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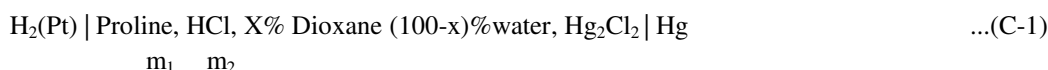
Determination of deprotonation constant of proline at 318.15K in 10, 20 and 30% dioxane (m/m) in dioxane-water and study of thermodynamic quantities by e.m.f measurement

Md. Shamsuddin¹, A.K. Ghosh²

Maharana Pratap Govt. P.G. College, Chittorgarh-312001 (Raj.), India

Ex-Head Department of Chemistry, Patma University, Patna, India

ABSTRACT: For determining deprotonation constant of proline at 318.15K in 10, 20 and 30% dioxane(m/m) in dioxane-water system 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:

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

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 and ΔS^0 can be calculated.

KEYWORDS: Deprotonation constant, Thermodynamic quantities, Modified Davies equation, Activity coefficient, Dioxane-water system

I. INTRODUCTION

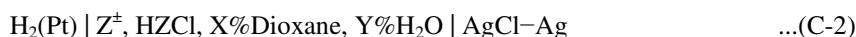
Proline is an important part of biomolecule also called proteinogenic amino acid used for biosynthesis of amino acid and it contain protonated NH_2^+ group under biological condition while the carboxylic group is found in

deprotonated carboxylate form and it has exceptional conformational rigidity affecting the secondary structure of protein.

Dissociation constant of proline and thermodynamic property are known in aqueous system but in aquo-organic system a little work²⁻⁸ has been done for the dissociation constant of amino acids 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 valid⁹⁻¹³ upto 0.07mol kg⁻¹ in aqueous and aquo-organic system.

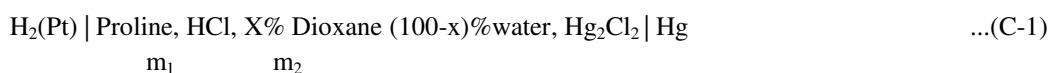
Hence, curiosity arose to determine acidic dissociation constant of Proline in 10, 20 and 30% dioxane (m/m) in dioxane-water system at 318.15K. Dioxane has been taken into consideration because it being protic solvent and so solubility of Proline is much affected and therefore in dioxane- water system 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 Birdsall⁸ setup the following cell:



II. EXPERIMENTAL DETAIL

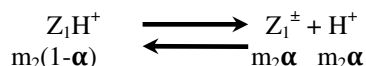
To determine acidic dissociation constant of Proline in 10, 20 and 30% dioxane (m/m) in dioxane-water at 318.15 K a cell C-1 was setup.



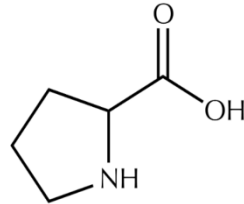
The glass cell made up of corning glass was setup in duplicate and the electrodes were fitted in interchangeable cones and could be put in and test from the cell as and when needed. All chemical used for the purpose are of AR or GR quality. Buffer solution of Proline was prepared by mixing one molar 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^+ in the buffer of 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 , Δ 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

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

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

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

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

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

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

$$m_H^+ = m_2 \alpha$$

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

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

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

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 μ for 10, 20 and 30% dioxane (m/m) at 318.15 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	$-q$
0.011234	2.248
0.020926	2.238
0.033217	2.227
0.041962	2.221
0.053206	2.202

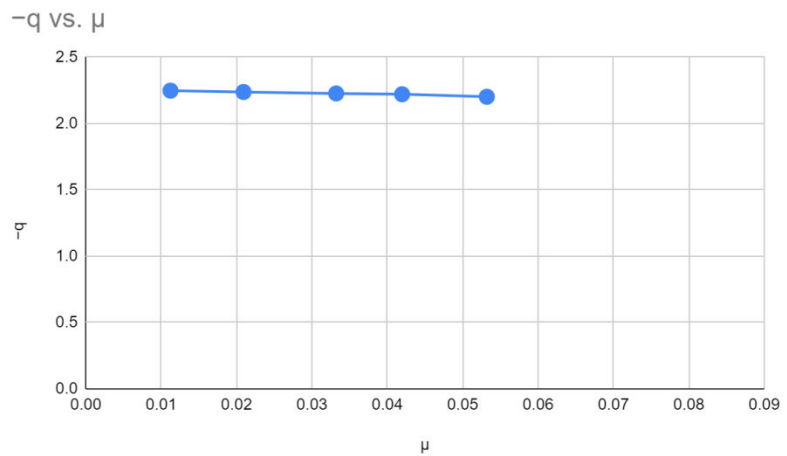


Fig. 1: The plot of $-q$ against μ for the dissociation constant of proline in 10% dioxane at 318.15 K.

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	$-q$
0.010236	2.418
0.023125	2.413
0.032153	2.408
0.046138	2.400
0.057322	2.393
0.0669295	2.390

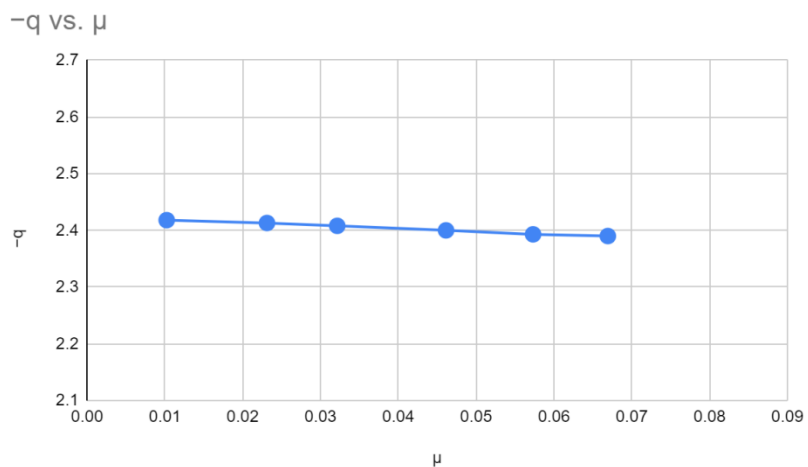


Fig. 2: The plot of $-q$ against μ for the dissociation constant of proline in 20% dioxane at 318.15 K.



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	$-q$
0.009163	2.522
0.017392	2.521
0.029144	2.514
0.041235	2.508
0.056127	2.501
0.067128	2.498

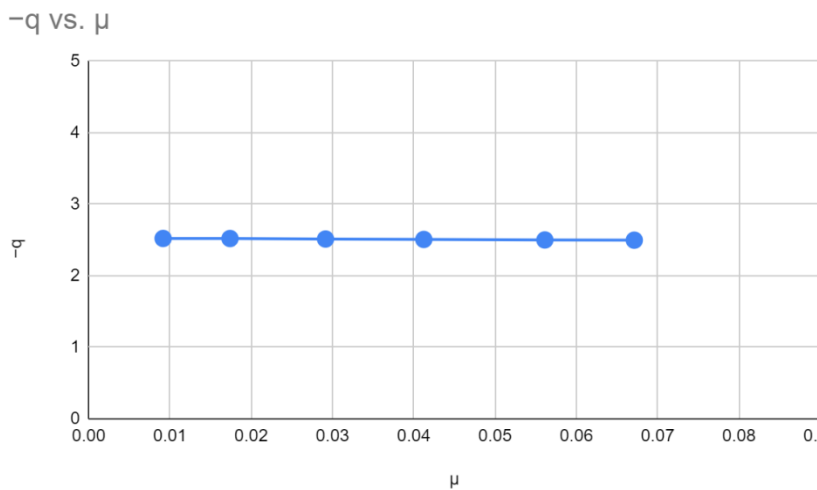


Fig. 3: The plot of $-q$ against μ for the dissociation constant of proline in 30% dioxane (m/m) at 318.15 K.

In Fig 1, 2 and 3 the plots have been extrapolated to $\mu = 0$ and we have get the value of pK_1 at 318.15 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 .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	2.26	13.763	64.103	-6.635
20	2.42	14.281	16.730	8.960
30	2.53	15.434	64.687	-5.146

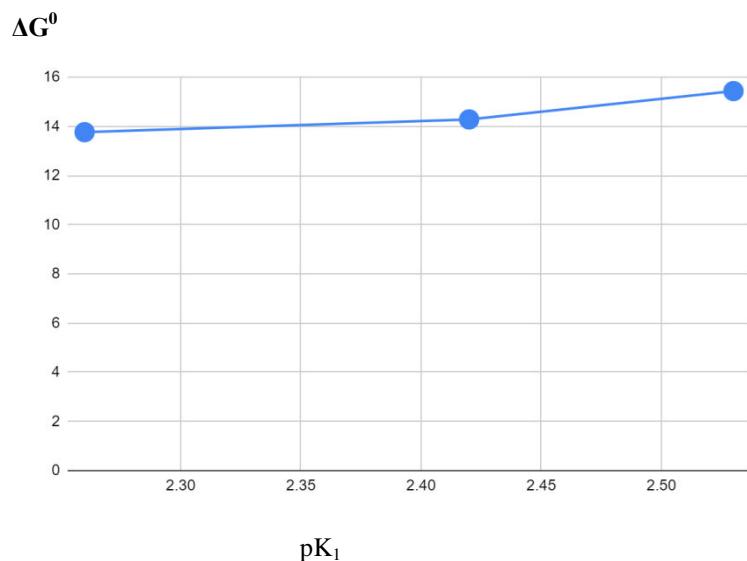


Fig. 4: The plot of ΔG^0 against pK_1 for the dissociation constant of proline in 10, 20 ad 30% dioxane (m/m) at 318.15 K.

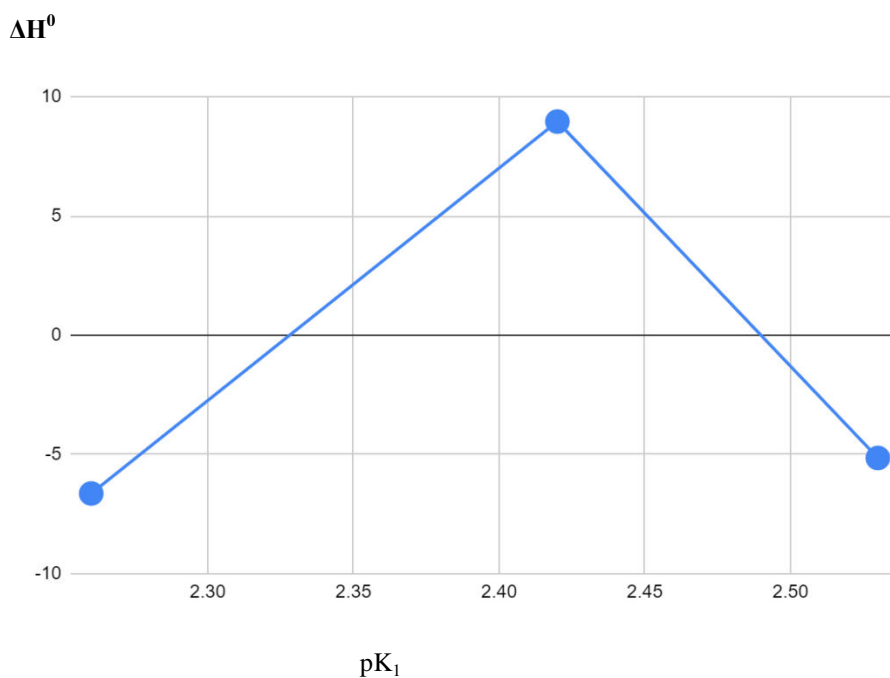


Fig. 5: The plot of ΔH^0 against pK_1 for the dissociation constant of proline in 10, 20 ad 30% dioxane (m/m) at 318.15 K.

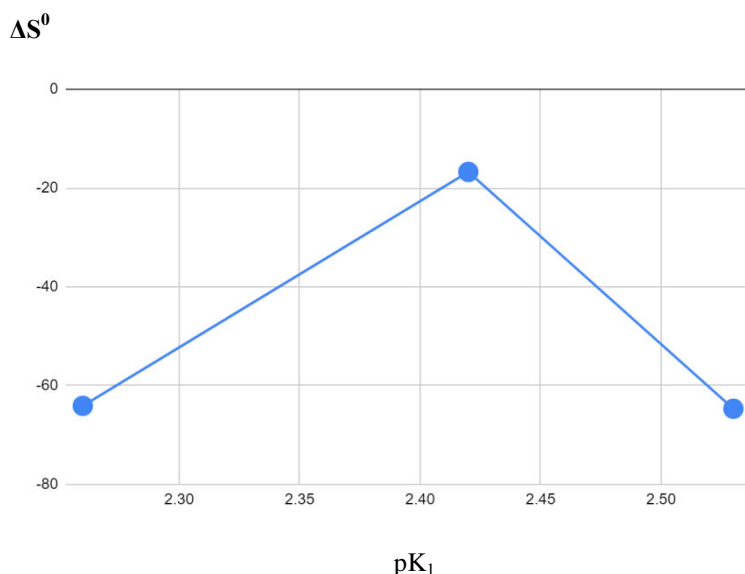


Fig. 6: The plot of ΔS^0 against pK_1 for the dissociation constant of proline in 10, 20 ad 30% dioxane (m/m) at 318.15 K.

The values obtained by least square method¹⁴ 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 318.15K 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.

Study of thermodynamic quantities: From table 4, it is evident that value of standard free change value at 318.15K 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 but the increase in pK_1 is not smooth with increase in standard free energy change rather there is a slight curvature.

Further it is noticed from table 4, that value of standard enthalpy change is negative for 10 and 30% whereas for 20% dioxane (m/m) content the value of standard enthalpy change is positive indicating that the reaction is exothermic in 10 and 30% whereas reaction is endothermic in 20% dioxane in dioxane water system at 318.15K.

Similarly, the value of standard entropy change at 10, 20 and 30% dioxane (m/m) in dioxane-water at 318.15K is negative but entropy increases from 10 to 20% and then decreases in 30%.

According to Frank and Evans¹⁶, 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 bonded¹⁷. Furthermore, dioxane molecule forms hydrogen bonding with hydrogen atoms of water molecules¹⁸ which affect structure of water and so ion-solvent interaction. Since addition of dioxane in dioxane-water system structure of water is affected and according to Frank and Wen¹⁹, water has quasi crystalline structure at ordinary temperature and dynamic structure exist between three 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 Wen¹⁹ 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 three dimensional structure of water. In such circumstances it is difficult to ascertain exact nature of detail molecular structure of water molecules and 318.15K 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 318.15K because of increase in standard free energy change, the value of pK_1 increases.

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