Study of Ion-Solvent Interaction during Acidic Dissociation of Glycine in 10, 20 And 30% Dioxane in Dioxane-Water System At 318.15K by Potentiometric Method

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ARTICLEINFO

ABSTRACT

Ion solvent interaction was studied by free energy transfer during acidic dissociation of Glycine in 10,20 and 30% dioxane in dioxane-water system at 318.15K and free energy was given by the thermodynamic relation

$\Delta G_t = 2.303RT\Delta pK_1$

where ΔG_t = free energy transfer when solvent change from water to dioxane-water.

$\Delta pK_1 = pK_{s1} - pK_{w1}$

where $pK_{w1} = -\log K_{w1}$ negative logarithmic of dissociation constant of glycine in water.

$pK_{s1} = -\log K_{s1}$ negative logarithmic of acid dissociation constant of glycine in dioxane-water.

For this purpose acidic dissociatio constant of glycine was determined potentiometrically by setting up the cell:

$H_2(Pt) \mid$ Glycine, HCl, X% Dioxane, $Hg_2Cl_2 \mid$ Hg   …(C-1)

m_1 m_2 (100-x)% water
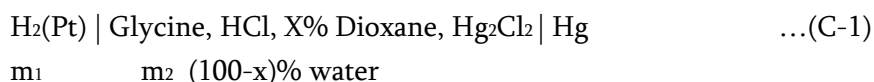
and e.m.f. of the cell was given by the formula:

$E = E^0 - 2.303RT/F (\log m_{H^+} m_{cl^-} + \log \Upsilon_{H^+} \Upsilon_{Cl^-})$ …(1)

In the equation (1) activity coefficient of the solution has been taken into consideration to understand ion solvent interaction and activity coefficient is given by the relation:

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

Equation (2) is modified Davies equation given by B. Prasad and hence acidic dissociation constant of glycine can be calculated by calculating m_{H^+} as: $\log m_{H^+} = (E^0 - E)/K - \log m_{Cl^-} + (2A'\sqrt{\mu}/(1+\sqrt{\mu})) - \beta_1\mu$ …(3)

Keywords: Ion solvent interaction, Free energy transfer, acidic dissociation constant, modified Davies equation.

I. INTRODUCTION

Property of electrolytes deped upon its nature and solvent used. Dissociation of aqueous solution[1-2] have been studied extensively. In general, when electrolytes dissociates it gives cation and anion but in case of glycine when dissolves in water gives zwitter ion. Dissociation of electrolyte in aquo organic or organic medium have been less extensively studied.[3-7] Different workers[8-10] have determined dissociation constant of monoprotic and diprotic acids using cell without liquid junction potential and deprotonation constant of amino acids[11-15] in water has been studied using cell of the same type.

Apart from these experiments, the dissociation constant of other types of electrolytes have been determined in aqueous solution potentiometrically using cell without liquid junction potential by different workers.[16-22] The deprotonation constant of glycine has been determined by Birdsall[23] in 20, 45 and 70% dioxane content of dioxane-water system using cell of the following type:

$$H_2(Pt) \mid Z^{\pm}, HZCl, X\%Dioxane, Y\%H_2O \mid AgCl-Ag \quad \ldots(C-2)$$
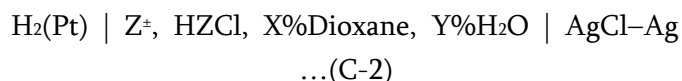
To study ion-solvent interaction in 10, 20 and 30% dioxane in dioxane-water system by calculating pK_1 following type of cell has been setup:

$$H_2(Pt) \mid Glycine, HCl, X\% Dioxane, Hg_2Cl_2 \mid Hg \quad \ldots(C-1)$$
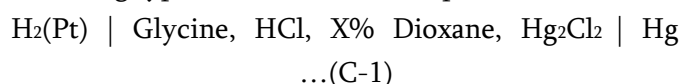
For which e.m.f of the cell is given by equation 1:

It is necessary to consider ion-solvent interaction in the system under study for which it is necessary to evaluate the value of the species involved in the medium. The study of ion-solvent interaction has been reported by different workers.[24-27] For this purpose, a equation has been given by Prasad[28] to determine activity coefficient:

$$\log \gamma_i = -A'z_i^2 \sqrt{\mu}/1 + \sqrt{\mu} + \beta_1\mu \quad \ldots(4)$$

For our experiment upto 30% dioxane content activity coefficient of HCl is given by the equation 2.
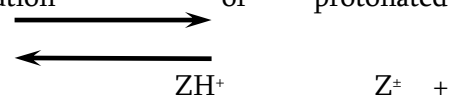
Where A' is Debye Huckel constant and β_1 is additive parameter.

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 318.15K. 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 chemicals 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.
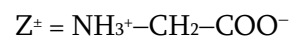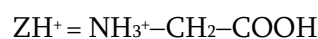
III.RESULT AND DISCUSSION

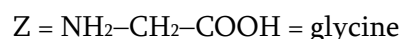It is assumed that the following equilibria take place during deprotonation of protonated Glycine.

$$ZH^+ \rightleftharpoons Z^{\pm} + H^+$$

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

where
$$ZH^+ = NH_3^+-CH_2-COOH$$
$$Z^{\pm} = NH_3^+-CH_2-COO^-$$
and
$$Z = NH_2-CH_2-COOH = glycine$$

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

$$m_{z^{\pm}} = m_1 + m_2\alpha$$
$$m_{H^+} = m_2\alpha$$
$$m_{ZH^+} = m_2(1-\alpha)$$
$$\mu = \tfrac{1}{2} m_{H^+} + \tfrac{1}{2} m_{ZH^+} + \tfrac{1}{2} m_{Cl^-}$$
$$= \tfrac{1}{2} m_2\alpha + \tfrac{1}{2} m_2(1-\alpha) + \tfrac{1}{2} m_2$$
$$\mu = m_2$$

In the cell C-1 and arbitrary value is assigned to μ and taking E^0, β and A', m_{H+} is calculated from equation3. Till constant value of m_{H^+} is obtained up to 6th places 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 protonatedglycine we have:

$$K_1 = (m_{H+}\, m_{z^\pm}/m_{ZH^+})\cdot(Y_{H^+}\, Y_{z^\pm}/\, Y_{ZH^+}) \quad …(5)$$

or

$$\log K_1 = \log K_1(A) + \log (Y_{H^+}\, Y_{z^\pm}/\, Y_{ZH^+}) \quad …(6)$$

$K_1(A)$ = Apparent dissociation constant

K_1 = Real dissociation constant

$$\log K_1 = \log K_1(A) - ((2A'\sqrt\mu) / (1+ \sqrt\mu)) + \beta_1\mu \quad …(7)$$

$$\log K_1(A) = m_{H+}\, m_{z^\pm} / m_{ZH+} = m_{H+}\cdot (m_1 + m_{H^+})/ m_2 - m_{H^+} \quad …(8)$$

where

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

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

Table 1: Plot of -q (-log $K_1(A)$ + (2A$^1\sqrt\mu$) / (1 + $\sqrt\mu$)) for 10% dioxane in dioxane-water syste at 318.15 K for cell C-1.

μ	$-q$
0.010346	2.3697
0.018327	2.3278
0.029326	2.31
0.042591	2.2709
0.056207	2.219
0.067298	2.172

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

and

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

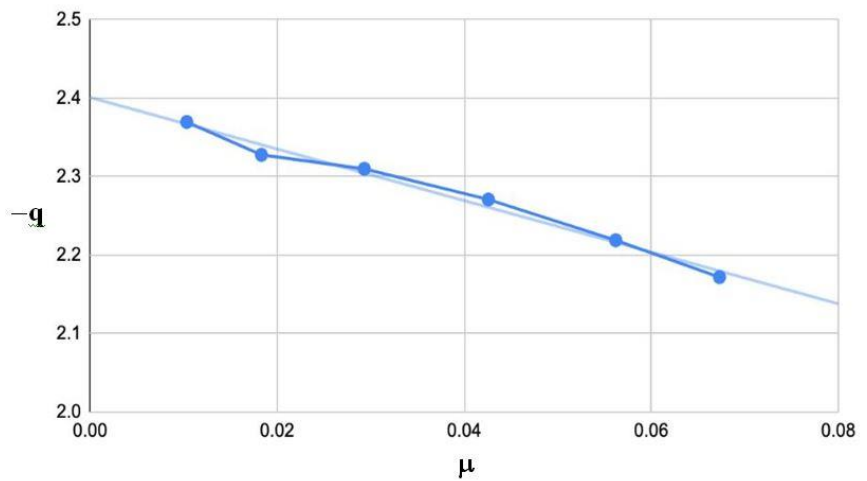$$\log K_1(A) = \log K_1 + (2A'\sqrt\mu) / (1 + \sqrt\mu) - \beta_1\mu \quad …(9)$$

or

$$\log K_1 - \beta_1\mu = \log K_1(A) - (2A'\sqrt\mu) / (1 + \sqrt\mu) \quad …(10)$$

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

or

$$q = \log K_1 - \beta_1\mu$$

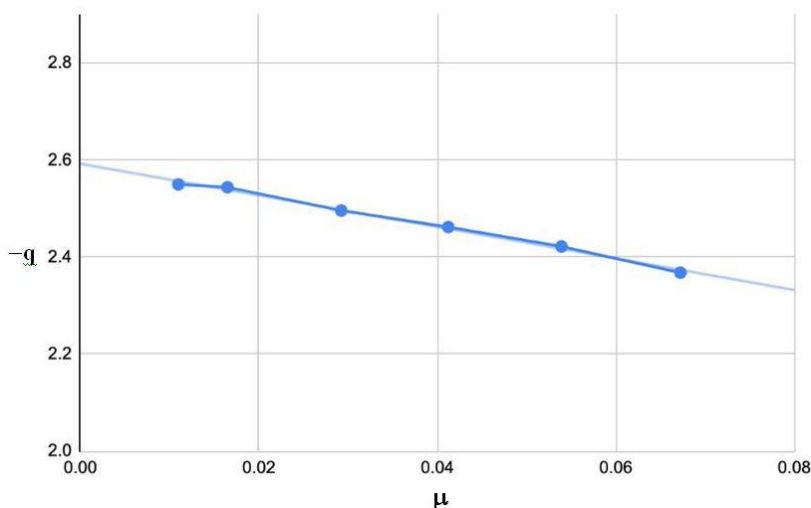$$-q = pK_1 + \beta_1\mu \quad …(11)$$

Now, $-q$ is plotted against μ for 10, 20 and 30% dioxane-water system at 318.15^0 K.

Fig. 1: The plot of $-q$ against μ for the dissociation constant of glycine in 10% diaoxane at 318.15 K.

Table 2: Plot of −q (−log K$_1$(A) + (2A′√μ) / (1 + √μ)) for 20% dioxane in dioxane-water system at 318.15 K for cell C-2.

μ	−q
0.010984	2.55
0.016497	2.544
0.029236	2.496
0.041224	2.462
0.053915	2.422
0.067237	2.368

Fig. 2: The plot of −q against μ for the dissociation constant of Glycine in 20% diaoxane at 318.15 K.

Table 3: Plot of −q (−log K$_1$(A) + (2A′√μ) / (1 + √μ)) for 20% dioxane in dioxane-water syste at 318.15 K for cell C-2.

μ	−q
0.012325	2.651
0.019027	2.63
0.027336	2.585
0.042129	2.523
0.057247	2.453
0.069413	2.419
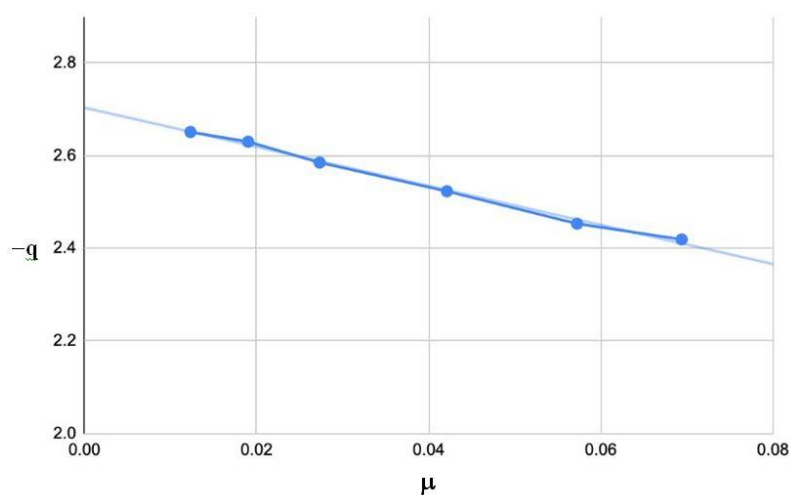
Fig. 3: The plot of −q against μ for the dissociation constant of glycine in 30% diaoxane at 318.15 K.

In Fig. 1, 2 and 3 the plots have been extrapolated at μ =0 and we get the value of pK$_1$ in 10, 20 and 30% dioxane in dioxane-water system at 318.15 K and the related thermodynamic quantities ΔG^0, ΔH^0 and ΔS^0 at 318.15K recorded in Table 4.

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 318.15K for the cell C-1.

% Dioxane water	pK$_1$	−β$_1$ Kg mol^{-1}	ΔG^0 KJ mol^{-1}	−ΔS^0 x 10^3 KJK^{-1}mol^{-1}	ΔH^0 KJ mol^{-1}
10	2.39	3.28	4.562	43.875	0.603
20	2.59	3.91	15.771	43.540	1.923
30	2.71	4.21	16.521	49.933	0.634

By the method of least square[29], the value of deprotonation constant are given by the equation:

$$\log K_1 = −A^*/ T + D^* − C^* T \qquad …(12)$$

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

For 10% (m/m) dioxane

$logK_1 = -4179.255/T + 23.723225 - 0.0409778T$

$$\dots(13)$$

For 20% (m/m) dioxane

$logK_1 = -678.3820/T + 1.4152361 - 0.0057964T$

$$\dots(14)$$

For 30% (m/m) dioxane

$logK_1 = -2117.1090/T + 10.4921639 - 0.0205886T$

$$\dots(15)$$

And 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 Table4. 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.

Table 5: The value of A*, D* and C* calculated by least square[29] method.

mass %Dioxane	A*	D*	C*
10	4179.2550	23.7823222	0.0409778
20	687.3820	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 318.15K in 10, 20 and 30% dioxane in dioxane-water system.
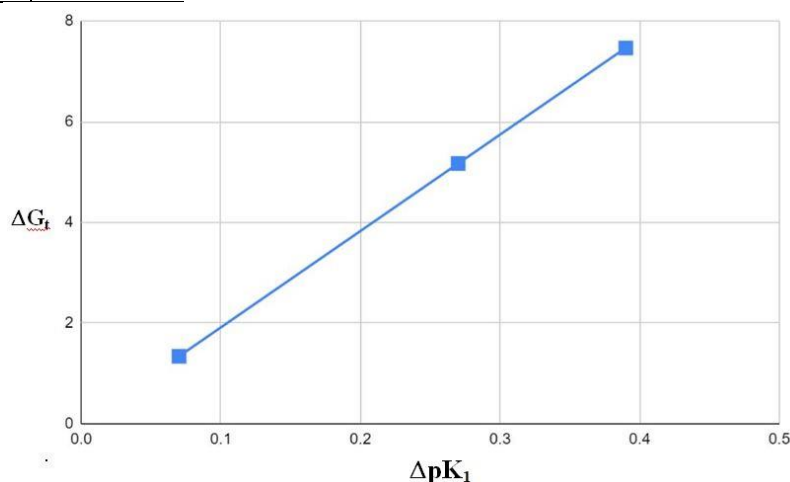
Mass %Dioxane	Experimental value	General equation value
10	2.39	2.39
20	2.59	2.58
30	2.71	2.71

Thermodynamic quantities for deprotonation of glycine in 10, 20 and 30% dioxane in dioxane-water system can be calculated by the following formula:

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

$$\dots(16)$$

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

$$\dots(17)$$

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

$$\dots(18)$$

Table: 7

Mass % dioxane	ΔpK_1	ΔG_t
10	0.07	1.34
20	0.27	5.169
30	0.39	7.466

Fig. 4: Free energy transfer (ΔG_t) for glycine in 10, 20 and 30% dioxane in dioxane-water system at 318.15K.

Ion-solvent interaction

The nature of ion-solvent interaction of glycine in 10, 20 and 30% dioxane in dioxane-water system at 318.15K can only be ascertained from free energy transfer ΔG_t. It is evident from Table 7, that free energy change of glycine increases with increase in dioxane-content and it can be concluded that change in free energy may be due to change from zwitter ion to neutral molecule but there is lesser probability of such contribution. The main contribution may be due to structural change of water, the structure formation of water molecule due to addition of dioxane on the one hand and hydrophilic addition of glycine and dioxane on the other hand but the change of zwitter ion to neutral molecule would be small, therefore zwitter ion must be in a lower free energy state due to solvation of amino acids by large number of water molecules[30] and it is evident from the ΔG_t that change inzwitter ion structure to neutral molecule is probably unfavorable. It is evident from the Table 7, in 10% dioxane in dioxane-water there is slight decrease in free energy change which may not be due to change of structure from zwitter ion into neutral molecule but it may be due to interaction between positive end of zwitter ion and oxygen atom of dioxane molecule. It is further evident from Table 7, when dioxane content is increased from 10 to 20% and 30% dioxane content in dioxane water system at 318.15K there is appreciable increase in ΔG_t value. According to Frank and Evans[31], ionization of uncharged molecules into ions causes immobilization of solvent molecules. In case of glycine, which is present in both $NH_3^+–CH_2–COOH$ and $NH_3^+–CH_2–COO^-$present in equal amount. Further dissociation of protonated glycine produces zwitter and H^+ ions. Therefore, there is probability of interaction of positive end of zwitter ion with oxygen atom of dioxane. Hence increase in dioxane content in dioxane water system is highly unfavorable in formation of zwitter and in our further study it has been found that temperature and virtually no significant role in this process.

Table: 8

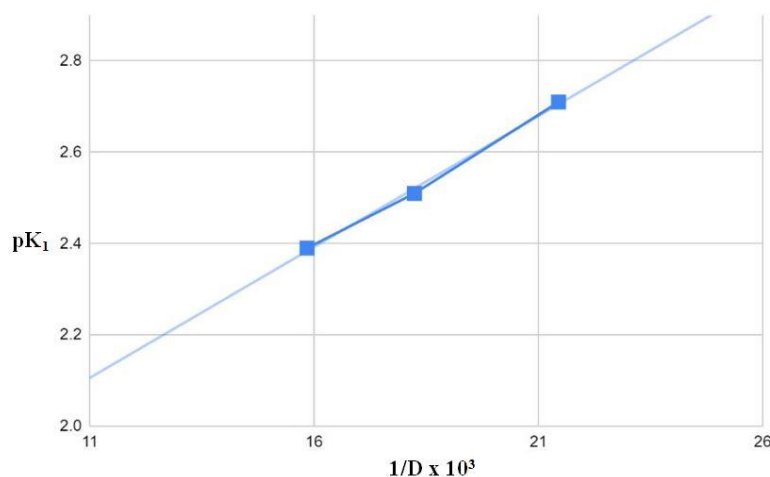| Mass % Dioxane	1/D x 10³	pK₁
10	15.84283904	2.39
20	18.23819077	2.51
30	21.45002145	2.71

Fig. 5: Plot of pK₁ against 1/D x 10³ at 318.15 K.

From the Fig. 5, it is evident that with increase in dioxane content from 10 to 30%, there is sharp increase in pK₁ value indicating that dissociation of glycine is unfavorable and the Fig.5 is straight line unlike[32,33] at 298.15 and 308.15K in which there are curvature.

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