



COMPLEXATION OF La(III) METAL ION WITH NOVEL SCHIFF BASES: THERMODYNAMIC STUDY

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ABSTRACT

In the present work we have investigated the stability constant of seven Schiff bases with trivalent rare earth metal ion Lanthanum using a pH metric titration technique in 80% (v/v) ethanol-water mixture at three different temperatures 298K, 308K & 318K at an ionic strength of 0.1M NaClO₄. The Calvin-Bjerrum method as adopted by Irving-Rossotti has been employed to determine metal-ligand stability constant logK values. The thermodynamic parameters such as, Gibb's free energy change (ΔG), entropy change (ΔS) and enthalpy change (ΔH) associated with the complexation reactions were calculated.

Keywords: Rare earth metal ion, Schiff bases, Stability constant, pH metry, Thermodynamic parameter.

1. INTRODUCTION

Metal complexes of Schiff bases play a central role in the development of coordination chemistry. Proton transfer plays an important role in the reactions such as complexation, acid-base catalyzing and enzymatic reaction in aqueous solution. The stability constants of significance in order to predict different chemical processes such as isolation, extraction, or preconcentration. Thus, the accurate determination of acidity and stability constants values are fundamental to understand the behavior of ligands and their interaction with metal ions in aqueous solution. pH metric titration technique is a powerful and simple electro analytical technique for determination of stability constants. There are different kinds of ligands used for complexation. For the present investigation, we have selected a series of seven Schiff bases. Synthesis of all seven Schiff bases was done by reported methods [1-2].

In continuation of our earlier work with complexation of Schiff bases [1, 2] and after a review of literature [3-9], it was a thought of interest to study the effect of temperature on thermodynamic parameters such as Gibb's free energy change ΔG , enthalpy change ΔH and entropy change ΔS of complexes of seven Schiff bases with rare earth metal ion La³⁺ pH metrically in 80% (v/v) ethanol-water mixture.

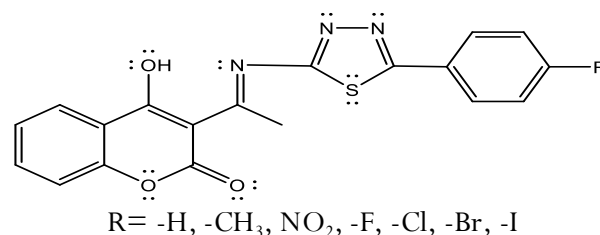


Fig. 1: Schiff base ligand (Molecular formula C₁₉H₁₂O₃N₃SR)

2. EXPERIMENTAL

2.1. Material and solutions

Lanthanum metal salt, NaOH, NaClO₄, HClO₄ used were of AR grade. The solutions used in the pH metric titration were prepared in double distilled CO₂ free water. The NaOH solution was standardized against oxalic acid solution and standard alkali solution was again used for standardization of HClO₄. The measurements were made at temperatures 298K, 308K and 318K in 80% (v/v) ethanol-water mixture at constant ionic strength (0.1M NaClO₄). The thermostat model SL-131 (Adar dutt and Co. India Pvt. Ltd. Mumbai) Narang Scientific Works Pvt. Ltd., New Delhi was used to maintain the temperature constant and the solutions were equilibrated in the thermostat for about 10-15 minutes before titration. The pH measurement was made using a digital Spectralab potentiometric titrator AT 38 C with combined glass electrode

consisting of glass and reference electrodes in the single entity. This digital potentiometric titrator has built in voltage stabilizer for $\pm 10\%$ fluctuations in voltage supply. The instrument has built in temperature compensator having range 0-99°C. The instrument could read pH in the range 0.001-14.000 with an accuracy of 0.0017 pH unit and (0.1mV). Provision of in built three way valves and gas tight burette with Teflon piston with an accuracy of 0.001mL enabled the required precision during the titration particularly near the equivalence point. The instrument was calibrated at pH 9.18, 7.00 and 4.00 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 with La^{3+} metal ion, the following sets of solutions were prepared in 80% (v/v) ethanol-water mixture (total volume 50 ml) and titrated pH metrically against standard NaOH solution at three different temperatures 298K, 308K and 318K.

- i. $\text{HClO}_4(\text{A})$
- ii. $\text{HClO}_4 + \text{Schiff base (A+L)}$
- iii. $\text{HClO}_4 + \text{Schiff base} + \text{Metal (A+L+M)}$

The above mentioned sets were prepared by keeping M:L ratio, the concentration of perchloric acid and sodium perchlorate (0.1M) constant for all sets.

2.3. Determination of the thermodynamic parameters

Thermodynamic parameters such as Gibb's free energy change (ΔG), entropy change (ΔS) and enthalpy change (ΔH) for formation of complexes were determined. The change in Gibb's free energy (ΔG) of the ligands was calculated by using the equation. $\Delta G = -2.303RT \log K$ Where R (ideal gas constant) = $8.314 \text{ JK}^{-1}\text{mol}^{-1}$, K is the dissociation constant for the ligand or the stability constant of the complex and T is absolute temperature in Kelvin.

The change in enthalpy (ΔH) is calculated by plotting $\log K$ vs $1/T$

The equation utilized for the calculation of changes in enthalpy is as Slope = $-(\Delta H/2.303R)$

The evaluation of changes in entropy (ΔS) is done by the equation: $\Delta S = (\Delta H - \Delta G)/T$

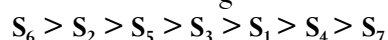
3. RESULTS AND DISCUSSION

The results obtained are analyzed by computer programme and stability constant values were calculated. The proton-ligand stability constant was determined by point wise calculation method as suggested by Irving and Rossoti. The proton ligand stability constant pK_a of all seven Schiff bases were determined in aqueous medium at three different temperatures 298K, 308K, 318K at 0.1M NaClO_4 ionic strength. The proton-ligand stability constants of all the Schiff bases are presented in table 1.

Table 1: Proton-ligand stability constant of Schiff bases

Temperature	Proton-ligand stability constant	Schiff bases						
		S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇
298K	pK ₁	3.2234	3.3961	3.0385	2.9744	3.6355	3.4792	--
	pK ₂	4.4968	5.1755	4.7142	3.6138	4.8790	5.3457	4.0972
308K	pK ₁	3.0782	3.2750	2.9374	2.8893	3.4614	3.3438	--
	pK ₂	4.3749	5.0532	4.5991	3.487	4.7013	5.1946	3.9860
318K	pK ₁	2.9303	3.1228	2.826	2.8061	3.3052	3.1451	--
	pK ₂	4.2027	4.8810	4.4339	3.3352	4.5062	5.0035	3.8637

The Schiff base S₇ has only one pK value where as S₁, S₂, S₃, S₄, S₅, and S₆ have two pK values. The ___ value ranges between 0.2 to 1.8 indicates the presence of two pK values whereas the range of ___ is in between 0.2 to 0.8 shows only one pK value. In the present investigation Schiff base selected contains hydroxyl group and azomethine nitrogen as bonding sites. The order of pKa values of seven ligands is as:



The above order indicates that S₇ has lowest basicity whereas S₆ has highest basicity Metal ligand stability constant $\log K$ of La (III) metal ion with Schiff bases are calculated by point wise and half integral method of Calvin-Bjerrum as adopted by Irving-Rossotti. The $\log K_1$ values calculated by point wise calculation method and half integral method, indicates simultaneous formation of 1:1 complex. We got values of proton-ligand formation number (___) between 0.2 to 0.8 and

1.2 to 1.8 indicating 1:1 and 1:2 complex formations. The proton-ligand stability constant pKa values decrease with increase in temperature i.e. the acidity of the ligands increases [10], which suggests that the liberation of proton becomes easier at higher temperature. Order of stability constants for La(III) complexes with Schiff bases (Table 2) found to be as follows:

$$S_6 > S_5 > S_3 > S_2 > S_1 > S_7 > S_4$$

The metal-ligand stability of bromo (Br) substituted Schiff base was found higher, while fluoro (F) substituted Schiff base lower $\{S_6 > S_5 > S_7 > S_4\}$ and the metal-ligand stability of nitro substituted Schiff base was found higher, while unsubstituted Schiff base lower. $\{S_3 > S_2 > S_1\}$

The negative ΔG values indicates that both dissociation of the ligand and the complexation process are spontaneous [10]. A decrease in metal-ligand stability constant $\log K$ with an increase in temperature and the negative values of enthalpy change ΔH for the complexation suggests that all the complexation

reactions are exothermic, favorable at lower temperature and the metal-ligand binding process is enthalpy driven [9] and metal-ligand bonds are fairly strong.

The positive entropy changes ΔS accompanying a given reaction are due to the release of bound water molecules from the metal chelates. The positive value of ΔS is considered to be the principal driving force for the formation of respective complex species. According to Martell-Calvin positive entropy effects was predicted towards an increase in the number of particles after the reaction and positive ΔS is responsible to give more negative ΔG . The positive values of ΔS in some cases indicate that the entropy effect is predominant over enthalpy effect. The positive ΔS values for metal complexes indicated that the formation of these complexes was entropy favored, while negative ΔS values (Table 3-5) for metal complexes suggesting a highly solvated metal complexes [10].

Table 2: La(III) Metal-ligand stability constant of Schiff bases

Temperature	298K			308K			318K		
La(III)-ligand stability constant \rightarrow Schiff Bases \downarrow	$\log K_1$	$\log K_2$	$\log \beta$	$\log K_1$	$\log K_2$	$\log \beta$	$\log K_1$	$\log K_2$	$\log \beta$
S_1	3.1622	2.9494	6.1116	3.1101	2.8978	6.0079	3.0589	2.8442	5.9031
S_2	3.5957	3.2905	6.8862	3.4532	3.1736	6.6268	3.3036	3.0684	6.3720
S_3	3.6670	3.2802	6.9472	3.5549	3.1845	6.7394	3.4602	3.0854	6.5456
S_4	2.9809	2.7094	5.6903	2.9061	2.6782	5.5843	2.8365	2.6482	5.4847
S_5	4.3008	3.6152	7.9160	4.1066	3.4794	7.5860	3.9202	3.3556	7.2758
S_6	4.7764	4.6792	9.4556	4.5564	4.4869	9.0433	4.3461	4.2880	8.6341
S_7	3.1319	2.9548	6.0867	3.0529	2.9012	5.9541	2.9842	2.8525	5.8367

Table 3: Thermodynamic parameters of Schiff base complex formation with La(III) at 298K

Schiff Bases	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
	$(KJmol^{-1})$		$(KJmol^{-1})$		$(JK^{-1}mol^{-1}) \cdot 10^3$	
S_1	18.043	16.829	9.371	9.541	0.0291	0.0245
S_2	20.517	18.775	26.490	20.159	-0.0200	-0.0046
S_3	20.923	18.716	18.777	17.667	0.0072	0.0035
S_4	17.009	15.459	13.104	5.553	0.0131	0.0332
S_5	24.540	20.628	34.533	23.561	-0.0335	-0.0098
S_6	27.253	26.699	39.043	35.480	-0.0396	-0.0295
S_7	17.870	16.860	13.408	9.285	0.0150	0.0254

Table 4: Thermodynamic parameters of Schiff base complex formation with La(III) at 308K

Schiff Bases	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
	$(KJmol^{-1})$		$(KJmol^{-1})$		$(JK^{-1}mol^{-1}) \cdot 10^3$	
S ₁	18.341	17.089	9.371	9.541	0.0291	0.0245
S ₂	20.365	18.716	26.490	20.159	-0.0199	-0.0047
S ₃	20.284	18.170	18.777	17.667	0.0051	0.0017
S ₄	16.582	15.281	13.104	5.553	0.0117	0.0326
S ₅	23.432	19.853	34.533	23.561	-0.0373	-0.0124
S ₆	25.998	25.602	39.043	35.480	-0.0438	-0.0331
S ₇	17.419	16.554	13.408	9.285	0.0135	0.0244

Table 5: Thermodynamic parameters of Schiff base complex formation with La(III) at 318K

Schiff Bases	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
	$(KJmol^{-1})$		$(KJmol^{-1})$		$(JK^{-1}mol^{-1}) \cdot 10^3$	
S ₁	18.625	17.318	9.371	9.541	0.0291	0.0245
S ₂	20.115	18.683	26.490	20.159	-0.0200	-0.0046
S ₃	19.743	17.605	18.777	17.667	0.0032	-0.0002
S ₄	16.185	15.110	13.104	5.553	0.0103	0.0321
S ₅	22.368	19.147	34.533	23.561	-0.0408	-0.0148
S ₆	24.798	24.467	39.043	35.480	-0.0478	-0.0370
S ₇	17.027	16.276	13.408	9.285	0.0121	0.0235

4. CONCLUSIONS

La(III) metal ion forms 1:1 and 1:2 complexes with all Schiff Bases. The metal-ligand stability constant $\log K$ decreases with an increase in temperature. The negative values of change in enthalpy ΔH for the complexation suggest that all the complexation reactions are exothermic, favorable at lower temperature. The negative change in free energy ΔG values indicates that both dissociation of the ligand and the complexation process are spontaneous. The positive ΔS values for some metal complexes indicated that the formation of these complexes was entropy favored, while negative ΔS values indicated a highly solvated metal complex.

5. ACKNOWLEDGEMENT

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Conflict of interest

None declared

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