

Comparative 4f-4f Spectral Analysis of Simultaneous Complexation of Pr(III) with L-Tryptophan in Presence and Absence of Ca²⁺ and Zn²⁺ Ions in Aqueous Medium: Energy, Intensity and Kinetic Studies

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The spectral analysis of the complexation of praseodymium (Pr³⁺) with L-tryptophan in various aqueous solvent applying a quantitative probe of 4f-4f transition spectra. The study is carried out by calculating various energy interaction parameters such as the nephelauxetic effect (β), percent covalency (δ), bonding parameter ($b^{1/2}$), Slater-Condon (F_k) and intensity parameters like oscillator strength (P) and intensity of Judd-Ofelt parameters T_λ ($\lambda = 2, 4, 6$). The paramagnetic behaviour of Pr³⁺ shows $^3H_4 \rightarrow ^1D_2$, $^3H_4 \rightarrow ^3P_0$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_2$ types of specific 4f-4f absorption bands and are observed at the visible region of 427-610 nm. The intensities of 4f-4f transition bands rise on the addition of Ca²⁺ and Zn²⁺ ions toward the complexation of praseodymium (Pr³⁺):Try and extended result in the case of Ca²⁺ ion compared to the Zn²⁺ ion due to increase in the interaction between ligand and 4f orbital of metal ions. These bands on immediate minor's coordination change around praseodymium (Pr³⁺) found to be highly sensitive due to the formation of heterobimetallic complex between L-tryptophan (Try) with Pr³⁺ in the existence of Zn²⁺ and Ca²⁺ ions. The complexation of Try with Pr³⁺ in the presence of Zn²⁺ and Ca²⁺ ions are monitored simultaneously from the sensitivity of the bands using energy parameters and oscillator strength. The rate of heterobimetallic complexation of both Zn²⁺ and Ca²⁺ ions was calculated from the 4f-4f transition at different temperatures. The thermodynamic parameters and activation energy calculated from the rate constants from different temperatures are more favourable in case of Try form complex with Pr³⁺ in the presence of Ca²⁺ ion as compared to Zn²⁺ ion.

Keywords: Nephelauxetic effect, Judd-Ofelt, Heterobimetallic, Oscillator strength, L-Tryptophan.

INTRODUCTION

The potential properties of the lanthanide complex for photoluminescent and many fields of applications have become attentiveness in research. Due to the spectral properties and isomorphous character of lanthanides is used as a technique of investigation in the biological and chemical mechanism involving zinc and calcium [1-3]. The comparable properties of lanthanide with calcium and zinc are the coordination number, ionic radii, the binding pattern [4]. Hence, lanthanide is used as an effective probe in determining the coordination and isomorphous character between calcium and zinc toward the complexation. The importance of calcium and zinc can explain by the study of lanthanide complexation with amino acids [5,6]. From the above properties, may be understandable the biological system and metal protein reaction. Some of the amino acids

are essential in human body since it considerably helps in the hormone melatonin production, the nervous system and also enzyme and protein synthesis. (2S)-2-Amino-3-(1H-indol-3-yl)-propionic acid (Try) has a unique structure, R-carbon or β -carbon bind with a side chain of indole ring so it is a non-polar aromatic amino acid but nitrogen present in indole ring gives polarity to the amino acid [7,8]. Try gives a peculiar role in protein folding conformation [9] and the recreation mechanism of different polypeptides and proteins [10].

In L-tryptophan due to -COOH group and nitrogen atom show unique complexation with lanthanides ions and gives interesting bio-logical and theoretical properties. Calcium and zinc ions do not exhibit sharp absorption in contrast to lanthanide ions in UV-visible regions due to Laported forbidden 4f-4f transition or obeying selection rule [11]. The absorption spectra are sensitive in the bonding of metal-ligand and symmetry of

complexation. This sensitivity helps to explain the inner and outer coordination sphere, binding position, degree of covalency nature. These bands are termed as “hypersensitive transition” [12]. The hypersensitive transition becomes an interesting topic for theoretical and experimental studies [13,14]. The special character shown by the hypersensitive transition in band transitions and oscillator strengths can be used as a probe in coordination geometry, complex formation, ligand structure and solvent effect in complexation [15] to explain the binding nature of bovine serum albumin (BSA) with Pr^{3+} and draw out this application.

Currently, both the transitions (hypersensitive and non-hypersensitive) band intensities and shape are also used to explain the change in $4f-4f$ transition spectra of Er^{3+} , Pr^{3+} and Ho^{3+} on complexation with 2,2'-bipyridine and thiocyanate (SCN^-) [16,17]. From the present studies, the complexation and behaviour change of Pr^{3+} with L-tryptophan (Try) on simultaneous addition of Zn^{2+} and Ca^{2+} ions, it is observed that the variation of $4f-4f$ absorption spectra with an increase in time and comparing the feasibility of complexation between the Zn^{2+} and Ca^{2+} ions. The metalloprotein coordination of Zn^{2+} and Ca^{2+} ions from stable complexes *in vitro* and *in vivo* [18]. Hence, Zn^{2+} and Ca^{2+} ions may involve simultaneously in the heterobimetallic complex of Try with praseodymium (Pr^{3+}). From complexation, the intensity and energy interaction parameters are calculated and used in explaining the ligand and metal ions bonding from the variation of these parameters.

The absorption spectra of the above complexes in different organic solvents are reported. With the peripheral change in coordination about Pr^{3+} , the sensitivity and intensity of $4f-4f$ transition bands also change with the oscillator strength and can be utilized in explaining the coordination between Try and Pr^{3+} in simultaneous addition of Zn^{2+} and Ca^{2+} ions. The rate of reaction of both the Zn^{2+} and Ca^{2+} ions complex with Try and Pr^{3+} are studied at different temperatures, the activation energy, thermodynamic parameters are calculated. From the kinetics and thermodynamic parameters, the heterobimetallic complex formation between the Ca^{2+} and Pr^{3+} with tryptophan are more feasible than Zn^{2+} .

EXPERIMENTAL

Praseodymium hexahydrate ($\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99% purity) was purchased from Central Drug House (P) Ltd. India, whereas L-tryptophan (Try) was purchased from Sigma-Aldrich used without purification. The organic solvents were acetonitrile, dioxane, methanol and dimethylformamide (DMF) of A.R. grade from E. Merck. Perkin-Elmer lambda-35 UV-Vis spectrometer was used for recording the absorption spectra of praseodymium (Pr^{3+}) with Try and simultaneous addition of Zn^{2+} and Ca^{2+} ions. For the kinetics studies, the required temperature *i.e.* 298, 303, 308 and 313 K were conserved by Peltier temperature controller.

Praseodymium nitrate (10^{-2} mol/L) and Try (10^{-2} mol/L) were mixed to form the complex ($\text{Pr}^{3+}:\text{Try}$). Zinc nitrate and calcium nitrate (10^{-2} mol/L) were further added to the complex solution in aqueous DMF solvent. The variation in $4f-4f$ transition, bonding parameters and oscillator strength were used as a probe in explaining the complex formation and the preferable

comparative study of heterobimetallic complex formation between Zn^{2+} and Ca^{2+} ions.

Methods

In the comparative absorption spectra, the energy (E_{so}) appears from two components: the spin-orbital interaction (A_{so}) and angular part of static electric charges (F_k).

$$E_{\text{so}} = \sum F_k + A_{\text{so}} \xi_{4f} \quad (1)$$

Here Lande's parameter (ξ_{4f}) is the radial integral part. Applying representation operator technique, the required values can be calculated. To determine $4f^n$ energy configuration the required four radial integrals parameters were F_2 , F_4 , F_6 and ξ_{4f} [19,20]. Wong gives the energy E_j of the j^{th} level by first order approximation [21] as:

$$E_j(F_k, \xi_{4f}) = F_{0j}(F_k^0, \xi_{4f}^0) + \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \quad (2)$$

where the energy of zero order at j^{th} level is E_{0j} and the partial

derivatives are $\left(\frac{\delta E_j}{\delta \xi_{4f}}\right)$, $\left(\frac{\delta E_j}{\delta F_k}\right)$. The least square technique is

used in calculating the correction values of F_k and put in the zero-order parameter to acquire the values of F_2 , F_4 , F_6 and ξ_{4f} . Thus

$$F_k = F_k^0 + \Delta F \quad (3)$$

$$\xi_{4f} = \xi_{4f}^0 + \Delta \xi_{4f} \quad (4)$$

The red shift in the spectra of all electronic transitions explains the complexation. The red shift is the main reason for the extension of metal electron cloud and decrease of Racah parameter or inter-electronic repulsion suggest that the complex has larger orbitals than the metal ion. The above experience is known as nephelauxetic effect (β) and used in calculating the change in F_k with free ions as:

$$\beta_1 = \frac{F_k^c}{F_k^f}$$

$$\beta_2 = \frac{\xi_{4f}^c}{\xi_{4f}^f}$$

$$\bar{\beta} = \frac{\beta_1 + \beta_2}{2} \quad (5)$$

where F_k^c ($k = 2, 4, 6$) are the different parameters of complex and free ions by F_k^f . The chemical bonding and intermixing of ligand orbital with metal $4f$ -orbital calculate from the bonding parameter $b^{1/2}$ and also used in measuring covalency nature of metal-ligand bond known as percent covalency $\delta\%$. Percent covalency and nephelauxetic ratio are related [22] and defined as:

$$b^{1/2} = \left(1 - \frac{\beta}{2}\right)^{1/2}$$

$$\delta = \left(1 - \frac{\beta}{2}\right) \times 100 \quad (6)$$

Oscillator strength (P_{obs}) are experimentally determined and used in measuring the absorption spectral band intensity given by Gaussian equation [23,24] as:

$$P = 4.6 \times 10^{-9} \times \epsilon_{\text{max}} \times \Delta\nu_{1/2} \quad (7)$$

where, the molar extinction coefficient is ϵ_{max} and the half band width is $\Delta\nu_{1/2}$. Judd-Ofelt give the idea of electric dipole oscillator strength (P_{obs}) as the intensity parameter of 4f-4f crystal field transition of lanthanides (Pr^{3+} , Nd^{3+} and Eu^{3+}) [25]. The calculated oscillator strength (P_{cal}) of electric dipole are concern with transition $\langle f^n \psi_J | f^n \psi_J^* \rangle$ of energy ($\bar{\nu}$, cm^{-1}) can be express as:

$$P_{\text{cal}} = \sum_{\lambda=2,4,6} T_{\lambda} \bar{\nu} \langle f^n \psi_J | U^{(\lambda)} | f^n \psi_J^* \rangle \quad (8)$$

The three electric dipole or Judd-Ofelt intensity parameters T_{λ} ($\lambda = 2, 4, 6$) homologous to the radial wave function ($4f^n$). Being perturbing configuration to the above wave function and ligand field parameters help in explaining the change of environment around the metal ion. The value of square matrix elements $U^{(\lambda)}$ taken from Carnall *et al.* [26,27]. The T_{λ} ($\lambda = 2, 4, 6$) parameters are calculated using the partial multiple linear regression method.

$$\frac{P_{\text{obs}}}{\bar{\nu}} = [U^{(2)}]^2 \cdot T_2 + [U^{(4)}]^2 \cdot T_4 + [U^{(6)}]^2 \cdot T_6 \quad (9)$$

The two activation energy (E_a) of praseodymium (Pr^{3+}): Try with Zn^{2+} and Ca^{2+} ions are simultaneously calculated for the comparison of the feasibility of complex formation using the graph of $\ln K$ versus $1/T$ of Arrhenius equation.

$$E_a = \text{Slope} \times R \quad (10)$$

The slope observed from the graph of $\ln K$ versus $1/T$ and the observed intercept of the linear plots of van't Hoff are used for thermodynamic parameters calculated.

$$\ln k = -\frac{\Delta G}{RT} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (11)$$

RESULTS AND DISCUSSION

The red shift observed in praseodymium (Pr^{3+}) complex, known as the nephelauxetic effect is used in determining metal-ligand mode of bonding. It is also observed the decline in spin-orbital (ξ_{4f}), Slater-Condon (F_k) and interelectronic repulsion parameters due to an extension of wave functions between the metal and ligand. Lanthanide shows the electrostatic nature of bonding due to Ln^{3+} ions are hard metal ions and highly favour in bond formation with non-polarizable donor atoms such as nitrogen and oxygen atoms. In Table-1 comparing with free ions the values of complexation have remarkable changes and more within Zn^{2+} and Ca^{2+} ions. The positive value of the bonding parameter ($b^{1/2}$) and minor variation in percentage covalency (δ) suggested that the bonding between ligand and metal have a covalent character. A notable increase was observed in bands oscillator strength and higher in the magnitude of 4f-4f transition. The observed values and calculated Judd-Ofelt or electric dipole intensity parameters T_{λ} ($\lambda = 2, 4, 6$) and oscillator strength values are shown in Table-2. In addition to Try with Pr^{3+} , a significant magnification in the intensity parameters T_{λ}

TABLE-1
CALCULATED VALUES OF ENERGY INTERACTION SLATER CONDON (F_k), SPIN ORBITAL INTERACTION (ξ_{4f}), THE NEPHELAUXETIC RATIO (β), BONDING PARAMETER ($b^{1/2}$) AND COVALENCY (δ) OF Pr^{3+} , Pr^{3+} :Try, Pr^{3+} :Try:Ca²⁺, Pr^{3+} :Try:Zn²⁺ SYSTEM AT AQUEOUS AND ORGANIC SOLVENT

Solvent	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
Water							
Pr^{3+}	309.26	42.693	4.67	722.75	0.9474	0.1621	309.26
Pr^{3+} :Try	309.27	42.686	4.669	722.77	0.9474	0.1622	309.2
Pr^{3+} :Try:Ca ²⁺	309.29	42.686	4.669	722.77	0.9474	0.1622	309.2
Pr^{3+} :Try:Zn ²⁺	309.28	42.686	4.669	722.77	0.9474	0.1622	309.2
Methanol							
Pr^{3+}	308.30	42.561	4.655	718.88	0.9434	0.1682	308.3
Pr^{3+} :Try	308.43	42.579	4.657	720.64	0.9448	0.1661	308.43
Pr^{3+} :Try:Ca ²⁺	308.97	42.653	4.665	719.59	0.9449	0.166	308.97
Pr^{3+} :Try:Zn ²⁺	308.96	42.652	4.663	719.58	0.9447	0.166	308.96
DMF							
Pr^{3+}	307.91	42.507	4.649	721.1	0.9443	0.1668	307.91
Pr^{3+} :Try	307.91	42.507	4.649	721.1	0.9443	0.1668	307.91
Pr^{3+} :Try:Ca ²⁺	307.82	42.494	4.648	720.25	0.9436	0.1679	307.82
Pr^{3+} :Try:Zn ²⁺	307.81	42.493	4.648	720.37	0.9437	0.1678	307.81
DXN							
Pr^{3+}	308.08	42.531	4.652	723.21	0.946	0.1642	308.08
Pr^{3+} :Try	308.09	42.532	4.652	717	0.9418	0.1706	308.09
Pr^{3+} :Try:Ca ²⁺	308.42	42.577	4.657	721.17	0.9451	0.1656	308.42
Pr^{3+} :Try:Zn ²⁺	308.49	42.588	4.658	720.61	0.9449	0.166	308.49
CH ₃ CN							
Pr^{3+}	308.29	42.559	4.655	718.51	0.9431	0.1686	308.29
Pr^{3+} :Try	308.11	42.535	4.653	724.54	0.947	0.1628	308.11
Pr^{3+} :Try:Ca ²⁺	308.95	42.65	4.665	719.02	0.9444	0.1667	308.95
Pr^{3+} :Try:Zn ²⁺	309.07	42.667	4.667	720.89	0.9459	0.1645	309.07

TABLE-2
OBSERVED AND CALCULATED VALUE OF OSCILLATOR STRENGTHS ($P \times 10^6$) AND JUDD-OFELT ($T_i \times 10^{10}$)
PARAMETER Pr^{3+} , $\text{Pr}^{3+}:\text{Try}$, $\text{Pr}^{3+}:\text{Try}:\text{Ca}^{2+}$, $\text{Pr}^{3+}:\text{Try}:\text{Zn}^{2+}$ IN AQUEOUS AND DIFFERENT ORGANIC SOLVENT

Solvent	${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$	${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$	${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$	${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$	T_2	T_2	T_4	RMS
	$P_{\text{(obs)}} (P_{\text{(cal)}})$	$P_{\text{(obs)}} (P_{\text{(cal)}})$	$P_{\text{(obs)}} (P_{\text{(cal)}})$	$P_{\text{(obs)}} (P_{\text{(cal)}})$				
Water								
Pr^{3+}	3.6084 (3.6084)	1.077 (1.077)	0.531 (0.522)	0.828 (0.828)	-51.453	2.219	11.229	102.95
$\text{Pr}^{3+}:\text{Try}$	3.4519 (3.4519)	1.037 (1.037)	0.4776 (0.47)	0.905 (0.9049)	-23.724	2.091	10.752	97.81
$\text{Pr}^{3+}:\text{Try}:\text{Ca}^{2+}$	3.2743 (3.2743)	0.962 (0.962)	0.4588 (0.451)	0.873 (0.8725)	-19.253	1.962	10.205	98.20
$\text{Pr}^{3+}:\text{Try}:\text{Zn}^{2+}$	3.1596 (3.1596)	0.925 (0.925)	0.4333 (0.426)	0.749 (0.7488)	-39.661	1.875	9.852	98.20
CH_3OH								
Pr^{3+}	2.8474 (2.8474)	0.573 (0.573)	0.3632 (0.358)	0.095 (0.095)	-166.885	1.297	9.005	147.44
$\text{Pr}^{3+}:\text{Try}$	4.0822 (4.0822)	0.847 (0.847)	0.4867 (0.48)	1.126 (1.1257)	-14.017	1.847	12.913	123.24
$\text{Pr}^{3+}:\text{Try}:\text{Ca}^{2+}$	4.3953 (4.3953)	0.838 (0.838)	0.5106 (0.502)	1.393 (1.3926)	25.702	1.863	13.937	121.22
$\text{Pr}^{3+}:\text{Try}:\text{Zn}^{2+}$	4.3953 (4.3953)	0.838 (0.838)	0.5106 (0.502)	1.393 (1.3926)	25.702	1.863	13.937	121.22
DMF								
Pr^{3+}	5.3455 (5.3455)	1.043 (1.043)	0.6183 (0.611)	1.26 (1.2604)	-67.139	2.302	16.979	130.46
$\text{Pr}^{3+}:\text{Try}$	5.6813 (5.6813)	1.198 (1.198)	0.4878 (0.482)	1.952 (1.9521)	68.497	2.336	18.076	123.49
$\text{Pr}^{3+}:\text{Try}:\text{Ca}^{2+}$	5.7829 (5.7829)	1.216 (1.216)	0.6662 (0.658)	1.998 (1.9979)	71.875	2.61	18.337	122.42
$\text{Pr}^{3+}:\text{Try}:\text{Zn}^{2+}$	5.884 (5.884)	1.349 (1.349)	0.7267 (0.716)	1.683 (1.6832)	-6.848	2.873	18.599	132.53
DXN								
Pr^{3+}	0.8198 (0.8198)	0.476 (0.476)	0.1668 (0.165)	0.301 (0.3009)	13.844	0.887	2.453	158.10
$\text{Pr}^{3+}:\text{Try}$	1.1884 (1.1884)	1.073 (1.073)	0.3927 (0.387)	0.898 (0.898)	125.694	2.025	3.358	189.63
$\text{Pr}^{3+}:\text{Try}:\text{Ca}^{2+}$	2.1806 (2.1806)	1.055 (1.055)	0.1927 (0.19)	0.468 (0.4682)	-38.66	1.721	6.701	126.02
$\text{Pr}^{3+}:\text{Try}:\text{Zn}^{2+}$	2.0157 (2.0157)	0.704 (0.704)	0.625 (0.616)	1.232 (1.2318)	146.454	1.84	6.124	145.87
CH_3CN								
Pr^{3+}	5.884 (5.884)	1.349 (1.349)	0.7267 (0.716)	1.683 (1.6832)	-6.848	2.873	18.599	132.53
$\text{Pr}^{3+}:\text{Try}$	3.6044 (3.6044)	0.386 (0.386)	0.2969 (0.293)	0.708 (0.7076)	-75.956	0.946	11.558	150.22
$\text{Pr}^{3+}:\text{Try}:\text{Ca}^{2+}$	3.9879 (3.9879)	0.693 (0.693)	0.4659 (0.458)	0.847 (0.8467)	-71.128	1.602	12.668	129.81
$\text{Pr}^{3+}:\text{Try}:\text{Zn}^{2+}$	4.2275 (4.2275)	0.78 (0.78)	0.5115 (0.503)	9.044 (9.0438)	1776.403	1.785	13.376	123.94

($\lambda = 2, 4, 6$) and oscillator strength is observed. The $4f$ orbital of metal interact with ligand wave function were determined from the strengthening of $4f-4f$ bands. The hetero bimetallic complexation of Ca^{2+} ions have notable intensity of $4f-4f$ transitions as compare to Zn^{2+} ion and binary complexation of Try with Pr^{3+} as shown in Fig. 1.

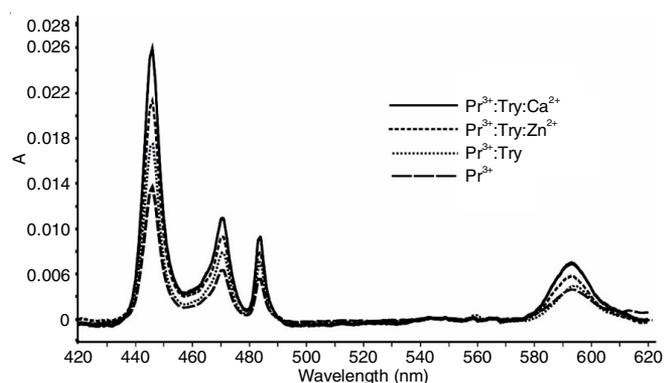


Fig. 1. Comparative absorption spectra of Pr^{3+} , $\text{Pr}^{3+}:\text{Try}$, $\text{Pr}^{3+}:\text{Try}:\text{Ca}^{2+}$ and $\text{Pr}^{3+}:\text{Try}:\text{Zn}^{2+}$ in DMF

Importance changes observed in the intensity parameters of Judd-Ofelt (T_λ) are used in the studies of the asymmetrical part of the crystal field. According to Devi & Singh [28], it gives the idea that the covalency parameters increase on complexation is not the single reason that influence T_λ values. The T_λ (T_2, T_4, T_6) values change at different solvents are related to the immediate coordination changes and variation in sym-

metry effects on the complex [29,30]. Different organic solvent shows the active participation on the coordination environment of the $4f-4f$ transition spectra of Pr^{3+} complex. The oscillator strength is changing and intensification of bands are observed at different organic solvents may be correlated to the coordination behaviour and shift in symmetry on complexation with ligand Try. From Fig. 2, DMF shows the strongest impact on Pr^{3+} complexation with Try and the next shown by dioxane and acetonitrile at last. It shows that solvent DMF has strong electric dipole intensity on $4f-4f$ transitions. The DMF can coordinate with two sites but it predominantly binds through oxygen when coordinates with lanthanides which is hard acid. The pseudo hypersensitive transition of Pr^{3+} ion *i.e.*, ${}^3\text{H}_4 \rightarrow {}^1\text{D}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$ and ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ show a red shift in all the tran-

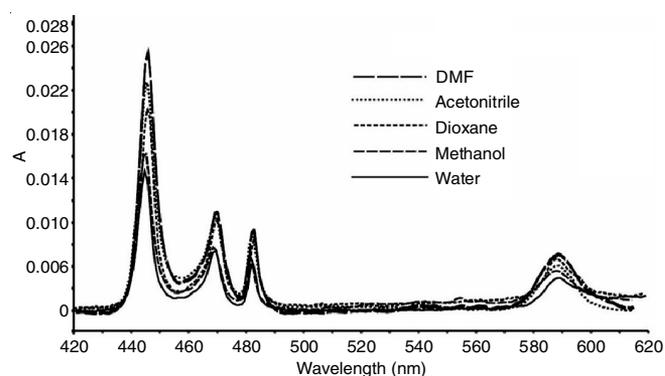


Fig. 2. Comparative absorption spectra of $\text{Pr}^{3+}:\text{Try}$ at different solvents- water, DMF, CH_3CN , dioxane, CH_3OH

sition, higher energies and most prominent effect is observed in solvent DMF. The nephelauxetic effect is mainly due to retrenchment in the bond length of metal-ligand which help in explaining the interaction and coordination between the inner sphere of metal Pr^{3+} and Try.

Due to the Zwitter ion effect on the complexation of Try and the lanthanide ions, it provides a remarkable electron density resulting in intensification in the Judd-Ofelt (T_λ) and oscillator strength of lanthanides. Hence, the pseudo hypersensitive transitions ${}^3\text{H}_4 \rightarrow {}^1\text{D}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$ and ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ sensitivity on the praseodymium (Pr^{3+}) complex and variation in intensity are observed on the coordination changes, different organic solvent interaction and binding nature of Pr^{3+} :Try. From the distinct spectra and variant in transitions, the 4f-4f comparative absorption transition use as a probe of the kinetic studies and comparison of spontaneity between the complex formation of Try and Pr^{3+} with Zn^{2+} or Ca^{2+} ions. In kinetic study, it is observed the variations in the 4f-4f transition concerning the time of all the hypersensitive and pseudo hypersensitive transitions on the Pr^{3+} . In Table-3 with the increase in time at 308 K, the absorbance also increases steadily. It is observed that the rate of complexation increases with the rise of temperature in both cases of Ca^{2+} and Zn^{2+} ions. The oscillator strength and T_2 , T_4 , T_6 parameters increase with respect to time. Initially the complexation and reaction were slow which is shown by minor variation in the oscillator strength and the values of T_2 , T_4 , T_6 parameters. Within the T_2 , T_4 , T_6 parameters T_4 , T_6 are more sensitive in the coordination and shift in asymmetry environment of Pr^{3+} so the variation of these parameter is use in explaining the shift in asymmetric structure of complex with the change of time and increase in temperature.

From the four-pseudo hypersensitive ${}^3\text{H}_4 \rightarrow {}^1\text{D}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$ and ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ of Pr^{3+} , the rate of complex is determined from the maximum height of complex absorbance at DMF medium of both Ca^{2+} and Zn^{2+} ions (Fig. 3). From the oscillator strength of four pseudo-hypersensitive transitions rate constant (K) were evaluated. To calculate the activation energy (E_a) of Pr^{3+} :Try: Ca^{2+} and Pr^{3+} :Try: Zn^{2+} , the Arrhenius equation is used and compared between the complex. The thermodynamic parameters (ΔH° , ΔS° and ΔG°) of Try with Pr^{3+} in the presence of Zn^{2+} and Ca^{2+} are calculated in addition to activation energy

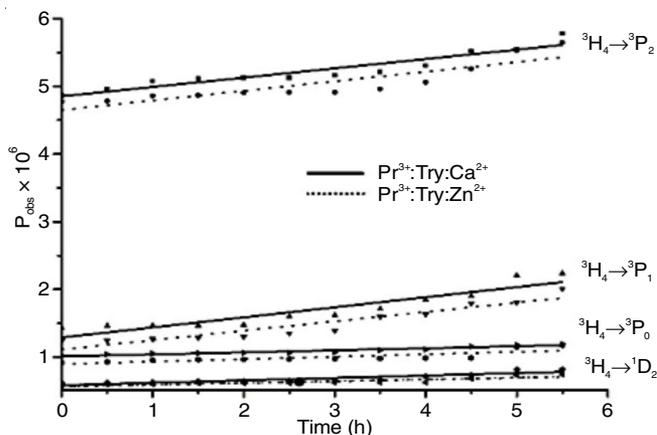


Fig. 3. Plot of Oscillator strength vs. time for four transition (${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$, ${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$) of Pr^{3+} :Try: Ca^{2+} and Pr^{3+} :Try: Zn^{2+}

and the rate of complexation are derived by graphing of $\ln k$ with $1/T$.

From Tables 4 and 5, the positive values of ΔH° and ΔS° shows that both complexation of Pr^{3+} :Try: Ca^{2+} and Pr^{3+} :Try: Zn^{2+} are endothermic, while increasing entropy and the negative values of ΔG° indicate the spontaneous process. The thermodynamic parameters of the complex are suitable in both Pr^{3+} :Try: Ca^{2+} and Pr^{3+} :Try: Zn^{2+} complexes. The hetero bimetallic complexation of Try with praseodymium (Pr^{3+}) in the presence of Ca^{2+} show more spontaneous and favourable compare to Zn^{2+} .

Conclusion

In summary, it is firmed that binary complexation of praseodymium (Pr^{3+}) with L-tryptophan (Try) is less stable but on complexation of Try with Pr^{3+} in the presence of Ca^{2+} and Zn^{2+} ions also. The intensification and enhancement of 4f-4f transition when Ca^{2+} ion hetero-bimetallic complex is more dominant than the Zn^{2+} ion due to spin-orbital coupling and the columbic force interaction parameter, which is connected with the polarization and asymmetry of complex.

The intensification and variation of pseudo hypersensitive transitions ${}^3\text{H}_4 \rightarrow {}^1\text{D}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$ and ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ of Pr^{3+} are used as a probe for kinetics and calculation of activation energy. With the increase of temperature from 298, 303, 308,

TABLE-3
OSCILLATOR STRENGTHS ($P \times 10^6$) AND JUDD-OFELT ($T_\lambda \times 10^{10}$)
PARAMETER OF Pr^{3+} :Try: Ca^{2+} , (Pr^{3+} :Try: Zn^{2+}) IN DMF MEDIUM OF 35 °C

Time (h)	${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ P_{obs}	${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$ P_{obs}	${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ P_{obs}	${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$ P_{obs}	T_2	T_4	T_6
0	4.8652 (4.775)	1.425 (1.243)	0.6158 (0.574)	1.021 (0.919)	22.261 (-8.473)	1.447 (2.140)	15.408 (15.127)
0.5	4.9592 (4.784)	1.460 (1.245)	0.6194 (0.596)	1.040 (0.930)	-15.189 (-32.150)	2.332 (2.142)	15.937 (15.138)
1.0	5.0758 (4.859)	1.462 (1.269)	0.6272 (0.602)	1.051 (0.953)	-69.697 (-38.386)	2.332 (2.153)	16.356 (15.417)
1.5	5.1095 (4.869)	1.464 (1.285)	0.6455 (0.615)	1.057 (0.964)	-4.234 (-42.371)	2.377 (2.160)	16.252 (15.449)
2.0	5.1270 (4.906)	1.474 (1.302)	0.6467 (0.616)	1.063 (0.965)	-5.297 (-30.030)	2.437 (2.165)	19.377 (15.562)
2.5	5.1271 (4.908)	1.599 (1.350)	0.6499 (0.617)	1.065 (0.972)	-13.123 (-40.964)	2.336 (2.198)	16.224 (15.594)
3.0	5.1585 (4.912)	1.615 (1.390)	0.6538 (0.623)	1.074 (0.976)	31.333 (-36.308)	2.449 (2.211)	16.194 (15.577)
3.5	5.2125 (4.961)	1.712 (1.598)	0.6631 (0.625)	1.106 (0.981)	135.659 (54.293)	2.381 (2.217)	16.503 (15.750)
4.0	5.5416 (5.061)	1.840 (1.631)	0.7137 (0.626)	1.111 (0.985)	54.907 (47.402)	2.736 (2.226)	16.071 (16.025)
4.5	5.5048 (5.260)	1.900 (1.793)	0.7349 (0.681)	1.158 (0.990)	66.191 (42.724)	2.652 (2.281)	17.536 (16.724)
5.0	5.5621 (5.528)	2.204 (1.807)	0.8168 (0.732)	1.180 (1.149)	67.478 (37.345)	2.641 (2.605)	17.370 (17.459)
5.5	6.0800 (5.649)	2.234 (2.010)	0.8175 (0.745)	1.194 (1.175)	-328.19 (123.266)	2.266 (2.659)	17.495 (17.841)

TABLE-4
RATE CONSTANT AND THERMODYNAMIC PARAMETERS FOR THE COMPLEXATION OF Pr³⁺:Try:Zn²⁺ AT DIFFERENT TEMPERATURES AND ACTIVATION ENERGY FOR THE COMPLEXATION REACTION ³H₄→³P₂

Temp. (K)	Rate constant (M ⁻¹ S ⁻¹)	ln K	E _a (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	ΔG (kJ mol ⁻¹)
298	17.08	2.838			23.64	-14.51
303	21.17	3.052			25.42	-19.34
308	21.47	3.067	14.076	14.076	25.54	-19.71
313	22.94	3.133			26.09	-21.51
318	23.22	3.145			26.19	-21.86

TABLE-5
RATE CONSTANT AND THERMODYNAMIC PARAMETERS FOR THE COMPLEXATION OF Pr³⁺:Try:Ca²⁺ AT DIFFERENT TEMPERATURES AND ACTIVATION ENERGY FOR THE COMPLEXATION REACTION ³H₄→³P₂

Temp. (K)	Rate constant (M ⁻¹ S ⁻¹)	ln K	E _a (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	ΔG (kJ mol ⁻¹)
298	17.11	2.839			23.66	-79.22
303	18.86	2.937			24.47	-80.59
308	19.61	2.976	9.1945	9.1945	24.79	-80.33
313	19.81	2.986			24.87	-79.31
318	21.75	3.079			25.65	-80.52

313 K the rate of reaction increases and the calculated value of activation energy shows that the complexation of Pr³⁺ ions with Try is the presence of Ca²⁺ ions show more effective than Zn²⁺ ions. And from the thermodynamic parameters (ΔH°, ΔS° and ΔG°) proved that the complexation in the presence of Ca²⁺ ions is more favoured than Zn²⁺ ions.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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