

Calculation of Energy Interaction and Electric Dipole Intensity Parameters to Explore the Interaction between the Trivalent Praseodymium and Uracil Using 4f-4f Transition Spectra as an Absorption Probe

Victory Devi Ch. and Rajmuhon Singh N*.

Department of Chemistry, Manipur University, Canchipur-795003, India

Abstract. The spectroscopic techniques involving comparative absorption, absorption difference and quantitative intensity analysis using 4f-4f transitions are used as a tool to understand the interaction of Pr(III) and uracil in different aquated organic solvents. The change in coordination in different medium is observed from the absorption intensity analysis when Pr(III) interacts with uracil. The interaction induced substantial changes in the intensities of 4f-4f bands and their perturbation was reflected through oscillator strength and Judd-Ofelt intensity (T_{λ}) parameters. It is suggested that the changes in the oscillator strengths of different 4f-4f bands and Judd-Ofelt intensity parameters can be used to predict in vivo intracellular complexation of uracil with Ca(II) through Pr(III)-uracil absorption spectral analysis studies in vitro as both Pr(III) and Ca(II) have unique similarity in their coordination behavior. Other parameters namely energy interaction parameters like Slater-Condon (F_k 's), spin-orbit Lande (ξ_{4f}), Racah parameter (E^k), nephelauxetic effect (β), bonding ($b^{1/2}$) and percent covalency (δ) parameters are calculated to further characterize the interaction between the Pr(III) and uracil.

Keywords: absorption difference, Pr(III), 4f-4f transition, oscillator strength, nephelauxetic effect

1. Introduction

The unique similarities in terms of coordination and binding characteristics between the paramagnetic lanthanides with calcium makes the lanthanides to act as an "absorption probes" [1,2] in understanding the biochemical reactions and functions involving the isomorphous substitution of Ca(II) by Ln(III) [3,4]. Lanthanides are finding selective applications in sol gel [5] process, which is found to be one of the most effective and extensively used method for generation of multicomponent novel materials like metal oxide and thin films. Recently, there has been renewed interest in the absorption of 4f-4f transitions and their intensity analysis to probe the finer details of structure in lanthanide complexes. Misra *et al* [6], made a detail studies on the interaction of Pr(III) and Nd(III) with β -diketones and diols using the comparative absorption spectrophotometry and reported a relation between the magnitude and variation of intensity parameters and structural and compositional changes in these complexes. David *et al* [7,8] have also used the electric dipole intensity and variation in the spectral parameters to explore the interaction between the Pr(III) and Nd(III) with glutathione. Only a few references are available on lanthanide-organic metabolite interactions [9] and studies on lanthanide-nucleic acid interaction are still fewer [10,11]. Thus, it was though worthwhile to explore the interaction between Pr(III) with uracil in solution by employing electronic spectral studies.

In the present study, the interaction of uracil with Pr(III) is carried out by selecting different aquated organic solvents and the corresponding changes in oscillator strengths of different 4f-4f bands and experimentally determined Judd-Ofelt intensity (T_{λ}) parameters are correlated with the binding of uracil. We

also manifested particular interest in the effect of different solvent media on the relatively sharp absorption bands seen in the 400-620 nm regions.

2. Experimental

Praseodymium nitrate hexahydrate of 99% purity was purchased from CDH, Mumbai and uracil from the Acrose company, U.S.A. The solvents used were CH₃CN, CH₃OH, DMF and Dioxane of A.R. grade from E.Merk .

The absorption spectral data are 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 uracil were maintained at .001 mol L⁻¹ and spectral analysis were carried out by using different solvents. The temperature of all observations was maintained by using Perkin Elmer PTP1 Peltier -temperature system.

3. Methods

Judd-Ofelt[12,13] theory predicts that the intensity of 4f-4f transition arise principally from forced electric dipole mechanism. Thus the electric dipole oscillator strength (P) is expressed as the product of T_λ parameters and appropriate transition matrix element U^(λ) at frequency of transition J→ J'.

$$P_{cal} = \sum_{\lambda=2,4,6} T_{\lambda} v \left(f^n \psi_J \parallel U^{\lambda} \parallel f^n \psi_{J'} \right)^2 \quad (1)$$

The Judd-Ofelt intensity parameters are empirical, yet these show high sensitivity towards even minor changes in the coordination environment and symmetry of the molecule.[14]. These parameters have been widely used in the structure elucidation of lanthanoid coordination compounds in solution.

The energy of 4f-4f transitions comprises of two main components : coulombic (represented by inter-electronic repulsion (F_k, Slater Condon) and spin-orbit (Lande-ξ_{4f}) components. The complexation of lanthanoids bring about lowering of nephelauxetic effect represented by nephelauxetic ratio ($\bar{\beta}$) :

$$\beta_1 = \frac{F_k^c}{F_k^f} \quad \beta_2 = \frac{\xi_{4f}^c}{\xi_{4f}^f} \quad \bar{\beta} = \frac{\beta_1 + \beta_2}{2} \quad (2)$$

$$b^{1/2} = \left[1 - \frac{\beta}{2} \right]^{1/2} \quad \delta = \left(1 - \frac{\beta}{\bar{\beta}} \right) \times 100 \quad (3)$$

Bonding (b) and percent covalency parameter (δ) which are related to nephelauxetic ratio (β) are also used to describe the structural features of a lanthanoid complexes. The significance and evaluation of these (F_k, $\bar{\beta}$, δ, E^k, ξ_{4f} and b) parameters have been discussed in our earlier papers [15,16].

4. Results and discussions

From fig. 1. we can see that there is a red shift as uracil is added to Pr(III). Table 1 shows the variation of the magnitude of energy interaction parameters like Slator-Condon(F_k), spin-orbit coupling constant (ξ_{4f}), Racah parameters (E^k), nephelauxetic ratio (β), bonding parameter (b^{1/2}) and covalency parameter (δ). The binding of uracil to Pr(III) brings about changes in energies of various 4f-4f bands which causes the degree of lowering in the energy interaction parameters like Slator-Condon and inter-electronic repulsion parameters, which lead to nephelauxetic effect. The data in Table 1 shows that significant lowering of these parameters takes place in complexes as compared to the values for aquo ions indicating the expansion of the central metal ion orbital on complexation. The positive values of b^{1/2} indicates some covalent character in metal-ligand bond. The small value and small variation of it suggests that the 4f-orbitals are very slightly involved in the interaction of uracil to Pr(III).

Since lanthanides are hard metal ions, their preference will be for hard donor site like oxygen atom. The absolute values of oscillator strengths and Judd-Ofelt intensity (T_λ) parameters are determined under different experimental conditions for Pr(III) and Pr(III)-uracil (Table 2.) This clearly shows a significant change in the oscillator strengths of 4f-4f bands of the Pr(III) ion. Comparative absorption spectra of Pr(III)

and Pr(III)-uracil in DMF (Fig. 1) clearly show that the addition of uracil to Pr(III) results in significant enhancement in the oscillator strengths of different 4f-4f transitions. We also observe noticeable increase in the magnitude of Judd-Ofelt parameters suggesting the binding of the uracil to Pr(III) in solution. T_2 values appear to be negative which is meaningless. T_4 and T_6 are affected significantly. Both parameters are related to changes in symmetry properties of the complex species. At the same time, the extent of mixing of 4f and 4d orbital also influences T_6 parameter predominantly, while some influences on T_4 can also be extended. Comparative absorption spectra of Pr(III)-uracil in different aquated organic solvents (Fig. 2) clearly suggest the significant role of solvents on complexation. DMF appears to induce the strongest influence on Pr(III)-uracil complexes. The red shift is observed in the energies of all bands. The influence of solvents like methanol and acetonitrile are less on complexation of Pr(III)-uracil. 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 resulting in the decrease of inter-electronic repulsion which leads to the phenomenon of nephelauxetic effect and thus can lead to lowering of coordination number [17]. Table 2 also clearly shows that T_4 and T_6 parameters are effected significantly in the presence of different solvents, suggesting that not only immediate coordination environment of Pr(III), but symmetry of the complex species is also changed dramatically.

5. Conclusions

From the above discussions through variation in the magnitude of energy interaction and intensity parameters we can suggest that minor coordination changes in the Pr(III) complexes are caused by the different coordinating sites of uracil, coordination number, denticity, solvent nature and nature of Pr(III)-uracil bond, which do induce significant variation in the intensity of f-f transitions.

6. Acknowledgment

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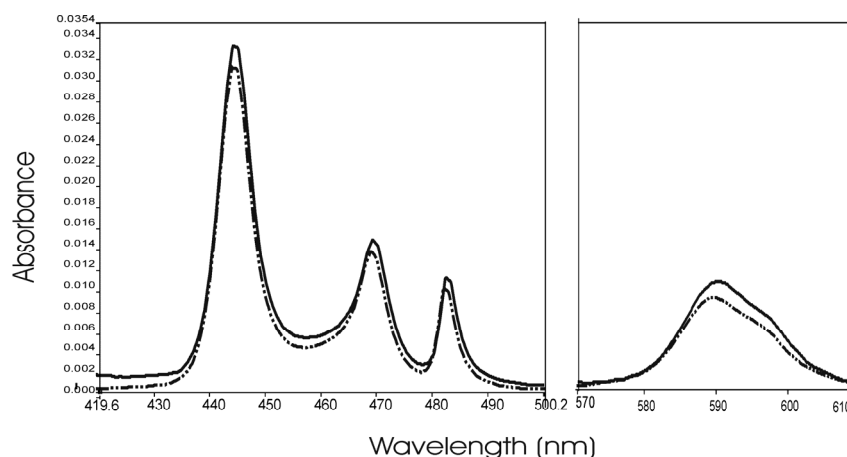


Fig. 1. Comparative absorption spectra of Pr(III) — — — — — and Pr(III):uracil ————— in DMF.

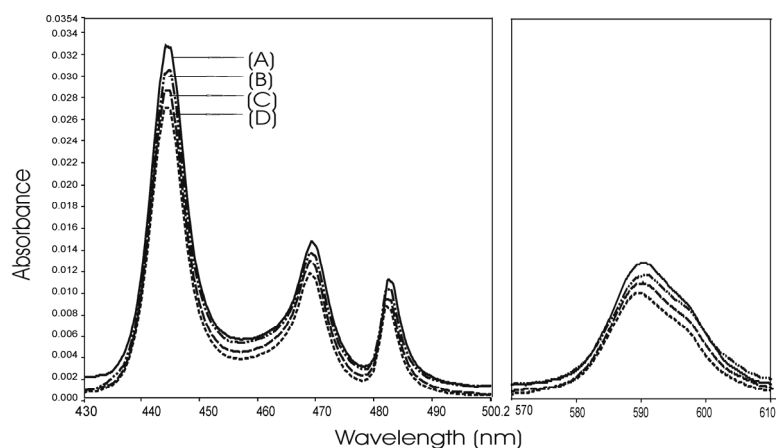


Fig. 2. Comparative absorption spectra of Pr(III)-uracil in different solvents (A) DMF (B) dioxane (c) acetonitrile and (D) MeOH

Table 1. Calculated values of energy interaction parameters (F_k), spin-orbit coupling constant (ξ_{4f}), Racah parameters (E^k), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and covalency parameter (δ) for the interaction of Pr(III) with Uracil in different medium at 25°C.

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
Pr(III) aquo ion	308.96	42.65	4.66	722.60	3508.10	23.73	614.22	0.9460	0.1632	5.6719
Pr(III):uracil										
MeOH	308.95	42.65	4.66	722.24	3508.09	23.73	614.22	0.9463	0.1638	5.6719
DMF	308.81	42.63	4.66	721.84	3506.48	23.72	613.94	0.9458	0.1646	5.7261
Acetonitrile	308.93	42.64	4.66	722.23	3507.88	23.73	614.18	0.9463	0.1639	5.6755
Dioxane	308.95	42.65	4.66	722.60	3508.10	23.74	614.22	0.9466	0.1634	5.6442
DMF:Dioxane	308.83	42.63	4.66	722.14	3506.76	23.73	613.99	0.9461	0.1642	5.6991
DMF:Acetonitrile	308.62	42.60	4.66	720.69	3504.29	23.71	613.56	0.9448	0.1662	5.8454
MeOH:Acetonitrile	308.95	42.65	4.66	721.98	3508.07	23.73	614.22	0.9461	0.1641	5.6923
MeOH:Dioxane	308.93	42.64	4.66	722.58	3507.86	23.73	614.18	0.9465	0.1635	5.6495
MeOH:DMF	308.85	42.63	4.66	722.51	3506.92	23.73	614.02	0.9464	0.1638	5.6684

Table 2. Calculated values of oscillator strengths ($P \times 10^6$) and Judd-Ofelt ($T_\lambda \times 10^{10}$) parameters for Pr(III)-uracil in different medium.

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}			
Pr(III) aquo ion	3.2475	3.2475	0.7819	0.4360	0.1517	0.4576	1.1800	1.1800	-8.03	1.69	10.30
Pr(III):uracil											
MeOH	3.2490	3.2490	0.7820	0.4730	0.1615	0.4657	1.1801	1.1801	52.97	1.30	10.31
DMF	3.5459	3.5459	0.8785	0.6903	0.4943	0.6796	1.1566	1.1566	-27.69	1.89	11.12
Acetonitrile	3.5175	3.5175	0.8211	0.6319	0.4359	0.6222	0.9467	0.9467	-18.10	1.73	11.07
Dioxane	3.5283	3.5283	0.9101	0.6955	0.4735	0.6847	1.067	1.067	-8.16	1.91	11.06
DMF:Dioxane	3.1170	3.1170	0.8307	0.6346	0.4315	0.6246	0.947	0.947	-8.34	1.74	9.76
DMF:Acetonitrile	3.2677	3.2677	0.8426	0.6515	0.4532	0.6414	0.9825	0.9825	-6.19	1.79	10.24
MeOH:Acetonitrile	2.9153	2.9153	0.9365	0.6966	0.4497	0.6859	0.8525	0.8525	-0.11	1.91	9.05
MeOH:Dioxane	3.2785	3.2785	0.6946	0.5536	0.4062	0.545	0.936	0.936	-4.62	1.52	10.34
MeOH:DMF	1.2912	1.2912	0.9081	0.6939	0.4721	0.6830	0.7540	0.7540	-84.0	1.90	3.72

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