INTRODUCTION

Certain transitions 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 noted that these hypersensitive bands are associated with large values of $[U(2)]$ matrix elements of Judd-Ofelt theory. Jorgensen and Judd 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.

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). 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

HoCl₃ (99.9% purity) was obtained from Aldrich, TmCl₃.6H₂O (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 HoCl₃ or TmCl₃ 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\textsuperscript{III} doped systems, we got eight peaks in the range of 370-800 nm region, corresponding to \(^5\text{G}_4, \ ^5\text{G}_5, \ ^5\text{G}_4, \ ^3\text{K}_8, \ ^5\text{F}_2, \ ^5\text{F}_4, \ ^5\text{F}_5, \ ^5\text{G}_6\) level is hypersensitive. In case of Tm\textsuperscript{III} doped systems, we got four peaks, corresponding to \(^3\text{H}_4, \ ^3\text{F}_3, \ ^3\text{F}_2, \ ^1\text{G}_4\) levels. Hypersensitive transition obtained from \(^3\text{H}_4\) level.

**Calculation of thermodynamic parameters**

(a) **Thermodynamic efficiency**

By using thermodynamic relations

\[ A = E - T S \text{ and } S = -K \ln P, \]

the following relation may be obtained

\[ A = E + KT \ln P \quad \ldots(1) \]

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

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

(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 (\( \beta \)) and covalency factor (\( b^{(i)} \))**

\( \beta \) may be given as

\[ \beta = \frac{\nu_{\text{doped system (cm}^{-1})}}{\nu_{\text{aqua ion (cm}^{-1})}} \]

Covalent factor (\( b^{(i)} \)) may be given as

\[ b^{(i)} = \left[ (1-\beta)/2 \right]^{1/2} \]

where

\( \nu_{\text{doped system}} = \) Energy of transition for doped system
\( \nu_{\text{aqua}} = \) 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 (\( b^{(i)} \)) along with nephaleuxetic ratio (\( \beta \)) for Ho\textsuperscript{III} and Tm\textsuperscript{III} doped systems have been tabulated in Tables 1 and 2.

(A) **Tm\textsuperscript{III} doped systems**

The value of partition function (Q) for Tm\textsuperscript{III} doped systems varies from 3.4352 x 10\textsuperscript{-26} to 4.3253 x 10\textsuperscript{-26} and ratio of partition function (R\( _p \)) varies from 1.00 to 1.2591. The data reported in Table 1 reveals that covalency factor (\( b^{(i)} \)) has a linear correlation with oscillator strength (P). In \( \beta \)-alanine system, we have observed highest value of oscillator strength (7.82 x 10\textsuperscript{6}) and highest value of bonding parameter (covalency factor) \( b^{(i)} \), 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 (\( b^{(i)} \)). The order of covalency for the Tm\textsuperscript{III} doped systems is given by \( \beta \)-alanine = Aspartic acid = Threonine = Proline = Lencine > Arginine = Cystine.

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

The nephelauxetic ratio (\( \beta \)) value varies from 1.00 to 0.9962 showing very small covalency in metal-ligand linkage.
### Table - 1: Computed value of thermodynamic and bonding parameters for hypersensitive transition $^3\text{H}_6 \rightarrow ^3\text{H}_4$ of Tm$^{ll}$ doped systems. ($T = 300$ K)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Tm$^{ll}$ doped systems</th>
<th>Energy of $^3\text{H}_6$ band (cm$^{-1}$)</th>
<th>Oscillator strength Pobs x $10^6$ (cm$^{-1}$)</th>
<th>Work function (A) (cm$^{-1}$)</th>
<th>Thermodynamic efficiency TET</th>
<th>Partition function Q x $10^{-6}$</th>
<th>Ratio of partition function (Rp)</th>
<th>Nephelauxetic ratio (β)</th>
<th>Covalency factor (b$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Tm$^{ll}$ Aqua ion</td>
<td>12674</td>
<td>6.125</td>
<td>10172.69</td>
<td>0.8026</td>
<td>3.4352</td>
<td>1.000</td>
<td>1.00</td>
<td>0.0000</td>
</tr>
<tr>
<td>2.</td>
<td>Tm$^{ll}$ + Arginine</td>
<td>12658</td>
<td>7.360</td>
<td>10194.97</td>
<td>0.8054</td>
<td>3.7095</td>
<td>1.0798</td>
<td>0.9987</td>
<td>0.0254</td>
</tr>
<tr>
<td>3.</td>
<td>Tm$^{ll}$ + β-Alanine</td>
<td>12626</td>
<td>7.820</td>
<td>10175.60</td>
<td>0.8059</td>
<td>4.3253</td>
<td>1.2591</td>
<td>0.9962</td>
<td>0.0435</td>
</tr>
<tr>
<td>4.</td>
<td>Tm$^{ll}$ + Aspartic acid</td>
<td>12626</td>
<td>6.702</td>
<td>10143.45</td>
<td>0.8033</td>
<td>4.3253</td>
<td>1.2591</td>
<td>0.9962</td>
<td>0.0435</td>
</tr>
<tr>
<td>5.</td>
<td>Tm$^{ll}$ + Threonine</td>
<td>12626</td>
<td>6.900</td>
<td>10149.52</td>
<td>0.8038</td>
<td>4.3253</td>
<td>1.2591</td>
<td>0.9962</td>
<td>0.0435</td>
</tr>
<tr>
<td>6.</td>
<td>Tm$^{ll}$ + Cystine</td>
<td>12658</td>
<td>6.405</td>
<td>10166.01</td>
<td>0.8031</td>
<td>3.7098</td>
<td>1.0798</td>
<td>0.9987</td>
<td>0.0254</td>
</tr>
<tr>
<td>7.</td>
<td>Tm$^{ll}$ + Proline</td>
<td>12626</td>
<td>6.288</td>
<td>10130.17</td>
<td>0.8023</td>
<td>4.3253</td>
<td>1.2591</td>
<td>0.9962</td>
<td>0.0435</td>
</tr>
<tr>
<td>8.</td>
<td>Tm$^{ll}$ + Leucine</td>
<td>12626</td>
<td>6.210</td>
<td>10127.56</td>
<td>0.8021</td>
<td>4.3253</td>
<td>1.2591</td>
<td>0.9962</td>
<td>0.0435</td>
</tr>
</tbody>
</table>

### Table - 2: Computed value of thermodynamical and bonding parameters for hypersensitive transition $^1\text{I}_8 \rightarrow ^3\text{G}_4$ Hg$^{ll}$ doped systems. ($T = 300$ K)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Energy of transition $^1\text{I}_8$ band (cm$^{-1}$)</th>
<th>Oscillator strength Pobs x $10^6$ (cm$^{-1}$)</th>
<th>Work function (A) (cm$^{-1}$)</th>
<th>Thermodynamic efficiency TET</th>
<th>Partition function Q x $10^{-6}$</th>
<th>Ratio of partition function (Rp)</th>
<th>Nephelauxetic ratio (β)</th>
<th>Covalency factor (b$^{1/2}$)</th>
<th>Ho$^{ll}$ doped systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>22471</td>
<td>9.567</td>
<td>20062.66</td>
<td>0.8928</td>
<td>1.8807</td>
<td>1.000</td>
<td>1.00</td>
<td>0.0000</td>
<td>Ho$^{ll}$ Aqua ion</td>
</tr>
<tr>
<td>2.</td>
<td>22222</td>
<td>12.403</td>
<td>19867.72</td>
<td>0.8940</td>
<td>6.2580</td>
<td>3.3273</td>
<td>0.9889</td>
<td>0.0744</td>
<td>Ho$^{ll}$ + Arginine</td>
</tr>
<tr>
<td>3.</td>
<td>22321</td>
<td>16.247</td>
<td>20022.98</td>
<td>0.8970</td>
<td>3.8723</td>
<td>2.0588</td>
<td>0.9933</td>
<td>0.0578</td>
<td>Ho$^{ll}$ + β-Alanine</td>
</tr>
<tr>
<td>4.</td>
<td>22321</td>
<td>7.984</td>
<td>19874.93</td>
<td>0.8904</td>
<td>3.8723</td>
<td>2.0588</td>
<td>0.9955</td>
<td>0.0474</td>
<td>Ho$^{ll}$ + Aspartic acid</td>
</tr>
<tr>
<td>5.</td>
<td>22321</td>
<td>12.730</td>
<td>19972.14</td>
<td>0.8947</td>
<td>3.8723</td>
<td>2.0588</td>
<td>0.9933</td>
<td>0.0578</td>
<td>Ho$^{ll}$ + Threonine</td>
</tr>
<tr>
<td>6.</td>
<td>22222</td>
<td>8.830</td>
<td>19796.92</td>
<td>0.8908</td>
<td>6.2580</td>
<td>3.3273</td>
<td>0.9889</td>
<td>0.0744</td>
<td>Ho$^{ll}$ + Cystine</td>
</tr>
<tr>
<td>7.</td>
<td>22321</td>
<td>11.787</td>
<td>19956.11</td>
<td>0.8940</td>
<td>3.8723</td>
<td>2.0588</td>
<td>0.9933</td>
<td>0.0578</td>
<td>Ho$^{ll}$ + Proline</td>
</tr>
<tr>
<td>8.</td>
<td>22222</td>
<td>13.983</td>
<td>19892.71</td>
<td>0.8951</td>
<td>6.2580</td>
<td>3.3273</td>
<td>0.9889</td>
<td>0.0744</td>
<td>Ho$^{ll}$ + Leucine</td>
</tr>
</tbody>
</table>
(B) Ho\textsuperscript{III} doped systems

The value of partition function (Q) for Ho\textsuperscript{III} doped systems varies from 1.8807 x 10\textsuperscript{-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\textsuperscript{-6} to 16.3247 x 10\textsuperscript{-6}. Trends in the variation of oscillator strength value for Ho\textsuperscript{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\textsuperscript{III} doped systems.

The value of work function (A) varies from 1987.72 cm\textsuperscript{-1} to 20062.66 cm\textsuperscript{-1}. Thermodynamic efficiency is almost constant for Ho\textsuperscript{III} doped systems, its value is about 89%. The value of nephelauxetic ratio (β) value varies from 0.9955 to 0.9889 for Ho\textsuperscript{III} doped systems, and covalency factor (b\textsuperscript{-}) 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\textsuperscript{III} aqua ion < Aspartic acid < Threonine = Proline = β-Alanine < Leucine = Cystine = Arginine.

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

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

In case of Ho\textsuperscript{III} aqua ion, we have observed oscillator strength value equal to 9.567 x 10\textsuperscript{-6} which is considerably higher than aspartic acid and cystine medium. This reveals that in Ho\textsuperscript{III} doped systems water (H\textsubscript{2}O) 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 → f transition in lanthanides.

ACKNOWLEDGEMENTS

Authors are thankful to Dr. H.K. Pandey, Head, Department of Chemistry and Principal, Sh. R.S. Meena, for providing necessary facilities. Authors are also thankful to Dr. R.P. Mathur for general discussion and for giving good suggestions.

REFERENCES