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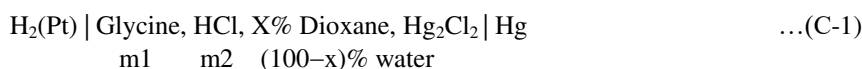
Study of Effect of 10, 20 and 30% Dioxane (m/m) in Dioxane-Water System on Acidic Dissociation Constant of Glycine and Related Thermodynamic Quantities at 288.15⁰K by Potentiometric Method

Md. Shamsuddin¹, Anil Kumar Chaohadia¹, D. P. Goyal¹, A. K. Ghosh²

¹Maharana Pratap Govt. P.G. College, Chittorgarh (Raj.), India

²Department of Chemistry, Patna University, Science College, Patna (Bihar), India

ABSTRACT: The acidic dissociation constant of glycine at 10%, 20% and 30% dioxane at 288.15⁰K was determined using the cell:



and e.m.f. of the cell was given by

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

$$\text{Where } \log \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} = -2A' \sqrt{\mu} / (1 + \sqrt{\mu}) + \beta_1 \mu \quad (\text{modified Davies equation}) \quad \dots(2)$$

Which has been given by B Prasad in our laboratory called modified Davies equation for calculating activity coefficient in the system under study acidic dissociation constant was calculated by calculating m_{H^+} given by the formula:

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

By determining the acidic dissociation constant of glycine at 288.15⁰ K in 10, 20 and 30% dioxane-water systems, the effect of dioxane in dissociation of glycine was studied and related thermodynamic quantities were determined.

KEYWORDS: Acidic dissociation constant, Dioxane-water, Modified Davies equation, solvent effect, free energy transfer.

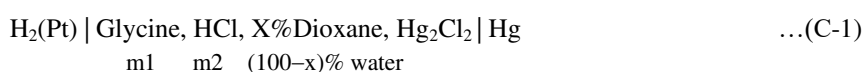
I. INTRODUCTION

Glycine is an important biomolecule and essential for life. Therefore it is necessary to study dissociation in Aquo organic solvent. The dissociation constant of monoprotic and diprotic acid, have been determined in water and dioxane water systems by different workers¹⁻³ using cells without liquid junction potential besides acidic dissociation constant of amino acids⁴⁻⁸ in water have been determined using cells 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.⁹⁻¹⁵ The acidic dissociation constant of glycine has been determined by Birdsall¹⁶ in 20, 45 and 70% dioxane content of dioxane-water system using cell of the following type.





Therefore, it is well established that e.m.f measurement with a cell having no liquid junction potential gives the most accurate result. Acidic dissociation constant indicates the nature of the substance to donate hydrogen ions. Furthermore, acidic dissociation constant is also important for a chemical in biochemistry and pharmaceutical and by studying acidic dissociation constant we can get information about fraction of biomolecules to get absorbed and from pK value we get information about ionization behavior and so pK_a is of great importance to explain drug absorption and biodistribution in the systematic circulation. Further, pK_a measurement enables the determination of proportion of the molecules in the ionized or deionized state. Apparently pK_a is an experimentally determined value of molecules or bio-molecules, the value is the pH at which the number of ionized and deionized are equal. Knowing the importance of pK_a value, curiosity arose to determine the pK_a value of glycine in 10, 20 and 30% dioxane in dioxane-water systems at 288.15⁰K by setting up the following cell.



The main problem in determination of ionization constant of an electrolyte is value of activity coefficient of the species involved in the medium under study so that ion solvent interaction must be taken into consideration resulting it would be helpful in understanding the structure of the medium. In this regard, a modified Davies equation has been found more suitable, given by Prasad¹⁷ in our laboratory.

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

and for our experiment up to 30% dioxane content activity coefficient of HCl is given by the following equation.

$$\log \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} = -2A'\sqrt{\mu}/1 + \sqrt{\mu} + \beta_1\mu \quad \dots(5)$$

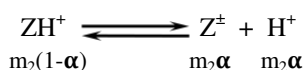
Where A' is Debye Huckel constant and β₁ is additive parameter.

II. EXPERIMENTAL DETAIL

The acidic dissociation constant of Glycine for 10, 20 and 30% dioxane (m/m) in dioxane-water system was determined by the EMF measurement for the cell (C-1) at 288.15⁰ K. 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 chemical 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:



where $\text{ZH}^+ = \text{NH}_3^+ - \text{CH}_2 - \text{COOH}$

$\text{Z}^\pm = \text{NH}_3^+ - \text{CH}_2 - \text{COO}^-$

and $\text{Z} = \text{NH}_2 - \text{CH}_2 - \text{COOH} = \text{glycine}$

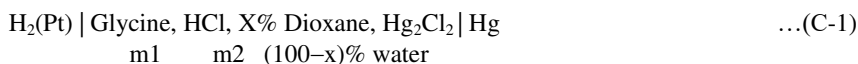
If α be the degree of dissociation of ZH⁺ in the buffer of Glycine and hydrochloric acid

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

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



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



In the cell C-1 and arbitrary value is assigned to μ and taking E^0 and β and A' , m_{H^+} is calculated from equation (3).

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

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).

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

Till constant value of m_{H^+} is obtained up to 6 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 protonation of glycine we have

$$K_1 = (m_{H^+} m_z^\pm / m_{ZH^+}) \cdot (V_H^+ V_Z^\pm / V_{ZH^+}) \quad \dots(6)$$

$$\text{or } \log K_1 = \log K_1(A) + \log (V_H^+ V_Z^\pm / V_{ZH^+}) \quad \dots(7)$$

$K_1(A)$ = apparent dissociation constant

K_1 = real dissociation constant (acidic dissociation constant)

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

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

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

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

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

$$-q = -\log K_1 + \beta_1 \mu \quad \dots(10)$$

$$-q = p K_1 + \beta_1 \mu \quad \dots(11)$$

Now, $-q$ is plotted against μ at 288.15⁰ K for 10, 20 and 30% dioxane in dioxane-water systems.

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	$-q$
0.010675	2.48136
0.018248	2.435
0.028722	2.385
0.040074	2.325
0.052240	2.285
0.065480	2.205
0.074800	2.175

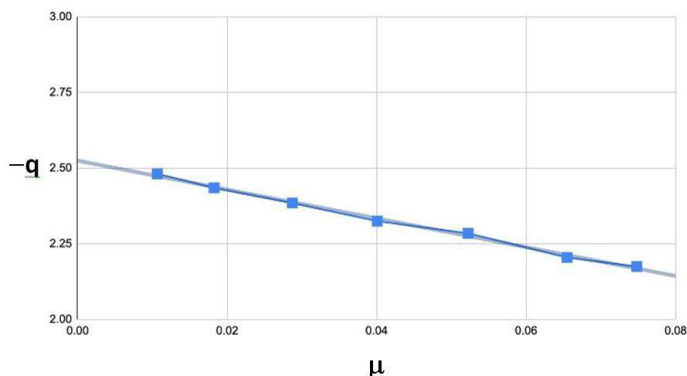


Fig. 1: The plot of $-q$ against μ for the dissociation constant of Glycine in 10% dioxane in dioxane-water system at 288.15⁰ K.



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	$-q$
0.009725	2.588
0.019736	2.529
0.026740	2.477
0.041450	2.358
0.052260	2.284
0.065520	2.236

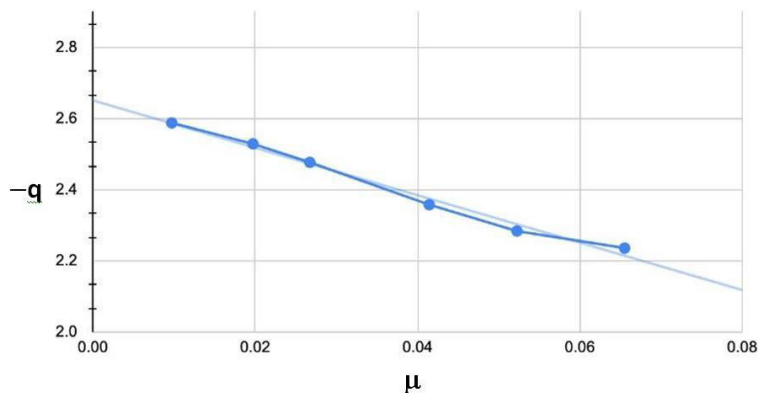


Fig. 2: The plot of $-q$ against μ for the dissociation constant of Glycine in 20% dioxane in dioxane-water system at 288.15⁰ K.

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	$-q$
0.015235	2.678
0.018342	2.656
0.030450	2.571
0.041220	2.52
0.055750	2.445
0.065240	2.4

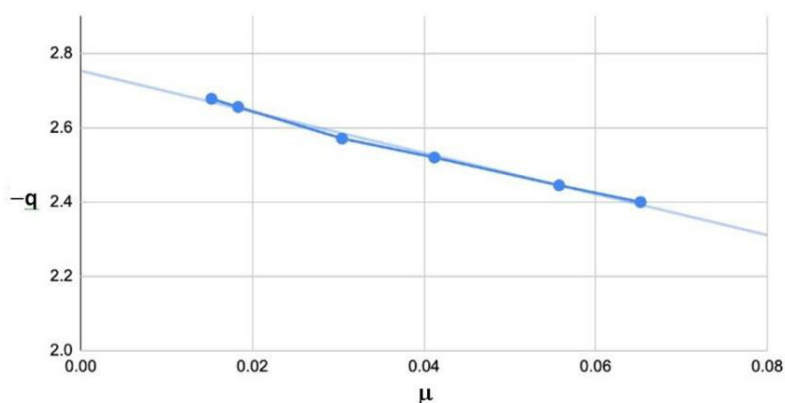


Fig. 3: The plot of $-q$ against μ for the dissociation constant of Glycine in 30% dioxane in dioxane-water system in at 288.15⁰ K.

In the Fig. 1, 2 and 3, the plots have been extrapolated at $\mu = 0$ and we get the value of pK_1 at 288.15⁰K in 10, 20 and 30% dioxane in dioxane-water systems and related thermodynamic quantities ΔG^0 , ΔS^0 and ΔH^0 at 288.15⁰K recorded in table 4.

Table- 4: The Value of pK_1 , ΔG^0 , ΔS^0 , ΔH^0 and β_1 have been recorded in table 4 for the cell C-1 in the 10, 20 and 30% dioxane in dioxane-water systems at 288.15⁰K.

% Dioxane (m/m)	pK_1	$-\beta_1$ Kg mol ⁻¹	ΔG^0 KJ mol ⁻¹	$-\Delta S^0 \times 10^3$ KJ K ⁻¹ mol ⁻¹	ΔH^0 KJ mol ⁻¹
10	2.52	4.73	13.952	3.193	14.872
20	2.64	5.40	14.566	36.950	3.945
30	2.79	6.69	15.378	26.284	7.803

By the method of least square²⁰, the value of deprotonation constant are given by the equation

$$\log K_1 = -A^*/T + D^* - C^*T \quad \dots(12)$$



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

For 10% (m/m) dioxane

$$\log K_1 = -4179.255/T + 23.723225 - 0.0409778T \quad \dots(13)$$

For 20% (m/m) dioxane

$$\log K_1 = -678.3820/T + 1.4152361 - 0.0057964T \quad \dots(14)$$

For 30% (m/m) dioxane

$$\log K_1 = -2117.1090/T + 10.4921639 - 0.0205886T \quad \dots(15)$$

The value of A*, D* and C* have been recorded in Table 5 for 10, 20 and 30% (m/m) dioxane in dioxane-water content. The values pK₁ calculated from these equations are in good agreement with the experimental values as shown in Table 6. The values of pK₁ increases with the increase in dioxane content of dioxane-water system as evident from Table 4. 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 method have been recorded.

mass % Dioxane	A*	D*	C*
10	4179.255	23.782	0.041
20	687.382	1.415	0.006
30	2117.1090	10.4921639	0.021

Table- 6: Comparison of values of pK₁ for general equation and experimental value at 288.15⁰K in the 10, 20 and 30% dioxane in dioxane-water systems.

mass % Dioxane	Experimental value	General equation value
10	2.52	2.53
20	2.64	2.64
30	2.79	2.78

Thermodynamic quantities can be calculated by the following formula:

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

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

$$\Delta S^0 = -19.1438 (D^* - 2C^* T) \quad \dots(18)$$

IV. SOLUTE-SOLVENT INTERACTION

Glycine exists in zwitter ion form and there is possibility of interaction between glycine zwitter ion and dioxane and there may be large number of dioxane molecules involved forming layered structure with glycine and hence no further decrease in dielectric constant.

Dominating role played by dielectric constant because with increase in dioxane-content there is increase in pK₁ values which indicates that there is lesser dissociation of glycine. Free energy transfer from water to aquo-organic system is measure of ion-solvent interaction. The purpose of calculating free energy transfer is mainly study of effect of aquo-organic solvent upon structure of zwitter ion hence may be used for purification and separation of amino acids. The free energy transfer of cation and anion from water to aquo-organic system usually negative and positive respectively.²²⁻²⁴



Change in enthalpy ΔH^0 is measure of bond breaking and bond making in solution. According to Frank and Evan²⁵ when a neutral molecule dissociates, it forms a charged ions which immobilizes solvent molecules causing decrease in entropy. We are studying dioxane-water system in which dissociation of glycine takes place and we know that dioxane is more basic than water and it enhances the acidity of water molecules to which it is bonded²⁶; this is because of inductive effect of two methylene groups in each side of oxygen atoms of dioxane molecules. Further, dioxane molecules form hydrogen bonding with water molecules.²⁷ This causes dioxane molecule becomes more basic and less acidic than water. It is evident that a cation will interact more strongly with the oxygen atom in dioxane-water system moiety in dioxane-water system while anion will interact more strongly with other hydrogen atom of hydrogen bonded water dioxane moiety and not with hydrogen atom of methylene group of dioxane. This type of ion solvent interaction will cause a primary solvation sheath around the ions. This is the region “A” of Frank and Wen.²⁸ Water has quasi-crystalline structure at ordinary temperature and a dynamic equilibrium probably exists between 3-dimensional hydrogen bonded clusters and the denser monomer. In the region “A” around the ion, water molecules are in a sort of frozen state while a bit away there is the normal 3-dimensional water structure called region “C”. In between region “A” and region “C”, there is region “B” where the water molecules are disorganized but in case of aquo-organic solvent Frank and Wen²⁵ simple model needs to be modified because of structural change of water molecule due to addition of organic solvent and structural change of water may also depend upon mass % of organic component added. It is expected that addition of small amount of dioxane may give rise to two changes, the first is dioxane may be accumulated with solvent structure or it may strengthen water structure; since water is better proton acceptor, in case it is not accommodated because of its large size it may cause a breakdown in 3-dimensional structure of water but it is evident from viscometric study of dioxane-water mixture, the dioxane is not accommodated in the solvent structure and it breaks down 3-dimensional structure of water. But it is very difficult to ascertain the exact nature of detailed molecular structure in different mass % of organic content and how it changes with change of mass % of organic content at a given temperature. Therefore, it becomes a tedious job in these circumstances to correlate quantitatively the variation of ΔH^0 and ΔS^0 both change in concentration of organic components at a given temperature. In our study of acidic dissociation of glycine in 10, 20 and 30 % dioxane in dioxane-water system at 288.15⁰K there is an increase in pK_1 value with increase in mass % of dioxane. Hence it can be concluded that up to 30% of dioxane content dioxane in dioxane-water system dissociation of glycine is not favored.

The variation in thermodynamic quantities like ΔG^0 , ΔH^0 and ΔS^0 have been studied by the graph. It is evident from fig. 4 that there is an increase in standard free energy change with increase in pK_1 value which indicates that acidic dissociation of glycine is not favorable with increase in dioxane content.

Table- 7: Variation of ΔG^0 with pK_1 for 10, 20 and 30% dioxane in dioxane–water system at 288.15⁰K recorded.

Mass % dioxane	ΔG^0	pK_1
10	13.952	2.52
20	14.566	2.64
30	15.378	2.79

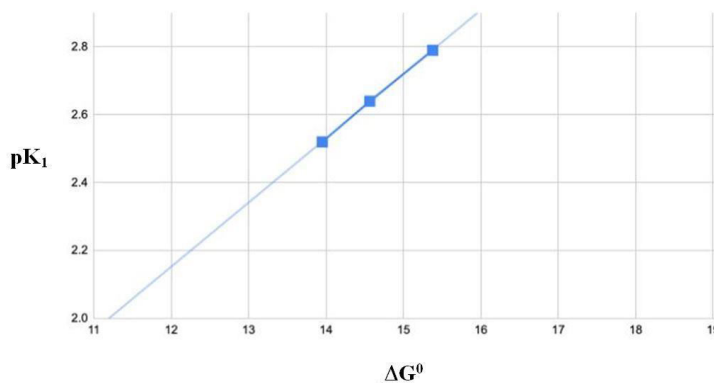


Fig. 4: Plot of pK_1 against ΔG^0 at 288.15⁰ K for 10, 20 and 30 % dioxane in dioxane-water system.

It is evident from the fig. 5 that there is maximum entropy in 10% dioxane-content, it means the dioxane is not immobilized with presence of zwitter ion of glycine as percent of dioxane is increased from 10 to 20%, there is sharp decrease in entropy indicating that the dioxane is more organized with glycine system. As dioxane-content is increased from 20 to 30%, there is slight increase in entropy indicating that the dioxane is slightly mobilized in the glycine system.



Table- 8: The variation of ΔS^0 with pK_1 for 10, 20 and 30% dioxane in dioxane–water system at 288.15⁰K recorded.

Mass % dioxane	pK_1	ΔS^0 KJ K ⁻¹ mol ⁻¹
10	2.52	-3.193
20	2.64	-36.950
30	2.79	-26.284

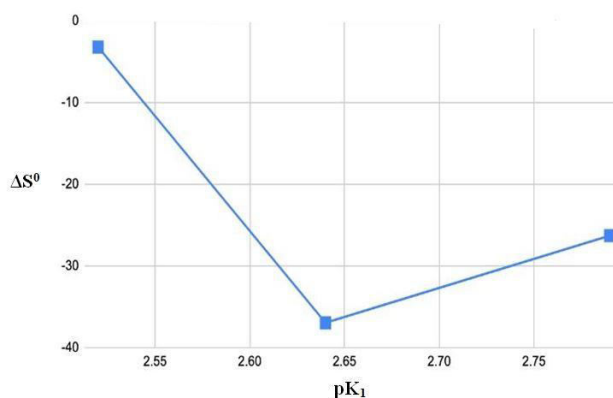


Fig. 5: Plot of pK_1 against ΔS^0 at 288.15⁰ K for 10, 20 and 30 % dioxane in dioxane-water system.

From table 9, it is evident that the value of standard enthalpy change is positive so the reaction is endothermic throughout the dissociation process. In 10% dioxane content the value of standard enthalpy change is maximum, indicating maximum endothermic reaction in the process of acidic dissociation of glycine. In 20% dioxane-content the value of standard enthalpy change is minimum so the acidic dissociation is least endothermic. As the percent of dioxane increases to 30, standard enthalpy change is increased but less than in 10% dioxane-content so in 30% dioxane contents the reaction is not as much endothermic as in 10% dioxane content.

Table- 9: Variation of ΔH^0 with pK_1 for 10, 20 and 30% dioxane in dioxane–water system at 288.15⁰K recorded.

Mass % dioxane	pK_1	ΔH^0 KJ mol ⁻¹
10	2.52	14.872
20	2.64	3.945
30	2.79	7.803

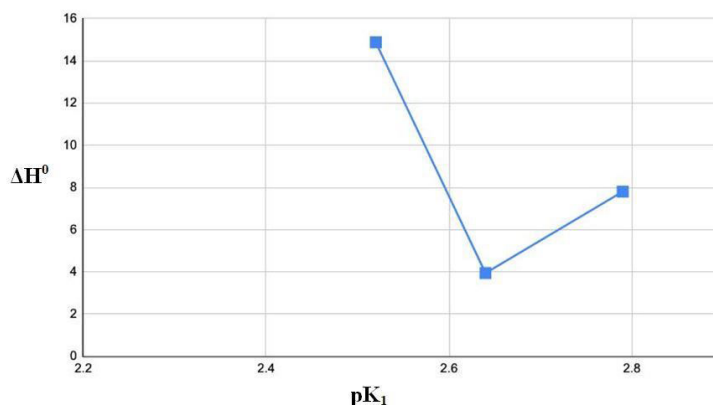


Fig. 6: Plot of pK_1 against ΔH^0 at 288.15⁰ K for 10, 20 and 30 % dioxane in dioxane-water system.

From fig. 10, it is evident that with increase in dioxane content the value of pK_1 which indicates that in higher content of dioxane in dioxane-water system, the acidic dissociation is unfavourable.²⁹

Table- 10: Variation of pK_1 with dielectric constant of 10, 20 and 30% dioxane in dioxane-water system at 288.15^0K .

Mass % dioxane	pK_1	$1/D \times 10^3$
10	2.52	13.657
20	2.64	15.625
30	2.79	18.262

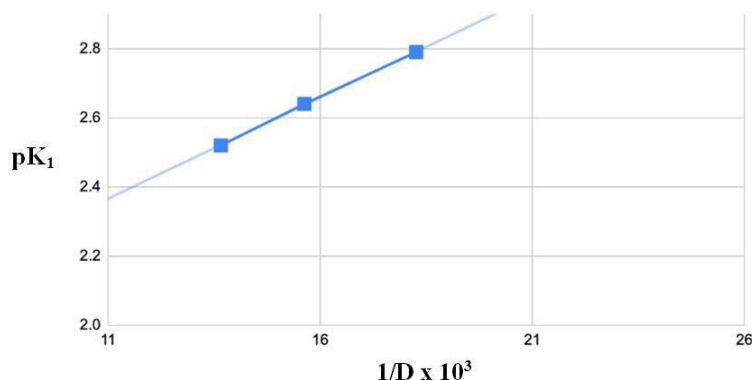


Fig. 7: Plot of pK_1 against $1/D \times 10^3$ at $288.15^0 K$

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