

Determination of the stability Constants of the Complexes of Lanthanoid metals with tridentate ligands containing N, O/S as donor atoms

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Abstract

In Continuation of our previous work, stability constants of complexes of Pr(III), Sm(III) and Gd(III) with glutamic acid as ligand have been determined. The stability constant has been determined by the study of proton ligand stability constants.

The stability constant of metal chelates has been determined potentiometrically by Bjerrum method¹ involving Irving – Rossotti pH metric titration technique²⁻⁵ at constant ionic strength of (0.01M) KNO₃ and at constant temperature 20±1⁰ C in water dioxane (60:40) medium. The stability constant of metal complexes with Glutamic acid shows the sequence Sm(III) > Gd(III) > Pr(III).

Key words : Stability Constant, Lanthanoids (III), Tridentate ligands.

Introduction

Glutamic acid complexes¹ have many pharmacological and physiological activity. These complexes also have some antifungal and antitubercular activity. A number of complexes of lanthanoid (III) ions with amino acid as ligand have been reported because of their

biochemical importance⁸⁻⁹. But very less is known about the stability constant of rare earth metals with amino acid as ligands. Thus this project has been undertaken to investigate the stability constant of complexes of lanthanoid metals *i.e.* Pr(III), Sm(III) and Gd(III) with glutamic acid as ligand.

Experimental

All titrations were done in aqueous 1, 4 – dioxane medium (60:40). The solvent 1, 4 – dioxane (GR grade) was purified by standard method⁶ and the purity of solvent was ascertained by determining its refractive index value (reported 1.437, observed 1.437).

E. Merck sample of sodium hydroxide and Anala R grade (BDH) (E. Merck Germany) of KNO_3 was used.

The metal ion solution of Pr(III), Sm(III) and Gd(III) metal nitrate were prepared from weighed quantity of metal oxide (99.8% purity) by treatment with stoichiometric amount of nitric acid (G. F. Smith Chemical Company). The solution was diluted to 0.1 M and standardized titrimetrically using xylenol orange as an indicator.¹⁰⁻¹¹

Glutamic acid solution was prepared

by dissolving requisite amount of Glutamic acid (99.8% pure, sisco chem.) in 40% dioxane water mixture.

All other solutions were prepared in double distilled CO_2 free conductivity water pH metric titration were carried out with the help of systronic model 335 pH meter supplied with calomel and glass electrode. The titration cell consists of a long beaker (100 mL) in water thermostat maintained at $20 \pm 1^\circ\text{C}$ temperature. Constant ionic strength was maintained by adding calculated amount of KNO_3 , $\mu = 0.10$ M KNO_3 . Analytical concentration of ion were calculated for the use of mixed solvent. The cell is accompanied with a glass stirrer and a micro burette and inlet for nitrogen gas. Inert atmosphere was maintained by passing nitrogen gas. Total volume in each set was maintained at 40 mL and water dioxane ratio 60:40 (v/v). Concentrations used in the experiment are shown in table 1.

Table 1.

Metal	V_0	Y	N	E_0	T_L	T_M
Sm(III)	40.0 mL	2	0.5 M	0.02M	5.0×10^{-3}	1.0×10^{-3}
Gd (III)	10.0mL	2	0.5 M	0.02 M	5.0×10^{-3}	1.0×10^{-3}
Pr(III)	40.0 mL	2	0.5 M	0.02 M	5.0×10^{-3}	1.0×10^{-3} M

Acid mixture, a mixture of acid + ligand solution and a mixture of acid + ligand solution + metal salt solution was titrated with standard alkali solution.

The change in pH with each addition of alkali was recorded. During the titration the change of colour and appearance of turbidity at particular pH values were recorded simultaneously.

Table 2.

The pH titration reading of acid, acid + ligand & acid + ligand + metal ions.

Temperature 20±1°C, water: Dioxane = 40/60 (V/V) $\mu = 1.0$ (M) KNO_3

Volume of alkali added in mL	Acid	Acid + ligand	pH-meter reading [B]		
			Acid + ligand + Sm(III)	Acid + ligand + Gd(III)	Acid + ligand + Pr(III)
0.20	2.10	2.28	2.28	2.28	2.24
0.40	2.16	2.40	2.40	2.40	2.40
0.60	2.20	2.50	2.50	2.50	2.50
1.00	2.30	2.90	2.90	2.90	2.90
1.10	2.44	3.08	3.08	3.08	3.08
1.20	2.54	3.32	3.32	3.32	3.32
1.30	2.70	3.64	3.64	3.64	3.64
1.40	2.90	3.98	3.98	3.98	3.98
1.50	3.20	4.46	4.46	4.46	4.46
1.60	3.80	5.18	4.90	4.90	5.05
1.70	8.70	6.40	5.25	5.40	5.55
1.72	11.00	7.00	5.55	5.65	6.15
1.74	11.22	8.80	5.90	6.10	6.75
1.78	11.32	9.50	—	—	7.25
1.80	11.50	9.64	6.35	6.65	7.95
1.84	11.60	9.88	6.90	7.55	8.34
1.90	—	10.22	—	—	—
1.96	—	10.52	—	—	—

Results and Discussion

A graph between pH meter reading [B] and volume of alkali added was plotted. Three titration curve for three metal ions and one curve each for acid and ligand solution were obtained (Fig. 1)

The values of volumes (V_1 , V_2 & V_3) corresponding to the same pH values were obtained from experimental titration curve of acid, ligand and complexes.

The values of \bar{n}_A , \bar{n} and P^L were calculated using standard expressions

$$\bar{n}_A = 1 + \frac{V_1 - V_2}{V_0 + V_1} \times \frac{N_0 + E_0}{T_L}$$

$$\bar{n} = \left(\frac{V_3 - V_2}{V_0 + V_1} \right) \times \frac{N + E}{T_M} \times \frac{1}{\bar{n}_A}$$

$$P^L = \log \frac{\sum P^{B_nH} \frac{1}{(\text{anti log } B)^n} (V_0 + V_3)}{T_L \cdot T_M \cdot \bar{n} \cdot V_0}$$

Proton ligand stability constant :

The ligand titration curve is well separated from the acid titration curve at pH = 6.8. The

ligand curve is parallel to the acid titration curve indicating the smooth dissociation of ligand.

The value of \bar{n}_A at various pH reading [B] calculated from the acid and ligand titration curves are given in table 3.

The formation curve obtained from the plot of \bar{n}_A versus [B] extends from 0.4 to 2.55. As the value of A does not go beyond³ which indicates that the ligand is triprotic and protonated ligand dissociates as given below:



The value of the proton ligand stability constant was calculated by half integral method³ and it was further corroborated by linear plot method ($\text{Log } \bar{n}_A / 1 - \bar{n}_A$) vs [B] and $\log (2 - \bar{n}_A / \bar{n}_A - 1)$ vs [B].

Table 3

Ligand – Glutamic acid Temperature 201⁰C
 $\mu = 0.10$ (M) KNO₃

[B]	\bar{n}_A
2.25	2.51
2.50	2.45
2.75	2.35
3.00	2.20
3.50	1.93
4.00	1.50
4.50	1.29
5.00	1.11
5.50	1.02
8.00	0.81
8.50	0.74
9.00	0.68
9.50	0.60
10.00	0.50
10.50	0.40

Table 4

Ligand-Glutamic acid Temperature 20±1⁰C
 $\mu = 0.10$ (M) KNO₃

[B]	\bar{n}_A	$\log \bar{n}_A / 1 - \bar{n}_A$
8.00	0.81	0.63
8.50	0.74	0.45
9.00	0.68	0.33
9.50	0.60	0.18
10.00	0.52	0.03
10.50	0.40	0.18

The complex titration curve crossed the ligand titration curve at pH = 3.2 for Sm(III) at pH = 3.70 for Gd(III) and pH = 4.0 for Pr(III) – GA system indicating the starting of complex formation.

For Sm(III) – GA system the curve is very regular in shape and during the titration the system attained equilibrium rapidly, it was therefore understood that there is no hydrolysis during the titration as well as formation of other species. The turbidity appeared in the titration vessel at pH = 7.2 in Gd(III) – GA (system) and at pH = 8.4 in case of Pr(III) – GA system so the study was limited up to these pH in both the cases.

The values of \bar{n} extended from 0.15 to 0.95 for Sm(III), 0.075 to 0.90 for Gd(III) and from 0.03 to 0.80 for Pr(III). As the value of \bar{n} is limited to less than one indicating the formation of ML type of complexes in all the three cases.

Table 5

Temperature $20 \pm 1^\circ\text{C}$

Sm(III) G.A. system

\bar{n}	pL
0.15	7.02
0.25	6.75
0.40	6.42
0.475	6.25
0.55	6.12
0.625	6.00
0.80	5.55
0.85	5.275
0.90	5.18
0.95	5.00

Gd(III) - G.A.
system

\bar{n}	pL
0.90	4.72
0.845	5.0
0.79	5.2
0.75	5.3
0.60	5.7
0.55	5.8
0.45	5.94
0.30	6.12
0.15	6.6
0.075	6.68

 $\mu = 0.10$ (M) KNO_3 Pr (III) - G.A.
system

\bar{n}	pL
0.03	6.00
0.115	5.80
0.17	5.60
0.25	5.40
0.30	5.30
0.35	5.20
0.40	5.06
0.54	4.80
0.61	4.70
0.675	4.60
0.80	4.32

From the formation curve of \bar{n} vs pL the value of $\log K$ were calculated by half integral method. It was further verified by the linear plot¹³ of $\log \frac{\bar{n}}{1-\bar{n}}$ Vs pL

The values of proton ligand stability constant and metal ligand stability constant are calculated by various computational methods and the most representative value are recorded in table.

Table 6

Values of practical proton ligand and metal ligand stability constant.

Temperature $20 \pm 1^\circ\text{C}$

Metal ion		
	$\text{Log } {}_1^H$	10.10
	$\text{Log } {}_2^H$	4.05
	$\text{Log } {}_3^H$	2.35
Sm(III)	$\text{Log } K_1$	6.20
Gd(III)	$\text{Log } K_2$	5.88
Pr (III)	$\text{Log } K_3$	4.88

The thermodynamic function ΔG of chelation of metal ions with glutamic acid was calculated using well known equations.

- $\Delta G = 2.303 RT \log K$ is given as under

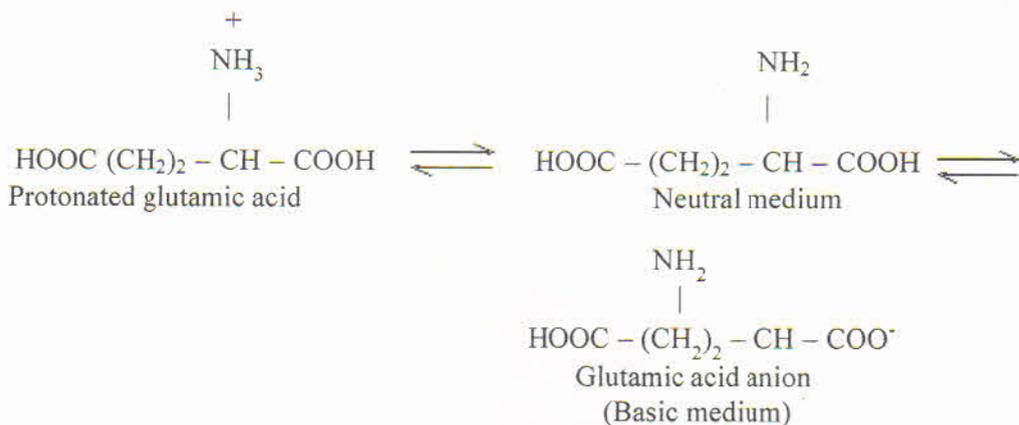
Table 7

Values of Gibb's free energy Change at 293°K

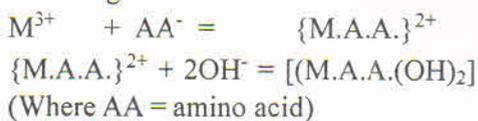
Metal ions	- G (k.Cal. Mol)
Sm(III)	8.28
Gd(III)	7.86
Pr(III)	6.52

Discussion

Proton ligand stability constant : In the initial stage of the titration, the ligand titration curve was above the acid titration curve; due to basic properties of amino group present in glutamic acid which can easily accept a proton from the strongly acidic medium. Reaction occurring during the dissociation of the protonated glutamic acid molecule can be shown as :-



Therefore, three values of proton ligand stability constant are obtained. The metal ligand formation curve for Sm(III) complex shows that n values lie between 0.17 to 0.97 indicating the formation of 1:1 complex of the type ML. Precipitation was observed in all the three metal ligand titration mixture and hence calculation were done only in lower pH range where there was no precipitation. The precipitaton may be due to hydroxyl complex formation which can be explained in the following manner.



It can be seen that the trend of stability constant with the amino acid under investigation is Sm(III) > Gd(III) > Pr(III). Thus the statement "Stability increase with the decreases in ionic radii" is proved¹³⁻¹⁴ in the present case also. The observation is due to lanthanoid contraction, in the lanthanoid series, which has been discussed by many authors¹²⁻¹⁵ It is suggested¹⁶ that these trends in the values of formation constant may be due to varying degree of stabilization arising out of the interactions of

4f metal orbitals with ligand field.

The same stability order¹⁷⁻¹⁹ of binary & ternary complexes is found to be in accordance with the increasing ionic potential of metal ions which is also in agreement with the Debye Huckel equation²⁰.

The thermodynamic function ΔG have been found to be negative in all the case showing complex formation spontaneously. ΔG values have been found to increase with increasing temperature, indicating that low temperature favours complexation. This is also confirmed by negative enthalpy values (H). The positive entropy (S) show increase in randomness in the GA – metal ion system indicating the presence of larger number of species. Similar observation have been reported by other workers²¹ also

Changes in enthalpy and entropy of complex formation with atomic number of trivalent lanthanoides show a complex pattern¹³. The observation is wroth stressing that an interpretation may be made in terms of the structure of the reacting species.

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