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"Studies on the Quaternary Complexes of La (III), Pr (III) and Nd (III)"

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INTRODUCTION

The metal complexes are formed by thecombination of one or different type of complexing agents with the central metal ion-resulting in the formation of binary or mixed ligand complexes respectively. The mixed ligand complexes are further divided as Binary, Ternary and quaternary complexes depending on the type of ligands.

Mixed-ligand chelates of amino poly carboxylic with other acids such as NTA[1] EDTA[2-4] and CDTA[5] with mltidentate ligands have been studied extensively Koch et. al[6-7] investigated some metal chelates of analytical importance[8]potentiometrically as well as spectrophotometrically

Recently, Sharma et al[9-11] studied Ternary as well as quaternary complexes of PDA in different systems involving CDTA, DTPA, NTA, EDTA, IMDA and GLY. In these complexes, Lanthanide ions attain an unusual co-ordination number greater than six and thus the study of quaternary complexes of these metals with multidentates ligands would be more interesting.

A survey of the literature revealed that 1:1:1:1, M(III)-NTA-PDA-GLY quaternary systems, have not been studied so far and, therefore, it was considered of interest to investigate, these systems potentiometrically with a view to determine their stability constants.

EXPERIMENTAL

The pH-metric titrations of the following systems were carried out at 25 ± 1°C against 0.1 M KOH solution keeping the ionic strength (μ= 0.1 M KNO_3) and total volume (50 ml) constant in the begining of each titration as described earlier.

System: 1:1:1:1 M(111)-K_2NTA-PDA-GLY

(where M(III) = La (III), Pr (III) and Nd (III)

1. 10 ml (0.025) metal nitrates + 5 ml (14) KNO_3 curve 'a'
diluted to 50 ml. with conductivity water (Figs. 4.1 – 4.3)
2. 10 ml (0.025 M) K_2NTA + 5 ml (M) KNO_3 curve 'b'
diluted to 50 ml with conductivity water (Figs. 4.1 – 4.3)
3. 10 ml (0.025 m) PDA + 5 ml (M) KNO_3+ diluted curve 'c'
to 50 ml with conductivity water (Figs. 4.1 – 4.3)
4. 10 ml (0.025 m) GLY + 5 ml km) KNO_3 curve 'd'
diluted to 50 ml with conductivity water (Figs. 4.1 – 4.3)
5. 10 ml (0.025 M) metal nitrates + 10 ml curve 'e'
(0.025 M)-K_2NTA+ diluted to 50 ml with C.W (Figs. 4.1 – 4.3)
(1:1, M(III) -K_2NTA)
6. 10 ml (0.025 M) metal nitrate + 10 ml (0.025 M) curve 'f'
PDA + 5 ml (M) KNO_3 + diluted to 50 ml with C.. (Figs. 4.1-4.3)
(1:1, M (III) - PDA)
7. 10 ml (0.025 M) metal nitrate + 10 ml (0.025 M) curve 'g'
GLY+5 ml (M) KNO_3 + diluted to 50 ml with C.W (Figs. 4.1 – 4.3)
(1:2, M (III) - GLY)
8. 10 ml (0.025 M) metal nitrate + 10 ml (0.025 m) curve 'h'
NTA + 10 ml (0.025 M) PDA + 5ml (M) KNO_3 + diluted (Figs. 4.1 – 4.3)
to 50 ml with conductivity water.
[1:1:1:1M III) -NTA-PDA]
9. 10 ml (0.025 M) metal nitrate + 10 ml. curve '1'
(0.025 M) NTA + 10 ml (0.025 M)-GLY + 5 ml (M) KNO_3+
diluted to 50 ml with conductivity water. (Figs. 4.1 – 4.3)
[1:1:1; M (III) – NTA - GLY]
10. 10 ml (0.025 M) metal nitrate + curve 'j'
10 ml (0.025 M) NTA + (Figs. 4.1 – 4.3)
10 ml (0.025 M) PDA +
10 ml. (0.025 M) GLY +

5 ml. (M) KNO_3 + diluted to 50 ml with Conductivity water.

[1:1:1:1, M(III) – NTA – PDA-GLY

RESULTS AND DISCUSSION:

Curve ‘a’ (Figs. 4.1-4.3) for metal nitrates, Curve 'b' (Figs. 4.1-4.3) for K_2NTA, Curve 'd' (Figs. 4.1- 4.3) for GLY, Curve 'e' (Figs. 4.1-4.3) for 1:1, M(III)-K_2NTA, Curve 'g' (Figs. 4.1-4.3) for 1:1, M(III)-GLY, and Curve 'i' (Figs. 4.1-4.3) for 1:1:1;,M(III)-K_2NTA-GLY systems have already been explained. Curve 'c' (Figs. 4.1-4.3) ascribes the titration of PDA showing a single well-defined inflection at m = 2 showing the titration of both the carboxylic protons leading to the normal salt formation.

BINARY SYSTEM :

Curve 'f' (Figs. 4.1-4.3) depicts the titration of 1:1, metal nitrate and PDA. An initial lowering in the pH followed by an inflection at m = 2 may be attributed to the formation of soluble 1:1, M(III)-PDA binary complex. An appearance of solid phase at m ~2 followed by another inflection at m = 3 is probably due to the disproportionation of the initially formed 1:1, M(III) binary complex into 1:3, M(III) binary complex, and the remaining metal precipitated as metal hydroxide.

$$M^{3+} + PDA + 2OH^- \xrightleftharpoons{O < m < 2} [M^{3+} - PDA^{-2}] + 2H_2O$$

$$M^{3+} + PDA^{2-} + 2OH^- \xrightleftharpoons{2 < m < 3} \frac{1}{3}[M^{3+} - (PDA)_3^{2-}] + \frac{2}{3}M(OH)_3$$

TERNARY SYSTEM:

pH-metric titration of 1:1:1, M(III) – K_2NTA-PDA system is represented by Curve 'h' (Figs. 4.1 to 4.3). The lowering in initial pH as compared to the Curve 'f' for 1:1,M(III)-PDA binary system and a sharp inflection at m=3 may be ascribed to the simultaneous addition of both the ligands to the metal ion. Forming 1:1:1, M(III)-K_2NTA-PDA biligand species:

$$M^{3+} + NTA^{2-} + PDA + 3OH^- \xrightleftharpoons{O < m < 3} [NTA^{3-} - M^{3+} - PDA^{2-}] + 3H_2O$$

QUATERNARY SYSTEM :

Curve ‘j’ (Figs. 4.1-4.3) depicts the pH-metric titration of 1:1:1:1, M(III)-K_2NTA-PDA-GLY quaternary system. This curve runs parallel to the Curve 'h' (Figs. 4.1- 4.3) upto m = 2 with an initial lowering in pH and there, after gives an inflection at m = 3 which indicate the initial formation of 1:1:1, M(III)-K_2NTA-PDA ternary species. The occurrence of one more inflection at m-4 further shows the stepwise formation of 1:1:1:1, M(III)-K_2NTA-PDA-GLY quaternary species resulted by the addition of glycine in the higher pH range.

$$M^{3+} + NTA^{2-} + 3OH^{-} \xrightleftharpoons{O < m < 3} [NTA^{3-}\_M^{3+} - PDA^{2-}]$$

+ PDA

$$\Big\Updownarrow \; 3<m<4 \qquad +GLY^{-} \quad +OH^{-}$$

$$[NTA^{3-}\_M^{3+} - PDA^{2-}]$$
$$|$$
$$GLY^{1-}$$

The formation of above quaternary complexes hasbeen further supported by the following facts.

1. Non-appearance of any solid phase in the region of quaternary complex formation.

2. By the constancy observed in the calculated values of stability constants.

3. Non-superimposable nature of the theoretical composite Curve (T) with the experimental Curve 'j representing the quaternary system.

Formation Constants (log KMLLL) of the mixed ligand Complexes :

The calculated values of the formation constants (log $K_{ML'L''}$) of the 1:1:1:1, M(III)-K_2NTA-PDA-GLY quaternary species at 25± 1°C are recorded in Table 4.1. The relative order of stability of quaternary species (10g $K_{MLL'L''}$) in terms of the metal ions has been found to be: La(III) <Pr(III) <Nd (III), and may be explained on the basis of decreasing size and increasing ionization potential (Charge/radius ratio) of the metal ions.

Table 4.1: System:1:1:1:1 M(III)-NTA-PDA-GLYQuaternary System

(where M(III) = La (III), Pr(III) and Nd (III))

Temperature = 25 ± 1°C, μ = 0.1 MKNO_3, KOH= 0.1 M

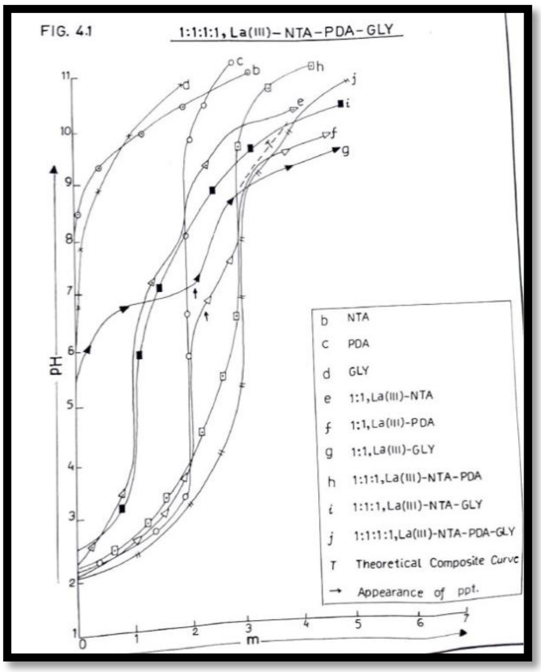
Concentration = M(III) NTA = PDA = GLY = 5 × 10^{-3}M

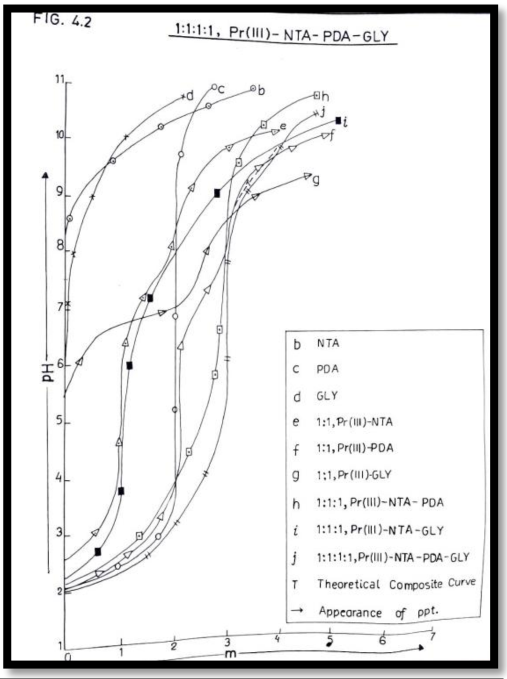
S.No.	M 3-4	La (III)-NTA-PDA-GLY pH	log $K_{MLL'L''}$	Pr(III)-NTA-PDA-GLY pH	log $K_{MLL'L''}$	Nd (III)-NTA-PDA-GLY pH	log $K_{MLL'L''}$
1	0.1	8.70	2.92*	8.01	-	6.10	-
2	0.2	8.90	3.46*	8.60	3.41*	7.20	-
3	0.3	9.06	3.92*	9.20	3.97*	8.25	3.96*
4	0.4	9.20	4.13	9.28	4.16	8.50	4.17
5	0.5	9.38	4.16	9.40	4.21	8.74	4.24
6	0.6	9.50	4.19	9.55	4.27	8.96	4.26
7	0.7	9.57	4.23	9.66	4.31	9.22	4.33
8	0.8	9.68	4.41	9.75	4.51	9.34	4.49
9	0.9	9.75	4.54	9.91	4.63	9.40	4.68

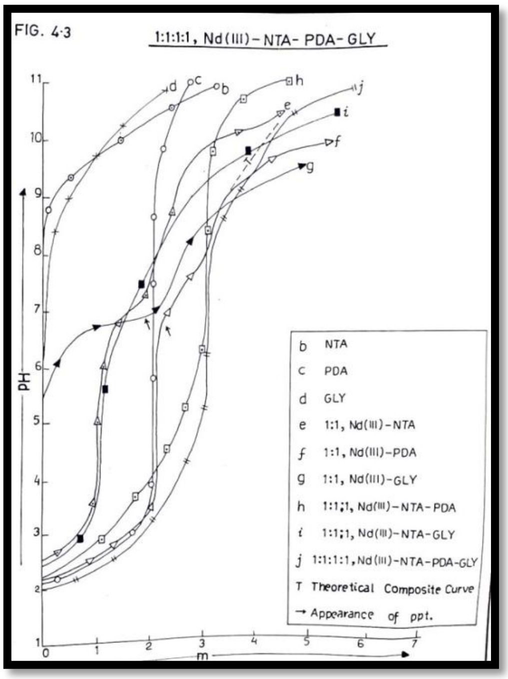
log $K_{MLL'L''}$ = 4.27±.20 ΔG° = – 5.82K.Cal/mole

log $K_{MLL'L''}$ = 4.34 ±.23 ΔG° = – 5.91 K.Cal/mole

log $K_{MLL'L''}$ = 4.36 ±.25 ΔG° = – 5.94 K.Cal/mole







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