RJC

STUDY OF THERMODYNAMIC BEHAVIOUR OF HYPERSENSITIVE TRANSITION OBSERVED IN SOME LANTHANIDE (III) DOPED SYSTEMS

Mahendra Vyas[1,*] and H. K. Pandey[2]

[1]P. G. Department of Chemistry, Govt. Engineering College, Bikaner (Raj.)
[2]P. G. Department of Chemistry, Govt. Dungar College, Bikaner (Raj.)
*E-mail: mkvyas2007@rediffmail.com

ABSTRACT

The spectroscopic data for hypersensitive transition have been correlated with the thermodynamic parameters including Thermodynamic efficiency of the transition (TET), partition function of the transition, Peacock relation (K') and (Q),Ratio of partition function (r_p) .
Keywords: Hypersensitive transition, Lanthanide, N, S and O donor ligands.

INTRODUCTION

The intensities of most of the f-f transitions of trivalent lanthanides are little affected by environment of surrounding ions. However, a few transitions are very sensitive to the environment and in the complexed lanthanide ion. They are usually more intense as compared to that of independent lanthanide ion present in the solvent medium. Such transitions are called hypersensitive transitions.

The study of hypersensitive transitions plays an important role in evaluating the effect of ligand environment on 4f orbital of lanthanide ion[1-3]. The recent theories given by Slater-Condon, Lande, Carnall[4] and Judd-Ofelt[5-6] about the lanthanide f-f spectra correlate the involvement of 4f-orbitals in terms of the various energy and intensity parameters.

The present paper describes the thermodynamic treatment of hypersensitive transitions of various ligands doped with Tm (III) ion. The transition $^3H_6 - {}^3H_4$ are said to be hypersensitive in case of Tm (III) ion. The thermodynamic treatment involves the determination or work function and thermodynamic efficiency from the spectroscopic data obtained for the present systems. The thermodynamic parameters resulting from spectroscopic data support the covalency between lanthanide ion and the surrounding ligand.

The present work includes systems of saturated solutions in DMSO involving eight ligands. These include Salicylaldoxime,Vanillinoxime, Ethylvanillinoxime, Veratraldoxime, Acetylbenzoyloxime, Protocatechualdehydeoxime, Acetylacetoneoxime and Diacetylmonoxime.

These systems provide saturated ligand environment around Tm (III) ion. The solution spectra have been recorded for the various systems in the visible region (400-850 nm). The spectroscopic data (oscillator strengths and energy of transition) have been used to compute thermodynamic parameters. These parameters represent the microscopic behavior of the hypersensitive transition.

EXPERIMENTAL

By employing doped model, eight systems were prepared involving Tm (III) and different ligands. Solution spectra of these systems have been recorded by a standard spectrophotometer in the range 400 to 820 nm.

Calculation of work function and thermodynamic efficiency of the transition
Thermodynamic parameters may also support covalency (if any in the systems), in metal-ligand interaction in addition to spectral parameters for hypersensitive transitions.

Thermodynamic Efficiency of Transition (TET) = Work Function for transition / Energy absorbed for transition

By using thermodynamic relation-

$$A = E - TS \text{ and } S = K \ln P_{obs} \tag{1}$$

Following relation may be obtained-

$$A = E - KT \ln P_{obs}$$

Where, A = Work function (cm^{-1})

E = Energy absorbed for hypersensitive transition (cm^{-1})

K = Boltzmann constant = 0.6945 cm^{-1}

T = Absolute temp

P_{obs}= Oscillator strength of transition (from eq.1)

S = Absolute energy.

Thermodynamic efficiency of transition may be expressed as-

$$TET = \text{Work function for transition (cm) / Energy absorbed for transition (cm)} \tag{2}$$

Calculation of partition function (Q) and ratio of partition function

$$(Q) = g_i \, e^{-E/kT} \tag{3}$$

Where,

For Tm - $g_i = 2J + 1 = 9$

Ratio of Partition (r_p) = Q for lanthanide ion system (doped) / Q for lanthanide ion (free ion in solvent)

$$\tag{4}$$

RESULTS AND DISCUSSION

The computed values of the thermodynamic parameters (for hypersensitive transition) from the spectroscopic data have been tabulated in Table-1.

The values of work function (A) have been found to be from 12461.06 to 12500.The values of TET vary from 1.1909 to 1.1917.The values of partition function (Q) have been found to be from 7.9187 to 9.9983.The values of ratio of partition function (r_p) vary from 2.8746 to 3.5368 for Tm(III) doped systems. The significance of thermodynamic parameters is well understood but their computation from spectroscopic data proposes a microscopic behavior of the f-f transition. The present study finds that the microscopic behavior with respect to TET for Tm (III) doped systems is almost the same but there is a variation in partition function values.

Table-1: Values of Thermodynamic Parameters of Tm(III) SYSTEMS

S. No.	Tm(III) doped systems	Energy for hypersensitive transition ($^3H_4$) (cm^{-1})	Oscillator strength for hypersensitive transition ($^3H_4$) (X 10^6)	Work function (A) (cm^{-1})	Thermo dynamic efficiency of the transition (TET)	Partition function $Q = g_i e^{-E/KT}$ (X 10^{26})	Ratio of partition function (r_p)	Peacock relation ($K^/$) = P_{obs} / νT_6
1.	Tm(III) + L_1	12484.39	10.5570	14871.82	1.19123	8.5346	3.0981	4.9581
2.	Tm(III) + L_2	12461.06	10.5309	14849	1.1916	9.5461	3.4653	5.5212
3.	Tm(III) + L_3	12461.06	10.5309	14849	1.1916	9.5461	3.4653	5.1039

4.	Tm(III) + L_4	12461.06	10.5570	14848.48	1.1915	9.5461	3.4653	5.0877
5.	Tm(III) + L_5	12500	10.4266	14890.01	1.1912	7.9187	2.8746	5.0709
6.	Tm(III) + L_6	12453.30	10.5309	14841.24	1.1917	9.9983	3.5368	5.6168
7.	Tm(III)+L_7	12500	10.5570	14887.42	1.1909	7.9187	2.8746	5.5654
8.	Tm(III)+L_8	12492.19	10.5570	14879.62	1.1911	8.2211	2.9843	7.5340

Where, K = 0.6945 , T = 300

REFERENCES
1. S. N. Mishra, S.B. Mehta and K. Venkatsubramaniyam, *Asian J. Chem. Rev.* Vol. **2**, 100,(1991).
2. S.H. Maran and C.P. Prutton, Principles of Physical Chemistry, Amerind Publishing Co. Pvt. Ltd., Delhi (1972).
3. S. Maurya, D. Balani and G.K.Joshi, *Asian J. Chem.*, **7**, 523(1995).
4. B.R. Judd, *Phy. Rev.*,**127**, 750(1962).
5. G.S. Ofelt, *J. Chem. Phys.*,**37**, 511(1962).
6. W.T. Carnall, *J. Chem. Phys.*,4**2**, 3797(1965).

[RJC-1137/2014]