

**NOTE****Thermodynamic Behaviour of Hypersensitive Transitions Observed in Some Pr<sup>3+</sup> and Nd<sup>3+</sup> Doped Pharmaceutical Compounds**

Ms. ARYAMITRA PANDEY\*, P.C. TATER, K.P. SONI and G.K. JOSHI

*Rare Earth Research Laboratory, Department of Chemistry  
Government Dungar College, Bikaner-334 003, India*

The saturated anionic ligand environment produced by various pharmaceutical compounds, viz., thiabendazole, mebendazole, albendazole and diethylcarbamazine in alcohol around Pr<sup>3+</sup> and Nd<sup>3+</sup> ions has been studied with respect to the hypersensitive transition involved in the system. The spectroscopic data for the hypersensitive transition has been correlated with the thermodynamic parameters (work function and thermodynamic efficiency) which yield the thermodynamic behaviour of the said transition.

The intensities of most of the  $f \leftrightarrow f$  transitions of trivalent lanthanides are little affected by the environment of the ions. However, a few transitions are very sensitive to the environment and in the complexed ion they are usually more intense as compared to that in aquo ions. Such transitions are called hypersensitive transitions. Thus the study of hypersensitive transitions plays an important role to estimate the effect of ligand environment of 4f-orbitals<sup>1</sup>. The recent theories given by Slater-Condon, Landé and Judd-Ofelt about the lanthanide  $f \leftrightarrow f$  spectra correlate the involvement of 4f-orbitals in terms of the various energy and intensity parameters. The present paper describes thermodynamic treatment of the hypersensitive transitions of the various ligands doped with Pr<sup>3+</sup> and Nd<sup>3+</sup> ions<sup>2</sup>. There are several organic ligands having either nitrogen or oxygen or both as donor atoms which are found in most commonly used medicines. These medicines have effective interaction with inorganic ions such as Ca<sup>2+</sup>, Na<sup>+</sup>, Fe<sup>3+</sup>, La<sup>3+</sup> etc. Lanthanide ions show weak complexing behaviour in many cases similar to alkali and alkaline earth metals. The role of La<sup>3+</sup> ion in medicinal field has been studied as an antagonist of Ca<sup>2+</sup> ion in biological interactions. All these facts lead to the selection of ligands of medicinal importance in the present study. The ligands include thiabendazole, mebendazole, albendazole, and diethylcarbamazine.

The transitions  ${}^3H_4 \rightarrow {}^3P_2$  in case of Pr<sup>3+</sup> ion and  ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$  in case of Nd<sup>3+</sup> ion are said to be hypersensitive. The thermodynamic treatment involves the determination of work function and thermodynamic efficiency from the spectroscopic data obtained for the present systems. The thermodynamic para-

meters resulting from spectroscopic data also support the covalency in between the lanthanide ion and the surrounding ligands.

In the present work some saturated solutions of various pharmaceutical compounds have been prepared in alcohol. To these solutions a constant amount (100 mg/10 mL) of  $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  has been added. Solution spectra of these systems have been recorded by using a standard spectrophotometer in the region 400 to 900 nm.

### Calculation of Work function and Thermodynamic Efficiency of the Transition (TET)<sup>3</sup>

Using the thermodynamic relations  $A = E - TS$  and  $S = K \log_e W$ , the following analogous relation may be obtained:

$$A = E - 2.303 \times TK \log P \quad (1)$$

where

A = Work function ( $\text{cm}^{-1}$ )

E = Energy absorbed for the transition ( $\text{cm}^{-1}$ )

K = Boltzmann constant ( $\text{cm}^{-1}$ )

P = Oscillator strength of the transition or probability of the occurring transition.

Thermodynamic efficiency of transition (TET) may therefore be given analogous to thermodynamic relations as:

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

The computed values of the thermodynamic parameters like work function and thermodynamic efficiency for the hypersensitive transitions from the spectroscopic data for  $\text{Pr}^{3+}$  ion systems and  $\text{Nd}^{3+}$  ion systems have been reported in Tables 1 and 2 respectively.

TABLE-1  
VALUES OF THERMODYNAMIC PARAMETERS (A AND T.E.T.) FOR  
HYPERSENSITIVE TRANSITION IN  $\text{Pr}^{3+}$  ION DOPED SYSTEMS

Ligand	Energy	Oscillator strength ( $P \times 10^6$ )	Work function ( $A \times 10^{15}$ )	T.E.T. $\times 10^{17}$
Thiabendazole	22471	10.90	4953	22.04
Mebendazole	22471	12.40	4948	22.02
Albendazole	22471	6.80	4973	22.13
Diethylcarbamazine	22471	8.56	4964	22.09

The order of magnitude of work function is as follows:

(i) In  $\text{Pr}^{3+}$  Systems:

Albendazole > Diethylcarbamazine > Thiabendazole > Mebendazole

(ii) In  $\text{Nd}^{3+}$  Systems:

Mebendazole > Diethylcarbamazine > Thiabendazole > Albendazole

Order of T.E.T. is as follows:

(i) In Pr<sup>3+</sup> systems:

Albendazole > Diethylcarbamazine > Thiabendazole > Mebendazole

(ii) In Nd<sup>3+</sup> systems:

Mebendazole > Diethylcarbamazine > Thiabendazole = Albendazole.

TABLE-2  
VALUES OF THERMODYNAMIC PARAMETERS (A AND T.E.T.) FOR  
HYPERSENSITIVE TRANSITION IN Nd<sup>3+</sup> ION DOPED SYSTEMS

Ligand	Energy	Oscillator strength (P × 10 <sup>6</sup> )	Work function (A × 10 <sup>15</sup> )	T.E.T. × 10 <sup>17</sup>
Thiabendazole	17241	18.1	3892	22.57
Mebendazole	17241	14.1	3903	22.64
Albendazole	17241	10.6	3891	22.57
Diethylcarbamazine	17241	16.1	3895	22.59

The significance of thermodynamic parameters is well understood but their computation for the hypersensitive transitions and that too from spectroscopic data proposes the microscopic behaviour of the f ↔ f transitions.

The present study finds that the microscopic behaviour of f ↔ f transitions with respect to T.E.T. for both Pr<sup>3+</sup> and Nd<sup>3+</sup> ion systems is almost same but the work function involved in Pr<sup>3+</sup> systems is definitely greater in comparison to Nd<sup>3+</sup> ion systems. Moreover it is found that thermodynamic parameters are slightly affected with a variation of ligand environment around lanthanide ion.

### ACKNOWLEDGEMENTS

The authors are thankful to Dr. H.K. Pandey, Dungar College, Bikaner and Mr. Rudradev Pandey (M.B.B.S.), S.P. Medical College, Bikaner for their valuable suggestions and help.

### REFERENCES

1. Sudhindra N. Misra, S.B. Mehta and K. Venkatasubramaniam, *Asian J. Chem. Rev.*, **2**, 100 (1991).
2. B.K. Gupta, G.K. Joshi and P.R. Bhati, *Indian J. Pure and Appl. Phys.*, **23**, 525 (1990).
3. S.H. Maron and C.F. Prutton, *Principles of Physical Chemistry*, Amerind Publication Co. Pvt. Ltd, New Delhi (1972).