

Determination of Deprotonation Constant of Glycine in 10, 20 and 30% Dioxane in Dioxane-Water System and Related Thermodynamic Quantities at 308.15K by E.M.F. Measurement

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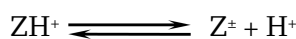
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ABSTRACT

The deprotonation constant (pK_1) of glycine in 10, 20 and 30% dioxane in dioxane-water system at 308.15K was determined by potentiometric method using calomel electrode with the help of modified Davies equation, the dissociation of glycine is given as:



$$m_2(1-\alpha) \qquad m_2\alpha \quad m_2\alpha$$

where $ZH^+ = NH_3^+-CH_2-COOH$

$Z^+ = NH_3^+-CH_2-COO^-$ (Zwitter ion)

and $Z = NH_2-CH_2-COOH =$ glycine

$k_1 =$ acidic dissociation constant

k_1 is given by:

$$\log k_1 = \log k_1(A) - (2A'\sqrt{\mu}/(1 + \sqrt{\mu})) + \beta_1\mu$$

where k_1 real dissociation constant

$k_1(A) =$ Apparent Dissociation Constant

Rearranging the above equation we have:

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

$$= q \text{ where } q = \log K_1(A) - (2A'\sqrt{\mu}) / (1 + \sqrt{\mu})$$

$$\text{or } q = \log K_1 - \beta_1\mu$$

$$-q = pK_1 + \beta_1\mu$$

The constant value of m_{H^+} was calculated by:

$$\log m_{H^+} = (E^0 - E)/K - \log m_{Cl^-} + (2A'\sqrt{\mu}/(1 + \sqrt{\mu})) - \beta_1\mu$$

The value of deprotonation constant was calculated by extrapolating graph at $\mu = 0$ where μ is ionic strength. The related thermodynamic quantities ΔG^0 , ΔH^0 and ΔS^0 and free energy transfer ΔG_t were calculated by the following least square method. The deprotonation constant was calculated by least square method:

$$\log K_1 = -A'/T + D^* - C^*T$$

The related thermodynamic quantities ΔG^0 , ΔH^0 and ΔS^0 and free energy

transfer ΔG_r was calculated by the following least square method:

$$\Delta G^0 = -19.1438(-A^* + D^*T - C^*T^2)$$

$$\Delta H^0 = -19.1438(-A^* - C^*T^2)$$

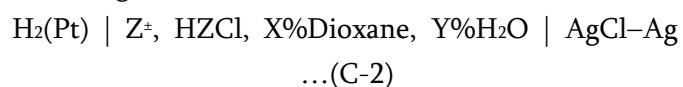
$$\Delta S^0 = -19.1438(D^* - 2C^*T)$$

Keywords : Deprotonation constant, aquo-organic system, thermodynamic quantities.

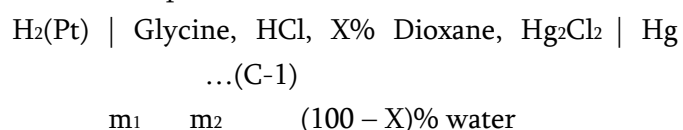
I. INTRODUCTION

Glycine is important biomolecule which is of great value in Biological system and in pharmaceutical industries. Therefore it is necessary to understand its ionization behavior in water and in aquo-organic solvent. It is known that glycine in aqueous medium exists as zwitter ion but as medium is changed from aqueous to aquo-organic how its ionization behavior changes and what is degree of ion solvent interaction. To study the ionization behavior of glycine we have chosen 10, 20 and 30% dioxane in dioxane-water system at 308.15K using modified Davies equation given by Prasad¹⁷ and deprotonation constant was determined by potentiometric method because deprotonation constant gives quantitative information about dissociation of electrolyte.

The dissociation constant of monoprotic and diprotic acids have been determined in water, dioxane-water and water-ethanol by different workers¹⁻³ using cell without liquid junction potential besides acidic dissociation constant of amino acids⁴⁻⁸ water and dissociation constant of other electrolytes have been determined by different workers⁹⁻¹⁵ potentiometrically using cell without liquid junction potential. The acidic dissociation constant of glycine has been determined by Birdsall¹⁶ in 20, 45 and 70% dioxane in dioxane-water system dioxane using the following cell:



Therefore to determine, acidic dissociation of glycine potentiometrically in 10, 20 and 30% dioxane in dioxane-water system at 308.15K following type of cell was setup:



And E.M.F. of the cell(C-1) is given by

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

In this process, activity coefficient of ions to know ion-solvent interaction in the system modified Davies equation was given by Prasad¹⁷ which is upto 30% dioxane content as. In our experiment at 308.15K is given by the equation:

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

where A is Debye-Hackle constant and β_1 is additive parameter.

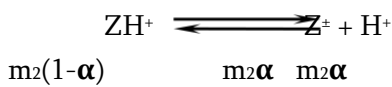
II. EXPERIMENTAL DETAIL

The acidic dissociation constant of Glycine at 10, 20 and 30% dioxane (m/m) in dioxane-water system was determined by the EMF measurement for the cell (C-1) at 308.15K. The Glass cell was set up in duplicate. The electrodes were fitted in interchangeable cones and could be put in and test from the cell as and when needed. All chemical used for the purpose are of AR or GR quality. Buffer solution of glycine was prepared by mixing one molar solution of glycine and half

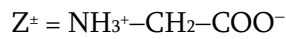
molar of hydrochloric acid. After attaining equilibrium the EMF value have been noted for 10, 20 and 30% dioxane in dioxane-water system and the values are mean of two reading of the two cell. After correction for barometric pressure, vapour pressure and bubbler depth.

III. RESULT AND DISCUSSION

It is assumed that the following equilibria take place during deprotonation of protonated Glycine



where $\text{ZH}^+ = \text{NH}_3^+-\text{CH}_2-\text{COOH}$



and $\text{Z} = \text{NH}_2-\text{CH}_2-\text{COOH} = \text{glycine}$

If α be the degree of dissociation of ZH in the buffer of Glycine and hydrochloric acid

$$m_{Z^{\pm}} = m_1 + m_2\alpha$$

$$m_{\text{H}^+} = m_2\alpha$$

$$m_{\text{ZH}^+} = m_2(1-\alpha)$$

$$\mu = \frac{1}{2} m_{\text{H}^+} + \frac{1}{2} m_{\text{ZH}^+} + \frac{1}{2} m_{\text{Cl}^-}$$

$$= \frac{1}{2} m_2\alpha + \frac{1}{2} m_2(1-\alpha) + \frac{1}{2} m_2$$

$$\mu = m_2$$

In the cell C-1 and arbitrary value is assigned to μ and taking E^0 , β and A' , m_{H^+} is calculated from equation(3).

$$\log m_{\text{H}^+} = (E^0 - E)/K - \log m_{\text{Cl}^-} + (2A'\sqrt{\mu}/(1 + \sqrt{\mu})) - \beta_1\mu \quad \dots(3)$$

and when this m_{H^+} value is put in $m_{\text{H}^+} = m_2\alpha$ and $\mu = m_2$, a new value of μ is obtained. This value of μ is again put in the equation(3).

$$\log m_{\text{H}^+} = (E^0 - E)/K - \log m_{\text{Cl}^-} + (2A'\sqrt{\mu}/(1 + \sqrt{\mu})) - \beta_1\mu$$

Till constant value of m_{H^+} is obtained up to the 6th place of decimal and from this value of m_{H^+} , $m_{Z^{\pm}}$ and m_{ZH^+} and this value is put in tabular form.

From dissociation of protonated glycine we have

$$K_1 = (m_{\text{H}^+} m_{Z^{\pm}}/m_{\text{ZH}^+}) \cdot (\gamma_{\text{H}^+} \gamma_{Z^{\pm}}/\gamma_{\text{ZH}^+}) \quad \dots(4)$$

$$\text{or} \quad \log K_1 = \log K_1(A) + \log (\gamma_{\text{H}^+} \gamma_{Z^{\pm}}/\gamma_{\text{ZH}^+}) \quad \dots(5)$$

$K_1(A)$ = apparent dissociation constant

K_1 = real dissociation constant

$$\log K_1 = \log K_1(A) - ((2A'\sqrt{\mu}) / (1 + \sqrt{\mu})) + \beta_1\mu \quad \dots(6)$$

$$K_1(A) = m_{\text{H}^+} m_{Z^{\pm}} / m_{\text{ZH}^+} = m_{\text{H}^+} \cdot (m_1 + m_{\text{H}^+}) / m_2 - m_{\text{H}^+} \quad \dots(7)$$

$$m_{Z^{\pm}} = m_1 + m_2\alpha$$

$$m_{\text{H}^+} = m_2\alpha$$

$$m_{\text{ZH}^+} = m_2 (1-\alpha)$$

$$\beta_1 = \beta_{\text{H}^+} + \beta_{\text{ZH}^+} + \beta_{Z^{\pm}}$$

$$\log K_1(A) = \log K_1 + (2A'\sqrt{\mu}) / (1 + \sqrt{\mu}) - \beta_1\mu \quad \dots(8)$$

$$\text{or} \quad \log K_1 - \beta_1\mu = \log K_1(A) - (2A'\sqrt{\mu}) / (1 + \sqrt{\mu}) \quad \dots(9)$$

$$= q \text{ where } q = \log K_1(A) - (2A'\sqrt{\mu}) / (1 + \sqrt{\mu})$$

$$+ \sqrt{\mu}$$

$$\text{or} \quad q = \log K_1 - \beta_1\mu$$

$$-q = pK_1 + \beta_1\mu$$

$$\dots(10)$$

Table 1: The value of μ and $-q$ ($-\log K_1(A) + (2A'\sqrt{\mu}) / (1 + \sqrt{\mu})$) recorded in Table 1 for cell C-1.

μ	$-q$
0.010234	2.39
0.01425	2.378
0.019036	2.367
0.026758	2.34
0.049443	2.28
0.056298	2.26

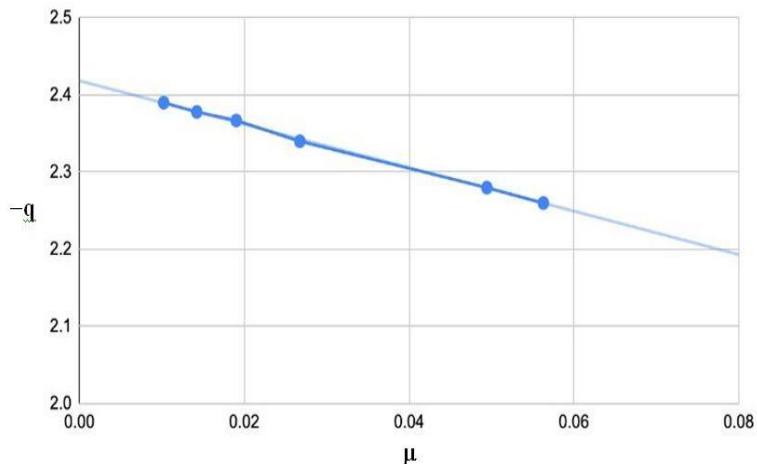


Fig. 1: The plot of $-q$ against μ for the dissociation constant of glycine in 10% diaoxane at 308.15 K.

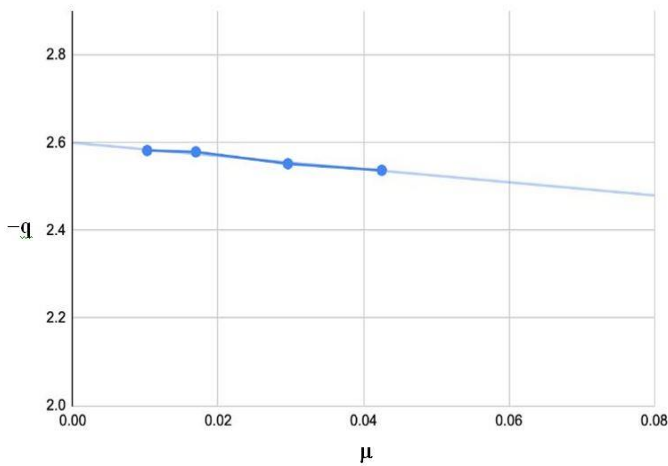


Fig. 2: The plot of $-q$ against μ for the dissociation constant of glycine in 20% diaoxane at 308.15 K.

Table 2: The value of μ and $-q$ ($-\log K_1(A) + (2A'\sqrt{\mu}) / (1 + \sqrt{\mu})$) recorded in Table 2 for cell C-1.

μ	$-q$
0.010235	2.582
0.016936	2.579
0.029598	2.552
0.042513	2.537

Table 3: The value of μ and $-q$ ($-\log K_1(A) + (2A'\sqrt{\mu}) / (1 + \sqrt{\mu})$) recorded in Table 3 for cell C-1.

μ	$-q$
0.012364	2.66
0.019286	2.624
0.027026	2.57
0.042366	2.521
0.057396	2.45
0.0657	2.398

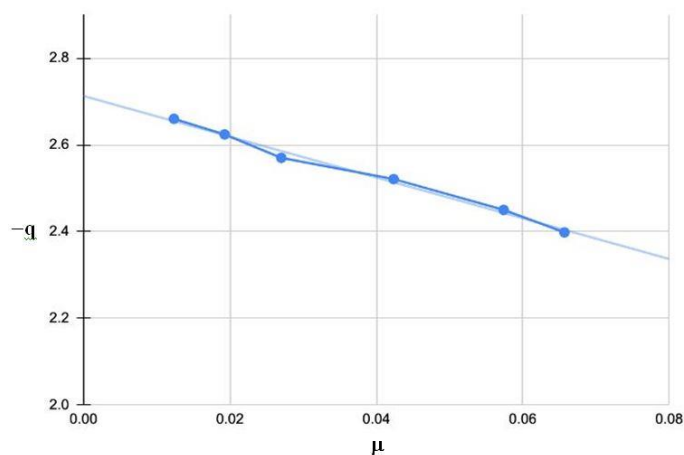


Fig. 3: The plot of $-q$ against μ for the dissociation constant of glycine in 30% diaoxane at 308.15 K.

In Fig 1,2 and 3 the plots have been extrapolated at $\mu=0$ and we have get the value of pK_a at 308.15K in 10, 20 and 30% dioxane in dioxane-water system and related thermodynamic quantities ΔG^0 , ΔS^0 and ΔH^0 have been calculated at recorded in Table4.

By the method of least square²⁰, the value of deprotonation constant are given by the equation

$$\log K_1 = -A^*/T + D^* - C^*T \quad \dots(11)$$

and for 10, 20 and 30%(m/m) dioxane in dioxane-water system are given by the following equation:

For 10% (m/m) dioxane

$$\log K_1 = -4179.255/T + 23.723225 - 0.0409778T \quad \dots(12)$$

For 20% (m/m) dioxane

$$\log K_1 = -678.3820/T + 1.4152361 - 0.0057964T \quad \dots(13)$$

For 30% (m/m) dioxane

$$\log K_1 = -2117.1090/T + 10.4921639 - 0.0205886T \quad \dots(14)$$

The value of A^* , D^* and C^* have been recorded in Table5 for 10, 20 and 30%(m/m) dioxane in dioxane-water content. The values pK_1 calculated from these equations are in good agreement with the experimental values as shown in Table6. The values of pK_1 increases with the increase in dioxane content of dioxane-water system as evident from Table4. These results are similar to the results of other workers^{13,14,16,18,19,21} in dioxane-water system and it is Crystal clear an effect due to lowering of dielectric constant of the medium under consideration. Thermodynamic quantities for deprotonation of glycine in 10, 20 and 30% dioxane in dioxane-water system can be calculated by the thermodynamic equations.

$$\Delta G^0 = -19.1438(-A^* + D^*T - C^*T^2) \quad \dots(15)$$

$$\Delta H^0 = -19.1438(-A^* - C^*T^2) \quad \dots(16)$$

$$\Delta S^0 = -19.1438(D^* - 2C^*T) \quad \dots(17)$$

Table 4: The values of pK_1 , ΔG^0 , ΔS^0 and ΔH^0 in 10, 20 and 30% dioxane in dioxane-water system at 308.15K for the cell C-1.

% Dioxane-water	pK_1	$-\beta_1$ Kg mol^{-1}	ΔG^0 KJ mol^{-1}	$-\Delta S^0 \times 10^3$ $\text{KJK}^{-1}\text{mol}^{-1}$	ΔH^0 KJ mol^{-1}
10	2.40	2.63	14.202	28.185	5.516
20	2.60	1.53	15.347	41.295	2.622
30	2.73	4.85	16.061	42.051	3.103

Table 5: The value of A^* , D^* and C^* calculated by least square²⁰ method.

mass %Dioxane	A^*	D^*	C^*
10	4179.2550	23.7823222	0.0409778
20	678.3820	1.4152361	0.0057964
30	2117.1090	10.4921639	0.0205886

Table 6: Comparison of values of pK_1 for general equation and experimental value at 308.15K in 10, 20 and 30% dioxane in dioxane-water system.

mass %Dioxane	Experimental value	General equation value
10	2.40	2.41
20	2.60	2.60
30	2.73	2.72

The variation of ΔG^0 , ΔH^0 and ΔS^0 have been studied by graph. It is evident from Fig. 4 that there is increase in standard free energy change with increase in dioxane content which indicates that the acidic dissociation of glycine is not favorable with increase in dioxane content.

Table: 7

% Dioxane (m/m)	pK ₁	ΔG ⁰
10	2.40	14.202
20	2.60	15.347
30	2.73	16.061

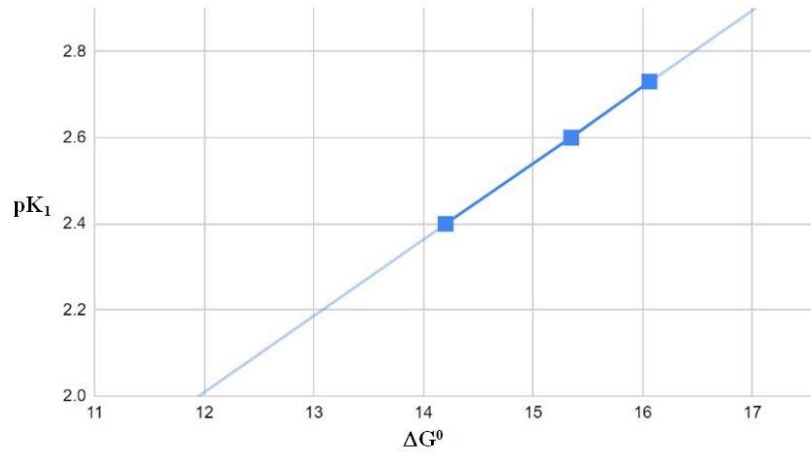


Fig. 4: Plot of pK₁ against ΔG⁰ at 308.15 K for 10, 20 and 30 % in dioxane-water system.

Table: 8

% Dioxane (m/m)	pK ₁	-ΔS KJ K ⁻¹ mol ⁻¹
10	2.40	28.185
20	2.60	41.295
30	2.73	42.051

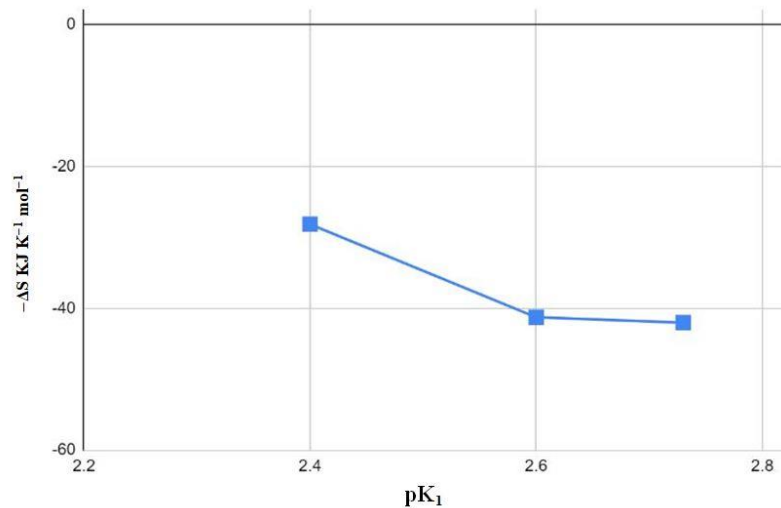


Fig. 5: Plot of pK₁ against ΔS⁰ at 308.15 K for 10, 20 and 30% in dioxane water system.

It is clear from Fig. 5 that there is maximum entropy in 10% dioxane content in dioxane-water system at 308.15 K then there is decrease in entropy with increase in 20% dioxane-content when dioxane content is 30% there is slight decrease in entropy. It means that when dioxane content is increased from 10 to 20% dioxane content there is sharp decrease in entropy indicating that the dioxane molecules are more associated with glycine at 20% dioxane content at 308.15 K. When dioxane content is increased to 30% there is slight decrease in entropy indicating when

dioxane content is increased from 20 to 30% association of dioxane molecules with glycine is slightly increased.

Table: 9

Mass % dioxane (m/m)	pK ₁	ΔH° KJ mol ⁻¹
10	2.40	5.516
20	2.60	2.622
30	2.73	3.103

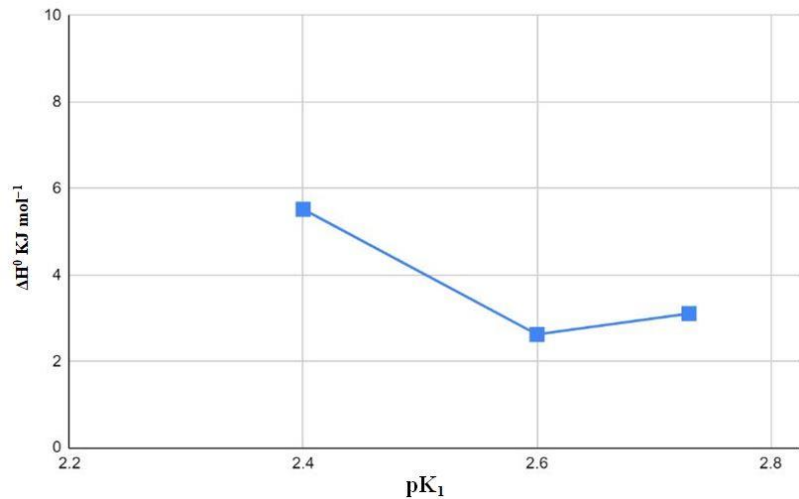


Fig. 6: Plot of pK₁ against ΔH° at 308.15 K for 10, 20 and 30% in dioxane water system

From Table 9, it is clear that the value of standard enthalpy change is positive indicating that the reaction is endothermic throughout the dissociation process and according to Le Chatelier's principle the dissociation of glycine is favored at high temperature. For 10% dioxane content enthalpy change is maximum, indicating maximum endothermic process.

Table:10

mass % Dioxane	1/D x 10 ³	pK ₁
10	15.07840772	2.40
20	17.32201628	2.60
30	20.32933523	2.73

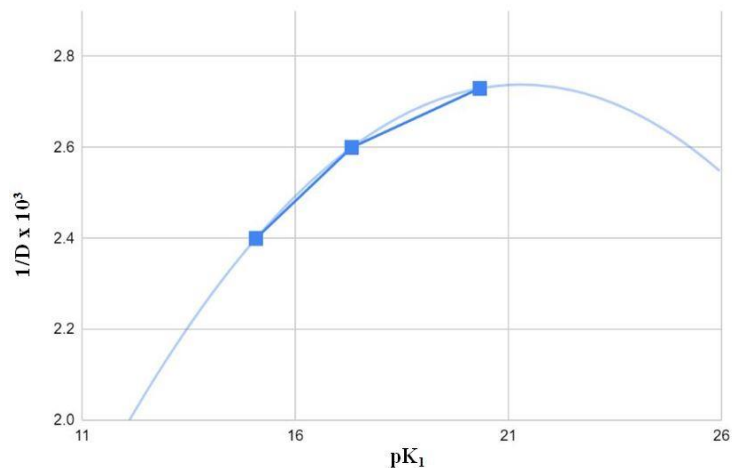


Fig. 7: Plot of pK₁ against 1/D x 10³ at 308.15 K for 10, 20 and 30% dioxane. (Born Plot)

From Fig. 7 variation of pK₁ against 1/D x 10³ at 10, 20 and 30% dioxane in dioxane–water system, but the remarkable point to note that at 308.15K is that there is curvature unlike the variation of pK₁ with dielectric constant at 288.15K straight line has been found.²² It

means when temperature is increased from 288.15K to 308.15K there is greater association between dioxane molecules and glycine. According to Frank and Evans²³, when a neutral molecule dissociates it forms charged ions which immobilizes solvent

molecules. In our study for dissociation of glycine in dioxane water system in which dissociation of glycine takes place and therefore, it is necessary to study the structure of resulting system at 308.15 K. We know that dioxane is more basic than water and it increases the acidity of water molecules to which it is bonded²⁴, this is due to inductive effect of two methylene groups in each side of oxygen atom of dioxane molecule; besides dioxane molecule forms hydrogen bonding with water molecule.²⁵ In this process, cation will attract more strongly with oxygen atom and anion will more strongly with other hydrogen atom of hydrogen bonded water-dioxane system. This type of ion-solvent interaction will cause a primary solvation sheath around the ion. This is the region "A" of Frank and Wen.²⁶ We know that quasi crystalline structure at ordinary temperature and dynamic equilibrium exist between 3-Dimensional hydrogen bonded clusters and the denser monomer. In the region "A" around the ion, water molecules are in a sort of froze state while a bit away there is 3-dimesional water structure called the region "C". In between region "A" and region "C", there is region "B" where the water molecules are disorganized but in case of aquo-organic solvent Frank and Wen simple model needs to be modified because of structural change of water molecule. Due to addition of organic solvent and structural change of water may also depend upon mass % of organic component added. Due to addition of dioxane, there may be changes in dioxane water system, the dioxane can be accommodated with water molecule and strengthen water structure because water is better proton acceptor. If dioxane is not accommodated due to its large size the 3-dimensional structure of water may breakdown. From viscometric study of dioxane water mixture, the dioxane is not accommodated in the solvent structure and it breaks down the 3-dimensional structure of water. Therefore, with increase in dioxane content in dioxane-water system, it is difficult to conclude exact nature of glycine in dioxane-water system upto 30% dioxane content. In

our study it has been found that the acidic dissociation constant of glycine at 308.15K decreases with increase in dioxane content that is pK_1 value increases with increase in mass % of dioxane, hence upto 30% of dioxane content in dioxane water system at 308.15K, dissociation of glycine is unfavorable.

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