INTENSITY PARAMETERS AND BIOLOGICAL EVALUATION ON TERBIUM (III) COMPLEX WITH 4-NITROACETOPHENONE THIOSEMICARBAZONE

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Abstract **:** Intensity parameters for the complex of Terbium with 4- Nitroacetophenone thiosemicarbazone (doped study) have been analysed by application of Judd ofelt theory . Absorption spectrum has been recorded in organic and micellar medium (HTAB, SDS AND TRITON X-100). The antibacterial activity of complex was tested against two bacterial strains: *Escherichia coli*, *Staphylococcus aureus.* Complex possess inhibitory action against the tested strains.

Keywords – Judd Ofelt parameter, Thiosemicarbazone , antibacterial activity

INTRODUCTION

Terbium has applications in medicinal field, energy transfer processes, radionuclide, luminescent properties, dopants, green phosphors and as alloys [1-7]. The Judd Ofelt theory predicts an increase in the Ω_2 parameter as the reciprocal energy difference between the 4f and 5d orbitals of the rare earth ions increases, the peak wavelength increases with increasing covalency of the rare earth sites due to increasing polarizibility of the ligands [8]. Studies on transition metal thiosemicarbazones complexes have been investigated using different mediums. [9].

Thiosemicarbazones as one of the important compounds attracted researchers due to their potential biological activities. (10). Kanika Solanki et al. have prepared three novel green chelating resins and their analytical potentialities have also explored. Determination of different

toxic and non-toxic residues present in various food materials is also carried out. Anti microbial activities of chelating resins were also evaluated against two bacterial strains i.e. *E. coli* and *S. aureus* (11).

MATERIAL AND METHOD:

PREPARATION OF SOLUTION OF METAL - Terbium (III) Chloride (Acros organics, New Jersy, USA) of 99.90% was used

SYNTHESIS OF LIGANDS - ligand 4-Nitroacetophenone thiosemicarbazone [4NAT] was synthesized as given in literature [12].

PREARATION OF MICELLAR SOLUTIONS - The solvents used in doped system are Ethyl Alcohol (AR 99.9%, Jiangsu-Hliaxi International Trade Co. Ltd., Made in China) and Triton-X-100, HTAB and SDS, (Loba Chemia Pvt.Ltd., Mumbai, India).

The saturated solution of ligand and metal Tb (III) ion (0.05 M) was prepared in different solvents [Triton X-100 of 100 CMC (1.8×10^{-2} M), Sodium Dodecyl sulphate, (SDS) of 75 CMC (0.05 M), and Hexadecyl Trimethyl Ammonium Bromide, (HTAB) of 100 CMC (9.2×10^{-2} M)]. 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) upgraded with resolution and expansion of scale in the region 190 nm to 1100 nm.

INTENSITY PARAMETERS

These parameters include oscillator strengths and Judd-Ofelt intensity (T_λ) parameters.

(a) OSCILLATOR STRENGTH

The observed spectra in the present study are due to $f \leftrightarrow f$ transitions, which are forbidden ones. Thus the intensity of these transitions, which is measured in terms of oscillator strength

(P) must be zero. But the observed oscillator strength (P_{obs}) has to be explained. The first successful theory has been proposed by Judd & Ofelt.

The observed oscillator Strength (P_{obs}) may be considered to be due to the contribution from induced electric dipole, magnetic dipole and electric quadrupole.

Thus

$$P_{obs} = P_{ed} + P_{md} + P_{eq}$$

The intensity of an absorption band can be indicated by the molar absorptivity commonly called the extinction coefficient. A parameter of greater theoretical significance is P, the oscillator strength of integrated intensity, often simply called the integrated intensity.

$$P = 4.315 \times 10^{-9} \int \in d\ \bar{\nu}$$

Here $\in$ is the absorptivity and $\bar{\nu}$ is the frequency expressed in wave numbers. For a fully allowed electronic transition P=1. The quantity P is evaluated graphically from equation written above by plotting $\in$ on a linear scale versus the wave number $\bar{\nu}$ in cm^{-1} and calculating the area of the band. For a single, symmetrical peak, P can be approximated by the expression. [13]

$$P \approx (4.6 \times 10^{-9}) \times \in_{max} \times \Delta\ \bar{\nu}^{1/2}$$

(b) JUDD-OFELT PARAMETERS

According to Judd-Ofelt theory, the oscillator strength, P_{ed} of the induced electric dipole transition $\Psi \rightarrow \Psi_{J'}$ of energy $\bar{\nu}$ cm^{-1}, can be expressed as a sum of products of parameters T_λ and matrix element of unit tensor $U^{(\lambda)}$, and is given by

$$P_{ed} = \sum_{\lambda = 2,4,6} T_\lambda\ \bar{\nu}\ \left[f^N \Psi_J \left\| U^{(\lambda)} \right\| f^N \Psi_{J'} \right]^2$$

The parameters (T_λ) (λ =2, 4, 6) are called Judd-Ofelt parameters (T_2, T_4 & T_6). The observed oscillator strength of the transition of energy ($\bar{\nu}$) can be expressed in terms of T_2, T_4 & T_6 parameters (Judd-Ofelt) [14] as follows-

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

The values of $[U^{(2)}]^2$, $[U^{(4)}]^2$ and $[U^{(6)}]^2$ have been taken from Carnall et.al. to compute the values of T_2, T_4 & T_6 parameters. [15-20]

For various peaks of Tb (III) Intensity (Judd Ofelt T_2, T_4, T_6 and oscillator strength $P_{obs} \times 10^6$, Symmetry (T_4/T_6) and Coordination (T_4/T_2) RMS deviation σ parameters have been computed using partial and multiple regression methods

ANTIBACTERIAL STUDIES

The antibacterial activity of ligand and their corresponding complex with Terbium ions were assayed simultaneously against the bacteria *Escherichia coli* and *Staphylococcus aureus* by disc diffusion method. [21]

RESULT AND DISCUSSION

Five bands in the case of Tb^{3+} have been observed which have been recorded in the region 200 nm to 400 nm of electronic spectrum. In computing the values of oscillator strength, the value of $\nu^{1/2}$ (half band width) have been determined by resolving the observed bands into Gaussian shape curve which provides better investigations of different parameters.

The spectra of doped systems were recorded in various mediums, i.e. in organic (alcoholic) and micellar medium. In general, organic media (alcoholic system) was found best comparative to micellar medium ((HTAB, SDS AND TRITON X-100). Oscillator strength results are showen in table 1. Judd ofelt parameter are showen in table 2. and antibacterial results are showen in table 3.). The antibacterial activity of complex was tested against two bacterial strains: *Escherichia coli, Staphylococcus aureus.* Complex possesses inhibitory action against the tested strains and results found better against *Staphylococcus aureus.*

TABLE 1

Computed values of oscillator strength (P X 10^6) for Tb(III) complexes with 4NAT in alcoholic and micellar medium

S.NO.	LEVEL / Tb-SYSTEMS (MEDIUM)	$^5F_3$		$^5H_4$		$^5H_6$		$^5H_7$		$^5D_1$		r.m.s dev.±σ
		P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	
1	Tb-4NAT (HTAB)	1.09	19.28	8.56	0.29	60.52	71.82	71.42	5.06	16.42	-153.45	0.000579
2	Tb-4NAT (SDS)	2.77	381.50	0.12	8.29	0.11	14.20	1.15	522.27	24.54	-309.51	0.0001464
3	Tb-4NAT (TRITON-X-100)	2.64	25.94	0.18	0.41	0.16	96.63	80.35	6.11	59.86	-410.04	0.0001944
4	Tb-4NAT (ETOH)	0.01	2.98	0.19	401.80	2.14	0.11	2.38	0.95	0.29	2,625.85	0.001374

TABLE 2

Computed values of T_λ ,T_4 / T_2 and T_4 / T_6 parameters for Tb(III) complexeswith 4NAT in alcoholic and micellar medium

S.N.	COMPOUND	T_2 X 10^8	T_4 X 10^8	T_6 X 10^8	T_4/T_2	T_4/T_6
1	Tb-4NAT (HTAB)	60.11	-1.19	6.30	-1.98	-1.89
2	Tb-4NAT (SDS)	1.21	-2.40	1.24	-1.98	-19.29
3	Tb-4NAT(Triton-X- 100)	1.60	-3.18	8.48	-1.98	-3.76
4	Tb-4NAT(ETOH)	-0.10	2.04	9.75	-1.97	2.09

TABLE 3

Antibacterial activity of ligand and complex

S.NO	Compounds	Zone of inhibition (in mm) against Staphylococcus aureus at 200 ppm	Zone of inhibition (in mm) against Escherichia coli at 200 ppm
1	4NAT	12	11
2	Tb (III)-4NAT	16	14

CONCLUSION

The absolute value of oscillator strength and Judd Ofelt parameter determined under different experimental condition for Tb (III)-complex, (Table-1-2). This clearly shows a significant change in the oscillator strength with respect to change in solvents. The T_2 (Judd-Ofelt parameter) has been found to be positive in micellar medium which has significance. The constant value of Co-ordination parameter (T_4/T_2) is suggesting the no change in coordination environment around the lanthanide ion. The value of T_4/T_6 shows a change in symmetry around central metal ion.

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