

Characterization of Some Electronic Spectral Parameters for Doped Nd(III) Ion in Saturated Aqueous Solution of Some Pharmaceutical Compounds

NEELAM NAULAKHA, K.P. SONI and P.R. BHATI*

*Rare Earth Research Lab., Department of Chemistry
Government Dungar College, Bikaner-334 001, India*

The stereo-environment of doped Nd(III) ion in various saturated solutions of some medicinal compounds has been studied for various electronic spectral parameters. The various electronic parameters, viz., Slater Condon (F_k), Lande (ζ_{4f}), intensity of hypersensitive band (${}^4G_{5/2}$), bonding parameter ($b^{1/2}$), Judd-Ofelt parameter (T_λ) and Racah parameter (E^k) for Nd(III) ion doped in saturated solution of diphenylhydramine, tripeleennamine, chlorophenaramine, promethazine, terfinadine, naproxen, fenoprofen, flurbiprofen, oxaprozine, ketoprofen and ibuprofen have been studied.

INTRODUCTION

In the present discussion the study has been made to explore the extent of coordination behaviour of Nd(III) ion with some medicinal importance compounds for their pharmaceutical application, on the ground of Judd-Ofelt and Slater-Condon theory. A great deal of work has been reported on the measurement of $f \leftrightarrow f$ transition of free and aquo-ion of Nd(III) ion in different saturated solutions by several workers.¹⁻⁷ The lanthanide(III) ion exhibits absorption spectra characterized by the bands in the visible region, but these spectra have not been studied extensively⁴⁻⁷ in terms of various electronic spectral parameters. The present investigation has been undertaken with a view to make comparative study of the various energy and intensity parameters resulting from $f \leftrightarrow f$ transition in different energy levels of doped Nd(III) ion in aqueous solution.

The values of various electronic spectral parameters like Judd-Ofelt (T_λ), Slater-Condon (F_k), Racah (E^k), Lande (ζ_{4f}), oscillator strength (P), nephelauxetic ratio (β) and bonding ($b^{1/2}$) give useful information regarding spin-orbit interaction and inter-electronic repulsions, nephelauxetic effect and bonding around the doped Nd(III) ion have been calculated by using partial and multiple regression method involving theories given by Slater-Condon, Lande and Judd-Ofelt. Saturated solutions in aqueous media were made by dissolving Diphenylhydramine, tripeleennamine, chlorophenaramine, promethazine, terphenadine, naproxen, fenoprofen, oxaprozine, ketoprofen and ibuprofen at room temperature ($30 \pm 2^\circ\text{C}$) and a constant amount of Nd(III) chloride had been added to each of the solutions and observations were made for characterisation of electronic parameters spectrophotometrically. The Nd(III) ion yields ten bands in the region 390 nm to 900 nm, viz., ${}^2P_{1/2}$, ${}^4G_{11/2}$, ${}^4G_{9/2}$, ${}^2G_{9/2}$, ${}^4G_{7/2}$, ${}^4G_{5/2}$, ${}^4F_{9/2}$, ${}^4F_{7/2}$, ${}^4F_{5/2}$, ${}^4F_{3/2}$, and the change in the intensity of these bands is indicated by the red shift change in the coordination environment around the ion resulting from $f \leftrightarrow f$ transitions in lanthanides⁸⁻¹¹.

EXPERIMENTAL

The various saturated aqueous solutions of diphenhydramine, tripeleminamine, chlorpheniramine, promethazine, terfenadine, naproxen, fenopropfen, flurbiprofen, oxaprozine, ketoprofen and ibuprofen of I.P. grade were prepared at room temperature ($30 \pm 2^\circ\text{C}$) and 0.14 m of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9% purity supplied by Indian Rare Earth Udyogmandalam, Kerala) had been added to each of the saturated solutions. Solution spectra of these saturated solutions were recorded spectrophotometrically by using standard spectrophotometer (SPECTRONIC-20) in the visible region¹²⁻¹⁵. The computation of various electronic parameters was made by computerized statistical method reported earlier¹⁶⁻¹⁸

RESULTS AND DISCUSSION

The computed values of various spectral electronic parameters has been given in Tables 1 to 3. The present study shows that the $f \leftrightarrow f$ transition resulting from spin orbit interaction in Nd(III) ion is due to the interaction of f -orbital with the ligand present in the saturated solution which is remarkably manifested in terms of change in the various energy and intensity parameters. The energies of the various bands observed have been recalculated by applying Slater-Condon-Lande's equation^{16, 17}. The comparison of the observed and calculated values of the various energy levels (Table-2) shows the average r.m.s. deviation within the range ± 61 to $\pm 85 \text{ cm}^{-1}$ which indicates good results. The red shift in all energy bands from the free ion value supports the change in coordination environment around the central metal ion^{19, 20}.

The various energy parameters F_k ($k = 2, 4, 6$), *i.e.*, Slater-Condon parameter, β nephelauxetic ratio, ζ_{4f} Lande parameter and $b^{1/2}$ bonding parameter (extent of covalency around the metal ion in the solution) and $\%rF_2$ have been reported in Table-1 which shows fair agreement with the theory involved in doped Nd(III) ion. The decrease in the parametric values of F_k , E^k and ζ_{4f} indicates the decrease in the inter electronic repulsion and spin-orbit interactions which suggests that expansion of the central metal ion takes place orbital on being doped in saturated solution and in accordance with the theory of $f \leftrightarrow f$ transition reported earlier⁸⁻¹⁰.

The average value of F_4/F_2 in Nd(III) doped ion (0.1572 to 0.1698) is nearer to the value for free ion (0.1531). The same trend has been observed for the ratio F_6/F_2 (0.016). The values of nephelauxetic ratio $\beta < 1$ and bonding parameter $b^{1/2}$ indicate some extent of covalent bonding in Nd(III) doped ion. The small value of $b^{1/2}$ and little variation in it suggest that the $4f$ orbitals are very slightly involved in the bonding in the saturated solution with ligands. Thus the spectral characterizations of the doped Nd(III) ion are found to be much more important as these involve very little crystal field.

The intensities of the observed bands have been given in terms of oscillator strength (P). The observed values of the oscillator strength have been compared with those of the calculated ones (Judd-Ofelt equation). The r.m.s. deviation within the range of 1.61×10^{-6} to 1.92×10^{-6} has been reported in Table-3. The small deviation for the calculated and observed (P) value suggests the validity of Judd-Ofelt equation for $f \leftrightarrow f$ transition for the present study.

TABLE-1
 COMPUTED VALUES OF VARIOUS ELECTRONIC SPECTRAL PARAMETERS F_6 , $\%F_2$, E^k , ζ_{4f} , $\%r\zeta_{4f}$, β , $b^{1/2}$, T_2 , T_4 FOR Nd(III) ION DOPED IN AQUEOUS SATURATED SOLUTIONS OF VARIOUS PHARMACEUTICAL ORGANIC COMPOUNDS

Compounds	F_2	F_4	F_6	F_4/F_2	F_6/F_2	$\% xF_2$	E^1	E^2	E^3	ζ_{4f}	$\%r\zeta_{4f}$	β	$b^{1/2}$	$\times 10^{-10}$			
														T_2	T_4	T_2/T_4	
Nd-Diphenhydramine	326.88	52.41	5.23	0.160354	0.016333	1.289500	5075.52	23.00	487.89	854.99	3.28	0.9858	0.083	8.53	9.30	12.8	0.72
Nd-Tripelenn-amine	326.45	53.01	5.23	0.162402	0.016030	1.421772	5063.93	22.62	491.37	839.79	5.00	0.9845	0.087	12.2	15.4	10.3	1.49
Nd-Chlorpheni-ramine	327.96	51.38	5.29	0.156689	0.016134	0.963700	5046.89	23.42	488.88	860.28	2.68	0.9891	0.073	12.3	13.6	11.1	1.23
Nd-Promethazine	329.88	51.42	5.31	0.155885	0.016111	0.384083	5067.97	23.64	491.44	846.29	4.26	0.9949	0.050	6.5	20.0	10.1	1.97
Nd-Terfinadine	328.17	51.52	5.22	0.157004	0.015910	0.902007	5036.34	23.34	491.62	845.74	4.32	0.9897	0.071	13.7	13.5	10.1	1.32
Nd-Naproxen	326.64	52.75	5.29	0.161506	0.016198	1.362946	5071.61	22.82	489.42	845.83	4.31	0.9851	0.086	12.5	13.6	11.8	1.14
Nd-Fenoprofen	330.01	51.38	5.32	0.155705	0.016134	0.345703	5070.08	23.68	491.28	844.53	4.46	0.9953	0.048	10.1	2.5	15.3	0.16
Nd-Flurbiprofen	330.02	51.47	5.31	0.155982	0.016114	0.342605	5071.14	23.64	491.67	842.78	4.66	0.9953	0.048	12.5	13.4	11.9	1.13
Nd-Oxaprozoin	322.67	54.80	5.20	0.169846	0.016129	2.562833	5074.01	21.63	489.52	843.83	4.54	0.9731	0.115	11.6	19.4	3.2	6.10
Nd-Ketoprofen	327.62	52.14	5.30	0.159169	0.016195	1.065993	5067.02	23.14	489.39	855.16	3.26	0.9881	0.077	6.7	12.2	10.8	1.12
Nd-Ibuprofen	328.54	51.67	5.28	0.157281	0.016094	0.788160	5057.91	23.39	490.53	847.70	4.10	0.9908	0.067	2.0	16.9	13.0	1.30

TABLE-2
COMPUTED VALUES OF ENERGIES (in cm^{-1}) OF THE BANDS FOR THE VARIOUS Nd(III) IONS DOPED IN AQUEOUS SATURATED SOLUTIONS OF VARIOUS PHARMACEUTICAL ORGANIC COMPOUNDS

Group level	Nd-Diphenhydramine		Nd-Tripelenamine		Nd-Chlorpheniramine		Nd-Promethazine		Nd-Terfenadine		Nd-Naproxen	
	E _{exp}	E _{cal}	E _{exp}	E _{cal}	E _{exp}	E _{cal}	E _{exp}	E _{cal}	E _{exp}	E _{cal}	E _{exp}	E _{cal}
² P _{1/2}	23130	23119.61	23082	23078.93	23082	23077.22	23121	23117.89	23034	23030.93	23094	23097.38
⁴ G _{11/2}	21460	21327.36	21500	21347.24	21620	21390.33	21525	21379.83	21510	21381.81	21460	21323.98
⁴ G _{9/2}	21150	21150.55	21140	21126.91	21090	21094.75	21030	21044.36	21010	21025.29	21145	21130.45
² G _{9/2}	19460	19431.41	19445	19464.30	19430	19448.31	19490	19445.60	19490	19445.45	19420	19438.69
⁴ G _{7/2}	19100	19118.70	19140	19164.07	19127	19110.81	19125	19122.55	19125	19116.67	19090	19134.78
⁴ G _{5/2}	17180	17078.67	17220	17177.58	17160	17127.24	17250	17193.65	17240	17197.85	17182	17122.34
⁴ F _{9/2}	14625	14641.18	14600	14626.99	14650	14634.41	14650	14634.41	14640	14624.28	14620	14625.86
⁴ F _{7/2}	13090	13160.66	13120	13184.39	13080	13202.10	13110	13211.26	13110	13209.99	13100	13165.26
⁴ F _{5/2}	12290	12338.93	12330	12375.08	12290	12379.37	12290	12396.88	12310	12398.71	12270	12350.58
⁴ F _{3/2}	11310	11339.46	11425	11394.46	11420	11370.35	11445	11411.33	11440	11409.42	11425	11363.14
	r.m.s. dev ± 61.3		r.m.s. dev ± 58.4		r.m.s. dev ± 89.3		r.m.s. dev ± 70.3		r.m.s. dev ± 62.8		r.m.s. dev ± 62.6	

Group level	Nd-Fenoprofen		Nd-Flubiprofen		Nd-Oxaprozoin		Nd-Ketoprofen		Nd-Ibuprofen	
	E _{exp}	E _{cal}	E _{exp}	E _{cal}	E _{exp}	E _{cal}	E _{exp}	E _{cal}	E _{exp}	E _{cal}
² P _{1/2}	23121	23115.52	23121	23117.02	23100	23093.24	23121	23119.03	23094	23083.10
⁴ G _{11/2}	21505	21363.17	21505	21364.82	21450	21329.73	21500	21379.14	21551	21362.41
⁴ G _{9/2}	21008	21027.58	21010	21028.49	21320	21292.77	21160	21144.19	21052	21056.00
² G _{9/2}	19493	19431.63	19495	19435.92	19580	19501.44	19510	19464.19	19417	19436.99
⁴ G _{7/2}	19120	19110.63	19125	19117.21	19090	19221.97	19050	19143.54	19138	19114.59
⁴ G _{5/2}	17250	17186.34	17245	17196.77	17200	17116.37	17210	17135.33	17250	17164.70
⁴ F _{9/2}	14640	14623.18	14640	14622.43	14610	14654.32	14650	14660.17	14612	14628.25
⁴ F _{7/2}	13100	13202.60	13100	13204.91	13110	13155.95	13110	13195.96	13090	13195.66
⁴ F _{5/2}	12280	12389.13	12285	12392.67	12270	12343.05	12310	12375.33	12350	12380.96
⁴ F _{3/2}	11425	11406.79	11445	11412.76	11400	11352.97	11430	11374.54	11360	11391.51
	r.m.s. dev ± 71.7		r.m.s. dev ± 70.5		r.m.s. dev ± 75.8		r.m.s. dev ± 67.9		r.m.s. dev ± 75.7	

TABLE-3

COMPUTED VALUES OF OSCILLATOR STRENGTH OF THE BANDS OBSERVED FOR THE VARIOUS Nd(III) ION DOPED IN AQUEOUS SATURATED SOLUTION OF VARIOUS PHARMACEUTICAL ORGANIC COMPOUNDS

Level	Nd-Diphenhydramine $P_{exp} \times 10^6$	Nd-Tripeleminamine $P_{exp} \times 10^6$	Nd-Chlorpheniramine $P_{exp} \times 10^6$	Nd-Promethazine $P_{exp} \times 10^6$	Nd-Terfenadine $P_{exp} \times 10^6$	Nd-Naproxen $P_{exp} \times 10^6$
$^2P_{1/2}$	0.986	1.48	1.41	1.14	1.64	1.43
$^4G_{11/2}$	1.25	0.517	0.472	0.384	0.604	0.499
$^4G_{9/2}$	4.21	4.48	4.83	4.93	4.68	3.63
$^2G_{9/2}$	0.743	1.05	1.38	0.831	1.18	1.63
$^4G_{7/2}$	6.57	5.02	7.82	7.90	7.39	8.10
$^4G_{5/2}$	18.1	20.5	26.4	21.6	28.5	27.3
$^4F_{9/2}$	1.02	0.857	1.27	1.04	1.67	4.34
$^4F_{7/2}$	7.49	7.65	6.28	5.45	5.75	6.74
$^4F_{5/2}$	5.34	8.97	5.35	6.77	4.88	6.24
$^4F_{3/2}$	1.51	3.21	2.14	3.43	2.22	2.56
	r.m.s. dev ± 1.68	r.m.s. dev ± 1.88	r.m.s. dev ± 1.90	r.m.s. dev ± 1.84	r.m.s. dev ± 1.84	r.m.s. dev ± 1.92

level	Nd-Fenoprofen $P_{exp} \times 10^6$	Nd-Flurbiprofen $P_{exp} \times 10^6$	Nd-Oxaprozoin $P_{exp} \times 10^6$	Nd-Ketoprofen $P_{exp} \times 10^6$	Nd-Ibuprofen $P_{exp} \times 10^6$
$^2P_{1/2}$	71.0	21.7	1.43	1.18	1.60
$^4G_{11/2}$	78.2	29.1	.499	.357	.542
$^4G_{9/2}$	2.52	1.72	3.63	2.86	3.11
$^2G_{9/2}$	50.3	49.4	1.63	.716	1.14
$^4G_{7/2}$	2.90	3.41	8.10	6.59	5.06
$^4G_{5/2}$.170	.184	27.3	29.6	17.9
$^4F_{9/2}$	4.88	.902	4.34	.868	4.52
$^4F_{7/2}$	8.72	8.66	6.74	7.35	6.31
$^4F_{5/2}$	5.62	8.19	6.24	9.69	7.18
$^4F_{3/2}$	1.19	1.60	2.51	4.28	3.12
	r.m.s. dev ± 1.61	r.m.s. dev ± 1.92	r.m.s. dev ± 1.66	r.m.s. dev ± 1.61	r.m.s. dev ± 1.63

The ratio T_4/T_6 has been reported along with T_2 in Table-1. The T_4/T_6 ratio qualitatively suggests to have a common symmetry around the Nd(III) ion in the solution.

The hypersensitive transition (which is sensitive to environmental changes) ${}^4G_{5/2} \leftarrow {}^4I_{9/2}$ exhibit (Table-1) the increase in the intensity with increase in covalency around the Nd(III) ion in the solution. The hypersensitivity has been found to be proportional to nephelauxetic ratio β . This is in confirmation of the observation reported earlier by Peacock^{9, 10}.

The trend of decrease in ζ_{4f} value for the Nd(III) ion doped in saturated solution in comparison to free value (384.00 cm^{-1}) varies between 839.79 cm^{-1} to 860.28 cm^{-1} and suggests fair interaction as given in Table-1.

The various other parameters have their usual significance as reported earlier¹⁶.

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