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Few bonding parameters study, on the basis of spectral intensity of Dy3+ ion in solution of some organic oximes

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Abstract: *The ligand environment produced by various oximes in 60% ethanol around doped systems of Dy3+ ions have been studied and characterized with respect to electronic spectral parameters. The parameters viz. Judd-Ofelt (T_λ), intensity of hypersensitive band, bonding parameters (b½, δ% &η) for doped in solution of organic oximes have been studied. The study provides useful information about interelectronic repulsion and spin interaction involved in metal-liand bond.*
Keywords*: Hypersensitive transition, Doped systems.*

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I. Introduction

Due to their outstanding luminescent properties and numerous applicationslanthanoides (Ln^{3+}) are a unique class of materials[1-8].Electronic spectral studies of lanthanoide ion complexes with reference to Judd-Ofelt parameters have been found to have due significance[9].

In the present study six organic oximes viz. acetoxime (A), acetophenoneoxime (B), bcnzophenoneoxime(C). diacetylmonooxime (D), cyclooctanoneoxime (E) and camphoreoxime (F) have been used as ligands. The solution of each ligand was prepared in 60% aqueous ethanol solution (v/v) and a constant volume of $DyCI_3.6H_20$ salt solution (w/v) has been added to this solution. Dy^{3+} ion has been doped in solutions of these oximes separately in the metal ligand ratio of 1:1 and 1:2.

For these doped systems, we have observed six peaks for Dy^{3+} in the visible region,
these are due to $^4M_{19/2}$, $^4F_{7/2}$, $^4I_{15/2}$, $^6F_{3/2}$, $^6F_{5/2}$ and $^6F_{7/2}$ levels The transition $^6H_{15/2} \rightarrow {}^4I_{15/2}$ is hypersensitive transition.

II. Results and discussion:-

The calculation of parameters viz. Oscillator strength (P), Judd-Ofelt (T_λ) bonding parameters ($b^{½}$, δ% &η) have been computed by the programme developed by earlier workers [13- 19]. The computed values of oscillator strength, Judd-Ofeltparameter , bonding parameters and nephelauxetic ratio have been tabulated (Tables 1-4). Here 'M : La' and 'M : Lb' represents metal to ligand ratio 1:2 and 1:1 respectively in the tables.

Spectral intensity parameters:

The computed values of oscillator strength (P_{obs} and P_{cal}) of various bands for Dy^{3+}-doped systems have been tabulated in Table-1 and 2. The observed values of oscillator strength for $^4I_{15/2}$ band varies from 5.67×10^{-7} to 1.58×10^{-5}

Trend with respect to $^4I_{15/2}$ level

Fb > Db > Ca >Cb> Ba > Bb >Aa> Eb > Ab > Fa >Ea> Da

The r.m.s. deviation between P_{obs} and P_{cal} varies from $1.624x10^{-6}$ to $3.543x10^{-6}$.

The low value of r.m.s. deviation proved validity of Judd-Ofelt theory.

Trend with respect to r.m.s. deviation

Ba >Cb>Ea> Ca > Bb > Da > Eb > Fb >Aa> Ab > Fa > Db

from the above trends, we can infer that Camphoroxime (Fb) with metal-ligand ratio 1:1 is stronger ligand for metal-ligand interaction,

Judd-Ofelt Parameters:-

These parameters(T_2 ,T_4 and T_6) for Dy^{3+} doped systems have been tabulated in Table-3.The values of T_2, T_4 and T_6 are positive for present systems. The values of T_2 varies from $2.33x10^{-9}$ to $7.33x10^{-8}$. The values of T_4 varies from $5.02x10^{-10}$ to $1.16x10^{-9}$. The values of T_6 varies from $4.15x10^{-11}$ to $1.56\ x10^{-10}$. The values of T_4 / T_6 varies from 3.4450 to 21.4211 . The values of T_4 / T_2 varies from 0.014to 0.787.

The general sequence in the value of T_2, T_4 and T_6 is
$T_2 > T_4 > T_6$
On the basis of T_4/T_6 values, the doped Dy^{3+} ion systems have been classified in the following CLASSES.
(1) CLASS-1: T_4/T_6 values varying in between 3.4000 to 7.4000. Ligands were Aa, Ab, Da, Fa & Fb..
(2) CLASS-2: T_4/T_6 values varying in between 9.8000 to 14.2000. Ligands were Ba, Bb, Ca& Eb.
(3) CLASS-3: T_4/T_6 values varying in between 18.5000 to 21.5000. Ligands were Cb, Db &Ea
These three CLASSES (1,2 &3) reveal that on changing the metal to ligand ratio for ligands C, D & E, symmetry around the cation or symmetry of stereo environment around the doped Dy^{3+} ion changes.
There is much variation in Judd-Ofelt parameters, shows that the sequence $T_6 < T_4 < T_2$ in most of the cases, which is in good agreement with lanthanide metal ion characteristics.

Energy of hypersensitive transitions: -
The values of energies (observed) vary from 21915.1cm^{-1}to22100.5cm^{-1}. Trend with respect to energy of hypersensitive transitionDa >Cb> Db > Ca >Aa> Fa > Ab > Ba > Bb >Fb >Ea>Eb
Red shift is observed in the energy level of each band in Dy^{3+} doped systems as compared to that of free ion and solvent.

Nephelauxetic ratio and Bonding parameters ($b^{½}$, δ% &η):-
The values of nephelauxetic ratio(β) and various bonding parameters for Dy^{3+} doped systems have been tabulated in Table-4. The value of nephelauxetic ratio (β), for Dy^{3+} doped system varies from 0.9830 to 0.9914. Since the value of β is less than one for all the systems hence presence of covalent character in metal-ligand linkage is proved.
The value of bonding parameter ($b^{½}$) varies from 0.0657 to 0.0921. The value of $b^{1/2}$ represents the mixing of metal ion 4 *f* orbitals with the ligand orbitals. The positive value of bonding parameter indicates covalent character in metal-ligand bond . The value of Sinha's covalency parameter (δ%) varies from 0.8706 % to 1.7244 % and value of covalency angular overlap parameter (η) varies from 0.0043 to 0.0086.Trend with respect to β
Da >Cb> Db> Ca > Aa > Ab = Fa > Ba = Bb >Ea> Fb > Eb
From the above trend, Dy^{3+} systems surrounded by cyclooctanoneoxime having metal-ligand ratio1:1 (Eb) have the highest covalent character in metal- ligand bond.

Validity of Peacock's relation ($P\alpha\ \bar{\nu}\ T_6$):-
In Dy^{3+} ion, the transition $^6H_{15/2} \rightarrow {}^4I_{15/2}$, is regarded as hypersensitive transition. The values of proportionality constant K for the relation $P\alpha\ \bar{\nu}\ T_6$ or $P\ \alpha\ \bar{\nu}\ T_4$,as proposed by R.D.Peacock, should be constant for the present systems. The value of proportionality constant K_2 (= $P/\ \bar{\nu}\ T_6$), is approximately constant for Dy^{3+} doped systems and value of K_1 (= $P/\ \bar{\nu}\ T_4$), is also constant for certain ligands. In the present study of Dy^{3+} doped systems, constancy is found more in K_1 in comparison to K_2.

Materials and method :-
All the chemicals and the solvent used were of analytical grade. $DyCI_3.6H_20$ having 99.1% purity was supplied by Indian Rare Earths Ltd. The ligands were dissolved to prepare 0.32 M and 0.16 M solutions in 60% aqueous ethanol (v/v) at room temperature (35 °C). Equal volume (10 ml) of each of these 0.32 M and 0.16 M ligand solution was added in 10 ml solution of 0.16M $DyCI_3.6H_20$ to get systems of having metal to ligand ratio I : 2 and I : I respectively. Solution spectra of these twelve systems were recorded by using standard spectrophotometer (Biomate UV-Visible spectro-photometer v7.07) in the range of 350 to 1000 nm.

Table-1.Computed values of oscillator strength for Dy^{3+} doped systems:-

SN	Levels	Dy^{3+}+ solvent		Dy^{3+}+Aa		Dy^{3+}+Ab		Dy^{3+}+Ba		Dy^{3+}+Bb		Dy^{3+}+ Ca		Dy^{3+}+Cb	
		P obs	P Cal	P obs	P Cal	Pobs	P obs	P obs	P Cal	P obs	P Cal	Pobs	PCal	P obs	P Cal
1	$^4M_{19/2}$	8.1029 X10^{-6}	1.7237 X10^{-6}	6.3059 X10^{-6}	1.2685 X10^{-6}	6.1557 X10^{-6}	1.1564 X10^{-6}	1.029 X10^{-5}	1.8825 X10^{-6}	7.33976 X10^{-6}	1.3339 X10^{-6}	8.2391 X10^{-6}	1.510X 10^{-6}	9.8393 X10^{-6}	1.5822 X10^{-6}
2	$^4F_{7/2}$	3.4557 X10^{-6}	1.7745 X10^{-6}	2.8207 X10^{-6}	1.5086 X10^{-6}	2.6583 X10^{-6}	1.3240X 10^{-6}	3.293 X10^{-6}	1.8081 X10^{-6}	3.22709 X10^{-6}	1.7008 X10^{-6}	3.6897 X10^{-6}	1.984X 10^{-6}	3.5796 X10^{-6}	1.7683 X10^{-6}
3	$^4I_{15/2}$	1.4342 X10^{-6}	1.5928 X10^{-6}	9.6712 X10^{-7}	9.7983 X10^{-7}	9.2508 X10^{-7}	1.0435X 10^{-6}	1.065 X10^{-6}	1.94111 X10^{-6}	1.00234 X10^{-6}	1.2491 X10^{-6}	1.0955 X10^{-6}	1.372X 10^{-6}	1.0955 X10^{-6}	1.6358 X10^{-6}
4	$^6F_{3/2}$	4.7644 X10^{-7}	1.1362 X10^{-7}	5.7308X 10^{-7}	1.2540 X10^{-7}	3.4796 X10^{-7}	7.0303 X10^{-8}	3.872 X10^{-7}	7.2026 X10^{-8}	3.22876 X10^{-7}	4.7690 X10^{-8}	3.6564 X10^{-7}	5.94 X10^{-8}	4.259 X10^{-7}	3.3378 X10^{-8}
5	$^6F_{5/2}$	1.6173 X10^{-6}	6.0265 X10^{-7}	1.4348 X10^{-6}	6.6599 X10^{-7}	1.1783 X10^{-6}	3.7307 X10^{-7}	1.357 X10^{-6}	3.8194 X10^{-7}	1.18898 X10^{-6}	2.5310 X10^{-7}	1.3614 X10^{-6}	3.152X 10^{-7}	1.3057 X10^{-6}	1.7693 X10^{-7}
6	$^6F_{7/2}$	3.0973 X10^{-6}	2.37289 X10^{-6}	2.9176 X10^{-6}	2.2799 X10^{-6}	2.2055 X10^{-6}	1.6379X 10^{-6}	2.786 X10^{-6}	2.0173 X10^{-6}	2.35957 X10^{-6}	1.7145 X10^{-6}	2.7589 X10^{-6}	2.037X 10^{-6}	2.4763 X10^{-6}	1.6313 X10^{-6}
7	rms→deviations	σ = ±2.745 X10^{-6}		σ =±2.1716 X10^{-6}		σ =±2.153 X10^{-6}		σ = ±3.5431 X10^{-6}		σ = ±2.5764 X10^{-6}		σ =±2.885 X10^{-6}		σ =±3.509 X10^{-6}	

Table-2.Computed values of oscillator strength for Dy^{3+} doped system:-

SN	Level	Dy^{3+}+Da		Dy^{3+}+Db		Dy^{3+}+Ea		Dy^{3+}+Eb		Dy^{3+}+Fa		Dy^{3+}+Fb	
		Pobs	P Cal	Pobs	P Cal	P Cal	P obs	P Cal	P Cal	P obs	P Cal	P obs	P Cal
1	$^4M_{19/2}$	7.45433 X10^{-6}	1.41724 X10^{-6}	8.86533 X10^{-6}	8.29912 X10^{-6}	7.54888 X10^{-6}	8.24209 X10^{-7}	6.19218 X10^{-6}	8.65599 X10^{-7}	5.97104 X10^{-6}	1.17024 X10^{-6}	9.00296 X10^{-6}	8.87891 X10^{-6}
2	$^4F_{7/2}$	1.97171 X10^{-6}	1.09351 X10^{-6}	5.03127 X10^{-6}	2.34108 X10^{-6}	4.10345 X10^{-6}	1.83119 X10^{-6}	3.9482 X10^{-6}	1.87579 X10^{-6}	2.99868 X10^{-6}	1.60677 X10^{-6}	5.61858 X10^{-6}	2.13261 X10^{-6}
3	$^4I_{15/2}$	5.66772 X10^{-07}	1.36581 X10^{-6}	1.36379 X10-5	1.12903 X10-5	7.77563 X10^{-7}	4.77899 X10^{-7}	9.41678 X10^{-7}	4.76594 X10^{-7}	8.59412 X10^{-7}	8.74993 X10^{-7}	1.57559 X10-5	1.19339 X10^{-5}
4	$^6F_{3/2}$	3.08987 X10^{-07}	1.17343 X10^{-7}	7.01164 X10^{-7}	4.37246 X10-8	5.53257 X10^{-7}	3.94724 X10^{-8}	4.97573 X10^{-7}	5.50882 X10^{-8}	3.91897 X10^{-7}	1.02322 X10^{-7}	1.78856 X10^{-6}	1.15745 X10^{-7}
5	$^6F_{5/2}$	1.22776 X10^{-6}	6.22453 X10^{-7}	1.5719 X10^{-6}	2.31898 X10^{-7}	1.52644 X10^{-6}	2.09362 X10^{-7}	1.47426 X10^{-6}	2.91984 X10^{-7}	1.37269 X10^{-6}	5.42847 X10^{-7}	2.20596 X10^{-6}	6.1336 X10^{-7}
6	$^6F_{7/2}$	2.39772 X10^{-6}	1.89017 X10^{-6}	2.89058 X10^{-6}	2.15881 X10^{-6}	2.64077 X10^{-6}	1.74119 X10^{-6}	2.68668 X10^{-6}	1.916 X10^{-6}	2.71682 X10^{-6}	2.14378 X10^{-6}	3.92559 X10^{-6}	2.6602 X10^{-6}
7	rms→deviations	σ = ± 2.5336X10^{-6}		σ =±1.62441X10^{-6}		σ = ±2.97999X10^{-6}		σ = ±2.41768X10^{-6}		σ = ±2.08511X10^{-6}		σ = ± 2.3703X10^{-6}	

Table-3. Computed values of Judd-Ofelt parameters for Dy^{3+} doped systems:-

SN	Systems	M:L	T_2	T_4	T_6	T_4/T_6	T_4/T_2
1	Dy^{3+} + Solvent		$8.5889X10^{-9}$	$8.47613X10^{-10}$	$1.41008X10^{-10}$	6.0111	0.0986
2	Dy^{3+}+Aa	1:2	$4.66321X10^{-9}$	$7.09239X10^{-10}$	$1.55764X10^{-10}$	4.5533	0.1520
3	Dy^{3+}+Ab	1:1	$5.67548X10^{-9}$	$6.39252X10^{-10}$	$8.73836X10^{-11}$	7.3155	0.1249
4	Dy^{3+}+Ba	1:2	$1.12251X10^{-8}$	$8.83448X10^{-10}$	$8.94625X10^{-11}$	9.8751	0.7870
5	Dy^{3+}+Bb	1:1	$7.19792X10^{-9}$	$8.38527X10^{-10}$	$5.92538X10^{-11}$	14.1514	0.1165
6	Dy^{3+}+Ca	1:2	$7.82494X10^{-9}$	$9.7669X10^{-10}$	$7.37746X10^{-11}$	13.2388	0.1248
7	Dy^{3+}+Cb	1:1	$9.73933X10^{-9}$	$8.7735X10^{-10}$	$4.14665X10^{-11}$	21.1580	0.0900
8	Dy^{3+}+Da	1:2	$7.13905X10^{-9}$	$5.0221X10^{-10}$	$1.45781X10^{-10}$	3.4450	0.0703
9	Dy^{3+}+Db	1:1	$6.95506X10^{-8}$	$1.16323X10^{-9}$	$5.43029X10^{-11}$	21.4211	0.0167
10	Dy^{3+}+Ea	1:2	$2.51004X10^{-9}$	$9.10041X10^{-10}$	$4.90277X10^{-11}$	18.5618	0.3625
11	Dy^{3+}+Eb	1:1	$2.32817X10^{-9}$	$9.26056X10^{-10}$	$6.8407X10^{-11}$	13.5375	0.3977
12	Dy^{3+}+Fa	1:2	$4.26689X10^{-9}$	$7.69191X10^{-10}$	$1.27058X10^{-10}$	6.0539	0.1802
13	Dy^{3+}+Fb	1:1	$7.32516X10^{-8}$	$1.03016X10^{-9}$	$1.43756X10^{-10}$	7.1660	0.0140

Table-4. Computed values of bonding parameters for Dy^{3+}doped systems.

SN	Systems	M:L	β	$b^{1/2}$	δ %	η
1	Dy^{3+} + Solvent	-	0.9900	0.0709	1.0143	0.0051
2	Dy^{3+}+Aa	1:2	0.9890	0.0741	1.1118	0.0055
3	Dy^{3+}+Ab	1:1	0.9889	0.0746	1.1242	0.0056
4	Dy^{3+}+Ba	1:2	0.9888	0.0749	1.1333	0.0057
5	Dy^{3+}+Bb	1:1	0.9888	0.0750	1.1366	0.0057
6	Dy^{3+}+Ca	1:2	0.9891	0.0739	1.1052	0.0055
7	Dy^{3+}+Cb	1:1	0.9906	0.0684	0.9457	0.0047
8	Dy^{3+}+Da	1:2	0.9914	0.0657	0.8706	0.0043
9	Dy^{3+}+Db	1:1	0.9899	0.0711	1.0203	0.0051
10	Dy^{3+}+Ea	1:2	0.9832	0.0916	1.7052	0.0085
11	Dy^{3+}+Eb	1:1	0.9830	0.0921	1.7244	0.0086
12	Dy^{3+}+Fa	1:2	0.9889	0.0744	1.1185	0.0056
13	Dy^{3+}+Fb	1:1	0.9832	0.0916	1.7052	0.0085

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