Absorption spectra of ternary complex of neodymium in different solvents

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The optical absorption spectra of complex of neodymium in different solvents i.e water (18), methanol (32.04), ethanol (46.07) and acetic acid (60.05) have been recorded in visible region (360-900 nm for Nd3+) using amino acid primary ligand and diol as secondary ligand in ratio (1:2:1). The values of energies and intensities of various transition have been calculated using Judd-Ofelt relation which are found to be in good agreement with experimental results. The complexes studied are found to be ionic in nature. The effect of various ligand on the position and intensity of the observed transition in different environments has been discussed in terms of metal-ligand co-ordinate. Transition also involves change in the vibrational modes of the complex comprising a rare earth ion and its surroundings which provides a contribution to oscillator strength of precisely similar form.

Keywords: UV-Vis spectra, Rare earth metals, Amino acid, Judd-Ofelt parameters

1 Introduction

Information regarding composition and structure of lanthanide complexes with non-aqueous solvent molecules is in lesser stage but has been obtained mainly from spectrophotometric studies[1-7]. Studies of absorption spectra of tri-positive neodymium ion with different ligands have been reported[8-10]. The mixed ligand complexes of Nd^{3+} in different environments have been reported in the present paper. Much work has been done on rare earth complex with oxygen ligands[11-15]. It is considered as important lasing material due to narrow line width and weak crystal field interaction. Most $f \leftrightarrow f$ transitions in rare earths are found to be weak in comparison to one which are called as hypersensitive transition[16,17]. The intensity of hypersensitive transition changes with change of environment of metal ion in different complex[18]. Various intensity parameters i.e Judd-Ofelt parameters (T_2, T_4, T_6), bonding parameters $b^{1/2}$ of complex, energy parameters (F_2, F_4, F_6) and covalency of complexes have been calculated and discussed.

2 Experimental Details

Neodymium ternary complex ML_2L^1 with amino acid proline as primary ligand (L) and propane-1,3 diol (L′) as secondary ligand were prepared following Whan and Crossby. The complexes were crystallized under vacuum. The elemental analysis of the complexes was also carried out. The complexes of Nd^{3+} were prepared[19] and the chemicals used were of AR grade and metals 99.9%. Pure (Indian Rare earth Ltd.) were used and the complexes were prepared in molar ratio 1:2:1. The visible spectra was recorded on model uv-2601 spectrophotometer (rayleigh analytical instrument corp) in the laboratory.

3 Evaluation of Parameters

3.1 Energy levels

The parameters have been evaluated expressing the energy as a Taylor series expansion as:

$$E_j (F_k , \zeta_{4f}) = E_{oj}(F_k^0 , \zeta_{4f}^0)$$
$$+ \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \xi_{4f}} \Delta \zeta_{4f} \quad \ldots(1)$$

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

The relation for nephelauxetic ratio β and degree of covalency $b^{1/2}$ is given by:

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

The value of Nephelauxetic[20] ratio has been obtained using relation $\beta = F_2^c / F^f$, where subscript c and f refer to complex and free ion. The β value for $Nd^{3+} > 1.0$ shows that complex is ionic in nature. Also

with change of metal i.e as the atomic number of metal ion increases the covalency decreases.

3.2 Intensity Parameter

Oscillator strength of each transition has been calculation using the formula.

$$P_{exp} = 4.6 \times 10^{-9} \times \varepsilon_m \times \Delta y_{1/2}$$

where ε_m and $\Delta y_{1/2}$ are the molecular extinction coefficient and half band width, respectively.

The experimentally observed values of oscillator strength for Nd^{3+} complex along with their calculated values have been shown in Table 3. The values of F_2, F_4 and F_6 parameter were computed using Judd-Ofelt relation[21] by partial multiple regression method and have been presented in Table 2. The values of reduced matrix elements were collected from Carnall *et al*[22]. The values in parenthesis indicates the corresponding molecular weight. It has been observed that the value of T_2 changes linearly with molecular weight of amino acid. Figure 1 shows the variation of optical density with wavelength in all solvents for Nd^{3+} complex in visible region (360-900 nm).

4 Results and Discussion

Table 1 presents the observed energy (have been converted into wave numbers) as well as calculated values of energy levels using above equation for Nd^{3+} complex in different solvents. Here we find that calculated value of energy level parameters matches with observed value. RMS deviation between calculated and observed value is very low which actually supports the validity of relation used in case of Nd^{3+} complexes . We also observed that calculated

and observed values of energy are roughly the same in all the solvent. It has been clearly observed from the low value of rms deviation as well. From Table 1, we also find that the value of energy levels calculated for neodymium matches with observed value which clearly indicates that the formation of complex is perfect.

The calculated values of Slater-Condon parameters F_2, F_4 & F_6 Lande's parameters ζ_{4f}, nephelauxetic ratio β, & bonding parameters $b^{1/2}$ in different solvent are presented in Table 2 in different solvent and the value matches with free ion value. From Table 2, we also observe that parameter values are roughly same in different environments. The value of β is slightly greater than 1 which indicates that complexes are ionic in nature.

The decrease in value of F_2 from that of free ion may support the complexation. This decrease shows that on complexation the contraction of 4f-orbital is reduced[20] with the increase of atomic number of metal
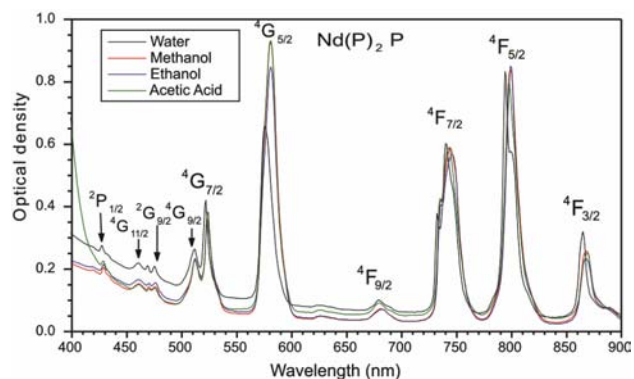

Fig. 1 — Variation of optical density with wavelength for Pr^{3+} complex in different solvent

Table 1 — Observed and calculated values of energy levels (in cm^{-1}) for Nd^{3+} complex in different solvent

Levels	Water		Methanol		Ethanol		Acetic Acid	
	Cal. cm^{-1}	Obs. cm^{-1}	Cal. Cm$^{=1}$	Obs. cm^{-1}	Cal. cm^{-1}	Obs. cm^{-1}	Cal. cm^{-1}	Obs. cm^{-1}
$^2P_{1/2}$	23420.32	23419.20	23358.68	23364.48	23356.20	23364.48	23361.61	23364.48
$^4G_{11/2}$	21675.33	21739.13	21614.04	21739.13	21594.77	21739.13	21654.29	21739.13
$^2G_{9/2}$	21290.78	21367.52	21213.88	21276.59	21212.56	21276.59	21216.68	21276.59
$^4G_{9/2}$	19677.23	19569.47	19596.02	19531.25	19591.18	19531.25	19606.08	19531.25
$^4G_{7/2}$	19332.17	19193.85	19232.96	19120.45	19237.12	19120.45	19224.03	19120.45
$^4G_{5/2}$	17380.28	17391.30	17273.29	17241.37	17277.70	17241.37	17263.49	17241.37
$^4F_{9/2}$	14838.61	14727.54	14805.65	14684.28	14792.92	14662.75	14832.15	14727.54
$^4F_{7/2}$	13389.39	13513.51	13344.94	13440.86	13335.46	13422.81	13364.56	13458.95
$^4F_{5/2}$	12556.25	12594.45	12505.42	12515.64	12499.17	12515.64	12518.28	12547.05
$^{+4}F_{3/2}$	11541.41	11574.07	11477.52	11520.73	11478.69	11520.73	11474.62	11507.47
rms deviation		84.3162		79.6169		83.7511		70.2651

ion. Ten peaks in case of Nd^{3+} complexes have been observed. The difference of energy value between observed and calculated is very small which supports the formation of complex well. The variation of wave length with optical density for Nd^{3+} have been shown in graph in visible region.

Table 3 reported the calculated value of oscillator strength for Nd^{3+} complex in different solvents which is in good agreement with observed value. The values of all parameters for $^4G_{5/2}$ levels are maximum because of hypersensitive transition. The observed and calculated values of oscillator strength for hypersensitive transition i.e. $^4G_{5/2}$ are almost the same in all solvents. The values of reduced matrix elements have been taken from Carnall *et al*[22]. For hypersensitive transition in case of Nd^{3+} the value of

oscillator strength observed is max i.e highest among all transition in all solvents.

Table 4 presents the T_λ parameters and the ratio of T_4/T_6 is almost constant in all solvent, low value of rms deviation confirms the formation of complex. We observed that the ratio of T_4/T_6 is low in each metal. The complexes under study have ratio (T_4/T_6) lies between 0.19-0.28 supporting that they have oxygen/nitrogen-donor liquids. Also it has been observed that value of T_4 and T_6 remains nearly invariant in Table 4.

Table 5 presents the value of refractive index for Nd^{3+} complex which is in the increasing order as is the increasing order of molecular weight of the solvents. The values of refractive index have also been obtained which are in order. Water-1.356, Methanol-1.360, Ethanol-1.381, Acetic acid-1.391. Table 6

Table 2 — Computed value of Slater-Condon parameters and Landes parameters β and $b^{1/2}$ for Nd^{3+} complexes in different solvent

	Water	Methanol	Ethanol	Acetic Acid
F_2 (cm^{-1})	335.32	335.0459	334.7203	335.6692
F_4 (cm^{-1})	51.0195	50.0145	50.3495	49.3181
F_6 (cm^{-1})	5.4324	5.4740	5.4662	5.4883
ζ_{4F} (cm^{-1})	869.5471	879.2255	874.1093	890.0094
E^1 (cm^{-1})	5125.862	5107.298	5111.612	5097.436
E^2 (cm^{-1})	24.4776	24.8134	24.6594	25.1258
E^3 (cm^{-1})	496.1156	492.3918	492.7580	491.6065
F_4/F_2	0.1521	0.1492	0.1504	0.1469
F_6/F_2	1.6200E-02	1.6338E-02	1.6330E-02	1.6350E-02
E^1/E^3	10.3319	10.3724	10.3734	10.3689
E^2/E^3	4.9338E-02	5.0393E-02	5.0043E-02	5.1109E-02
β'	1.0125	1.0117	1.0107	1.0136
$b1/2$	7.9252E-02	7.6596E-02	7.3317E-02	8.2511E-02

Table 4 — Computed value of Judd-Ofelt parameters and ratio of (T_4/T_6) for Nd^{3+} complex in different solvent

	Water	Methanol	Ethanol	Acetic Acid
$T_2 \times 10^{10}$	4.2168	7.6284	4.6381	5.1414
$T_4 \times 10^{10}$	0.9335	2.2637	5.6438	5.4784
$T_6 \times 10^{10}$	5.6182	6.6422	7.7724	7.3357
T_4/T_6	0.1661	0.3408	0.7261	0.7468

Table 5 — Refractive index value observed for complex Pr^{3+} in different solvents

Complex	Solvent	Refractive index
	Water	1.356
$Nd(P)_2P$	Methanol	1.360
	Ethanol	1.381
	Acetic acid	1.391

Table 3 — Observed and calculated value of oscillator strength for Nd^{3+} complexes in different solvent

Levels	Water		Methanol		Ethanol		Acetic Acid	
	Cal. × 10^{-6}	Obs. × 10^{-6}	Cal. × 10^{-6}	Obs. × 10^{-6}	Cal. × 10^{-6}	Obs. × 10^{-6}	Cal. ×10^{-6}	Obs. × 10^{-6}
$^2P_{1/2}$	0.1083	0.2110	0.2277	.0680	0.5247	0.1093	0.5083	0.2293
$^4G_{11/2}$	0.1084	0.3078	0.1416	0.2439	0.2002	0.1655	0.1906	0.2567
$^2G_{9/2}$	0.2452	0.1050	0.3773	.0530	0.6465	0.0497	0.6226	0.0380
$^4G_{9/2}$	0.7621	1.6355	1.0725	2.5835	1.6026	1.6540	1.5389	1.9771
$^4G_{7/2}$	1.3228	2.3104	2.1841	3.8140	3.0038	3.4973	2.9609	2.8242
$^4G_{5/2}$	9.1172	9.3845	16.3423	16.6294	14.9431	14.6413	15.5501	15.2918
$^4F_{9/2}$	0.4536	0.2278	0.5589	0.3642	0.6990	0.3809	0.6664	0.2997
$^4F_{7/2}$	5.0709	5.8278	6.0365	6.7814	7.2288	6.6966	6.8512	6.2660
$^4F_{5/2}$	3.9680	3.4725	5.0515	4.6183	6.7749	6.9999	6.4668	6.7886
$^4F_{3/2}$	0.6047	1.1674	1.0181	1.3681	1.9825	1.1924	1.9090	1.1976
rms deviation	5.5367E-07		7.7883E-07		4.3893E-07		4.2286E-07	

Table 6 — Observed value of omega parameters complex Pr^{3+} in different solvents

	Water	Methanol	Ethanol	Acetic acid
$\Omega_2 \times 10^{20}$	3.2193	5.8082	3.4810	3.8321
$\Omega_4 \times 10^{20}$	0.7126	1.7235	4.2359	4.0833
$\Omega_6 \times 10^{20}$	4.2892	5.0573	5.8334	5.4677

presents the value of omega parameters for Nd^{3+} in different solvents.

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