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Characterization of Some Rare Earth-Sulphonanilide Complexes in Terms of Thermodynamic Parameters

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ABSTRACT: *The twenty systems of Sm(III) with O, N, and S containing ligands have been characterized on the basis of various thermodynamic parameters viz; oscillator strength of transition (P), work function (A), partition function (Q), thermodynamic efficiency of transition (TET) & ratio of partition function (r_p). The study provides useful information about M-L interactions.*

KEYWORDS: *Thermodynamic parameters, Doped Sm(III) system.*

I. INTRODUCTION

The lanthanide(III) ion exhibits absorption spectra characterized by the bands in the visible region, but these spectra have not been studied extensively in terms of various electronic spectral parameters. A great deal of work has been reported on the measurement of $f \rightarrow f$ transition of free and aquo-ion of Sm(III) ions in different saturated solutions by several workers. **(1-8)**

Most of $f \rightarrow f$ transitions of trivalent lanthanide, have intensities, which are little affected by environment of ligands. A few however, are very sensitive to ligand environment, are usually more intense when complexed, such transitions have been called hypersensitive transitions**(9-10)**.The intensity of hypersensitive transitions can be up to 200 times greater than corresponding aqua ion transition depending upon particular complex.

The transition , $^6H_{5/2} - {}^6F_{1/2}$ and $^6H_{5/2} - {}^6P8_{/2}$ are said to be hypersensitive in case of Sm(III) ion.
Oscillator strength of the hypersensitive transitions exhibit greater variation than the oscillator strength of non hypersensitive transitions.

The study of hypersensitive transitions play an important role in evaluating the effect of ligand environment on 4f orbital of lanthanide ion[11-13]. The recent theories given by Slater-Condon, Lande, Carnall and Judd-Ofelt about the lanthanide f-f spectra correlate the involvement of 4f-orbitals in terms of the various energy and intensity parameters[14-16].

The present paper describes the thermodynamic treatment of hypersensitive transitions of various sulphonanilide ligands doped with Sm(III) ion.

II. EXPERIMENT

Twenty systems were prepared (table I) for Sm(III) ions and substituted sulphonailides ligands. Solution spectra of these systems have been recorded by using a standard spectrophotometer .

Calculation of work function and thermodynamic efficiency of the transition (TET)-

(A) TET:-

By using thermodynamic relation[1-3]

$$A = E - TS \text{ and } S = K \ln p$$

following relation may be obtained

$$A = E - KT \ln p$$

Where-

A = Work function (cm^{-1})
E = energy absorbed for transition (cm^{-1})
K = Boltzmann Constant = 0.6945 cm^{-1}
T = Absolute temp
P = Oscillator strength of transition
S = Absolute energy.

Thermodynamic efficiency of transition (TET) may be expressed as-

$$TET = \frac{\text{Work function for transition } (cm^{-1})}{\text{Energy absorbed for transition } (cm^{-1})}$$

(B) Calculation of Partition function (Q) and ratio of partition function (r_p) :

$Q = g_i\, e^{-E / KT}$

Where $g_i = 2J + 1$ ($g_i = 6$ for $^4G_{5/2}$)

$$r_p = \frac{\text{Q for lanthanide ion system}}{\text{Q for lanthanide ion in solvent}}$$

III. RESULT & DISCUSSION

The computed values of the thermodynamic parameters (for hypersensitive transition) from the spectroscopic data have been tabulated in Table – II & table-III.

 The observed oscillator strength values for $^6P_{8/2}$ band were found between 6.2789 X 10^{-6} & 64.7972 X 10^{-6}.

Sm(III)-L_6 < Sm(III)-L_8 < Sm(III)-L_{12} < Sm(III)-L_9 < Sm(III)-L_1 < Sm(III)-L_2 < Sm(III)-L_3 < Sm(III)-L_4 < Sm(III)-L_{14} < Sm(III)-L_{17} < Sm(III)-L_7 < Sm(III)-L_{10} < Sm(III)-L_5 < Sm(III)-L_{19} < Sm(III)-L_{11} < Sm(III)-L_{13} < Sm(III)-L_{16} < Sm(III)-L_{15} <Sm(III)-L_{18} < Sm(III)-L_{20}

- The values of work function for Sm(III) systems were found between 26579.40 & 27.186.60.
- The order of work function was found as given below-
- Sm(III)-L_{20} < Sm(III)-L_{16} < Sm(III)-L_{18} < Sm(III)-L_{13} < Sm(III)-L_5 < Sm(III)-L_{15} < Sm(III)-L_{11} < Sm(III)-L_{17} < Sm (III)-L_{19} < Sm (III)-L_{14} < Sm (III)-L_{10} < Sm (III)-L_4 < Sm (III)-L_8 < Sm (III)-L_7 < Sm (III)-L_9 < Sm (III)-L_6 < Sm (III)-L_3 < Sm (III)-L_{12} < Sm (III)-L_2 < Sm (III)-L_1
- The values of TET for Sm(III) systems were found between 1.0817 & 1.0956, and the order of TET was found as given below-
- Sm(III)-L_{20} < Sm(III)-L_{18} < Sm(III)-L_{15} < Sm(III)-L_{16} < Sm(III)-L_{13} < Sm(III)-L_{11} < Sm(III)-L_{19} < Sm (III)-L_5 < Sm (III)-L_{10} < Sm (III)-L_7 < Sm (III)-L_{17} < Sm (III)-L_3 < Sm (III)-L_4 < Sm (III)-L_{14} < Sm (III)-L_2 = Sm (III)-L_1 < Sm (III)-L_9 < Sm (III)-L_{12} < Sm (III)-L_8 < Sm (III)-L_6
- Thus, the order of partition function and ratio of partition function are found as given below-
- Sm(III) - L_c = Sm (III) - L_a < Sm (III) - L_e = Sm (III) - L_d < Sm (III) -L_b < Sm (III) - L_i = Sm (III) - L_g < Sm (III) - L_h

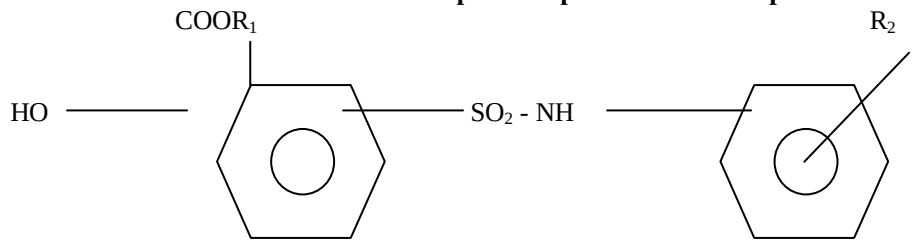
- Where a = 4, 19
- b = 7, 10,15
- c = 9,
- d = 12
- e = 1, 2, 3
- g = 8, 17, 20
- h = 5,13,14, 16, 4
- I = 20,6,11,18

The thermodynamic parameters resulting from spectroscopic data support the covalency between lanthanide ion and the surrounding ligand.

The significance of thermodynamic parameters are well understood but their computation from spectroscopic data proposes the microscopic behavior of the f-f transition.

IV. TABLES

TABLE – I A Simplified representation of sulphonanilides:



Sulphonanilide	Groups and their Position	
	R^1	R^2
L_1	H	o - CH_3
L_2	H	m - CH_3
L_3	H	p - CH_3
L_4	CH_3	o - CH_3
L_5	CH_3	m - CH_3
L_6	CH_3	p - CH_3
L_7	H	o – Cl
L_8	H	m – Cl
L_9	H	p - Cl
L_{10}	CH_3	o – Cl
L_{11}	CH_3	m – Cl
L_{12}	CH_3	p - Cl
L_{13}	C_2H_5	o – Cl
L_{14}	C_2H_5	m – Cl
L_{15}	C_2H_5	p - Cl
L_{16}	H	o - OCH_3
L_{17}	H	p - OCH_3
L_{18}	CH_3	o - OCH_3
L_{19}	CH_3	p - OCH_3
L_{20}	C_2H_5	o - OCH_3

TABLE-3.22 THERMODYNAMIC PROPERTY

S. N.	Sm(III) doped systems	Energy for hypersensitive transition ($^6P_{3/2}$) (cm^{-1})	Oscillator strength for hypersensitive transition ($^6P_{3/2}$)(X 10^6)	Work function (A) (cm^{-1})	Thermo Dynamic efficiency of the transition (TET)	Partition function $Q=g_ie^{-E/KT}$ (X 10^{26})	Ratio of partition function (r_p)	$K) = P_{obs} / vT_6$
1.	Sm(III) + L_1	24813.89	11.3297	27186.60	1.0956	1.7021	1.9217	0.381578
2.	Sm(III) + L_2	24813.89	11.3297	27186.60	1.0956	1.7021	1.9217	0.360160
3.	Sm(III) + L_3	24813.89	12.2738	27169.93	1.0949	1.7021	1.9217	0.402372
4.	Sm(III) + L_4	24660.91	12.5890	27011.66	1.0953	3.5471	4.0048	0.247179
5.	Sm(III) + L_5	24600.24	18.7908	26867.54	1.0921	4.7461	5.3585	0.235102
6.	Sm(III) + L_6	24630.54	6.2789	27126.22	1.1013	4.1038	4.6333	0.021394
7.	Sm(III) + L_7	24691.35	14.0225	27019.64	1.0942	3.0649	3.4603	0.473674
8.	Sm(III) + L_8	24570.02	7.8680	27018.70	1.0996	5.4869	6.1949	0.404711
9.	Sm(III) + L_9	24721.87	9.9570	27121.49	1.0970	2.6472	2.9888	0.572633
10.	Sm(III) + L_{10}	24691.35	17.2944	26975.94	1.0925	3.0649	3.4603	0.463709
11.	SmIII) + L_{11}	24630.54	19.4419	26890.74	1.0917	4.1038	4.6333	0.079071
12.	Sm(III) + L_{12}	24752.47	8.9248	27174.89	1.0978	2.2857	2.5806	0.364964
13.	Sm(III) + L_{13}	24600.24	21.9230	26835.42	1.0908	4.7461	5.3585	0.166006
14.	Sm(III) + L_{14}	24600.24	12.7591	26948.20	1.0954	4.7461	5.3585	0.241572
15	Sm(III) + L_{15}	24691.35	26.8770	26884.08	1.0888	3.0649	3.4603	0.297856
16.	Sm(III) + L_{16}	24390.24	26.2254	26588.08	1.0901	1.3004	14.6818	0.443521
17.	Sm(III) + L_{17}	24570.02	13.8851	26900.36	1.0948	5.4869	6.1949	0.165986
18.	Sm(III) + L_{18}	24630.54	27.9075	26815.43	1.0887	4.1038	4.6333	0.393623
19.	Sm(III) + L_{19}	24660.91	18.8839	26927.18	1.0918	3.5471	4.0048	0.493156
20.	Sm(III) + L_{20}	24570.02	64.7972	26579.4	1.0817	5.4869	6.1949	0.425239

Where;- K = 0.6945 , T = 300K gi=9

TABLE III Comparative Value Of Thermodynamic Parameter For Sm (Iii) Systems

S.N.	A-value for Er(III) systems		TET value for Er(III) systems		Q-value for Er(III) systems ($X\ 10^{40}$)		r_p value for Er(III) systems	
	Max A -value	Min A-value	Max TET	Min TET	Max Q -value	Min Q-value	Max r_p	Min r_p
1	L_9	L_8	L_8	L_7	L_8	L_9	L_8	L_9
2	L_1	L_{13}	L_6	L_{13}	L_5	L_3	L_5	L_3
3	L_{19}	L_{20}	L_{17}	L_{20}	L_{16}	L_{19}	L_{16}	L_{16}

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