



FORMATION OF RARE EARTH METAL COMPLEXES WITH 2-HYDROXY-5-METHYL ACETOPHENONE-N-(4-ETHOXYPHENYL) IMINE IN ETHANOL-WATER MIXTURE

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ABSTRACT:

The stability constant of schiff base 2-hydroxy-5-methyl acetophenone-N-(4-ethoxy phenyl) imine with trivalent 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 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, rare earth metal ions, Schiff base, pH meter etc.

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-ethoxyphenyl) imine, having molecular formula $\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$

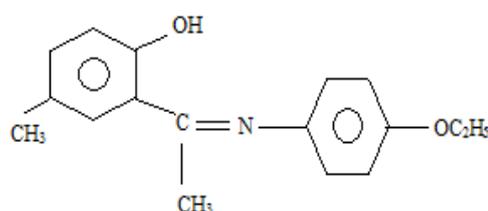


Figure: 2-hydroxy-5-methyl acetophenone-N-(4-ethoxyphenyl) imine

In recent years, there has been an increased interest in the study of the rare earth metal 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-ethoxyphenyl) imine with ten 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 SECTION:

I. Materials and Solution:

All rare earth metal salts, NaOH, NaClO_4 and 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 rare earth 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.

II. 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 .

- Free Acid HClO_4 (A)
- Free Acid HClO_4 + Ligand (schiff base) (A+L)
- Free Acid HClO_4 + Ligand (schiff base) + Metal solution (A+L+M)

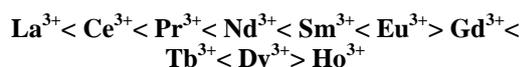
The above mentioned sets prepared by keeping M: L ratio, the concentration of perchloric acid and sodium perchlorate were kept constant for all sets.

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-ethoxyphenyl)imine is determined by point wise calculation method as suggested by Irving and Rossoti. Metal ligand stability constant ($\log K$) of rare earth metal ions with schiff base 2-hydroxy-5-methyl acetophenone-N-(4-ethoxyphenyl) imine are calculated by point wise

and half integral method of Calvin and Bjerrum as adopted by Irving and Rossoti 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, which indicates simultaneous formation of 1:1 and 1:2 complexes. Since we got values of proton-ligand formation number (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.

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	
		$\log K_1$	$\log K_2$ $\log \beta$
La(III)	$pK_1 = 5.00$	7.30	5.68
		12.98	
Ce(III)	$pK_2 = 11.26$	7.54	5.83
		13.37	
Pr(III)		8.13	6.27
		14.40	
Nd(III)		8.24	6.53
		14.77	
Sm(III)		8.28	6.86
		15.14	
Eu(III)		8.34	6.97
		15.31	
Gd(III)		8.08	6.80
		14.88	
Dy(III)		7.89	6.91
		14.80	
Ho(III)		7.94	7.20
		15.14	
		7.78	6.68
		14.46	

4. CONCLUSIONS

The rare earth metal ion forms 1:1 and 1:2 complexes with schiff base 2-hydroxy-5-methyl acetophenone-N-(4-ethoxy phenyl) imine. These complexes show a regular increase of stability constants from La to Eu with a discontinuity at Gd which is commonly known as gadolinium break. After Gd, stability constant increases up to Dy and then decreases for Ho.

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