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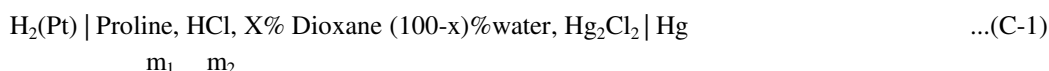
# Study of Free Energy Transfer and Related Thermodynamic Quantities during Determination of Deprotonation Constant of Proline at 298.15K in 10, 20 and 30% Dioxane (m/m) in Dioxane-Water System by e.m.f Measurement

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## ABSTRACT

Deprotonation constant of Proline was determined by potentiometric method using following type of cell:



and emf of the cell is given by:

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

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

The equation (2) is Modified Davies Equation<sup>1</sup> which is used for calculating activity coefficient in a system and which is measure of deviation from ideality of solution. Hence, taking into account activity coefficient, acidic dissociation constant of Proline can be calculated by calculating  $m_{\text{H}^+}$  given by the formula:

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

and hence acidic dissociation constant of Proline is given by:

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

and hence by calculating acidic dissociation constant of Proline, thermodynamic quantities  $\Delta G^0$ ,  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G_f$  can be calculated.

**KEYWORDS:** Free energy transfer, Thermodynamic quantities, Deprotonation constant, Modified Davies equation

## I. INTRODUCTION

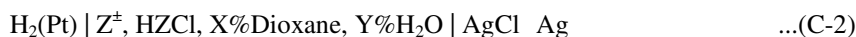
Proline is an important part of biomolecule and its acidic dissociation constant and thermodynamic property are known in aqueous system but in aquo- organic system a little work<sup>2-8</sup> has been done for the dissociation constant of amino acids in dioxane-water system. The dissociation constant and thermodynamic property are directly related to



stability of a substance in a medium and so it may be helpful in its purification and separation. It is well established that e.m.f. Measurement with cells having no liquid junction potential give the most accurate result. Furthermore for determining activity coefficient of ionic species present in solution, modified Davies equation(2) has been taken into consideration because this equation has been found to be satisfactory upto 30% dioxane (m/m) in dioxane-water and 2-propanol-water besides in aqueous solution of uni-univalent ion and also been found to be valid<sup>9-13</sup> upto 0.07mol kg<sup>-1</sup> in aqueous and aquo-organic system.

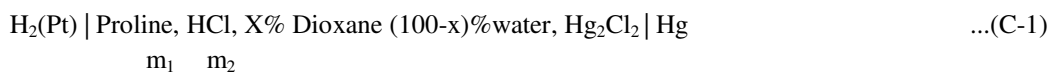
Hence, curiosity arose to determine acidic dissociation constant of Proline in 10, 20 and 30% dioxane (m/m) in dioxane-water system at 298.15K. Dioxane has been taken into consideration because it being protic solvent and so solubility of Proline is much affected and therefore in dioxane- water system ion-solvent interaction can be studied during acidic dissociation of Proline by free energy transfer.

For acidic dissociation of Glycine in 20, 45 and 70% dioxane system from 0 to 50<sup>0</sup> Birdsall<sup>8</sup> setup the following cell:



### II. EXPERIMENTAL DETAIL

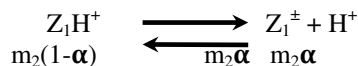
To determine acidic dissociation constant of Proline in 10, 20 and 30% dioxane (m/m) in dioxane-water at 298.15 K a cell C-1 was setup.



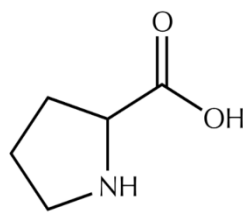
The glass cell made up of corning glass was setup in duplicate and the electrodes were fitted in interchangeable cones and could be put in and test from the cell as and when needed. All chemicals used for the purpose are of AR or GR quality. Buffer solution of Proline was prepared by mixing one molar solution of proline and half molar solution of hydrochloric acid. After attaining equilibrium the EMF value have been noted for 10, 20 and 30% dioxane (m/m) in dioxane-water system and the values are mean of two reading of the two cells 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 proline



where  $Z_1$  = Proline and structure is given as:





If  $\alpha$  be the degree of dissociation of  $Z_1H^+$  in the buffer of Proline and hydrochloric acid

$$m_z^\pm = m_1 + m_2\alpha$$

$$m_H^+ = m_2\alpha$$

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

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

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

$$\mu = m_2$$

In the cell C-1 and arbitrary value is assigned to  $\mu$  and taking  $E^0$ ,  $\beta$  and  $A'$ ,  $m_{H^+}$  is calculated from equation (3), and when this  $m_{H^+}$  value is put in  $m_H^+ = m_2 \alpha$  and  $\mu = m_2$ , a new value of  $\mu$  is obtained. This value of  $\mu$  is again put in the equation (3) 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 Proline we have

$$K_1 = (m_H^+ m_{Z_1}^\pm / m_{Z_1H^+}) \cdot (V_H^+ V_{Z_1}^\pm / V_{Z_1H^+}) \quad \dots(4)$$

or 
$$\log K_1 = \log K_1(A) + \log (V_H^+ V_{Z_1}^\pm / V_{Z_1H^+}) \quad \dots(5)$$

$K_1(A)$  = apparent dissociation constant

$K_1$  = real dissociation constant

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

From equation (2), by putting the value of  $\log V_H^+ \cdot V_{Cl^-}$

$$K_1(A) = m_H^+ m_{Z_1}^\pm / m_{Z_1H^+} = m_H^+ \cdot (m_1 + m_H^+) / m_2 - m_H^+ \quad (7)$$

$$m_z^\pm = m_1 + m_2\alpha$$

$$m_H^+ = m_2\alpha$$

$$m_{Z_1H^+} = m_2 (1-\alpha)$$

$$\beta_1 = \beta_H^+ + \beta_{Z_1H^+} + \beta_{Z_1}^\pm$$

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

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

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

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

$$-q = pK_1 + \beta_1\mu \quad \dots(10)$$

Now  $-q$  is plotted against  $\mu$  for 10, 20 and 30% dioxane (m/m) at 298.15 K for the cell C-1.



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

$\mu$	$-q$
0.010446	2.166
0.021334	2.113
0.032776	2.073
0.041365	1.971
0.057325	1.913
0.071623	1.842

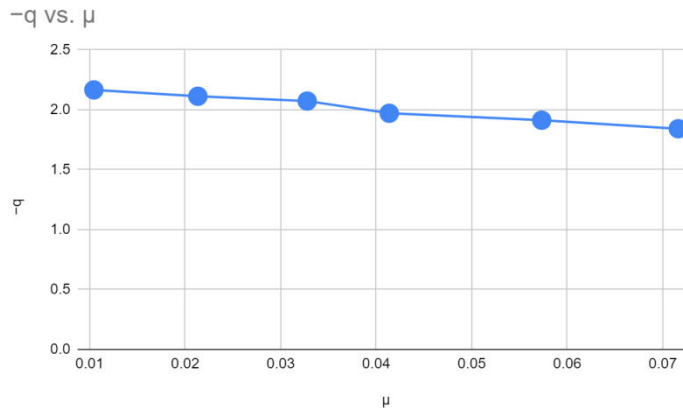


Fig. 1: The plot of  $-q$  against  $\mu$  for the dissociation constant of proline in 10% dioxane at 298.15 K.

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

$\mu$	$-q$
0.011224	2.350
0.021336	2.338
0.034937	2.311
0.047962	2.308
0.059611	2.284
0.066124	2.281

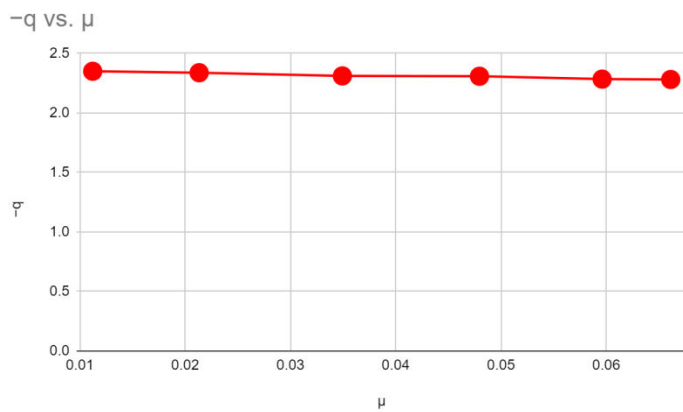


Fig. 2: The plot of  $-q$  against  $\mu$  for the dissociation constant of proline in 20% dioxane at 298.15 K.



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

$\mu$	$-q$
0.010223	2.451
0.019347	2.440
0.028925	2.428
0.041663	2.42
0.058693	2.387
0.071335	2.375

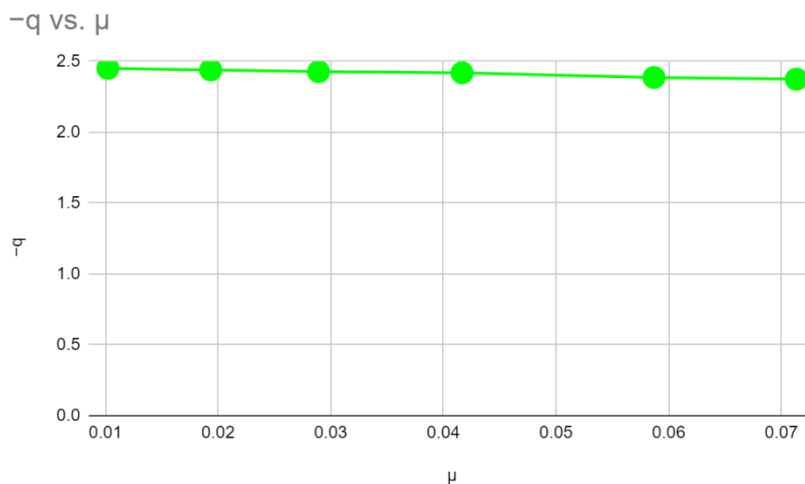


Fig. 3: The plot of  $-q$  against  $\mu$  for the dissociation constant of proline in 30% dioxane (m/m) at 298.15 K.

In Fig 1, 2 and 3 the plots have been extrapolated to  $\mu = 0$  and we have get the value of  $pK_1$  at 298.15 K in 10, 20 and 30% dioxane (m/m) in dioxane-water system and related thermodynamic quantities  $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$  have been calculated by least square method<sup>14</sup> and recorded ion table 4.

Table 4: The values of  $pK_1$ ,  $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$  in 10, 20 and 30% dioxane (m/m) in dioxane-water system at 298.15 K for the cell C-1.

% Dioxane-water (m/m)	$pK_1$	$\Delta G^0$ KJ mol <sup>-1</sup>	$-\Delta S^0 \times 10^3$ KJK <sup>-1</sup> mol <sup>-1</sup>	$-\Delta H^0$ KJ mol <sup>-1</sup>
10	2.21	12.540	<u>50.966</u>	2.519
20	2.36	13.554	56.568	3.317
30	2.47	14.164	62.135	4.392

The values obtained by least square method are in good agreement to experimental values and it is clear from Table (4) that  $pK_1$  increases with increase in dioxane-content from 10 to 30% dioxane(m/m) at 298.15K and the results are similar to other workers<sup>6-8,12,13,15</sup> in aquo-organic solvent and it is mainly due to lowering of dielectric constant of the medium under study.





**Free energy transfer:** Free energy transfer of proline from water to 10, 20 and 30% dioxane(m/m) in dioxane-water system have been calculated with thermodynamic relation:

$$\Delta G_t = 2.303RT \Delta pK_1$$

Table: 5 :- Value of  $\Delta pK_1$  and  $\Delta G_t$  for 10, 20 and 30% dioxane(m/m) in dioxane-water system

% Dioxane (m/m)	$\Delta pK_1$	$\Delta G_t$
10	0.27	5.167
20	0.42	8.040
30	0.53	10.146

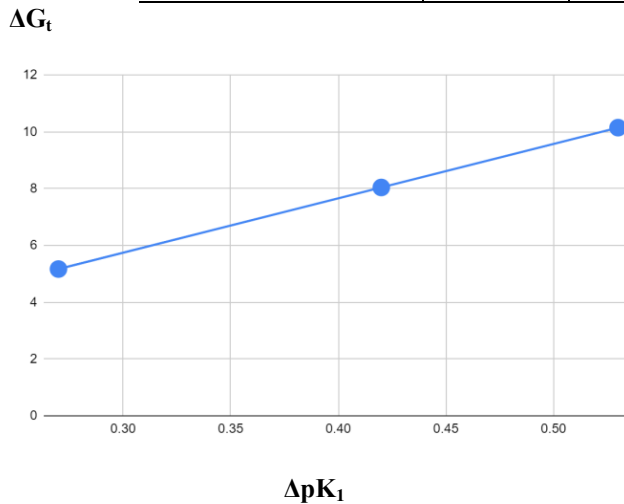


Fig:4 Free energy transfer ( $\Delta G_t$ ) for Proline in 10, 20 ad 30% dioxane (m/m) in dioxane-water system at 298.15K

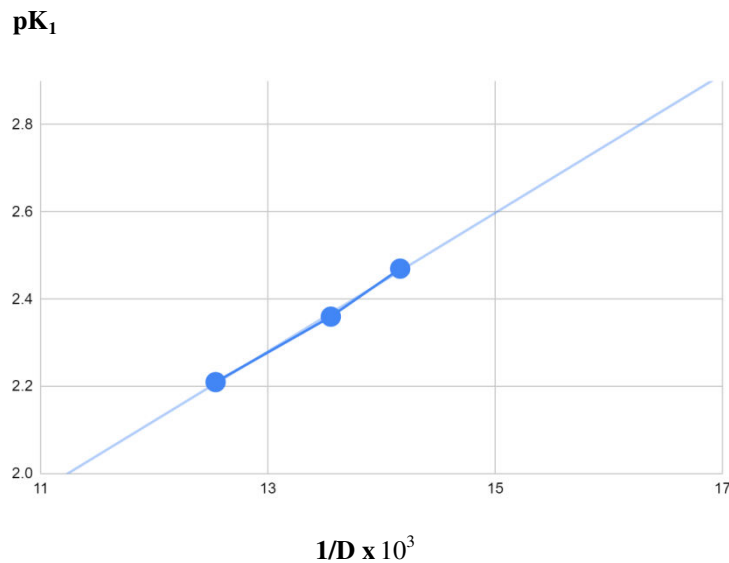


Fig 5 :- Plot of  $1/D \times 10^3$  against  $pK_1$  at 298.15K for 10, 20 and 30% dioxane(m/m) in dioxane-water system for acidic dissociation of Proline

Free energy transfer from water to aquo-organic solvent is measure of ion-solvent interaction and it is evident from table 5 that free energy transfer increases with increase in dioxane-content at 298.15K. It can be inferred that increase in free energy change with increase in dioxane content from 10 to 30% dioxane (m/m) may rise due to change from zwitter ion to neutral molecule but this contribution seems to be small and the main contributory factor may be due to structural change of water- and the structural change of water molecules may be due to addition of dioxane on the one hand, and hydrophobic interaction of proline on the other.

Free energy transfer of cation and anion from water to aquo-organic system are usually negative and positive respectively<sup>16-18</sup> and with the help of Born<sup>19</sup> or modified<sup>20-21</sup> Born equation, the role of solvent on the ionization of weak acid and weak bases is not clearly understood. Therefore in such circumstances the problem is extremely complicated in case of zwitter ion upon addition of solvent in aquo-organic medium. The role of water is very important for the solvation of amino-acids by large number of water molecules<sup>22</sup>, this causes zwitter ion must be lower free energy state.

It is clear from value of  $\Delta G_t$  from table 5 that change of zwitter ion to neutral molecule is probably unfavourable due to increase in  $\Delta G_t$  value with increase in dioxane-content therefore formation of zwitter ion is highly unfavourable. Further it is noticed that from the graph 5, there is sharp increase in  $pK_1$  with dielectric constant indicating that there is least probability of interaction of proline molecules with dioxane.

**Study of thermodynamic quantities:** From table 4, it is evident that value of standard free change value at 298.15K increases with increase in dioxane-content from 10 to 30% dioxane (m/m) in dioxane-water system due to decrease in dielectric constant of the medium. Remarkable point to note that there is increase in standard free energy change indicating that dioxane molecules are not well interacted with proline molecules which is due to its ring structure and low charge existence. Further it is noticed from table 4, that value of standard enthalpy change is negative for 10, 20 and 30% dioxane (m/m) content in dioxane water system at 298.15K. This indicates that the reaction is exothermic. Similarly, the value of standard entropy change at 10, 20 and 30% dioxane (m/m) in dioxane-water at 298.15K is negative and there is smooth decrease in entropy from 10% to 30% dioxane (m/m) at 298.15K. According to Frank and Evans<sup>23</sup>, ionization of uncharged molecules into ions causes immobilization of solvent molecule around the ion and so there is decrease in entropy and in case of proline it is due to dissociation of  $Z_1H^+$  produces  $Z_1^\pm$  and  $H^+$  ions. Further, we know that interaction of dioxane molecules to proline depend upon nature of dioxane which is more basic than water and it increases the acidity of water molecules to which it is bonded<sup>24</sup>. Furthermore, dioxane molecule forms hydrogen bonding with hydrogen atoms of water molecules<sup>25</sup> which affect structure of water and so ion-solvent interaction. In the study of such ion-solvent interaction, the region A of Frank and Wen<sup>26</sup>, water has quasi crystalline structure at ordinary temperature and dynamic structure exist between 3-Dimensional hydrogen bonded clusters and the denser monomer. In the region 'A' around the ion, water molecules are in sort of frozen state while a bit away there is the normal three dimensional structure of water called region 'C' and in between region 'A' and 'C' there is region 'B' where water is disorganised. But in case of dioxane-water system, Frank and Wen<sup>26</sup> simple water model needs to be modified due to addition of dioxane.

Due to ring structure of proline and large size of dioxane molecule, there is greater probability of breakdown of 3-dimensional structure of water. In such circumstances it is difficult to ascertain exact nature of detail molecular structure of water molecules and 298.15K in 10, 20 and 30% dioxane (m/m) in dioxane-water system. Therefore, it can be concluded that dissociation of proline is less favoured with increase in dioxane content at 298.15K because of increase in standard free energy change, the value of  $pK_1$  increases.

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