Determination of Stability Constant and Related Thermodynamics of Complex Formation of Glutamic Acid with Some Rare Earth Metals

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Practical proton ligand and metal ligand stability constants of the metal ions Y(III), Nd(III) and Pr(III) with glutamic acid ligand at temperature 293 K at constant ionic strength of 0.1 M KNO_3 was determined. The stability constant was determined by the method of Bjerrum Calvin pH titration technique as adopted by Irving and Rossotti. The stability constant of metal complexes with glutamic acid shows the sequence Y (III) > Nd(III) > Pr (III). Thermodynamic parameters such as free energy (ΔG), enthalpy charge (ΔH) and entropy charge ΔS have also been calculated.

Key Words: Stability constant, Rare earth complexes, Glutamic acid.

INTRODUCTION

Amino acids which form stable metal complexes have analytical importance in separation of transition metals and rare earths. A study of these complexes is also important in biological chemistry and the accumulation of sufficient data on amino acid complexes with metal ions may contribute to a better understanding of the types of linkages involved in metal protein fraction. Extensive work has been reported on metal chelates of amino acids with various metal ions. But so as to obtain the trend and values of stability constant of the complexes of rare earth metals with amino acids as ligands are comparatively less studied. Therefore, it was proposed to study the complexes of some rare earth metals with glutamic acid.

EXPERIMENTAL

The solvent 1,4-dioxane (GR grade) was purified by standard method[1] and purity was ascertained by determining its refractive index. Sodium hydroxide used was E. Merck. AnalaR grade (BDH) of nitric acid was used. AnalaR quality (E. Merck, Germany) of KNO_3 was used.

The solution of Y(III), Nd(III) and Pr(III) metal nitrate were prepared by dissolving their oxide (G.F. Smith chemical company) in nitric acid. These metal nitrate solutions are standardized titrimetrically using xylenol orange as an indicator[2].

Glutamic acid (Sisco chem.) solution was prepared in 40 % dioxane water mixture. All other solutions were prepared in doubly distilled CO_2 free conductivity water. pH metric titrations were carried out with the help of pH meter (Systronics model No. 331) supplied with calomel and glass electrode in water thermostat maintained at 293 ± 1 K at constant ionic strength $\mu = 0.10$ M was maintained by adding calculated amount of KNO_3. Analytical concentrations of hydrogen ion were corrected for the use of mixed solvent[3]. Inert atmosphere was maintained by passing nitrogen gas. Total volume in each set was maintained at 40 mL. Concentrations used in the experiment are shown in Table-1.

TABLE-1

Metal	V^0 (mL)	Y	N (M)	E^0 (M)	T_L (M)	T_M (m)
Y(III)	40	2	0.5	0.02	5.0×10^{-3}	1.0×10^{-3}
Nd(III)	40	2	0.5	0.02	5.0×10^{-3}	1.0×10^{-3}
Pr(III)	40	2	0.5	0.02	5.0×10^{-3}	1.0×10^{-3}

The mixtures were titrated against standard alkali. The change in pH with each addition of alkali was recorded in Table-2. Five titrations were carried out one for acid one for ligand and three for different metal ions. The titrations were repeated several times to get identical results. During the titrations, the change in colour and appearance of turbidity, if any, at the particular pH values were recorded simultaneously.

A graph between pH-meter reading [B] and volume of alkali added was plotted in each case. The three titration curves so obtained are referred as (a) acid-titration curve, (b) liquid titration curve and (c) complex titration curve, respectively.

The values of volume (V_1, V_2 and V_3) corresponding to the same pH values were read from acid, ligand and complex titration curves.

The $\bar{n}_A$, $\bar{n}$ and pL values were calculated using standard expressions.

$$\bar{n}_A = 1 + \left(\frac{v_1 - v_2}{v_0 + v_1} \right) \left(\frac{v^n}{T_1^n} + \frac{E^0}{T_1^m} \right) \tag{1}$$

$$\bar{n} = \left(\frac{v_3 - v_2}{v_0 + v_1} \right) \left(\frac{v^n}{T_M^0} + \frac{E^0}{T_M^0} \right) \left(\frac{1}{\bar{n}_A} \right) \tag{2}$$

$$pL = \text{Log} \frac{\left\{ \sum_{n=0}^{n=n} P\beta_n^H \left(\frac{1}{\text{anti log B}} \right)^n (v_0 + v_3) \right\}}{\left(T_1^0 + \bar{n} T_M^0 \right) V^0} \tag{3}$$

TABLE-2
pH TITRATION READING OF ACID, ACID + LIGAND AND
ACID LIGAND + METAL IONS, TEMPERATURE 293 ± 1 K,
WATER:DIOXANE = 40/60 (v/v), μ = 1.0 (M) KNO$_3$

Volume of alkali added (mL)	pH meter reading [B]				
	Acid	Acid + ligand	Acid + ligand + Y(III)	Acid + ligand + Nd(III)	Acid + ligand + Pr(III)
0.20	2.10	2.28	2.23	2.28	2.28
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	8.35
1.90	–	10.22	–	–	–
1.96	–	10.52	–	–	–

RESULTS AND DISCUSSION

Proton ligand stability constant: The ligand titration curve is well separated from the acid titration curve at pH = 6.8. The ligand curve parallel to the acid titration curve indicating the smooth dissociation of ligand.

The values of $\overline{n}_A$ at various pH reading [B] was calculated from the acid and ligand titration curves.

The formation curve obtained from the plot of $\overline{n}_A$ *versus* [B] extends from 0.4 to 2.55. As the value of $\overline{n}_A$ does not go beyond 3, so this indicates that the ligand is biprotic.

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

In Y(III)-GA system the complex titration curves crossed the ligand mixture curve at pH = 3.2 indicating the starting of complex formation. As 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 value of $\overline{n}$, extends from 0.15 to 0.95 indicating the formation of ML complex only. In Nd(III) GA system the complex titration

curve separates from the ligand mixture curve at pH = 3.70 indicating the start of the complexation. The turbidity appeared in the titration vessel at pH = 7.2. So the study was limited up to this pH.

The value of $\bar{n}$, extended from 0.75 to 0.90 indicating the formation of ML complex. Pr(III) GA system the complex titration curve separates from the ligand mixture curve at pH = 4.0 indicating the start of the complexation. The turbidity appeared in the titration vessel at pH = 8.4. So the study was limited up to this pH.

The value of $\bar{n}$ extended from 0.03 to 0.80 indicating the formation of ML complex. For all the three systems the values of log K was calculated by half integral method[4] from the formation curve and verified by the linear plot of log $(\bar{n}_A / 1 - \bar{n}_A)$ *vs.* pL. The most representative values of proton ligand stability constant and metal ligand stability constant are recorded in Table-3.

TABLE-3
VALUES OF PRACTICAL PROTON LIGAND AND METAL LIGAND
STABILITY CONSTANTS, TEMPERATURE 293 ± 1 K

	Constants	Values
Ligand	$\log K_1^H$	10.10
	$\log K_2^H$	4.05
	$\log K_3^H$	2.35
Y (III)	log K	6.20
Nd (III)	log K	5.88
Pr (III)	log K	4.88

The thermodynamic function ΔG of chelation of metal ions with glutamic acid was calculated recorded in Table-4.

TABLE-4

Metal ions	Values of Gibb's free energy change at 293 K ΔG (k cal mol^{-1})
Y(III)	-8.28
Nd(III)	-7.86
Pr(III)	-6.52

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. Reactions occurring during the dissociation of the protonated glutamic acid molecule can be shown as:

Protonated glutamic acid (I)   Glutamic acid (II)

Glutamic acid monoanion (III)   Glutamic acid dianion (IV)

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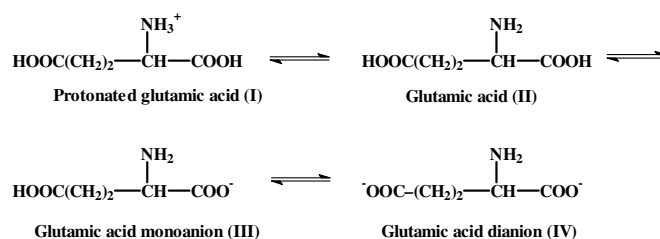
Therefore, three values of proton ligand stability constant are obtained. The metal ligand formation curve for Y(III) complex shows that $\bar{n}$ values lie between 0.17 to 0.97 indicating the formation of 1:1 complex of the type ML. Precipitation was observed in all the three metal ligand titration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

$$M^{3+} + AA^- = (M.AA)^{2+}$$
$$(M.AA)^{2+} + 2OH^- = [(M.AA)(OH)_2]\downarrow$$
(where AA = amino acid)
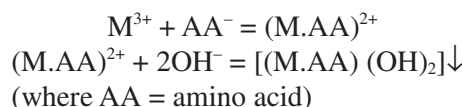
It can be seen that the trend of stability constant with the amino acid under investigation is Y(III) > Nd(III) > Pr(III). Thus the statement 'stability increases with the decrease in ionic radii is proved[4,5] in the present case also. The observation is due to lanthamide contraction. In lanthamide series, lanthanum is known to show abnormal trends. The reason for such deviation have been discussed by previously[6]. It is suggested[7] 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 order[8] of binary tertiary complexes is found to be accordance with the increasing ionic potential of metal ions which is also in agreement with the Debye Huckel equation[9]. The thermodynamic function ΔG have been found negative in all the cases showing complex formation is spontaneous[10].

REFERENCES

1. A.J. Vogel, A Text Book of Practical Organic Chemistry, Longman, edn. 3, p. 177 (1994).
2. A.J. Bernard Jr., W.C. Broad and H. Flaska, *Chemist Analyst*, **45**, 88 (1956).
3. A. Dogan and E. Kilic, *Indian J. Chem.*, **42A**, 1632 (2003).
4. D.S. Makhijani and P.S. Sangal, *J. Indian Chem. Soc.*, **54**, 670 (1977).
5. M.M. Suvarna, V.S. Panse, U.P. Fulwadva and P.K. Jadhav, *Asian J. Chem.*, **7**, 495 (1995).
6. G. Scwarzenbach, R. Gnt and G. Anderegg, *Helv. Chem. Acta*, **39**, 1989 (1956).
7. L.A.K. Stravely and J. Rondell, *Discuss. Faraday Soc.*, **26**, 157 (1958).
8. V. Kolhe and K. Diwedi, *Asian J. Chem.*, **7**, 568 (1995).
9. R. Nasanen and A. Ekman, *Acta Chem. Scand.*, **6**, 1369 (1952).
10. R. Kaur and B.S. Sekhon, *J. Indian Chem. Soc.*, **83**, 645 (2006).