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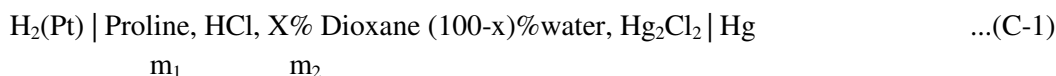
Determination of acidic dissociation constant of Proline at 308.15K using modified Davies equation in 10, 20 and 30% dioxane (m/m) in dioxane-water system and related thermodynamic quantities by e.m.f measurement

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ABSTRACT: For determining acidic dissociation constant in 10, 20 and 30% dioxane at 308.15K following type of cell has been setup:



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) $\dots(2)$

The equation (2) is Modified Davies Equation¹ 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_{H^+} given by the formula:

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

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 ΔG^0 , ΔH^0 , ΔS^0 and ΔG_t can be calculated.

KEYWORDS: Free energy transfer, Thermodynamic quantities, De-protonation constant, Modified Davies equation

I. INTRODUCTION

Proline is an important part of biomolecule. It is also called Protienogenic amino acid used in biosynthesis of protein. It contains protonated NH^+_2 group under biological condition while the carboxylic group is found in deprotonated carboxalate form and it has exceptional conformational rigidity affecting the secondary structure of protein. When proline is bond as an amide in peptide bond its nitrogen is not bonded to any hydrogen meaning it cannot act as hydrogen atom donor but can be hydrogen acceptor based upon the characteristic it has biological and chemical importance therefore it will highly informative to know thermodynamic property by determining acidic dissociation of proline.

Acidic dissociation constant of proline and thermodynamic property are known in aqueous system but in aquo- organic system a little work²⁻⁹ has been done for the dissociation constant of amino acid in dioxane-water system because 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 univalent ion and also been found to be valid¹⁰⁻¹⁴ upto 0.07mol kg^{-1} in aqueous and aquo-organic system.

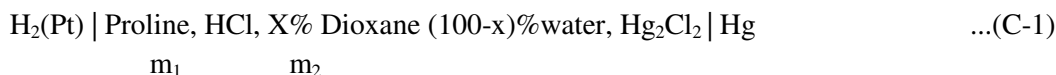
Hence, curiosity arose to determine acidic dissociation constant of Proline in 10, 20 and 30% dioxane (m/m) in dioxane-water system at 308.15K. Dioxane has been taken into consideration because it being protic solvent and so solubility of Proline is much affected and therefore in dioxane-water system 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 50⁰ Birdsall⁹ setup the following cell:



II. EXPERIMENTAL DETAIL

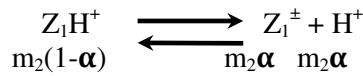
To determine acidic dissociation constant of Proline in 10, 20 and 30% dioxane (m/m) in dioxane-water at 308.15 K a cell C-1 was setup.



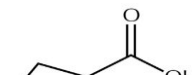
The glass cell made up of corning glass was setup in duplicate and the electrodes were fitted in interchangeable cones and could be put in and test from the cell as and when needed. All chemical used for the purpose are of AR or GR quality. Buffer solution of Proline was prepared by mixing one molar 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 α be the degree of dissociation of Z_1H  proline and hydrochloric acid

$$\begin{aligned} m_z^\pm &= m_1 + m_2\alpha \\ m_H^+ &= m_2\alpha \\ m_{ZH^+} &= m_2(1-\alpha) \\ \mu &= \frac{1}{2} m_H^+ + \frac{1}{2} m_{ZH^+} + \frac{1}{2} m_{Cl^-} \\ &= \frac{1}{2} m_2 \alpha + \frac{1}{2} m_2 (1-\alpha) + \frac{1}{2} m_2 \\ \mu &= m_2 \end{aligned}$$

In the cell C-1 and arbitrary value is assigned to μ and taking E^0 , \square 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 μ is obtained. This value of μ 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

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

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

$K_1(A)$ = apparent dissociation constant

K_1 = real dissociation constant

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

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

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

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

$$m_H^+ = m_2 \alpha$$

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

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

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

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 μ for 10, 20 and 30% dioxane (m/m) at 308.15 K for the cell C-1.

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	$-q$
0.010435	2.204
0.021922	2.184
0.033425	2.16
0.046126	2.149
0.057163	2.133
0.069193	2.111

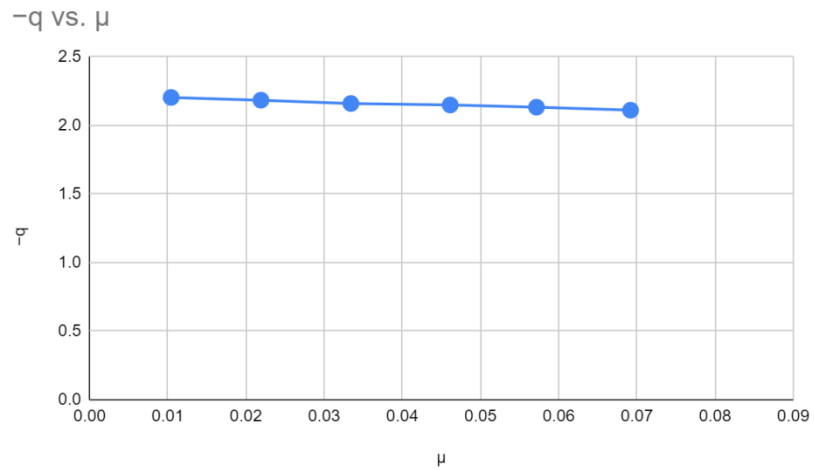


Fig. 1: The plot of $-q$ against μ for the dissociation constant of proline in 10% dioxane at 308.15 K.

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	$-q$
0.010002	2.376
0.021922	2.361
0.030051	2.354
0.042552	2.344
0.058632	2.328
0.69126	2.311

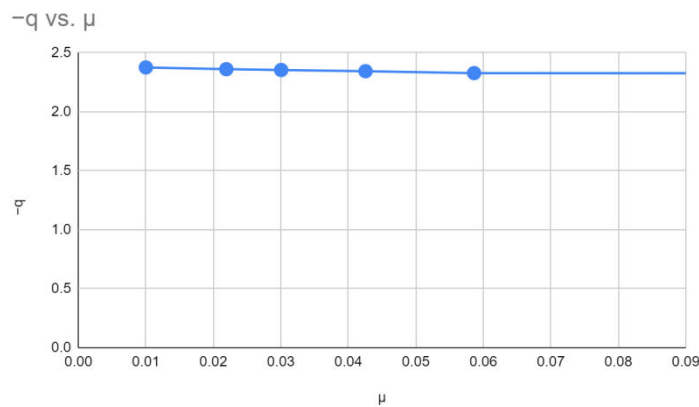


Fig. 2: The plot of $-q$ against μ for the dissociation constant of proline in 20% dioxane at 308.15 K.

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	$-q$
0.010233	2.501
0.021944	2.481
0.033425	2.460
0.046926	2.438
0.057327	2.420
0.069129	2.326

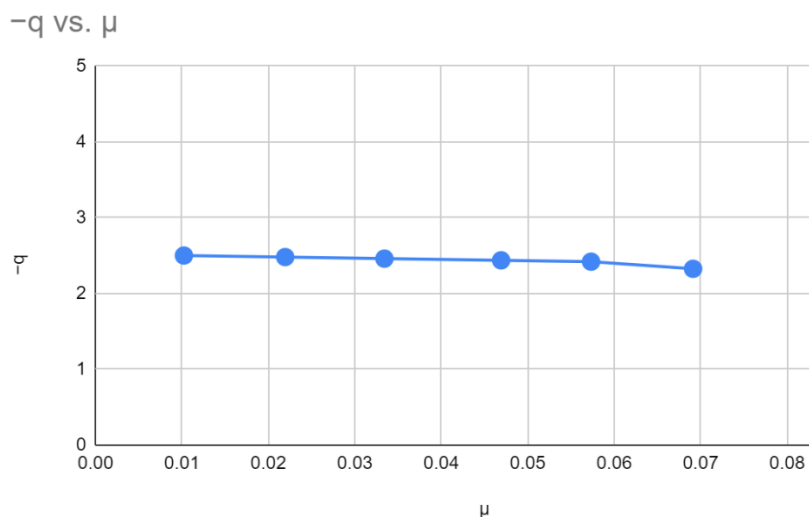


Fig. 3: The plot of $-q$ against μ for the dissociation constant of proline in 30% dioxane (m/m) at 308.15 K.

In Fig 1, 2 and 3 the plots have been extrapolated to $\mu = 0$ and we have get the value of pK_1 at 308.15 K in 10, 20 and 30% dioxane (m/m) in dioxane-water system and related thermodynamic quantities ΔG^0 , ΔS^0 and ΔH^0 have been calculated by least square method¹⁴ and recorded ion table 4.

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

% Dioxane-water (m/m)	pK_1	ΔG^0 KJ mol ⁻¹	$-\Delta S^0 \times 10^3$ KJK ⁻¹ mol ⁻¹	ΔH^0 KJ mol ⁻¹
10	2.23	13.151	<u>57.555</u>	-4.576
20	2.39	14.015	36.649	2.722
30	2.52	14.793	63.452	-4.763

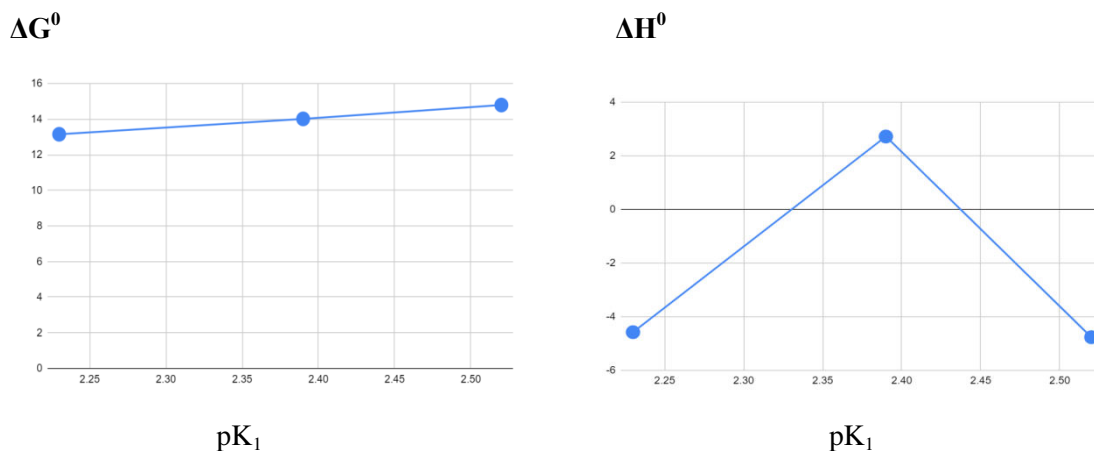


Fig. 4: The plot of pK_1 against ΔG^0 for dissociation constant of proline in 10, 20 and 30% dioxane (m/m) at 308.15K

Fig. 5: The plot of pK_1 against ΔH^0 for the dissociation constant of proline in 10, 20 ad 30% dioxane (m/m) at 308.15K.

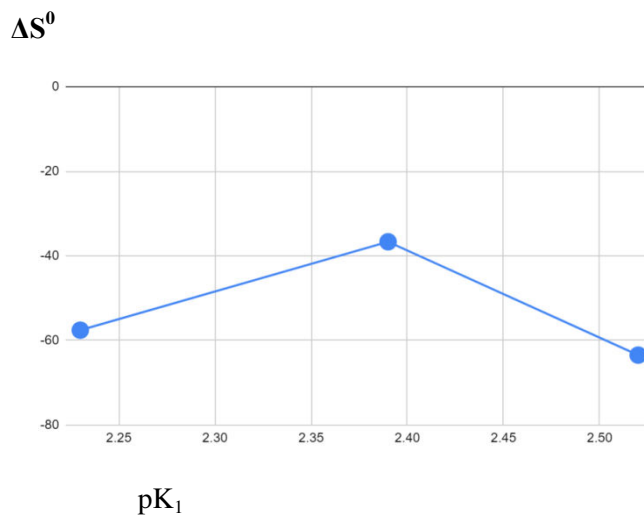


Fig. 6: The plot of pK_1 against ΔS^0 for the dissociation constant of proline in 10, 20 ad 30% dioxane (m/m) at 308.15 K.

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 308.15K and the results are similar to other workers^{6-8,12,13,15} 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 ΔpK_1 and ΔG_t for 10, 20 and 30% dioxane(m/m) in dioxane-water system

% Dioxane (m/m)	ΔpK_1	ΔG_t
10	0.29	5.552
20	0.45	8.614
30	0.58	11.103

% Dioxane-water (m/m)	pK_1	$1/D \times 10^3$
10	2.23	15.07840772
20	2.39	17.32201628
30	2.52	20.32933523

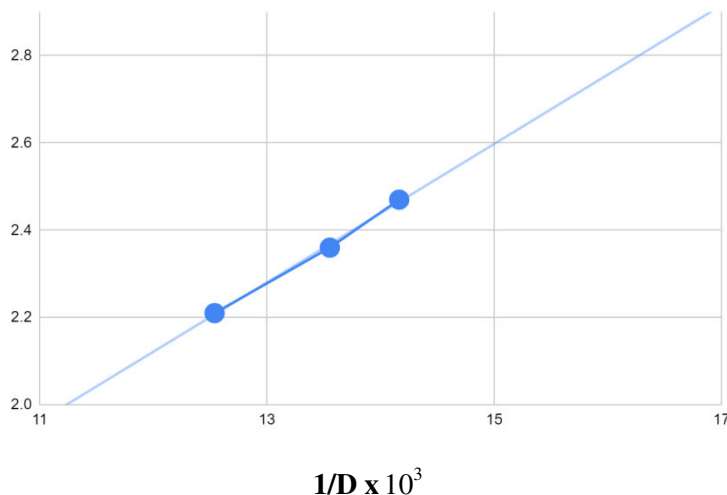


Fig 5 :- Plot of $1/D \times 10^3$ against pK_1 at 308.15K for 10, 20 and 30% dioxane(m/m) in dioxane-water system for acidic dissociation of Proline

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 308.15K. 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 respectively¹⁶⁻¹⁸ and with the help of Born¹⁹ or modified²⁰⁻²¹ 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 molecules²², this causes zwitter ion must be lower free energy state.

It is clear from value of ΔG_t from table 5 that change of zwitter ion to neutral molecule is probably unfavourable due to increase in ΔG_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 308.15K 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 and 30% dioxane (m/m) content and positive for 20% in dioxane water system at 308.15K. This indicates that the reaction is exothermic for 10 and 30% and endothermic for 20% means acidic dissociation of glycine is favoured for 10 and 30% and not for 20%. Similarly, the value of standard entropy change at 10, 20 and 30% dioxane (m/m) in dioxane-water at 308.15K is negative and there is increase in entropy when dioxane-content changes from 10 to 20% then the entropy further decreases from 20 to 30% i.e. maximum entropy is at 20% dioxane-content which is more favourable.

According to Frank and Evans²³, 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 bonded²⁴. Furthermore, dioxane molecule forms hydrogen bonding with hydrogen atoms of water molecules²⁵ which affect structure of water and so ion-solvent interaction. In the study of such ion-solvent interaction, the region A of Frank and Wen²⁶, 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 Wen²⁶ 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 308.15K 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 308.15K because of increase in standard free energy change, the value of pK_1 increases.

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