



Stability constants of binary complexes of some rare earth and nuclear metal ions with some peptides at 0.1 M ionic strength pH-metrically

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ABSTRACT

Interaction of Pm(III), Gd(III), HO(III), Er(III), Ce(IV), Pr(IV), Tb(IV), UO₂(II), Th(IV) metal ions with Glycyl-Glycyl-Glycine (L₁), L-Alanyl-L-Alanyl-L-Alanine (L₂), DL-Alanyl-DL-Phenyl-Alanine (L₃) and DL-Alanyl-Glycine (L₄) have been studied at 0.1 M ionic strengths [NaClO₄, 1 M] pH-metrically. The deviation between ligand curves and free acid curves showed the dissociation of -COOH and -NH₃⁺ group. The deviation between ligand curves and metal curves showed the commencement of complex formation. Proton-ligand stability constant (pK) and metal-ligand stability constant of the binary complex are evaluated using Irving-Rossotti's expression. Complex systems are carried out by using Calvin-Bjerrum titration method in an inert atmosphere.

Keywords : NaClO₄, HClO₄, peptides, lanthanide metal ions, pH-meter instrument.

INTRODUCTION

The interaction of metal ion with amino acid and peptides of amino acid gained much interest as these bases constitute the back bone of DNA and RNA molecules.

Metal-ligand stability constant of complex of transition metal ions and nuclear metal ions with sulphonic acid, carboxylic acid, phenols, amino acid etc. have been studied by many workers [1,2]. The study of interaction of chloro and bromo succinimides in dioxane-water mixture has been done by Ishwar Bhat and Shivakumar [3]. The synthesis of bivalent Hg(II) and Sn(II) metal ion complexes with L-lysine monohydrochlorides and their properties have been investigated using X-ray diffraction process by Usha Sharma [4]. Gulwade et al [5] have studied acoustical properties of substituted azoles in N-N-dimethylformamide at different temperature. Khobragade and Narwade [6] have studied the interaction between Fe(III) and 1,2-dihydroxy benzene and 1,5-disulphonic acid. Theoretical study of some substituted pyrazoles and rare earth metal complexes has been studied by Kuznetsov et al [7]. Parallel solution phase synthesis of N-substituted 2-pyrazoline has been carried out by Udobanes et al [8].

The study of metal complexes with peptides was still lacking, moreover peptides are having some remarkable characters. In the body, peptides are formed during the initial digestion of the proteins and inside the cells by synthesis from amino acids [8].

Some small peptides which have significant biological activities. This wide range of peptide is related with several interlinked brain system. Peptides are potent painkillers and also able to potentiate the action of pharmacologic agents.

Peptides are immense biomedical interest particularly in endocrinology [9].

Due to above good characters and complexing agent, the complex study of some peptides with lanthanide and nuclear metal ions has been undertaken in the present work.

MATERIALS AND METHODS

In the present investigation, following peptides and metal ions are used for complex study pH-metrically at 0.1 M ionic strength.

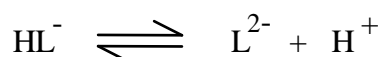
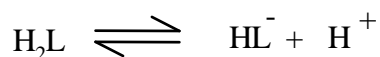
Ligands :- Glycyl-Glycyl-Glycine (L_1), L-Alanyl-L-Alanyl-L-Alanine (L_2), DL-Alanyl-DL-Phenyl-Alanine (L_3) and DL-Alanyl-Glycine (L_4).

Metal ions :- Pm(III), Gd(III), HO(III), Er(III), Ce(IV), Pr(IV), Tb(IV), $UO_2(II)$ and Th(IV).

pH-Metric measurement involved pH-metric titration which are adopted by Calvin-Bjerrum in present work. Acid, ligand and metal titration are carried out in an inert atmosphere by bubbling nitrogen gas. Ionic strength (0.1 M) was maintained constant by adding an appropriate amount of 1 M $NaClO_4$ solution. pH-Meter was standardized before titration by buffer solution pH = 0.4, pH = 7.0 and pH = 9.2.

RESULTS AND DISCUSSION

The (acid + ligand) curves started to deviate from acid curves at pH 3.0 and continued up to pH 12.0. It clearly indicated the dissociation of $-COOH$ and $-NH_3^+$ groups from peptides.



Proton-ligand formation number \bar{n}_A are evaluated using Irving-Rossotti's expression [10]. Proton-ligand stability constants are determined from half integral and point wise calculation which are shown in Table-1.

It could be seen from Table-1 that dissociation of $-COOH$ group occurs above pH 7.0 and $-NH_3^+$ group dissociates above pH 9.0 except the dissociation of ligand (L_4) this may be due to simple peptide linkage.

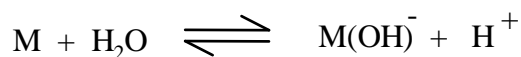
The standard deviation σ is evaluate for the current values of \bar{n}_A . It is calculated for two sets (Set I and Set II) using same procedure except the concentration of NaOH as shown in Table-2.

The value of standard deviation σ is found to be very less that showed the correct values of \bar{n}_A .

Metal-Ligand Stability Constant :-

Metal in hydrolysis :-

The pH at which metal ion starts hydrolyzing should be known to ascertain the complex formation with the ligand. The information of hydroxide $M(OH)$ is given by the equation



[i] Polynuclear complexes

Since the solutions were dilute, the probability of existence of polynuclear species under present experimental condition was not expected to be highly. The values of \bar{n} (metal-ligand formation number) are calculated by Irving-Rossotti's expression.

Metal-ligand stability constant $\log K_1$ and $\log K_2$ for 1:1 and 1:2 complex respectively are evaluated as shown in Table-3 & 4. There is no as such appreciable difference between $\log K_1$ and $\log K_2$ values. This clearly indicates the formation of 1:1 and 1:2 complexes occur simultaneously Pm(III), Gd(III), HO(III), Er(III). Pm(III) and Gd(III) formed pale green colour and HO(III) formed light pink colour with all system around pH 4.20. The systematic values of \bar{n} obtained upto the highest value around 2.00, indicating the formation of 1:1 and 1:2 complexes.

[ii] Trivalent hard acid metal ions :-

The peptides give characteristic colouration with Pm(III) immediately after mixing the two solutions. Deviation for Ce(IV) and Pr(IV) was observed at around pH 3.00 and for Tb(IV) at around pH 3.5. This indicated the formation of complexes.

Table 1 : Proton-ligand stability constant (pK)

| System | Half integral method | | Point wise calculation | |
|--------------------------|----------------------|-----------------|------------------------|-----------------|
| | pK ₁ | pK ₂ | pK ₁ | pK ₂ |
| Ligand (L ₁) | 7.45 | 10.30 | 7.50 ± 0.05 | 10.30 ± 0.03 |
| Ligand (L ₂) | 7.15 | 9.30 | 7.10 ± 0.4 | 9.20 ± 0.06 |
| Ligand (L ₃) | 7.25 | 9.50 | 7.36 ± 0.03 | 9.05 ± 0.02 |
| Ligand (L ₄) | 6.30 | 9.65 | 6.23 ± 0.022 | 9.75 ± 0.04 |

Table 2 : Determination of standard deviation (σ) system ligand L₄

| pH | \bar{n}_A (Set - I) N = 0.101 M NaOH | \bar{n}_A (Set - II) N = 0.125 M NaOH | \bar{n}_A (Set - I) - \bar{n}_A (Set - II) = $\Delta \bar{n}_A$ | $\sigma = \left[\frac{\Delta(\bar{n}_A)^2}{n'-1} \right]^{1/2}$ n' = number observation |
|-------|--|---|---|---|
| 4.00 | 1.8940 | 1.8719 | 0.0020 | 0.014418 |
| 4.50 | 1.7865 | 1.7823 | 0.0142 | |
| 5.00 | 1.5837 | 1.5640 | 0.0298 | |
| 5.50 | 1.5403 | 1.5200 | 0.0102 | |
| 6.00 | 1.5201 | 1.5011 | 0.0093 | |
| 6.50 | 1.5113 | 1.4915 | 0.1000 | |
| 7.00 | 1.4851 | 1.4895 | -0.0042 | |
| 7.50 | 1.4150 | 1.4552 | -0.0302 | |
| 8.00 | 1.3842 | 1.4250 | -0.0313 | |
| 8.50 | 1.3001 | 1.3092 | -0.00190 | |
| 9.00 | 1.0012 | 1.0002 | 0.0010 | |
| 9.50 | 0.7222 | 0.7100 | 0.0020 | |
| 10.00 | 0.4248 | 0.4260 | 0.00050 | |

Table 3 : Metal-ligand stability constant of binary complexes

| Sr. No. | System | Stability Constant | |
|---------|--------------------------|--------------------|--------------------|
| | | log K ₁ | log K ₂ |
| 1. | Gd(III) - L ₁ | 13.50 | 12.03 |
| 2. | Gd(III) - L ₂ | 11.02 | 10.02 |
| 3. | Gd(III) - L ₃ | 11.08 | 10.25 |
| 4. | Gd(III) - L ₄ | 11.38 | 10.35 |
| 5. | Ho(III) - L ₁ | 13.04 | 11.20 |
| 6. | Ho(III) - L ₂ | 11.02 | 9.12 |
| 7. | Ho(III) - L ₃ | 11.17 | 9.30 |
| 8. | Ho(III) - L ₄ | 11.30 | 8.30 |
| 9. | Er(III) - L ₁ | 13.15 | 10.60 |
| 10. | Er(III) - L ₂ | 10.60 | 8.20 |
| 11. | Er(III) - L ₃ | 13.30 | 8.60 |
| 12. | Er(III) - L ₄ | 11.60 | 7.30 |

Table 4 : Metal-ligand stability constant of binary complexes

| Sr. No. | System | Stability Constant | |
|---------|---------------------------------------|--------------------|--------------------|
| | | log K ₁ | log K ₂ |
| 1. | Ce(IV) - L ₁ | 13.00 | 10.50 |
| 2. | Ce(IV) - L ₃ | 12.25 | 8.30 |
| 3. | Ce(IV) - L ₄ | 12.55 | 8.50 |
| 4. | Pr(IV) - L ₁ | 13.14 | 10.45 |
| 5. | Pr(IV) - L ₃ | 10.55 | 8.04 |
| 6. | Pr(IV) - L ₄ | 10.98 | 8.20 |
| 7. | Tb(IV) - L ₁ | 12.54 | 10.85 |
| 8. | Tb(IV) - L ₃ | 10.65 | 8.90 |
| 9. | Tb(IV) - L ₄ | 10.98 | 8.98 |
| 10. | UO ₂ (II) - L ₁ | 13.64 | 10.65 |
| 11. | UO ₂ (II) - L ₃ | 10.30 | 8.15 |
| 12. | UO ₂ (II) - L ₄ | 12.08 | 9.00 |
| 13. | Th(IV) - L ₁ | 11.50 | 8.85 |
| 14. | Th(IV) - L ₃ | 11.02 | 8.35 |
| 15. | Th(IV) - L ₄ | 11.68 | 10.20 |

[iii] Nuclear metal ions UO₂(II) and Th(IV) :-

The color of uranyl complex was observed light yellow for all the systems in the range of pH 3.50 to 5.50 and then changed to dark yellow after pH 5.50. This indicated the commencement of complex formation.

pK and log K₁ and log K₂ values are less for (L₃) ligand this may be due to presence of phenyl ring as electron withdrawing group in ligand (L₃).

Linear relationship of log K = a.pK + b is tested at observed rare relationship which has been found by many workers.

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