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Micellar Investigations on Hypersensitive Transitions for Doped Pr(III) Ion in Saturated Alcoholic Solution of Semicarbazones

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The interactions of semicarbazones (*p*-methoxyacetophenone semicarbazone, *p*-anisaldehyde semicarbazone and *p*-hydroxybenzaldehyde semicarbazone) with Pr(III) ion have been studied in different media. The absorption spectra have been recorded in visible range. Various energy and intensity parameters such as Racah (E^K), Slater-Condon (F_K), Lande (ζ_{4f}), Oscillator strength (P) and Judd-Ofelt parameter (T_λ) etc. have been computed using partial and multiple regression methods. Also, the nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$) have been evaluated. Results were compared for micellar medium and alcoholic medium.

Key Words: Micellar, Doped Pr(III), Semicarbazone.

INTRODUCTION

The coordination chemistry of semicarbazones is very significant because of their biological[1, 2] and analytical[3] importance. Various spectral and intensity parameters of complexes of lanthanides with several ligands have been widely studied for the interpretation of sharp line bands, which appears due to *f-f* transitions. Judd and Ofelt derived equation for the oscillator strength (P) of a transition between ground state and excited state[4, 5]. The equation can be explored for the determination of probability of an electronic transition for lanthanide solution as well as in doped state[6]. For a symmetrically allowed transition P is equal to one. Since *f-f* transitions are induced electric dipole transitions, the value of P is much less than one. Magnetic dipole oscillator strength is of the order of 10^{-8} while electric quadrupole oscillator strength is 10^{-10}. A comparative study of oscillator strength can further be used to evaluate the T_4/T_6 parameter and Judd-Ofelt parameter (T_λ). T_λ values have been used to predict the symmetry environment in doped system. Literature survey reveals that no systematic study has been carried on complexes of Pr(III) with semicarbazone with reference to statistical thermodynamic calculations. Further studies have been restricted to simple solutions. So the present study has been undertaken with doped systems of Pr(III) in alcoholic solution of semicarbazone as well as in

micellar medium. However, this study is far from being complete. It is important and significant to report the results of the effect of micellar medium on the statistical thermodynamical studies of lanthanide complexes.

EXPERIMENTAL

The semicarbazones were synthesized by refluxing semicarbazide in equimolar ratio with *p*-methoxyacetophenone, *p*-anisaldehyde and *p*-hydroxybenzaldehyde for 5–6 h at temperature 70–80°C. The compounds were purified and crystallized in ethanol.

The saturated solution of *p*-methoxyacetophenone semicarbazone (*p*-MAPSC), *p*-anisaldehyde semicarbazone (*p*-ASC) and *p*-hydroxybenzaldehyde semicarbazone (*p*-HBSC) were prepared by dissolving them in ethanol and $PrCl_3 \cdot 6H_2O$ was added to the solution. Triton X-100 surfactant was used (1.8×10^{-2} M).

The solution spectra of the systems were recorded by using standard spectrophotometer in the visible region. The calculation for various electronic parameters was made by the computerized statistical method reported earlier[7].

RESULTS AND DISCUSSION

The semicarbazones were characterized on the basis of m.p., IR, NMR and electronic spectral studies. The computed values of electronic spectral parameters (energy and intensity parameters) have been given in Tables 1 and 2. Wong method has been used to calculate the Slater-Condon parameter (F_K) and Lande's parameter (ζ_{4f}). The values of Slater-Condon parameter (F_K) were found to decrease in comparison to free metal ion. The values for Lande's parameter (ζ_{4f}) were also found to be decreasing. The spin-orbit interaction has been found to show much variation as a result of this. Spin-orbit interactions in $f \leftrightarrow f$ transition are much more affected in comparison to inter-electronic interaction. The intensity of hypersensitivity band also shows a similar trend.

The decrease in computed values of spin orbit interaction parameter (ζ_{4f}), Judd-Ofelt parameter (T_λ) and Slater-Condon parameter (F_k) in comparison to free ion values show clearly symmetry change around the metal ion in the solution.

The T_4/T_6 ratio reflects the change in stereo-environment around the metal ion present in the solution and thereby change in coordination number. Therefore the change in the surrounding environment around the metal ion involving a suitable interaction between the metal ion and ligand has been well characterized by decrease in the various inter-electronic repulsion and spin-orbit interactions.

The parametric values provide useful information regarding the coordination behaviour of Pr(III) ion. The coordination behaviour varies as the change in ratio of T_4/T_6 takes place. Similar values indicate similar stereo-environment around Pr(III) due to solute-interaction present in the solution.

The nephelauxetic ratio as indicated by the positive values of $b^{1/2}$ reflects some bonding character in the form of change in stereo-environment around the central metal ion.

TABLE-1

COMPUTED VALUES OF ENERGY (cm^{-1}) OF OSCILLATOR STRENGTH T_λ AND T_4/T_6 FOR Pr(III) ION DOPED IN ALCOHOLIC SATURATED SOLUTION OF VARIOUS SEMICARBAZONES OF CARBONYL COMPOUNDS

Compound	$^3P_2 \times 10^6$		$^3P_1 \times 10^6$		$^3P_0 \times 10^6$		$^1D_2 \times 10^6$		$T_2 \times 10^{10}$	$T_4 \times 10^{10}$	$T_6 \times 10^{10}$	T_4/T_6
	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}				
p-MAPSC + Pr	20.30	20.30	9.17	9.17	4.40	4.40	3.95	3.95	–454.0	18.7	61.60	0.30
p-MAPSC + Pr (in micellar medium)	28.50	28.50	11.70	11.70	5.08	5.06	5.17	5.17	–713.0	23.1	86.90	0.27
p-ASC + Pr	23.70	23.69	10.30	10.20	5.25	5.26	6.82	6.80	–3.20	2.15	7.25	0.30
p-ASC + Pr (in micellar medium)	29.20	29.00	14.90	14.70	5.60	5.60	8.33	8.31	–4.58	2.83	8.78	0.32
p-HBSC + Pr	12.30	12.29	5.05	5.05	2.26	2.25	2.58	2.60	–223.0	10.00	37.10	0.27
p-HBSC + Pr (in micellar medium)	33.30	33.20	16.00	16.01	6.24	6.24	9.36	9.34	–9.35	3.07	10.20	0.30

TABLE-2

COMPUTED VALUES OF ENERGY (F_k, ζ_{4f}, E_k, %r ζ_{4f}, β and $b^{1/2}$) FOR Pr(III) ION DOPED IN ALCOHOLIC SATURATED SOLUTION OF VARIOUS SEMICARBAZONES OF CARBONYL COMPOUNDS

Compound	F_2	F_4	F_6	%r F_2	ζ_{4f}	%r ζ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$
p-MAPSC + Pr	310.71	42.89	4.690	3.430	692.31	6.560	4566.50	23.880	461.69	0.9657	0.1310
p-MAPSC + PR (in micellar medium)	314.34	43.39	4.740	2.405	621.36	16.146	4615.14	24.140	466.61	0.9760	0.1097
p-ASC + Pr	309.07	42.66	4.670	4.030	693.00	6.450	4537.00	2.373	458.79	0.9889	0.0741
p-ASC + Pr (in micellar medium)	310.02	42.80	4.684	3.747	723.35	2.380	4551.66	23.810	460.19	0.9625	0.1368
p-HBSC + Pr	310.51	42.86	4.690	3.590	662.00	10.620	4558.00	23.840	460.92	0.9867	0.0815
p-HBSC + Pr (in micellar medium)	315.73	43.59	4.770	1.974	634.80	14.331	4635.46	24.248	468.67	0.9802	0.0993

On comparing the results for both meda, oscillator strength (P), Judd-Ofelt parameters (T_λ), Slater-Condon parameters (F_K), Racah parameter (E_K) and nephelauxetic ratio (β) have been found to be increasing in micellar medium. A decreasing value of Lande's parameter (ζ_{4f}) in micellar medium has been observed. Lesser value of Slater-Condon parameter than free ion value suggests a decrease in spin-orbit interaction and interelectronic repulsion indicating a general red shift, but less decrease in value of F_K has been observed for micellar medium. Greater values of Judd-Ofelt (T_λ) parameters and Racah parameter (E_K) have been observed. Also the value of β has been found to be less than one for micellar medium.

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