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STUDY OF THE STABILITY CONSTANT OF THE LANTHANIDE (III) ION COMPLEXES WITH SCHIFF BASES

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ABSTRACT

The present work is undertaken to make a systematic solution study of the complex formation of lanthanide (III) ions with the Schiff bases synthesized from salicylhydrazide with (i) 4- methoxy benzaledehde (ii) 3,4,5, trimethoxybenzaledehde and (iii) furfuraladehyde. The stability constants of their complexes with lanthanides (III) ions have been determined at 30 ± 0.1ºC potentiometrically in 40% THF-water mixture and 0.1M ($NaClO_4$) ionic strength. The lanthanides form 1 : 1 and 1 : 2 complexes with all the Schiff bases and log k values show a break at gadolinium.

Key words: Lanthamide, Schiff bases, Complexes, Stability constant.

INTRODUCTION

Complexes of Schiff bases are widely used in biological[1], germicidal[2], bactericidal[3], fungicidal and carcinogenic activities. In view of the analytical, biological importance and manifold uses of metal complexes with Schiff bases, a study of their stability is therefore required, which is an important factor in determining the effectiveness of these chelates in above fields.

The literature survey revealed that no systematic study of the binary complexes of rare earth metal ions with present substituted Schiff bases has been reported. Hence, the study of their complexes with rare earth metal ions like La (III). Ce (III). Pr (III), Nd (III), Sm (III), Eu (III). Gd (III), Tb (III), Dy (III) and Ho (III) were undertaken.

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EXPERIMENTAL

All the chemicals used were of A. R. grade. The Schiff bases were synthesized by the condensation of salicylhydrazide with 4 - methoxy benzaldehyde, 3,4,5- trimethoxy benzaldehyde and furfuraldehyde and their purity was checked by M. P., TLC, elemental analysis and IR spectra. The metal nitrates were dissolved in double distilled water and standardized by the known methods[4]. All other solutions were also prepared in double distilled water. A digital pH meter (Elico model LI-120) in conjunction with a combined electrode was used for pH measurements. The Calvin-Bjerrum methods modified by Irving and Rossotti[5] was used to obtain pk and log k values. The measurement were made at 30 ± 0.1°C and $\mu = 0.1$ M ($NaClO_4$) in 40% (v/v) tetrahydrofuran- water medium.

RESULTS AND DISCUSSION

The pk values of Schiff bases, which represent the deprotonation of phenolic - OH group were determined. It can be seen from Table 1 that the pk value of R_1 is higher than R_2 and R_3. This may be attributed to the fact that in R_1, only one methoxy group at 4-position minimizes the election density on phenolic - OH group, whereas in R_2 the electron density on - OH group is minimized by three methoxy groups present at 3, 4, 5 – position. This is the combined effect of three $-OCH_3$ group, which decreases the pk value of R_2 as compared to R_1.

The lower value of R_3 can be explained on the basis that the more electronegative oxygen atom in furan ring having a lone pair of electrons minimizes the electron density of phenolic – OH, which affects the deprortonation of - OH group.

The displacement of metal titration curve from the ligand titration curve is in between 3.5-7.0 pH. The highest values of $\bar{n}$ obtained was about 2.0 indicating the formation of both 1 : 1 and 1 : 2 complexes. The values of log k_1 and log k_2 were calculated by pointwise calculation method, half integral method and least squares methods. The values of log k_1, log k_2 and log k_3 are shown in Table 1.

Lanthanides from mostly ionic compounds due to the shilding of f -electron. If the bonds in the lanthanide compounds are ionic, the Born relation $E = (e^2/2r)(1-1/D)$ must be followed for the ions. Since, the stability constants are related directly to this energy, it is expected that the log k values for various rare earths should increase in early with e^2r. Such a relationship has been tested for number of rare earth complexes[6-8] Moeller et al.[9] observed the regular increase in stabilities with increase in atomic number from La (III) to

Eu (III) and however, there is a discontinuity at Gd (III).

Table 1. Proton ligand and metal ligand stability constants of Schiff bases.

Medium-40% (v/v) THF-water medium; Temp. = 30 ± 0.1°C; μ = 0.1M ($NaClO_4$)

(a) pk values of the ligands

Ligand	Name of the lignad	pk
R_1	1-(2' - Hydroxy benzamido) -2 (4'-methoxyphenyl) -azomethine	8.49
R_2	1-(2'- Hydroxy benzamido) -2 (3',4,5 trimethoxyphenyl) - azomethine	8.30
R_3	1-(2'- Hydroxy benzamido)-2 (fur-2'-yl)-azomethine	4.63

(b) log k_1 and log k_2 values of lanthanide (III) complexes

Lanthanide	Stability	R_1	R_2	R_3
La (III)	log k_1	4.10	4.30	2.78
	log k_2	3.98	4.17	2.73
	log β	8.08	8.47	5.51
Ce (III)	log k_1	4.14	4.38	2.82
	log k_2	4.05	4.26	2.76
	log β	8.19	8.64	5.58
Pr (III)	log k_1	4.17	4.47	2.84
	log k_2	4.10	4.28	2.74
	log β	8.27	8.75	5.58
Nd (III)	log k_1	4.20	4.50	2.86
	log k_2	4.04	4.41	2.72
	log β	8.24	8.91	5.58

Cont…

Lanthanide	**Stability**	**R_1**	**R_2**	**R_3**
Sm (III)	log k_1	4.25	4.52	2.88
	log k_2	4.12	4.32	2.81
	log β	8.37	8.84	5.69
Eu (III)	log k_1	4.27	4.57	2.93
	log k_2	4.16	4.38	2.84
	log β	8.43	8.95	5.77
Gd (III)	log k_1	4.21	4.18	2.91
	log k_2	4.02	4.13	2.86
	log β	8.23	8.49	5.77
Tb (III)	log k_1	4.29	4.49	2.86
	log k_2	4.09	4.20	2.74
	log β	8.38	8.69	5.60
Dy (III)	log k_1	4.31	4.82	2.76
	log k_2	4.12	4.36	2.67
	log β	8.43	9.18	5.43
Ho (III)	log k_1	4.23	4.32	2.79
	log k_2	3.99	4.06	2.74
	log β	8.22	8.38	5.51

In the present complexes, the rare earth metal ions bind predominantly to oxygen and weakly to nitrogen in Schiff bases. The plot of log k_2 vs 1/r for these complexes shows a regular increase of stability constants from La (III) to Eu (III) with a discontinuity at gadolinium. The values of stability constants increase up to Dy (III) and then there is a decrease for Ho (III). Such behaviour was found for most of the rare earth complexes with various ligands [10-12]

When log β values were plotted against pk values, no linearity could be obtained, lonisation potential of the metal ion and donor atoms, tendency of metal ions to form π bonds and ligand field stabilization of ligands are some of the factors, which affect the linear relationship. Such a behaviour was found with various ligands[8.9]

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