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Stability constant of the lanthanide (III) ion complexes with schiff bases

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Abstract

In this paper the stability constants of Schiff base and their Lanthanide metal complexes, hence on interest is taken to study the Schiff base and Lanthanide. Metal complexes in the present investigation. An attempt has been made to study the stability constant, effect of ionic strength and thermodynamic parameter of the Lanthanide metal complexes.

Keywords: Complexes, deprotonation, schiff bases, phenolic – OH group

1. Introduction

In continuation of our earlier work [1-6] deals with the stability constants of Schiff bases and their transition metal (Co^{II} , Ni^{II} , Cu^{II} and Zn^{II}) & Lanthanide metal complexes. The Schiff base derived from substituted amino thiazole i.e. 2-aminothiazole, 2,4-diaminothiazole and 2,4-diamino-5-chloro thiazole and 0-hydroxy aldehyde i.e. (5- CH_3 , 5-Cl and 2-hydroxy-1-nathaldehydes).

Complexes of Schiff bases are widely used in biological [7], germicidal [8], bactericidal [9], 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.

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 [10]. 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 [11] was used to obtain $\text{p}K$ and $\log k$ values. The measurement were made at $30 \pm 0.1^\circ\text{C}$ and $\mu = 0.1 \text{ M}$ (NaClO_4) in 40% (v/v) tetrahydrofuran- water medium.

Result and Discussion

The $\text{p}K$ values of Schiff bases, which represent the deprotonation of phenolic – OH group were determined. It can be seen from Table 1 that the $\text{p}K$ 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 electron 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 $\text{p}K$ value of R_2 as compared to R_1 .

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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 deprotonation 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.

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

(a) pK values of the ligands

Ligand	Name of the ligand	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

Medium-40% (v/v) THF-water medium; Temp. = $30 \pm 0.1^\circ\text{C}$; $\mu = 0.1\text{M}$ (NaClO_4)

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

Lanthanide	Stability	R1	R2	R3
La (III)	$\log k_1$	4.10	4.30	2.78
	$\log k_2$	3.98	4.17	2.73
	$\log \beta$	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
	$\log \beta$	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
	$\log \beta$	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
	$\log \beta$	8.24	8.91	5.58
Sm (III)	$\log k_1$	4.25	4.52	2.88
	$\log k_2$	4.12	4.32	2.81
	$\log \beta$	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
	$\log \beta$	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
	$\log \beta$	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
	$\log \beta$	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
	$\log \beta$	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
	$\log \beta$	8.22	8.38	5.51

Proton-ligand stability constant (P_K) values of the ligands $(2\text{H5MPM})_2$ DCT, $(2\text{H5CPM})_2$ DCT, and $(2\text{HN})_2$ DCT, were calculated using Half-Integral Method.

The ligand possesses two pK value due to dissociable proton of the two phenolic – OH group. The protonation of imino nitrogen ($\text{HC}=\text{N}$) does not take place in the pH range under study. The pK values of ligands follows the trend: ligand $(2\text{H5MPM})_2$ DCT > $(2\text{H5CPM})_2$ DCT > $(2\text{HN})_2$ DCT, and it is explained on the grounds of basic nature of azomethine nitrogen and phenolic oxygen [15, 16].

The ligand $(2\text{H5CPM})_2$ DCT exhibit higher proton-ligand stability constant values than the ligand $(2\text{HN})_2$ DCT and this may be due to presence of Cl group in the aromatic ring.

Lanthanides from mostly ionic compounds due to the shielding 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 [12, 13] Moeller *et al.* [14] 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).

Cl behave as electron releasing group due to mesomeric effect (+M) rather than (–I) effect (inductive effect). Hence electron density on phenyl ring increases and azomethine nitrogen and phenolic oxygen become more basic.

The ligands $(2\text{H5MPM})_2$ DCT possess methyl group at meta position with respect to azomethine group. Due to (+I) effect of methyl group, electron density over phenyl ring increases and azomethine nitrogen and phenolic oxygen become more basic. Hence the ligand possesses higher stability constant values.

Thus (+I) effect of methyl and stronger (+M) of halogen group present in the phenyl ring in the series of the Schiff base support the trend proposed for proton-ligand stability values.

Metal–Ligand stability constants

The titration curves of acid, ligands and the metal ions are studied. The metal ion curve shows departure from ligand curves at pH much lower than the pH of hydrolysis of metal ion and therefore the liberation of proton is due to chelation [17]. The order of stability constant for the trivalent Lanthanide complexes have no regular trends that is in many cases no order is apparent [18, 19].

Few observations were made for Lanthanide complexes, were the increasing stability constants with increasing atomic number up to Tb(III) and Yb(III) [20, 21] respectively.

In present observation complexes of Lanthanide trivalent metal (III) ions and Schiff bases I, II and III shows increasing in stability from La(III) to Yb(III) in agreement with increasing Lewis acidity of the metal ions. The order of stability constant of Lanthanide complexes with Schiff bases I, II and III has been found to be as follows.

La(III) < Ce(III) < Pr(III) < Nd(III) > Sm(III) < Eu(III) < Gd(III) < Tb(III) and Dy(III) < Gd(III) has low value of stability constant then Sm(III) indicates the Gadolinium break. The Ce(III) cerium show higher value due to the partial conversion of Ce(III) to Ce(III).

The value of stability constants are decreased with increasing ionic strength which is an agreement with Debye-Hukel equation.

To study the effect of temperature on complexation observed that the value of proton-ligand and metal-ligand decreases with increasing temperature suggesting that low

temperature is favorable for complexation. These results are good agreement with Pitzer and Garge [22].

Conclusion

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 [23, 24]

When $\log \beta$ values were plotted against pK values, no linearity could be obtained, ionisation 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

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