

# Effect of solvent on sensitivity of hypersensitive transition for Pr (III) complexes with quinoline derivatives in doped system

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**Abstract:** Studies on the oscillator strength as Judd-Oflet parameters (1,2) were carried out for some f-f transitions specially on Hypersensitive or pseudoquadrupolar transitions for Pr (III) complexes with N and O containing ligands (viz: 2-Hydroxyquinoline, 8-Hydroxyquinoline, and 8-Aminoquinoline) in organic (Et-OH) as well as micellar medium as a doped system. The oscillator strength was calculated by Judd-Oflet method. The variation in oscillator strength ( $P_{obs} \times 10^6$ ) as well as in Judd-Oflet Parameter  $T_2 \times 10^9$  was reported as solvent changed.

**Keywords:** Pr (III), Quinoline Derivatives, oscillator strength and TET

## I. INTRODUCTION

Certain absorption band due to f-f transitions of lanthanide is particularly susceptible to intensity change and splitting. These are termed as hypersensitive transitions. The intensity of some absorption line in the solution spectra of rare earth ions is sensitive to the solvent. Generally the intensity of hypersensitive transitions is directly proportional to the basic nature of the ligand as well as the number of coordinating ligand and inversely proportional to the Metal-Ligand bond distance. An extensive study about Hyper sensitive transitions has been made by Karraker (3-4) particularly for Nd (III), Ho (III) and Er (III) complexes of  $\beta$ -diketone having 6, 7 and 8 coordination number. The Hypersensitive or pseudoquadrupolar transitions obey the selection rule  $\Delta J \leq 2$ . The term on Hypersensitive refer to the transitions which show a relatively large variability in the magnitude of oscillator strength caused by the eigen perturbation (5-6). In our case hypersensitive transitions for Pr (III)  $^3H_4 \rightarrow ^3P_2$  the Hyper sensitive transitions show a significant Red shift. The higher values of P and  $T_\lambda$  parameters of salt solutions in comparison to Pr (III) aqueous solutions show an involvement of 4f-orbital of Pr (III) ion. In the past year change in magnitude of oscillator strength of Hyper sensitive transition were successfully used to determine the stability constant as a function of ligand concentration.

## II. 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<sup>-2</sup> M, Sodium Dodecyl sulphate, (SDS) of 75 CMC (0.05 M), and Hexadecyl Trimethyl Ammonium Absorption spectra of each solution at room temperature in  $P_{cal} = T_2 v [U^{(2)}]^2 + T_4 [U^{(4)}]^2 + T_6 v [U^{(6)}]^2$  ----- (3)

Bromide, (HTAB) of 100 CMC (9.2 x 10<sup>-2</sup> M) is used for preparing saturated solution of ligand and metal.

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), 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<sup>-2</sup> M, Sodium Dodecyl sulphate, (SDS) of 75 CMC (0.05 M), and Hexadecyl Trimethyl Ammonium Bromide, (HTAB) of 100 CMC (9.2 x 10<sup>-2</sup> 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). 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  $T_\lambda$  ( $\lambda=2, 4, 6$ ) parameters 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.  $P = 4.315 \times 10^{-9} \int \epsilon dv$  ----- (1)

Here,  $\epsilon_{max}$  = Molar Absorptivity or molar extinction Coefficient = O.D. / C x L

The equation may be expressed in terms half band width

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

OD = Optical Density or Absorbance

C = Concentration

L = Path Length

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

$$\Delta v^{1/2} = \{1/(\lambda - 0.5bw) - 1/(\lambda + 0.5bw)\} \times 10^{-7}$$

Where  $[U^{(2)}]^2$ ,  $[U^{(4)}]^2$ ,  $[U^{(6)}]^2$  are matrix elements (7-8)

For hypersensitive transitions, oscillator strength (P) is found directly proportional to  $vT_6$ . This linear correlation

has been proposed by R. D. Peacock (9). addition to spectral parameters for hypersensitive transitions (12-13).  

$$K^{\prime} = P_{obs} / v_{obs} \times T_6 \dots \dots \dots (4)$$

Thermodynamic parameters may also support covalency (if any in the systems), in metal-ligand interaction in TET =  $\frac{A}{E_{obs}}$  ..... (5)

**TABLE I**  
Observed and calculated values of thermodynamic parameters of HyperSensitive Transition for Pr (III) doped system in alcoholic (Et-OH) medium

Hyper.Sens.Trans.		Energy cm <sup>-1</sup>		oscillato Strength		Thermodynamic Efficiency of transition		Peacock Constant
<sup>3</sup> H <sub>4</sub> → <sup>3</sup> P <sub>2</sub>								
S.N	complex	E <sub>obs</sub>	E <sub>cal</sub>	P <sub>obs</sub> ×10 <sup>6</sup>	P <sub>cal</sub> ×10 <sup>6</sup>	TET <sub>obs</sub> ×10 <sup>17</sup>	TET <sub>cal</sub> ×10 <sup>17</sup>	K <sup>∧</sup>
1	Pr(III)-2HQ	22522.52	22523.17	14.627	27.386	0.9962	0.9965	0.1248
2	Pr(III)-8HQ	23337.22	23334.72	29.371	193.952	0.9966	0.9972	0.0552
3	Pr(III)-8AQ	22246.94	22249.19	5.305	10.191	0.9958	0.9961	0.1560

**TABLE II**  
Observed and calculated values of thermodynamic parameters of Hypersensitive Transition for Pr (III) doped system in micellar (TX-100) medium

Hyper.Sens.Trans.		Energy cm <sup>-1</sup>		oscillato Strength		Thermodynamic Efficiency of transition		Peacock Constant
<sup>3</sup> H <sub>4</sub> → <sup>3</sup> P <sub>2</sub>								
S.N	complex	E <sub>obs</sub>	E <sub>cal</sub>	P <sub>obs</sub> ×10 <sup>6</sup>	P <sub>cal</sub> ×10 <sup>6</sup>	TET <sub>obs</sub> ×10 <sup>17</sup>	TET <sub>cal</sub> ×10 <sup>17</sup>	K <sup>∧</sup>
1	Pr(III)-2HQ	22446.60	22447.18	12.019	12.019	0.9962	0.9961	0.1746
2	Pr(III)-8HQ	23337.22	23334.80	51.401	50.864	0.9968	0.9969	0.1376
3	Pr(III)-8AQ	23337.22	23374.84	43.741	43.662	0.9968	0.9967	0.9967

**TABLE III**  
Observed and calculated values of thermodynamic parameters of Hypersensitive Transition for Pr (III) doped system in micellar (HTAB) medium

Hyper.Sens.Trans.		Energy cm <sup>-1</sup>		oscillato Strength		Thermodynamic Efficiency of transition		Peacock Constant
<sup>3</sup> H <sub>4</sub> → <sup>3</sup> P <sub>2</sub>								
S.N	complex	E <sub>obs</sub>	E <sub>cal</sub>	P <sub>obs</sub> ×10 <sup>6</sup>	P <sub>cal</sub> ×10 <sup>6</sup>	TET <sub>obs</sub> ×10 <sup>17</sup>	TET <sub>cal</sub> ×10 <sup>17</sup>	K <sup>∧</sup>
1	Pr(III)-2HQ	22522.50	22523.01	0.207	17.696	0.9964	0.9963	0.1593
2	Pr(III)-8HQ	23577.10	23553.94	66.844	60.684	0.9969	0.9968	0.1500
3	Pr(III)-8AQ	22522.20	22523.23	14.042	12.106	0.9963	0.9962	0.1579

**TABLE IV**  
Observed and calculated values of thermodynamic parameters of Hypersensitive Transition for Pr (III) doped system in micellar (SDS) medium

Hyper.Sens.Trans.		Energy cm <sup>-1</sup>		oscillato Strength		Thermodynamic Efficiency of transition		Peacock Constant
<sup>3</sup> H <sub>4</sub> → <sup>3</sup> P <sub>2</sub>								
S.N	complex	E <sub>obs</sub>	E <sub>cal</sub>	P <sub>obs</sub> ×10 <sup>6</sup>	P <sub>cal</sub> ×10 <sup>6</sup>	TET <sub>obs</sub> ×10 <sup>17</sup>	TET <sub>cal</sub> ×10 <sup>17</sup>	K <sup>∧</sup>
1	Pr(III)-2HQ	22471.90	22472.39	9.5336	7.515	0.99612	0.9960	0.1727
2	Pr(III)-8HQ	23310.02	23307.83	65.296	59.064	0.9968	0.9966	0.1505
3	Pr(III)-8AQ	22197.50	22199.02	11.66	6.911	0.9961	0.9960	0.2297

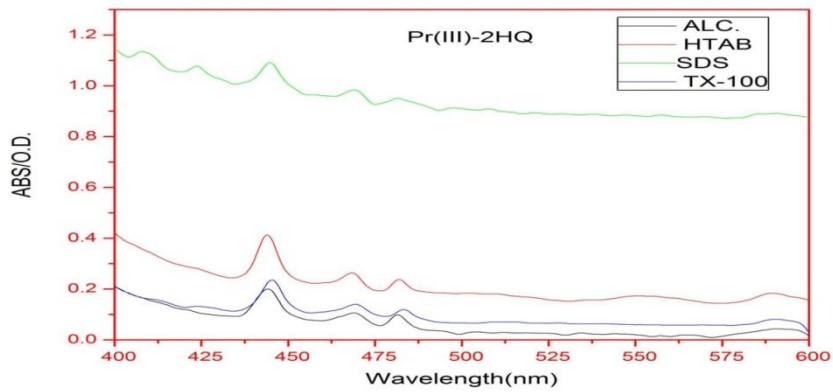


Fig.1 Variation of optical density with wavelength for Pr (III)-2HQ complex in different solvent

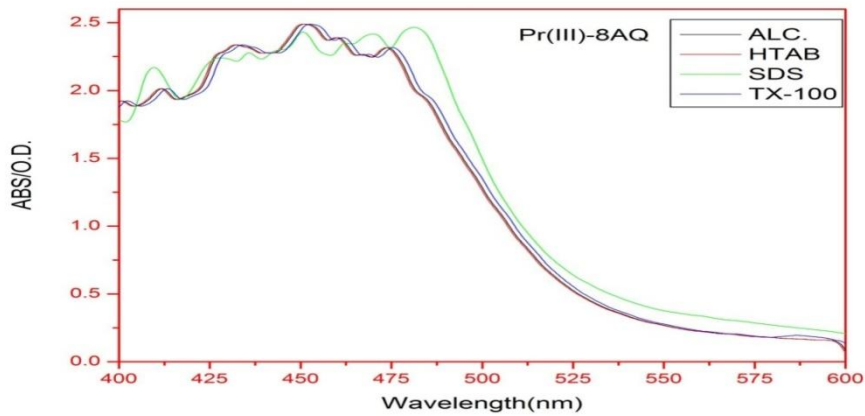


Fig.2 Variation of optical density with wavelength for Pr (III)-8AQ complex in different solvent

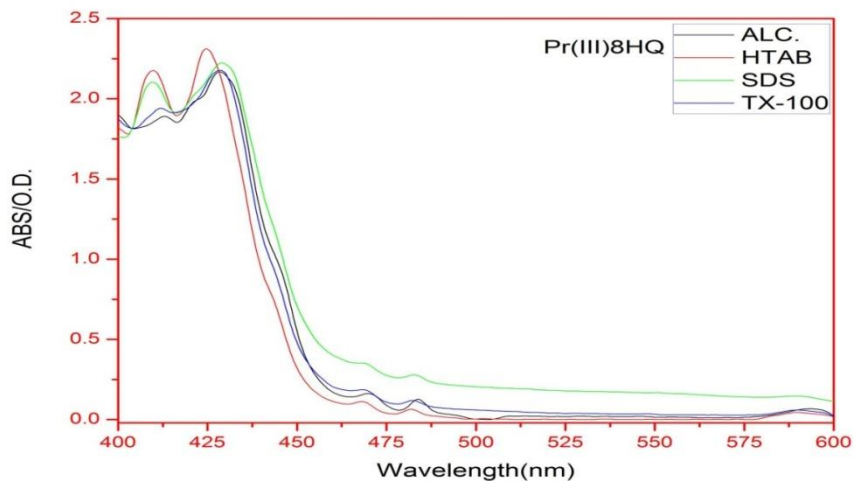


Fig.3 Variation of optical density with wavelength for Pr (III)-8HQ complex in different solvent

### III. RESULT AND DISCUSSION

The absolute value of oscillator strength and TET are determined under different experimental condition for Ln (III)-complexes (Table-1–IV). A significant change in the oscillator strength of f-f transition ( i.e.  $^3H_4 \rightarrow ^3P_2$ ) for Pr (III) ion have been observed. In fig 1 to 3 a comparative absorption spectra of Pr (III)-complexes in alcoholic and micellar medium has clearly revealed that a significant enhancement in the oscillator strength of f-f transition is observed which is in agreement with previous studies (13-14). In the present study the value of Peacock constant has been found to be constant in (HTAB) medium which signifies the validity of Judd-Oflet Theory.

### IV. CONCLUSION

The results reported in this study indicated that Pr (III) Complexes with quinoline derivatives with nitrogen and oxygen donor ligands creates high degree of intensification to hypersensitive transitions in different medium. Thus hypersensitive transitions can be used to study for instance the metal–ligand interaction in complexes.

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### BIOGRAPHY



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