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Thermodynamic behaviour of hypersensitive transitions observed in some Ho^{III} and Tm^{III} doped systems

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ABSTRACT

The saturated ligand environment produced by various amino acids in 50% ethanol (v/v) around Ho^{III} and Tm^{III} ions have been studied with respect to hypersensitive transitions. The thermodynamics of hypersensitive transitions have been studied and correlated with spectral parameters. The thermodynamic parameters include work function, thermodynamic efficiency and partition functions of the said transitions. Tm^{III} doped systems exhibit 80% thermodynamic efficiency where as Ho^{III} doped systems show 89% efficiency.

Key words: Thermodynamic behaviour, hypersensitive transitions, Tm^{III} Ho^{III} doped systems.

INTRODUCTION

Certain transitions[1,2] which show relatively strong sensitivity of oscillator strength to the environment about the ion are called hypersensitive transitions. The oscillator strength of the hypersensitive transitions exhibit a relatively greater variability than do the oscillator strengths of non-hypersensitive transitions, Judd[3] noted that these hypersensitive bands are associated with large values of $[U^{(2)}]^2$ matrix elements of Judd-Ofelt theory. Jorgensen and Judd[4] have concluded from a detailed study that the transitions following the selection rules $\Delta J \leq 2$, $\Delta L \leq 2$ and $\Delta S = 0$ should be considered in this category.

In Ho^{III} doped system, the transition $^5I_8 \rightarrow {}^5G_6$ is hypersensitive. For Tm^{III} doped systems, the transition $^3H_6 \rightarrow {}^3H_4$ is considered hypersensitive[6,7].

In the present study Ho^{III} and Tm^{III} ions have been doped with the saturated solution of various amino acids in 50% ethanol (v/v). The saturated solutions have been prepared by dissolving amino acids (which include L-Cystine, L-Leucine, L-Proline, L-Threonine, β-Alanine, L-Arginine and aspartic acid) in 50% ethanol. A constant amount of lanthanide ion (0.1gm) has been added to each saturated solution of amino acid to prepare doped system. Now this doped system has been subjected to measure electronic spectra in the visible and near IR region. By using electronic spectra of each doped systems, various thermodynamic parameters have been computed. Thermodynamic studies also help to support covalent linkage between metal and ligand.

EXPERIMENTAL

$HoCl_3$. (99.9% purity) was obtained from Aldrich, $TmCl_3.6H_2O$. (99.9%) produced from Fluka. All amino acids were of A.R. grade (BDH) and spectrapure ethanol was used as solvent.

I) Preparation of doped system

The saturated solution of amino acids were prepared in 50% ethanol at room temperature (32 ± 2°C). The amino acids include arginine, β-alanine, aspartic acid, threonine, cystine and leucine, seven saturated ligand (amino acid) solutions were prepared, 0.1 gm of $HoCl_3$ or $TmCl_3$ has been added to 10ml of each saturated solution. In this way seven doped systems for each metal ion has been prepared.

II) Recording of solution spectra

Now each metal ion doped system was

subjected to record solution spectra in the range of 370-800 nm region. Solution spectra were recorded by using nm region. Solution spectra were recorded by using systonics - 106 (Spectrophotometer).

In case of Ho^{III} doped systems, we got eight peaks in the range of 370-800 nm region, corresponding to $^5G_4$, $^5G_5$, $^5G_4$, $^3K_8$, $^5F_2$, $^5F_4$ and $^5F_5$, $^5G_6$ level is hypersensitive. In case of Tm^{III} doped systems, we got four peaks, corresponding to $^3H_4$, $^3F_3$, $^3F_2$ and $^1G_4$ levels. Hypersensitive transition obtained from $^3H_4$ level.

Calculation of thermodynamic parameters

(a) Thermodynamic efficiency

By using thermodynamic relations A=E -T S and S = -K In P, the following relation may be obtained

$$A = E + KT \ln P \quad ...(1)$$

where,

P = Oscillator strength of the hypersensitive peak,
A = Work function,
E = Energy of transition
K = Boltzman constant,
T = Absolute temperature

Thermodynamic efficiency of transition (TET) may be given as

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

(b) Partition function of the electronic transition

It is given as

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

where

$g_i = (2J + 1)$, statistical weight factor,
T = Absolute temperature,
E = Energy of transition

Ratio of partition may be given as

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

(c) Nephelauxetic ratio (β) and covalency factor ($b^{½}$)

β may be given as

$$\beta = \frac{\upsilon_{doped} \text{ system } (cm^{-1})}{\upsilon_{aqua} \text{ ion } (cm^{-1})}$$

Covalent factor ($b^{½}$) may be given as

$$b^{½} = [(1-\beta)/2)^{½}$$

where

υ_{doped} system = Energy of transition for doped system
υ_{aqua} = Energy of transition for aqua ion

RESULTS AND DISCUSSION

The computed values of thermodynamic parameters like work function (A), thermodynamic efficiency (TET), partition function (Q) covalency factor ($b^{½}$) along with nephaleuxetic ratio (β) for Ho^{III} and Tm^{III} doped systems have been tabulated in Tables 1 and 2.

(A) Tm^{III} doped systems

The value of partition function (Q) for Tm^{III} doped systems varies from 3.4352×10^{-26} to 4.3253×10^{-26} and ratio of partition function (R_p) varies from 1.000 to 1.2591. The data reported in Table 1 reveals that covalency factor ($b^{½}$) has a linear correlation with oscillator strength (P). In β-alanine system, we have observed highest value of oscillator strength (7.82×10^{-6}) and highest value of bonding parameter (covalency factor) $b^{½}$, however, in some systems deviation from this behaviour is also observed.

A perusal of data reveals that there is a linear correlation between partition function (Q) of hypersensitive transition and covalency factor (b½). The order of covalency for the Tm^{III} doped systems is given by β-alanine = Aspartic acid = Threonine = Proline = Lencine > Arginine = Cystine.

Five amino acids show identical metal - ligand interactions in Tm^{III} doped systems. For Tm^{III} doped systems, the values of work function (A) varies from 10172.69 cm^{-1} to 10127.56 cm^{-1}. The thermodynamic efficiency varies from 0.8021 to 0.8059. These values show that for Tm^{III} doped systems, thermodynamic efficiency is almost constant and about 80%.

The nephelauxetic ratio (β) value varies from 1.000 to 0.9962 showing very small covalency in metal-ligand linkage.

Table - 1: Computed value of thermodynamic and bonding parameters for hypersensitive transition $^3H_6 \rightarrow {}^3H_4$ of Tm^{III} doped systems. (T = 300 K)

S. No.	Tm^{III} doped systems	Energy of $^3H_4$ band (cm^{-1})	Oscillator strength Pobs x 10^{-6}	Work function (A) (cm^{-1})	Thermodynamic efficiency TET	Partition function Q x 10^{-26}	Ratio of partion function (Rp)	Nephelauxetic ratio (β)	Covalency factor ($b^{½}$)
1.	Tm^{III} Aqua ion	12674	6.125	10172.69	0.8026	3.4352	1.0000	1.000	0.0000
2.	Tm^{III} + Arginine	12658	7.360	10194.97	0.8054	3.7095	1.0798	0.9987	0.0254
3.	Tm^{III} + β-Alanine	12626	7.820	10175.60	0.8059	4.3253	1.2591	0.9962	0.0435
4.	Tm^{III} + Aspartic acid	12626	6.702	10143.45	0.8033	4.3253	1.2591	0.9962	0.0435
5.	Tm^{III} + Threonine	12626	6.900	10149.52	0.8038	4.3253	1.2591	0.9962	0.0435
6.	Tm^{III} + Cystine	12658	6.405	10166.01	0.8031	3.7098	1.0798	0.9987	0.0254
7.	Tm^{III} + Proline	12626	6.288	10130.17	0.8023	4.3253	1.2591	0.9962	0.0435
8.	Tm^{III} + Leucine	12626	6.210	10127.56	0.8021	4.3253	1.2591	0.9962	0.0435

Table - 2: Computed value of thermodynamical and bonding parameters for hypersensitive transition ($^5I_8 \rightarrow {}^5G_6$) Hg^{III} doped systems. (T = 300 K)

S. No.	Energy of transition (cm^{-1})	Oscillator strength of $^5G_6$ band Pobs x 10^{-6}	Work function (A) (cm^{-1})	Thermodynamic efficiency TET	Partition function Q x 10^{-46}	Ratio of partion function (Rp)	Nephelauxetic ratio (β)	Covalency factor ($b^{½}$)	Ho^{III} doped systems
1.	22471	9.567	20062.66	0.8928	1.8807	1.000	1.000	0.0000	Ho^{III} Aqua ion
2.	22222	12.403	19867.72	0.8940	6.2580	3.3273	0.9889	0.0744	Ho^{III} + Arginine
3.	22321	16.247	20022.98	0.8970	3.8723	2.0588	0.9933	0.0578	Ho^{III} + β-Alanine
4.	22321	7.984	19874.93	0.8904	3.8723	2.0588	0.9955	0.0474	Ho^{III} + Aspartic acid
5.	22321	12.730	19972.14	0.8947	3.8723	2.0588	0.9933	0.0578	Ho^{III} + Threonine
6.	22222	8.830	19796.92	0.8908	6.2580	3.3273	0.9889	0.0744	Ho^{III} + Cystine
7.	22321	11.787	19956.11	0.8940	3.8723	2.0588	0.9933	0.0578	Ho^{III} + Proline
8.	22222	13.983	19892.71	0.8951	6.2580	3.3273	0.9889	0.0744	Ho^{III} + Leucine

(B) Ho^{III} doped systems

The value of partition function (Q) for Ho^{III} doped systems varies from 1.8807 x 10^{-46} and ratio of partition function varies from 1.000 to 3.3273.

Oscillator strength values for hypersensitive peak varies from 7.984 x 10^{-6} to 16.3247 x 10^{-6}. Trends in the variation of oscillator strength value for Ho^{III} doped systems is Aspartic acid < Cystine < Proline < Arginine < Threonine < Leucine < β-Alanine.

Since metal-ligand interaction is directly proportional to the oscillator strength value of the peaks, hence β-Alanine doped system represents highest metal - ligand interactions in Ho^{III} doped systems.

The value of work function (A) varies from 1987.72 cm^{-1} to 20062.66 cm^{-1}. Thermodynamic efficiency is almost constant for Ho^{III} doped systems, its value is about 89%. The value of nephelauxetic ratio (β) value varies from 0.9955 to 0.9889 for Ho^{III} doped systems, and covalency factor ($b^{1/2}$) varies from 0.0474 to 0.0744. These values represents very slight covalent character in metal - ligand linkage.

The trend in the variation of covalency factor is Ho^{III} aqua ion < Aspartic acid < Threonine = Proline= β-Alanine < Leucine = Cystine = Arginine.

From the above trend it is clear that aspratic acid medium (system) represent very small covalent interaction in the doped system. We have observed highest value of oscillator strength for hypersensitive peak fo β-Alanine system in both the metal ion (Tm^{III} and Ho^{III}) doped systems. This shows that metal -ligand interaction in β-Alanine medium (system) is highest, although, we got lesser character in Ho^{III} doped systems.

For Ho^{III} doped systems the trend for the vale of partition function (Q) is as follow- Ho^{III} aqua ion < Aspartic acid = Proline = Threonine = β-Alanine < Leucine = Arginine = Cystine.

In case of Ho^{III} aqua ion, we have observed oscillator strength value equal to 9.567 x 10^{-6} which is considerably higher than aspartic acid and cystine medium. This reveals that in Ho^{III} doped systems water (H_2O) also behave as a good ligand for metal-ligand interaction. Thus, the present study also correlate the thermodynamic parameters with the covalency in the metal - ligand linkage. The significance of thermodynamic parameters are well understood but their computation from electronic spectral data propose the microscopic behavior of $f \leftrightarrow f$ transition in lanthanides.

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