MICELLAR SPECTROPHOTOMETRIC STUDIES OF DOPED Pr(III) ION AND CODOPED WITH Ca^{+2}Mg^{+2},Sr^{+2} IONS WITH 2-HBT SYSTEM

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ABSTRACT

Electronic absorption studies of the complexes in solution state with benzothiazole derivative doped in Pr(III) ion and codoped with Ca^{+2}Mg^{+2},Sr^{+2}ions have been calculated in alcoholic (C$_2$H$_5$OH) as well as micellar in medium. In present work, we describes the spectral characterization of the complexes of benzothiazole derivative with Nd(III) ion and codoped with Ca^{+2}Mg^{+2},Sr^{+2} ions in agreement to Green chemistry approach. Various spectroscopic parameters viz- Intensity parameters: Oscillator strength(P$_{obs}$x10^{-6}), r.m.s. deviation (σ), Judd-Ofelt Parameter (T$_2$, T$_4$, T$_6$), Bonding parameters : Nephelauxetic ratio (β), Bonding(b$^{1/2}$), Sinha Covalency (δ %) and Covalency-Angular Overlap (η) Symmetry Parameter (T$_4$ / T$_2$)and Coordination Parameter (T$_4$ / T$_6$)have been computed using partial and multiple regression method. This work describes investigations on Nd(III) ion and codoped with Ca^{+2}Mg^{+2},Sr^{+2} systems with benzothiazole derivatives(2-HBT)in alcoholic as well as micellar in medium.

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Keywords: *Oscillator Strength, Spectral Characterization, Judd-Ofelt Parameter.*

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Introduction
Material and Method

Praseodymium chloride of 99.9% was purchased from Ms. Indian Earth limited and ligand were synthesized in our laboratory. 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, 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) upgraded with resolution and expansion of scale in the region 190nm to 1100nm at Green chemistry research center (GCRC).

Methods

Oscillator strength was calculated as a function of hyper sensitive transition. Judd-Oflet theory (1-2) predicts that the intensity of f-f transitions arise principally from forced electric dipole mechanism. Thus the electric dipole oscillator strength (P) is expressed as the product of T$_λ$(λ=2, 4, 6) parameters

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and appropriate transition matrix element U $^{(\lambda)}$ at frequency of transition J-J' the intensity of an absorption band is measured by Oscillator strength, which is directly proportional to area under the absorption curve.

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

here, ε_{max} = Molar Absorptivity or molar extinction Coefficient

The equation may be expressed in terms half band width

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

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

Where $[U^{(2)}]^2$, $[U^{(4)}]^2$, $[U^{(6)}]^2$ are matrix elements (9-10)

For hypersensitive transitions, oscillator strength (P) is found directly proportional to νT_6. This linear correlation has been proposed by R. D. Peacock (11).

$$K^{/} = P_{obs} \, / \, \nu_{obs} \text{x} T_6 \text{------------------------------------- (4)}$$

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$$T_2 = C_{11}\sum x_1 y + C_{12}\sum x_2 y + C_{13}\sum x_3 y \text{------------ (5)}$$

$$T_4 = C_{12}\sum x_1 y + C_{22}\sum x_2 y + C_{23}\sum x_3 y \text{------------ (6)}$$

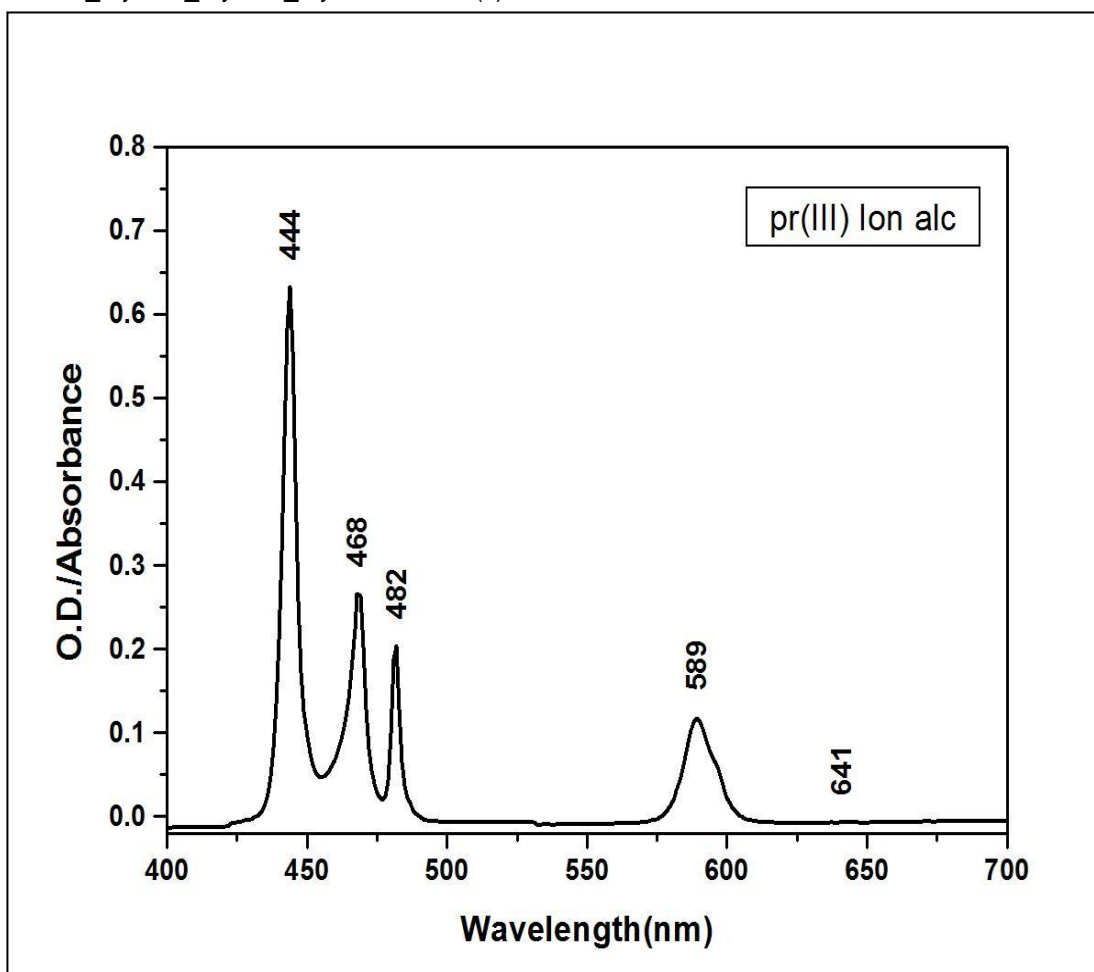$$T_6 = C_{13}\sum x_1 y + C_{23}\sum x_2 y + C_{33}\sum x_3 y \text{---------------- (7)}$$

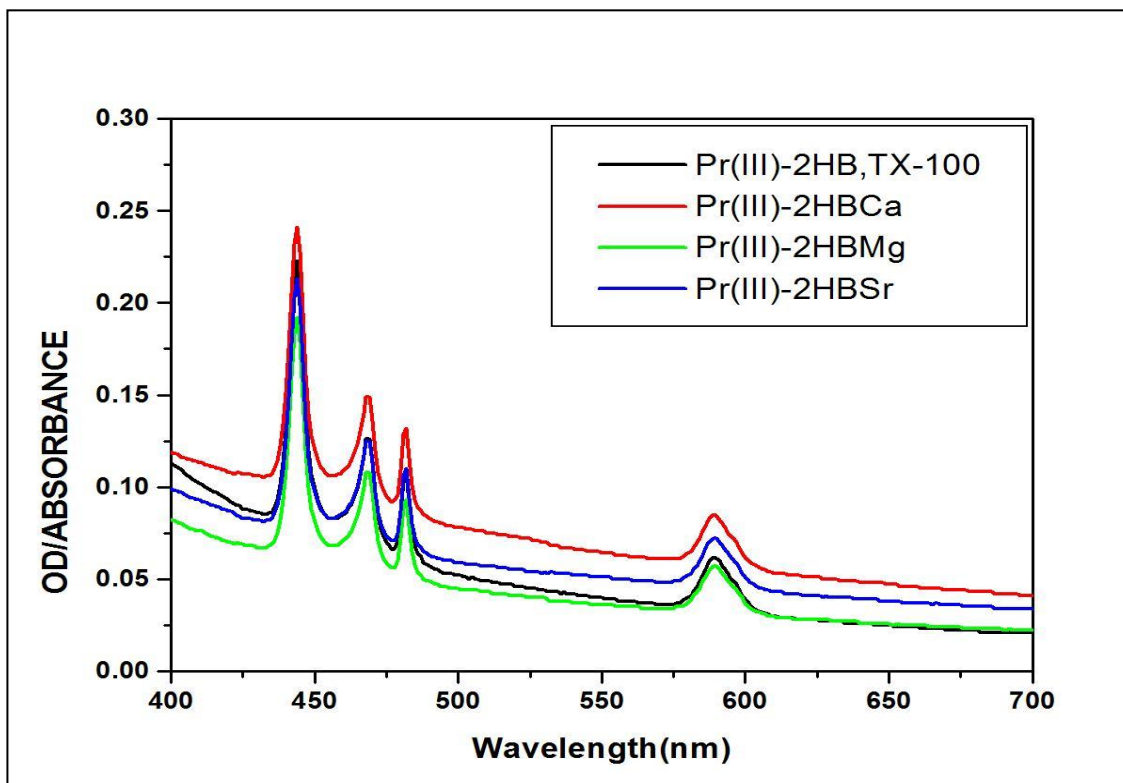

Figure 1: Room Temperature Absorption Spectra of Pr (III) Ion

Figure 2: Room Temperature Absorption Spectra of Pr(III)-2HBT-Ca^{+2}, Mg^{+2} and Sr^{+2} Doped System

Observed and calculated values of Oscillator strength (Px10^6) of various Absorption transitions ofPr(III)-2-HBT system in Micellar medium

Table 1

Complex		Pr(III)-2-HBT		Pr(III)-2-HBT-Ca^{+2}		Pr(III)-2-HBT-Mg^{+2}		Pr(III)-2-HBT-Sr^{+2}	
S. N.	Energy Levels	P_{obs}x10^6	P_{cal}x10^6	P_{obs}x10^6	P_{cal}x10^6	P_{obs}x10^6	P_{cal}x10^6	P_{obs}x10^6	P_{cal}x10^6
1	$^3H_4 \rightarrow ^3P_2$	5.306	6.191	43.742	43.662	8.042	5.1107	11.660	6.2911
2	$^3H_4 \rightarrow ^3P_1$	1.591	1.886	0.252	0.106	2.192	0.2189	7.162	0.1169
3	$^3H_4 \rightarrow ^3P_0$	2.553	2.650	1.310	0.107	1.380	0.2193	1.1907	0.1171
4	$^3H_4 \rightarrow ^1D_2$	1.056	2.516	4.532	6.630	5.080	4.6111	2.539	2.632
5	r.m.s.(σ) dev. (±)	3.263		6.080		3.238		4.393	

Computed values of juddOfelt Parameter (Tλ) ,Symmetry Parameter (T4/T2), and Coordination Parameter (T4/T6) of Pr(III)-2HBT Complex in micellar medium

Table 2

S.N.	Parameter	Pr(III)-2-HBT	Pr(III)-2-HBT-Ca^{+2}	Pr(III)-2-HBT-Mg^{+2}	Pr(III)-2-HBT-Sr^{+2}
1	T2 x 10^9	142.778	-0.238	-0.349	-1.128
2	T4 x 10^9	1.411	0.008	0.011	0.036
3	T6 x 10^9	5.204	3.931	5.769	18.603
4	T4/T6	0.271	0.002	0.002	0.002
5	T4/T2	0.010	-0.032	-0.032	-0.032

Observed and calculated value of Energy (cm^{-1}) of various energy level of Pr(III)-2HBT Complex in Micellar medium

Complex		Pr(III)-2-HBT		Pr(III)-2-HBT-Ca^{+2}		Pr(III)-2-HBT-Mg^{+2}		Pr(III)-2-HBT-Sr^{+2}	
S. No.	Levels	E$_{cal}$	E$_{obs}$	E$_{cal}$	E$_{obs}$	E$_{cal}$	E$_{obs}$	E$_{cal}$	E$_{obs}$
1	$^3P_2$	22523.1	22522.5	22447.2	22446.6	22523.0	22522.5	22472.4	22471.9
2	$^3P_1$	21344.8	21344.7	21322.0	21322.0	21344.8	21344.7	21322.0	21322.0
3	$^3P_0$	20767.3	20768.4	20681.6	20682.5	20745.9	20746.9	20724.6	20725.4
4	$^1D_2$	16949.4	16949.2	16963.7	16963.5	16963.7	16963.5	17007.0	17006.8

Results and Discussion

The computed values of the data have been tabulated in (Table-1 –3). This clearly shows a significant change in the oscillator strength of f-f transition particularly for $^3H_4 \rightarrow {}^3P_2$ transition of Pr (III) ion. Comparative absorption spectra of Pr (III)-complexes in micellar medium (13-16) (Fig.1 to 2) clearly show a significant enhancement in the oscillator strength of f-f transition. From data it is clear that Pr (III)-2HBT complex show maximum variation in all parameters in all system when there is codoping of ca^{+2} mg^{+2} and sr^{+2} ion

- Observed oscillator strength (P$_{obs}$) ca^{+2}>sr^{+2}>mg^{+2}

Conclusion

The significance of thermodynamic parameters are that there are more covalent characteror metal-ligand interaction between Pr(III)-2HBT complex in micellar medium.

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