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Stability constant of metal proton of Lanthanum (III), Neodymium (III) and Praseodymium (III) chelates with substituted Schiff's bases

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Abstract
The interactions of La(III), Nd(III) and Pr(III) with 2-hydroxy-5-chloro-1-(a-phenylimino) ethyl benzene (Ligand-L_1), 2-hydroxy-5-chloro-1-(a-para methylphenylimino) ethyl benzene (Ligand-L_1) and 2-hydroxy-3-bromo-5-chloro-1-(a-phenylimino) ethyl benzene (Ligand-L_1) have been investigated by pH-metric technique at 0.1 M ionic strength at 26 ± 0.1°C in 70% DMF-water mixture. The data obtained were used to estimate the values of proton-ligand stability constants (pK) and metal-ligand stability constants (log K). It is observed that La (III), Nd(III) and Pr(III) metal ions formed 1:1 and 1:2 complex with all the three ligands.

Keywords: Stability constant, chelates, schiff's base, metal, proton, ligands

Introduction

The substituted Schiff's bases are good chelating agents as they bear -OH group in the vicinity of >CN group. The study of their metal complexes is very interesting because of their unusual stability, chemical, electrical and magnetic properties. Metal-ligand stability constants of some lånthanides with some substituted sulphonic acids have also been investigated [1]. The stability constants of Pr(III), Nd(III), Sm(III), Eu(III), Tb(III) metal ion complexes with some substituted isoxazolines have been reported [2]. The stability constants of Pr(III), Nd(III) and Sm(III) chelates with some substituted pyrazolines have also been reported [3].

Materials and Methods

Substituted Schiff's bases were synthesised in laboratory and their purity was checked by I.R., N.M.R. and m.p. The solutions of ligands were prepared in DMF water (70% v/v) solvent. Dimethyl formamide (DMF) was dried over calcium sulphate for 72 hours followed by distillation under reduced pressure. The solvent thus obtained is used for the experimental purpose. $HClO_4$ and NaOH were used of AR-grade. Metal nitrates were dissolved in perchloric acid and their concentrations were estimated by standard methods [4]. The other solutions were prepared in double distilled water pH measurements were carried out with ELICO-LI-10 pH-meter (accuracy ± 0.05 unit) using glass electrode and calomel electrodes at 26 ± 0.1°C. pH-meter was calibrated by standard buffer solution of pH 4.00, 7.00 and 9.20 pH. The β -values (pH-meter reading in 70% DMF-water mixture) were converted to $[H^+]$ values by applying the corrections proposed by Van Uitert and Hass [5].

The overall 0.1 M ionic strength of solution was calculated by the expression

$$u= \frac{1}{2} + \sum_{i=1} cizi^2$$

The contribution of the other ions in addition to Na and ClO, were also taken into consideration.

Experimental procedure involves following three sets of experiments.

1. Free Acid $HClO_4$ (1×10^{-2} M)
2. Free Acid $HClO_4$ ($1x10^{-2}$ M) + substituted ligand solution (20×10^{-4} M)
3. Free Acid $HClO_4$ ($1x10^{-2}$ M) + substituted ligand solution (20×10^{-4} M) + Metal ions (4×10^{-4} M)

Three sets were titrated separately against standard solution of 0.2 M NaOH and 0.1 M ionic strength was maintained constant by adding an appropriate amount of 1 M NaClO, solution. All the titrations were carried out in 70% DMF-water mixture.

Results and Discussion

Proton-Ligand Stability Constants: Substituted Schiff's bases may be considered as monobasic acids having only one dissociable H^+ ion from -OH group. It can therefore be represented as HL.

$HL \rightleftharpoons H^+ + L^-$

The titration data were used to construct the curves between volume of NaOH as pH the proton ligand formation numbers (n_A) were calculated by Irving and Rossotti's expression [6]. pK values were calculated from the formation curves between pH vs n_A by noting the pH at which $n_A = 0.5$ (half integral method). It could be observed from Table-1, that pK, values increase in the following order.

Ligand (L_1) >Ligand(L_2)>Ligand(L_3)

Metal-Ligand Stability Constant: The stepwise formation constants of La (IIII), Nd(III) and Pr(III) with ligand (L_1) ligand (L_2)and ligand (L_3) in 70% DMF-water mixture were determined. The values of log(K_1) and log(K_2) were directly computed from the formation curves (n vs pL) using half integral method shown in Table-2.

The deviation between acid curve and (Acid + Ligand) curve showed the dissociation of-OH group from ligand.

The departure between (Acid + Ligand) curve and (Acid + Ligand + Metal) curve showed the commencement of formation of complex. The colour of complexes was observed in the pH range from 5 to 10 shows the formation of complex. The values of (log K_1 -log K_2) and logK_1 /log K_2 are presented in Table-3. It could be observed from Table-3 shows that there is a difference in log K_1 and log $_{K2}$ values that showed the stepwise formation of complexes. The smaller may to trans-structure.

Table 1: Proton-ligand stability constants of substituted Schiff's bases in 70% DMF-water mixture

Sr. No.	System	Constant by half integral method
1.	2-Hydroxy-5-chloro-1-(*a*-phenyl imino) ethyl benzene -Ligand (L_1)	6.975
2.	2-Hydroxy-5-chloro-1-(*a*-para methyl phenyl imino) ethyl benzene- Ligand (L_2)	5.530
3.	2-Hydroxy-3-bromo-5-chloro-1-(*a*-phenyl imino) ethyl benzene- Ligand (L_3)	4.210

Table 2: Metal-ligand stability constants of La(III), Nd(III) and Pr(III) complexes with substituted Schiff's bases at 0.1 M ionic strength

Sr. No.	System	Constant	
		Log k_1 *i.e.* pL_1	Log K_2 i.e. pL_2
1.	La(III) – Ligand (L_1)	5.0099	4.3289
2.	Nd(III) – Ligand (L_1)	5.0198	4.5789
3.	Pr(III) – Ligand (L_1)	4.8297	4.1890
4.	La(III) – Ligand (L_2)	3.4748	3.0347
5.	Nd(III) – Ligand (L_2)	3.9248	3.5839
6.	Pr(III) – Ligand (L_2)	4.0848	3.9463
7.	La(III) – Ligand (L_3)	3.3780	3.3433
8.	Nd(III) – Ligand (L_3)	3.0139	2.9618
9.	Pr(III) – Ligand (L_3)	2.8541	2.6682

The results show that the ratio log(K_1 /log K_2 is +ve in all cases. This implies that there is little or no steric hindrance to the addition secondary molecules. It could be seen from Table-I that pK value of ligand (L_1) is greater as compared to ligand and ligand (L_3) It showed that, the dissociation of-OH group is at a low extent of (L_1) ligand (L_1)

Validity of gK = a pK + b relation: Many workers have investigated linear relationship between pK and log K [7, 8, 9]. The order of stability of complex is as follows

1. log K_1 for ligand (L_1)
   Nd(III)>La(III)>Pr(III)
2. log K_1 for ligand (L_2)
   Pr(III) > Nd(III) > La(III)
3. log K_1 for ligand (L_3)
   La(III) >Nd(IIII)>Pr(III)

Table 3: Metal-ligand stability constant at 0.1 M ionic strength

Sr. No.	System	Log K_1 – log K_2	Log k_1 / log k_2
1.	La(III) – Ligand (L_1)	0.6810	1.1573
2.	Nd(III) – Ligand (L_1)	1.4409	1.0963
3.	Pr(III) – Ligand (L_1)	0.6407	1.1529
4.	La(III) – Ligand (L_2)	0.4401	1.1450
5.	Nd(III) – Ligand (L_2)	0.3409	1.0951
6.	Pr(III) – Ligand (L_2)	0.1385	1.0351
7.	La(III) – Ligand (L_3)	0.0347	1.0104
8.	Nd(III) – Ligand (L_3)	0.0521	1.0176
9.	Pr(III) – Ligand (L_3)	0.1859	1.0697

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