



## Studies on Variation In Electronic – Spectral Parameters of Sm (III) Ion in Different Ligand Environment

Sudhir N. Limaye\* and Sneha Wanakr

\*Department of Chemistry, Dr.H.S.Gour Central University, Sagar 470003, **INDIA**

Email: [snehawanker21@yahoo.com](mailto:snehawanker21@yahoo.com), [snl222@yahoo.co.in](mailto:snl222@yahoo.co.in)

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### ABSTRACT

Studies on electronic spectral behavior of Sm (III) in different ligand environments at controlled pH medium in aqueous media have been carried out with a function to observe the influence of different ligand environments on the spectral parameters viz., oscillator strengths and the radioactive parameters of Sm(III). The experimental data have been evaluated using Judd's relation. In all cases it has been found that the oscillator strength values increases near about pH ~3-4 at which complexation occurs. The metal ligand interaction were obtained from  $\Omega_\lambda$  parameters where ( $\lambda=2,4,6$ ). The  $\tau_R$  values of complexes [Sm:L-Isoleucine], [Sm:L-Histidine], [Sm:Glycylglycine] at different pH showed better correlation with respect to their partial charge on -O atom.

**Keywords:** Oscillator strength, Judd-Ofelt parameters.

### INTRODUCTION

The coordination chemistry of the lanthanides is of great interest due to their unique electronic properties with very little structural changes. These properties create possibilities of designing new compounds with associated structural modification. Much attention is being paid on their magnetic, optical and electronic properties of these elements[1]. Simultaneously, lanthanide ions have comparable ionic radii with biologically significant metal ions like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions generate exploration possibilities for studying their interaction with biologically significant ligands. These studies lend lanthanides a status of structure probes. Simultaneously, radioactive  $\text{Sm}^{153}$  has also been used in medical field for radiotherapy[2]. Julia Torres *et al.* reported the preparation of new Sm(III)-complexes with glutamic acid[3]. Spectroscopic studies on various Ln(III) ion are carried out with different amino acids in solid state by Yue-tao Yang *et al.* [4]. Some solution studies on rare earth complexes of drug and related amino acid has been carried out from our laboratory.

As regards to their complexing behavior of amino acids, these ligands exhibit better complex formation with transition ( $3d^-$ ) metals than lanthanide ( $4f^-$ ), because of hard acid character of later elements[5-9a]. Studies on molecular structure, photo physical and thermal properties of Sm(III) with some organic ligand has been reported in literature [10]. At the same time it has been found that Ln(III) other than Sm(III) have also showed their behavior with biologically active compounds.[20].

The present work aims at evaluating and comparing the electronic spectral parameters for Sm(III) viz, Oscillator strengths, Judd-Ofelt parameters and radioactive parameter in different ligand environment such as L-Alanine, L-Isoleucine, L-Histidine, Glycylglycine, L-Arginine, which possess potential biological application. Evaluation of parameters has been made by using Judd-Ofelt theory. This theory define that the susceptibility of the  $4f$ -orbital and their electronic interaction in different environment are governed by set of three intensity parameters  $\Omega_\lambda$  ( $\lambda = 2, 4, 6$ ) (Tensor Operators) indicative of direct Ln-ligand interaction, changes in symmetry and the nature of the environment around  $4f$ -Ln(III) ion [11,12].

The Judd-Ofelt intensity parameters[13] are capable to provide information about partial covalence of the chemical bond, changes in the symmetry around lanthanide ion (long range effects:  $\Omega_4$ , rigidity of system:  $\Omega_6$ ) and the concomitant reflections in radiative parameters as direct evidence for the  $4f$ -involvement in bonding.

**Theory of Ln(III) electronic spectra:** In case of  $4f$ - $4f$  transition in lanthanides arises from mutual interaction of electric- and magnetic- dipoles. But in case of free  $4f$ -ion the electric dipole transitions are *parity forbidden* while magnetic dipole and quadrupolar transitions are allowed[14]. The transition probability that depends on the type of matrix developed around metal ion with change of environments. Since the oscillator strengths are the sole parameters to examine these changes, a systematic analysis of changes in these parameters under the influence of different ligand, may help to reveal the  $4f$ -behavior. This is the basis of the objectives of the present studies.

The oscillator strength, ( $f_{exp}$ ) a parameter informative of intensity and susceptibility of specific electronic transitions may be calculated using the following relation:

$$f_{exp} = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu \quad (1)$$

where,  $\epsilon$  is the molar extinction coefficient which corresponds to energy ( $\text{cm}^{-1}$ ).

$$f_{cal} = \left[ \frac{8\pi^2 m c \nu}{3h(2J+1)} \right] \times \left[ \frac{(n^2+2)^2}{9n} \right] \sum_{\lambda=2,4,6} \Omega_\lambda (\psi_J \| U^\lambda \| \psi'_{J'})^2 \quad (2)$$

Where, the transparency of the medium observed by  $n$  is Refractive index,  $m$  is mass of electron,  $\nu$  is frequency of transition,  $h$  is Plank's constant.

The expression for Judd-Ofelt is complex one but it correlate the radial wave function of the state, refractive index of the medium and field parameter of particular environment[15].

$$\Omega_t = [2t+1 \sum |A_{s,p}|^2 \mathcal{E}^2(s,t)(2s+1)^{-1}] \quad (3)$$

Where,  $|A_{s,p}|^2$  and  $\mathcal{E}^2(s,t)$  represented the crystal field parameters and consequential nephelauxetic effect ( $4f$ -cloud expansion)  $\beta$  respectively.  $\mathcal{E}$  is proportional to  $\beta$  which indicates the bonding pattern of Ln(III)-O bond [16]. The value  $\Omega_\lambda$  is obtained from squared matrix (Tensor). The values for  $U^\lambda$  ( $\lambda = 2, 4, 6$ ) were calculated by Carnell *et al.* [17].

The electrical and magnetic dipole of the transition susceptibility is further evaluated in terms of spontaneous emission probability,  $A_{Rad}$ , from an initial state  $aJ \rightarrow bJ'$  for a particular electric dipole transition given by,

$$A_{Rad} = 64\pi^4 \nu^3 n (n^2+2)^2 e^2 / 27hc^2 (2J+1) \left[ \sum_{t=2,4,6} \Omega_t | \langle aJ | U^t | bJ' \rangle |^2 \right] \quad (4)$$

Total probability,  $A_T$ , obtained by carrying out the summation of all the transitions to the final states,  ${}_b J^0$ , is given by

$$A_T = \sum A_{Rad} \quad (5)$$

The values of  $A_{rad}$  and  $A_T$  can be used to calculate the fluorescence branching ratio  $\beta_r$  given by

$$\beta_r = \frac{A_{Rad}}{A_T} \quad (6)$$

The radiative lifetime of the excited states is represented by

$$\tau_R = \frac{1}{A_T} \quad (7)$$

## MATERIALS AND METHODS

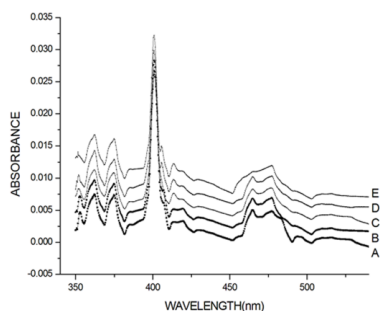
The stock solution were prepared using  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  from CDH and standardized. Rest all chemicals used were of AR grade, procured commercially and used without further purification viz., NaOH,  $\text{NaClO}_4$ ,  $\text{HClO}_4$  and amino acids. The sets were prepared using 5mL of 0.5M of  $\text{HClO}_4$  and 5mL of 0.5M amino (ligand) acid and 5mL of 0.5 M  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  making the total volume of 50mL. The pH of the sets were maintained on Orion 900 (CH-150) pH meter,  $\text{pH} \pm 0.001$  using aqueous HCl or NaOH and the absorbance of the sets have been recorded at pH range of 3 to 5. The absorption spectra were recorded by using Spectrophotometer Systronic 2201 in  $\lambda$  range of 350nm-550nm. The obtained spectra were used to compare the absorption of the particular transition at different pH. All the electronic and spectral parameters mentioned above were calculated using the spectra. The oscillator strength for all allowed transitions at each pH values has been calculated. Evaluated oscillator strengths have been further used to determine the  $T_\lambda$  and  $\Omega_\lambda$  value using

$$f = \Omega_2 \|U^2\| + \Omega_4 \|U^4\| + \Omega_6 \|U^6\|$$

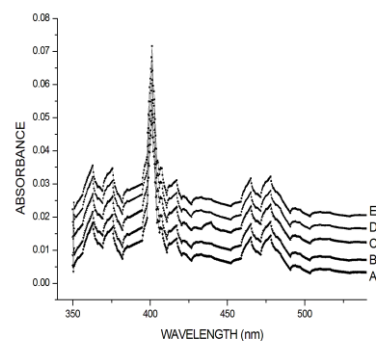
self-devised PASCAL compiled programme. Tensor operator values ( $U^\lambda$ ) for each value  $\lambda$  and for each spectral assignment for Sm(III) have been recorded from standard references [18].

## RESULTS AND DISCUSSION

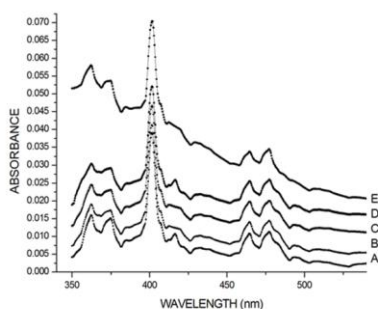
A perusal of the oscillator strength values (Table 1) exhibit a dependence on pH of the medium as well as the changed ligand environments. This is indicative of the susceptibility of specific electronic transitions even towards minor changes in  $4f$ -environment. The present studies have been performed at controlled pH in different ligand environments in order to examine the influence of complexation on the electronic spectral parameters *vis-à-vis* electronic environment. Figure 1-5 exhibits the variation in the oscillator strengths with pH of the solutions. Almost all the ligands exhibit a maxima around pH 3-4 which suggests that the oscillator strength values depend upon the degree of complexation. For brevity assignment corresponding to  $24500\text{-}25200 \text{ cm}^{-1}$  have been utilized for the graphical demonstration, however, almost all the assignments exhibited almost similar pattern. This pH of observance corresponds with the Irving – Rosotti titrimetric studies performed earlier from our laboratories[19].



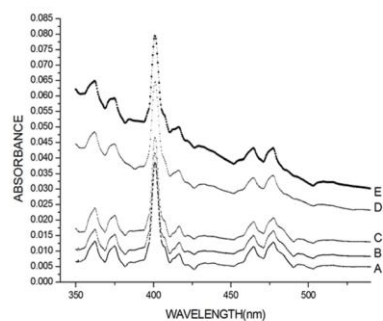
**Fig.1** Representing absorption spectra [Sm(III)-L-Alanine] at different pH A,B,C,D,E at 3,3.5,4,4.5,5 respectively.



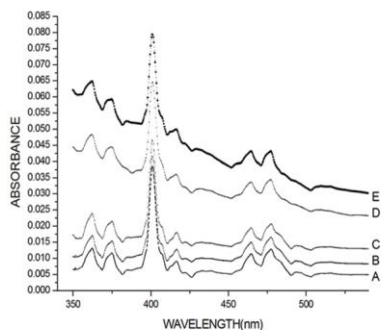
**Fig.2** Reporting absorption spectra [Sm(III)-L-Isoleucine] at different pH A,B,C,D,E at 3,3.5,4,4.5,5 respectively



**Fig.3** Representing the absorption spectrum [Sm(III)-L-Histidine] at different pH A,B,C,D,E at 3,3.5,4,4.5,5 respectively.



**Fig.4** Representing absorption spectra [Sm(III)-L-Glycylglycine] at different pH A,B,C,D,E at 3,3.5,4,4.5,5 respectively.



**Fig.5** Representing absorption spectra [Sm(III)-L-Arginine] at different pH A,B,C,D,E at 3,3.5,4,4.5,5 respectively.

The highest values for oscillator strength for [Sm:Arginine] as compared to [Sm:Alanine] and [Sm:Histidine] may attribute to the complexing tendencies of the ligands. A variation in the oscillator strengths with respect to ligand environments in the present case, exhibit their dependence on the ligand basicity. This varied response in the susceptibility of specific electronic transitions towards changed cation environment, clearly indicate a positive response of 4*f*-orbitals towards its environment. The 4*f* orbitals in lanthanides are, however, deeply seated and effective screening and high shielding make these orbitals less available for direct metal ligand interaction leading to sharp, fine peaks. This may attribute to weak influence of ligand field on the 4*f* electron. Thus the ligand may only influence the inter-configurational transitions of the rare earth ions in terms of magnitude and ratio of transition intensities. These may get reflected into the symmetry parameters in varied environment of ligands.

**Table 1.** Oscillator Strength values for some transition from ground state level  ${}^6H_{5/2}$  ( $P \times 10^{-6}$ )

COMPLEXES	E ( $\text{cm}^{-1}$ )	Assig- nment	pH 3		pH 3.5		pH 4		pH 4.5		pH 5	
			$P_{cal}$	$P_{exp}$	$P_{cal}$	$P_{exp}$	$P_{cal}$	$P_{exp}$	$P_{cal}$	$P_{exp}$	$P_{cal}$	$P_{exp}$
[Sm(III):Alanine]	24999	${}^4F_{7/2}$	5.20	4.65	5.22	4.54	4.32	4.08	3.34	2.15	4.44	2.34
[Sm(III):Isoleucin]	24999	${}^4F_{7/2}$	9.41	7.48	7.70	5.47	5.60	5.34	9.13	7.50	5.15	5.10
[Sm(III):Histidine]	24999	${}^4F_{7/2}$	0.95	1.36	7.97	6.07	6.63	6.96	6.79	5.85	3.23	1.40
[Sm(III):Glycylglycine]	24999	${}^4F_{7/2}$	8.41	8.17	5.85	5.32	1.04	0.70	8.05	7.98	4.16	3.95
[Sm(III):Arginine]	24999	${}^4F_{7/2}$	3.76	3.52	4.04	3.92	1.63	3.50	1.84	3.35	2.38	2.76

The oscillator strength values are composed of three components expressed in terms of Judd Ofelt parameters. The three parameters are indicative of the physical interaction in the metal and the ligand donor atoms, the transparency of the medium and the symmetry changes associated with complexation. The magnitude of the three components is expressed in terms of Tensor operators  $\Omega_\lambda$  [18]. Evaluated values for the three parameters for present set of ligand environments are recorded in table 2. According to Judd- Ofelt theory the  $\Omega_2$  are expected to be smaller than  $\Omega_6$ , however, the observed trend is reverse for the present set of ligands. This may attribute to increase in the covalent nature of Sm(III) and O bond. As a result of covalency asymmetric dipole generate around the Sm(III) ion, the Sm(III) ion is get more interacted with -O atom and results in higher values  $\Omega_2$ . The larger value obtained for  $\Omega_2$  in case of Sm-Arginine, may be on account of larger size of the L-Arginine molecule.

**Table 2.** Judd-Ofelt intensity parameters  $\Omega_\lambda$  (10-20cm<sup>2</sup>) where  $\lambda=2,4$  and 6

COMPLEXES	ENERGY ( $\text{cm}^{-1}$ )	$\Omega_\lambda$	pH 3	pH 3.5	pH 4	pH 4.5	pH 5
		$\Omega_4$	1.51	0.15	1.23	1.02	1.39
		$\Omega_6$	3.49	0.18	3.12	1.10	1.01
[Sm(III):Isoleucine]	24999	$\Omega_2$	5.74	2.88	3.07	2.08	1.90
		$\Omega_4$	2.68	2.25	1.69	3.05	1.63
		$\Omega_6$	3.75	0.74	3.48	4.19	1.01
[Sm(III):Histidine]	24999	$\Omega_2$	2.54	3.29	8.54	1.58	6.3
		$\Omega_4$	2.20	2.23	7.31	1.79	0.90
		$\Omega_6$	0.46	1.54	4.27	0.95	1.70
[Sm(III):Glycylglycine]	24999	$\Omega_2$	7.01	3.02	2.66	9.85	2.71
		$\Omega_4$	1.39	1.58	2.55	2.44	2.37
		$\Omega_6$	1.01	0.96	3.41	2.64	2.99
[Sm(III):Arginine]	24999	$\Omega_2$	6.34	17.4	35.5	0.28	6.95
		$\Omega_4$	1.14	1.25	2.89	3.63	1.52
		$\Omega_6$	0.95	0.96	1.27	1.43	1.72

Table 3 records the variation in the transition probability, branching ratios and the relaxation timings for the prominent transition. There is no particular trend obtained for  $T_R$  values, all the complexes have shown their highest values at different pH range.

**Table 3.** Variation in the Transition Probabilities, Branching ratio and Relaxation timings  $A_T$ ,  $\beta_R$ ,  $\tau_R$  respectively, for Sm(III) in different ligand environments at varied pH ranges.

[Sm(III):L.]	ENERGY ( $\text{cm}^{-1}$ )	pH 3			pH 3.5			pH 4			pH 4.5			pH 5					
		$A_T$ ( $\text{s}^{-1}$ )	$\beta_R$ (%)	$\tau_R$ (ms)	$A_T$ ( $\text{s}^{-1}$ )	$\beta_R$ (%)	$\tau_R$ (ms)	$A_T$ ( $\text{s}^{-1}$ )	$\beta_R$ (%)	$\tau_R$ (ms)	$A_T$ ( $\text{s}^{-1}$ )	$\beta_R$ (%)	$\tau_R$ (ms)	$A_T$ ( $\text{s}^{-1}$ )	$\beta_R$ (%)	$\tau_R$ (ms)			
[Sm(III):Ala]	24999	1.4426	0.2854	0.6930	0.1440	0.2846	0.6913	1.225	0.2843	0.8162	0.8950	0.2755	0.4548	0.3127	0.2929	1.1172	0.3213	0.2464	0.8484
[Sm(III):Isoleu]	24999	2.6253	0.0540	0.3808	2.5964	0.2127	0.3851	1.3960	0.2813	0.7163	2.3625	0.3302	0.4686	0.3519	0.1542	0.4232	1.1178	0.2622	0.8263
[Sm(III):His]	24999	2.4480	0.219	0.4080	2.8610	0.2775	0.3490	8.3862	0.2362	0.119	1.820	0.2375	0.4686	0.2690	0.0033	0.5492	1.0378	0.0884	0.3977
[Sm(III):Glycylgly]	24999	1.2619	0.2129	0.7924	2.2804	0.1347	0.4385	3.0713	0.2813	0.119	2.2447	0.2265	0.4686	0.2690	0.0027	0.5492	1.0378	0.2819	0.5079
[Sm(III):Arg]	24999	1.0800	0.2538	0.9250	0.9670	0.2129	1.0330	2.074	0.2375	0.119	2.412	0.2265	0.4686	0.2690	0.0027	0.5492	1.0378	0.2819	0.8351
			0.1293			1.1591			0.1654				0.1738					0.2519	
			0.4219			0.4645			0.4146				0.2416					0.3378	
			0.1948			0.1633			0.1823				0.3580					0.0879	
			0.3001			0.1895			0.2265				0.2416					0.3378	
			0.2301			0.1342			0.2416				0.3580					0.0879	
			0.2394			0.5307			0.3580				0.3580					0.0879	
			0.2303			0.1454			0.1738				0.2416					0.3378	
			0.2897			0.3532			0.3790				0.2416					0.3378	
			0.2365			0.2783			0.2368				0.2416					0.3378	
			0.2515			0.0974			0.0933				0.2416					0.3378	
			0.2223			0.2710			0.2908				0.2416					0.3378	

It is observed that the sequence for the relaxation timings approximately follow the sequence L-Isoleucine < L-Histidine < L-Arginine < Glycylglycine < L-Alanine. Deviations in these case may be on account of some cooperative structural modifications which might influence the relaxation timings of these ligands. This certify i.that the 4f orbitals preserve their core like behavior even in complex ligand environment, besides ii. their increased partial covalency with increased complexing behavior of the ligands.

Table 4.  $T_R$  values at different pH

Complex	pH3	pH3.5	pH4	pH4.5	pH5
[Sm(III)-LAlanine]	0.693	0.6913	0.8162	<b>1.1172</b>	0.8484
[Sm(III)-L-Isoleucine]	0.3808	0.3851	<b>0.7163</b>	0.5492	0.3977
[Sm(III)-L-Histidine]	0.4080	0.3490	0.1190	0.4232	<b>0.8263</b>
[Sm(III)-Glycylglycine]	0.9250	<b>1.0330</b>	0.3255	0.4454	0.5079
[Sm(III)-L-Arginine]	0.7924	0.4385	0.4820	0.4145	<b>0.8351</b>

## APPLICATIONS

These results provide the better knowledge of complexing behavior of amino acid with Ln(III). The Sm(III) shows its bonding nature with various amino acids, therefore it is required to study the behavior these lanthanides in biological environment.

## CONCLUSIONS

Due to the presence of comparable ionic radii of Sm(III) with  $\text{Ca}^{2+}$ , which is found to be spectroscopically silent are biologically active in nature. This element shows its bonding nature with various amino acids, therefore it is required to study the behavior these elements in biological environment. The attempt is put forward to carry out the pH dependence study of lanthanide complexes with amino acid. This provides the better knowledge of complexing behavior of amino acid with Ln(III).

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