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THERMODYNAMIC AND SPECTRAL PARAMETERS OF DOPED Nd (III) IONS IN SATURATED ALCOHOLIC SOLUTION OF VARIOUS SEMICARBAZONES DERIVED FROM CARBONYL COMPOUNDS

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ABSTRACT

The thermodynamic parameters and stereic environment of Nd (III) ion with a series of semicarbazone in saturated alcoholic solution has been discussed on the basis of electronic spectral data. The variosu energy parameters such as Racah (E^k) Slater–Condon (F_k) Lande parameter (ζ_{4f}) and the intensity parameters such as oscillator strength (P), Judd–Ofelt parameter (T_λ) have been computed using partial and regression methods. The bonding parameter ($b^{1/2}$) and nephelauxetc ratio (β) have also been evaluated.

Key words : Nd (III), Semicarbazones, Spectral, Thermodynamic

INTRODUCTION

Semicarbazones have been found of vital importance due to their biological and analytical applicability and strong coordination behaviour[1,2]. The energy and intensity parameters of lanthanon chelates with variety of ligands have widely been studied for the interpretation of sharp line like bands arising from the transition among different level of $4f^n$ configuration.[3,4] Doped study of certain systems finds immense applications.[5–7], therefore, the present work deals with the study of various energy and electronic parameters viz. Judd–Ofelt intensity (T_λ), Slater–Condon (F_λ), Lande's (ζ_{4f}) intensity of hypersensitive band ($^3P_2$) and Racah's (E_k) as well as bonding parameters $b^{1/2}$ for Nd (III) ion doped in alcoholic saturated solution of semicarbazones derived from carbonyl compounds. In these studies, a saturated solution in alcoholic media has been made by dissolving some semicarbazones derived from carbonyl compounds at room temperature and a constant amount of Nd (III) chloride has been added to each of the solutions. Spectrophotometry has been used for the characterisation and determination of electronic parameters for Nd (III) ion doped in saturated alcoholic solution. Several bands including $^4G_{5/2}$ are characterized for Nd (III) ion in the visible region and the change in the intensity of these bands in indicated by red shift caused by the change in coordination environment around the ion resulting from $f \leftrightarrow f$ transition in lanthanides.

EXPERIMENTAL

Synthesis of ligands

Eight semcarbazones were synthesized by refluxing semcarbazide in equimolar ratio with p–hydroxyacetophenone, o–hydroxyacetophenone, m–hydroxyacetophenone, ethyl vanilline, phenazone, p–aminoacetophenone, o–aminoacetophenone and m–aminoacetophenone, respectively for 5 to 6 h at temperature 70 to 80°C. Each compound was purified and crystallized in ethanol.

Preparation of saturated ligand solutions containing doped Nd (III) ion

The saturated solutions of p–hydroxyacetophenonesemicarbazone (p–HAP–SC), o–hydroxyacetophenonesemicarbazone (o–HAP–SC), m–hydroxyacetophenonesemicarbazone (m–HAP–SC), ethylvanillinesemicarbazone (EV–SC), phenazonesemicarbazone (P–SC), p–aminoacetophenonesemicarbazone (p–AAP–SC), o–aminoacetophenonesemicarbazone (o–AAP–SC) and m–aminoacetophenonesemicarbazone (m–AAP–SC) were prepared by dissolving each of them in ethanol and 0.014 M of $NdCl_3.6H_2O$ was added to each of the solutions.

The solution spectra of these systems were recorded by using standard spectrophotometer (Spectronic–20) in the visible region. The calculation for various electronic parameters was made by computerized statistical method reported earlier[8]. All chemicals used were of A.R. Grade. $PrCl_3.6H_2O$ (99.9% purity) was supplied by Indian Rare Earth's Udyogmandalam, Kerala.

RESULTS AND DISCUSSION

The value of energies (E) for peaks of various transitions and the parameters of all the compounds are summarized in Table 1 and 2. The decrease in values of the Slater–Condon, Lande and the Racah parameters of the doped system as compared to those of the free metal ion may be attributed to chelation of Nd (III) ion with the ligand present in the surrounding environment and this in turn indicates the expansion of metal orbital, which is in accordance with $f \leftrightarrow f$ transtions. The decrease in the value of the Lande parameter (ζ_{4f}) is more than the Slater–Condon (F_k) parameter. It indicates that the ligand affects the spin orbit coupling more than electrostatic repulsion. The order of Slater–Condon parameter is found to be $F_2 > F_4 > F_6$. The observed values of F_6/F_2 are less than F_4/F_2. The solution spectra are analyzed by resolving each band into Gussian curve shape to enable evaluation of oscillator strength. The observed oscillator strength has maximum contribution from the induced electric dipole mode in comparison to magnetic dipole and electric quadripole modes. Comparing the values of energies with corresponding energy level in free metal ion, the bands for the different transitions are identified.

Table 1. Computed values of energy (cm^{-1}) of oscillator strength for Nd (III) ion doped in alcoholic saturated solution of various semicarbazones of carbonyl compounds

COMPOUND	$^2P_{1/2}$		$4G_{11/2}$		$4G_{9/2}$		$2G_{9/2}$		$4G_{7/2}$		$4G_{5/2}$		$^4F_{9/2}$		$^4F_{7/2}$		$^4F_{5/2}$		$4F_{3/2}$		σ^{rms}
	P_{exp} x 10^6	P_{cal} x 10^6	P_{exp} x 10^6	P_{cal} x 10^6	P_{exp} x 10^6	P_{cal} x 10^6	P_{exp} x 10^6	P_{cal} x 10^6	P_{exp} x 10^6	P_{cal} x 10^6	P_{exp} x 10^6	P_{cal} x 10^6	P_{exp} x 10^6	P_{cal} x 10^6	P_{exp} x 10^6	P_{cal} x 10^6	P_{exp} x 10^6	P_{cal} x 10^6	P_{exp} x 10^6	P_{cal} x 10^6	
Nd–p–HAP–SC	1.520	1.430	0.780	0.325	6.620	2.920	1.620	0.697	9.370	7.020	28.800	30.900	2.130	0.707	5.910	5.550	4.530	8.850	3.470	4.770	2.180
Nd–o–HAP–SC	1.080	1.300	1.790	0.365	4.970	2.960	0.965	0.735	7.475	6.410	20.200	22.700	1.400	0.866	7.490	7.350	5.670	10.000	3.330	4.580	1.850
Nd–m–HAP–SC	1.330	1.600	0.421	0.362	4.620	3.210	0.894	0.770	8.690	7.380	24.700	27.700	1.130	0.780	5.520	6.100	5.400	9.810	3.350	5.340	1.910
Nd–EV–SC	1.120	1.160	2.050	0.340	5.240	2.730	2.000	68.200	7.890	5.830	18.500	20.100	2.820	0.830	7.760	7.100	5.830	9.450	3.410	4.160	1.890
Nd–P–SC	1.060	1.270	0.360	0.290	3.710	2.540	0.760	0.610	6.900	5.820	19.400	21.700	0.980	0.620	4.450	4.870	4.310	7.760	2.680	4.220	1.500
Nd–p–AAPSC	1.010	0.880	0.490	0.240	3.750	2.020	1.240	0.500	5.800	4.670	18.800	20.500	1.310	0.580	5.250	4.870	3.400	6.710	2.470	3.090	1.400
Nd–o–AAPSC	0.940	1.190	0.450	0.290	4.380	2.470	0.830	0.600	6.050	5.530	17.800	19.500	2.850	0.640	4.970	5.140	4.990	7.850	2.930	4.040	1.490
Nd–m–AAPSC	0.900	1.050	0.460	0.170	3.160	1.760	1.030	0.400	5.480	4.420	16.800	17.900	1.330	0.280	1.870	1.740	2.060	4.440	2.710	3.250	1.100

Table 2. Computed values of energy (F_k, $\zeta_{4f, Ek}$, %r $\zeta_{4f,}$ β and $b^{1/2}$) Nd (III) ion doped in alcoholic saturated solution of various semicarbazones of carbonyl compounds

COMPOUND	F_2 (in cm^{-1})	F_4 (in cm^{-1})	F_6 (in cm^{-1})	%rF_2	ζ4f (in cm–1)	%rζ_{4f}	E1 (in cm^{-1})	E^2 (in cm^{-1})	E^3 (in cm^{-1})	β	$b^{1/2}$
A	331.160	50.71	5.15	–	884.06	–	5024.00	23.90	497.00	–	–
1	331.130	50.09	5.30	0.0080	873.17	1.2247	5047.54	24.03	490.82	0.9969	0.0383
2	330.810	50.25	5.30	0.1032	876.60	0.8366	5041.11	24.21	491.18	0.9986	0.256
3	330.560	50.46	5.30	0.1784	875.84	0.9230	5042.11	24.12	491.07	0.9977	0.0236
4	330.560	50.46	5.30	0.1784	873.17	1.2247	5047.54	24.03	490.82	0.9969	0.0388
5	330.810	50.25	5.30	0.1032	875.84	0.9230	5042.11	24.12	491.07	0.9977	0.0336
6	331.130	50.09	5.30	0.0080	876.60	0.8366	5041.11	24.21	491.18	0.9986	0.0256
7	330.770	50.36	5.30	0.1170	873.69	1.1666	5045.11	24.09	491.13	0.9976	0.0346
8	330.810	50.25	5.30	0.1032	875.84	0.9230	5042.11	24.12	491.07	0.9977	0.3360

Nephelauxetic ratio has been found less than one for all the complexes, which reflects the mixing of metal–ligand orbitals and covalent nature of metal–ligand bond. To establish the validity of the theory given by Judd–Ofelt with reference to the result obtained for the systems, T_2, T_4 and T_6 Judd–Ofelt parameters (T) have been further used to classify the symmetry environment around Nd (III) ion. The values of oscillator strength were found in the order of p–HAP–SC > m–HAP–SC > o–HAP–SC > P–SC > p–AAP–SC > EV–SC > o–AAP–SC > m–AAP–SC. The r.m.s. deviations with respect to oscillator strength were in the acceptable range.

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