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NOTE

Microscopic Behaviour of Hypersensitive Transition Observed in Some Er(III) Doped Systems

R.S. VERMA* and G.K. JOSHI
Department of Chemistry
Government Dungar Postgraduate College, Bikaner-334 001, India

The saturated organic ligand environment produced by various ligands in 50% ethanol, around Er(III) ion has been studied with respect to hypersensitive transition involved in the system. The spectroscopic data for the hypersensitive transition has been correlated with the thermodynamic behaviour of the said transition. Thermodynamic parameters include thermodynamic efficiency, work function and partition function of the said transition.

The study of the substances doped with certain impurities has been found very useful in the field of science and technology.[1] In the present work Er(III) ion was doped with 50% ethanolic saturated solution of some organic ligands, *e.g.*, seven amino acids (*viz.*, L-cystine, L-proline, L-threonine, L-arginine, L-leucine, β-alanine and aspartic acid), hippuric acid, ascorbic acid, indole, α-benzoin oxime, salicyl aldoxime and diacetyl monoxime.

The saturated solutions were prepared by dissolving organic ligands in 50% ethanol. A constant amount (0.05 g) of $Er(NO_3)_3$ was added to 10 mL of each saturated solution.[2] The solution spectra were recorded for the various systems in the region 400–850 nm. These spectra were used to compute spectroscopic data and from spectroscopic data, thermodynamic parameters were evaluated.

The transition $^4I_{15/2} \rightarrow {}^2H_{11/2}$ in case of Er(III) ions is said to be hypersensitive. The thermodynamic treatment involves evaluation of thermodynamic efficiency and partition function from the spectroscopic data for the systems. The thermodynamic parameters also support the covalency in between Er(III) ion and the surrounding ligands.

1. Calculation of thermodynamic parameters[3, 4]

(a) *Thermodynamic efficiency*—By using the thermodynamic relations $A = E - TS$ and $S = -k \ln P$ the following relation may be obtained:

$$A = E + KT \ln P \tag{1}$$

Thermodynamic efficiency of transition (TET) may be given as:

$$TET = \frac{\text{Work function for the transition } (cm^{-1})}{\text{Energy absorbed for the transition } (cm^{-1})} \tag{2}$$

TABLE-1
COMPUTED VALUES OF THERMODYNAMIC PARAMETERS FOR Er(III) DOPED SYSTEMS

S. No.	Er(III) doped systems	Energy for hypersensitive transition (cm^{-1}) ($^2H_{11/2}$)	Oscillator strength for hypersensitive transitions ($\times 10^{-6}$)($^2H_{11/2}$)	Work function A (cm^{-1})	T.E.T. (Thermodynamic efficiency)	Partition function $Q = g_i e^{-E/KT}$ ($\times 10^{-40}$)	Ratio of Partition function (r_p)
1.	Er(III) aqua ion	19305	3.761	16702.06	0.8651	7.2150	–
2.	Er(III) + L-Cystine	19230	4.375	16658.58	0.8662	10.3395	1.433
3.	Er(III) + Ascorbic acid	19194	3.321	16564.57	0.8630	12.2886	1.703
4.	Er(III) + L-Proline	19193	5.888	16683.34	0.8692	12.3477	1.711
5.	Er(III) + L-Leucine	19193	4.140	16610.07	0.8654	12.3477	1.711
6.	Er(III) + Indole	19230	3.942	16636.86	0.8651	10.3395	1.433
7.	Er(III) + α-Benzoin-oxime	19193	5.092	16653.20	0.8676	12.3477	1.711
8.	Er(III) + Salicyl-aldoxime	19230	3.285	16598.86	0.8631	10.3395	1.433
9.	Er(III) + Diacetyl monoxime	19267	3.469	16647.22	0.8640	8.6578	1.199
10.	Er(III) + L-Threonine	19193	3.942	16599.86	0.8648	12.3477	1.711
11.	Er(III) + Hippuric acid	19193	3.154	16553.38	0.8624	12.3477	1.711
12.	Er(III) + Arginine	19230	3.548	16614.91	0.8640	10.3395	1.433
13.	Er(III) + β-Alanine	19194	5.520	16671.02	0.8685	12.2886	1.703
14.	Er(III) + Aspartic acid	19195	5.913	16686.35	0.8693	12.2298	1.695

k = 0.6945; T = 300 K.

where A = work function, E = energy absorbed, K = boltzmann constant = 0.6945 cm^{-1}, T = absolute temp., P = oscillator strength or probability of occurring of transition.

(b) Partition function of the transition[4, 5]: The partition function Q of the electronic transition may be given as

$$Q = g_i \times e^{-E/KT} \tag{3}$$

where $g_i = (2J + 1)$, statistical weight factor.

(c) Ratio of partition (r_p): This may be given as

$$r_p = \frac{\text{Q for lanthanide ion system (doped)}}{\text{Q for lanthanide aqua ion (or free ion)}}$$

The computed values of thermodynamic parameters (work function, thermodynamic efficiency and partition function) for Er(III) doped system have been tabulated in Table-1.

These values reveal that the magnitude of work function (A) ranges from 16553.38 to 16702.06 cm^{-1}. Thermodynamic efficiency of hypersensitive transition for Er(III) doped systems has been found to be almost the same for all the systems. Its value is 0.86 for all the systems.

The computed values of partition function for the present systems range from 0.657×10^{-40} to 12.347×10^{-40}. When the values are compared with those of aqua ion, then the ratio (r_p) is found to be from 1.199 to 1.711.

The significance of thermodynamic parameters is well understood but their computation for the hypersensitive transitions porposes the microscopic behaviour of $f \leftrightarrow f$ transitions. It is found that thermodynamic parameters are very slightly affected by variation of ligands.

Hence the present study finds that the microscopic behaviour of $f \leftrightarrow f$ transition with respect to TET for Er(III) doped systems is almost the same.

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