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Biligand complexes of terbium with DTPA-alanine and phenylalanine

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ABSTRACT

The interaction of Tb(III) ions with DTPA alanine and phenylalanine have been followed potentiometrically. The stability constants of the formed complexes were determined at three different ionic strengths.

Key words: Ternary complex, terbium, DTPA-alanine, phenylalanine.

INTRODUCTION

The studies on mixed ligand complexing equilibria have fascinated the chemists because of the fact such complexes are of much importance in industrial, analytical and biological filed[1-3]. DTPA (Diethelene –triaminepenta acetic acid) is an important octadentate chelating ligand belongs to the class of aminopolycarboxylic acids and find many applications[4-6].

In this paper we have reported the complexes of lanthanide metal ion with DTPA, alanine and phenylalanine.

EXPERIMENTAL

Following sets of titration mixtures were prepared and titrated against standard alkali solution at three different ionic strengths (m = 0.05M, 0.10M and 0.15M) maintained in each set was kept at 50.00ml.

1. HNO_3 (2.0×10^{-3}M)
2. HNO_3 (2.0×10^{-3}M) + ligand L (1.0×10^{-3}M)
3. HNO_3 (2.0×10^{-3}M) + ligand L (1.0×10^{-3}M) + metal ion (1.0×10^{-3}M)
4. HNO_3 (2.0×10^{-3}M) + ligand L' (1.0×10^{-3}M)
5. HNO_3 (2.0×10^{-3}M) + ligand L' (1.0×10^{-3}M) + metal ion (1.0×10^{-3}M)
6. HNO_3 (2.0×10^{-3}M) + ligand L (1.0×10^{-3}M)+ ligand L' (1.0×10^{-3}M) + Metal ion

RESULTS AND DISCUSSION

By plotting the formation cure, pH versus $\overline{n}$ H, the P^k values of the ligand were calculated. These values were in agreement with the literature value. The value of K_{ML} can also be calculated considering by Bjerrums function and P^L.

$$K_{ML} = \frac{C_L - Y_1[L]}{[L]^2 Y_1}$$

where ,

C_L = Total ligand concentration

L = Ligand

$$Y_1 = \left[\frac{[H]^2}{K_1^H K_2^H} + \frac{[H]}{K_2^H} + 1 \right]$$

where and K_2^H are the proton dissociated constant of primary and secondary ligand respectively.

Table 1: Conditional and thermodynamic formation constant

Mixed ligand complex system	μ=0.15M $\log K^{ML}_{MLL'}$	μ=0.10M $\log K^{ML}_{MLL'}$	μ=0.05M $\log K^{ML}_{MLL'}$	μ→0 M $\log K^{ML}_{MLL'}$
Tb(III)- H_2DTPA alanine	3.640	3.706	3.775	3.825
Tb(III)- H_2DTPA Phenylalanine	3.558	3.601	3.648	3.700

Further the value of formation constant of mixed ligand compelxis calculated by Thomsan and Loraas method[7].

The plot of moles of alkali per mole of ligand metal (a) vs P^H were obtained for the system. It shows studies that the primary complex is formed at a lower P^H and is stable even at higher pH value. The primary complex curve [c] and mixed ligand curve [D] overlap each other upto $P^H \approx 5.2$

This indicates that in this P^H range combination of secondary ligand with metal ion does not take place. The curve C and D diverse from each other after $P^H \approx 5.2$. At this P^H range combination of the secondary ligand with primary complex starts at "a" ≥ 2, the mixed titration curve is found to be displaced to the right of the theoretical composite curve, which provide the evidence for increased interaction in the presence of two ligand, which indicates the formation of 1:1:1 mixed ligand species. Non appearance of mixed ligand system supports the formation of ternary species.

From above discussion it is concluded that the formation of ternary complex take place by stepwise chelation in which DTPA acts as a primary ligand and alanine and phenylalanine act as a secondary ligand. The equilibria can be represented as

$$Ln^{3+} + H_2DTPA^{3-} \xrightleftharpoons{0<a<2} [Ln\text{-}DTPA]^{3-} + 2H^+$$

$$[Ln\text{-}DTPA]^{2-} + 2L' \xrightleftharpoons{2<a<3} [Ln\text{-}DTPA\text{-}L]^{3-} + H^+$$

where ,

HL' = alanine or Phenylalanine
Ln = Tb(III)

Thermodynamic stability constants of complex were obtained graphically by extrapolating to zero ionic strength [μ→0]. The graphical extrapolation was obtained by plotting V_μ Vs logK.

The stability order of mixed ligand complees w.r.t secondary ligand is found to be : alanine < phenylalanine which is the order of increasing P^K value of the secondary ligand.

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