Asian Journal of Chemistry Vol. 19, No. 1, (2007), 311–314

Mixed Ligand Complexation of Pr(III), La(III) and Ce(III) with Some Organic Ligands: A Potentiometric Study

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Interaction of La(III), Ce(III) and Pr(III) with N-2-mercapto propionyl glycine, phenyl alanine and tyrosine at 25°C in aqueous medium was studied. pH titration data based on Calvin-Bjerrum titration technique were employed for the calculation of proton-ligand and metal-ligand stability constants.

Key Words: Potentiometric studies, Stability constants, Calvin-Bjerrum method.

INTRODUCTION

The developments in the study of mixed ligand complexes have been very fast in recent years[1] and their study is of interest to analytical chemists[2] and bio-inorganic researchers[3]. An exhaustive literature survey was therefore undertaken and it was revealed that generally mixed ligand complexation has been studied potentiometrically by maintaining metal : primary ligand : secondary ligand ratio as 1 : 1 : 1 (M : X : Y). It was also revealed that not much work was done on the present ligands and their complexation with La(III), Ce(III) and Pr(III). Hence the present work was undertaken to investigate the mixed ligand complexation with these ligands by maintaining the metal : primary ligand : secondary ligand ratio as 1 : 5 : 5 (M : X : Y). The stability constants of ternary complexes log K_{MXY} were computed adopting the method given by Thompson Lorras[4].

EXPERIMENTAL

The metal salts of La(III), Ce(III) and Pr(III) were dissolved in doubly distilled water and standardized by the method of Flaschka[5]. All the other solutions were also prepared in doubly distilled water. The pH measurements were carried out on Elico digital model LI-127 pH-meter (accuracy up to ± 0.01 pH unit) with a combined electrode type CL-51B having range 0–14. The method of Calvin-Bjerrum[6] as modified by Irving and Rossotti was used to obtain log K_1^H and Thompson and Lorra's method[4] was employed to obtain log K_{MXY}.

Calculation of stability constants

(a) Proton-ligand stability constants: Proton-ligand stability constants have been calculated as a proton-ligand formation number (n_A). The proton-ligand stability constants log K_1^H are calculated by:

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(i) Half integral method,
(ii) Method of pointwise calculation, and
(iii) Least squares method.

(b) Calculation of stability constants of mixed-ligand complexes: For the calculation of stability constant of mixed ligand complexes, the two types of equilibria possible are given as:

$$\mathrm{M + X = MX,} \qquad \mathrm{MX + Y = MXY}$$

$$\mathrm{M + Y = MY,} \qquad \mathrm{MY + X = MXY}$$

$$\mathrm{M + X + Y = MXY} \text{ (simultaneous equilibria)}$$

where X and Y represent the two different ligands.

Simultaneous equilibria: When the mixed ligand titration curve MXY does not coincide with either MX or MY curve, the equilibrium involved is simultaneous and determination of stability constant has been carried out by Thomson and Lorras method[4].

When $T_M^0 = T_X^0 = T_Y^0$,

$$K_{MXY} = \frac{T_M^0 - (A)B/2}{(1/8)(A)^3B} \tag{1}$$

where

$$A = \frac{2T_X^0 + T_Y^0 + P - T_{OH—H^+}}{\dfrac{4[H^+]^2}{K_1K_2 + K_1' K_2'} + \dfrac{2[H^+]}{K_2 + K_2'}} \tag{2}$$

But when $T_M^0 \neq T_X^0 = T_Y^0$ (present work),

$$K_{MXY} = \frac{(1/2)(T_X^0 + T_Y^0) - ([A])X)}{\{T_M^0 - (1/2)(T_X^0 - T_Y^0) - ([A]X)\}(1/4)[A]2X} \tag{3}$$

where

$$A = \frac{\underline{\{2T_X^0 + 2T_Y^0 + P - T_{OH—[H]}\}}}{\dfrac{4[H^+]^2 + 2[H^+]}{(K_1K_2) + (K_1' K_2')(K_2 + K_2')}} \tag{4}$$

RESULTS AND DISCUSSION

Determination of proton ligand stability constants was carried out by the half integral method. Formation curve for n_A against pH was constructed and the values log K_1H were found out as the pH at $n_A = 0.5$ and 1.5 for all the three ligands and the results obtained are given in Table-1.

The log K_1^H values were also calculated adopting pointwise calculation and least squares method. It has been observed that log K_1^H values obtained by all the three methods were almost same.

N-2-Mercapto propionyl glycine is a ligand of novel type bearing —SH—CONH and —COOH groups; however, pH titration curves of this ligand show two well separated steps of neutralization and hence protonation constants are calculated.

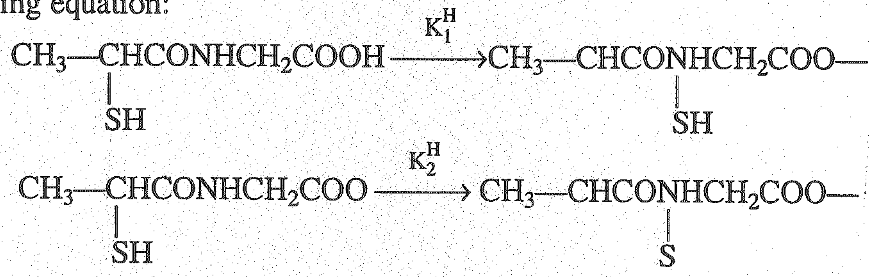
TABLE-1
PROTONATION CONSTANTS OF LIGANDS

$P = 0.008395$ M; $N = 0.3906$; $T^0{}_L = 0.002$ N;
$\mu = 0.1$ M (NaC10$_4$), $V^0 = 50$ mL

Ligand	log K_1^H	log K_2^H
2 MPG	8.380	3.500
PA	10.958	8.836
TR	10.596	8.845

2MPG:	N-2 mercapto propinonyl glycine
PA:	phenyl alanine
TR:	tyrosine

The ionization of N-2 mereapto propionyl glycine may be represented by the following equation:



$$CH_3\text{—}\underset{\substack{|\\ SH}}{C}HCONHCH_2COOH \xrightarrow{K_1^H} CH_3\text{—}CHCON\underset{\substack{|\\ SH}}{H}CH_2COO\text{—}$$

$$CH_3\text{—}\underset{\substack{|\\ SH}}{C}HCONHCH_2COO \xrightarrow{K_2^H} CH_3\text{—}CHCON\underset{\substack{|\\ S}}{H}CH_2COO\text{—}$$

PA and TR have been shown to be useful analytical reagents because of complexing properties. As our aim was to study the interaction of the present ligands with Pr(III), La(III) and Ce(III) ions, the protonation constants of these ligands were investigated at the identical experimental conditions set for La(III), Ce(III) and Pr(III) mixed ligand studies.

The formation of mixed ligand complexes can be concluded initially by noting the pH of precipitation for MX, MY and MXY titration curves. It is expected that the mixed ligand titration would give a higher value of pH precipitation than the binary metal complex formation. This can be further confirmed by comparing the mixed ligand curve with the theoretical composite curve. The composite curve was drawn by computing the difference between the titration curves as (NX – X) + (MY + Y) or (MX + MY) – (X – Y). The composite curve has been found to be non-superimposable on the experimental MXY curve.

The metal-ligand stability constant values ate tabulated in Table-2. The nature of complex equilibria was investigated according to the method suggested by Carey and Martell.

TABLE-2
METAL-LIGAND STABILITY CONSTANT

$P = 0.008395$ M; $N = 0.3906$; $T^0L = 0.002$ N;
$T^0M = 0.0004$ N; $u = 0.1$ M (NaClO$_4$); $V^0 = 50$ mL.

Metal ion	Ligand		
	2PMG	PA	TR
La(III)	5.32	3.19	3.21
Ce(III)	5.40	4.48	4.47
Pr(III)	5.55	3.36	3.79

The deviation of mixed ligand complex curve was from pH 2.80 to 3.95. The stability constants of mixed ligand complexes are tabulated in Table-3.

TABLE-3
STABILTY CONSTANTS OF MIXED LIGAND COMPLEX

Metal ion	Mixed ligand system	Log^{K} MXY
La(III)	2MPG-PA	5.415
	2MPG-TR	5.359
Ce(III)	2MPG-PA	7.221
	2MPG-TR	6.874
Pr(III)	2MPG-PA	7.154
	2MPG-TR	7.043

Since the mixed ligand curve did not coincide with either binary complex titration curve, the mixed ligand complex formation was therefore assumed to be taking place by simultaneous and not by stepwise equilibria and both the ligands were considered to have been attached simultaneously to the metal ion.

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(*Received*: 19 September 2005; *Accepted*: 5 June 2006) AJC-4941