

# Dissociation Constant of Proline in 10, 20 and 30% Dioxane in Dioxane-Water at 288.15K and Related Thermodynamic Quantities by e.m.f. Measurement

Md. Shamsuddin<sup>1</sup>, A. K. Ghosh<sup>2</sup>

<sup>1</sup>Maharana Pratap Govt. P.G. College, Chittorgarh, Rajasthan, India

<sup>2</sup>Ex Head of The Department of Chemistry, Patna University, Science College, Patna, Bihar, India

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## ABSTRACT

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

$H_2(Pt) | \text{Proline, HCl, X\% Dioxane, Hg}_2Cl_2 | Hg \dots(C-1)$

$m_1 \ m_2(100-x)\% \text{water}$

and emf of the cell is given by:

$$E = E_0 - (2.303RT/F) (\log m_{H^+} \ m_{Cl^-} + \log \gamma_{H^+} \ \gamma_{Cl^-}) \dots(1)$$

where

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

The equation (2) is Modified Davies Equation 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:

$$\log m_{H^+} = (E_0 - E)/K - \log m_{Cl^-} + (2A \sqrt{\mu} / (1 + \sqrt{\mu})) - \beta_1 \mu \dots(3)$$

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  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  can be calculated.

**Keywords** : Proline, Thermodynamic Quantities, Biomolecule, Barometric Pressure, Vapour Pressure, Bubbler Depth

## I. INTRODUCTION

Proline is an important part of biomolecule and its dissociation constant is known in aqueous system but in aquo organic system a little work<sup>1-8</sup> has been done

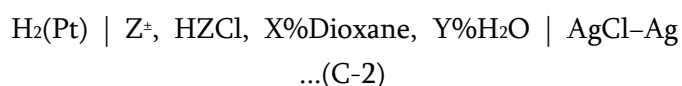
for the dissociation constant of amino acid in dioxane-water system because dissociation constant is directly related to stability of a substance in a medium and so it may be helpful in its purification and separation. Therefore, it is well established that e.m.f.

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% of 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  $0.07\text{mol kg}^{-1}$  in aqueous and aquo-organic system. The general modified Davies equation:

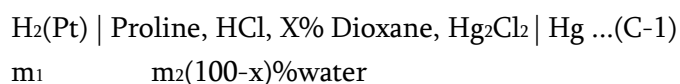
$$\log \gamma_i = - (2A'Z_i^2\sqrt{\mu}/(1+\sqrt{\mu})) + \beta_1\mu \quad (A)$$

Hence, curiosity arose to determine acidic dissociation constant of Proline in 10, 20 and 30% (m/m) dioxane in dioxane-water system at 288.15K. 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.

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



We set up cell without liquid junction potential to determine acidic dissociation of Proline in 10, 20 and 30%(m/m) dioxane in dioxane water system at 288.15K.



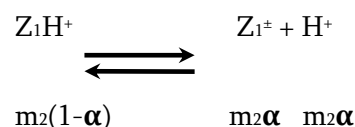
## II. Experimental Detail

To determine acidic dissociation constant of Proline in 10, 20 and 30% (m/m) dioxane in dioxane-water at 288.15 K a cell C-1 was setup. The glass cell made up of corning glass was setup in duplicate and the

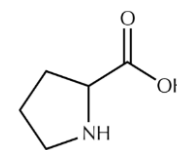
electrodes were fitted in interchangeable cones and could be put in and test from the cell as and when needed. All chemical used for the purpose are of AR or GR quality. Buffer solution of Proline was prepared by mixing one molar solution of proline and half molar solution of hydrochloric acid. After attaining equilibrium the EMF value have been noted for 10, 20 and 30% dioxane 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. RESULTS 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  $Z_1\text{H}^+$  in the buffer of Proline and hydrochloric acid

$$\begin{aligned} m_{\text{Z}^\pm} &= m_1 + m_2\alpha \\ m_{\text{H}^+} &= m_2\alpha \\ m_{\text{Z}_1\text{H}^+} &= m_2(1-\alpha) \\ \mu &= \frac{1}{2} m_{\text{H}^+} + \frac{1}{2} m_{\text{Z}_1\text{H}^+} + \frac{1}{2} m_{\text{Cl}^-} \\ &= \frac{1}{2} m_2 \alpha + \frac{1}{2} m_2 (1-\alpha) + \frac{1}{2} m_2 \\ \mu &= m_2 \end{aligned}$$

In the cell C-1 and arbitrary value is assigned to  $\mu$  and taking  $E^0$ ,  $\beta$  and  $A'$ ,  $m_{\text{H}^+}$  is calculated from equation (3), and when this  $m_{\text{H}^+}$  value is put in  $m_{\text{H}^+} = m_2\alpha$  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  $m_{\text{H}^+}$  is obtained up to the 6th place of decimal and from this value of  $m_{\text{H}^+}$ ,  $m_{\text{Z}^\pm}$  and  $m_{\text{Z}_1\text{H}^+}$  and this value is put in tabular form.

From dissociation of protonated Proline we have

$$K_1 = (m_{\text{H}^+} m_{\text{Z}_1^\pm} / m_{\text{Z}_1\text{H}^+}) \cdot (\gamma_{\text{H}^+} \gamma_{\text{Z}_1^\pm} / \gamma_{\text{Z}_1\text{H}^+}) \quad \dots(4)$$

Or

$$\log K_1 = \log K_1(A) + \log \left( \frac{Y_{H^+} Y_{Z1^{\pm}}}{Y_{Z1H^+}} \right) \quad \dots(5)$$

$K_1(A)$  = apparent dissociation constant

$K_1$  = real dissociation constant

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

$$K_1(A) = \frac{m_{H^+} m_{Z1^{\pm}}}{m_{Z1H^+}} = \frac{m_{H^+} \cdot (m_1 + m_{H^+})}{m_2 - m_{H^+}} \quad \dots(7)$$

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

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

$$m_{Z1H^+} = m_2(1 - \alpha)$$

$$\beta_1 = \beta_{H^+} + \beta_{Z1H^+} + \beta_{Z1^{\pm}}$$

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

or

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

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

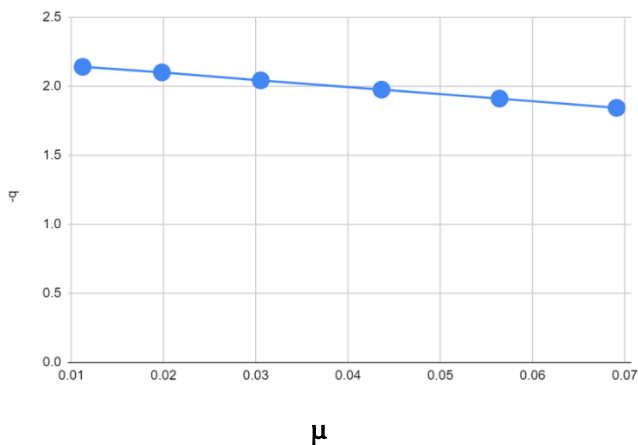
$$\text{or } q = \log K_1 - \beta_1\mu$$

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

Now  $-q$  is plotted against  $\mu$  for 10, 20 and 30% dioxane at 288.15 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.

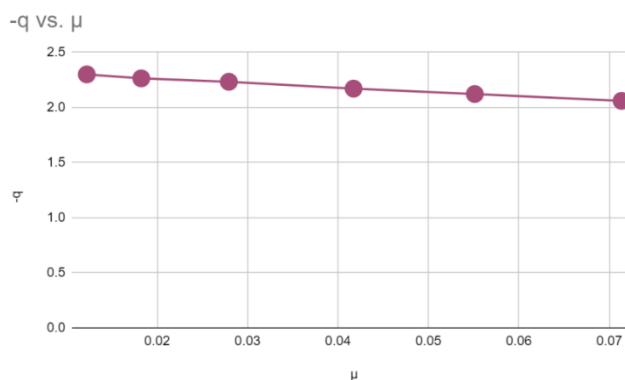
$\mu$	$-q$
0.011236	2.141
0.019825	2.101
0.030536	2.043
0.043637	1.976
0.056419	1.911
0.069112	1.844



**Fig. 1 :** The plot of  $-q$  against  $\mu$  for the dissociation constant of proline in 10% dioxane at 288.15 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.

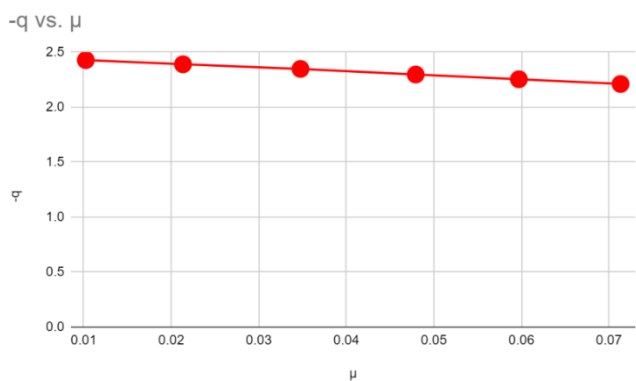
$\mu$	$-q$
0.012222	2.3
0.018247	2.264
0.027936	2.233
0.041726	2.171
0.055126	2.122
0.071362	2.06



**Fig. 2 :** The plot of  $-q$  against  $\mu$  for the dissociation constant of proline in 20% dioxane at 288.15 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

$\mu$	$-q$
0.010237	2.428
0.021339	2.39
0.034764	2.348
0.047926	2.297
0.059715	2.254
0.071334	2.211



**Fig. 3 :** The plot of  $-q$  against  $\mu$  for the dissociation constant of proline in 30% dioxane at 288.15 K.

**Table 4 :** The values of  $pK_1$ ,  $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$  in 10, 20 and 30% dioxane in dioxane-water system at 288.15 K for the cell C-1.

% Dioxane-water	$pK_1$	$-\beta_1$ Kg $\text{mol}^{-1}$	$\Delta G^0$ $\text{KJ mol}^{-1}$	$-\Delta S^0 \times 10^3$ $\text{KJK}^{-1}\text{mol}^{-1}$	$-\Delta H^0$ $\text{KJ mol}^{-1}$
10	2.20	5.11	12.132	43.967	0.663
20	2.34	3.95	12.884	76.487	9.156
30	2.45	3.52	13.548	61.0132	4.030

In Fig 1, 2 and 3 the plots have been extrapolated at  $\mu = 0$  and we have get the value of  $pK_1$  at 288.15 K in 10, 20 and 30% dioxane in dioxane-water system and related thermodynamic quantities  $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$  have been calculated at recorded in Table 4.

To know the acidic dissociation constant the following equation<sup>14</sup> is taken into consideration and the value of  $A^*$ ,  $D^*$  and  $C^*$  have been calculated by least square method. The general equation for 10, 20 and 30% dioxane content can be written as:

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

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

$$\log K_1 = -1388.5047/T + 7.5582986 - 0.0171427T \quad \dots(12)$$

For 20% (m/m) dioxane

$$\log K_1 = -4797.9309/T - 33.9773763 + 0.0171427T \quad \dots(13)$$

For 30% (m/m) dioxane

$$\log K_1 = -54.9631/T - 33.9773763 - 0.0031994T \quad \dots(14)$$

Thermodynamic quantity  $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$  can be calculated by the following thermodynamic equation:

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

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

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

The values obtained from equation (12) to (14) 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 at 288.15K 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.

From table (4), the value of standard free change is also same for 10 and 20% dioxane in dioxane-water system, but at 30% dioxane in dioxane-water system at the same temperature there is slight increase in standard free energy change which is due to decrease in dielectric constant of the medium, slight increase in standard free energy change means dioxane molecules are not well interacted with proline which is due to ring structure of proline and low charge existence of the zwitter ion. Free energy transfer of proline from water to 10, 20 and 30% dioxane in dioxane-water system have been calculated with thermodynamic relation:

$$\Delta G_T = 2.303RT \Delta pK_1$$

**Table: 5**

% Dioxane (m/m)	$\Delta pK_1$	$\Delta G^\ddagger$
10	0.24	4.594
20	0.38	7.275
30	0.50	9.572

It is clear from table 5 that with increase in dioxane content from 10 to 30%, free energy transfer increases. The purpose of calculating the free energy transfer from water to aquo organic solvent is measure of ion-solvent interaction and hence study of effect of aquo-organic solvent on zwitter ion which may be helpful in understanding its structure and it may give new way purification and separation of amino acids from a system. The free energy transfer of cation and anion from water to aquo organic system are usually negative and positive respectively<sup>16-18</sup>. It is known that from Born<sup>19</sup> equation or modified<sup>20-21</sup> equation the role of ionization of weak acids and bases is not clearly understood hence in such circumstances the problem is extremely complicated in the case of zwitter ion upon addition of organic component in aquo-organic medium. The main contributory factors in the study of ion-solvent interaction is structural change of water and zwitter ion existence and for proline molecule is due to its solvation by large number of molecules<sup>22</sup>. It is clear from table 4 that value of standard enthalpy change for 10, 20 and 30% dioxane water is negative at 288.15K means the reaction is exothermic. Similarly, the value of standard entropy change at 10, 20 and 30% dioxane in dioxane-water at 288.15K is negative and there is decrease in entropy from 10% to 20% dioxane at 288.15K and from 20 to 30% dioxane at 288.15K there is slight increase in entropy. 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. We know that standard enthalpy change is measure of bond breaking and bond forming in

solution and 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 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 large size of dioxane it may breakdown three dimensional structure of water and so it is difficult to ascertain exact nature of detail molecular structure of water molecules in 10, 20 and 30% dioxane in dioxane-water system at 288.15K. Hence, dielectric constant is the main factor responsible for dissociation of proline. It is evident from table 4 that there is increase in standard free energy change and  $pK_1$  value with increase in dioxane content. Hence it can be concluded that dissociation of Proline is less favored with increase in dioxane content at 288.15K.

#### IV. REFERENCES

- [1]. H. S. Harned and B. B. Owen, J. Am. Chem. Soc., 1930, 52(12), 5091-5102.
- [2]. H. S. Harned and B. B. Owen, Chem. Rev., 1939, 25(1), 31-65.
- [3]. B. B. Owen, J. Am. Chem. Soc., 1934, 56(8), 1695-1697.
- [4]. L. F. Nims and P. K. Smith, J. Bio. Chem., 1933, 101(2), 401-412.

- [5]. P. K. Smith and A. C. Taylor and E. R. B. Smith, J. Bio. Chem., 1937, 122(1), 109-123.
- [6]. J. T. Edsall and R. D. Blanchard, J. Am. Chem. Soc., 1933, 55(6), 2337-2353.
- [7]. A. K. Chattopadhyay, S. C. Lahri, Indian. J. Chem., 1977, 15A, 930.
- [8]. H. S. Harned and C. M., Birdsall, J. Am. Chem. Soc., 1943, 65(1), 54-57.
- [9]. A.K. Sinha, J.C. Ghosh and B. Prasad, Indian J. Chem. A, 1981, 20(01), 33-35.
- [10]. G. Sahu and Prasad B, Indian J. Chem. Soc, 1969, 46, 233.
- [11]. B. Prasad, J. Indian. Chem. Soc., 1977, 54, 588.
- [12]. A. Gupta, Ph.D Thesis, Patna University, Patna, 1986.
- [13]. S. Ghosh, Ph.D Thesis, Patna University, 1992.
- [14]. H. S. Harned and R. A. Robinson, Trans. Farad. Soc., 1940, 36, 973-978.
- [15]. B. M. Prasad and J. C. Gosh, Proc. Nat. Acad. Sc. India, 1990, 60A, III, 255.
- [16]. C. F. Well, J. Chem. Soc. Faraday Trans.- I, 1976, 72, 601-609.
- [17]. C. F. Well, J. Chem. Soc. Faraday Trans.-I, 1973, 69, 984-992.
- [18]. D. Feakins, Physico-chemical process and mixed aqueous solvents, Edited by F. Franks (Hienemann Educational Books Ltd., London), Jan. 1967, 7190.
- [19]. Born.M. ; Z Physik, 1920, 1, 45
- [20]. Sager, E.E.Robinson, R.A. and Bates, R.G. ; J. Res.Nat.Bur.Stand, 1965, A69, 263
- [21]. Parson,G.H. and Rochester;C.H. ; J.Chem.Soc.; Farad I; 1975, 71, 1068
- [22]. Chattopadhyay, A.K, and Lahiri, S.C.; Electrothermica Acta, 1982, 27, 269
- [23]. H. S. Frank and M. W. Evans, J. Chem. Phys., 1945, 13(11), 507-532.
- [24]. D. Feakins and P. Watson., J. Chem. Soc. (Resumed), 1963, 4734-4741.
- [25]. F. Frank, "Water, A Comprehensive Treatise" Vol. II, Edited by F. Frank, Plenum Press, New York, London, 1973, 1430.
- [26]. H. S. Frank and W. Y. Wen, Disc. Farad. Soc., 1967, 24, 133-1

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