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Archives of Applied Science Research, 2016, 8 (3):1-3
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Study of Spectral intensities and Judd-Ofelt parameters of some Pr (III)-Alkaloid doped systems

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ABSTRACT

The spectral properties of Pr (III) doped system with some biologically important alkaloids (i.e. atropine, brucine and caffeine) were investigated at different metal- ligand concentration and broad pH range (2 to 6). The analysis of oscillator strength values of the hypersensitive transition ($3H_4 \rightarrow 3P_2$) and Judd-Ofelt intensity parameters were performed in order to determine the formation of metal-ligand coordination complex and the type of bonding.

INTRODUCTION

Coordination complexes of lanthanide with alkaloids have found wide application in pharmaceutical and biological fields. In this study we took alkaloids having N & O i.e. atropine, brucine and caffeine, which are able to form coordination bond with lanthanide. Hence electronic spectra of such coordinated lanthanide alkaloid systems will help in the investigation of the nature of coordination bond and the participation of 5d & 4f orbitals. As we know that f-f transition in Ln (III) ions is Laporte- forbidden transition that's why the intensity of f-f transition is weak. In this present work we have composed some doped Pr (III) - alkaloid system with different M: L Ratio and different pH of solution. In electronic spectrum of Pr (III) ion of Pr-alkaloid doped system, we got four peaks corresponding to $3H_4 \rightarrow 3P_2$, $3H_4 \rightarrow 3P_1$, $3H_4 \rightarrow 3P_0$ & $3H_4 \rightarrow D_2$. $3H_4 \rightarrow 3P_2$ is a hypersensitive transition^(1,2) which have generally the largest oscillator strength among all possible final states and is more sensitive to the change to T₂ value than other transitions. A comparative study of oscillator strength of hypersensitive transition and Judd- Ofelt parameter have been used in to changes in the coordination environment of Pr (III) with different M:L ratio and at different pH.

Experimental: - Stock solution of .1M PrCl₃ was prepared from 99.9% praseodymium oxide, (Merk) in 50% ethanol solution. .1M, .2M, .3M solutions of atropine, brucine, and caffeine (Merk) were also made in 50% ethanol. Now 10 ml of each of these ligand solutions was added to 10 ml of .1M Pr (III) solution. In this way we got doped Pr : Alkaloid system of different M:L Ratio (1 : 1, 1 : 2 & 1 : 3). Electronic spectra of Pr (III) ion in such doped system was measured at pH 2 to 6. A carbonate free NaOH solution and HCl was used to adjust the pH of doped Pr-Alkaloid System

Measurement and calculation - All electronic spectra were measured by Systronic-2202 UV-Visible double beam spectrophotometer in the range of 400-625 nm. pH was recorded by using systronic μ -pH system 361, pH meter at room temp. 100% C₂H₅OH (Merk) was used to make solutions.

In the electronic spectra of Pr (III) ion four peaks corresponding to $3H_4 \rightarrow 3P_2$, $3H_4 \rightarrow 3P_1$, $3H_4 \rightarrow 3P_0$ & $3H_4 \rightarrow 1D_2$ transition have been obtained. $3H_4 \rightarrow 3P_2$ is hypersensitive peak⁽³⁾ which is highly affected by different concentrations of ligand and pH of solution.

Oscillator strength of only hypersensitive peak was calculated by the relation⁽⁴⁻⁷⁾ :-

$$P_{exp} = 4.60 \times 10^{-9} \times \Delta v_{1/2} \times \epsilon_{max}$$

Mostly the spectral studies of the solution have been done by utilizing the matrix element of carnall⁽⁹⁾ et al. The calculations of Judd-Ofelt parameters (T_2 , T_4 & T_6) have been made by computerizing program used by earlier workers.^(6, 8)

Table - 1

1	Pr:Atropine System	pH	Hyper Sensitive Peak (3P_2)	Pexp. $\times 10^{-6}$	T2 $\times 10^{-9}$	T4 $\times 10^{-9}$	T6 $\times 10^{-9}$	T4/T6
A M:L Ratio-1:1								
1	.1MPr:.1M Atropine	2	22676	5.18	-3.69	0.332	1.6	0.21
2	.1MPr:.1M Atropine	3	22676	5.65	-5.3	0.355	1.74	0.2
3	.1MPr:.1M Atropine	4	22676	6.24	-8.13	0.375	1.93	0.19
4	.1MPr:.1M Atropine	5	22676	5.61	-5.4	0.356	1.73	0.21
5	.1MPr:.1M Atropine	6	22676	7.17	-7.06	0.477	2.21	0.22
B M:L Ratio-1:2								
1	.1MPr:.2M Atropine	2	22676	6.81	-6.08	0.442	2.1	0.21
2	.1MPr:.2M Atropine	3	22676	6.54	-11.4	0.442	2.01	0.22
3	.1MPr:.2M Atropine	4	22676	8.57	-15.1	0.542	2.64	0.21
4	.1MPr:.2M Atropine	5	22676	7.57	-8.93	0.482	2.34	0.21
5	.1MPr:.2M Atropine	6	22676	7.34	-7.46	0.52	2.25	0.23
C M:L Ratio-1:3								
1	.1MPr:.3M Atropine	2	22676	5.45	-2.22	0.377	1.67	0.23
2	.1MPr:.3M Atropine	3	22676	5.81	-6.04	0.372	1.79	0.21
3	.1MPr:.3M Atropine	4	22676	8.57	-15.2	0.562	2.64	0.21
4	.1MPr:.3M Atropine	5	22676	6.08	-7.06	0.391	1.87	0.21
5	.1MPr:.3M Atropine	6	22676	7.17	-8.86	0.475	2.21	0.22

Table - 2

1	Pr-Brucine System	pH	Hyper Sensitive Peak (3P_2)	Pexp. $\times 10^{-6}$	T2 $\times 10^{-9}$	T4 $\times 10^{-9}$	T6 $\times 10^{-9}$	T4/T6
A M:L Ratio-1:1								
1	.1MPr.1MBrucine	2	22523	6.59	-13.4	0.472	2.03	0.23
2	.1MPr.1MBrucine	3	22523	11.2	-12.6	0.672	3.5	0.19
3	.1MPr.1MBrucine	4	22523	16.5	-19.8	1.04	5.13	0.2
4	.1MPr.1MBrucine	5	22523	20.8	-12.1	1.16	6.5	0.18
5	.1MPr.1MBrucine	6	22624	28	-17.4	2.28	8.52	0.27
B M:L Ratio-1:2								
1	.1MPr.2MBrucine	2	22727	6.81	-5.19	0.45	2.09	0.22
2	.1MPr.2MBrucine	3	22727	6.44	-4.61	0.428	1.98	0.22
3	.1MPr.2MBrucine	4	22727	5.98	-6.96	0.368	1.84	0.2
4	.1MPr.2MBrucine	5	22727	6.48	-9.49	0.384	2	0.19
5	.1MPr.2MBrucine	6	22727	8.27	-1.47	0.627	2.52	0.25
C M:L Ratio-1:3								
1	.1MPr.3MBrucine	2	22727	6.94	-3.18	0.474	2.13	0.22
2	.1MPr.3MBrucine	3	22727	6.38	-7.42	0.411	1.96	0.21
3	.1MPr.3MBrucine	4	22727	6.01	-8.28	0.377	1.85	0.2
4	.1MPr.3MBrucine	5	22727	7.17	-5.08	0.499	2.2	0.23
5	.1MPr.3MBrucine	6	22727	8.47	-1.69	0.644	2.58	0.25

Table - 3

1	Pr-Caffiene System	pH	Hyper sensitive peak (3P_2)	Pexp. $\times 10^{-6}$	T2 $\times 10^{-9}$	T4 $\times 10^{-9}$	T6 $\times 10^{-9}$	T4/T6
A M:L Ratio-1:1								
1	.1MPr-.1MCaffiene	2	22573	4.54	-3.44	0.242	1.42	0.17
2	.1MPr-.1MCaffiene	3	22573	4.09	-13.1	0.223	1.28	0.17
3	.1MPr-.1MCaffiene	4	22573	4.58	-15.2	0.246	1.43	0.17
4	.1MPr-.1MCaffiene	5	22573	4.88	-12.9	0.282	1.52	0.19
5	.1MPr-.1MCaffiene	6	22573	5.97	-17.1	0.343	1.86	0.18
B M:L Ratio-1:2								
1	.1MPr-.2MCaffiene	2	22573	4.39	-11.8	0.212	1.18	0.18
2	.1MPr-.2MCaffiene	3	22573	4.39	-14.5	0.244	1.37	0.18
3	.1MPr-.2MCaffiene	4	22573	4.39	-16.8	0.269	1.54	0.17
4	.1MPr-.2MCaffiene	5	22573	4.39	-16.9	0.32	1.77	0.18
5	.1MPr-.2MCaffiene	6	22573	4.39	-19.4	0.336	1.89	0.18
C M:L Ratio-1:3								
1	.1MPr-.3MCaffiene	2	22573	5.41	-11.6	0.31	1.68	0.18
2	.1MPr-.3MCaffiene	3	22573	5.74	-12.6	0.354	1.78	0.2
3	.1MPr-.3MCaffiene	4	22573	6.68	-17	0.399	2.08	0.19
4	.1MPr-.3MCaffiene	5	22573	7.77	-12.8	0.501	2.41	0.21
5	.1MPr-.3MCaffiene	6	22573	7.43	-0.77	0.37	2.33	0.16

RESULTS AND DISCUSSION

Hypersensitive peak⁽²⁾ is very sensitive to ionic environment of the solution. A red shift⁽¹⁰⁾ is observed in doped Pr-alkaloid system with Pr (III) ion compared to aqua ion. The comparative data of oscillator strengths and Judd-Ofelt parameters of doped Pr-Alkaloid systems (Pr-Atropine system, Pr-Brucine system and Pr-Caffeine system) with different metal-ligand concentration at different pH of solution are shown in table 1, 2, 3. At a broad range of pH with different M:L ratio, hypersensitive peak show wide variations of oscillator strength and binding characteristics. Results of doped Pr-alkaloid system^(3, 10) indicate that changes in oscillator strengths are connected with change in ligand concentration and pH. As the oscillator strength of hypersensitive peak⁽¹²⁾ is consider as a proof for the coordination state of the solutions we evaluated the bonding characteristics and coordination behavior of Pr (III) ion in doped Pr-alkaloid system.

Pr-Atropine system with M:L Ratio = 1 : 1, 1 : 2, 1 : 3

Highest value of oscillator strength for M:L Ratio 1 : 1 was obtained at pH = 6 where as in M:L Ratio = 1 : 2 and 1 : 3 highest value of oscillator strength was found at pH = 4. These data revealed that M:L ratio 1 : 1, Pr (III) forms strong coordinated complex in weak acidic solution and at higher concentration of alkaloid (M:Lratio 1:2&1:3), Pr (III) forms stable coordinated complex comparatively in high acidic solution.

Pr-Brucine system with M:L Ratio = 1 : 1, 1 : 2, 1 : 3

In this system for M:L Ratio 1 : 1, Pr (III) forms coordinated complex with brucine in strong acidic solution where as for M:L Ratio - 1 : 2 and 1 : 3, the highest value of oscillator strength was obtained at pH = 6 that exhibit Pr (III) forms coordination complex with brucine in weak acidic solution.

Pr-Caffeine system with M:L Ratio = 1:1, 1:2, 1:3

Pr-Caffeine system exhibit highest value of oscillator strength in weak acid solution (i.e. pH = 6) for each M:L Ratio. A systematic increase in oscillator strength values was observed together with all M:L Ratio and a broad range pH of solution.

In Pr-alkaloid system, value of nephelauxetic ratio (β) has been found to be less than one in all systems. Positive value of $b_{1/2}$ indicates some covalent character in Pr-alkaloid bond. The values of T_2 have been found to be negative⁽⁸⁾ for all systems. The values of T_2 , T_4 & T_6 are in the sequence $T_2 < T_4 < T_6$ and Ratio T_4/T_6 varies from $1.5 \cdot 10^{-1}$ - $2.6 \cdot 10^{-1}$ indicates a very slight change in the symmetry around Pr (III) ion in the present system under study.

CONCLUSION

From the above results it may be concluded that by measurement of electronic spectra of Lanthanide coordinated system, we can able to predict the coordination behaviour of Pr (III) and nature of coordination bond in a broad range of pH of solution.

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