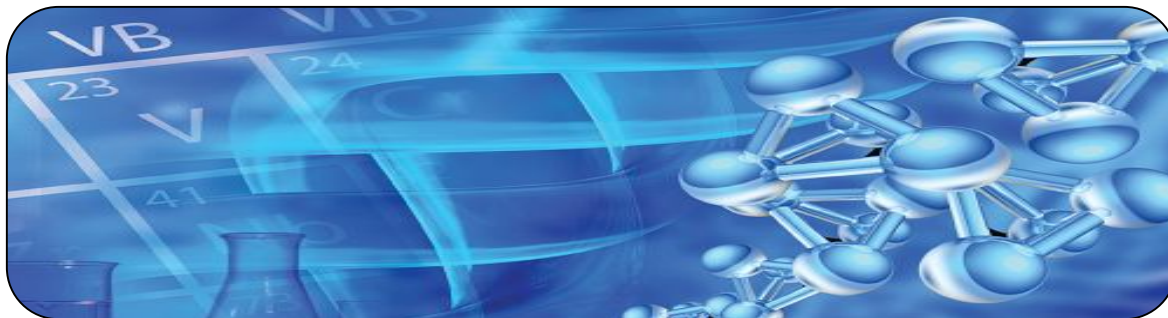




## Review Of Research



### THERMODYNAMIC STUDY OF COMPLEX FORMATION OF RARE EARTH SCHIFF BASE METAL COMPLEXES IN MIXED SOLVENT MEDIA



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#### ABSTRACT

The interaction of rare earth metals ion with (i) *P*-toluidine, (ii) *P*-anisidine, and (iii) *P*-phenetidine has been investigated potentiometrically in 50 % (v/v) ethanol-water medium at 0.1 M NaClO<sub>4</sub> ionic strength. The lanthanides form 1:1 and 1:2 chelates and the trend in log *K* values show a break of gadolinium. The study was carried out at 25, 35 and 45°C to determine thermodynamic parameters of the chelation process. The metal complexes are found to be enthalpy and entropy stabilized.

**KEYWORDS :** analytical reagent, fungicidal and insecticidal activity.

#### INTRODUCTION

The efficiency of Schiff bases as an analytical reagent, fungicidal and insecticidal activity and many other biochemically relevant aspects has been proved. The biological and analytical applications of Schiff bases can be correlated to their structure and substituent groups. In view of the above facts, we have reported the stability constants of transition metal complexes with aryl Schiff bases<sup>1-2</sup>. In continuation of our earlier work we report in this communication the thermodynamic study of chelation of rare earth metal ions with Schiff bases R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> in ethanol-water medium. The temperature effect, substituent effect and the effect of the atomic number of metal ions on the stability constants of the complexes have been discussed.

#### EXPERIMENTAL

The Schiff (R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>) were prepared by the condensation of 5-bromo-2-hydroxy acetophenone, with *p*-toluidine, *p*-anisidine and *p*-phenetidine respectively. The solution of rare earth nitrates (Indian Rare

Earths Limited, Udyogmandal, Kerla) were prepared in doubly distilled water and standardized by the method of Flaschka<sup>3</sup>. All other reagents were of AR grade. The pK and logK values were calculated by the method of Irving and Rossotti at 25, 35 and 45° C by adopting least squares method and were used for the calculation of thermodynamic parameters. The data are listed in Table 1

Complex	LogK <sub>1</sub>	LogK <sub>2</sub>	Logβ	-ΔG <sub>1</sub> -ΔG <sub>2</sub> -ΔH <sub>1</sub> -ΔH <sub>2</sub>				+ΔS <sub>1</sub> +ΔS <sub>2</sub>	
				(KJmol <sup>-1</sup> )				JK <sup>-1</sup> mol <sup>-1</sup>	
La (III) R <sub>1</sub>	7.62	7.00	14.62	43.480	39.943	18.840	14.495	82.687	85.395
La (III) R <sub>2</sub>	8.08	6.90	14.98	46.105	39.372	15.231	13.205	103.605	87.808
La (III) R <sub>3</sub>	7.30	5.68	12.98	41.654	32.410	9.032	8.206	109.472	81.223
Ce (III) R <sub>1</sub>	7.72	7.10	14.82	44.051	40.513	16.023	14.361	94.055	87.760
Ce (III) R <sub>2</sub>	8.22	7.31	15.53	46.904	41.711	17.096	12.818	100.027	96.957
Ce (III) R <sub>3</sub>	7.54	5.83	13.37	43.024	33.266	16.754	12.487	88.153	69.728
Pr (III) R <sub>1</sub>	8.03	7.15	15.18	45.820	40.798	15.044	11.754	103.276	97.464
Pr (III) R <sub>2</sub>	8.40	7.38	15.78	47.931	42.111	13.644	8.776	115.057	111.863
Pr (III) R <sub>3</sub>	8.13	6.27	14.40	46.39	35.777	12.067	13.677	115.180	74.162
Nd (III) R <sub>1</sub>	8.07	7.30	15.37	46.048	41.654	12.880	11.314	111.304	101.812
Nd (III) R <sub>2</sub>	8.46	7.43	15.89	48.274	42.396	17.839	11.979	102.128	102.111
Nd (III) R <sub>3</sub>	8.24	6.53	14.77	47.018	37.261	12.410	13.055	116.134	81.227
Sm (III) R <sub>1</sub>	8.10	7.38	15.48	46.219	42.111	13.240	10.637	110.668	105.6158
Sm (III) R <sub>2</sub>	8.50	7.46	15.96	48.502	42.567	13.644	10.226	116.971	108.527
Sm (III) R <sub>3</sub>	8.28	6.86	15.14	47.246	39.144	13.164	16.412	114.371	76.280
Eu (III) R <sub>1</sub>	8.14	7.55	15.69	46.448	43.081	14.361	9.265	107.674	113.477
Eu (III) R <sub>2</sub>	8.58	7.50	16.08	48.958	42.796	13.791	12.087	118.012	103.050
Eu (III) R <sub>3</sub>	8.34	6.97	15.31	47.589	39.771	14.246	140.19	111.890	86.418
Gd (III) R <sub>1</sub>	7.95	47.23	15.18	45.363	41.255	12.273	13.025	111.043	94.733
Gd (III) R <sub>2</sub>	8.19	7.32	5.51	46.733	41.769	14.272	12.882	108.929	96.936
Gd (III) R <sub>3</sub>	8.08	6.80	14.88	46.105	38.801	14.959	14.506	104.517	81.529
Tb (III) R <sub>1</sub>	8.06	7.41	15.47	45.991	42.282	12.822	9.813	111.307	108.957
Tb (III) R <sub>2</sub>	8.28	7.54	15.82	47.246	43.024	13.791	10.428	112.267	109.381
Tb (III) R <sub>3</sub>	7.89	6.91	14.80	45.021	39.429	19.538	13.055	85.512	88.503
Dy (III) R <sub>1</sub>	8.32	7.87	16.19	47.475	44.907	14.569	14.079	110.423	103.449
Dy (III) R <sub>2</sub>	8.36	7.61	15.97	47.703	43.423	14.069	14.361	112.866	97.526
Dy (III) R <sub>3</sub>	7.94	7.20	15.14	45.306	41.084	18.731	12.937	89.177	94.451
Ho (III) R <sub>1</sub>	8.16	7.76	15.92	46.562	44.279	14.959	8.921	106.051	118.652
Ho (III) R <sub>2</sub>	8.18	7.41	15.59	46.676	42.282	14.480	11.967	108.039	101.728
Ho (III) R <sub>3</sub>	7.78	6.68	14.46	44.393	38.117	14.480	13.677	100.379	82.013

## RESULT AND DISCUSSION

Due to the presence of azomethine nitrogen, protonation takes place in the initial stages of titration. The pK<sub>1</sub> and pK<sub>2</sub> corresponds to the proton association and proton dissociation constant were determined and are given below.

		25°C	35°C	45°C
Ligand R <sub>1</sub>	pK <sub>1</sub>	4.66	4.58	4.41
	pK <sub>2</sub>	11.25	10.96	10.68
Ligand R <sub>2</sub>	pK <sub>1</sub>	4.91	4.43	4.01
	pK <sub>2</sub>	11.27	11.07	10.87
Ligand R <sub>3</sub>	pK <sub>1</sub>	5.0	4.79	4.60
	pK <sub>2</sub>	11.26	11.01	10.77

The pK<sub>1</sub> value of R<sub>1</sub> is lower than that of R<sub>2</sub> and R<sub>3</sub>. The ligand R<sub>1</sub> is having methyl substituent at para position to amine group and the other ligands are having -OCH<sub>3</sub> and -OC<sub>2</sub>H<sub>5</sub> group respectively. This can be explained on the basis of dominating nature of +M effect of -OCH<sub>3</sub>/OC<sub>2</sub>H<sub>5</sub> group over +I effect of -CH<sub>3</sub>. This may be attributed to the fact that methoxy and ethoxy groups increases the electron density on the azomethine nitrogen to the more extent than methyl group resulting in stronger bonding. The metal-ligand titration curve deviates from the acid-dissociation curve in the pH range 5.0 to 6.0, indicating that the complexation takes place in this range. The highest value of n obtained was about 2.0, indicating the formation of 1:1 and 1:2 complexes. The values of logK<sub>1</sub> and logK<sub>2</sub> were determined by the half integral method and least squares method. The stability constants of present rare earth complexes (Table 1) shows a very little difference in their values with the increases in atomic number. This indicates the effect of shielding of 4f electrons in the stability constants of these complexes.

In the present complexation the rare earth metal ions predominantly to oxygen and weakly to nitrogen in the Schiff base<sup>4</sup>. These complexes show a regular increase of stability constants from lanthanum to europium with a discontinuity at gadolinium. After gadolinium, stability constants show occasional increase and decrease in their values. The relationship,  $\log K = a \text{ p}K + b$  was used to understand the effect of substituent groups on the chelating tendencies of ligands by plotting  $\beta$  v/s  $\sum \text{p}K$  values of Schiff bases. It was found that the linear relationship was not obeyed by the ligands<sup>5-7</sup>. The thermodynamic parameters of lanthanide complexes with Schiff bases were obtained from data of logK<sub>1</sub> and logK<sub>2</sub> at different temperatures.

It is seen from table 1 that the logK<sub>1</sub> and logK<sub>2</sub> values decreases with increase in temperature indicating that the high temperature does not favour the formation of stable complexes. The  $\Delta H_1$  and  $\Delta H_2$  values are all negative while  $\Delta S_1$  and  $\Delta S_2$  values are all positive and therefore the resulting  $\Delta G_1$  and  $\Delta G_2$  values are all negative. The more negative values of  $\Delta G_1$  and  $\Delta G_2$  indicate that 1:1 complex formation is energetically favoured. Further, the  $\Delta G$  values show the trend similar to the order of logK values of the complexes. This also confirms the order of stability.

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