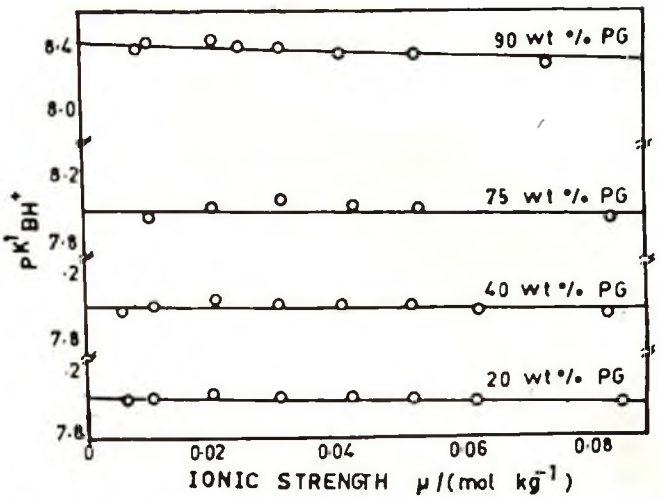


Fig. 1 Plots of pK'_{BH^+} (eqn.V.4) vs ionic strength, u in water - PG mixtures at 25° C for the evaluation of pK_{BH^+} (B=Tris)

TABLE 2

pK DATA OF TRIS H^+ IN MOLAL AND MOLE FRACTION SCALE IN WATER - PG MIXTURES AT 25 C

Weight % PG	$pK^m_{BH^+}$	$pK^N_{BH^+}$	$\Delta pK^m_{BH^+}$
0 (Ref-10)	8.08	9.82	0
20	8.05	9.72	- 0.03
40	8.01	9.60	- 0.07
75	7.98	9.36	- 0.10
90	8.39	9.63	+ 0.31
100 (Ref-7)	10.50	11.62	+ 2.42

* $\Delta pK^m_{BH^+}$ ' = $(pK^m_{BH^+})_S$ - $(pK^m_{BH^+})$

TABLE 3

SOLUBILITY AND TRANSFER FREE ENERGY DATA (MOLAL SCALE) OF TRIS IN WATER - PG MIXTURES AT 25° C. (as per equation 4)

Weight % PG	Solubility of Tris in mol/Kg	ΔGt (Tris)* J/mole
0 (Ref-10)	5.892	-
20	2.837	1812
40	2.299	2333
75	1.165	4018
90	0.6475	5475
100 (Ref-7)	0.4646	6298

* Values accurate to within ± 60 J/mole

$$pK^{N}_{BH^+} = pK^{m}_{BH^+} + \log \frac{1000}{M_{xy}} \quad \text{---} \quad (3)$$

where M_{xy} is the mean molecular weight of the solvent. All the data are given in Table 2.

The standard Gibbs energy of transfer of the base from water to mixed solvents, have been calculated from the solubility data of Tris (Table 3) using the relation.

$$\Delta G^{\circ}_{t(B)} = 2.303\ RT.\ \log \frac{S_{B(w)}}{S_{B(S)}} \quad \text{---} \quad (4)$$

where $S_{B(w)}$ and $S_{B(s)}$ represent the solubilities of Tris in water and solvent mixture respectively.

DISCUSSION

An examination of the results of pK_{BH^+} for Tris H^+ (Table II) indicates a slight decrease of pK_{BH^+} intially with the addition of PG which then reaches a minimum at about 75 wt. % PG and subsequently increases upto pure PG.

A comparison of these results with those in Water-Ethylene glycol mixtures<5> shows small differences between the two solvent systems. It is observed in Water-Ethylene glycol(EG) mixtures that the pK of Tris H^+ increases continuously with the addition of EG. However, the variation of pK of Tris H^+ in these mixtures (Water + PG) is similar to that in Water-methanol <6> methanol - PG mixtures <7> as well as to the variation of p_{NAH} and m_{NAH} <8> in water-PG mixtures. The observation of minimum around 75 wt. % PG in these mixtures may possiblity be due to the unusual influence of water <9> on the equilibrium process occuring in these media. Since the reaction

$$\text{Tris } H^+ \qquad \text{Tris} + H^+ \quad \text{-----} \quad (5)$$

is . isoelectric, the variation of pK may not be much influenced by the dielectric constant of the medium. In order to understand the effect of solvent on the equilibrium <3>, an examination of various thermodynamic quantities associated with it is necessary and this is done by considering the difference $(pK^{m}_{BH^+})_s - (pK^{m}_{BH^+})_w$ (where B = Tris) rather than p^{BH} itself. The difference may be expressed by equation(6)

$$(pK^{m}_{BH^+})_s - (pK^{m}_{BH^+})_w = \frac{1}{2.303RT}\left[\Delta G^{\circ}_{t(H)} + \Delta G^{\circ}_{t(B)} - \Delta G^{\circ}_{t(BH)}\right] \ldots (6)$$

Equation (6) may also be expressed in an equivalent from as

$$2.303\cdot RT\ \Delta pK = G^{\circ}_{t(diss)} = \Delta G^{\circ}_{t(HCL)} \quad \Delta G^{\circ}_{t(B)} - \Delta G^{\circ}_{t(BHCl)} \quad \ldots . (7)$$

TABLE 4

THERMODYNAMIC PARAMETERS OF VARIOUS SPECIES INVOLVING TRIS IN WATER - PG MIXTURES AT 25°C ON MOLAL SCALE. ALL VALUES GIVEN IN J.mol . THE G VALUES OF H AND BH IONS ARE THOSE BASED ON TATB METHOD.

Weight % PG	$\Delta G^{\circ}_{t(diss)}$	$\Delta G^{\circ}_{t(B)}$	$\Delta G^{\circ}_{t(BHCl)}$	$\Delta G^{\circ}_{t(BH^+)}$	ΔG^{*}_{change}	$\Delta G^{\circ}_{t(HCl)}$ **	$\Delta G^{\circ}_{t(H^+)}$ *	$\Delta G^{\circ}_{t(Cl^-)}$
20	- 171	1812	3469	-14427	- 1657	1486	-16410	17896
40	- 400	2333	5638	- 9633	- 3305	2905	-12366	15271
75	- 571	4018	11537	- 3677	- 7519	6948	- 8266	15214
90	1770	5475	15912	- 2327	- 10437	12207	- 6032	18239
100	13815	6298	17033	- 1064	- 10735	24550	6453	18097

* Values obtained from the solubilities of references a electrolyte (TATB) on molal Scale - Reference (8)

** Data from reference (3).

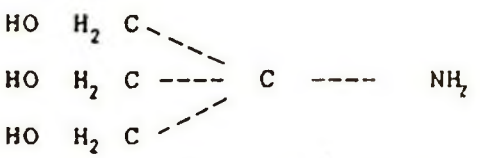
The different thermodynamic quantities i.e. $G^{\circ}_{t(B)}$, $G^{\circ}_{t(diss)}$, $G^{\circ}_{t(BHCl)}$, $G^{\circ}_{t(BH)}$ and $G^{\circ}_{t(B)} - G^{\circ}_{t(BHCl)}$ have been evaluated according to the earlier procedure <5> and the results are given in Table 4. The $\Delta G_{t(H^+)}$ and $\Delta G_{t(Cl^-)}$ are obtained from $\Delta G_{t(HCl)}$ following the procedure mentioned else where <3>. Thsese results are also shown in Table 4.

Variation of $G_{t(diss)}$

An examination of $G_{t(diss)}$ values (Table 4) for Tris H^+ shows a decrease initially with the addition of PG, which sunsequently passes through a minimum at about 75 wt.% PG and then increases attaining a positive value beyond this composition upto pure PG. These results suggest that the equilibrium eq.(5), is favoured (for Tris H^+) in the mixed solvent upto 75% PG as compared to water. From equation<4> it is seen that $\Delta G^{\circ}_{t(diss)}$ is a composite function of $\Delta G^{\circ}_{t(HCl)}$ and $G^{\circ}_{t(B)} - \Delta G^{\circ}_{t(BHCl)}$. While $\Delta G^{\circ}_{t(HCL)}$ increases continuously with the addition of PG, $\Delta G^{\circ}_{t(B)} - \Delta G^{\circ}_{t(BHCL)}$ continuously decreases upto pure PG (Table 4). The minimum observed in $\Delta G^{\circ}_{t(diss)}$ for Tris H^+ may thus be due to the opposite variations of the above two factors, the dominant factor being $\Delta G^{\circ}_{t(B)} - \Delta G^{\circ}_{t(BHCl)}$ upto 75 wt % PG. The large positive $\Delta G^{\circ}_{t(diss)}$ in pure PG possibly arises due to the dominance of $\Delta G_{t(HCl)}$ over $\Delta G^{\circ}_{t(B)} - \Delta G^{\circ}_{t(BHCl)}$

Variation of $G_{t(B)}$:

It is seen that $\Delta G^{\circ}_{t(B)}$ is positive through out and increases continuously with the addition of PG (Table 4) indicating that the transfer process for Tris from water to Water - PG mixtures is not favourable. In the case of Tris, which has the structure



the solvation should largely involve the N - atom of the - NH_2 group and the hydrogen bridge from H - atoms supplied by the solvent molecules. Since it has already been shown <8> that in water - PG mixtures $\partial^{+}_{PG} < \partial^{+}_{W}$, the resulting $\Delta G^{\circ}_{t(B)}$ values should be expected to increase continuously because of the decreased protonic character of H - atoms in the mixed solvents and hence the decreased interactions between the lone pair of electrons on the nitrogen of the - NH group and the H - atoms of the solvent mixtures. Further, the participation of the three terminal - OH groups in Tris molecule in the hydrogen bonded structure of water may play an important role and this hydrogen bonded interaction becomes less important as the proportion of water in the mixed solvent decreases. $\Delta G^{\circ}_{t(B)}$ may therefore be expected to increase on this account also, with the addition of PG.

Variation Of $G^{\circ}_{t(BH^+)}$

It is observed from Table 4, that $\Delta G^{\circ}_{t(BH^+)}$ initially decreases with the addition of PG to Water, reaches a minimum at about 20 wt.% PG and then increases with further addition of PG, the values however being negative throughout. The negative values of $\Delta G^{\circ}_{t(BH^+)}$ indicate that the species BH^+ is better solvated in these mixed solvents although the addition of PG tends to destabilize the solvation of species in the mixed solvent beyond 20 wt. % . It is significant to point out that the variation of $\Delta G^{\circ}_{t(BH^+)}$ of Tris H^+ with the addition of PG is essentially similar to that of $\Delta G^{\circ}_{t(H^+)}$ with the exception that in pure PG, $\Delta G^{\circ}_{t(BH^+)}$ of Tris H^+ is still negative, while $\Delta G^{\circ}_{t(H^+)}$ is positive. In these mixed solvents Tris H^+ is likely to be solvated through the partially protonated H - atoms attached to the nitrogen atom and tthe negatively charged oxygen centres of the solvent dipoles. Since $\Delta^{-}_{PG} > \Delta^{-}_{W}$ in the mixed solvents, the $\Delta G^{\circ}_{t(BH^+)}$ of Tris, should be increasingly negative with the addition of PG. Although, $\Delta G^{\circ}_{t(BH^+)}$ is negative in all Water PG mixtures, the values however, become less negative beyond 20 wt. % PG as observed in the case of $\Delta G^{\circ}_{t(H^+)}$. This is presumably due to the formation of some - bonded clusters between water and PG molecules beyond 20 wt.% PG, which result in a decrease in the number of negative charge centres on the oxygen atoms in the mixed solvents. This results in an increase of $G^{\circ}_{t(BH^+)}$, with increasing proportion of PG beyond 20 wt. % . It appears that the solvation of Tris H^+ through the terminal - OH groups, is not significant in the mixed solvents, whereas the same may be quite large in pure PG which accounts for the negative value of $\Delta G^{\circ}_{t(BH^+)}$ in pure PG.

Variation of $\Delta G^{\circ}_{t(BHCl)}$

It is seen that $\Delta G^{\circ}_{t(BHCl)}$ (Table 4) continuously increases with the addition of PG, the values being positive throughout. This suggests that Tris H(

is in a lower free energy state in water than in the mixed solvents and hence it is better solvated by water than the mixed solvents. The positive values of $\Delta G^{\circ}_{t(BHCL)}$ in the mixed solvents and the significant increase of the same with the addition of PG, may be attributed to the large contribution of $\Delta G^{\circ}_{t(Cl^-)}$ in these mixtures which outweighs the negative $\Delta G^{\circ}_{t(BH^+)}$. The large increase of $\Delta G^{\circ}_{t(BH^+)}$ (ie. the values become less negative) and the relatively smaller variation in $\Delta G^{\circ}_{t(Cl^-)}$ seem to result in a continuous increase of $\Delta G^{\circ}_{t(BHCL)}$ as observed in the present case.

Thus the overall variation of ΔpK, with solvent composition indicates the significant role of specific solute-solvent interactions in these equilibrium processes.

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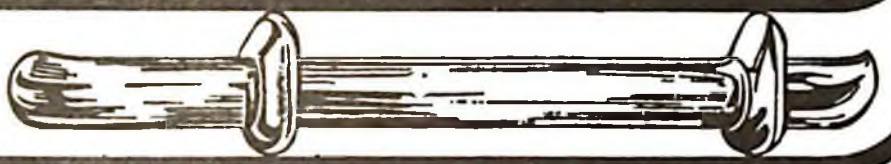
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