

Stabilities and thermodynamics of Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} complexes of 2,5-diamino-1-pentanoic acid

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ABSTRACT

The stability constant of Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} complexes of 2,5-diamino-1-pentanoic acid (DL-ornithine) have determined in aqueous medium at different temperature viz. 20°C, 30°C and 40°C and varying ionic strengths $\mu=0.05$, 0.1 and 0.2M NaClO_4 employing Irving-Rossotti method. The thermodynamic functions " G° ", " H° ", and " S° " accompanying complex formation have also been evaluated at 30°C.

Key words: Metal ions, Thermodynamics stabilities, complexes.

INTRODUCTION

From the survey of chemical literature¹⁻¹¹ it has been found that the thermodynamics and stability of binary and ternary metal complexes of Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} with different biologically important amino acids at various temperature and ionic strength has been carried out, this communication reports the formation, composition and stability constants of Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} complexes with 2,5-diamino-1-pentanoic acid at different temperatures viz. 20°C, 30°C and 40°C and ionic strengths $\mu=0.05$, 0.1 and 0.2M NaClO_4 by pH metric titration technique.

EXPERIMENTAL

2,5-diamino-1-pentanoic acid, commonly referred as DL-ornithine was obtained from BDH Poole, England and $\text{Co}(\text{NO}_3)_2$, NiSO_4 , CuSO_4 , ZnSO_4 and NaOH were of AnalR grade. Their solutions were prepared in double distilled water whose strength were checked by standard method¹². 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 standardized with standard buffers.

A thermostat of type U7^c made in GDR having an accuracy of 0.1°C to maintain the temperature of cell.

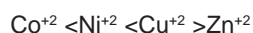
Procedure

The experimental procedure as described earlier involves a series of pH titrations of the ligand with 0.2M NaOH solution in the absence and presence of metal ions, at different metal-ligand ratio, keeping the total volume 25ml in each case. For qualitative detection of complex formation, stoichiometric pH titration were performed for the solution having metal-ligand ratio 1:1, 1:2, 1:3 and 1:4. After each addition of titrat NaOH, pH meter readings were noted on reaching equilibrium.

Curves were plotted between pH and volume of alkali required. The inflection in curves reveal the formation of complexes in the solutions from which the stoichiometry has been evaluated. Requisite amount of NaClO_4 were added to the solution mixture for maintaining the ionic strength. The stability constants of metal-ligand complexes were evaluated by employing Irving-Rossotti method¹³⁻¹⁴. In pH titrations, the ratio of metal to ligand kept constant at 1:5, using 4×10^{-2} M HClO_4 for initial lowering of buffer region.

RESULT AND DISCUSSION

The value of formation function n were plotted against the corresponding free ligand concentration (pL) values to get the formation curves of the metal-complexation equilibrium from these formation curves, the values of stability constants $\log K_1$ and $\log K_2$ were calculated which correspond to pL values at $n=0.5$ and 1.5 respectively. The $\log K$ values were determined at different temperatures viz. 20°C , 30°C and 40°C and at varying ionic strengths $0.05, 0.1$ and 0.2M in the pH range $6.0-10.0$ are tabulated (Table-1). The values are in agreement with Irving-William¹⁵⁻¹⁶ order of stability constants of bivalent metal complexes. The order of stability as follows:



The plot of $\log K_1$ or $\log K_2$ against atomic

number of these metal element (Fig.1) reveals that there is a monotonic rise to a maximum of copper followed by a lower value of zinc in accordance with Irving-Williams relationship¹⁵⁻¹⁶.

Similarly plot of $\log K_1$ or $\log K_2$ against reciprocal of ionic radii of metal ions (Fig.2) shows that the ligand forms least stable complex with Co^{+2} and more stable complex Cu^{+2} in comparison to other metal ions.

The second ionization potential rises along the first transition series to a maximum of copper and falls again at zinc. A correlation between second ionization potential and the formation constants of complexes was pointed out by Irving-Williams¹⁵⁻¹⁶, Schwarzenbach, Ackermann & Prue¹⁷ and Calving & Melchoir¹⁸. A similar correlation was observed in the present case of the plots of $\log K_1$ or $\log K_2$ against second ionization potential (Fig.3).

Table 1: Metal-ligand formation constants of the Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} complexes with DL-ornithine

Metal complexes		Temperature				
		20°C	30°C		40°C	
		0.1M	0.05M	0.1M	0.2M	0.1M
Co ⁺² -DL-ornithine	$\log K_1$	3.97	4.11	4.19	4.31	4.23
	$\log K_2$	3.07	2.82	3.09	3.12	3.14
Ni ⁺² -DL-ornithine	$\log K_1$	5.04	5.03	5.11	5.14	5.17
	$\log K_2$	4.08	4.10	4.12	4.15	4.19
Cu ⁺² -DL-ornithine	$\log K_1$	7.20	7.21	7.24	7.52	7.57
	$\log K_2$	6.43	6.44	6.45	6.53	6.56
Zn ⁺² -DL-ornithine	$\log K_1$	3.93	4.12	4.17	4.26	4.31
	$\log K_2$	2.69	2.84	2.87	2.90	2.91

Table 2: Thermodynamic parameters of Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} complexes with DL-ornithine at 30°C and $\mu=0.1\text{M}$

Metal complexes	$-\Delta G^\circ$ (Kcal/mole)	ΔH° (Kcal/mole)	ΔS° (Cal/deg/mole)
Co ⁺² -DL-ornithine	5.05	44.07	128.78
Ni ⁺² -DL-ornithine	6.40	41.18	114.78
Cu ⁺² -DL-ornithine	9.49	35.38	85.43
Zn ⁺² -DL-ornithine	4.88	55.09	165.71

The plots of electronegativity against $\log K_1$ or $\log K_2$ shows that the stability of these metal complexes increases with increasing electronegativity (Fig.4) which suggest that the metal-ligand bond would be covalent.

Effect of temperature and ionic strength

The data reveals that the stability constants gradually increases with rise in temperature showing thereby that higher temperature favours the formation of stabler complexes.

The effect of increase in ionic strength from 0.05 to 0.2M on the stability has been examined and it is observed that $\log K$ increases with increase

in ionic strength. These changes have also been shown in Table-1.

Thermodynamic parameters

Thermodynamic functions such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) accompanying complexation are determined at 30°C with help of standard equation¹⁹ are summarized in Table-2.

The negative value of ΔG° show that the reaction tends to proceed spontaneously. The positive value of enthalpy indicate the endothermic nature of the reaction process in fair agreement with increasing stability suggesting higher temperature favours the chelation process. A

Plots of $\log K_1$ Vs various physical properties for Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} complexes at temperature 30°C and $\mu=0.1\text{M}$

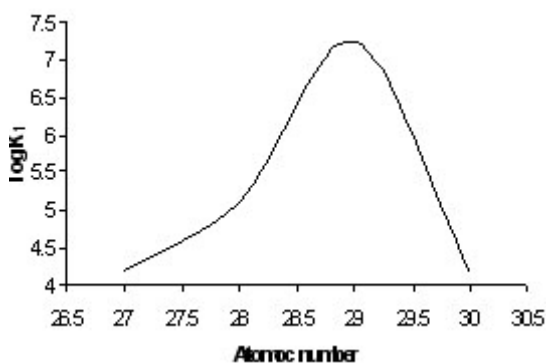


Fig. 1:

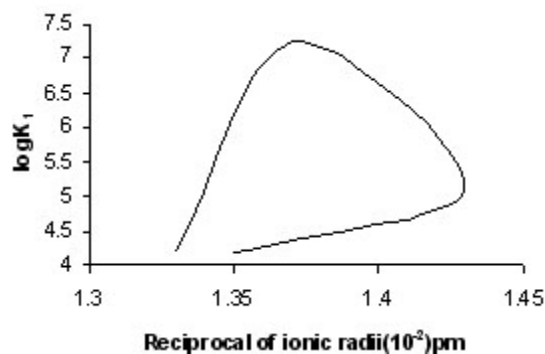


Fig. 2:

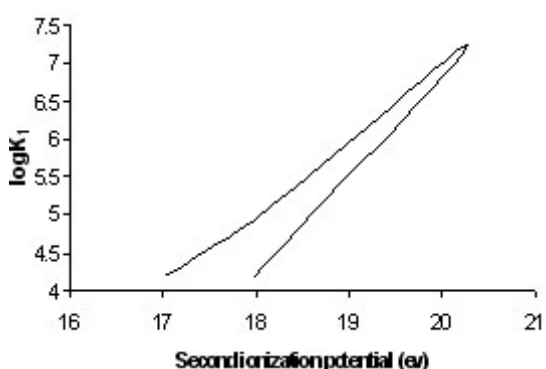


Fig. 3:

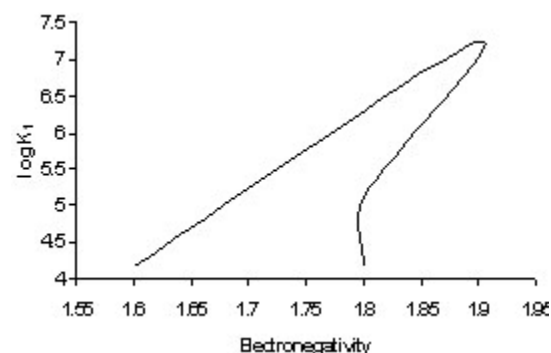


Fig. 4:

Note: Similar type of relationship were obtained when $\log K_2$ plot with physical properties as plotted above with $\log K_1$.

positive change in entropy strongly indicate the complex formation. The very large entropy changes are also justified by considering the greater availability of coordination sites of these metal ions.

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