

A Probe into the Kinetics of the Interaction of Pr(III) Ions with Some Selected Amino Acids: A 4f-4f Transition Spectral Study

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Abstract-The absorption spectra in transition metal ions involving d-d transitions have been used for following the kinetics of the chemical reaction leading to the development of the mechanism of chemical and biochemical reactions. The 4f-4f transition spectral intensity changes have very rarely been used for mechanistic and kinetic investigations. Thus, it has been considered quite interesting to explore the interaction of Pr³⁺ with biomolecules in presence of Ca²⁺ by employing absorption spectral research owing to the ease of Ln³⁺ ions to act as surrogates for Ca²⁺ ions.

The kinetics for the complexation of Pr(III): Amino acid with Ca(II) have been investigated in DMF medium at different temperatures viz., 298K, 303K, 308K, 313K and 318K. Three amino acids viz., Glycine, L-Alanine and L-Phenylalanine were selected for the kinetic study of the complexation reactions of Ln(III) ion and amino acid ligands in the presence of Ca(II) ion. From the values of the rate of reaction at different temperatures, the activation energy (E_a) of the various complexes are determined and from the calculated data of activation energies, thermodynamic parameters like ΔH^0 , ΔS^0 and ΔG^0 of the formation of complexes are evaluated. The determined activation energy parameters corresponding to the rate constants and thermodynamic parameters corresponding to the formation of the complexes of Pr(III): Amino acid: Ca(II) were found to be highly favourable.

Keywords- 4f-4f Transition; Absorption Spectral Studies; Kinetics; Activation Energy; Thermodynamic Parameters

I. INTRODUCTION

In lanthanides, rarely absorption spectra, involving 4f-4f transitions are used for mechanistic studies of the kinetic reactions involving lanthanide ions and coordinating ligands like biomolecules. The close resemblance between most abundant and biologically important Ca(II) ion and paramagnetic lanthanides(III) ions, in coordination and binding characteristics [1, 2], allow lanthanide(III) ion to act as an “absorption spectral probe” in understanding biochemical reactions and functions involving isomorphous Ca(II) ion substitution by Ln(III) [3-5].

In the previous work [6-7], the absorption difference and comparative absorption spectroscopy involving 4f-4f transitions of the heterobimetallic complexation of some selected amino acids with Pr(III) and Ca(II) was carried out in aqueous and different aquated organic solvents. The difference in the energy parameters like Slater Condon (F_k), and Lande Spin-orbit Coupling (ζ_{4f}), Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and percent covalency (δ) are calculated to explain the nature of complexation. The changes in the values of experimentally calculated oscillator strengths (P) and Judd–Ofelt electric dipole intensity parameter, T_λ ($\lambda = 2, 4, 6$) suggest the specific correlation between relative intensities, ligand structures and nature of complexation. The variation of intensities (oscillator strengths) of 4f-4f bands during hydrolysis, as well as the variation of Judd–Ofelt intensity parameters has helped in following the preliminary kinetic studies of hydrolysis. The kinetics for the formation of Pr(III): Amino acids: Ca(II) complex is evaluated at different temperatures in DMF medium. From the rates of reactions at different temperatures, the values of activation energy (E_a) of the formation of the complexes are evaluated.

II. EXPERIMENTAL

A. Materials

Praseodymium(III) nitrate of 99% purity, purchased from CDH, Mumbai and Amino acids viz; Glycine, L-Alanine and L-Phenylalanine from SRL Pvt. Ltd., Mumbai, are used for the present analysis. Solvent used is Dimethylformamide(DMF) since it showed maximum intensification among other organic solvents analysed [6-7].

B. Methods

The rates of the complexation of Pr³⁺: Amino acid with Ca²⁺ have been measured applying two different methods i.e., comparative absorption and absorption difference spectroscopy using 4f-4f transitions by monitoring the changes of absorbance and oscillator strength of multiplet to multiplet electronic transitions of Pr³⁺ ion. The activation energy of the complexation of Pr³⁺: Amino acid with Ca²⁺ has been explored from the data of rates at different temperatures by following

Arrhenius equation. The thermodynamic parameters for the complexation of Pr^{3+} : Amino acid: Ca^{2+} ion is calculated using Vant Hoff's plot of $\log k$ against $1/T$.

The calculation of the band intensities is based upon the theoretical treatment derived by Judd [8] and Ofelt [9]. They considered that the transitions are essentially electric dipole in character and the oscillator strength corresponding to the induced electric dipole transition $\Psi J \rightarrow \Psi' J'$ as given by

$$P = \sum_{\lambda=2,4,6} T_{\lambda} \sigma(f^n \Psi J \| U^{(\lambda)} \| f^n \Psi' J')^2 \quad (1)$$

where $U^{(\lambda)}$ is matrix element of rank λ . The three quantities T_2 , T_4 and T_6 are related to the radial parts of the $4f^n$ wave functions which are the wave functions of the perturbing configurations of the nearest $4f^{n-1} 5d$.

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

$$P = 2303 \text{ mc}^2 / N\pi e^2 \int \epsilon_i(\sigma) d\sigma$$

$$\text{or } P = 4.318 \times 10^{-9} \int \epsilon_i(\sigma) d\sigma \quad (2)$$

where ϵ is the molar absorptivity at the energy σ (cm^{-1}) and other symbols have their usual significance. From these values of T_2 , T_4 and T_6 are calculated applying

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

where $U^{(\lambda)}$ are the matrix elements of Pr^{3+} and Nd^{3+} system given by Carnall [10]. The activation energy for the complexation of $\text{Pr}^{3+}/\text{Nd}^{3+}$: Amino acid in DMF is calculated from the plot of $\log k$ (k = rate constant) against $1/T$ by using Arrhenius rate equation [11].

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T} \quad (4)$$

where A is the pre-exponential factor or frequency factor. From the slope the activation energy (E_a) is calculated as:

$$E_a = \text{Slope} \times 2.303 \times R \quad (5)$$

where R is the universal gas constant.

The thermodynamic parameters for the complexation of Pr^{3+} : Amino acid and Ca^{2+} ion is evaluated using Van't Hoff plot [12] of $\log k$ against $1/T$.

$$\ln k = -\frac{\Delta H^0}{R} \left[\frac{1}{T} \right] + \frac{\Delta S^0}{R}$$

$$\text{or } \ln k = -\frac{\Delta G^0}{RT} \quad (6)$$

III. RESULTS AND DISCUSSIONS

Figs. 1-2 show the time span absorption spectra of the formation of Pr(III) : L-Alanine with Ca(II) at 298K and 303K respectively.

It can be seen that there is an increase of absorbance and intensity with time. Both hypersensitive and pseudo-hypersensitive transitions of Pr(III) display significant changes during complexation, which can be seen from the spectral changes with time. The same trend was observed for Pr(III) : Glycine/L-Phenylalanine: Ca(II) at different temperatures:- 298K, 303K, 308K, 313K and 318K. On the other hand it was found that the bands other than hypersensitive bands can acquire sensitivity due to the binding characteristics of the coordinating ligands, change in denticity, nature of the donor sites as well as nature of Ln(III) - Ligand bond and nature of complex species, which have induced significant intensity to the non-hypersensitive $4f-4f$ bands. Such transitions are known as pseudo-hypersensitive transitions [13-15]. Judd marked the hypersensitivity as due to the changes in symmetry of the environment of a lanthanide ion. Therefore, it has been suggested

that the changes in the oscillator strengths of both hypersensitive and non-hypersensitive transitions should be considered for spectral structure correlation in Ln(III) complexes with coordination ligands including biomolecules.

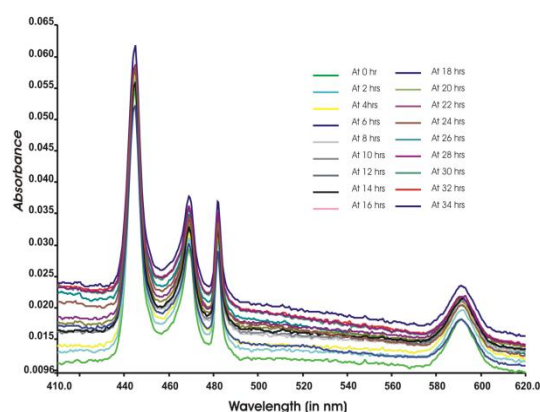


Fig. 1 Absorption Spectra of Pr(III): L-Alanine complexation with Ca(II) at different hours at 298K (25 °C)

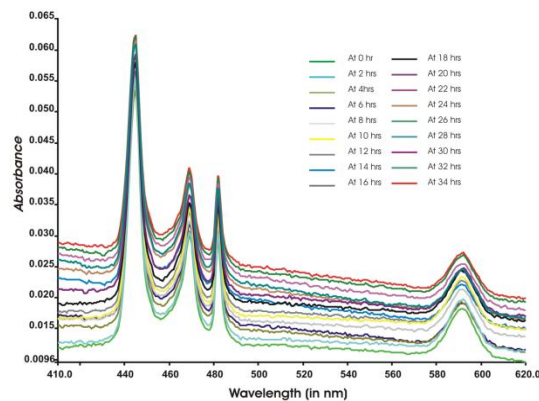


Fig. 2 Absorption Spectra of Pr(III): L-Alanine complexation with Ca(II) at different hours at 303K (300 °C)

Tables 1-5 show the observed (P_{obs}) and calculated (P_{cal}) values of oscillator strengths Judd- Ofelt intensity parameter, T_{λ} ($\lambda = 2,4,6$) for complexation of Pr(III): L Alanine with Ca(II) in DMF at different temperatures, viz; 298K, 303K, 308K, 313K and 318K.

TABLE 1 OBSERVED AND CALCULATED OSCILLATOR STRENGTHS ($\text{P} \times 10^6$) AND JUDD-OFELT INTENSITY PARAMETER (T_{λ} , $\lambda = 2,4,6 \times 10^{10} \text{ cm}^{-1}$ PARAMETERS FOR PR(III): L ALANINE: CA(II) COMPLEX AT 298K (25 °C) AT DIFFERENT TIME(HRS)

Time (in hour)	$^3\text{H}_4 \rightarrow ^3\text{P}_2$		$^3\text{H}_4 \rightarrow ^3\text{P}_1$		$^3\text{H}_4 \rightarrow ^3\text{P}_0$		$^3\text{H}_4 \rightarrow ^1\text{D}_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
0	0.8972	0.8972	0.2480	0.2154	0.1800	0.2121	0.4240	0.4240	36.7880	0.5917	2.7862
2	0.9240	0.9240	0.2440	0.2154	0.1840	0.2122	0.4140	0.4140	32.7450	0.5918	2.8744
4	0.9323	0.9323	0.2530	0.2194	0.1830	0.2161	0.4090	0.4090	31.0220	0.6028	2.8988
6	0.9459	0.9459	0.2460	0.2205	0.1920	0.2172	0.4070	0.4070	29.7480	0.6057	2.9425
8	1.0079	1.0079	0.2660	0.2340	0.1990	0.2305	0.4350	0.4350	31.9680	0.6430	3.1360
10	1.0089	1.0089	0.2670	0.2355	0.2010	0.2320	0.4580	0.4580	37.2030	0.6473	3.1388
12	1.0181	1.0181	0.2760	0.2405	0.2020	0.2370	0.4520	0.4520	35.1230	0.6610	3.1651
14	1.0289	1.0289	0.2670	0.2386	0.2070	0.2350	0.4620	0.4620	37.0220	0.6556	3.2021
16	1.0472	1.0472	0.2790	0.2466	0.2110	0.2429	0.4850	0.4850	40.7970	0.6776	3.2562
18	1.0525	1.0525	0.2800	0.2456	0.2080	0.2419	0.4780	0.4780	38.8320	0.6748	3.2740
20	1.0654	1.0654	0.2850	0.2496	0.2110	0.2459	0.4820	0.4820	38.8190	0.6859	3.3135
22	1.1128	1.1128	0.2910	0.2567	0.2190	0.2528	0.4910	0.4910	37.8600	0.7052	3.4639
24	1.1226	1.1226	0.2880	0.2572	0.2230	0.2533	0.5030	0.5030	39.8110	0.7067	3.4957
26	1.1305	1.1305	0.2930	0.2607	0.2250	0.2568	0.5050	0.5050	39.8630	0.7164	3.5191
28	1.1425	1.1425	0.2950	0.2627	0.2270	0.2588	0.5130	0.5130	40.8900	0.7219	3.5570
30	1.1532	1.1532	0.3040	0.2697	0.2320	0.2657	0.5280	0.5280	43.5220	0.7413	3.5867
32	1.1686	1.1686	0.3000	0.2682	0.2330	0.2643	0.5120	0.5120	38.9640	0.7372	3.6387
34	1.1872	1.1872	0.3090	0.2733	0.2340	0.2692	0.5240	0.5240	40.6690	0.7509	3.6956

TABLE 2 OBSERVED AND CALCULATED OSCILLATOR STRENGTHS ($\text{P} \times 10^6$) AND JUDD-OFELT INTENSITY PARAMETER (T_{λ} , $\lambda = 2,4,6 \times 10^{10} \text{ cm}^{-1}$ PARAMETERS FOR PR(III):L ALANINE: CA(II) COMPLEX AT 303K (30 °C) AT DIFFERENT TIME(HRS)

Time (in hour)	$^3\text{H}_4 \rightarrow ^3\text{P}_2$		$^3\text{H}_4 \rightarrow ^3\text{P}_1$		$^3\text{H}_4 \rightarrow ^3\text{P}_0$		$^3\text{H}_4 \rightarrow ^1\text{D}_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
0	0.8855	0.8855	0.2400	0.2098	0.1770	0.2067	0.1770	0.1770	-18.560	0.5765	2.7519
2	0.9033	0.9033	0.2430	0.2129	0.1800	0.2097	0.1800	0.1800	-19.000	0.5849	2.8079
4	0.9195	0.9195	0.2400	0.2134	0.1840	0.2102	0.1840	0.1840	-19.160	0.5863	2.8608
6	0.9345	0.9345	0.2430	0.2154	0.1850	0.2122	0.1850	0.1850	-19.900	0.5919	2.9093
8	0.9836	0.9836	0.2590	0.2264	0.1910	0.2231	0.1910	0.1910	-21.860	0.6222	3.0616
10	0.9952	0.9952	0.2590	0.2300	0.1980	0.2266	0.1980	0.1980	-21.050	0.6320	3.0979
12	1.0037	1.0037	0.2660	0.2345	0.2000	0.2310	0.2000	0.2000	-21.200	0.6444	3.1223
14	1.0183	1.0183	0.2680	0.2370	0.2030	0.2335	0.2030	0.2030	-21.390	0.6515	3.1680
16	1.0385	1.0385	0.2720	0.2390	0.2030	0.2355	0.2030	0.2030	-22.810	0.6569	3.2332
18	1.0375	1.0375	0.2750	0.2410	0.2040	0.2375	0.2040	0.2040	-22.490	0.6624	3.2278
20	1.0465	1.5465	0.2790	0.2451	0.2080	0.2414	0.2080	0.2080	-55.030	0.6734	4.8958
22	1.0992	1.0992	0.2820	0.2501	0.2150	0.2464	0.2150	0.2150	-24.110	0.6874	3.4241

24	1.1021	1.1021	0.2920	0.2582	0.2210	0.2543	0.2210	0.2210	-22.940	0.7095	3.4274
26	1.1184	1.1184	0.2940	0.2597	0.2220	0.2558	0.2220	0.2220	-23.780	0.7136	3.4804
28	1.1283	1.1283	0.2930	0.2617	0.2270	0.2578	0.2270	0.2270	-23.250	0.7192	3.5114
30	1.1354	1.1354	0.3000	0.2662	0.2290	0.2623	0.2290	0.2290	-23.330	0.7316	3.5311
32	1.1516	1.1516	0.2990	0.2662	0.2300	0.2623	0.2300	0.2300	-24.140	0.7316	3.5843
34	1.1723	1.1723	0.3000	0.2683	0.2330	0.2643	0.2330	0.2330	-24.820	0.7371	3.6508

TABLE 3 OBSERVED AND CALCULATED OSCILLATOR STRENGTHS ($\text{PX } 10^6$) AND JUDD-OFELT INTENSITY PARAMETER (T_λ , $\Lambda = 2,4,6 \times 10^{10} \text{ cm}^{-1}$ PARAMETERS FOR PR(III): L ALANINE: CA(II) COMPLEX AT 308K (35 °C) AT DIFFERENT TIME(HRS)

Time (in hour)	${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$		${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$		${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$		${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
0	0.8785	0.8785	0.2410	0.2068	0.1700	0.2037	0.3930	0.3930	31.114	0.5681	2.7306
2	0.8983	0.8983	0.2400	0.2104	0.1780	0.2072	0.4050	0.4050	32.433	0.5779	2.7939
4	0.9121	0.9121	0.2400	0.2144	0.1860	0.2112	0.4030	0.4030	31.089	0.5891	2.8357
6	0.9237	0.9237	0.2420	0.2139	0.1830	0.2107	0.4050	0.4050	30.785	0.5877	2.8745
8	0.9681	0.9681	0.2550	0.2234	0.1890	0.2201	0.4560	0.4560	39.406	0.6139	3.0136
10	0.9874	0.9874	0.2580	0.2270	0.1930	0.2236	0.4340	0.4340	33.085	0.6237	3.0745
12	0.9895	0.9895	0.2640	0.2315	0.1960	0.2280	0.4360	0.4360	33.449	0.6361	3.0778
14	1.0081	1.0081	0.2570	0.2300	0.2000	0.2266	0.4430	0.4430	33.912	0.6321	3.1401
16	1.0129	1.0129	0.2680	0.2345	0.1980	0.2310	0.4480	0.4480	34.633	0.6444	3.1524
18	1.0199	1.0199	0.2660	0.2355	0.2020	0.2320	0.4440	0.4440	33.533	0.6472	3.1744
20	1.0314	1.0314	0.2720	0.2395	0.2040	0.2360	0.4410	0.4410	31.833	0.6583	3.2095
22	1.0810	1.0810	0.2750	0.2461	0.2140	0.2425	0.4980	0.4980	41.439	0.6763	3.3674
24	1.0855	1.0855	0.2800	0.2496	0.2160	0.2459	0.4750	0.4750	36.034	0.6860	3.3789
26	1.0987	1.1000	0.2780	0.2501	0.2190	0.2465	0.4880	0.4880	38.063	0.6875	3.4269
28	1.1000	1.0987	0.2900	0.2567	0.2200	0.2529	0.4820	0.4820	36.637	0.7053	3.4176
30	1.1271	1.1271	0.2870	0.2577	0.2250	0.2539	0.4960	0.4960	37.941	0.7082	3.5100
32	1.1355	1.1355	0.2900	0.2592	0.2250	0.2554	0.5060	0.5060	39.711	0.7123	3.5364
34	1.1538	1.1538	0.2960	0.2637	0.2280	0.2598	0.5040	0.5040	38.148	0.7247	3.5930

TABLE 4 OBSERVED AND CALCULATED OSCILLATOR STRENGTHS ($\text{PX } 10^6$) AND JUDD-OFELT INTENSITY PARAMETER (T_λ , $\Lambda = 2,4,6 \times 10^{10} \text{ cm}^{-1}$ PARAMETERS FOR PR(III): L ALANINE: CA(II) COMPLEX AT 313K (40 °C) AT DIFFERENT TIME(HRS)

Time (in hour)	${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$		${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$		${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$		${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
0	0.8575	0.8575	0.2320	0.2053	0.1760	0.2023	0.3800	0.3800	29.537	0.5641	2.6628
2	0.8779	0.8779	0.2400	0.2098	0.1770	0.2067	0.4070	0.4070	34.236	0.5765	2.7267
4	0.8914	0.8914	0.2330	0.2053	0.1750	0.2023	0.4010	0.4010	31.991	0.5641	2.7744
6	0.9186	0.9186	0.2440	0.2134	0.1800	0.2102	0.4010	0.4010	30.296	0.5863	2.8580
8	0.9552	0.9552	0.2500	0.2214	0.1900	0.2181	0.4270	0.4270	33.771	0.6085	2.9725
10	0.9674	0.9674	0.2540	0.2254	0.1940	0.2221	0.4300	0.4300	33.647	0.6196	3.0101
12	0.9727	0.9727	0.2540	0.2280	0.1990	0.2246	0.4250	0.4250	32.146	0.6266	3.0253
14	0.9863	0.9863	0.2600	0.2310	0.1990	0.2276	0.4430	0.4430	35.364	0.6348	3.0674
16	1.0010	1.0010	0.2580	0.2295	0.1980	0.2261	0.4370	0.4370	32.985	0.6306	3.1169
18	1.0120	1.0120	0.2590	0.2320	0.2020	0.2286	0.4390	0.4390	32.646	0.6376	3.1510
20	1.0206	1.0206	0.2660	0.2370	0.2050	0.2335	0.4590	0.4590	36.633	0.6514	3.1754
22	1.0678	1.0678	0.2780	0.2471	0.2130	0.2434	0.4760	0.4760	37.335	0.6790	3.3235
24	1.0673	1.0673	0.2710	0.2441	0.2140	0.2405	0.4730	0.4730	36.923	0.6708	3.3236
26	1.0769	1.0769	0.2780	0.2471	0.2130	0.2434	0.4780	0.4780	37.165	0.6790	3.3528
28	1.0908	1.0908	0.2790	0.2501	0.2180	0.2464	0.4920	0.4920	39.557	0.6874	3.3962
30	1.1087	1.1087	0.2850	0.2541	0.2200	0.2504	0.4790	0.4790	35.284	0.6984	3.4522
32	1.1189	1.1189	0.2890	0.2552	0.2180	0.2513	0.4950	0.4950	38.357	0.7011	3.4851
34	1.1399	1.1399	0.2910	0.2622	0.2300	0.2583	0.4970	0.4970	37.476	0.7206	3.5484

TABLE 5 OBSERVED AND CALCULATED OSCILLATOR STRENGTHS ($\text{PX } 10^6$) AND JUDD-OFELT INTENSITY PARAMETER (T_λ , $\Lambda = 2,4,6 \times 10^{10} \text{ cm}^{-1}$ PARAMETERS FOR PR(III): L ALANINE: CA(II) COMPLEX AT 318K (45 °C) AT DIFFERENT TIME(HRS)

Time (in hour)	${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$		${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$		${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$		${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
0	0.8542	0.8542	0.2230	0.1973	0.1690	0.1943	0.3470	0.3470	22.286	0.5420	2.6577
2	0.8652	0.8652	0.2310	0.2048	0.1760	0.2018	0.3810	0.3810	29.157	0.5628	2.6883
4	0.8834	0.8834	0.2340	0.2084	0.1800	0.2053	0.3850	0.3850	28.981	0.5725	2.7464
6	0.8932	0.8932	0.2370	0.2099	0.1800	0.2067	0.4060	0.4060	33.075	0.5766	2.7773
8	0.9450	0.9450	0.2460	0.2189	0.1890	0.2157	0.4190	0.4190	32.533	0.6015	2.9402
10	0.9570	0.9570	0.2430	0.2189	0.1920	0.2157	0.4200	0.4200	32.092	0.6016	2.9801
12	0.9507	0.9507	0.2520	0.2250	0.1950	0.2216	0.4230	0.4230	33.228	0.6182	2.9556
14	0.9792	0.9792	0.2510	0.2234	0.1930	0.2202	0.4480	0.4480	36.956	0.6141	3.0496

16	0.9851	0.9851	0.2600	0.2310	0.1990	0.2276	0.4450	0.4450	35.767	0.6348	3.0638
18	0.9919	0.9919	0.2530	0.2280	0.2000	0.2246	0.4280	0.4280	31.507	0.6266	3.0882
20	1.0079	1.0079	0.2630	0.2350	0.2040	0.2316	0.4470	0.4470	34.720	0.6458	3.1353
22	1.0471	1.0471	0.2610	0.2371	0.2100	0.2336	0.4700	0.4700	37.481	0.6515	3.2622
24	1.0504	1.0504	0.2700	0.2416	0.2100	0.2380	0.4510	0.4510	32.962	0.6638	3.2697
26	1.0673	1.0673	0.2760	0.2441	0.2090	0.2405	0.4790	0.4790	38.031	0.6707	3.3237
28	1.0829	1.0829	0.2780	0.2481	0.2150	0.2445	0.4850	0.4850	38.456	0.6818	3.3716
30	1.0876	1.0876	0.2820	0.2516	0.2180	0.2479	0.4720	0.4720	35.125	0.6915	3.3845
32	1.0956	1.0956	0.2840	0.2521	0.2170	0.2484	0.4860	0.4860	37.772	0.6929	3.4110
34	1.1120	1.1120	0.2890	0.2587	0.2250	0.2549	0.4890	0.4890	37.404	0.7109	3.4595

The rate constants for the complexation at different temperatures were evaluated from the plots of oscillator strength versus time for Pr(III): Amino acid: Ca(II) complexation. From Tables 6-8, it can be clearly seen that the rates of complexation of Pr(III): Amino acid with Ca(II) linearly increases with the increase in time.

TABLE 6 RATE CONSTANT FOR THE COMPLEXATION OF PR(III): GLYCINE: CA(II) AT DIFFERENT TEMPERATURES AND ACTIVATION ENERGY(EA)

Temp (K)	1/T K ⁻¹ X 10 ⁻³	Rate Constant Mol L ⁻¹ hr ⁻¹	Rate Constant (k) Mol L ⁻¹ s ⁻¹ x 10 ⁻⁶	log k	Activation Energy Ea (KJ)
298	3.3557	0.00769	2.1361	0.329624	0.003529
303	3.3003	0.00793	2.2028	0.342971	
308	3.2468	0.00801	2.2250	0.34733	
313	3.1949	0.00837	2.3250	0.366423	
318	3.1447	0.00837	2.3250	0.366423	

TABLE 7 RATE CONSTANT FOR THE COMPLEXATION OF PR(III): L-ALANINE: CA(II) AT DIFFERENT TEMPERATURES AND ACTIVATION ENERGY(EA)

Temp (K)	1/T K ⁻¹ X 10 ⁻³	Rate Constant Mol L ⁻¹ hr ⁻¹	Rate Constant (k) Mol L ⁻¹ s ⁻¹ x 10 ⁻⁶	log k	Activation Energy Ea (KJ)
298	3.3557	0.00769	2.1361	0.329624	0.00319
303	3.3003	0.00793	2.2028	0.342971	
308	3.2468	0.00801	2.2250	0.34733	
313	3.1949	0.00829	2.3028	0.362252	
318	3.1447	0.00832	2.3111	0.363821	

TABLE 8 RATE CONSTANT FOR THE COMPLEXATION OF PR(III): L-PHENYLALANINE: CA(II) AT DIFFERENT TEMPERATURES AND ACTIVATION ENERGY(EA)

Temp (K)	1/T K ⁻¹ X 10 ⁻³	Rate Constant Mol L ⁻¹ hr ⁻¹	Rate Constant (k) Mol L ⁻¹ s ⁻¹ x 10 ⁻⁶	log k	Activation Energy Ea (KJ)
298	3.3557	0.00223	0.6194	-0.208	0.053036
303	3.3003	0.00371	1.0306	0.013071	
308	3.2468	0.0069	1.9167	0.282547	
313	3.1949	0.00758	2.1056	0.323367	
318	3.1447	0.0083	2.3056	0.362776	

Since the intensity of 4*f*-4*f* transitions show a substantial increase with Time, hence absorption spectral analysis of 4*f*-4*f* transitions can be used to explore the kinetics of the formation of the complexes. The observed values of rate (k) have been evaluated in terms of the complex formed during the progress of the reaction and the same has been evaluated from the plots of oscillator strength of ³H₁ → ³P₂ transition of Pr(III) complex formation versus time (in hour). The values of activation energy (E_a) and thermodynamic parameters are evaluated from the Van't Hoff plot of log k against 1/T (Fig. 3).

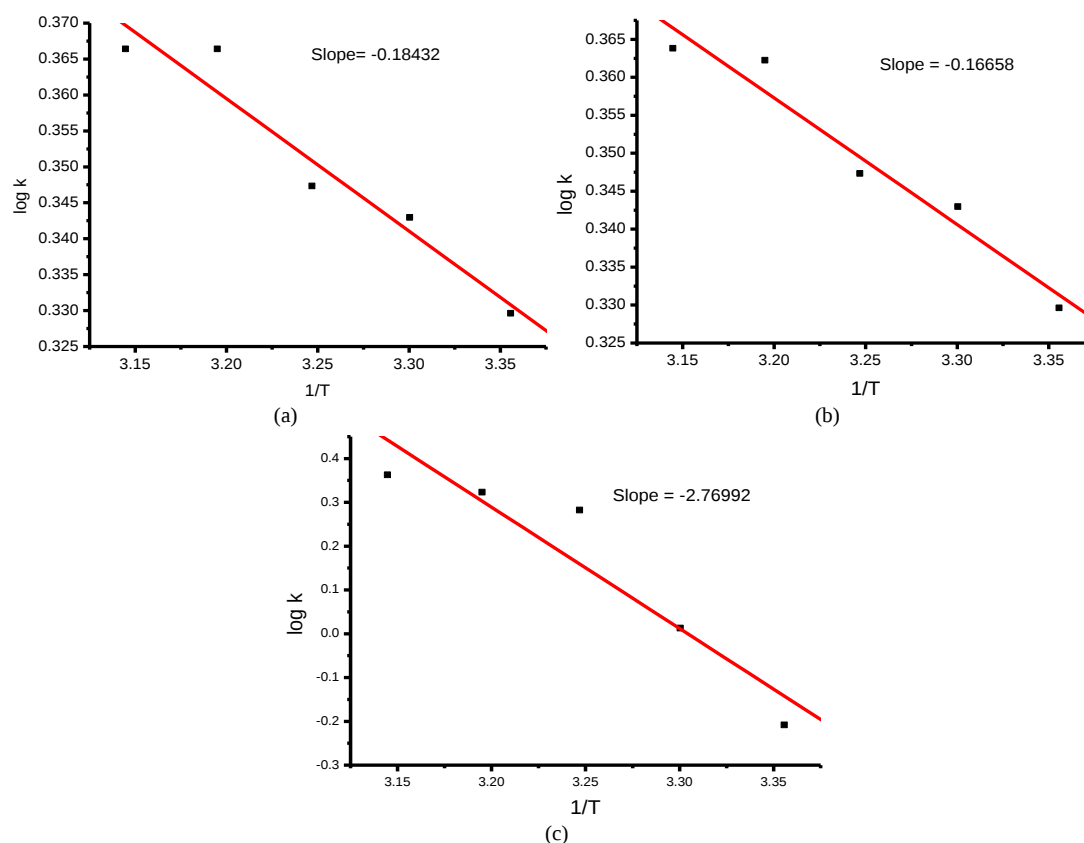


Fig. 3 Vant Hoff's plot of $\log k$ vs $1/T$ for (a) Glycine, (b) L-Alanine and (c) L-Phenylalanine

This technique can provide a means to determine indirectly the thermodynamic parameters of the complexation of Pr(III) and Ca^{2+} ions in DMF medium. It was clearly seen that the rate of complexation increases with increase in temperature and from which the activation energy E_a of the complexation is evaluated and consequently other thermodynamic parameters have been evaluated. The thermodynamic values are given in Table 9.

TABLE 9 THERMODYNAMIC PARAMETERS FOR THE COMPLEXATION OF PR(III); AMINO ACID; CA(II) AT DIFFERENT TEMPERATURES

T(K)	Rate constant (k) $\text{mol L}^{-1}\text{s}^{-1} \times 10^{-6}$			ΔH° (kJmol ⁻¹)			ΔS° (JKmol ⁻¹)			ΔG° (kJmol ⁻¹)		
	Gly	L-Ala	L-Phen	Gly	L-Ala	L-Phen	Gly	L-Ala	L-Phen	Gly	L-Ala	L-Phen
298	2.1361	2.1361	0.6194				0.006	0.006	-0.004	-1.881	-1.881	1.187
303	2.2028	2.2028	1.0306				0.007	0.007	0.000	-1.990	-1.990	-0.076
308	2.2250	2.2250	1.9167	0.003529	0.053036	0.053036	0.007	0.007	0.006	-2.048	-2.048	-1.666
313	2.3250	2.3028	2.1056				0.007	0.007	0.006	-2.196	-2.171	-1.938
318	2.3250	2.3111	2.3056				0.007	0.007	0.007	-2.231	-2.215	-2.209

IV. CONCLUSIONS

From the values of the thermodynamic parameters, it was found that:

The values of ΔH° and ΔS° are positive which indicates that the complexation reaction is endothermic and entropy increasing process.

Further, since $T\Delta S^\circ > \Delta H^\circ$ the coordination reaction is entropy driven process. Negative values of ΔG° predict that the complex formation is favourable and is spontaneous. The same trend was seen in all the complexes of Pr(III) with Glycine/ L-Alanine/ L-Phenylalanine in the presence of Ca(II).

Thus, it can be further justified that the simultaneous complexation reactions between Pr(III) ions with amino acids and metal ions, Ca(II) occur but at a spontaneous pace, following the randomness of the system when it approaches higher temperatures (increasing ΔS° values).

Further, from the Tables 6, 7, 8 it has been found that the activation energies (E_a) for L-Alanine in Pr(III) systems was the lowest i.e. 0.00319 KJ, which supports the earlier report that the most sensitive ligand (amino acid) in binding with Pr(III) was L-Alanine, which was followed by Glycine and the least sensitive was L-Phenylalanine.

The lower values of E_a substantiate further evidence that the reaction is a fast one.

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