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Spectrophotometric Study of Doped Pr(III) Ion in Saturated Solutions of Carbohydrates and Amides in Non-aqueous Solvents

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The stereo-environment of doped Pr(III) ion in saturated solutions of carbohydrates (glucose, fructose and sucrose) and amides (acetamide, urea and thiourea) in DMF as well as in DMSO has been discussed on the basis of Judd-Ofelt intensity parameteric ratio (T_4/T_6). Pr(III) ions doped with the various systems have been characterized on the basis of various electronic spectral parameters *viz.* Slater-Condon (F_k) Landé (ζ_{4p}) intensity of hypersensitive transition ($^3P_2$), Judd-Ofelt (T_λ) and bonding parameter ($b^{1/2}$).

INTRODUCTION

The study of the substances doped with certain known impurities has been found to be very useful[1, 2] in many of the fields of science and technology. In the present work Pr(III) ion has been doped with non-aqueous saturated solutions. The saturated solutions have been prepared by dissolving carbohydrates as well as amides in DMF and DMSO. Pr(III) chloride of constant amount (0.10 gm) has been added to each of the saturated solutions. Thus Pr(III) ion is surrounded by non-aqueous environment saturated with certain organic compound. The present systems of saturated solutions doped with Pr(III) ion have been characterized spectrophotometrically. Since Pr(III) ion absorption spectra yield four bands *viz.* $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ in visible region so in the doped systems prepared as above the changes in the intensities with a little red shift in the energy of these bands have been studied in terms of various electronic spectral parameters recently popularized in the field of lanthanide f↔f transitions[3, 4]

EXPERIMENTAL

The various saturated solutions at room temperature (35° ± 2°C) in DMF and DMSO have been prepared for carbohydrates including glucose, fructose and sucrose and amides including acetamide, urea and thiourea. 0.10 Gm. of $PrCl_3 \cdot 6H_2O$ (99.9% purity supplied by Indian Rare Earths, Udhyogmandalam, Kerala) has been added to each of these saturated solutions. The solution spectra of these systems have been recorded by using the standard spectrophotometer

(systronic) in the visible region. The calculation of the parameters were done as reported earlier.[5,6]

RESULTS AND DISCUSSION

The computed values of the various energy and intensity parameters have been reported in Tables 1 and 2. The parametric values show a remarkable variation in spin-orbit interaction parameter ζ_{4f}, oscillator strength of $^3P_2$-band and Judd-Ofelt parameters (T_λ) along with T_4/T_6 ratio for the systems under study. The spectrophotometric study infers that the f↔f transitions resulting from Pr(III) ion doped in the present systems are remarkably affected in terms of energy and intensity. Thus the surrounding environments involving suitable ligand saturated in a non-aqueous solvent can be well characterized in the form of decrease in interelectronic repulsions and spin-orbit interactions. The parametric values showing the said effect provide useful informations about the coordination behaviour of Pr(III) ion. The coordination behaviour of Pr(III) ion in the present doped systems has been found to be varied as the ratio T_4/T_6 changes. Pr(III) ion doped with symmetrical stereo environment has been reported to show similar value of T_4/T_6 ratio. In the present systems the stereo environments around doped Pr(III) ion have been classified in the various categories depending upon the value of T_4/T_6 ratio. This has been reported in Table 2.

It may be concluded for the present systems that the stereo-environment around doped Pr (III) ion has been found to show a change in coordination behaviour. Thus the change in stereo-environment around doped Pr (III) ion depends upon combined effect of solute-solvent interaction in these cases.

The values of F_2-parameter in the present systems find a close similarity whereas as the values of ζ_{4f}-parameter have been found to show much variation. This shows spin-orbit interactions in f↔f transitions are much more affected in comparison to interelectronic repulsions. The intensity of hypersensitive band, $^3P_2$ in the present systems of doped Pr(III) ion has also been found to show much variation.

In this way the various systems having saturated solutions of carbohydrates and amides in DMF and DMSO with Pr(III) ion doped in them have been characterized on the basis of spectrophotometric study. The study provides the useful informations regarding changes in stereo-environment around Pr(III) ion which have been remarkably indicated by T_4/T_6 ratio value. The study also suggests the variation in nephelauxetic effect by changing the ligand environment around Pr(III) ion. The various electronic spectral parameters reported in Tables 1 and 2 have the usual significance as have been reported earlier by one of the authors (G.K. Joshi).[5,7]

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TABLE 1

COMPUTED VALUES OF F, ζ_{4f}, E^k, % r ζ_{4f}, % r F_2, β and $b^{1/2}$ FOR Pr(III) ION DOPED WITH SATURATED NON-AQUEOUS ENVIRONMENT PRODUCT BY VARIOUS ORGANIC COMPOUNDS

Compound	Medium	F_2	F_4	F_6	ζ_{4f}	E^1	E^2	E^3	% r ζ_{4f}	% r F_2	β	$b^{1/2}$
1 Sucrose	DMSO	309.058	42.66	4.67	687.04	4537.53	23.736	458.765	7.28	4.046	0.95954	0.14233
	DMF	311.355	42.98	4.70	657.116	4571.26	23.91	462.176	11.320	3.333	0.96667	0.12910
2. Glucose	DMSO	311.60	43.020	4.71	648.654	4574.88	23.93	462.54	12.46	3.256	0.96743	0.12760
	DMF	311.48	43.000	4.70	640.88	4573.14	23.92	462.36	13.51	3.293	0.96707	0.1283
3. Fructose	DMSO	309.34	42.70	4.67	688.55	4541.61	23.76	459.10	7.07	3.96	0.96040	0.1407
	DMF	310.373	42.84	4.69	672.90	4556.83	23.84	460.72	9.20	3.64	0.9636	0.1348
4. Urea	DMSO	308.93	42.65	4.67	690.133	4535.756	23.72	458.58	6.86	4.08	0.9591	0.1429
	DMF	309.13	42.67	4.67	683.54	4538.57	23.74	458.87	7.75	4.024	0.9597	0.1418
5. Thiourea	DMSO	309.08	42.67	4.67	686.34	4537.84	23.73	458.80	7.37	4.04	0.9596	0.14211
	DMF	311.45	42.99	4.70	653.85	4572.69	23.92	462.32	11.76	3.30	0.9669	0.1285
6. Acetamide	DMSO	309.21	42.69	4.67	681.82	4539.74	23.74	458.99	7.98	3.99	0.9600	0.1414
	DMF	311.44	42.99	4.70	653.04	4572.53	23.92	462.30	11.87	3.30	0.9669	0.1285

TABLE 2

COMPUTED VALUES OF ENERGIES IN (cm^{-1}), P, T_λ and T_4/T_6 FOR Pr(III) ION DOPED WITH SATURATED NON-AQUEOUS ENVIRONMENT PRODUCED BY VARIOUS ORGANIC COMPOUNDS

Compound	Medium	Level (Observed)				T_λ			T_4/T_6
		$^3P_2$	$^3P_1$	$^3P_0$	$^1D_2$	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	
		$P \times 10^6$	$P \times 10^6$	$P \times 10^6$	$P \times 10^6$				
1. Source	DMSO	22451	21186	20618	16863	–31.08	0.853	4.999	.170
		15.9	3.823	2.313	3.266				
	DMF	22471	21177	20725	16906	–49.65	1.427	6.703	.213
		21.57	6.47	3.81	4.12				
2. Glucose	DMSO	22421	21164	20725	16906	–48.42	1.089	4.632	.23
		14.958	5.175	2.670	2.257				
	DMF	22441	21168	20703	16806	–38.20	1.631	7.106	.22
		22.93	7.51	4.23	5.007				
3. Fructose	DMSO	22441	21208	20639	16906	–58.62	.937	5.297	.177
		16.86	4.87	1.87	2.35				
	DMF	22446	21231	20682	16891	–65.58	1.175	8.182	.143
		25.842	5.323	3.154	4.64				

Compound	Medium	Level (Observed)				T_λ			T_4/T_6
		$^3P_2$	$^3P_1$	$^3P_0$	$^1D_2$	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	
		$P \times 10^6$	$P \times 10^6$	$P \times 10^6$	$P \times 10^6$				
4. Urea	DMSO	22471	21141	20618	16891	−10.596	1.027	3.925	.26
		12.78	5.28	2.103	3.277				
	DMF	22421	21119	20618	16906	−41.50	1.014	4.625	.22
		14.87	4.76	2.523	2.523				
5. Thiourea	DMSO	22446	21186	20618	16863	−15.59	9.379	6.2232	.150
		19.689	4.435	2.313	5.042				
	DMF	22461	21186	20725	16891	−26.80	.783	4.6900	.167
		14.909	3.530	2.119	3.1666				
6. Acetamide	DMSO	22421	21177	20618	16863	−37.28	1.363	6.2148	.22
		19.987	6.653	3.154	4.205				
	DMF	22471	21141	20725	16906	−94.21	1.370	10.676	.128
		33.622	6.470	3.391	5.640				

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