

## Review of Study of ion-solvent interaction during determination of deprotonation constant of glycine in 10, 20 and 30% dioxane (m/m) in the dioxane-water system at 288.15K, 298.15K, 308.15K and 318.15K potentiometrically

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### ABSTRACT

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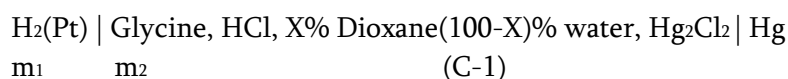
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To study ion-solvent interaction in the system, free energy transfer ( $\Delta G_t$ ) was calculated by determining acidic dissociation of Glycine<sup>1-4</sup> in 10, 20 and 30% dioxane content in dioxane-water system at 288.15K, 298.15K, 308.15K and 318.15K have been studied by measuring e.m.f of the cell:



in 10, 20 and 30% dioxane in dioxane-water system at 288.15K to 318.1K at an interval of 10K and e.m.f. of the cell was give by:

$$E = E^0 - (2.303RT/F) (\log m_{\text{H}^+} m_{\text{Cl}^-} + \log \gamma_{\text{H}^+} \gamma_{\text{Cl}^-}) \quad (1)$$

$$\text{where } \log \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} = - (2A \sqrt{\mu} / (1 + \sqrt{\mu})) + \beta_1 \mu \quad (2)$$

$$\log K_1 - \beta_1 \mu = \log K_1(A) - (2A \sqrt{\mu} / (1 + \sqrt{\mu})) \quad (3)$$

The equation (2) is called Modified Davies equation given by B.Prasad<sup>5</sup> for calculating activity coefficient in the system.

From equation (3), acidic dissociation constant of glycine were calculated by extrapolating the graph at  $\mu=0$  in 10, 20 and 30% dioxane in dioxane-water system from 288.15K to 318.5K at an interval of 10K and then free energy transfer was calculated by the formula:

$$\Delta G_t = 2.30259 RT \Delta p K_1 \quad (4)$$

Where  $\Delta p K_1 = pK_s - pK_w$

S – stand for mean mix solvent

W – stand for water

Keyword: Ion-Solvent Interaction, Free Energy Change, Dielectric Constant, Modified Davies Equation, Acidic Dissociation Constant

## I. INTRODUCTION

To study ion-solvent interaction it is necessary to know free energy transfer; for this purpose acidic dissociation constant has been determined from 288.15K to 318.15K at an interval of 10K in 10, 20 and 30% dioxane (m/m) in dioxane- water system..

Study of variation of acidic dissociation constant of different electrolytes in aqueous and aquo-organic solvent has been topic of great interest and challenging system because on knowing dissociation constant physico-chemical properties of electrolytes can be known. Electrolytes show varying properties in different medium depending upon their nature either singly or in mixed one and aqueous solution<sup>6-7</sup> have extensively studied in comparison to aquo-organic system. It is well established that water is good and exceptional solvent for large number of electrolytes but need of the hour workers to change attention from aqueous to aquo-organic system because to understand the course of the reaction in aquo-organic system<sup>8-14</sup>. When system is changed from water to non-aqueous medium changes have been observed in the reactivity of ions like solubility, oxidation-reduction and acid-base behavior.

Glycine is an important biomolecules; therefore it is very informative to study free energy transfer and thermodynamic quantities in aqueous and aquo-organic system. We have chosen aquo-organic system like dioxane -water system at 288.15K to 318.15K at an interval of 10K.

## II. Result and Discussion

After determining acidic dissociation constant of glycine in 10, 20 and 30% dioxane(m/m) in dioxane-water system from 288.15K to 318.15K at an interval of 10K were calculated and free energy transfer  $\Delta G_t$

was evaluated for the system under consideration for cell C-1 by thermodynamic equation :-

$$\Delta G_t = 2.30259 RT \Delta pK_1 \quad \dots(5)$$

and the values were tabulated in table 1.

Table 1 : - The value of  $pK_1$  and  $\Delta G_t$  in 10, 20 and 30% dioxane(m/m) in dioxane-water system for the given cell C-1 at given range of temperature:

Temp(K)	Mass % dioxane(m/m)					
	10		20		30	
	$pK_1$	$\Delta G_t$	$pK_1$	$\Delta G_t$	$pK_1$	$\Delta G_t$
288.15	2.52	2.872	2.64	4.977	2.79	7.845
298.15	2.45	1.914	2.62	5.169	2.74	7.47
308.15	2.40	1.531	2.60	5.169	2.73	7.657
318.15	2.39	1.34	2.59	5.169	2.71	7.466

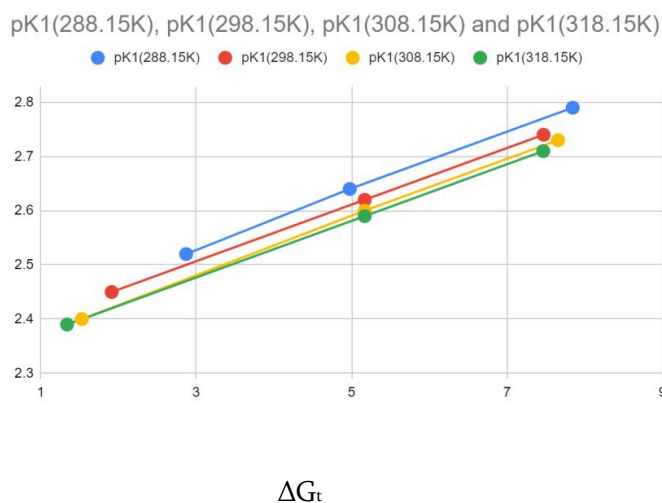


Fig 1 :- Plot between  $pK_1$  and  $\Delta G_t$  in 10, 20 and 30% dioxane (m/m) in dioxane-water system from 288.15 to 318.15K at 10K interval

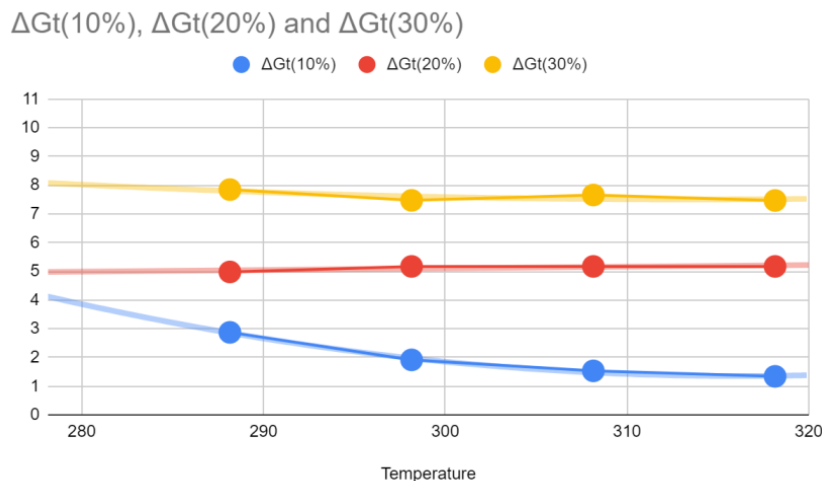


Fig 2

Fig 2 :- Plot between temperature and  $\Delta G_t$  in 10, 20 and 30% dioxane (m/m) in dioxane-water system from 288.15 to 318.15K at 10K interval

Table-2 : Variation of  $pK_1$  against  $1/D \times 10^3$  in 10, 20 and 30% dioxane at 288.15K

% Dioxane(m/m)	$1/D \times 10^3$	$pK_1$
10	13.65747064	2.52
20	15.625	2.64
30	18.26150475	2.79

Table-3 : Variation of  $pK_1$  against  $1/D \times 10^3$  in 10, 20 and 30% dioxane at 298.15K

% Dioxane(m/m)	$1/D \times 10^3$	$pK_1$
10	14.351	2.45
20	16.45	2.62
30	19.268	2.74

Table-4 : Variation of  $pK_1$  against  $1/D \times 10^3$  in 10, 20 and 30% dioxane at 308.15K

% Dioxane(m/m)	$1/D \times 10^3$	$pK_1$
10	15.07840772	2.4
20	17.32201628	2.6
30	20.32933523	2.73

Table-5 : Variation of  $pK_1$  against  $1/D \times 10^3$  in 10, 20 and 30% dioxane at 318.15K

% Dioxane(m/m)	$1/D \times 10^3$	$pK_1$
10	15.84283904	2.39
20	18.23819077	2.51
30	21.45002145	2.71

$pK_1$

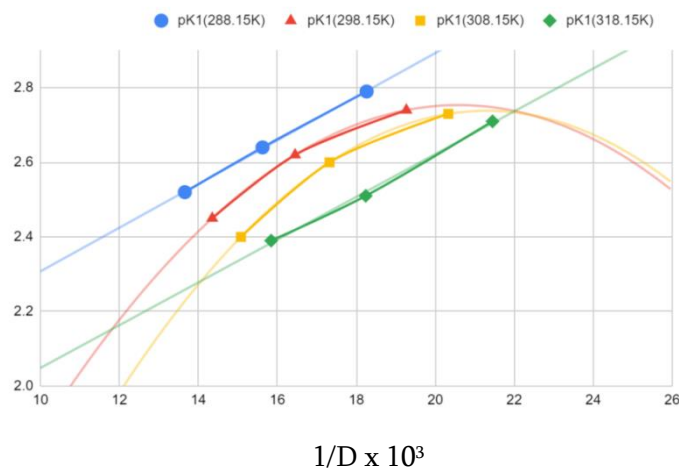


Fig-3 :- Plot of  $pK_1$  against  $1/D \times 10^3$

### Ion solvent Interaction :-

It is evident from table 1, that the value of  $pK_1$ , increases with increase in dioxane-content of dioxane-water system. The results are similar to the results of other workers<sup>13,14,15,16,17,18</sup> in dioxane water system and it is due to lowering of dielectric constant of the medium under consideration but with rise of temperature from 288.15K to 318.15K there is slight decrease in the  $pK_1$  value which is in agreement with observation of Harned<sup>19</sup>. Slight decrease in  $pK_1$  and  $\Delta G_t$  values with increase in temperature and the sharp increase in  $pK_1$  and  $\Delta G_t$  values with increase in dioxane content in dioxane water system as evident from the Fig 1. This may be due to existence of glycine in zwitter ion form. Hence, there is possibility of solute-solvent interaction between glycine and dioxane and perhaps positive end of the zwitter ion interact with the oxygen atom of dioxane and probably large number of dioxane molecules are involved in forming layered structure with glycine molecules and so no further decrease in dielectric constant. Further, it is evident from the table 1 that there is large increase in  $pK_1$  value with increase in dioxane content in dioxane-water system and smaller decrease in  $pK_1$  value with rise in temperature. This may be due to existence of glycine in "zwitter ion" form. Hence, increase in temperature favors dissociation of glycine. This reason may be taken into

account to explain the decrease in the  $pK_1$  values of glycine with rise in temperature. Therefore, dielectric constant of the medium plays dominating role and temperature least in dissociation of glycine.

Further to study ion-solvent interaction  $pK_1$  against  $1/D \times 10^3$  has been plotted and it is evident from the Fig 2 and straight line has been found at 288.15K and 318.15K indicating least ion solvent interaction between glycine and dioxane whereas curvature observed for 298.15K and 308.15K means greater ion-solvent interaction.

**Free energy and ion-solvent interaction :-** Free energy transfer from water to aquo-organic solvent is measure of ion-solvent interaction and free energy transfer can be calculated by thermodynamic equation (4) and the purpose of calculating free energy transfer is mainly study of effect of aquo-organic solvent upon structure of zwitter - ion and may be used for purification and separation of amino acids.

The free energy transfer of cations and anion from water to aquo-organic system are usually negative and positive respectively.<sup>20-22</sup>

From Born<sup>23</sup> or modified Equation<sup>24,25</sup> the role of solvent on the ionisation of weak acid and weak base is not clearly understood. Hence, in such circumstances the problem is extremely complicated in case zwitter ions upon addition of 10 to 30% dioxane content in dioxane-water system.

The nature of solute-solvent interaction can be explained by free energy transfer. It is clear from table 2, that free energy transfer of glycine increases with increase in dioxane content and this may be due to structural change from zwitter - ion to neutral glycine molecule but this is least probable.

The main contributory factor may be due to structural change of water molecules by addition of dioxane on the one hand and hydrophilic interaction of glycine and dioxane on the other therefore zwitter - ion must be in free energy state due to solvation of amino acids by large number of water molecules<sup>26</sup> and it is evident from table 1, the value of  $\Delta G_t$  that change of zwitter ion structure to neutral molecules is probably unfavourable and it is least affected by increase in temperature means temperature has virtually no significant role in this process. Therefore, role of solvent is dominating and this can be explained according to Frank and Evans<sup>27</sup> ionization of uncharged molecules into ions causes immobilization of solvent molecules around ions. Further dioxane is more basic than water and it increases the acidity of water molecules to which it is bonded<sup>28</sup> and so dioxane molecules form hydrogen bonding with hydrogen atom of water molecules<sup>29</sup>. Hence, a cation will interact more strongly with the oxygen atom of dioxane-water system while anion will interact with hydrogen atom of hydrogen bonded water dioxane moiety. This type of ion solvent interaction will cause primary solvation sheath. This is the region 'A' of Frank and Wen<sup>30</sup> water has quasi-crystalline structure at ordinary temperature and a dynamic equilibrium probably exist between three dimensional hydrogen bonded clusters and the denser monomer. In the region "A" around the ion, water molecules are

in a sort of frozen state while a bit away there is the normal three dimensional water structure called region C.

In between region "C" and region "A" there is the region "B" where the water molecules are disorganised. But in case of aquo-organic solvents frank and wen simple model needs to be modified because of structural change of water molecule due to addition of organic solvents and structural change of water may also depend upon mass percent of organic component added. It is expected that addition of small amount of dioxane may give rise to two effects.

If dioxane is accommodated with solvent structure, it may strengthen the water structure, since dioxane is better proton acceptor, incase it is not accommodated because of its large size it may cause a breakdown in three dimensional structure but it is evident from viscometric study of dioxane water mixture that dioxane is not accommodated in the solvent structure and it breakdown three dimensional structure of water. In such circumstances, it is very difficult to ascertain exact nature of the detailed molecular structure in different mass percent content and with temperature change.

In case of acidic dissociation of glycine there is decrease in pK<sub>1</sub> value with rise in temperature favouring dissociation of glycine but there is slight decrease in pK<sub>1</sub> value evident from table 1. But with increase in mass percent of dioxane in dioxane-water system there is appreciable increase in pK<sub>1</sub> value, hence role of organic solvent dioxane play important in acidic dissociation of glycine.

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