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Effect of Medium on Hypersensitive Transition and Calculation of Judd-oflet Intensity Parameters to Explore the Interaction between Sm(III)- Imidazole Derivative in Different Environment

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ABSTRACT

Thermodynamic parameters in micellar and alcoholic medium has been computed for Sm(III)- Imidazole systems. Various energies and intensities parameters for all the transitions were calculated using Judd-Ofelt relation which are perfectly matches with observed value. Eight bands $^6H_{5/2} \rightarrow H_{9/2}$, $^6H_{5/2} \rightarrow {}^4D_{3/2}$, $^6H_{5/2} \rightarrow {}^6P_{3/2}$, $^6H_{5/2} \rightarrow {}^4I_{15/2}$, $^6H_{5/2} \rightarrow {}^4I_{13/2}$, $^6H_{5/2} \rightarrow {}^4M_{15/2}$, $^6H_{5/2} \rightarrow {}^4G_{7/2}$, $^6H_{5/2} \rightarrow {}^4G_{5/2}$ in the case of Sm(III) have been observed in the region 300 nm to 600 nm. By applying the Judd-Ofelt theory a good correlation has been established between the experimental and calculated data.

Key words: Imidazole Derivative, Sm(III)ion, Judd Oflet parameters

INTRODUCTION

Certain absorption band due to f-f transitions of lanthanide is particularly susceptible to intensity change and splitting. These are termed as hypersensitive transitions. The intensity of some absorption line in the solution spectra of rare earth ions is sensitive to the solvent. Generally the intensity of hypersensitive transitions is directly proportional to the basic nature of the ligand as well as the number of coordinating ligand and inversely proportional to the Metal-Ligand bond distance.

An extensive study about Hyper sensitive transitions has been made by Karraker [1-2] particularly for Nd (III), Ho (III) and Er (III) complexes of β-diketone having 6, 7 and 8 coordination number.

The Hypersensitive or Pseudo-quadorpolar transitions obey the selection rule I ΔJ I ≤ 2. The term Hypersensitive refer to the transitions which show a relatively large variability in the magnitude of oscillator strength caused by the Eigen perturbation [3-6]. In our case hypersensitive transitions for Sm (III) 6H5/2 →4D3/2, the Hyper sensitive transitions show a significant Red shift. The higher values of P and Tλ (λ=2,4,6) parameters of M-L system in comparison to Sm (III) aqueous solutions show an involvement of 4f-orbital of Sm (III) ion. In the past year change in magnitude of oscillator strength of Hyper sensitive transition were successfully used to determine the stability constant as a function of ligand constration.

EXPERIMENT

The saturated solution of ligand and metal Sm (III) ion 0.05 M were prepared in different solvents (Triton X-100 of 100 CMC (1.8 x 10^{-2} M, Sodium Dodecyl sulphate, (SDS) of 75 CMC (0.05 M), and Hexadecyl Trimethyl Ammonium Bromide, (HTAB) of 100 CMC (9.2 x 10^{-2} M) is used for preparing saturated solution of ligand and metal.

Absorption spectra of each solution at room temperature in 1:3 ratio (Metal: Ligand) were recorded on UV Visible Double Beam Spectrophotometer (UV-5704-SS) in the region 400 nm to 900 nm at Green chemistry research center (GCRC).

CALCULATION

1.0 Oscillator strength:

The oscillator strength can be expressed as

$P = 4.315 \times 10^{-9} \int \varepsilon \, d\nu$ ---------- (1)

The equation may be expressed in terms half band width

$Pobs \approx 4.6 \times 10^{-9} \times \varepsilon_{max} \, \nu^{1/2}$ ---------- (2)

$P_{cal} = T_2\nu[U^{(2)}]^2 + T_4\nu[U^{(4)}]^2 + T_6\nu[U^{(6)}]^2$----------(3)

2.0 Judd-ofelt perameter

$T_2 = C_{11}\sum x_1 y + C_{12}\sum x_2 y + C_{13}\sum x_3 y$---------- (4)

$T_4 = C_{12}\sum x_1 y + C_{22}\sum x_2 y + C_{23}\sum x_3 y$---------- (5)

$T_6 = C_{13}\sum x_1 y + C_{23}\sum x_2 y + C_{33}\sum x_3 y$---------- (6)

RESULTS AND DISCUSSION

The various energy, intensity, bonding, symmetry and coordination parameters have been calculated by using the equations as described in the literature. In order to simplify the tedious and cumbersome calculations based on partial and multiple regressions, Microsoft Excel 2010 has been used. The values of the various spectroscopic parameters for the complexes under study have been reported in table I, II and III. Eight bands $^6H_{5/2} \rightarrow H_{9/2}$, $^6H_{5/2} \rightarrow {}^4D_{3/2}$, $^6H_{5/2} \rightarrow {}^6P_{3/2}$, $^6H_{5/2} \rightarrow {}^4I_{15/2}$, $^6H_{5/2} \rightarrow {}^4I_{13/2}$, $^6H_{5/2} \rightarrow {}^4M_{15/2}$, $^6H_{5/2} \rightarrow {}^4G_{7/2}$, $^6H_{5/2} \rightarrow {}^4G_{5/2}$ in case of of Sm (III) systems [7-9] Samarium (III) with imidazole derivatives (i.e. 2- methylimidazole and 4-methylimidazole) have been observed in the region 300 nm to 600 nm. In computing the values of oscillator strength, the value of half band width has been determined by resolving the observed bands into Gaussian shape curve, this has provided better investigations of different parameters. These parameters include the Oscillator strength and Judd- Ofelt parameters these are as follows: The values of the oscillator strength (P) for Sm (III) systems have order of 10^{-6} which shows the transitions are forbidden ones. The intensity of the hypersensitive transition, $^6H_{5/2} \rightarrow {}^4D_{3/2}$ in the Sm (III) systems depends much on the ligand. The higher value of oscillator strength (P) shows lower symmetry in complexes [10].The spectral intensities of observed bands have been reported in terms of T_2, T_4 and T_6 parameters [11-12]. Henrie D E and Choppin G R [5-6] have theoretically shown that among T_2, T_4 and T_6 parameters, T_2 is most sensitive to the environment [15-21].The higher values of P and T_λ parameters of salt solutions in comparison to Sm (III) aqueous solutions show an involvement of 4f-orbital of Sm (III) ion. Also these parameters show more increased values in case of more soluble salts [13-14]

Table -1 Observed and calculated values of Oscillator strength (Px10-6) of various Absorption Transitions of Sm(III)- 2-Methylimidazole (2MI) Complex in alcoholic (C2H5OH) and Micellar medium (Triton X-100, SDS and HTAB)

COMPLEX		Sm(III)-2MI (Et-OH)		Sm(III)-2MI (TX-100)		Sm(III)-2MI) (SDS)		Sm(III)-2MI (HTAB)	
S.N.	**Energy levels**	**$PobsX10^{-6}$**	**$PcalX10^{-6}$**	**$PobsX10^{-6}$**	**$PcalX10^{-6}$**	**$PobsX10^{-6}$**	**$PcalX10^{-6}$**	**$PobsX10^{-6}$**	**$PcalX10^{-6}$**
1	$^6H_{5/2} \rightarrow {}^4H_{9/2}$	5.68	1.57	6.169	3.60	7.54	2.32	6.89	6.16
2	$^6H_{5/2} \rightarrow {}^4D_{3/2}$	8.36	7.85	37.82	34.0	13.3	22.1	54.3	51.6
3	$^6H_{5/2} \rightarrow {}^6P_{3/2}$	7.44	6.54	3.316	.123	6.338	6.68	3.37	7.62
4	$^6H_{5/2} \rightarrow {}^4I_{15/2}$	1.63	0.234	1.844	.024	.857	.0193	8.76	0.239
5	$^6H_{5/2} \rightarrow {}^4I_{13/2}$	3.96	25.4	3.262	2.61	1.339	2.20	3.11	28.7
6	$^6H_{5/2} \rightarrow {}^4M_{15/2}$	48.2	32.3	7.93	3.40	3.808	2.71	46.4	34.1
7	$^6H_{5/2} \rightarrow {}^4G_{7/2}$	2.33	4.48	9.93	9.85	.616	5.98	2.21	15.5
8	$^6H_{5/2} \rightarrow {}^4G_{5/2}$	4.38	.832	9.89	4.05	.396	2.73	.958	5.93
9	R.M.S Deviation	9.69×10^{-6}		5.87×10^{-6}		3.09×10^{-6}		1.18×10^{-5}	

Table -2 Observed and calculated values of Oscillator strength (Px10-6) of various Absorption Transitions of Sm(III)- 4-Methylimidazole(4MI) Complex in alcoholic (C2H5OH) and Micellar medium

COMPLEX		Sm(III)-4MI (Et-OH)		Sm(III)-4MI (TX-100)		Sm(III)-4MI) (SDS)		Sm(III)-4MI (HTAB)	
ʊϐʊ	Energy levels	$PobsX10^{-6}$	$PcalX10^{-6}$	$PobsX10^{-6}$	$PcalX10^{-6}$	$PobsX10^{-6}$	$PcalX10^{-6}$	$PobsX10^{-6}$	$PcalX10^{-6}$
1	$^6H_{5/2}\rightarrow{}^4H_{9/2}$	1.28	2.31	4.527	3.57	3.42	2.05	7.54	4.55
2	$^6H_{5/2}\rightarrow{}^4D_{3/2}$	22.6	21.3	30.58	31.1	21.2	20.2	49.8	44.4
3	$^6H_{5/2}\rightarrow{}^6P_{3/2}$	1.85	.758	3.11	3.81	2.16	3.87	7.20	8.01
4	$^6H_{5/2}\rightarrow{}^4I_{15/2}$	3.63	.0164	1.844	.061	.298	.014	8.75	2.44
5	$^6H_{5/2}\rightarrow{}^4I_{13/2}$	2.63	1.58	2.36	6.57	1.64	1.65	3.91	2.82
6	$^6H_{5/2}\rightarrow{}^4M_{15/2}$	2.71	1.99	9.99	8.25	3.43	2.02	2.98	3.24
7	$^6H_{5/2}\rightarrow{}^4G_{7/2}$	7.77	6.32	9.76	9.49	.193	5.22	3.41	1.09
8	$^6H_{5/2}\rightarrow{}^4G_{5/2}$	2.45	2.66	.312	3.80	.327	2.33	.562	5.03
9	R.M.S Deviation	$1.62\ X10^{-6}$		$4.96\ X10^{-6}$		$2.97\ X10^{-6}$		$4.96X10^{-6}$	

(Triton X-100, SDS and HTAB)

Table -3 Computed value of judd Ofelt parameter (Tλ), Symmetry parameter (T4 / T2), Coordination Parameter (T4 / T6), of Sm(III) 2-methylimidazole and 4-Methylimidazole Complex in alc.(C2H5OH) and micellar medium.

S.N.	Sm (III) System	$T_{2\ X10^{-9}}$	$T_{4\ X10^{-9}}$	$T_{6\ X10^{-9}}$	T_4/T_6	T_4/T_2
1	Sm (III)-2MI C_2H_5OH	238	1.56	50.6	0.0308	0.0065
2	Sm (III)-2MI TX-100	1233	0.302	5.30	0.056	0.0002
3	Sm (III)-2MI SDS	786	1.51	4.30	0.352	0.0019
4	Sm (III)-2MI HTAB	1800	1.74	53.5	0.032	0.0009
5	Sm (III)-4MI C_2H_5OH	775	0.169	3.11	0.0543	0.0021
6	Sm (III)-4MI TX-100	1130	0.933	13.1	0.071	0.0008
7	Sm (III)-4MI SDS	692	0.923	3.27	0.282	0.0013
8	Sm (III)-4MI HTAB	1550	1.9	5.02	0.379	0.0012

CONCLUSIONS

The present study is based on DOPED crystal phenomenon. RMS deviation between Pobs and Pcal values indicates the applicability of Judd-Ofelt theory. Oscillator strength of transition 6H5/2 →4D3/2, is high value which exhibits hypersensitivity to changes in ligand environment. T4/T6 and T4/T2 values indicates almost identical stereo environment around Sm(III) Ion. Value of T2 found positive for all medium which shows existence of interaction between samarium and imidazole system. Micellar systems has increased the O.D/ Absorbance and luminescence properties as stability of complex is sufficient in Micellar system. Micellar medium is found to be best as intensity of Uv-visible spectra are high in Micellar medium than alcoholic medium.

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