Research Article

Calculation and Comparison of Energy Interaction and Intensity Parameters for the Interaction of Nd(III) with DL-Valine, DL-Alanine and β-Alanine in Presence and Absence of Ca^{2+}/Zn^{2+} in Aqueous and Different Aquated Organic Solvents Using 4f-4f Transition Spectra as Probe

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Absorption difference and comparative absorption spectrophotometric studies involving 4f-4f transitions of Nd(III) and different amino acids: DL-valine, DL-alanine, and β-alanine in presence and absence of Ca(II) and Zn(II) in aqueous and different aquated organic solvents have been carried out. Variations in the spectral energy parameters: Slater-Condon (F_K) factor, Racah (E^K), Lande factor (ξ_{4f}), nephelauxetic ratio (β), bonding ($b^{1/2}$), percentage covalency (δ) are calculated to explore the mode of interaction of Nd(III) with different amino acids: DL-valine, DL-alanine, and β-alanine. The values of experimentally calculated oscillator strength (P) and computed values of Judd-Ofelt electric dipole intensity parameters, T_λ ($\lambda = 2,4,6$), are also determined for different 4f-4f transitions. The variation in the values of P and T_λ parameters explicitly shows the relative sensitivities of the 4f-4f transitions as well as the specific correlation between relative intensities, ligand structures, and nature of Nd(III)-ligand interaction.

1. Introduction

Lanthanides ions are often used as spectroscopic probes as surrogates for calcium ions in studies of biological systems as well as promoters in the textile dyeing industry. Lanthanide elements have extensive application in industries, agriculture, and biomolecular reactions, so it has become very important to understand the behaviour of trivalent lanthanide ions in biological system [1, 2]. The co-ordination chemistry of lanthanide in solution state has become more important with the increase use of lanthanides as probes in the exploration of the structural function of biomolecular reactions [3–6] specially due to its ability to replace Ca(II) in a specific manner [7–10]. In our previous study [11], we have reported the interaction of Pr(III) with amino acids in aqueous and different aquated organic solvents

by using 4f-4f absorption spectra as probes and thereby calculating energy interaction parameters like Slater-Condon (F_K) factor, Racah (E^k), Lande factor (ξ_{4f}), nephelauxetic ratio (β), bonding ($b^{1/2}$), percentage covalency (δ), and parameters like calculated values of oscillator strength (P) and computed values of electric dipole intensity parameters, T_λ ($\lambda = 2, 4, 6$). We also studied [12] the energy interaction parameters for the complexation of Pr(III) with glutathione reduced (GSH) in presence and absence of Zn(II) in aqueous and aquated organic solvents using 4f-4f transition spectra as probe. The ligands we chose are amino acids, that is, DL-valine, DL-alanine, and β-alanine having two binding sites, namely, carboxylic acid group and an amino group.

Ca(II) which is a hard metal ion and Zn(II) which is a soft metal ion are endogenous metal ions that have different co-ordinating behaviour towards biological molecules. For

binding, Ca(II) prefers hard donor site like carboxylic acid group while Zn(II) prefers soft donor site like amino group which are found in amino acids. Since Nd(III) resembles Ca(II), its complexation can provide information about the co-ordination characteristics of diamagnetic Ca(II) with biomolecules during biochemical reactions. Hence, paramagnetic lanthanides are good spectral probes to explore the biological roles of Ca(II) by isomorphous substitution. In our present work, the absorption difference and comparative absorption spectroscopy involving 4f-4f transitions of the complexation of different amino acids with Nd(III) in presence and absence of Ca(II)/Zn(II) has been carried out in aqueous and aquated organic solvents. The variation in the energy parameters like Slater-Condon factor (F_K, K = 2, 4, 6), Lande-Spin-Orbit coupling (ξ_{4f}), nephelauxetic ratio (β), bonding ($b^{1/2}$), percentage covalency (δ) is calculated to explain the nature of complexation. The changes in the values of experimentally determined oscillator strength (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.

2. Experimental

$Nd(NO_3) \cdot 6H_2O$ of 99.9% purity was purchased from CDH analytical reagent and DL-valine, DL-alanine, and β-alanine were purchased from Loba-Chemie Indo-Australian Co. The solvents used are methanol, acetonitrile, dimethylformamide (DMF), and dioxane, and they are of AR grade from Qualigens.

The solutions of Nd(III), DL-valine, DL-alanine, β-alanine, Ca(II) and Zn(II) salts were prepared in different solvents in the concentration 10^{-2} M. For the present study, Nd(III) : ligand was kept at 1 : 1 molar ratio and in multimetal complexation like Nd(III) : ligand : Ca(II)/Zn(II) was also kept at 1 : 1 : 1 molar ratio. The absorption spectra were recorded at pH 4 on a Perkin Elmer Lambda-35 UV-Vis spectrophotometer upgraded with high resolution and expansion of scale in the region 350–1000 nm. The temperature for all the observations is maintained at 298 K for all the observations by using water circulating thermostat model DS-G HAAKE.

Nephelauxetic ratio has been regarded as a measure of covalency. The nephelauxetic effect has been interpreted in terms of Slater-Condon and Racah parameters, by the ratio of the free ion and complex ion [13, 14]

$$\beta = \frac{F_K^c}{F_K^f} \quad \text{or} \quad \beta = \frac{E_c^K}{E_f^K}, \tag{1}$$

where F_k (K = 2, 4, 6) is the Slater-Condon parameters, and E^K the Racah parameters for complex (c) and free ions (f), respectively.

The bonding parameter ($b^{1/2}$) is represented by the amount of mixing of 4f-orbital and ligand orbital and is related to the nephelauxetic effect as

$$b^{1/2} = \left[\frac{1 - \beta}{2}\right]^{1/2}, \qquad \delta = \left[\frac{1 - \beta}{\beta}\right] \times 100. \tag{2}$$

The energy of 4f-4f transitions is composed of two main components, that is, the electrostatic and spin-orbit interaction between 4f-electrons

$$E = \sum_k \int^K F_K + A_{so}\xi_{4f}, \tag{3}$$

where F_K and A_{so} are the angular part of electrostatic and spin-orbit interaction, respectively. F_K (Slater-Condon) and ξ_{4f} (Lande parameter) 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 [13, 15]. Then, energy E_j of the jth level is given by

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

where E_{oj} is the zero order energy of the jth level

$$F_K = F_K^0 + \Delta F_K, \tag{5}$$

$$\xi_{4f} = \xi_{4f}^0 + \Delta\xi_{4f}, \tag{6}$$

when $\Delta F_K \ll F_K^0$ and $\Delta\xi_{4f} \ll \xi_{4f}^0$.

The difference between the observed E_j values and the zero order value ΔE_j is evaluated by

$$\Delta E_j = \sum_{K=2,4,6} \frac{\delta E_j}{\delta F_K} + \frac{\delta E_j}{\delta\xi_{4f}}\Delta\xi_{4f}. \tag{7}$$

By using the zero-order energy and partial derivatives of Nd(III) ion given by Wong [14], the previous equation can be solved by least squares technique and the value of ΔF_K and $\Delta\xi_{4f}$ can be found out. From these values, the value of F_2, F_4, F_6, and ξ_{4f} are found out by using (5) and (6). The intensity of the absorption band is measured by the oscillator strength (P), which is directly proportional to the area under the absorption curve. It can be expressed in terms of molar extinction coefficient (ε_{max}), energy of the transition in wave number ($\bar{\nu}$), and the refractive index (η) of the medium by the relationship

$$P = 4.31 \times 10^{-9}\left[\frac{9\eta}{(\eta + 2)^2}\right]\int\varepsilon_{max}\bar{\nu}\delta\bar{\nu}, \tag{8}$$

where ε_{max} = molar extinction coefficient = Absorbance/Concentration $\times$ path length of the cell in cm (l = 1 cm), $\bar{\nu}$ is the energy of transition in wave number, and η is the refractive index of the medium.

The experimental values of oscillator strength (P_{obs}) of absorption band were given by Gaussian curve analysis as

$$P_{obs} = 4.6 \times 10^{-9} \times \varepsilon_{max} \times \Delta\bar{\nu}_{1/2}, \tag{9}$$

where $\Delta\bar{\nu}_{1/2}$ is half band width.

The observed oscillator strength (P_{obs}) of the transition energies was expressed in terms of parameters defined by
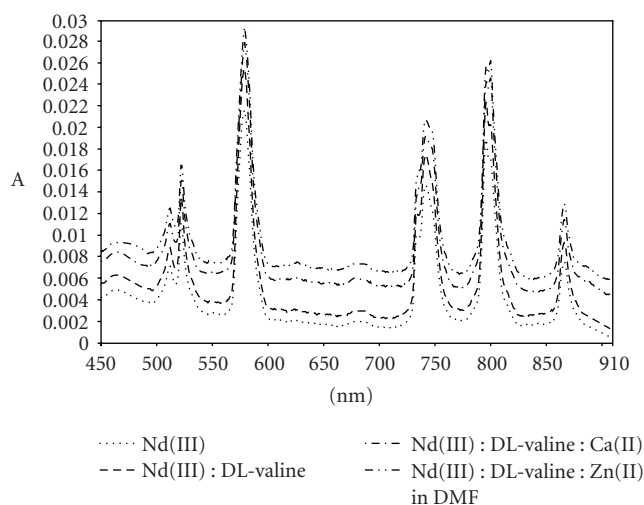
Figure 1: Comparative absorption spectra of Nd(III), Nd(III) : DL-valine, Nd(III) : DL-valine : Ca(II), and Nd(III) : DL-valine : Zn(II) in DMF.
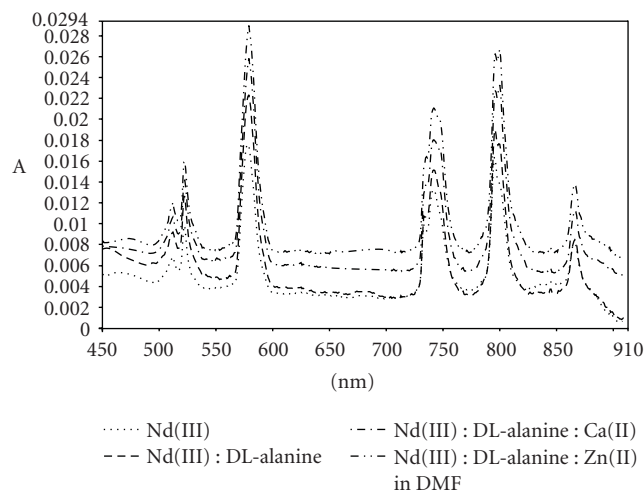

Figure 2: Comparative absorption spectra of Nd(III), Nd(III) : DL-alanine, Nd(III) : DL-alanine : Ca(II), and Nd(III) : DL-alanine : Zn(II) in DMF.

Ofelt [16] known as T_2, T_4, T_6 parameters which are given by the following equation:

$$\frac{P_{obs}}{\nu} = \left[\left(U^2\right)\right]^2 \cdot T_2 + \left[\left(U^4\right)\right]^2 \cdot T_4 + \left[\left(U^6\right)\right]^2 \cdot T_6, \quad (10)$$

where U^λ is the matrix element given by Carnall et al. [15] and ν is the frequency of transition.

3. Results and Discussion

Lanthanide complexes have very small crystal field stabilization energy and fast water exchange rate. Therefore, the conversion from one geometry to another is very convenient and facile. The sensitivity of hypersensitive bands in lanthanides towards coordination environment has been recognized since long. A few, however, are very sensitive
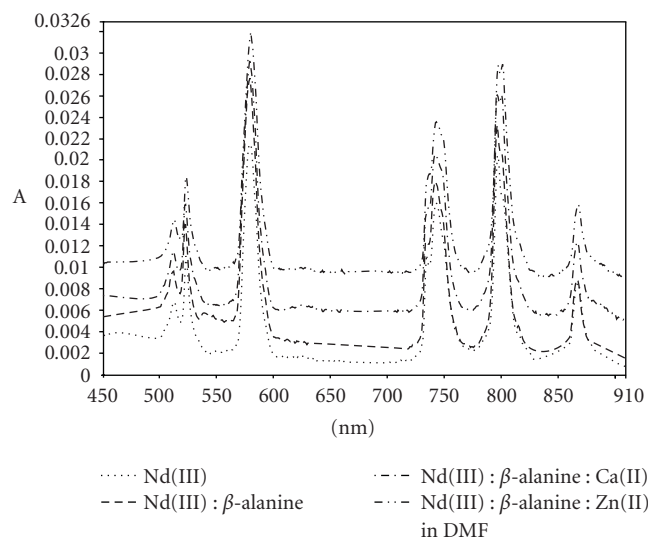

Figure 3: Comparative absorption spectra of Nd(III), Nd(III) : DL-β-alanine, Nd(III) : β-alanine : Ca(II), and Nd(III) : β-alanine : Zn(II) in DMF.

to the environment and are usually more intense when a lanthanide ion gets complexed than it is in the corresponding aquo ion. Such transitions are called hypersensitive transitions. The 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) do not obey the selection rules for hypersensitive transition but have been found to exhibit substantial sensitivity in the complexes. Such transitions are called "Ligand Mediated Pseudohypersentive" or Pseudohypersentive transitions [17]. Karraker [18, 19] showed that the shape, energy, and oscillator strength of hypersensitive or pseudohypersensitive transitions can be correlated with coordination number and are diagnostic of immediate coordination environment around lanthanide ions. The computed and observed values of energy interaction - Slater-Condon (F_k), Lande (ξ_{4f}), Nephelauxetic ratio (β), bonding ($b^{1/2}$), and percentage covalency (δ) parameters for Nd(III), Nd(III) : DL-valine/DL-alanine/β-alanine, Nd(III) : DL-valine/DL-alanine/β-alanine : Ca(II)/Zn in aqueous and different aquated organic solvents is given in Table 1.

The comparative absorption spectra of Nd(III), Nd(III) : DL-valine/DL-alanine/β-alanine, Nd(III) : DL-valine/DL-alanine/β-alanine : Ca(II), and Nd(III) : DL-valine/DL-alanine/β-alanine : Zn(II) in solvent DMF are given in Figures 1, 2, and 3.

From the figures, it is revealed that marginal red shift occurs as different amino acids are added to Nd(III). The wavelength further increases on addition of Ca(II) to Nd(III) : ligand. The same is also observed in case of Zn(II) but the increase in wavelength is more in the case when Zn(II) is added to Nd(III)-ligand. There is a slight decrease in Slater-Condon (F_k) and Spin-orbit interaction (ξ_{4f}) which indicates lowering of both coulombic and spin-orbit interaction parameters thus leading to the expansion of the central metal ion orbital as the complexation goes on

TABLE 1: Computed value of energy interaction parameters—Slater Condon F_K (cm-1), Spin Orbit Interaction ξ_{4f} (cm-1), Nephelauxetic ratio (β), bonding ($b^{1/2}$), and covalency (δ) parameters of Nd(III), Nd(III) : amino acid (1 : 1), Nd(III) : amino acid : Ca(II) (1 : 1 : 1), and Nd(III) : amino acid : Zn(II) (1 : 1 : 1) in aqueous and different aquated organic solvents (50 : 50) at pH4.

System	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
1. *Solvent—Water*							
Ligand—DL-valine							
Nd(III)	328.77	48.22	5.20	951.55	1.0220	0.1048	2.1527
Nd(III): L	328.21	48.21	5.19	951.54	1.0270	0.1161	2.6260
Nd(III) : L : Ca(II)	327.94	48.19	5.17	950.01	1.0293	0.1211	2.8498
Nd(III) : L : Zn(II)	327.83	48.12	5.17	950.00	1.0303	0.1231	2.9400
Ligand—DL-alanine							
Nd(III) : L	327.68	48.60	5.25	961.65	1.0308	0.1242	2.9904
Nd(III) : L : Ca(II)	327.55	48.69	5.24	961.62	1.0323	0.1270	3.1258
Nd(III) : L : Zn(II)	327.49	48.69	5.23	961.60	1.0330	0.1284	3.1928
Ligand—β-alanine							
Nd(III) : L	327.87	48.67	5.24	959.59	1.0295	0.1215	2.8672
Nd(III) : L : Ca(II)	327.84	48.66	5.23	959.57	1.0298	0.1221	2.8958
Nd(III) : L: Zn(II)	327.82	48.65	5.22	959.55	1.0301	0.1226	2.9172
2. *Solvent—Methanol*							
Ligand—DL-valine							
Nd(III)	330.12	48.10	5.13	928.15	1.0068	0.0583	0.6746
Nd(III) : L	330.02	48.09	5.13	928.14	1.0076	0.0618	0.7587
Nd(III) : L : Ca(II)	330.00	48.07	5.12	928.13	1.0083	0.0646	0.8263
Nd(III) : L : Zn(II)	329.95	48.05	5.10	928.12	1.0113	0.0752	1.1176
Ligand—DL-alanine							
Nd(III) : L	330.07	48.09	5.12	928.54	1.0077	0.0623	0.7711
Nd(III) : L : Ca(II)	330.00	48.08	5.10	928.52	1.0117	0.0766	1.1588
Nd(III) : L : Zn(II)	329.98	48.08	5.10	928.49	1.0119	0.0772	1.1786
Ligand—β-alanine							
Nd(III) : L	330.03	48.14	5.12	927.40	1.0080	0.0634	0.7973
Nd(III) : L : Ca(II)	329.99	48.13	5.10	927.39	1.0091	0.0673	0.8988
Nd(III) : L: Zn(II)	329.92	48.12	5.09	927.30	1.0125	0.0790	1.2333
3. *Solvent—MeCN*							
Ligand—DL-valine							
Nd(III)	330.11	48.13	5.13	928.06	1.0069	0.0587	0.6854
Nd(III) : L	330.08	48.12	5.11	928.02	1.0078	0.0623	0.7709
Nd(III) : L : Ca(II)	330.07	48.12	5.10	928.01	1.0079	0.0629	0.7846
Nd(III) : L : Zn(II)	330.06	48.11	5.05	927.95	1.0080	0.0633	0.7955
Ligand—DL-alanine							
Nd(III) : L	329.94	48.18	5.12	927.85	1.0083	0.0645	0.8250
Nd(III) : L : Ca(II)	329.92	48.14	5.11	927.83	1.0079	0.0628	0.7820
Nd(III) : L : Zn(II)	329.91	48.12	5.09	927.80	1.0086	0.0655	0.8501
Ligand—β-alanine							
Nd(III) : L	329.98	48.20	5.12	928.11	1.0081	0.0638	0.8085
Nd(III) : L : Ca(II)	329.97	48.19	5.11	928.10	1.0083	0.0642	0.8184
Nd(III) : L: Zn(II)	329.95	48.17	5.10	928.07	1.0084	0.0650	0.8304
4. *Solvent—DMF*							
Ligand—DL-valine							
Nd(III)	329.99	48.20	5.14	929.45	1.0082	0.0640	0.8122
Nd(III) : L	329.96	48.11	5.12	929.43	1.0113	0.0753	1.1216
Nd(III) : L : Ca(II)	329.29	48.61	5.11	929.40	1.0177	0.0941	1.7383
Nd(III) : L : Zn(II)	329.27	48.61	5.10	929.35	1.0180	0.0950	1.7726

TABLE 1: Continued.

System	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
Ligand—DL-alanine							
Nd(III) : L	329.77	48.15	5.14	933.42	1.0131	0.0809	1.2916
Nd(III) : L : Ca(II)	329.21	48.12	5.10	933.36	1.0182	0.0953	1.7848
Nd(III) : L : Zn(II)	329.21	48.08	5.05	933.30	1.0183	0.0956	1.7933
Ligand—β-alanine							
Nd(III) : L	329.80	48.12	5.14	934.58	1.0130	0.0805	1.2797
Nd(III) : L : Ca(II)	329.26	48.10	5.12	934.55	1.0182	0.0954	1.7894
Nd(III) : L: Zn(II)	329.25	48.61	5.21	934.53	1.0183	0.0956	1.7952
5. Solvent—Dioxane							
Ligand—DL-valine							
Nd(III)	330.15	48.14	5.13	927.18	1.0064	0.0567	0.6372
Nd(III) : L	330.11	48.14	5.12	927.16	1.0069	0.0591	0.6928
Nd(III) : L : Ca(II)	330.09	48.12	5.11	927.13	1.0071	0.0596	0.7050
Nd(III) : L : Zn(II)	330.02	48.10	5.10	927.12	1.0082	0.0642	0.8181
Ligand—DL-alanine							
Nd(III) : L	330.06	48.11	5.12	928.54	1.0074	0.0627	0.7793
Nd(III) : L : Ca(II)	330.04	48.10	5.11	928.50	1.0081	0.0637	0.8061
Nd(III) : L : Zn(II)	330.02	48.13	5.13	928.49	1.0083	0.0642	0.8186
Ligand—β-alanine							
Nd(III) : L	330.08	48.12	5.13	929.14	1.0081	0.0636	0.8026
Nd(III) : L : Ca(II)	330.06	48.11	5.12	929.13	1.0083	0.0642	0.8184
Nd(III) : L : Zn(II)	330.04	48.10	5.11	929.10	1.0085	0.0651	0.8405

which lead to increase in the values of nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), and percentage covalency (δ). This is in accordance with the theory of f ↔ f transitions reported earlier [20]. Ryan and Jørgensen [21] noticed the dependence of nephelauxetic effect on the coordination number. It was suggested that shortening in the metal-ligand distance occurs with decrease in the coordination number. Misra et al. [22] observed a general decrease in the values of Slater-Condon (F_2, F_4, F_6) and Spin-orbit interaction (ξ_{4f}) parameters as compared to the corresponding parameters of the free ion. In all the systems, the values of nephelauxetic effect (β) range from 1.0057 to 1.0200 and positive values of bonding parameter ($b^{1/2}$) indicate covalent bonding between Nd(III) and the ligand in the complexes. There is small variation in the bonding parameter ($b^{1/2}$) value and this suggests that the 4f-orbitals are very slightly involved in the bonding of lanthanide complexes. The same trend is also observed in case of Pr(III) in our previous work [11].

The observed and computed values of oscillator strengths and Judd-Ofelt parameters for Nd(III), Nd(III) : DL-valine/DL-alanine/β-alanine, Nd(III) : DL-valine/DL-alanine/β-alanine : Ca(II)/Zn in aqueous and different aquated organic solvents are given in Table 2.

On complexation the intensities of most of 4f-4f transition change slightly but the intensity of the hypersensitive transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$ of neodymium shows significant intensification and large variation with slight change in the immediate coordination environment around neodymium.

This clearly suggests a significant change, when Nd(III) interacts with the ligand in the solution. The comparative absorption spectra shown in Figures 1–3 clearly predict that the addition of ligand to Nd(III) results in significant enhancement in the oscillator strengths of different 4f-4f transitions. As a consequence, we have observed noticeable increase in the magnitude of Judd-Ofelt (T_λ) intensity parameters. These suggest the binding of the ligand to Nd(III) in solution. The introduction of Zn(II) in the Nd(III)-ligand yields noticeable changes in the oscillator strengths and in the magnitude of Judd-Ofelt (T_λ) intensity parameters. This result shows the enhancement in the interaction of Nd(III)-ligand in the solution. Among the five transitions of Nd(III) ion , that is, $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4G_{5/2}$, $^4G_{7/2}$, we observed the highest oscillator strength value for the hypersensitive transition ($^4G_{5/2}$) and the lowest oscillator strength value for the pseudohypersensitive transition ($^4F_{3/2}$). From these we can conclude that $^4G_{5/2}$ is the most sensitive transition and $^4F_{3/2}$ is the least sensitive transition.

The intensification of 4f-4f band specially hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$ and pseudohypersensitive $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$ transitions is reflected in the magnitude of T_λ ($\lambda = 2, 4, 6$) parameters. Intensification of the bands is due to the introduction of covalency in the metal-ligand bond as the oscillator strength of intra 4f-4f transitions and magnitude of T_λ increase with the increase in nephelauxetic effect. In general the oscillator strength for Nd(III) complexes can be expressed in terms of T_4 and T_6 parameters

TABLE 2: Observed and computed values of oscillator strengths ($P \times 10^6$) and Judd-Ofelt ($T_\lambda \times 10^{10}$) parameters for Nd(III), Nd(III) : amino acid (1 : 1), Nd(III) : amino acid : Ca(II) (1 : 1 : 1), and Nd(III) : amino acid : Zn(II) (1 : 1 : 1) in aqueous and different aquated organic solvents (50 : 50) at pH4.

System	$^4F_{3/2}$ P_{obs} (P_{cal})	$^4F_{5/2}$ P_{obs} (P_{cal})	$^4F_{7/2}$ P_{obs} (P_{cal})	$^4G_{5/2}$ P_{obs} (P_{cal})	$^4G_{7/2}$ P_{obs} (P_{cal})	T_2	T_4	T_6
1. *Solvent—Water*								
Ligand—DL-valine								
Nd(III)	0.5382 (0.4198)	2.0575 (2.2038)	2.4827 (2.3536)	4.0131 (4.0129)	0.7734 (0.7751)	2.1438	0.6251	4.0570
Nd(III): L	0.4072 (0.3676)	2.2170 (2.3319)	2.6887 (2.5857)	3.9798 (3.9899)	0.8439 (0.7101)	2.2494	0.3233	4.4939
Nd(III) : L : Ca(II)	0.3689 (0.3219)	2.0885 (2.1773)	2.5195 (2.4404)	2.3775 (2.3823)	0.6692 (0.6071)	1.9206	0.2077	4.2545
Nd(III) : L : Zn(II)	0.4088 (0.3761)	2.1681 (2.2927)	2.6359 (2.5239)	3.6058 (3.6189)	0.8570 (0.6862)	1.9889	0.3822	4.3838
Ligand—DL-alanine								
Nd(III) : L	0.3056 (0.2909)	1.9257 (1.9753)	2.2794 (2.2422)	3.3356 (3.3622)	0.6579 (0.5788)	1.9218	0.1801	3.8840
Nd(III) : L : Ca(II)	0.3121 (0.2922)	1.9702 (2.0387)	2.3572 (2.2957)	3.0413 (3.0480)	0.6358 (0.5467)	1.7396	0.1538	4.0098
Nd(III): L : Zn(II)	0.3067 (0.3288)	1.9206 (1.9985)	2.2665 (2.1973)	2.9533 (2.9565)	0.6234 (0.5808)	1.6044	0.3382	3.8197
Ligand—β-alanine								
Nd(III) : L	0.2905 (0.2733)	1.8900 (1.9546)	2.2677 (2.2097)	3.3155 (3.3221)	0.6417 (0.5538)	1.9382	0.1174	3.8595
Nd(III) : L : Ca(II)	0.2767 (0.2777)	1.8648 (1.8972)	2.1583 (2.1289)	2.9898 (2.9950)	0.5988 (0.5302)	1.7094	0.1690	3.7139
Nd(III) : L : Zn(II)	0.3079 (0.3004)	1.9670 (2.0266)	2.3233 (2.2695)	3.1427 (3.1505)	0.6685 (0.5661)	1.7875	0.1971	3.9577
2. *Solvent—MeOH*								
Ligand—DL-valine								
Nd(III)	0.4041 (0.3260)	1.9600 (2.1704)	2.6143 (2.4258)	4.0093 (4.0269)	0.9013 (0.6708)	2.3215	0.2279	4.2042
Nd(III) : L	0.4285 (0.3497)	2.0521 (2.2567)	2.6912 (2.5081)	4.1627 (4.1793)	0.9258 (0.7088)	2.3888	0.2841	4.3440
Nd(III) : L : Ca(II)	0.4246 (0.3544)	2.1591 (2.3001)	2.6845 (2.5588)	4.1744 (4.1827)	0.8223 (0.7131)	2.3895	0.2808	4.4329
Nd(III) : L : Zn(II)	0.4263 (0.3616)	2.1397 (2.2681)	2.6226 (2.5081)	4.0071 (4.0145)	0.8052 (0.7074)	2.2676	0.3304	4.3399
Ligand—DL-alanine								
Nd(III) : L	0.4554 (0.3549)	1.9846 (2.1861)	2.5897 (2.4101)	3.9740 (3.9857)	0.8545 (0.6990)	2.2423	0.3466	4.1656
Nd(III) : L : Ca(II)	0.4090 (0.3329)	2.0653 (2.2347)	2.6522 (2.5009)	3.8331 (3.8446)	0.8126 (0.6606)	2.2079	0.2231	4.3365
Nd(III) : L : Zn(II)	0.4355 (0.3653)	2.0472 (2.2229)	2.5538 (2.2611)	3.8471 (3.8574)	0.8347 (0.6993)	2.1491	0.3844	4.1734
Ligand—β-alanine								
Nd(III) : L	0.4075 (0.3252)	2.0011 (2.2015)	2.6460 (2.4668)	4.1290 (4.1442)	0.8797 (0.6801)	2.4039	0.2073	4.2797
Nd(III) : L : Ca(II)	0.4097 (0.3206)	2.0661 (2.2702)	2.7444 (2.5620)	4.0224 (4.0369)	0.8529 (0.6630)	2.3555	0.1493	4.4521
Nd(III) : L: Zn(II)	0.4246 (0.3450)	2.0005 (2.1983)	2.6151 (2.4382)	3.9467 (3.9620)	0.8876 (0.6865)	2.2548	0.2964	4.2217

Table 2: Continued.

System	$^4F_{3/2}$ P_{obs} (P_{cal})	$^4F_{5/2}$ P_{obs} (P_{cal})	$^4F_{7/2}$ P_{obs} (P_{cal})	$^4G_{5/2}$ P_{obs} (P_{cal})	$^4G_{7/2}$ P_{obs} (P_{cal})	T_2	T_4	T_6
3. *Solvent—MeCN* *Ligand—DL-valine*								
Nd(III)	0.4654 (0.3341)	2.0211 (2.0906)	2.5481 (2.4163)	3.8651 (3.8631)	0.6374 (0.6645)	2.2005	0.2629	4.1849
Nd(III) : L	0.4533 (0.3682)	2.0730 (2.2109)	2.6396 (2.4257)	3.9117 (3.9167)	0.7719 (0.7068)	2.1767	0.3913	4.1887
Nd(III) : L : Ca(II)	0.4056 (0.3475)	2.1228 (2.2649)	2.6491 (2.5227)	3.8211 (3.8319)	0.8160 (0.6740)	2.1701	0.2706	4.3687
Nd(III) : L : Zn(II)	0.3988 (0.3505)	2.1140 (2.2397)	2.5979 (2.4853)	3.8153 (3.8255)	0.8113 (0.6776)	2.15662	0.2979	4.3022
Ligand—DL-alanine								
Nd(III) : L	0.4834 (0.3824)	2.1427 (2.2505)	2.7069 (2.5021)	4.1569 (3.8295)	0.8468 (0.6742)	2.3264	0.3935	4.4049
Nd(III) : L : Ca(II)	0.4205 (0.3321)	2.0668 (2.1883)	2.5482 (2.4408)	3.7227 (3.7245)	0.6728 (0.6491)	2.1175	0.2456	4.2303
Nd(III) : L: Zn(II)	0.4466 (0.3930)	2.2284 (2.3528)	2.6906 (2.5795)	3.9167 (3.9256)	0.8482 (0.7308)	2.1578	0.4216	4.4549
Ligand—β-alanine								
Nd(III) : L	0.4355 (0.3308)	2.0135 (2.1907)	2.6027 (2.4452)	4.0408 (4.0481)	0.7737 (0.6777)	2.3290	0.2379	4.2405
Nd(III) : L : Ca(II)	0.4179 (0.3535)	2.1261 (2.2871)	2.6866 (2.5427)	4.0171 (4.0297)	0.8629 (0.6983)	2.2897	0.2839	4.4063
Nd(III) : L: Zn(II)	0.4009 (0.3671)	2.0267 (2.2065)	2.5826 (2.4206)	3.8324 (3.8536)	0.9801 (0.6998)	2.1376	0.3884	4.1832
4. *Solvent—DMF* *Ligand—DL-valine*								
Nd(III)	0.3055 (0.1700)	1.9017 (2.0571)	2.6091 (2.4723)	4.0810 (4.0790)	0.4783 (0.5045)	2.6337	-0.3942	4.3484
Nd(III) : L	0.4041 (0.2355)	1.9303 (2.0890)	2.5715 (2.4327)	4.3778 (4.3705)	0.5022 (0.6051)	2.7092	-0.1245	4.2534
Nd(III) : L : Ca(II)	0.4223 (0.2684)	2.1369 (2.2479)	2.7100 (2.6135)	4.5944 (4.5821)	0.4947 (0.6563)	2.8116	-0.0746	4.5643
Nd(III) : L : Zn(II)	0.4429 (0.3655)	2.0428 (2.2011)	2.5727 (2.4309)	4.4178 (4.4276)	0.8804 (0.7524)	2.5197	0.3781	4.2017
Ligand—DL-alanine								
Nd(III) : L	0.3438 (0.1322)	1.8281 (1.9717)	2.6197 (2.4075)	4.2702 (3.8322)	0.7772 (0.4428)	2.5939	0.0022	4.2575
Nd(III) : L : Ca(II)	0.4706 (0.3942)	2.1870 (2.3526)	2.7420 (2.5931)	4.6832 (4.6942)	0.9500 (0.6473)	2.6618	0.4195	4.4819
Nd(III) : L: Zn(II)	0.4612 (0.3954)	2.1165 (2.2722)	2.6264 (2.4865)	4.5428 (4.5543)	0.9475 (0.7953)	2.5563	0.4696	4.2905
Ligand— β-alanine								
Nd(III) : L	0.3787 (0.2472)	1.8832 (2.0896)	2.6023 (2.4191)	4.1236 (4.1303)	0.6836 (0.5958)	2.5327	-0.0738	4.2253
Nd(III) : L : Ca(II)	0.4314 (0.3278)	2.0987 (2.1482)	2.6559 (2.4090)	4.6990 (4.7217)	1.0386 (0.7393)	2.7727	0.2422	4.1759
Nd(III) : L: Zn(II)	0.4198 (0.3553)	2.0497 (2.2005)	2.5898 (2.4498)	4.6047 (4.6166)	0.9137 (0.7584)	2.6620	0.3307	4.2389

TABLE 2: Continued.

System	$^4F_{3/2}$ P_{obs} (P_{cal})	$^4F_{5/2}$ P_{obs} (P_{cal})	$^4F_{7/2}$ P_{obs} (P_{cal})	$^4G_{5/2}$ P_{obs} (P_{cal})	$^4G_{7/2}$ P_{obs} (P_{cal})	T_2	T_4	T_6
5. *Solvent—Dioxane*								
Ligand—DL-valine								
Nd(III)	0.3837 (0.2162)	1.9097 (2.1350)	2.7146 (2.5155)	3.6947 (3.6973)	0.5531 (0.5182)	2.3115	-0.2341	4.4073
Nd(III) : L	0.3967 (0.2932)	1.9273 (2.1396)	2.6150 (2.4257)	3.9279 (3.9409)	0.7972 (0.6271)	2.3231	0.1013	4.2177
Nd(III) : L : Ca(II)	0.3792 (0.3167)	1.9952 (2.1706)	2.5942 (2.4371)	3.8846 (3.8997)	0.8473 (0.6486)	2.2571	0.1871	4.2292
Nd(III) : L : Zn(II)	0.3922 (0.3175)	1.9089 (2.0779)	2.4651 (2.3143)	3.7077 (3.7195)	0.7906 (0.6359)	2.1258	0.2421	4.0112
Ligand—DL-alanine								
Nd(III) : L	0.4084 (0.3108)	1.9472 (2.1129)	2.5166 (2.3693)	3.6940 (3.7009)	0.7157 (0.6254)	2.1312	0.1936	4.1102
Nd(III) : L : Ca(II)	0.4059 (0.3507)	2.0237 (2.1723)	2.5298 (0.3968)	3.8291 (3.8415)	0.8439 (0.6814)	2.1555	0.3360	4.1444
Nd(III) : L: Zn(II)	0.4059 (0.3561)	2.0071 (2.1410)	2.4694 (2.3495)	3.7984 (3.8095)	0.8318 (0.6854)	2.1197	0.3769	4.0579
Ligand—β-alanine								
Nd(III) : L	0.4519 (0.3538)	1.9815 (2.1732)	2.5661 (2.3953)	3.9877 (3.9984)	0.8415 (6.9959)	2.2506	0.3491	4.1393
Nd(III) : L : Ca(II)	0.4269 (0.3396)	2.0128 (2.2022)	2.6199 (2.4508)	3.9708 (3.9834)	0.8457 (0.6813)	2.2727	0.2705	4.2441
Nd(III) : L: Zn(II)	0.3974 (0.3267)	1.9757 (2.1539)	2.5630 (2.4036)	3.8762 (3.8902)	0.8433 (0.6596)	2.2295	0.2408	4.1652

but the effect of solvent or ligand on the intensity of a hypersensitive transition can be explained by T_2 parameters only. The value of T_2 parameter which increased in the presence of organic solvents suggests that organic solvents have a better coordinating power in comparison with water as a result of solvation. T_4 and T_6 parameters which are related to changes in symmetry properties of the complex species are slightly affected in comparison with T_2 parameter. At the same time, T_6 parameter is also influenced by the extent of mixing of $4f^n$ and $5d$ orbital. It is noted that T_4 and T_6 parameters are affected significantly in the presence of different solvents. These suggest that symmetry of the complex species is changed significantly and not only the immediate coordination environment of Nd(III). These changes are considered to be good evidence for the involvement of amino acids (ligand) in the inner sphere coordination of Nd(III). Amino acids are expected to form inner sphere complexes by forming an ionic linkage with carboxylic oxygen and an additional linkage due to the amino group. All the results obtained clearly suggest that minor coordination changes in the Nd(III) complexes are caused by the coordinating sites of amino acid, nature of solvent, coordination number, nature of Nd(III)-amino acid bond, which induces significant variation in the intensity of 4f-4f transitions.
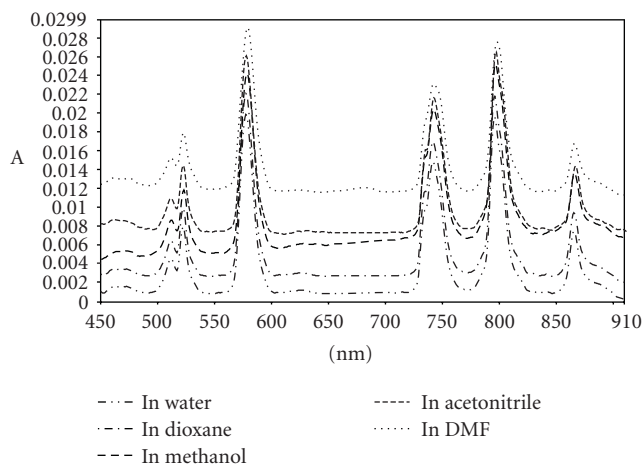

FIGURE 4: Comparative absorption spectra of Nd(III) : DL-alanine : Zn(III) in water, methanol, acetonitrile, dioxane, and DMF.

The comparative absorption spectra of Nd(III) : DL-alanine : Zn(II), given in Figure 4, shows the effect of solvents.

When the different ligands, that is, DL-valine, DL-alanine, and β-alanine are added to Nd(III) in different

solvents, maximum intensity is observed when the solvent is DMF. Again, when Ca(II) is added to Nd(III) : DL-valine, Nd(III) : DL-alanine, Nd(III) : β-alanine in different solvents, maximum intensification of bands is observed when the solvent is DMF. Similarly, when Zn(II) is added to Nd(III) : DL-valine, Nd(III) : DL-alanine, Nd(III) : β-alanine in different solvents, maximum intensity is observed when the solvent is DMF. From these observation, it can be concluded that intensification is maximum in the case of DMF because of the participation of N-donor site of DMF in the complexation of Nd(III) and the amino acid ligands.

4. Conclusion

From the present studies, it has been observed the involvement of Ca(II)/Zn(II) in the complexation of Nd(III) with amino acids (ligand). There is a slight decrease in the values of F_k and ξ_{4f} which leads to an increase in the values of nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) , and percentage covalency (δ) indicating stronger binding of metal ions, that is, Nd(III) with Ca(II)/Zn(II) and amino acids. Same changes are also observed in intensity parameters—oscillator strength (P) and Judd-Ofelt parameter, T_λ ($\lambda = 2, 4, 6$). The variation of the solvent has significant effect on the oscillator strength (P) and Judd-Ofelt parameter, $T_\lambda(\lambda = 2, 4, 6)$. Among all the solvents used, maximum intensification is observed in the case of DMF and this is because of the participation of N-donor site of DMF in the complexation.

Acknowledgment

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