

Potentiometric study of trivalent Lanthanide complexes with 2-hydroxy-5-methyl acetophenone-N-(4-methyl phenyl) imine in 50% ethanol-water media

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ABSTRACT

The stability constant of schiff base 2-hydroxy-5-methyl acetophenone-N-(4-methyl phenyl) imine with trivalent lanthanide metal ions La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} and Ho^{3+} using a pH metric titration technique in 50% (v/v) ethanol-water mixture at 25°C temperature and at an ionic strength of 0.1M NaClO_4 were studied. The method of Calvin and Bjerrum as adopted by Irving and Rossotti has been employed to determine metal-ligand stability constant ($\log K$) values. The trend in the formation constants follows the order: $\text{La}^{3+} < \text{Ce}^{3+} < \text{Pr}^{3+} < \text{Nd}^{3+} < \text{Sm}^{3+} < \text{Eu}^{3+} > \text{Gd}^{3+} < \text{Tb}^{3+} < \text{Dy}^{3+} > \text{Ho}^{3+}$.

Keywords: Stability Constant, Lanthanides, Schiff base, pH meter, thermodynamic parameter.

1. INTRODUCTION

The stability of metal complexes with schiff bases plays a major role in the biological and chemical activity. Metal complexes of schiff bases have played a central role in the development of coordination chemistry. Metal complexes are widely used in various fields, such as biological processes pharmaceuticals, separation techniques, analytical processes etc. pH metric titration is accepted as a powerful and simple electro analytical technique for determination of stability constants. It is also well known that some schiff bases exhibit increased activity when administered as metal complexes. Most of the f-block elements form complexes. There are different kinds of ligands used for complexation. For the present investigation, we have selected schiff base 2-hydroxy-5-methyl acetophenone-N-(4-methylphenyl) imine, having molecular formula $\text{C}_{16}\text{H}_{17}\text{ON}$

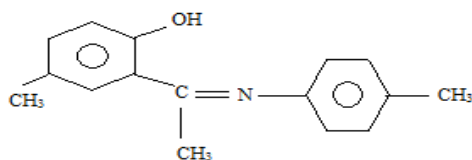


Figure: 2-hydroxy-5-methyl acetophenone-N-(4-methylphenyl)imine

In recent years, there has been an increased interest in the study of the lanthanide complexes. Owing to the unique properties of the lanthanide ions, lanthanides have often been effectively employed as active Ca^{2+} and Mg^{2+} substitutes in many metalloproteins as chiral NMR shift reagents. MRI contrast agents and also luminescent probes of metal binding in biological systems.¹ Thus keeping the above facts in mind and in continuation of our earlier work with complexation of Schiff bases, we have carried out a solution study on the complexation of

schiff base. It was thought of interest to study the complexes of 2-hydroxy-5-methyl acetophenone-N-(4-methylphenyl) imine with rare earth metal ions La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} and Ho^{3+} using pH metrically in 50% (v/v) ethanol-water mixture.

2. EXPERIMENTAL

2.1 Materials and Solution

All metal salts, NaOH, NaClO_4 , HClO_4 are of AR grade. The solutions used in the pH metric titration were prepared in double distilled CO_2 free water. The NaOH solution was standardized against oxalic acid solution (0.1M) and standard alkali solution was again used for standardization of HClO_4 . The metal salt solutions were also standardized using EDTA titration.² All the measurements were made at temperature 25°C in 50% (v/v) ethanol-water mixture at constant ionic strength of 0.1M NaClO_4 . The water thermostat model SL-131, scientific isothermometer refrigerated circulator accurate to $\pm 0.1^\circ\text{C}$ is used to maintain the temperature constant. The solutions were equilibrated in the thermostat for about 15 minutes before titration. The pH measurement was made using a digital pH meter model Elico L1-120 in conjunction with a glass and reference calomel electrode (reading accuracy ± 0.01 pH units). The instrument was calibrated at pH 4.00, 7.00 and 9.18 using the standard buffer solutions.

2.2 pH metric procedures: For evaluating the protonation constant of the ligand and the formation constant of the complexes in 50% (v/v) ethanol-water mixture with different metal ions the following sets of solutions were prepared (total volume 50 ml) and titrated pH metrically against standard NaOH solution at different temperature 25°C .

- i. Free Acid HClO_4 (A)
- ii. Free Acid HClO_4 + Ligand (Schiff base)(A+L)
- iii. Free Acid HClO_4 + Ligand (Schiff base) + Metal solution (A+L+M)

The above mentioned sets prepared by keeping M: L ratio, the concentration of perchloric acid and sodium perchlorate were kept constant for all sets.

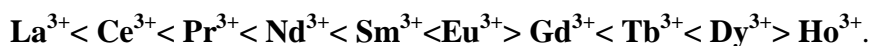
Table 1: Proton-ligand and metal-ligand stability constant of Schiff base with Rare earth metal ions in 50% ethanol-water media at 25°C .

Metal ion	Proton-ligand stability constant	Metal-ligand stability constant			$\log K_1 - \log K_2$	$\log K_1 / \log K_2$
		$\log K_1$	$\log K_2$	$\log \beta$		
La(III)	$\text{pK}_1 = 4.66$ $\text{pK}_2 = 11.25$	7.62	7.00	14.62	0.62	1.088
Ce(III)		7.72	7.10	14.82	0.62	1.087
Pr(III)		8.03	7.15	15.18	0.88	1.123
Nd(III)		8.07	7.30	15.37	0.77	1.105
Sm(III)		8.10	7.38	15.48	0.72	1.097
Eu(III)		8.14	7.55	15.69	0.59	1.078
Gd(III)		7.95	7.23	15.18	0.72	1.099
Tb(III)		8.06	7.41	15.47	0.65	1.087
Dy(III)		8.32	7.87	16.19	0.45	1.057
Ho(III)		8.16	7.76	15.92	0.40	1.051

3. RESULTS AND DISCUSSION

The results obtained are analyzed by the computer programme and the stability constant values are calculated. The proton-ligand stability constant (pK_a) of schiff base 2-hydroxy-5-methyl acetophenone-N-(4-methylphenyl)imine is determined by point wise calculation method as suggested by Irving and Rossoti. Metal ligand stability constant ($\log K$) of lanthanide metal ions with schiff base 2-hydroxy-5-methyl acetophenone-N-(4-methyl phenyl) imine are calculated by point wise and half integral method of Calvin and Bjerrum as adopted by Irving and Rossotti has been employed. The difference between the $\log K_1$ and $\log K_2$ values calculated by point-wise calculation method and half integral method was less than one log unit, indicating simultaneous formation of 1:1 and 1:2 complexes. Therefore least-squares method was used to calculate accurate values. Since we got values of proton-ligand formation number ($\overline{n_A}$) between 0.2 to 0.8 and 1.2 to 1.8 indicating 1:1 and 1:2 complex formations.

The shielding of the 4f electrons is exhibited in the stability constants of the present rare earth metal complexes with schiff base reported in **Table 1** which shows that there is very little difference in these values with the increase in atomic number. In the present complexes the rare earth metal ions bind predominantly to oxygen and weakly to nitrogen in the schiff base. The plot of $\log K$ vs $1/r$ for these complexes shows a regular increase of stability constants from lanthanum to europium with a discontinuity at gadolinium which is commonly known as gadolinium break. After gadolinium, stability constant increases up to dysprosium and then decreases for holmium. Thus showing occasional maxima and minima after gadolinium break. The order of stability constants for these metal complexes found to be:



The gadolinium break which is observed may be related to discontinuity in crystal radii at gadolinium. In all the cases Gd(III) chelates have lower values of stability constant in relation to those of Eu(III) and Tb(III) chelates. As we proceed through the lanthanide series, the nuclear charge and the number of 4f electrons increase by one at each step. The shielding of the 4f electrons by another is quite imperfect owing to the shifts of orbitals, so that at each increase the effective nuclear charge experience by each 4f electron increases. Thus causing a reduction in the size of the entire 4f shell. The lowering in the $\log K$ values in the Gd(III) chelates in relation to the corresponding Eu(III) and Tb(III) chelates may be due to the fact that progressively smaller radii of Gd(III) impose increasingly greater steric hinderance on the ligands on account of metal–ligand interaction. The graphs of $\log k$ vs atomic number, atomic radii, were plotted & found in good agreement with earlier studies. The ratio of $\log k_1 / \log k_2$ is positive & greater than one in all cases .

4. REFERENCES

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