INVESTIGATIONS ON GADOLINIUM (III) COMPLEXES WITH SOME N,S,O MOEITY LIGANDS AS DOPED SYSTEMS IN MICELLAR MEDIUM : A GREEN CHEMISTRY APPROACH

[1]YADUVEER SINGH[*], [2]H S BHANDARI, [3]KAILASH DAGA
[1]RESEARCH SCHOLAR, [2]ASST. PROFESSOR, [3]PROFESSOR
[1,] DEPARTMENT OF CHEMISTRY, J N V UNIVERSITY, JODHPUR, RAJ, INDIA.

ABSTRACT: Investigations on Gd (III) systems have been carried out in organic and micellar (HTAB, SDS And Triton X-100) medium.. Study is based on doped crystal phenomenon. The intensity parameters interaction has been described in terms of Oscillator Strength (P) and Judd- Ofelt parameters (T_λ).

Keywords – Gadolinum complexes, doped study, Judd Ofelt parameter, N,S,O moiety ligands

INTRODUCTION

Gadolinium is used in many ways in nuclear power plant, microwave, manufacturing appliance computer hardware, magnetic refrigeration and specifically in medical field. [1-5] Utility of surfactant systems (micelles) as green chemical reagents exclusively focus on surfactants and their relationships with the chemical with which they interact [6]. 4f valence electrons shielded by 5s and 5p electrons made lanthanide elements unique and versatile consequently an expeditious focus is laid by scientist towards the lanthanide chemistry [7] The magnetic susceptibility data obtained for lanthanide complexes are not much different from that of the respective free ions and a vast majority of the lanthanide complexes have colors similar to that of the free lanthanide ions showing the non-involvement of 4f orbitals in bonding [8].The participation of 4f electrons in the bonding of some lanthanide complexes has been investigated at the density functional theory level. Structural parameter obtained with small core potential suggests the non participation of the electron to the Ln-ligand bonding [9]. The ligand field splitting parameter obtained free embedding calculations are reported and calculation confirms localising the cation and ligand orbitals in different region space [10]. The 4f orbitals are largely prevented from interactions with ligands orbitals, although the 4f orbitals are spatially oriented towards favourable donor sites for the high coordination numbers observed.The oscillator strengths, transition rates, and branching ratios associated with known and potential laser transitions in trivalent holmium are discussed. Laser transitions between the $^5F_5$ and $^5I_5$ energy manifolds are found to have abnormally low average oscillator strength is reported and an alternative explanation of the laser observation is suggested [11].Recently research relating with metal complexes of N,S,O- moiety ligands have expanded enormously and now comprising their interesting aspects in coordination chemistry with a special emphasis in bioinorganic chemistry[12]. It is well known that N and S play a key role in the coordination of metals at the active sites of numerous metallobiomolecules. The metal complexes having N,S,O- moiety ligands posses unusual confriguration structural liability and are sensitive to molecular environment[13]. Micellar chemistry is one of the emerging areas of study at present. The importance and versatility of N,S,O- moiety ligands in biological systems have promoted the selection of this class of ligands and their complexes for the study. lanthanide metal complexes with potential biological activity are the focus of extensive investigations [14].

MATERIAL AND METHOD:

Gd(III) perchlorate were prepared by heating their oxides with perchloric acid and evaporating off the excess perchloric acid [15] and ligands (1) 2-Hydroxy benzaldehyde thiosemicarbazone [2HBT] (2) 2-Methoxy benzaldehyde thiosemicarbazone [2MBT] were synthesized as given in literature[16]. 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 Gd (III) ion (0.005 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.

Experimental Oscillator strength:

The strength of electronic transition is generally expressed in terms of a quantity called “Oscillator Strength” represented by ‘P’. It is defined as the ratio of the experimental transition probability to that of the ideal case of a harmonic oscillator that is P_{obs}., when the transition probability is unity. The oscillator strength can also be expressed. [17-21]

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

The equation may be expressed in terms half band width

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

$\Delta\nu^{1/2}$ = Half Band Width

Judd ofelt parameter

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

For various peaks of Ho (III) Intensity (Judd Ofelt T_2, T_4, T_6 and oscillator strength $P_{obs}\times10^6$, RMS deviation σ parameters have been computed using partial and multiple regression methods.

RESULT AND DISCUSSION

Four bands in the case of Gd^{3+} has been observed which have been recorded in the region 300 nm to 650 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 ((HATB, SDS AND TRITON X-100). Oscillator strength results are showen in table 1. Judd ofelt parameter are showen in table 2.

CONCLUSION

The absolute value of oscillator strength, energy and judd ofelt parameter determined under different experimental condition for Gd (III)-complexes, (Table-1-2). This clearly shows a significant change in the oscillator strength with respect to change in solvents. Comparative absorption spectra of Gd (III)- 2HBT complexes in alcoholic and micellar medium and Gd (III)- 2MBT complexes in alcoholic and micellar medium (clearly show a significant enhancement in the oscillator strength of f-f transition. The T_2 (Judd-Ofelt parameter) has been found to be positive in except few cases which has significance.

TABLE - 1

Computed values of oscillator strength (P X 10^6) for Gd(III) complexes with N,S,O moeity ligands in alcoholic and micellar medium

S.NO.	LEVEL Gd-SYSTEMS (MEDIUM)	$^6D_{5/2}$		$^3I_{15/2}$		$^6I_{7/2}$		$^6P_{3/2}$		r.m.s dev.±σ
		P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	
1	Gd-2HBT (HTAB)	1.9	98.84	3.91	253.69	2.86	36.48	0.78	0.00	0.00018978
2	Gd-2HBT (SDS)	2.53	20.037	2.55	65.12	1.59	9.36	2.38	0.00	4.2725E-05
3	Gd-2HBT (TRITON-X-100)	2.74	-902.15	2.01	-700.66	16.51	-100.77	0.40	0.00	0.00086263
4	Gd-MBT (ALCOHOLIC)	13.1	118.82	14.34	19.3	10.39	2.77	15.80	0.00	4.363E-05
5	Gd-MBT (HTAB)	1.66	42.62	17.54	90.41	6.62	486.67	3.38	0.00	0.00033025
6	Gd-MBT (SDS)	2.63	94.3	14.14	200.03	1.69	564.52	0.35	81.19	0.00046061
7	Gd-MBT (TRITON-X-100)	31.91	1270.56	12.95	2695.14	0.508	-438.74	11.61	-63.1	0.00170343
8	Gd-MBT (ALCOHOLIC)	7.55	127.12	16.52	269.66	8.48	369.36	5.45	53.12	0.00039063

TABLE - 2

Computed values of T_λ parameters for Gd(III) complexes with N,S,O moeity ligands in alcoholic and micellar medium

S.N.	Gd-SYSTEMS (MEDIUM)	$T_2 X 10^8$	$T_6 x 10^8$
1	Gd-2HBT (HTAB)	129.28	33.94
2	Gd-2HBT (SDS)	26.2	8.71
3	Gd-2HBT (TRITON-X-100)	-117.99	-93.76
4	Gd-MBT (ALCOHOLIC)	15.54	2.58
5	Gd-MBT (HTAB)	55.75	65.16
6	Gd-MBT (SDS)	123.34	75.54
7	Gd-MBT (TRITON-X-100)	166.184	-58.71
8	Gd-MBT (ALCOHOLIC)	166.27	49.42

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