Int. J. Chem. Sci.: 10(2), 2012, 1074-1078
ISSN 0972-768X
www.sadgurupublications.com

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

MAHENDRA VYAS*, PRAVEEN PUROHIT and H. K. PANDEY[a]

Department of Chemistry, Govt. Engineering College, BIKANER (Raj.) INDIA
[a]Department of Chemistry, Government College, Phalodi, JODHPUR (Raj.) INDIA

ABSTRACT

The Er (III) doped systems with various ligands studied with respect to hypersensitive transition. The spectroscopic data for hypersensitive transition have been correlated with the thermodynamic parameters. The thermodynamic parameters include thermodynamic efficiency and partition function of the transition.

Key words: Hypersensitive transition, Erbium, 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 4-f 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 4-f 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 Er(III) ion. The transition $^4I_{15/2} - {}^4G_{11/2}$ and $^4I_{15/2} - {}^2H_{11/2}$ are said to be hypersensitive in case of Er(III) ion. The thermodynamic treatment involves the determination of work function and thermodynamic efficiency from the

---

*Author for correspondence; E-mail: mkvyas2007@gmail.com

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 Diacetyl-monoxime.

These systems provide saturated ligand environment around Er(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 (Table 1) involving Er (III) and different ligands. Solution spectra of these systems have been recorded by a standard spectrophotometer in the range 400 to 850 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.

(a) Thermodynamic Efficiency of transition (TET) = $\dfrac{\text{Work function for transition}}{\text{Energy absorbed for transition}}$

By using thermodynamic relation-

$$A = E - TS \text{ and } S = K \ln P_{obs} \qquad \ldots(1)$$

Following relation may be obtained-

$$A = E - KT \ln P_{obs} \qquad \ldots(2)$$

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-

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

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

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

Where:

For Er - $g_i = 2J + 1 = 12$

(c) Ratio of partition (r_p) = $\frac{\text{Q for lanthanide ion system (doped)}}{\text{Q for lanthanide ion (free ion in solvent)}}$ ....(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 19138.7559 to 19249.2781 (cm^{-1}).
- The values of TET vary from 1.1022 to 1.1036.
- The values of partition function (Q) have been found to be from 9.0174 to 15.3272.
- The values of ratio of partition function (r_p) vary from 1.0327 to 1.7554 for Er(III) doped systems.

The significance of thermodynamic parameters are 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 Er (III) doped systems is almost the same but there is a variation in partition function values.

Table 1: Thermodynamic parameters of Er(III) systems

S. No.	**Er (III) doped systems**	**Energy for hypersensitive transition ($^2H_{11/2}$) (cm^{-1})**	**Oscillator strength for hypersensitive transition ($^2H_{11/2}$) (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 ($K^/$) = $P_{obs} / \nu T_6$**
1.	Er (III) + L_1	19157.0881	79.1046	21124.90	1.1027	14.0362	1.6075	1.3100
2.	Er (III) + L_2	19249.2781	79.0466	21217.24	1.1022	9.0174	1.0327	1.3653
3.	Er (III) + L_3	19230.7692	79.0466	21198.73	1.1023	9.85528	1.1287	1.3666
4.	Er (III) + L_4	19157.0881	79.1046	21124.90	1.1027	14.0362	1.6075	1.2995
5.	Er (III) + L_5	19138.7559	73.4754	21121.95	1.1036	15.3272	1.7554	1.2224
6.	Er (III) + L_6	19249.2781	79.1046	21217.09	1.1022	9.0174	1.0327	1.3636
7	Er (III)+L_7	19138.7559	80.6437	21102.55	1.1026	15.3272	1.7554	1.3792
8.	Er (III)+L_8	19157.0881	73.3968	21140.50	1.1035	14.0362	1.6075	1.2186

ACKNOWLEDGEMENT

The authors are grateful to Principal, Dungar College, Bikaner for providing necessary facilities. The authors are also highly thankful to Prof. R. S. Yadav, Principal, Govt. Engineering College, Bikaner, Dr. Chanchal Kachhawa and Mr. R. C. Beniwal, Govt. Engineering College, Bikaner for their whole hearted full co-operation.

REFERENCES

1. S. N. Mishra, S. B. Mehta and K. Venkat Subramaniyam, Asian J. Chem. Rev., **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., **42**, 3797 (1965).

Accepted : 28.04.2012