

pH Metric Study On Thermodynamic And Ionization Constant Of 2,5-Diaminopentanoic Acid (DL-ornithine)

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Abstract- pH metric titration technique is by far the most convenient for the determination of ionization constant of 2,5-diaminopentanoic acid (DL-ornithine). Their ionization constant have been evaluated in aqueous and aqua-organic media at different temperatures viz. 20°C, 30°C and 40°C and varying ionic strengths $\mu=0.1, 0.2, 0.5$ and 1.0M NaClO₄ by employing Henderson-Hasselbalch, Irving-Rossotti and Albert-Serjeant method. The decrease of ionization constant with increase of temperature and ionic strength has been proposed by Pitzer and Debye-Huckel theory, respectively.

The effect of change of solvent on the ionization constant are discussed and be explained according to Bates and Coworkers and Braude by employing Albert-Serjeant method in same percentage (20%) of 1,2-ethanediol, propane-2-ol, ethanol, DMF, acetonitrile, DMSO and 20, 30, 40 and 50 percentage of DMSO.

1. INTRODUCTION

Perusal of literature reveals a few references⁽¹⁻¹⁰⁾ on behavior, isolation, application and ionization constant of 2,5-diaminopentanoic acid (DL-ornithine). The present work describe the pH metric determination of ionization constants (pK₁, pK₂ and pK₃) of 2,5-diaminopentanoic acid (DL-ornithine) at different temperatures viz. 20°C, 30°C and 40°C and varying ionic strengths $\mu=0.1, 0.2, 0.5$ and 1.0M NaClO₄. The effect solvent and thermodynamic functions viz. free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of the ionization reaction have also been determined and explained.

2. EXPERIMENTAL

2,5-diaminopentanoic acid (DL-ornithine) were supplied by "Sarabhai M. Chemical, Baroda" and other reagents of Anala R, BDH grade. pH measurements were made on a Toshniwal digital pH meter (accuracy ± 0.01 pH) with combined glass electrode assembly in a nitrogen atmosphere. The instrument was standardised with standard buffers. A thermostat of type U7^C made in GDR having an accuracy of 0.1°C to maintain the temperature of the Cell.

3. PROCEDURE

The experimental procedure involves a series of pH titrations of water blank and ligand with 1M HCl (for pK₁) and 0.1M NaOH (for pK₂, pK₃) by Henderson-Hasselbalch method, 0.1M NaOH (for pK₁, pK₂ and pK₃) by Irving-Rossotti method and 0.1M HClO₄ (for pK₁), 0.1M NaOH (for pK₂, pK₃) by Albert-Serjeant

method, keeping the total volume 25ml in each case and for maintaining the ionic strength requisite amount of NaClO₄ were added to the solution mixture.

The ionization constant of ligand were evaluated by employing Henderson-Hasselbalch⁽¹¹⁾, Irving-Rossotti⁽¹²⁾ and Albert-Serjeant method⁽¹³⁾. In each pH metric titration, ligand concentration maintained 3.37mg/25ml for Henderson-Hasselbalch method and 0.001M for Irving-Rossotti and Albert-Serjeant method by using 0.006M (Irving-Rossotti) and 0.002M (Albert-Serjeant method) HClO₄ for initial lowering of the pH.

Albert⁽¹¹⁾ method is determined the all three pK values pK₁, pK₂ and pK₃ of DL-ornithine (0.001M Vs 0.1M NaOH) at 20°C, 30°C and 40°C ($\mu=0.1$ M) and at varying of ionic strength 0.1, 0.2, 0.5 and 1.0M. The varying ionic strength maintained by NaClO₄ (Temp.= 30°C) in aqueous media and V/V 20%, 30%, 40% and 50% of DMSO and in 20% aqua-organic solvents i.e 1,2-ethanediol, propane-2-ol, ethanol, DMF, acetonitrile, DMSO at 30°C, $\mu=0.1$ M NaClO₄.

4. RESULT AND DISCUSSION

Values of milliequivalent of acid and alkali were plotted against corresponding pH (Henderson-Hasselbalch method) and formation function \bar{n}_A against pH (Irving-Rossotti method) values to get the formation curves of ionization reaction equilibrium. From these formation curves, the values of ionization constants pK₁, pK₂ and pK₃ were calculated which is corresponding to inflection (H.H. Method) and pH values at $\bar{n}_A=2.5, 1.5$

and 0.5 respectively. The pK_1 , pK_2 and pK_3 values were also determined at different temperatures viz. 20°C, 30°C and 40°C and at varying ionic strength 0.1, 0.2, 0.5 and 1.0M in pH range 1.5-12.8 are summarized in Table (1), which is in agreement with Pitzer⁽¹³⁾ and Debye-Huckel Theory^(15,16) in order of ionization constant of ligand.

However, it is indicated from the titration that **two** ionizing α -amino and ω -amino groups are separated by less than 2.7 limits of pK_a , the usual calculation can only give results of poor precision⁽¹³⁾. Hence, accurate results can be obtained from Noye's modification⁽¹⁷⁾.

It is evident from the detail of all three methods that the normal titration set does not yield pH to the extent form where all the pK values be evaluated by Albert-Serjeant method as refined by Noye's and Irving-Rossotti method. the titration set requires adjustment keeping in view the known values of pK and therefore the values of ionization constants of unknown sample can not be evaluated from these **Two** method whereas there is no such limitations in case of Handerson-Hasselbalch method.

5. EFFECT OF SOLVENT

The behavior of ligand in aqua-organic solvent to be explained according to Bates and Coworkers and Braude^(18,19) as indicated in Table (2). Here it is observed that pK_1 , pK_2 and pK_3 values were increases with the increase in organic solvent content of the mixture, but increase has not been found to be appreciable due to difference in solubility and ionization of DL-ornithine in varying solvent-water mixture.

But for the same v/v composition pK values have the following sequence which is in regard to

change in dielectric constant for 20% solvent-water mixture.

DMSO > DMF > Acetonitrile > Ethanol > Propane-2-ol > 1,2-Ethanediol

(The dielectric constant follow the order: 1,2-Ethanediol > Propane-2-ol > Ethanol > Acetonitrile > DMF > DMSO)

6. EFFECT OF TEMPERATURE AND IONIC STRENGTH

It is observed from the Table (1) that the ionization constant generally decreases with rise of temperature, it is showing that lower temperature favors the ionization constant of ligand which is in agreement with relationship proposed by Pitzer⁽¹⁴⁾. The Table (1) reveals that the ionization constant (pK_1 , pK_2 and pK_3) values also decreases with increase in ionic strength from 0.1 to 1.0M which is in accordance with Debye-Huckel theory⁽¹⁵⁾.

7. THERMODYNAMIC FUNCTIONS

Thermodynamic functions such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) accompanying ionization is determined at 30°C with the help of equation⁽²⁰⁾ which is summarized in Table (3).

Negative value of ΔG° indicates that under standard conditions, the ionization reaction is exothermic and tends to proceed spontaneously. The decrease of pK 's values with increase in temperature support the negative values of ΔH° . Positive change in the entropy (ΔS°) strongly favours the ionization process.

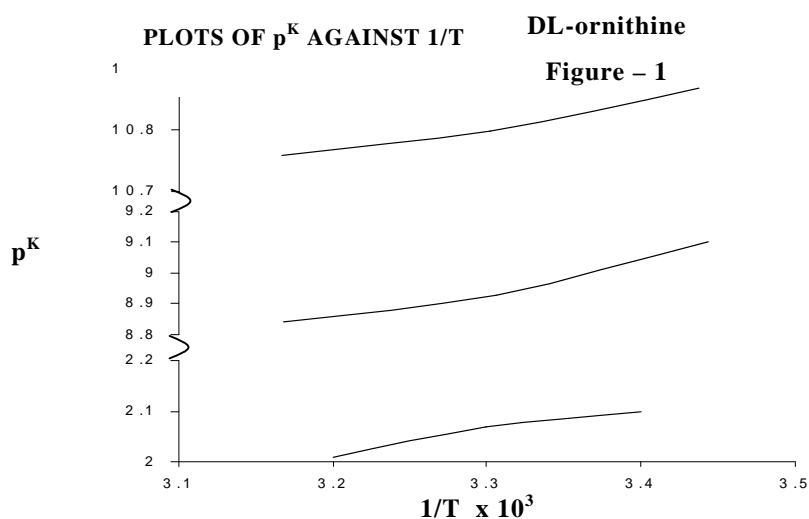
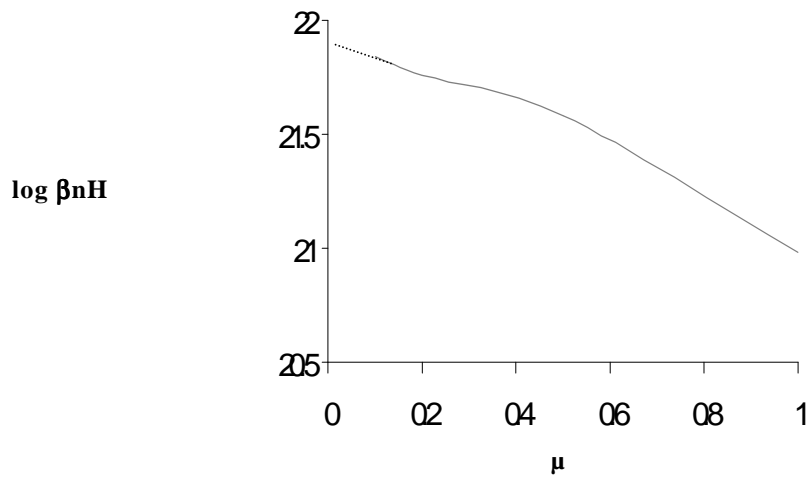
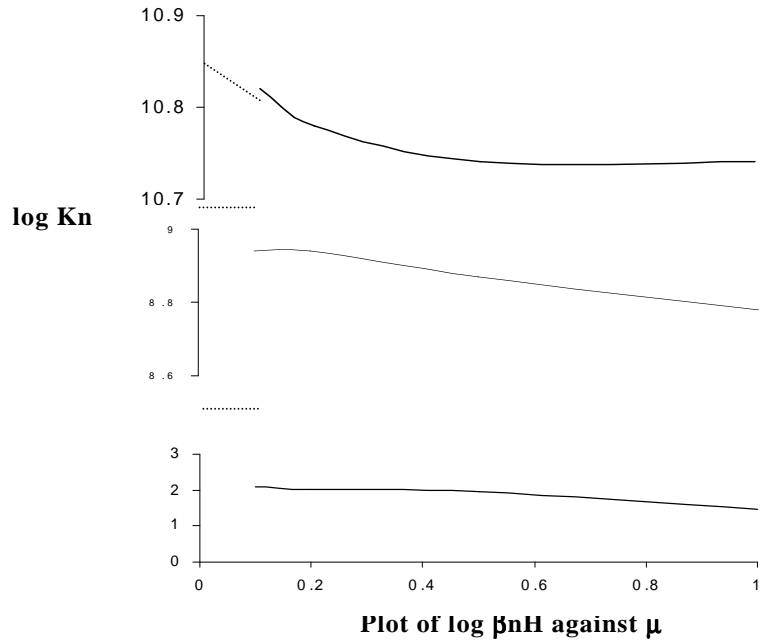


Figure - 2

LOTS OF log Kn AGAINST μ



8. TABLES

Table - 1

p^K_1 , p^K_2 and p^K_3 values of DL-orinithine in aquas medis at various temperature and ionic strength

Henderson-Hasselbatch Method

pK	Temp. 20°C				$\mu = 0.1 \text{ M}$		
	0.1M	0.2M	0.5M	1.0M	20°C	30°C	40°C
p^K_1	2.05	2.01	1.94	1.86	2.05	2.01	1.96
p^K_2	8.91	8.85	8.74	8.63	8.91	8.86	8.81
p^K_3	10.87	10.84	10.78	10.69	10.87	10.84	10.79

Irving-Rossotti Method

pK	Temp. 30°C				$\mu = 0.1 \text{ M}$		
	0.05M	0.1M	0.2M	0.5M	20°C	30°C	40°C
p^K_1	2.45	2.40	2.34	2.30	2.46	2.40	2.37
p^K_2	9.46	9.38	9.34	9.05	9.39	9.38	9.22
p^K_3	10.94	10.82	10.72	10.62	10.84	10.82	10.78

Albert-Serjeant Method

pK	Temp. 20°C				$\mu = 0.1 \text{ M}$		
	0.1M	0.2M	0.5M	1.0M	20°C	30°C	40°C
p^K_1	1.804	1.77	1.68	1.06	1.804	1.790	1.71
p^K_2	8.54	8.63	8.81	8.94	9.00	8.54	8.50
p^K_3	10.75	10.79	10.78	10.80	10.90	10.75	10.70

Table - 2

p^K_1 , p^K_2 and p^K_3 values of DL-orinithine in 20% (v/v) aqua-organic media at 30°C ($\mu = 0.1\text{M}$)

Solvent	$1/\epsilon$	p^K_1	p^K_2	p^K_3
1,2-Ethandiol	0.06258	2.04	8.61	10.45
Propane-2-ol	0.05464	2.13	8.84	11.12
Ethanol	0.04073	2.14	8.74	10.87
DMF	0.02724	2.43	7.93	10.50
Acetonitrile	0.02666	2.11	8.64	10.86
DMSO	0.02146	2.20	8.95	11.12

p^K_1 , p^K_2 and p^K_3 values of DL-orinithine in varying percentage aqua-organic media at 30°C ($\mu = 0.1M$)

organic content in aqua-organic media	p^K_1	p^K_2	p^K_3
20% DMSO	2.20	8.95	11.12
30% DMSO	2.43	9.04	11.56
40% DMSO	2.56	9.21	11.94
50% DMSO	2.70	9.31	12.44

Table - 3

Values of thermodynamic functions for DL-orinithine at 30°C in aqueous media ($\mu=0.1M$)

Ionization constants	$-\Delta G^\circ$ (KCal/mole)	$-\Delta H^\circ$ (KCal/mole)	ΔS° (Cal/Deg/mole)
$\log K_1^{\mu \rightarrow 0} = 1.71$	2.37	0.57	5.94
$\log K_2^{\mu \rightarrow 0} = 8.46$	11.73	5.86	19.37
$\log K_3^{\mu \rightarrow 0} = 10.66$	14.78	7.12	25.28
Calculated $\log K_C^{\mu \rightarrow 0} = 20.83$	Experimental $\log K_C^{\mu \rightarrow 0} = 20.81$		

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