

Review of effect of temperature and thermodynamic quantities upon acidic dissociation of Glycine in 10, 20 and 30% dioxane (m/m) in dioxane-water system at 288.15K, 298.15K, 308.15K and 318.15K by e.m.f. measurement

Md. Shamsuddin

Maharana Pratap Govt. P.G. College, Chittorgarh, Rajasthan, India

Email :- mail2shams63@gmail.com

ARTICLE INFO

Article History:

Accepted: 10 Oct 2023

Published: 30 Oct 2023

Publication Issue

Volume 10, Issue 5

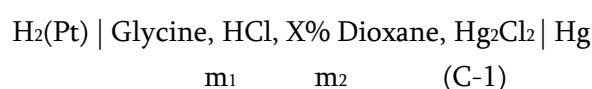
September-October-2023

Page Number

605-611

ABSTRACT

For study of effect of temperature and thermodynamic quantities upon acidic dissociation of Glycine in 10, 20, and 30% dioxane(m/m) content in dioxane-water system at 288.15K, 298.15K, 308.15K, and 318.15K, the following types of cell has been set up:



in 10, 20, and 30% dioxane in dioxane-water system at 288.15K to 318.15K at an interval of 10K, and e.m.f. of the cell was given by:

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

where,

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

$$\log K_1 - \beta_1 \mu = \log K_1(A) - (2A \sqrt{\mu} / (1 + \sqrt{\mu})) \quad (3)$$

The equation (2) is called Modified Davies equation given by B. Prasad¹ for calculating activity coefficient in the system.

From equation (3), acidic dissociation constant of glycine was calculated²⁻⁵ by extrapolating the graph at $\mu=0$ in 10, 20, and 30% dioxane (m/m) in dioxane-water system from 288.15K to 318.5K at an interval of 10K, and then standard free energy change, standard enthalpy change, and standard entropy change were calculated by thermodynamic relations:

$$\Delta G^0 = -RT \ln K_1 \quad (4)$$

$$\text{and } \Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (5)$$

and by least square method⁶.

Keywords: Thermodynamic Quantity, Acidic Dissociation Constant, Modified Davies Equation, Least Square Method.

I. INTRODUCTION

The dissociation of different electrolytes depends on their nature, temperature, and solvent. The study of the variation of dissociation constant of different electrolytes in aqueous and aquo-organic solvents has been a topic of great interest because, by knowing the dissociation constant, the physico-chemical properties of electrolytes can be known. Electrolytes show varying properties in different mediums depending upon their nature, either singly or in a mixed solution, and aqueous solution⁷⁻¹² have been extensively studied in comparison to aquo-organic systems. It is well established that water is good and exceptional solvent for a large number of electrolytes, but workers need to shift their attention from aqueous to aquo-organic systems to understand the course of the reaction in aquo-organic system¹³⁻

¹⁵. When system is changed from water to aquo-organic medium, changes have been observed in the reactivity of ions like solubility, oxidation-reduction and acid-base behavior.

Glycine is an important biomolecule; therefore, it is very informative to study effect of temperature on acidic dissociation of glycine and determination of thermodynamic quantities in aqueous and aquo-organic systems. We have chosen aquo-organic system like dioxane-water system at 288.15K to 318.15K at an interval of 10K.

Result and Discussion:

After determining acidic dissociation constant of glycine related thermodynamic quantities in 10, 20, and 30% dioxane in dioxane-water system were calculated by thermodynamic equations(4), (5) and least square method, and the values are given in table 1.

Table-1

The values of pK_1 , ΔG^0 , ΔS^0 and ΔH^0 in 10, 20, and 30% dioxane in dioxane-water system ranged from 288.15 K to

Temp (K)	mass % Dioxane											
	10				20				30			
	pK_1	ΔG^0 KJ mol ⁻¹	$\Delta S^0 \times 10^3$ KJ K ⁻¹ mol ⁻¹	ΔH^0 KJ mol ⁻¹	pK_1	ΔG^0 KJ mol ⁻¹	$-\Delta S^0 \times 10^3$ KJ K ⁻¹ mol ⁻¹	ΔH^0 KJ mol ⁻¹	pK_1	ΔG^0 KJ mol ⁻¹	$-\Delta S^0 \times 10^3$ KJ K ⁻¹ mol ⁻¹	ΔH^0 KJ mol ⁻¹
288.15	2.52	13.495 2	3.193	14.872	2.64	14.566	36.950	3.945	2.79	15.379	26.284	7.803
298.15	2.45	13.998	-12.497	10.272	2.62	14.945	39.0673	3.295	2.74	15.80	36.168	5.493
308.15	2.40	14.202	-28.185	5.516	2.60	15.347	41.295	2.622	2.73	16.061	42.051	3.103
318.15	2.39	14.562	-43.875	0.603	2.59	15.771	43.54	1.923	2.71	16.521	49.933	0.634

318.15K at an interval of 10K for cell C-1.

pK_1

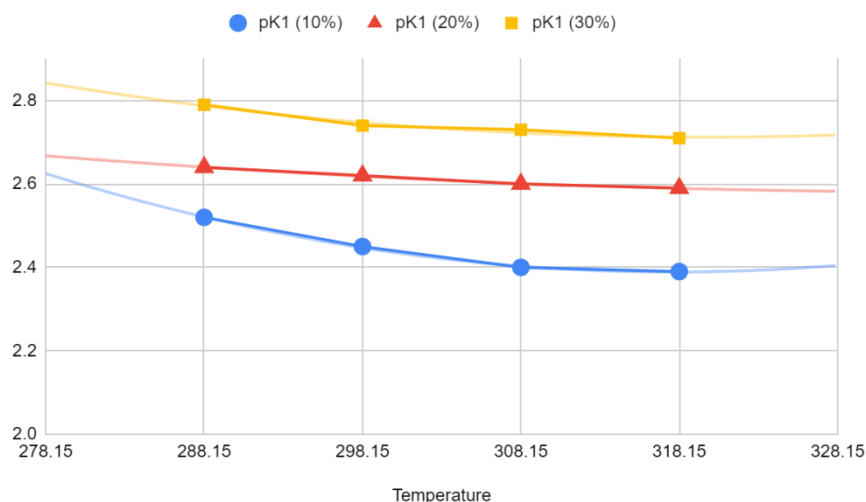


Fig-1 Graph for variation of pK₁ with temperature in 10, 20 and 30% dioxane-water system

Different colors indicates mass percent of dioxane in dioxane-water system.

● pK₁(10%) ▲ pK₁ (20%) ■ pK₁ (30%)

ΔG^0

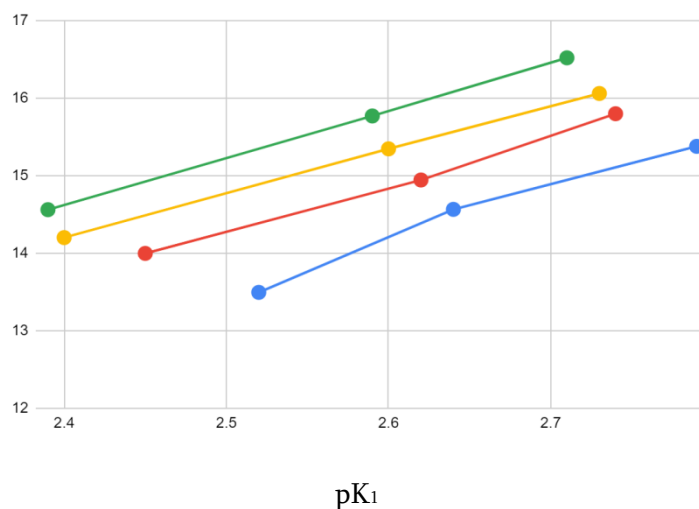


Fig 2 :- Plot of ΔG^0 against pK₁ in 10, 20 and 30% dioxane(m/m) in dioxane water system from 288.15K to 318.15K at an interval of 10K

Different colors indicates temperature as follows:

- - 288.15K
- - 298.15K
- - 308.15K
- - 318.15K

ΔH^0

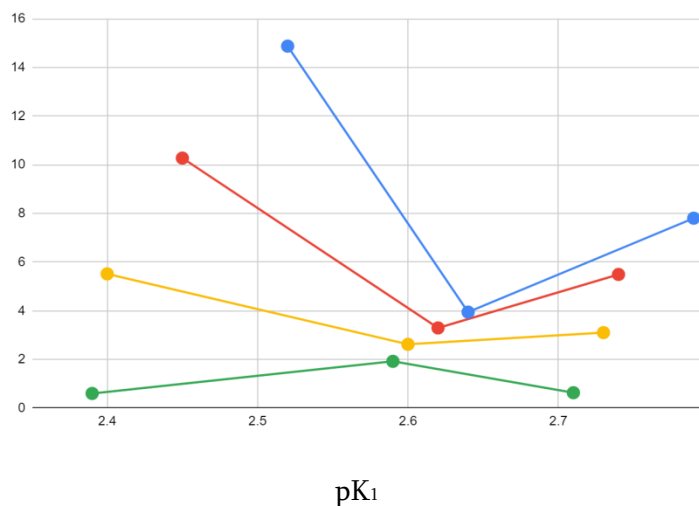


Fig 3 :- Plot of ΔH^0 against pK_1 in 10, 20 and 30% dioxane(m/m) in dioxane water system from 288.15K to 318.15K at an interval of 10K

Different colors indicates temperature as follows:

- - 288.15K
- - 298.15K
- - 308.15K
- - 318.15K

ΔS^0

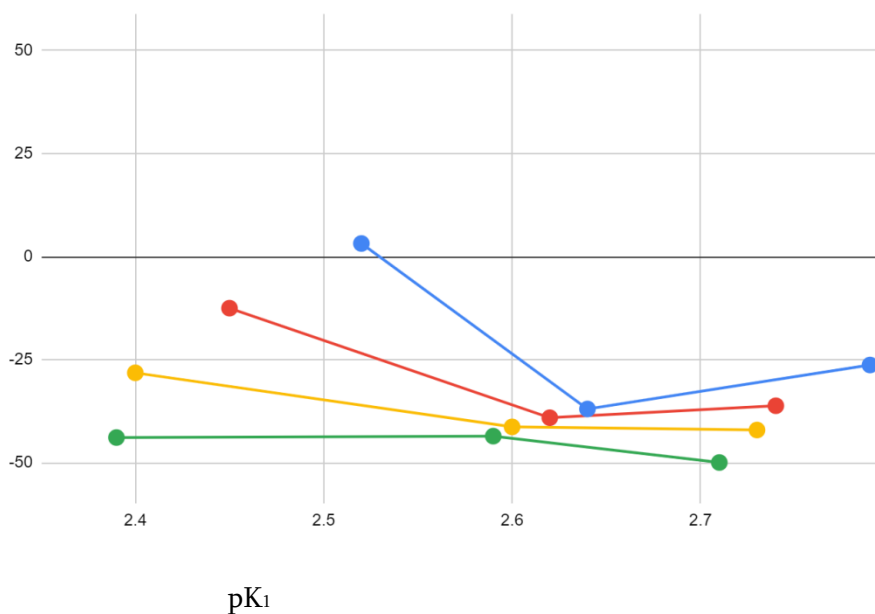






Fig 4 :- Plot of ΔS^0 against pK_1 in 10, 20 and 30% dioxane(m/m) in dioxane water system from 288.15K to 318.15K at an interval of 10K

Different colors indicates temperature as follows:

-  - 288.15K
-  - 298.15K
-  - 308.15K
-  - 318.15K

Effect of Temperature on acidic dissociation of Glycine :-

From Table 1, it is evident that the value of pK_1 decreases with an increase in temperature. The results are similar to the results of other workers¹⁶⁻¹⁷ in dioxane-water system, and it is due to the endothermic nature of the reaction, which favors a decrease in pK_1 value with an increase in temperature from 10 to 30% dioxane water at 288.15K to 318.15K, which is in agreement with observation of Harned¹⁸. Generally, in case of monoprotic and diprotic acids, it has been observed^{14,15,22} that the value of pK_1 increases with an increase in temperature, which is due to a decrease in the dielectric constant of the medium, but in the case of glycine, the pK_1 value decreases with a rise in temperature. It means that the dissociation of glycine is favored with an increase in temperature, and temperature play important role in comparison to dielectric constant of the medium at 10, 20 and 30% dioxane content in the dioxane water system. This may be due to existence of glycine in “zwitter ion” form. So there is possibility of solute-solvent interaction between glycine and dioxane and perhaps the positive end of the zwitter ion interacts with the oxygen atom of dioxane, and probably a large number of dioxane molecules are involved in forming a layered structure with glycine, so there is no further decrease in the dielectric constant. Hence, an increase in temperature favors the dissociation of glycine. This reason may be taken into account to explain the decrease in the pK_1 values of glycine with a rise in temperature. Further, it is evident from Table 1 that there is large increase in pK_1 value with an increase in dioxane content in the dioxane-

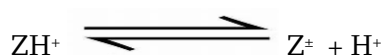
water system and a smaller decrease in pK_1 value with a rise in temperature. Therefore, the dielectric constant of the medium plays a dominant role, and temperature plays the least role in the dissociation of glycine.

From Fig. 1 between temperature and pK_1 for 10, 20, and 30% dioxane (m/m) at 288.15K to 318.15K at 10K interval, it has been observed that there is more curvature in 10 and 30% dioxane content and slight curvature in 20% dioxane content. A greater curvature in 10% dioxane content indicates that there is large solute-solvent interaction.

Further, in the case of 30% dioxane content, there is slight curvature in the plot indicating ion-solvent interaction, and a medium effect is visible. It can be concluded that between 10 and 30% dioxane, there is greater interaction between glycine and dioxane molecules.

Standard Free energy change and pK_1 variation:

It is evident from table 1, that value of standard free energy change of the reaction,



throughout the temperature and mass % of dioxane content of dioxane-water system are positive, the value of ΔG^0 increases with an increase in temperature and dioxane-content water and the increase in standard free energy change is more with increase in dioxane content of dioxane- water system and with an increase in temperature, therefore acidic dissociation of glycine is less favoured with increase of dioxane content but there is decrease in pK_1 value

with an increase in temperature in spite of an increase in standard free energy change as evident from Fig 2. This is perhaps due to interaction of positive end of zwitter ion of glycine with electronegative oxygen atom of dioxane. Therefore, dissociation of glycine may depend upon dielectric constant of the medium, temperature and solute-solvent interaction but the dominating role played by dielectric constant as has been seen in dissociation of acids in aquo-organic system.

It is evident from fig 2, at 308.15K, and 318.15K, there is smooth increase in ΔG^0 value with an increase in pK_1 in 10, 20, and 30% dioxane, whereas at 288.15K there is slight curvature and appreciable curvature at 288.15K.

Standard enthalpy change and pK_1 variation :-

From table 1. it is evident that the enthalpy change is positive, indicating that the reaction is endothermic. means increase in temperature favors the dissociation of glycine. With increase in temperature, there is decrease in standard enthalpy change and the change is remarkable in 288.15K, 298.25K and 308.15K. From table 1, it is evident that at all the temperature under consideration there is decrease in enthalpy change from 10 to 20% dioxane-content and then increase in 30% dioxane-content and minimum value of standard enthalpy change in all the temperature is in 20% dioxane-content and the value surge to exothermic nature i.e., there is remarkable change in 20% dioxane-content.

Further, it is noticed from Fig. 3 that the value of standard enthalpy change decreases at a particular temperature with an increase in dioxane-content from 10 to 20%, but then there is increase in standard enthalpy change when dioxane content increases to 30%, it means the first endothermic nature of the reaction decreases and then there is increase in the endothermic nature of the reaction.

Standard entropy change and pK_1 variation :-

It is evident from table 1, that there is decrease in entropy with increase in temperature and the value of entropy is negative in all the dioxane-content and temperature under consideration except at 288.15K in 10% dioxane-content, the value of entropy is positive. The remarkable point to note that there is greater decrease for 10% dioxane-content from 288.15K to 318.15K at an interval of 10K and least decrease in 20% dioxane-content for 288.15K to 318.15K at an interval of 10K.

Further, on the Fig 4 regarding variation of acidic dissociation of glycine with entropy it has been observed that in all the temperature and dioxane-content entropy first decreases and then there is slight increase in entropy. But the value of pK_1 increases with increase in dioxane- content from 288.15K to 318.15K at an interval of 10K.

According to Frank and Evans¹⁹, ionization of uncharged molecules into ions causes immobilization of solvent molecules around the ions, causing decrease in entropy. In case of glycine, which is both present in form of protonated glycine and zwitter ion in equal molecule, dissociation of protonated glycine gives zwitter ion and proton H^+ . In these circumstances, there is probability of interaction of positive end of zwitter ion with oxygen atom of dioxane; this may cause larger immobilization of solvent molecules, causing decrease in entropy, as evident from Table 1. Further, with rise in temperature, there is decrease in entropy, which is due to dissociation of protonated glycine, forming zwitter ion, and interaction with oxygen atom of dioxane. Therefore, decrease in entropy with increase in temperature favors the formation of zwitter ions.

Therefore, it may be concluded regarding effect of temperature and thermodynamic quantities upon dissociation of glycine that dissociation of glycine is

avored by increase of temperature, decrease in entropy, and endothermic nature of the reaction; but there is greater increase in pK_1 value with increase in dioxane-content in comparison to decrease in pK_1 value with increase in temperature. Therefore, in case of aquo-organic solvent, Frank and Wen²⁰ simple model needs to be modified because of structural change of water molecules due to addition of organic solvent, and structural change of water also depends on the mass percentage of organic solvent.

II. REFERENCES

- [1]. B. Prasad, J. Indian. Chem. Soc., 1977, 54, 588.
- [2]. Md Shamsuddin , Anil Kumar Chouhadia, DP Goyal, A.K. GHosh, IJRSET, PP. 5229-5236, VOL 12, ISSUE 5, 2023
- [3]. Md Shamsuddin, Anil Kumar Chouhadia, IJSRCH, PP. 09-21, VOL 8, ISSUE 3, 2023
- [4]. Md Shamsuddin, IJRSET, PP. 221-229, VOL 10, ISSUE 3, 2023
- [5]. Md Shamsuddin, IJSRST, PP. 405-411, VOL 10, ISSUE 3, 2023
- [6]. H. S. Harned and R. A. Robinson, Trans. Farad. Soc., 1940, 36, 973-978.
- [7]. C. W. Davies, H. W. Jones and C. B. Monk, Trans. Farad. Soc., 1952, 48, 921-928.
- [8]. V. S. K. Nair and G. H. Nancollas, J. Chem. Soc., 1958, 4144-4147.
- [9]. L. Sharma, B. Prasad, J. Ind. Chem. Soc., 1969, 46.
- [10]. A. K. Covington, J. V. Dobson and Lord Wynne Jones, Trans. Farad. Soc., 1965, 61, 2050-2056.
- [11]. B. M. Prasad and J. C. Gosh, Proc. Nat. Acad. Sc. India, 1990, 60A, III, 255.
- [12]. A. Gupta, Ph.D Thesis, Patna University, Patna, 1986.
- [13]. H. S. Harne d and L. D. Fallon, J. Am. Chem. Soc., 1939, 61(9), 2374-2377.
- [14]. H. S. Harned and T. R. Dobell, J. Am. Chem. Soc., 1941, 63(12), 3308-3312.
- [15]. H. S. Harned and R. S. Done, J. Am. Chem. Soc., 1941, 63(10), 2579-2582.
- [16]. J. T. Edsall and R. D. Blanchard, J. Am. Chem. Soc., 1933, 55(6), 2337-2353.
- [17]. A. K. Chattopadhyay, S. C. Lahri, Indian. J. Chem., 1977, 15A, 930.
- [18]. H. S. Harned and C. M., Birdsall, J. Am. Chem. Soc., 1943, 65(1), 54-57.
- [19]. H. S. Frank and M. W. Evans, J. Chem. Phys., 1945, 13(11), 507-532.
- [20]. H. S. Frank and W. Y. Wen, Disc. Farad. Soc., 1967, 24, 133-140.

Cite this article as :

Md. Shamsuddin, "Review of effect of temperature and thermodynamic quantities upon acidic dissociation of Glycine in 10, 20 and 30% dioxane (m/m) in dioxane-water system at 288.15K, 298.15K, 308.15K and 318.15K by e.m.f. measurement", International Journal of Scientific Research in Science and Technology (IJSRST), Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 10 Issue 5, pp. 605-611, September-October 2023. Available at doi : <https://doi.org/10.32628/IJSRST52310596>
Journal URL : <https://ijsrst.com/IJSRST52310596>