

Optical Absorption, Photoluminescence and Kinetics Studies of Pr^{3+} and Nd^{3+} with L-cysteine in the Presence of Zn^{2+} ions.

Thiyam Samrat Singh¹ and Thiyam David Singh^{*2}

^{1,2}Chemistry department, NIT Manipur, Langol, Manipur-795004

E-mail: ¹samratth@gmail.com, ²davidthiyam@gmail.com

Abstract— By using the absorption and emission analysis, the variation and changes of the hypersensitive and pseudo hypersensitive transition of Pr^{3+} and Nd^{3+} with the complexation of L-cysteine in the presence and absence of Zn^{2+} ions at different organic solvent are reported. To determine the nature of complexation, Slater Condon (F_k), Lande factor (\square_{4f}), Racah Parameter (E^k), The Nephelauxetic ratio (\square), bonding parameter ($b^{1/2}$) and percent covalency (\square) are calculated. Oscillator strength (P_{obs}) and Judd-Ofelt parameter (T_{\square} , $\square = 2, 4, 6$) are calculated to explain the intensities and electrostatic nature of the complex, Photoluminescence, Kinetics and Thermodynamic parameter are also reported.

Keywords: The Nephelauxetic ratio, Judd-Ofelt parameter, Hypersensitive, pseudo hypersensitive, oscillator strength parameter.

1. “INTRODUCTION”

Lanthanides elements are used as probes in biochemical reactions mechanism and for structural studies of the bio, molecule compounds due to the paramagnetic nature and the presence of 4f electrons [1-4]. Lanthanides mainly Pr (III) and Nd (III) are used in exploring selective applications in sol-gel [5] and laser emission in NIR region [6]. There has been a different aspect and interest in the study of absorption of 4f-4f transitions in intensity analysis to explain the details of structure in Lanthanide complexes. Using the comparative absorption spectrophotometer and reported a relationship between the magnitude and variation of intensity parameters and structural and compositional changes in these complexes. Zn(II) is an endogenous metal and isomorphous character so there is a similarity between the lanthanides and zinc in terms of size and higher coordination numbers hence they can replace Ln (III) to form a very stable complex [7].

The present work reports the hypersensitive transition $^4I_{9/2} \rightarrow ^4G_{5/2}$ and pseudo hypersensitive transitions $^4I_{9/2} \rightarrow ^4F_{3/2}$, $^4I_{9/2} \rightarrow ^4F_{5/2}$, $^4I_{9/2} \rightarrow ^4F_{7/2}$ and $^4I_{9/2} \rightarrow ^4G_{7/2}$ of Nd(III) and $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$ transitions of Pr(III) by using the magnitude and variation of Slater-Condon (F_k), spin-orbit coupling constant (ξ_{4f}), Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and percentage covalency (δ) parameters in further support, intensity parameters like Judd-Ofelt parameters (T_{λ} , $\lambda=2,4,6$) which is calculated from oscillator strength (P), which are correlated with the binding and complexation of L-Cysteine with Pr(III) and Nd(III) in presence and absence of Zn(II). Photo Luminescent properties of the complex with L-Cysteine also reported and from kinetics studies of the formation of Nd(III): L-Cysteine: Zn(II) complex, the activation energy (E_a) and thermodynamic parameters like $\square H^0$, $\square S^0$, $\square G^0$ are evaluated.

2. “MATERIALS AND METHODS”

The chemicals used for analysis, praseodymium nitrate and neodymium nitrate of 99% purity from M/S Indian Rare Earths Ltd., and L-Cysteine from sigma. The solvents used were CH_3OH , DMF and dioxane of A/R grade from Merck. The solution of ligand and lanthanides of 10^{-2} M were prepared in a different solvent. For the kinetics and thermodynamic studies, the electronic transition of Nd(III): L-Cysteine: Zn(II) complex in DMF medium is recorded at different temperature i.e. 298K, 303K, 308K, 313K and 318K. The temperature of all the observation is maintained by using Perkin Peltier temperature Controller. All the spectra are recorded on a temperature controlled Perkin Elmer Lambda-35 UV-Visible Spectrophotometer. Luminescence properties of the samples were measured by Hitachi F-7000 Spectrophotometer.

3. “RESULTS AND DISCUSSIONS”

3.1 Uv-visible Spectrophotometer Study

Nephelauxetic ratio [8-9] is used in the measure of covalency. And it can express in terms of Slater-Condon and Racah parameters as well as by the ratio of the complex ion and free ion [10-12]

$$\beta = \frac{F_k^C}{F_k^f} \text{ or } \frac{E_c^K}{E_f^K}$$

Where F_k ($k=2,4,6$) is the Slater- Condon parameter and E^k the Racah parameter; C and f stand for complex and free ions respectively. The bonding parameter and percent covalency are calculated as

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

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

The angular part of the spin-orbit interaction and ξ_{4f} is the radial integral known as Lande’s parameter. By first order approximation, the energy E_j of the j^{th} level is given by Wong [13]

$$E_j(F_k, \xi_{4f}) = E_{oj}(F_k^0, \xi_{4f}^0) + \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \xi_{4f}} \Delta \xi_{4f}$$

By using the zero order energy and partial derivatives of Pr(III) and Nd(III) ion given by Wong [14], the above equation can be solved by least square technique and the value of ΔF_k and $\Delta \xi_{4f}$ can be found out. From these values, the values of F2, F4, F6 and ξ_{4f} are calculated.

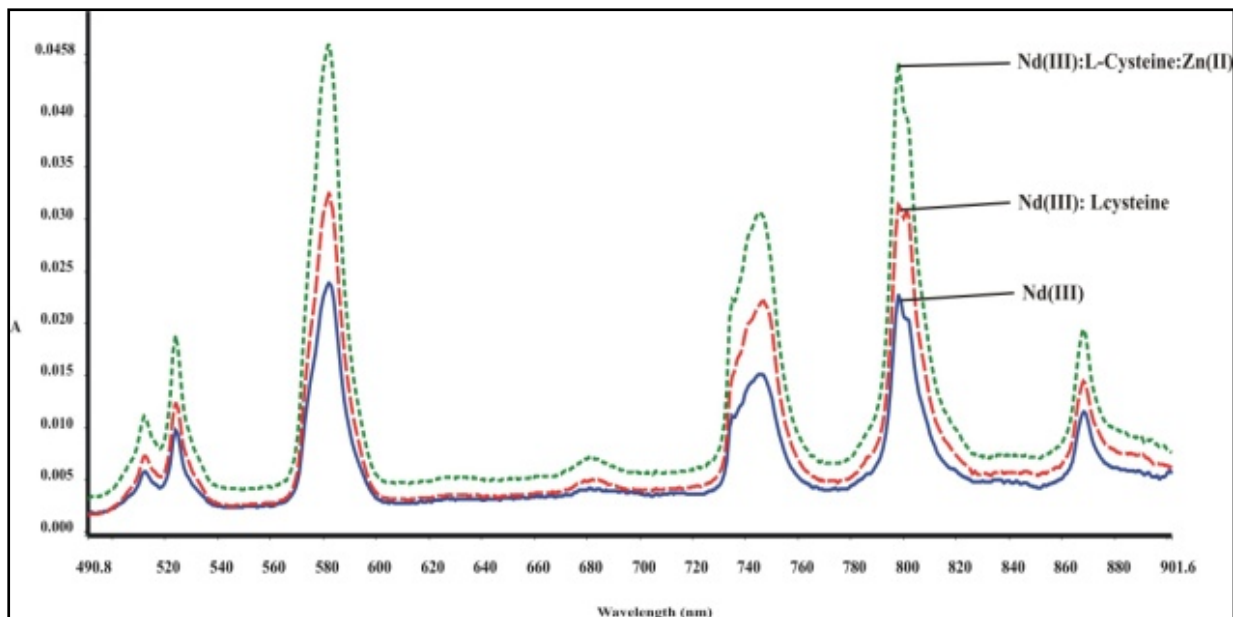


Figure 1: comparative absorption spectra of Nd(III), Nd(III): L-Cysteine and Nd(III): L-Cysteine:Zn(II) complex at DMF medium

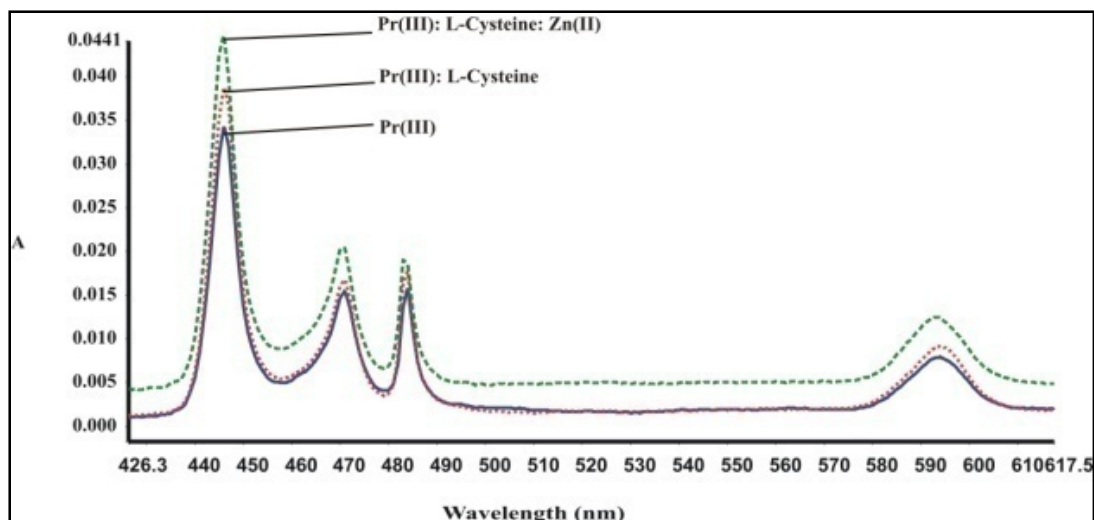


Figure 2: comparative absorption spectra of Pr(III), Pr(III): L-Cysteine and Pr(III): L-Cysteine:Zn(II) complex at DMF medium

Table 1: Computed value of energy interaction Slater Condon $F_k(\text{cm}^{-1})$, spin orbital interaction $\square_{4f}(\text{cm}^{-1})$, Racah energy $E^k(\text{cm}^{-1})$, Nephelauxetic ratio ($\square\square\square$ bonding ($b^{1/2}$) and covalency ($\square\square\square$ parameters of Pr(III), Pr(III):L-Cysteine, Pr(III):L-Cysteine:Zn(II) are given below (L=L-Cysteine).

SYSTEM	F_2	F_4	F_6	$\square\square f$	E^2	E^4	E^6	\square	$b^{1/2}$	\square
Solvent(CH3OH)										
Pr	308.13	42.54	4.65	720.79	3498.733	23.6	584.12	0.9445	0.1666	5.88
Pr:L	308.37	42.57	4.66	719.62	3501.487	23.7	585.13	0.944	0.1673	5.93
Pr:L:Zn	308.38	42.57	4.66	719.96	3501.496	23.7	585.67	0.9442	0.167	5.94
Solvent(DMF)										
Pr	307.82	42.49	4.65	719.23	3495.139	23.65	584.07	0.9429	0.1689	6.05
Pr:L	307.85	42.5	4.65	718.63	3495.545	23.65	584.14	0.9426	0.1695	6.09
Pr:L:Zn	308.08	42.53	4.65	718.88	3498.168	23.67	584.58	0.9425	0.1687	6.1
Solvent(DXN)										
Pr	307.92	42.51	4.65	720.28	3496.356	23.66	584.21	0.9438	0.1676	5.95
Pr:L	308.42	42.58	4.66	720.28	3501.986	23.7	585.27	0.9445	0.1665	5.87
Pr:L:Zn	308.46	42.58	4.66	721.28	3502.448	23.7	585.29	0.9443	0.1654	5.99

Table 2: Computed value of energy interaction Slater Condon $F_k(\text{cm}^{-1})$, spin orbital interaction $\square_{4f}(\text{cm}^{-1})$, Racah energy $E^k(\text{cm}^{-1})$, Nephelauxetic ratio ($\square\square\square$ bonding ($b^{1/2}$) and covalency ($\square\square\square$ parameters of Pr(III), Pr(III):L-Cysteine, Pr(III):L-Cysteine:Zn(II) are given below (L=L-Cysteine).

Solvent (CH ₃ OH)	F_2	F_4	F_6	\square_{4f}	E^2	E^4	E^6	\square	$b^{1/2}$	\square
Nd	328.78	47.95	5.165	949.04	3790.38	24.565	628.372	1.018	0.7006	1.4083
Nd:L	329.1	48.05	5.171	945.61	3794.45	24.571	628.487	1.017	0.701	1.4133
Nd:L:Zn	329.61	47.5	5.142	946.21	3894.24	24.789	629.924	1.015	0.7018	1.4806
Solvent (DMF)										
Nd	327.76	48.4	5.258	965.67	3803.21	24.274	627.223	1.033	0.6958	2.0651
Nd:L	327.54	48.58	5.265	965.65	3806.13	24.295	627.265	1.032	0.6956	2.1334
Nd:L:Zn	327.94	48.36	5.246	962.86	3809.55	24.398	627.549	1.029	0.6965	2.9811
Solvent (DXN)										
Nd	329.38	47.44	5.159	952.21	3790.95	24.397	628.37	1.018	0.7005	1.3203
Nd:L	329.83	47.72	5.151	941.93	3801.62	24.474	629.704	1.013	0.7022	1.3602
Nd:L:Zn	335.26	50.49	5.313	874.59	3915.31	24.553	643.808	0.994	0.7092	1.6033

Lanthanides are spectroscopically active due to the paramagnetic nature so the 4f-4f transitions are very sensitive towards immediate coordination or complexation with the metal ion. Judd [15] explain the hypersensitivity and pseudohypersensitive nature lanthanide ions, due to the changes in the symmetry of the environment. Four transitions of Pr (III) ions are ³H₄→³P₂, ³H₄→ ³P₁, ³H₄→ ³P₀, ³H₄→ ³D₂ which are recorded between 426-617nm spectral region. For Nd(III) ⁴I_{9/2}→ ⁴G_{5/2} is a hypersensitive transition as it obeys selection rule and the transitions ⁴I_{9/2}→ ⁴F_{3/2}, ⁴I_{9/2}→ ⁴F_{5/2}, ⁴I_{9/2}→ ⁴F_{7/2} and ⁴I_{9/2}→ ⁴G_{7/2} are pseudohypersensitive transitions due to ligand-mediated. In Table 1 the values of energy interaction parameters like Slatore-Condon (F_k), spin-orbit coupling constant (ξ_{4f}), Nephelauxetic ratio (β), bonding parameter (b^{1/2}) and percentage covalency (δ) parameters and Judd-Ofelt electric dipole intensity parameters(T_□, □=2,4,6) are reported at different organic solvent for Pr(III) ion, Pr(III):L-Cysteine and Pr(III): L-Cysteine: Zn(II). Table 2 for Nd(III) ion, Nd(III): L-Cysteine and Nd(III): L-Cysteine:Zn(II). The comparative absorption spectra of Pr (III) and Nd (III) in DMF solvent are shown in fig.1 and fig. 2 respectively.

Table 3: Observed and computed values of Oscillator strengths (P x 10⁶) and Judd-Ofelt (T_□ x 10¹⁰) parameters for Pr(III), Pr(III):L, Pr(III):L:Zn(II) in different organic solvent (L= L-Cysteine).

SYSTEM	3H4 → 3P2		3H4 → 3P1		3H4 → 3P0		3H4 → 1D2		T2	T4	T6
	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal			
Solvent(CH3OH)											
Pr	1.9687	1.9687	0.535	0.535	0.0925	0.091	0.506	0.5058	-15.152	0.865	6.243
Pr:L	2.1821	2.1821	0.54	0.54	0.1951	0.192	0.339	0.3388	-67.344	1.016	6.899
Pr:L:Zn	2.9124	2.9124	0.511	0.511	0.2789	0.275	0.706	0.7063	-31.464	1.092	9.273
Solvent(DMF)											
Pr	4.4513	4.4513	0.889	0.889	0.5486	0.542	0.987	0.9875	-69.96	1.994	14.121
Pr:L	5.0253	5.0253	0.907	0.907	0.6862	0.678	1.116	1.116	-78.582	2.211	15.954
Pr:L:Zn	5.6851	5.6841	1.285	1.285	0.8232	0.814	1.144	1.1443	-116.342	2.784	17.963
Solvent(DXN)											
Pr	3.1386	3.1396	0.536	0.556	0.3962	0.391	0.875	0.8746	-14.814	1.292	10.305
Pr:L	3.2121	3.2132	0.575	0.535	0.4398	0.434	1.168	1.1678	271.799	1.488	-0.766
Pr:L:Zn	3.5343	3.5383	0.623	0.603	0.432	0.426	1.823	1.8228	-46.187	1.296	11.256

Table 4: Observed and computed values of Oscillator strengths (P x 10⁶) and Judd-Ofelt (T_□ x 10¹⁰) parameters for Nd(III), Nd(III):L, Nd(III):L:Zn(II) in different organic solvent (L= L-Cysteine).

Solvent CH3OH	4I9/2 → 4G5/2		4I9/2 → 4G7/2		4I9/2 → 4F3/2		4I9/2 → 4F5/2		4I9/2 → 4F7/2		T2	T4	T6
	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal			
Nd	0.284	0.234	1.195	1.145	0.551	0.318	0.301	1.204	0.252	0.202	1.52	0.22	0.284
Nd:L	0.445	0.446	1.787	1.776	0.923	0.922	0.972	1.66	0.361	0.296	2.53	0.06	0.445
Nd:L:Zn	0.699	0.606	3.438	3.468	1.615	2.441	2.622	2.224	0.399	0.376	3.5	0.42	0.699
Solvent (DMF)													
Nd	2.151	2.785	3.851	3.165	1.785	1.623	1.430	2.254	0.359	0.350	3.89	0.15	2.151
Nd:L	2.994	2.915	5.367	5.869	2.791	3.181	3.184	2.761	0.373	0.328	4.93	0.09	2.994
Nd:L:Zn	3.626	3.692	7.610	7.400	3.872	3.851	3.959	3.513	0.538	0.540	4.56	0.1	1.626
Solvent (DXN)													
Nd	1.007	1.003	2.799	2.752	2.772	0.677	0.495	0.746	0.28	0.242	1.44	0.65	2.307
Nd:L	1.051	1.052	2.787	2.817	2.876	1.566	1.232	2.638	0.424	0.421	3.18	1.12	1.051
Nd:L:Zn	2.113	2.297	3.120	2.973	2.97	2.967	2.342	2.724	0.453	0.433	-0.54	3.58	2.113

From the figures 1 and 2, it can explain that the addition of ligand (L-Cysteine) to the metal ion show a red shift. With the addition of ligand changes in the intensity are observed from the intensification of the 4f-4f transition bands. This intensification of bands can explain the increased interaction between 4f orbital of lanthanides and ligand orbital. This intensification of bands is correlated with lowering of the coordination number as well as shortening of the metal-ligand bond distance. The values of the Nephelauxetic ratio in all the systems are low and the values of bonding parameter are positive which explain covalent bonding.

The calculation of the band intensities is based upon the theoretical treatment derived by Judd and Ofelt [16-18].

The measured intensity of an absorption band is related to the probability (P) for the absorption of radiant energy (oscillator strength) by the expression

$$P = 4.31 \times 10^{-9} \int \epsilon_{\max} \bar{\nu} d\bar{\nu}$$
 Where $\bar{\nu}$ (cm^{-1}) is the energy of the transition and ϵ_{\max} is the molar extinction coefficient. From these values, the value of T_2 , T_4 , and T_6 are calculated by partial and multiple regression methods using the Judd-Ofelt expression.

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

From table 3 and 4 the increased in the values of oscillator strength and Judd-ofelt intensity T_λ ($\lambda=2,4,6$) parameters in both Pr(III) and Nd(III) it indicates

complexation. Where T_2 is negative and is meaningless. Hence, it is favored by T_4 and T_6 followed by T_2 .

3.2 Photoluminescence studies:

The excitation and emission of Pr(III), Pr(III): L-Cysteine and Pr(III): L-Cysteine: Zn(II) are displayed in Figure: 3 . The excitation spectrum was obtained by monitoring emission of Pr(III) ion at 530 nm at room

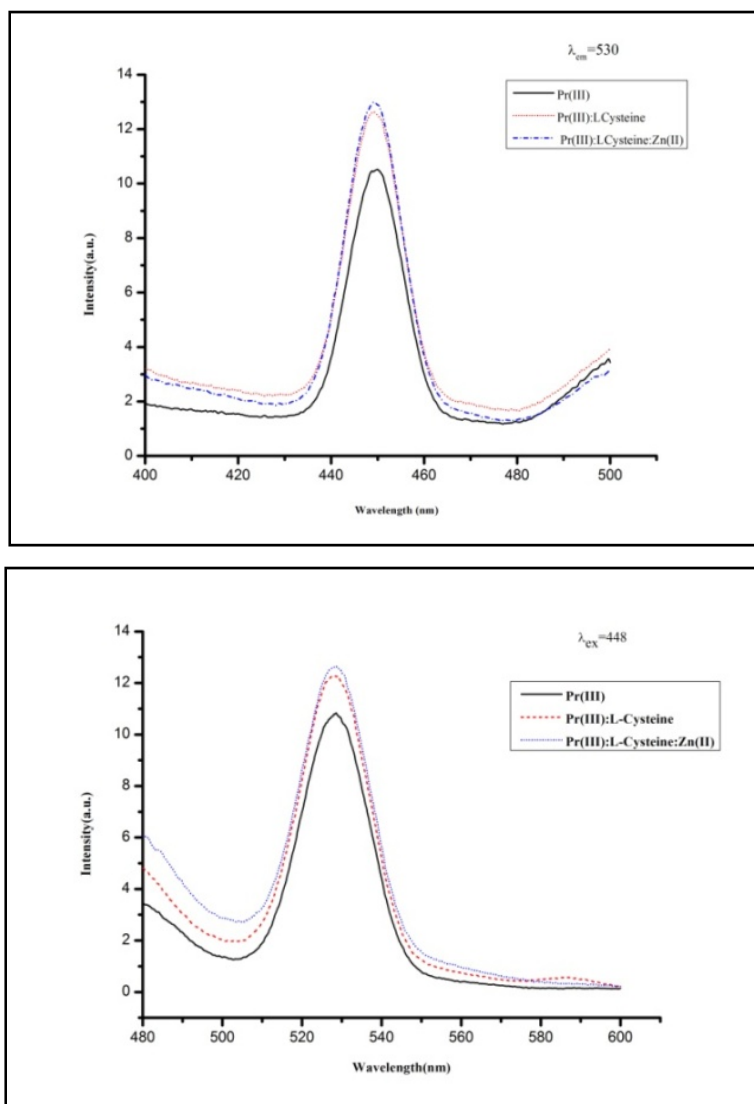


Figure 3 Emission and excitation spectrum of Pr(III), Pr(III): L-Cysteine and Pr(III): L-Cysteine:Zn(II).

Temperature and we consider only one excitation band at 448 nm ($^3H_4 \rightarrow ^3P_2$). Figure 3 present the emission spectrum with 448 nm excitation wavelength, here also we consider only one emission band at 528nm ($^3P_0 \rightarrow ^3H_5$). From the excitation and emission spectrum, we observed the enhancement of the spectrum. This enhancement is mainly due to the formation of complexation in Pr(III) ion with L-Cysteine in the presence of Zn(II) ion. The photoluminescence enhancement may be due to the difference in the binding of metals and interfacial ligand. The thiol group present in L-Cysteine has a strong affinity and this coordination generally caused quenching of photoluminescence.

3.3 Kinetics and Thermodynamic studies

By using absorption different of 4f-4f transitions of Nd(III) ion, the activation energy of the complexation of Nd (III): L-Cysteine with Zn(II) are explored from the data at different temperatures from table 5, using Arrhenius rate equation.

$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$, Where A is the pre-exponential factor and Ea is calculated as Ea=Slope x R

Thermodynamic parameters corresponding to rate constant is found to be favourable in studies of complexation of L-Cysteine with Nd(III) and Zn (II) is calculated by using van't Hoff plot of $\ln k$ vs $1/T$.

Table 5: Experimental value of Oscillator strength (P_{obs}) of (The hypersensitive transition $^4I_{9/2} \rightarrow ^4G_{5/2}$ of Nd) Nd(III): L- Cysteine :Zn(II) at 298K, 303K, 308K, 313K, 318K.

Time	298K	303K	308K	313K	318K
0	8.236	8.396	8.155	8.102	7.859
2	8.350	8.396	8.298	8.123	7.980
4	8.366	8.411	8.300	8.213	8.253
6	8.415	8.447	8.468	8.281	8.262
8	8.41	8.464	8.620	8.454	8.331
10	8.436	8.473	8.633	8.518	8.338
12	8.438	8.503	8.651	8.580	8.366
14	8.447	8.508	8.696	8.590	8.415
16	8.461	8.527	8.698	8.618	8.421
18	8.463	8.618	8.715	8.725	8.425
20	8.466	8.641	8.763	8.738	8.484
22	8.500	8.655	8.806	8.754	8.496
24	8.543	8.674	8.807	8.763	8.696
26	8.622	8.713	8.825	8.808	8.549

Table 6: Rate constant and thermodynamic parameter for the complexation of Nd(III): L- Cysteine :Zn(II) at 298K, 303K, 308K, 313K, 318K and activation energy (E_a).

Temp (K)	Rate Mol L ⁻¹ S ⁻¹	Ea KJ mol ⁻¹	ΔH^0 KJ mol ⁻¹	ΔS^0 JK ⁻¹ mol ⁻¹	ΔG^0 KJ mol ⁻¹
298K	3.27			0.1	-29.3
303K	3.68			0.11	-32.8
308K	6.66	0.095	0.095	0.16	-48.5
313K	7.6			0.17	-52.7
318K	8.43			0.18	-56.3

$$\ln k = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^0}{R}$$

From table 6 we observed that the value of ΔH^0 and ΔS^0 are positive which indicates that the complexation reaction is endothermic and the entropy increasing process. $T\Delta S^0 > \Delta H^0$ the coordination reaction is entropy driven (randomness) process. ΔG^0 is negative predict that the complex formation is favorable and is spontaneous. The rate of reaction has been found to increase with temperature and from which the activation energy has been determined.

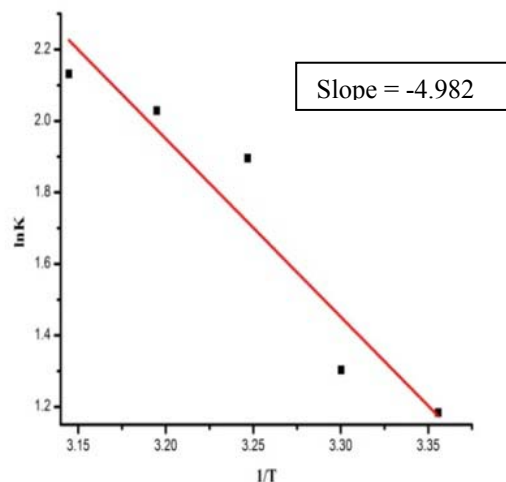


Figure: 4 Plot of $\ln k$ vs $1/T$ for the complex Nd(III)-L-Cysteine: Zn(II) in DMF medium.

4. "CONCLUSION"

From the present study, we can conclude that the involvement of Zn(II) in the complexation of Nd(III)/Pr(III) with L-Cysteine there is an increase in the value of bonding parameter and percent covalency. It shows strong binding with metal ions and ligands. The absorption of the complexation of Nd(III) and Pr(III): L-Cysteine with Zn(II) ion increase with time and the rate of complex formation is determined at different temperature i.e. 298K, 303K, 308K, 313K, 318K. ΔH^0 and ΔS^0 are positive hence the complexation is endothermic and the entropy increasing process. The activation energy (E_a) of the complex formation is determined as $0.9523 \text{ kJmol}^{-1}$. The thermodynamic parameters of the complex formation show that the complexation of Nd(III) and Pr(III) with L- Cysteine in the presence of Zn(II) ion is highly favored.

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