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Spectrophotometric study of kinetics and associated thermodynamics for the complexation of Pr(III) with L-proline in presence of Zn(II)

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Abstract The complexation of L-proline with Pr(III) has been studied in presence and absence of Zn(II) in different environments by employing 4f–4f absorption transition spectra. The study was carried out through the computation of various spectral parameters namely energy interaction (Slator–Condon (F_k's), nephelauxetic effect (β), bonding ($b^{1/2}$) and percent covalency (δ) parameters) and intensity parameters (oscillator strength and Judd–Ofelt parameters). Pr(III), being a paramagnetic shows characteristic 4f–4f transition bands ($^3H_4 \rightarrow {}^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$) in the visible region. The intensities of these bands became more prominent in presence of Zn(II) suggesting the evolvement of Zn(II) towards the complexation of Pr(III) and L-proline. This intensification of bands is visualized to be due to the increased probability of interaction between 4f-orbital of metal ion and ligand. As well as these bands have been found to be highly sensitive to even minor changes in the immediate coordination around Pr(III), occurring as a result of the progress of heterobimetallic complexation of L-proline with Pr(III) and Zn(II). The sensitivities of these bands in terms of oscillator strength have been utilized to monitor the simultaneous coordination of L-proline with Pr(III) and Zn(II). The rate of complexation with respect to 4f–4f transition bands has been determined. The determined activation and thermodynamic parameters corresponding to rate constant were found to be highly favourable for the heterobimetallic complexation of L-proline with Pr(III) and Zn(II).

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1. Introduction

The photophysical property of lanthanides has been becoming an active area of research to both chemists and spectroscopists for many years, because of their potential applications in many fields. Most of these applications are based on their luminescent and absorption spectral properties of lanthanides (Jorgensen, 1962; Kostova et al., 2008; Liang-Cai et al., 2008). Recently, lanthanides are frequently used as an

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absorption probe in studying the biochemical systems involving calcium ion (Supkowski et al., 1999; Sudhindra et al., 2003). Lanthanides have comparable properties with calcium in terms of ionic radii, coordination number and binding pattern (Evans, 1999). Because of these properties lanthanides are effectively used as a probe for providing coordination characteristics of calcium towards biomolecules. From this point of view, the study of interaction between lanthanides and amino acids are important for understanding the role of calcium ions in biological systems (Bukistynska and Mondry, 1985; Kremer et al., 2005). They are used as models in metal-protein reactions and biological systems where the properties of proteins are attached to them. Amino acids are considered very crucial for our good health, since they contribute considerably to the health of the human nervous system, hormone production, and muscular structure aside from playing an important role in protein and enzyme synthesis. In addition, they are needed for vital organs and cellular structure. Among 20 naturally occurring amino acids, proline has a unique structure; the amino nitrogen binds with the side chain, leading to the formation of a pyrrolidine ring with the R-carbon. This structure necessarily restricts the conformations that proline can adopt within a peptide or protein, giving proline a unique role in the secondary and tertiary structures of proline-containing proteins. With this conformation proline is often found in the turns in complex proteins (Rai et al., 2006) and plays a binding role in collagen, which has a high proline content (Bronco et al., 2004). Proline-rich regions in proteins are also found in many kinase binding sites (Ferreon and Hilser, 2004) and are linked to many other cellular processes (Stapley and Creamer, 1999). Proline-rich regions can adopt a left-handed helical conformation and this conformation has been linked to ligands for signalling proteins and is important for the structural integrity of many proteins (Kelly et al. 2001; Ostrander et al., 1999). That proline is a very rigid amino acid and is exemplified by the fact that it is one of the largest components of the protein collagen, the main protein that forms connective tissue in humans and other higher organisms. From this theoretical and biological point of view, L-proline (2-pyrrolidinecarboxylic acid) is an interesting amino acid and its complexing properties are due to the ring nitrogen atom and COOH group in the molecule. Lanthanide ions, in contrast of calcium ions exhibit sharp absorption bands in the uv–visible region of the spectrum due to Laported forbidden 4f–4f transitions. These absorption bands are sensitive to both the symmetries of the complex environment and the strength of the metal–ligand bond. The sensitivities of these bands provide an excellent means of extracting information regarding the outer and inner coordination sphere, relative binding capability of the binding sites of the ligand, and incidence of covalence character in predominantly ionic-ligand bond. Such bands have been given the name "hypersensitive transition" by Jorsensen and Judd (1964)). Many experimental and/or theoretical studies have been devoted to hypersensitivity (Hopkin et al., 1996; Mondry and Starynowicz, 1997; Khan and Iftikhar, 1994; Sharma et al., 1992) and this work has been renewed recently by (Goerller-walrand and Binnemans, 1998). And the practical interest has been given to the oscillator strength and band shapes of the hypersensitive transitions because of their ability to probe the complex formation, coordination geometry, ligand structure and complex–solvent interaction. In the past years, the changes in the magnitude of oscillator strength of hypersensitive transition were successfully used to determine the stability constant as a function of ligand concentration (Bukietynska et al., 1981). Birnbaum et al. (1970) extended this application in exploring the binding of Nd(III) with bovine serum albumin (BSA). The hypersensitive transitions of Ln(III) were further used in studying the binding of Ln(III) with bovine trypsin (Abolt et al., 1975). Recently, Khan et al. (2004) have used the intensity and band shapes for both hypersensitive and non-hypersensitive transitions in studying the effect of changes in the environment upon 4f–4f absorption spectra of Ho(III) and Er(III) complexes with thiocyanate and 2,2-bipyridine. Our interest in the present study lies in investigating the complexation behaviour of Pr(III) with L-proline in presence of Zn(II) by monitoring the absorption changes with time. In our earlier paper it has been shown that the heterobimetallic complexation was more stable than binary complexation (Victory Devi and Rajmuhon Singh, 2011). Zn(II), an endogenous metal occurs intracellularly and is known to form a very stable complex in vivo. So, Zn(II) may involve in heterobimetallic simultaneous complexation with L-proline.

The main aim of the present paper was to study the nature of complexation of Pr(III) with L-proline in presence of Zn(II) through the computation of energy interaction parameters and intensity parameters. The variation of these parameters is correlated with the type of bonding between ligand and metal ion. We have reported optical absorption spectra in a series of aquated organic solvents. The sensitivities of 4f–4f bands (in terms of oscillator strength) towards the minor coordination changes around Pr(III) have been utilized to study the rate of simultaneous coordination of L-proline with Pr(III) and Zn(II). The rate of reaction has been determined in terms of complex formed during the progress of the reaction and this study is carried out at different temperatures. From this, we have determined the activation energy and thermodynamic parameters associated with the reaction.

2. Experimental

2.1. Materials

Praseodymium hexahydrate of 99% purity was purchased from CDH, Mumbai, Zn(II) nitrate (Aldrich USA) and L-proline of G R grade from SRL India, were used as such. The solvents used were CH_3CN, CH_3OH, DMF and Dioxane of A.R. grade from E. Merk.

The absorption spectra of Pr(III) complex with L-proline in presence of Zn(II) were recorded on Perkin Elmer Lambda-35 UV–Vis Spectrometer equipped with a device for kinetic and high resolution spectral analysis. The concentrations of Pr(III) and Zn(II) were maintained at 0.01 mol L^{-1}; and L-proline at 0.03 mol L^{-1}. Pr(III):L-proline was kept at 1:1 M ratio and for multimetal interaction, Pr(III):L-proline:Zn(II) was also kept in 1:1:1 M ratio for spectral analysis in different solvents. The temperature of all observations was maintained by using Perkin Elmer PTP1 Peltier-temperature system. For kinetic studies, the electronic transition spectra of Pr(III):L-proline: Zn(II) were recorded in DMF medium at different temperatures, i.e. 298, 303 and 308 K.

Pr(III) nitrate (0.01 mol L^{-1}) and L-proline (0.03 mol L^{-1}) were added and the resultant mixture was stirred for sufficient time to form the complex in solution (solution A). Stock

solution of Zn(II) was prepared by adding $Zn(NO_3)_2$ (0.01 mol L^{-1}) in double distilled water (solution B). On mixing Pr(III) and L-proline(solution A) and Zn(II) (solution B), the increase in absorbance and oscillator strength of four bands of Pr(III) were observed indicating the formation of complex in solution.

2.2. Methods

The energy of 4f–4f transitions comprises of two main components, i.e., the electrostatic and spin–orbit interaction between 4f-electrons.

$$E = \sum_K \int^K F_k + A_{so}\xi_{4f} \tag{1}$$

where, F_k and A_{so} are the angular part of electrostatic and spin–orbit interaction respectively. Their values can be calculated applying tensor operator technique. F_k and ξ_{4f} are radial integrals. Thus to define energy level scheme of $4f^n$ configuration it is necessary to have four radial integrals F_2, F_4, F_6 and ξ_{4f} which are evaluated by Hartree–Fock method (Carnall et al., 1968; Judd, 1962)

The energy E_j of the ith level may be written as

$$E_j(F_k, \xi_{4f}) = E_{0j}\left(F_k^0, \xi_{4f}^0\right) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k}\Delta F + \frac{\partial E_j}{\partial \xi_{4f}}\Delta\xi_{4f} \tag{2}$$

where E_{0j} is the zero-order energy of the jth level and $(\partial E_j/\partial F_k)$, $(\partial E_j/\partial \xi_{4f})$ are the partial derivatives. Using experimental energy levels for E_j and numerical values of zero-order energy and partial derivatives (Wong, 1963) a number of linear equations equal to the number of the observed levels were formed. By employing the least square fit method, the values of the correction factors ΔF_k, $\Delta\xi_{4f}$ were calculated. These were added to the zero-order parameter to obtain the parameters F_2, F_4, F_6 and ξ_{4f}. Thus,

$$F_k = F_k^0 + \Delta F$$

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

The effect of complexation on the spectra is the red shift of all the electronic transitions. The red shift is due to the expansion of the metal orbital radius resulting in lowering of the inter-electronic repulsion parameters (Slator–Condon F_k's or Racah E^k) as compared to those of aquo ion. This phenomenon is known as nephelauxetic effect, which measures the change in F_k with respect to free ion, and expressed by a nephelauxetic ratio β which is defined as:

$$\beta_1 = F_k^c/F_k^f; \beta_2 = \xi_{4f}^c/\xi_{4f}^f; \overline{\beta} = \frac{\beta_1 + \beta_2}{2} \tag{3}$$

where F_k^c (k = 2, 4, 6) and F_k^f refer to the parameters for complex and free ions respectively. There is ample evidence to the fact that 4f orbitals do participate in chemical bonding. The amount of mixing of 4f-orbital and ligand orbital can be given by another bonding parameter $b^{1/2}$, which measures the covalency in metal–ligand bond. This is in turn, expressed by parameters called percent covalency, δ. These parameters are related to nephelauxetic ratio (Sinha, 1966; Jorgensen, 1971; Itikhar et al., 1982) and are defined as:

$$b^{1/2} = [1 - \beta/2]^{1/2} \quad \delta = (1 - \beta/\beta) \times 100 \tag{4}$$

The intensity of the absorption band is measured by experimentally determined oscillator strength (P_{obs}), which is directly proportional to the area under the absorption curve and is found out by Gaussian curve analysis (Kothari and Misra, 1983) as

$$P = 4.6 \times 10^{-9} \times \varepsilon_{max} \times \Delta\upsilon_{1/2} \tag{5}$$

where ε_{max} is the molar extinction coefficient and $\Delta\upsilon_{1/2}$ is the half band width.

Theoretical treatment of 4f–4f band intensity is based on the Judd–Ofelt theory which proposed that the intensity of 4f–4f transition arises principally from forced electric dipole mechanism (Judd, 1962; Ofelt, 1962). Thus the electric dipole oscillator strength (P_{cal}) can be expressed relating to energy of transition ($\overline{\upsilon}$), square of the matrix element of unit tensor operator, $U^{(\lambda)}$ connecting initial $\langle f^n\psi_J|$ and final $|f^n\psi'_J\rangle$ through three phenomenological parameters T_λ (λ = 2, 4, 6) and is given by

$$P = \sum_{\lambda=2,4,6} T_\lambda \overline{\upsilon}\langle f^n\psi_J \| U^{(\lambda)} \| f^n\psi'_J\rangle \tag{6}$$

The three phenomenological parameters are called Judd–Ofelt parameters and are related to the radial wave function of the state, refractive index of the media and the ligand field parameters that characterize the environmental field. The values of T_λ parameters have been computed from the Judd–Ofelt expression by using the partial multiple regression method where the reported values of reduced matrix element are taken from Carnall et al. (1968). For Pr(III) complexes, The Judd–Ofelt relation is applicable in the present form:

$$P_{cal}/v = [U^{(2)}]^2 \cdot T_2 + [U^{(4)}]^2 \cdot T_4 + [U^{(6)}]^2 \cdot T_6 \tag{7}$$

The energy of activation E_a for the complexation of Pr(III):L-proline with Zn(II) was determined from Arrhenius equation by plotting ln k versus $1/T$:

$$E_a = \text{slope x R} \tag{8}$$

The thermodynamic parameters were also determined from slope and intercept of the linear Van't Hoff plot based on ln k versus $1/T$:

$$\ln k = -\frac{\Delta G}{RT} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \tag{9}$$

3. Results and discussions

On complexation of Pr(III), we observed prominent red shift, which leads to a reduction in the values of interelectronic repulsion parameters, Slator–Condon and spin–orbit coupling constant. This phenomenon is referred to as nephelauxetic effect. Nephelauxetic effect is taken as a measure of metal–ligand covalent bonding. This effect may be visualized to be due to an expansion of the wave functions which results from interaction between the metal cations and neighbouring ligands.

Since lanthanides are hard metal ions and thus, their preference will be for hard donor sites like the oxygen atoms and hence their bonding is basically electrostatic in nature. However, data in Table 1 shows no significant variation as compared to the values for free ion taken as standard. The positive value of $b^{1/2}$ and small variation in δ indicates the incidence of some covalent character in the metal–ligand bond. Therefore, we do

Table 1 Computed values of energy interaction Slator–Condon F_k (cm^{-1}), Spin–orbit interaction ξ_{4f}(cm^{-1}), Racah energy E^k(cm^{-1}), Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and Covalency percentage (δ) of Pr(III); Pr(III):L-proline (1:1) and Pr(III):L-proline:Zn(II) (1:1:1) in aqueous and aquated organic solvents at 25 °C.

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
H_2O										
Pr(III)	309.404	42.713	4.672	722.62	3513.17	23.771	587.08	0.9472	0.1624	5.5699
Pr(III): L-proline	309.305	42.699	4.670	722.25	3512.05	23.763	586.89	0.9468	0.1630	5.6142
Pr(III):L-proline:Zn(II)	309.390	42.711	4.619	722.55	3513.03	23.760	587.03	0.9472	0.1625	5.5760
CH_3CN										
Pr(III)	309.474	42.720	4.755	722.00	3514.02	23.780	587.22	0.9469	0.1629	5.6049
Pr(III): L-proline	309.292	42.698	4.678	722.54	3511.96	23.768	586.88	0.9470	0.1627	5.5933
Pr(III):L-proline:Zn(II)	309.291	42.697	4.670	722.47	3511.89	23.765	586.86	0.9470	0.1628	5.5999
CH_3OH										
Pr(III)	309.309	42.699	4.679	721.51	3511.82	23.767	586.89	0.9463	0.1639	5.6751
Pr(III): L-proline	309.301	42.697	4.675	721.50	3511.81	23.767	586.89	0.9471	0.1627	5.5902
Pr(III):L-proline:Zn(II)	309.263	42.694	4.669	721.30	3510.79	23.763	586.88	0.9467	0.1632	5.6300
DMF										
Pr(III)	309.030	42.657	4.666	720.23	3508.59	23.748	586.38	0.9450	0.1658	5.8193
Pr(III): L-proline	309.029	42.650	4.665	720.21	3508.58	23.744	586.35	0.9454	0.1653	5.7782
Pr(III): L-proline:Zn(II)	309.028	42.630	4.659	719.79	3508.49	23.743	586.32	0.9452	0.1656	5.8016
Dioxane										
Pr(III)	309.279	42.726	4.678	722.34	3511.70	23.768	586.83	0.9469	0.1630	5.6121
Pr(III): L-proline	309.270	42.721	4.674	721.99	3511.70	23.775	587.21	0.9469	0.1629	5.6072
Pr(III): L-proline:Zn(II)	309.244	42.716	4.670	721.74	3511.62	23.770	587.15	0.9467	0.1633	5.6309

not find significant variation in nephelauxetic parameters, yet we find appreciable changes in the oscillator strength of different 4f–4f transitions; hence we have given more emphasis to quantitative f–f transition intensity analysis. The absolute values of oscillator strength and Judd–Ofelt parameters are determined under the experimental conditions and listed in Table 2. Table 2 shows that the addition of L-proline to Pr(III) brings about a noticeable enhancement in the oscillator strength of pseudohypersensitive 4f–4f bands (irrespective of solvent nature). Consequently, marked variation in the experimentally determined Judd–Ofelt (T_λ) intensity parameters was found. This intensification of 4f–4f bands can be interpreted in terms

Table 2 Experimental and computed values of oscillatory strength ($P \times 10^6$) and Judd–Ofelt ($T_\lambda \times 10^{10}$) parameters for Pr(III); Pr(III): L-proline (1:1) and Pr(III):L-proline:Zn(II) (1:1:1) in aqueous and aquated organic solvents at 25 °C.

System	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
H_2O											
Pr(III)	0.7390	0.7390	0.3570	0.9054	1.4761	0.9193	3.6924	3.6924	−77.67	1.87	7.42
Pr(III): L-proline	0.7690	0.7699	0.3667	0.5385	0.7213	0.5469	0.5469	2.5633	−04.71	1.50	7.90
Pr(III): L-proline:Zn(II)	0.8430	0.8430	0.8736	1.2745	1.7017	1.2945	1.2945	2.0350	−53.46	3.55	8.72
CH_3OH											
Pr(III)	0.7137	0.7137	0.3861	0.5430	0.7108	0.5514	2.7599	2.7599	−20.95	1.51	8.65
Pr(III): L-proline	0.9526	0.9526	0.2696	0.5044	0.7504	0.5121	2.7822	2.7822	−31.94	1.40	8.75
Pr(III): L-proline:Zn(II)	1.1665	1.1665	0.7063	0.8622	0.8622	0.6541	2.8243	2.8243	−35.68	1.41	8.88
Dioxane											
Pr(III)	1.0576	1.0576	0.4632	0.7554	1.0640	0.7752	3.6771	3.6771	−03.78	2.11	11.48
Pr(III): L-proline	1.1839	1.1839	0.4343	0.5909	0.7591	0.6001	3.0247	3.0247	−68.74	2.65	15.49
Pr(III): L-proline:Zn(II)	1.3362	1.3362	0.4543	0.6091	0.7957	0.6185	3.0007	3.0007	−07.18	17.0	19.40
DMF											
Pr(III)	1.3044	1.3044	0.7103	0.6589	1.2256	0.9733	4.2912	4.2912	−11.63	2.07	13.37
Pr(III): L-proline	1.3198	1.3198	0.7435	0.6803	0.8092	0.6297	4.3278	4.3278	−11.54	2.73	17.46
Pr(III): L-proline:Zn(II)	1.4300	1.4300	0.8695	0.8969	1.3444	0.9105	4.3807	4.3807	−10.34	3.50	21.20
CH_3CN											
Pr(III)	1.0210	1.0210	0.5462	0.6368	0.8050	0.8499	3.4941	3.4967	−33.18	2.33	10.82
Pr(III): L-proline	1.0954	1.0954	0.4726	0.6678	0.8154	0.6477	3.9266	3.9266	−54.40	2.77	19.20
Pr(III): L-proline:Zn(II)	1.1947	1.1947	0.6469	0.8443	1.0375	0.8472	3.8919	3.8919	−78.64	2.92	20.86

of interaction of 4f-orbital with ligand wavefunction. The intensification of bands and red shift were taken as an evidence for the involvement of ligand in complexation. This intensification of 4f–4f bands became more prominent in presence of Zn(II) (Fig. 1). This clearly suggests that the heterobimetallic complexation of L-proline was much stronger than binary complexation of L-proline. We also have shown that the binding of hard metal ion, Pr(III) strengthens the complexation of Zn(II) and L-proline and vice versa. This means that the probability of interaction of 4f-orbital with ligand wavefunction increases leading to the intensifications of bands.

The significant changes in the T_λ parameters in absence of significant nephelauxetic effect (as observed in present study) show that the unsymmetrical part of the field has major influence on these parameters. Regarding this, Reisfeld (2004) has argued that an increase in covalency is not the sole factor that influences T_λ parameters. The nephelauxetic effect, which is caused by lowering of the excited states of lanthanide ion by the surrounding crystal field, is influenced mainly by the asymmetric part of the crystal field. The change in T_λ parameter, in the presence of negligible changes in the nephelauxetic effect, shows that the asymmetric part of the field has major influences on these parameters. The values of T_λ parameters change significantly on varying the composition of solvents. T_2 is found to be negative so it is meaningless in the present study. T_4 and T_6 are affected significantly. Both parameters are related not only to the immediate coordination changes but also to changes in symmetry properties of the complex species (Misra and Mehta, 1991).

Absorption spectra of Pr(III) complex in different aquated organic solvents (Fig. 2) clearly shows the affinity of solvents towards the Pr(III) coordination environment. The small differences in the 4f–4f band shape in the different solvents may be related to differences in how the donor groups interact with

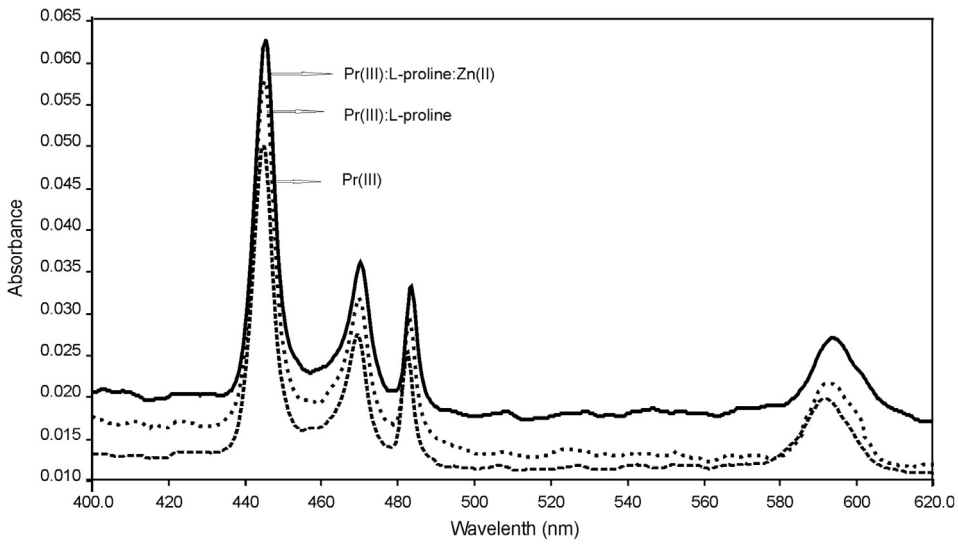

Figure 1 Comparative absorption spectra of Pr(III) with L-proline in presence of Zn(II) in DMF.

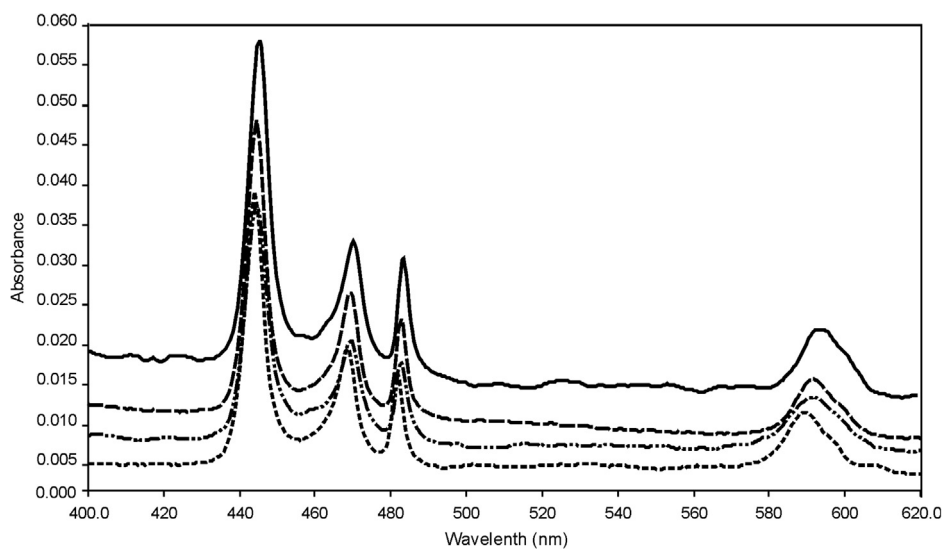

Figure 2 Comparative absorption spectra of Pr(III): L-proline in ——— DMF – – – Dioxane —·· —· CH_3CN - - - - CH_3OH.

f-electrons of the lanthanide ion. DMF appears to have strongest influence on Pr(III):L-proline followed by dioxane and least in acetonitrile. This means that DMF is effective in replacing nitrate ion from solvated species and promote 4f–4f electric dipole intensity, which is in accordance with our previous studies (Victory Devi and Rajmuhon Singh, 2011a, 2011b). Invasion of the hydration sphere about the praseodymium ion by DMF could be expected to cause alternation in strength and symmetry of field about Pr(III). Changes in symmetry around Pr(III) along with invasion of solvent type lead to the intensification of 4f–4f bands.

The difference in oscillator strength in different solvents may be associated to ligand (solvent) structure and their coordination behaviours around Pr(III). The DMF has two coordination sites but it generally binds via oxygen when it coordinates to hard acids like lanthanides. The red shift is observed in the energies of all the pseudohypersensitive bands which are considered as a marker for quantitative analysis in Pr(III) ion i.e. $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$. Although we have found red shift in energies of all transitions, the effect is more pronounced in DMF. The red shift is due to the expansion of the metal orbital radius bringing about a shortening of the metal–ligand bond length thereby increasing the probability of interaction between metal and ligand orbitals. This clearly shows the involvement of L-proline in the inner sphere coordination around the metal ion. However, a small magnitude of oscillator strength is observed. This might be due to the promotion of classical zwitterion resonance form of the acid by lanthanide ions. This in fact contributes a significant amount of electron-density to the lanthanides. This might be one of the reasons why low intensities of bands are observed in the present study. All results obtained clearly show the sensitivities of pseudohypersensitive transitions of Pr(III) on minor coordination changes, being caused by solvent nature, coordination number, and nature of Pr(III):L-proline band which do induce significant variation in the intensity of pseudohypersensitive transitions. Hence we have employed the comparative absorption and absorption difference spectroscopy along with variation of different spectral parameters, involving 4f–4f transitions as a probe to follow the kinetics of simultaneous complexation of L-proline with Pr(III) and Zn(II).

The kinetic study is carried out by monitoring the change in absorbance with time corresponding to four bands and their spectral changes. Four sets of kinetic experiment were conducted at different temperatures and for brevity only one set of kinetic run showing changes in absorbance with time at 308 K is given in Fig. 3. The comparative absorption spectra, showing an increase in absorbance with time, during the complexation of L-proline with Pr(III) and Zn(II) are given in Fig. 3. The data showing an increase in oscillator strengths with time during complexation reaction are given in Table 3. Data given in Table 3 shows that T_2, T_4 and T_6 parameters show a progressive increase with oscillator strengths of observed 4f–4f transition bands. The addition of Zn(II) to Pr(III):L-proline leads to sharp changes in the oscillator strengths of 4f–4f bands, as well as substantial variation in the magnitude of T_λ parameters.

The reaction appears to be quite slow in a initial stage as shown by only marginal variation of oscillator strength of pseudohypersensitive transitions of Pr(III) as well as by the magnitude of T_4 and T_6. For Pr(III), T_4 and T_6 are known to be extremely sensitive to even the minor changes in the immediate coordination environment, hence small variation of these two parameters can be ascribed to only very minor changes in the immediate coordination environment around Pr(III).

The rate of complexation corresponding to all pseudo hypersensitive transitions of Pr(III) were evaluated spectrophotometrically

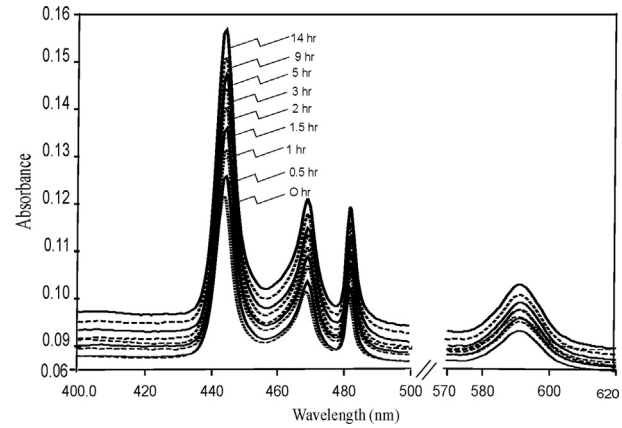

Figure 3 Time dependant absorption spectra of Pr(III):L-proline:Zn(II) in DMF at different time intervals (h) measured at 35 °C.

Table 3 Experimental values of oscillator strength ($P_{obs} \times 10^6$) and computed values of Judd–Ofelt intensity ($T_\lambda \times 10^{10}$) parameters for the complexation of Pr(III):L-proline and Zn(II) in DMF at different time intervals (35 °C).

Time (h)	$^3P_2$	$^3P_1$	$^3P_0$	$^1D_2$	T_2	T_4	T_6
0	4.410	1.465	0.722	1.357	−76.62	3.020	13.608
0.5	4.481	1.479	0.735	1.384	−68.13	3.029	13.638
1	4.757	1.507	0.744	1.396	−17.65	3.191	13.882
1.5	4.891	1.517	0.763	1.480	−82.43	3.291	14.106
2	5.187	1.538	0.733	1.506	−70.36	3.599	17.643
3	5.214	1.580	0.801	1.531	−54.21	3.617	17.892
5	5.463	1.690	0.846	1.633	−76.32	3.652	18.100
9	5.793	1.704	1.105	1.696	−82.22	3.851	19.201
14	6.329	1.795	1.138	1.803	−43.28	4.106	19.873

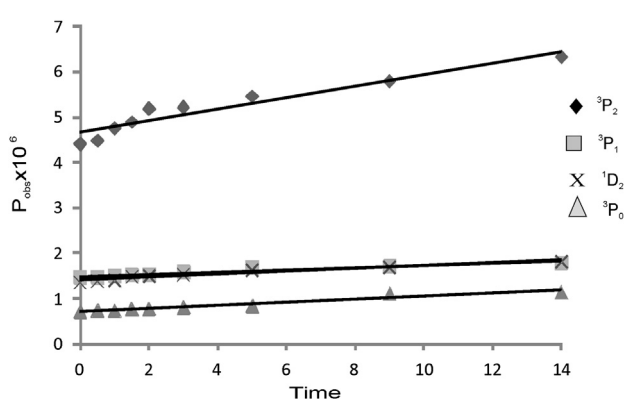

Figure 4 Plot of oscillator strength vs. time for four transitions of Pr(III) complex Pr(III):L-proline:Zn(II) in DMF at 35 °C.

Table 4 Rate constant and thermodynamic parameters for the complexation of Pr(III):L-proline with Zn(II) at different temperatures and activation energy for the complexation reaction.

Temp. (K)	Rate constant (M^{-1} s^{-1})				E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (JK^{-1} mol^{-1})	ΔG (kJ mol^{-1})
	$^3P_2$	$^3P_1$	$^3P_0$	$^1D_2$				
298	0.051	0.0161	0.005	0.010				−76.510 ± 0.001
303	0.090	0.0181	0.008	0.031	0.0759	0.0759	257.38	−77.795 ± 0.001
308	0.128	0.0312	0.024	0.033				−79.080 ± 0.001

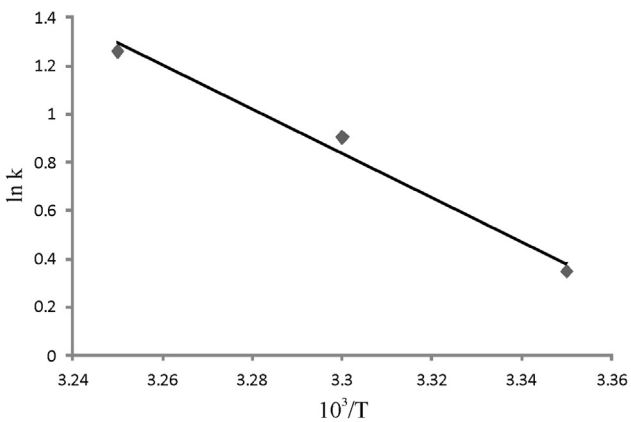

Figure 5 Plot of ln k versus $10^3/T$ for the complexation of Pr(III):L-proline and Zn(II) in DMF.

by determining the maximum absorbance reached for complexation. The rate of complexation was determined in terms of complex formed during the progress of the reaction and the observed values of rate constant (k) were evaluated from the plot of oscillator strength of four 4f–4f bands of Pr(III) viz, $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$ versus time (Fig. 4). The activation energy for the complexation was determined from Arrhenius equation. The rate of reaction was found to increase with temperature. This approach provides a good means to determine indirectly the thermodynamic parameters of simultaneous complexation of L-proline with Pr(III) and Zn(II) from the Van't Hoff plots of 1/T versus ln k (Fig. 5). The evaluated thermodynamic parameters are given in Table 4 along with the rate of complexation and activation energy. The positive values of ΔH and ΔS indicate that the complexation is an endothermic and entropy increasing process. Since $T\Delta S^\circ > \Delta H^\circ$, the entropy increasing effect results in $\Delta G^\circ < 0$, the reaction is an entropy driven process. The negative value of standard Gibbs energy indicates that the process is a spontaneous one. Overall speaking, the magnitude of the thermodynamic parameters were found to be highly favourable for the heterobimetallic complexation of L-proline with Pr(III) and Zn(II).

4. Conclusion

From the above discussion through the variation of spectral parameters, it can be concluded that the heterobimetallic complexation of L-proline with Pr(III) in presence of Zn(II) is more stable than binary complexation of Pr(III) with L-proline. It further, suggest the stimulative effect of Zn(II) on the complexation of Pr(III) with L-proline. The intensification of 4f–4f band in absence of prominent changes in the coulombic and spin–orbit coupling interaction parameter is attributed to the polarization caused by the asymmetric part of the field. Moreover, the symmetry of the complex species has been found to play a major role towards the intensification of bands. The unusual intensification of pseudo hypersensitive transitions of Pr(III) has been utilized to study the kinetics of heterobimetallic complexation of L-proline with Pr(III) and Zn(II) in DMF. The absorption spectra of complexation of Pr(III):L-proline with Zn(II) increases with time. The rate of complexation is determined in terms of complex formed during the progress of the reaction by monitoring the variation of oscillator strength with time. The rate of reaction has been found to increase with temperature and from which the activation energy of the complexation has been determined. Further, the magnitude of determined thermodynamic parameters of the complex formed have shown that the heterobimetallic complexation of L-proline with Pr(III) and Zn(II) is highly favoured in solution.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2013.07.044.

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