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RESEARCH ARTICLE

DERIVATIVE MICELLAR SPECTRAL ANALYSIS AND BIOLOGICAL EVOLUTION OF PR (III)-8HQ COMPLEXES.

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Abstract

Optical spectral investigations in micellar medium have been carried out for derivative spectra of Pr(III)-quinoline systems. The 4f-4f transition spectra yield sharp bands which were analyzed individually by Gaussian curve analysis. Various energies and intensities of all the transitions were calculated using Judd-Ofelt relation and are perfectly matches with observed value. Low rms deviation confirms the formation of complex. Lande spin orbit coupling (ξ_{4f}), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Percent covalency (δ), have been computed on computer using partial multiple regression analysis. The Judd-Ofelt intensity (T_2 , T_4 , T_6) parameters also have been evaluated by Using a least-squares fit method. From the magnitude of the bonding parameter (δ), which suggests covalency in complex. By applying the Judd-Ofelt theory a good correlation has been established between the experimental and calculated data.

Biological evolutions of these systems on three microorganisms have also been reported first time. A trend for antibacterial studies has been observed.

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Introduction:-

It is Interesting part of lanthanide chemistry that the efficient shielding of the 4f shells by closed 5s² and 5p⁶ shells leads the trivalent lanthanide ions to exhibit unique spectroscopic properties. Since the 4f lie deep in the nucleus core, the ligand environment only weakly affects the lanthanide electron cloud which is small in magnitude. The line width of the 4f-4f bands is considerably smaller than that observed for transition metal ions and the peak position of the spectral band reveals a part of 4fn configuration. (1-4) In the present study, the properties of lanthanides are mainly focused on the comparative absorption spectrometry and the corresponding changes in oscillator strength of different 4f-4f transition spectra as probe (5-6) in understanding the characteristics of Pr(III) ion and Pr(III) with 8-Hydroxy quinoline in alcoholic (Et-OH) and Micellar medium (viz: TX-100, HTAB and SDS) have been calculated.

Material and Method:-

Praseodymium chloride of 99.9% and ligand was procured from Ms. Indian Earth limited. 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 (100 CMC solution, Loba Chemia Pvt.Ltd., Mumbai, India). The saturated solution of ligand and metals Pr(III) ion 0.05 M were prepared in different solvents (Triton X-100 of 100 CMC (1.8 x 10⁻² M, Sodium

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Dodecyl sulphate, (SDS) of 75 CMC (0.05 M), and Hexadecyl Trimethyl Ammonium Bromide, (HTAB) of 100 CMC (9.2×10^{-2} M) is used for preparing saturated solution of ligand and metal. The UV-visible (normal and derivative) spectra from 400 nm to 600 nm were recorded on (5704-SS) UV Visible Double Beam spectrophotometer at room temperature in 1:3 ratio (Metal: Ligand) at Green chemistry research center (GCRC) Bikaner.

Oscillator strength:-

The intensity of a band is measured in term of Oscillator strength which is expressed in term of molar extinction coefficient (ϵ) and the energy of transition in term of wave number (ν) by the following equation

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

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

According to Judd-Ofelt theory, the oscillator strength for transition of energy can be calculated by using Judd-Ofelt parameters (T_2, T_4 and T_6) with the help of formula-

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

Where $[U^{(2)}]^2, [U^{(4)}]^2, [U^{(6)}]^2$ are matrix elements (13-14).

Slater- Condon (F_2, F_4 , & F_6) and Lande parameter (ζ_{4f}):-

The values of Slater-Condon parameters (F_k) and Lande para-meters (ζ_{4f}) are then evaluated using following equations-

$$F_k = F_k^0 + \Delta F_k \text{ ----- (9)}$$

$$\zeta_{4f} = \zeta_{4f}^0 + \Delta \zeta_{4f} \text{ ----- (10)}$$

Where, $\Delta F_k \ll F_k^0$, $\Delta \zeta_{4f} \ll \zeta_{4f}^0$ and F_k^0 and ζ_{4f}^0 are the zero -order values of Slater-Condon and spin-orbit interaction parameters as reported by Wong (16).

Racah Parameters or Energy parameters (E^1, E^2 and E^3):-

The Slater- Condon F_2, F_4 , & F_6 and Lande parameter or Spin-Orbit Coupling Constant (ζ_{4f}) may be evaluated by expressing energy as Taylor series expansion may be used to express the energy of j^{th} electronic energy level and The Racah parameters E^k ($k = 1, 2$, and 3) are related to F_k ($k=2,4$ and 6) parameters by the following relations -

$$E^1 = (1/9) (70F_2 + 231F_4 + 2002F_6) \text{ ----- (11)}$$

$$E^2 = (1/9) (F_2 - 3F_4 + 7F_6) \text{ ----- (12)}$$

$$E^3 = (1/3) (5F_2 + 6F_4 - 91F_6) \text{ ----- (13)}$$

By assuming wave functions to be hydrogenic as E^k 's (racah parameters) are the linear combination of F_k 's, they may be calculated by using the following relation the Racah parameters reduces to in case of Pr^{+3} complexes which have been evaluated using these equations.

$$E^1 = 14.6818F_2 \text{ ----- (11)}$$

$$E^2 = 0.0768F_2 \text{ ----- (12)}$$

$$E^3 = 1.4844 F_2 \text{ ----- (13)}$$

The F_2 values thus obtained for Pr(III)-8HQ in different medium alcoholic (301.12) TX- 100 (303.55), HTAB(303.40), SDS (302.44) are in close agreement with the values derived from the Racah parameters (E^1, E^2, E^3) by the relation (Table-8)

Bonding Parameters:-

These parameters consist of Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha's Covalency Parameters ($\delta\%$) and Covalency angular overlap Parameter (η) (16-18).

Nephelauxetic Ratio (β):-

The effect of complexation on the free ion is the red shift of the electronic transition. This effect can be represented in terms of Nephelauxetic ratio (β) as follows -

$$\beta = \nu_c / \nu_f \text{ ----- (15)}$$

Where, ν_c and ν_f are wave numbers of f-f transition for spectra of complex and free ion respectively.

Bonding parameter ($b^{1/2}$):-

The Nephelauxetic ratio value can be used to calculate the bonding parameter, from the relation given as -
 $b^{1/2} = [\frac{1}{2} (1-\beta)]^{1/2}$ ----- (16)

Positive value of bonding parameter ($b^{1/2}$) indicates covalent character in metal-ligand bond while negative value shows ionic character in metal-ligand interaction.

Sinha's Covalency Parameters ($\delta\%$):-

Percentage covalent character in metal ligand bond can be expressed by

Sinha's covalency parameter ($\delta\%$)

$$\delta = [1 - \beta / \beta_0] \times 100 \text{----- (17)}$$

Covalency angular overlap parameter (η):-

Covalency angular overlap parameter (η) represents extent of Overlapping

Between metal ion orbital and ligand orbital

$$\eta = [1 - \beta^{1/2} / \beta_0^{1/2}] \text{----- (18)}$$

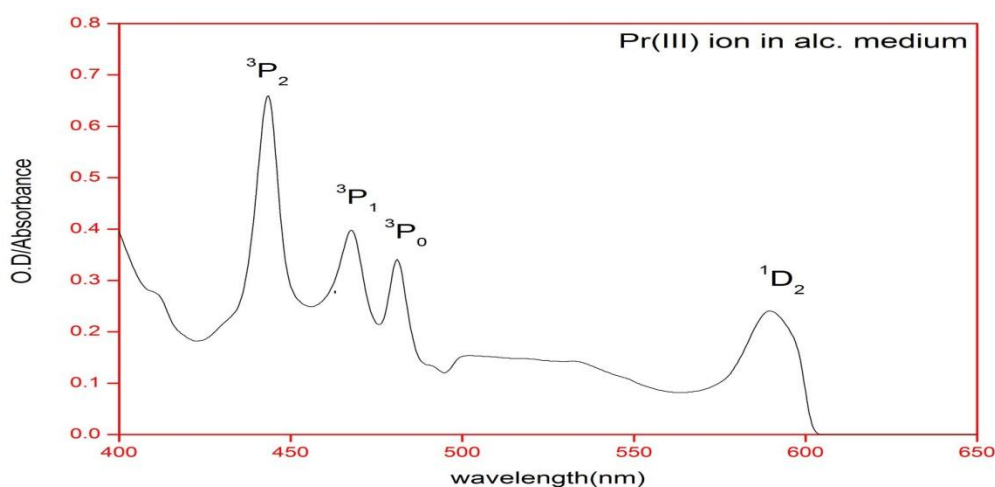
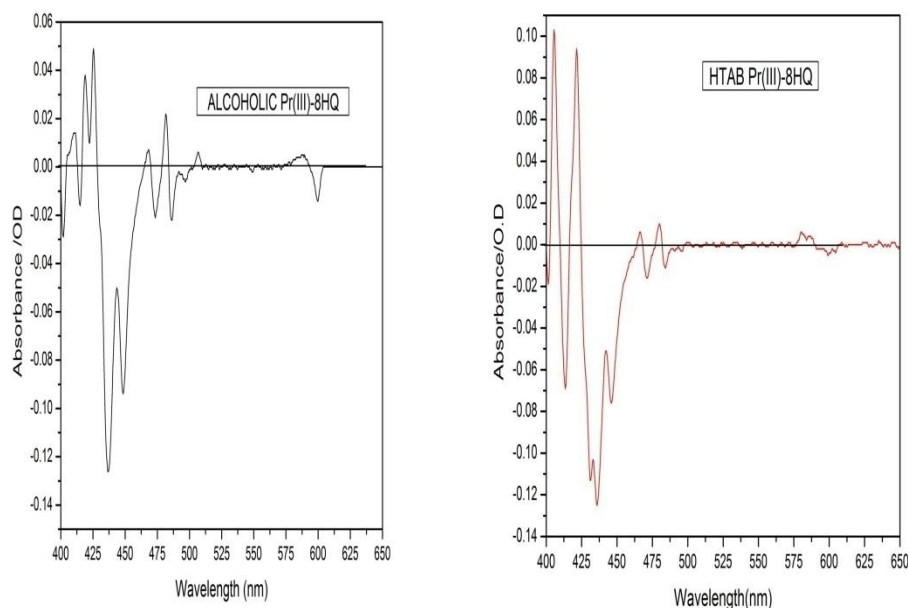


Fig 1:- Normal Electronic Spectrum Of Pr(III)-8HQ In Alcoholic Medium



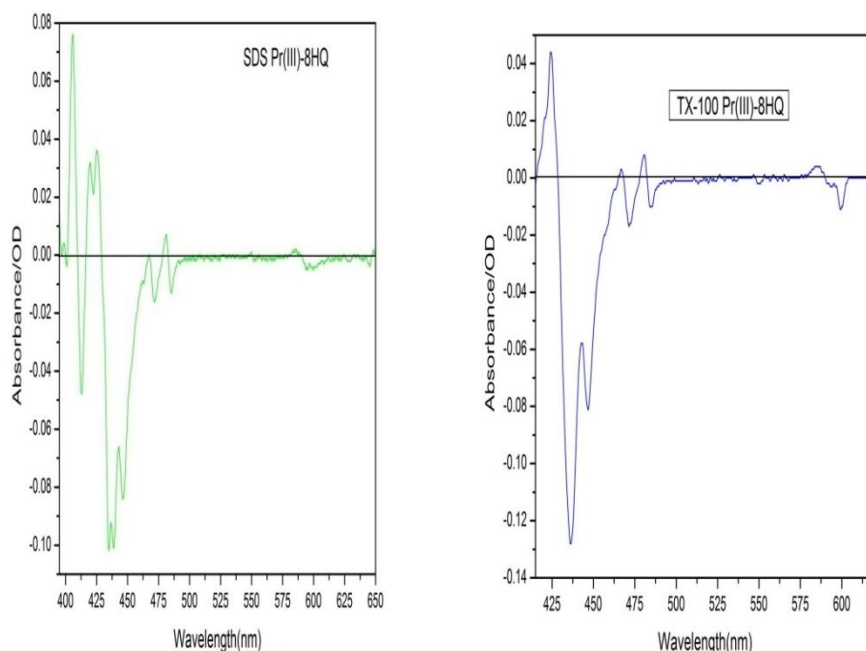


Fig.2:-Derivative Electronic Spectrum Of Pr (III)-8HQ in Different Solvent

Table 1:- Computed values of judd Ofelt Parameter (T_λ), Symmetry Parameter (T_4/T_2), and Coordination Parameter (T_4/T_6) of Pr(III)-8HQ Complex in alcoholic and micellar medium.

Coordination Parameter (T_4/T_6) of Pr(III)-8HQ Complex in alcoholic and micellar medium					
S.N.	Parameter	Pr(III)-8HQ (EtOH)	Pr(III)-8HQ (TX-100)	Pr(III)-8HQ (HTAB)	Pr(III)-8HQ (SDS)
1	$T_2 \times 10^9$	123.815	-0.970	-1.146	-1.128
2	$T_4 \times 10^9$	14.437	0.031	0.037	0.036
3	$T_6 \times 10^9$	22.766	16.002	18.897	18.603
4	T_4/T_6	0.634	0.002	0.002	0.002
5	T_4/T_2	0.117	-0.032	-0.032	-0.032

Table 2:- Observed and calculated values of Oscillator strength ($P \times 10^6$) of various Absorption transitions of Pr(III)-8HQ Complex in organic and Micellar medium.

COMPLEX		Pr(III)-8HQ (EtOH)		Pr(III)-8HQ (TX-100)		Pr(III)-8HQ (HTAB)		Pr(III)-8HQ (SDS)	
S.N.	Energy Levels	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$
1	$^3H_4 \rightarrow ^3P_2$	29.371	193.952	51.401	50.864	66.844	60.684	65.296	59.064
2	$^3H_4 \rightarrow ^3P_1$	5.510	11.450	0.311	1.235	10.533	0.148	8.948	0.144
3	$^3H_4 \rightarrow ^3P_0$	2.391	58.218	2.072	0.125	1.902	1.495	3.282	0.146
4	$^3H_4 \rightarrow ^1D_2$	3.062	40.867	3.746	19.373	5.418	23.113	2.539	22.495
5	r.m.s. (σ)	93.757		7.879		10.747		11.450	
	dev. (\pm)								

Table 3:- Observed and calculated value of Energy (cm^{-1}) of various energy level of Pr(III)-8HQ Complex in Organic and Micellar medium.

COMPLEX		Pr(III)-8HQ (EtOH)		Pr(III)-8HQ (TX-100)		Pr(III)-8HQ (HTAB)		Pr(III)-8HQ (SDS)	
S.N.	LEVELS	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}
1	3P_2	23334.7	23337.2	23334.9	23337.2	23553.9	23557.1	23307.8	23310.0
2	3P_1	21279.4	21276.6	21347.3	21344.7	21325.1	21321.9	21370.0	21367.5
3	3P_0	20661.5	20661.2	20747.3	20746.9	20747.8	20746.9	20725.7	20725.4
4	1D_2	16863.0	16863.4	16963.1	16963.5	16977.4	16977.9	16948.8	16949.2

Table 4:- Computed values of Bonding parameters : Nephelauxetic ratio (β), Bonding ($b^{1/2}$), Sinha Covalency ($\delta\%$) and Covalency-Angular Overlap (η) Parameters of Pr(III)-8HQ Complex in (SDS) micellar medium

Energy Levels	$\nu_c(\text{cm}^{-1})$ Obs	β	$b^{1/2}$	$\delta\%$	η
3P_2	23310.02	1.036	0.134	-3.487	-0.018
3P_1	21367.52	1.002	0.033	-0.213	-0.001
3P_0	20725.39	1.000	0.000	0.000	0.000
1D_2	16949.15	1.003	0.036	-0.254	-0.001

Table 5:- Computed values of Bonding parameters in (T X-100) micellar medium

Energy Levels	$\nu_c(\text{cm}^{-1})$ Obs	β	$b^{1/2}$	$\delta\%$	η
3P_2	23337.22	1.037	0.137	-3.600	-0.018
3P_1	21344.72	1.001	0.023	-0.107	-0.001
3P_0	20746.89	1.001	0.023	-0.104	-0.001
1D_2	16977.93	1.001	0.021	-0.085	0.000

Table 6:- Computed values of Bonding parameters in (HTAB) micellar medium

Energy Levels	$\nu_c(\text{cm}^{-1})$ Obs	β	$b^{1/2}$	$\delta\%$	η
3P_2	23557.13	1.045	0.150	-4.284	-0.022
3P_1	21321.96	0.997	0.040	0.321	0.002
3P_0	20746.89	0.998	0.032	0.208	0.001
1D_2	16977.93	1.001	0.021	-0.085	0.000

Table 7:- Computed values of Bonding parameters in (EtOH) Alcoholic medium

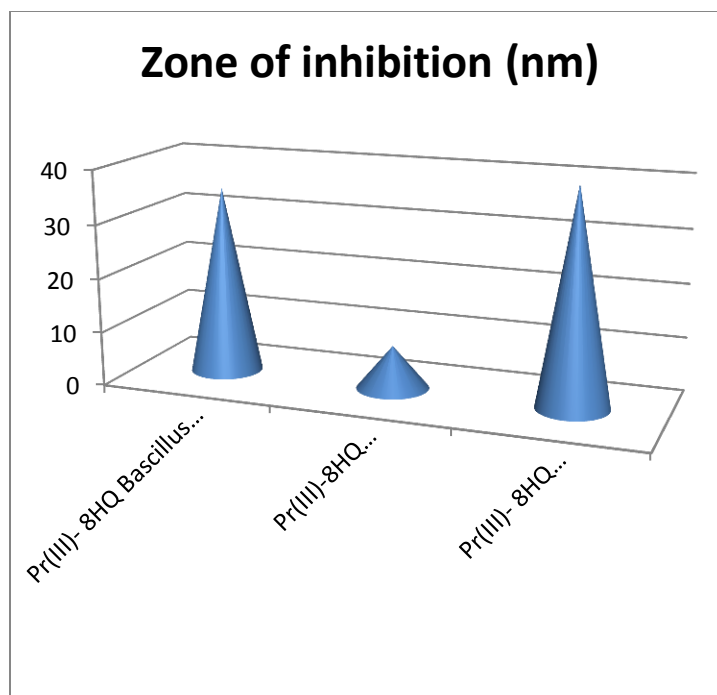
S.N.	Energy Levels	$\nu_c(\text{cm}^{-1})$ Obs	β	$b^{1/2}$	$\delta\%$	η
1	3P_2	23337.22	1.035	0.132	-3.382	-0.017
2	3P_1	21276.60	0.995	0.052	0.535	0.003
3	3P_0	20661.16	0.994	0.056	0.624	0.003
4	1D_2	16863.41	0.994	0.054	0.594	0.003

Table 8:- Computed value of energy interaction: Slater-Condon $F_k(\text{cm}^{-1})$, Spin-Orbit interaction Lande $\zeta_{4f}(\text{cm}^{-1})$ Racah $E_k(\text{cm}^{-1})$ parameters and Hydrogenic Ratio (F_4/F_2), (F_6/F_2) and (E_1/E_3), (E_2/E_3) of Pr (III)-8HQ Complexes in Alcoholic and micellar medium.

Complex		Pr(III)-8HQ	Pr(III)-8HQ	Pr(III)-8HQ	Pr(III)-8HQ
S.N.	Parameters	(EtOH)	(TX-100)	(HTAB)	(SDS)
1	E ₁	4421.05	4456.68	4454.50	4440.42
2	E ₂	23.13	23.31	23.30	23.23
3	E ₃	446.99	450.59	450.37	448.95
4	F ₂	301.12	303.55	303.40	302.44
5	F ₄	373.06	349.53	443.67	323.12
6	F ₆	26.57	25.04	31.35	23.24
7	ζ _{4f}	1184.83	1144.71	1262.39	1129.75
8	% _r ζ _{4f}	-64.45	-58.85	-73.46	-62.59
9	% _r F ₂	1.81	1.01	0.98	0.21
10	F ₄ /F ₂	1.239	1.151	1.462	1.068
11	F ₆ /F ₂	0.088	0.082	0.103	0.077
12	E ₁ /E ₃	9.891	9.891	9.891	9.891
13	E ₂ /E ₃	0.052	0.005	0.052	0.052

Table 9:- Biological Investigation of Pr (III)-8HQ Complex Against *Bacillus Subtilis*, *Escherichia coli*, *Staphylococcus aureus*.

S.N.	complexes	Zone of inhibition (in mm)
		100 ppm
1.	Pr(III)- 8HQ <i>Bacillus Subtilis</i>	35
2.	Pr(III)-8HQ <i>Escherichia coli</i>	8
3.	Pr(III)- 8HQ <i>Staphylococcus aureus</i>	40



Result and Discussion:-

The normal and derivative electronic spectrum of Pr(III) ion and Pr(III)-8HQ complex in different solvent in UV-visible regions are shown in Fig 1-2. The observed value of oscillator strength for Pr^{3+} complex along with their calculated value has been shown in table-1. The value of T_2 , T_4 and T_6 parameter was computed using Judd-Ofelt relation by partial multiple regression method for Pr(III)-complexes (Table-2). Comparative absorption spectra of Pr(III)-complexes in alcoholic and micellar medium (Fig-1) clearly show a significant enhancement in the oscillator strength and intensity parameter T_2 , T_4 and T_6 . It is observed that all three Judd-Ofelt parameters (T_2, T_4, T_6) have positive values. The reason for T_2 being negative for Pr(III)-8HQ in micellar medium has been attributed to f-d mixing. A similar conclusion was earlier made by Reisfeld(17). The wave numbers of the observed bands along with their assignments are presented in Table 3. Using the partial derivatives (9-11) for the Pr^{3+} ions and the calculated partial derivatives of the Pr^{3+} ion, the Racah (E^1, E^2, E^3), spin-orbit (ζ_{4f}) and the configuration interaction parameters were determined using the least squares fit method. They are presented in Table 8. The band positions have been calculated with these parameters. The rms deviations are reasonable. The intensities of the bands were measured only for the clear bands (15). The Judd-Ofelt intensity parameters were evaluated (Table 1) from the measured intensities of the absorption bands and the squared reduced matrix elements determined by the intermediate coupling scheme (11). The results are presented in Table 3. Derivative spectra would sometimes be helpful in resolving closely lying levels. It is very interesting to note that four bands $3P^2, 3P^1, 3P^0$ and $1D^2$. Each found split into two in the derivative spectrum shown in Fig. 2. However in all the complexes in to two components each. Although $3P^2$ have one additional component in TX -100 micellar medium and $3P^1$ have additional component in HTAB and in SDS micellar medium. A significant change in the oscillator strength of f-f transition (ie. $3H^4 \rightarrow 3P^2$) hypersensitive transitions(12). for Pr(III) ion have been observed in alcoholic and micellar medium has clearly revealed that a significant enhancement in the oscillator strength of f-f transition is observed. Structure activity relationship for Pr(III)-8HQ system following results were obtained as *Staphylococcus aureus* > Pr(III)-8HQ *Bacillus Subtilis* > Pr(III)-8HQ *Escherichia coli*

References:-

1. Wilkinson G, Gillard R and Mc J. Cleverty, *Comprehensive Coord. Chem Pergamon Press Oxford, Chapter 39. (1987).*
2. Misra S.N. and M. Indira Devi. *The synthesis and determination of the octacoordinated structure of Pr(III) and Nd(III) complexes with β -diketones and diols in non aqueous solutions: evidence of some participation of π -electron density of diols with Pr(III) and Nd(III) in complexation. Spectrochim. Acta A. (53) 1941-1946 (1997).*
3. Wybourne B G. *Spectroscopic Properties of Rare Earth. Inter Conference. New York (1955).*

4. Hufner S. *Optical Spectra of Transparent Rare Earth Compounds*. Academic Press, New York, (1978).
5. Mishr S N, Joshi G K and Bhutra M P, *Indian J. Chem.*, 21A(1982)278.
6. Mishra S N and Joshi G K, *Indian J. of Pure and Applied Chemistry*, 19(3) (1981)279.
7. Judd B R, *Phys. Rev.*, 127(1962)750.
8. Ofelt G S, *J. Chem. Phys.*, 37(1962)511.
9. Lakshman S. V. J. and Suresh Kumar A.. *J. Non-Cryst. Solids* 85, 162 (1986).
10. Lakshman S. V. J. and Jayasankar C. K., *Spectrochim. Acta. A* 48, 642 (1982). 16
11. Lakshman S. V. J. and Jayasankar C. K., *Proc. Indian Natn. Acad. A* 48, 642 (1982).
12. Jatolia S.N, Bhandari H.S, Bhojak N, *Int. A. R. J.Sc. Eng.Tech.*, 1, 4(2014)201
13. Carnall W T, Fields P R and K Rajnak, *J. Chem. Phys.*, 49 (1968)4424.
14. Carnall W T, Fields M H and Wybourn B C, *J.Chem.Phys.*, 42(11)(1965)3797.
15. Wybourn W G, *Spectroscopic properties of rare earth*, Interscience publishers, New York, (1965).
16. Wong E Y, *J. Chem. Phys.*, 35(1961)544.
17. R. Reisfeld, *Structure and Bonding*, 22 (1975) 123.