A Thermodynamic Study of Complex Formation of La(III) and Ce(III) with Glutamic Acid.

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The thermodynamic functions of La(III) and Ce(III) with glutamic acid were determined potentiometrically in aqueous solution at $30° \pm 0.1°$ and $40° \pm 0.1°$ in an ionic strength of 0.1 M KCl. The stability constants (log k) changes in free energy ($\triangle$G), enthalpy ($\triangle$H) and entropy ($\triangle$S) for complexes are reported.

AMINO ACIDS are of great biological importance as many of them are essential for human life. Therefore study of nature of linkage formed between amino acids and metal ions is of great importance. The complexes of many amino acids with several metal ions in aqueous solutions are reported in literature. The complexes of Ce(III) and Y(III) with arginine, lysine, methionine, threonine, tryptophan, histidine and phenylalanine were studied by Rogozine et al[1,2]. Sekhon and Chopra[3] determined thermodynamic parameters of Ce(III) and Y(III) with leucine, valine, proline, and hydroxyproline by potentiometric titration technique. Trivedi and Sunar[4] and Agarwal[5] have reported the stability constants and thermodynamic functions of Nd(III), Sm(III), Pr(III) and Gd(III) with aspartic acid respectively. The literature survey reveals that no work has been reported so far with glutamic acid (another amino acid) with rare earth metals. Therefore the study of interaction of glutamic acid with rare earth metals has been taken. In this paper the pH–metric investigation was made to study the stability constants, overall change in free energy ($\triangle$G), enthalpy ($\triangle$H) and entropy ($\triangle$S) of LA(III) and Ce(III) complexes with glutamic acid at different temperatures.

Experimental

La(NO$_3$)$_3$ and Ce(NO$_3$)$_3$ were dissolved in conductivity water. The metal content of the solutions were gravimatically estimated by precipitating as oxalate and then igniting as oxide[5-7]. Standard carbonate free NaOH was used for potentiometric titrations. Glutamic acid was used in the form of mono sodium glutamate. All the chemicals used were Anal—R(B.D.H. or equivalents).

The experimental procedure involved a series of pH-titrations of glutamic acid with standard NaOH solution in the absence of and in the presence of metal ions at 30° and 40° in a constant temperature water bath where the temperature was electrically controlled within 0.1°. The following sets were prepared for pH-titrations.

(i)   10 ml. of 0.05M HCl + 9.5 ml. of 1M KCl + 30.5 ml. of H$_2$O.

(ii)   10 ml of 0.05M HCl + 8.5 ml. of 1M KCl + 20 ml. of 0.05 M Ligand solution + 11.5 ml. of H$_2$O.

(iii)   10 ml. of 0.05M HCl + 7.9 ml. of 1M KCl + 20 ml. of 0.05M Ligand solution + 10 ml. of 0.01M La (NO$_3$)$_3$ + 2.1 ml. of H$_2$O.

(iv)   10 ml. of 0.05M HCl + 7.9 ml. of 1M KCl + 20 ml. of 0.05M Ligand solution. + 10ml. of 0.01 M Ce(NO$_3$)$_3$ + 2.1 ml. of H$_2$O.

In all the titrations volume (50 ml.) and ionic strength (0.1M KCl) were kept constant.

Results and Discussion

The curve for set II shows only one point of inflection, hence there is only one dissociable hydrogen ion in this glutamic acid. Although there are two carboxylic groups in the glutamic acid showing two dissociable H$^+$ ions, but one carboxylic group's activity is hindered by the presence of amino group adjacent to it, only one dissociable H$^+$ ion was observed. The proton-ligand stability constant and metal ligand stability constant were calculated by Calvin-Bjerrum[8,9,10] pH-titration technique as adopted by Irving and Rossotti[11].

At different pH, the horizontal distances between the curves of sets II and III and sets II IV measures quite accurably the additional base consumed due to complex formation, i.e.,

$$M^3 + NaG.H \text{———————} NaG:M^{2+} + H^+$$

(where M^3 denotes rare earth metals and NaG.H denotes sodium glutamic acid)

* For correspondence.
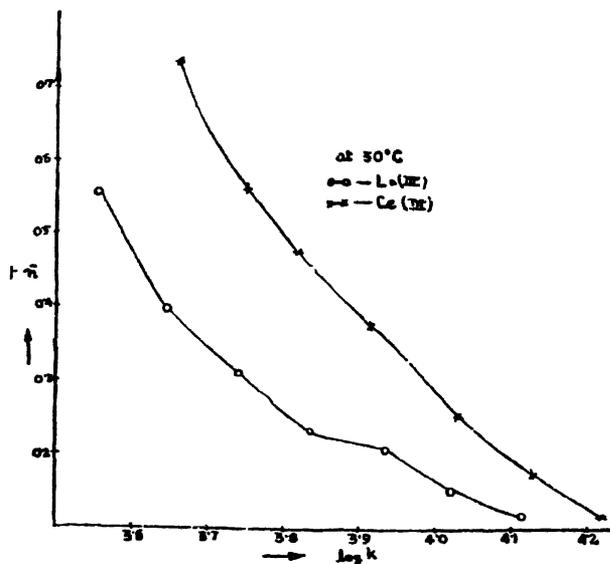
Fig. 1. Formation Curves at 30°
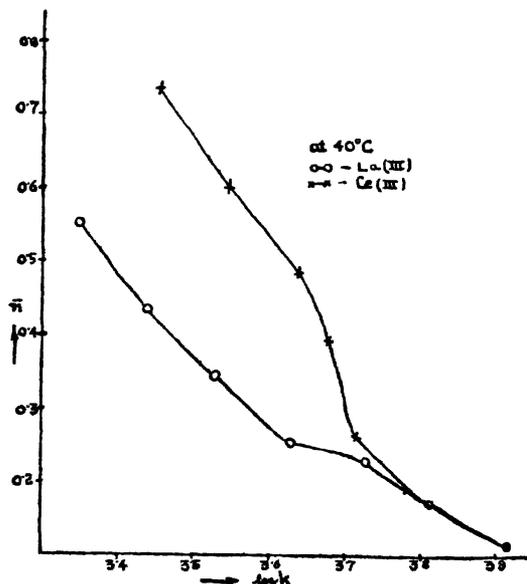
Fig. 2. Formation Curves at 40°

Therefore at various pH, different ñ and log $\left(\frac{1}{A}\right)$ i.e. log k values were obtained for each metal at $30\pm0.1°$ and $40°\pm0.1°$ by integral method. The above ñ and log k values are plotted for each temperatures and log k were read directly from graphs at ñ = 0.5.

Stoichimetry (1 : 1) of metal-ligand were determined by pH-titration method as well as by conductometric titration method as adopted by Job[12] as shown in the Fig. 3. In both the cases the complex formation occurs in the pH-range $6.25 - 7.75$ after that hydroxide formation takes place.
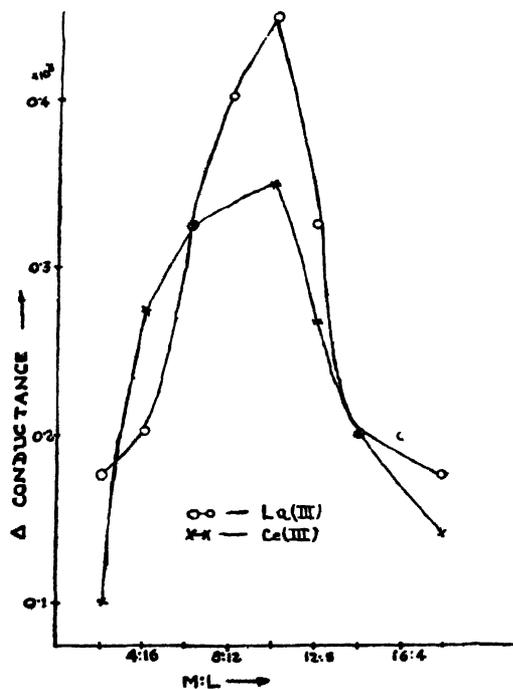
Fig. 3. Stoichiometry by Job's method.

The proton-ligand stability constant and dissociation constant of ligand, the metal-ligand stability constant and the thermodynamic functions of the complexes at $30°\pm0.1°$ and $40°\pm0.1°$ are all summarized in the following Table.

TABLE—PROTON-LIGAND, METAL-LIGAND STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF THE COMPLEXES AT μ=0.1 M KCl.

		30°±0.1°	40°±0.1°
Proton-Ligand stability constant (log pkH)		9.675	9.465
Dissociation constant of ligand		2.113×10^{-10}	3.428×10^{-10}
Metal-Ligand stability	La (III)	3.585	3.390
constant (log k)	Ce(III)	3.795	3.630
Change in free energy	La (III)	−4.971	−4.855
(Δ G) in KCal./mole	Ce (III)	5.261	−5.199
Change in enthalpy	La (III)	−8.461	For the difference
(Δ H) in KCal./mole	Ce (III)	−7.160	of 10°
Change in entropy	La (III)	−11.52	−11 52
(Δ S) in Cal./degree/mole	Ce (III)	−6.269	−6.266

The thermodymanic parameters of the complexes were calculated by the following relationships

$$\triangle G = \quad -RT \log k$$

$$\text{Log } \frac{k_2}{k_1} = \frac{\triangle H}{R}\left(\frac{T_2 - T_1}{T_1 \cdot T_2}\right)$$

$$\triangle G = \triangle H - T.\triangle S$$

Acknowledgement

References

1. E. M. Rogozina and T. M. Ponikarova, *Zh. Obshch. Khim.*, 1970, 40, 2357.
2. E. M. Rogozina, D. K. Popov and T. M. Ponikarova, *Zh. Obshch. Khim.*, 1968, 38, 1959.
3. B. S. Sekhon and S. L. Chopra, *Thermochimica Acta*, 1973, 7, 151.
4. C. P. Trivedi and O. P. Sunar, *J. Indian Chem. Soc.*, 1971. 48, 803.
5. R. C. Agarwal *J. Indian Chem. Soc.*, 1974, 51, 772.
6. N. K. Dutta and S. Rahul, *J. Inorg. Nuclear Chem.*, 1970, 32, 2905 ; 1969, 31, 3177.
7. J. F. Spencu, "The Metals of Rare Earth", Longmans, London, 1919, p. 105.
8. M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, 1945, 67, 2003.
9. M. Calvin and N. C. Melchior, *J. Amer. Chem. Soc.*, 1948, 70 3270.
10. J. Bjerrum, "Metal Amine Formation in Aqueous Solution". P. Hasse & Son, Copenhagen, 1941.
11. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904 ; 1953. 3397.
12. P. Job, *Compt. rend.*, 1927, 184, 204 ; 1925, 180 928. 1923, 176, 422 ;