Thermodynamic Behaviour of Hypersensitive Transitions Observed in Some Pr(III) and Nd(III) Systems

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The saturated anionic ligand environment produced by various organic acids in DMF and DMSO around Pr(III) and Nd(III) ions has been studied with respect to the hypersensitive transition involved in the system. The spectroscopic data for the hypersensitive transition have been correlated with the thermodynamic parameters which yield the thermodynamic behaviour of the said transition. Thermodynamic parameters include thermodynamic efficiency and partition functon of the said transition.

INTRODUCTION

The study of hypersensitive transitions[1] plays an important role to estimate the effect of ligand environment of 4f orbitals. The recent theories given by Slater-Condon-Landé and Judd Ofelt about the lanthanide f $\longleftrightarrow$ f spectra correlate the involvement of 4f orbitals in terms of the various energy and intensity parameters. The present paper describes thermodynamic treatment for the hypersensitive transitions of the various systems involving Pr(III) and Nd(III) ions.

The transitions $^3H_4 \longrightarrow {}^3P_2$ in case of Pr(III) ion and $^4I_{9/2} \longrightarrow {}^4G_{5/2}$ in case of Nd(III) ion are said to be hypersensitive. The thermodynamic treatment involves the determination of thermodynamic efficiency and partition function from the spectroscopic data obtained for the present systems. The thermodynamic parameters resulting from spectroscopic data also support the covalency in between the lanthanide ion and the surrounding ligands.

The present work includes systems of saturated solutions in DMF as well as in DMSO involving various organic acids like adipic acid, ascorbic acid, malonic acid, succinic acid, citric acid and tartaric acid. These systems provide saturated anionic ligand environment around Pr(III) ion as well as around Nd(III) ion. The solution spectra recorded for the various systems in the visible region which have been used to compute spectroscopic data which have been further used to compute thermodynamic parameters show the microscopic behaviour for the hypersensitive transitions with regard to thermodynamic efficiency and partition function.

EXPERIMENTAL

In the presnt work some saturated solutions of various organic acids have been

prepared in the different solvents like DMF and DMSO. To these solutions a constant amount (0.10 gm.) of $PrCl_3 \cdot 6H_2O$ (or $NdCl_3 \cdot 6H_2O$) has been added.

Solution spectra for these systems have been recorded by using a standard spectrophotometer (systronic) in the region 350 nm to 950 nm.

The present systems may be considered as modified doped crystal approach[2].

Calculation of Thermodynamic Parameters[3]

(a) *Thermodynamic efficiency of the transition (T.E.T.)*: Using the thermodynamic relations $A = E - TS$ and $S = K \log_e W$, the following analogous relation may be obtained:

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

Where

A = work function (in cm^{-1})

E = energy absorbed for the transition (in cm^{-1})

K = Bolzmann constant (in cm^{-1})

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

Thermodynamic efficiency of transition (T.E.T.) may therefore be given analogous to thermodynamic relation as:

$$T.E.T. = \frac{\text{work function for the transition } (cm^{-1})}{\text{energy absorbed for the transition}} \qquad (2)$$

(b) *Partition function of the transition (P.F.T.)*: The partition function (Q) of the electronic transition may be given as

$$Q = g_i \times e^{-E/KT} \qquad (3)$$

where

$g_i = 2J + 1$ (*e.g.* $g_i = 9$ for $^3H_4$)

E = energy absorbed for the transition (in cm^{-1})

K = Bolzmann constant (in cm^{-1})

The number of particles in any state of energy (n_i) with reference to ground to state (n_0) may be given as

$$n_i = \frac{n_0}{g_0} \times Q_i \qquad (4)$$

Thus values computed for n_i in case of lanthanide free or aquo ion may be compared with that of lanthanide ion systems. This ratio (r_p) may be expressed as

$$r_p = \frac{Q_i \text{ (P.F.T.) for lanthanide ion system}}{Q_i \text{ (P.F.T.) for lanthanide free or aquo ion}}$$

RESULTS AND DISCUSSION

The computed values of the thermodynamic parameters like work functions and thermodynamic efficiency for the hypersensitive transitions from the spectro-

scopic data for Pr(III) ion systems and Nd(III) ion systems have been reported in Tables 1 and 2 respectively.

TABLE-1

COMPUTED VALUES OF THERMODYNAMIC PARAMETERS (A AND T.E.T.)
FROM SPECTROSCOPIC DATA FOR HYPERSENSITIVE TRANSITION
IN Pr(III) ION SYSTEMS

S. No.	Ligand used	Solvent used		Energy	Oscillatior strength $\rho \times 10^6$	Work function $(A \times 10^{15})$	T.E.T. $\times 10^{15}$
1.	Adipic acid	(i)	DMF	22471	16.2	4937	0.2197
		(ii)	DMSO	22471	16.1	4936	0.2196
2.	Ascorbic acid	(i)	DMF	22321	21.6	4894	0.2192
		(ii)	DMSO	22321	12.3	4918	0.2203
3.	Malonic acid	(i)	DMF	22471	18.3	4933	0.2195
		(ii)	DMSO	22471	22.9	4921	0.2190
4.	Succinic acid	(i)	DMF	22421	17.1	4923	0.2195
		(ii)	DMSO	22421	11.5	4941	0.2204
5.	Citric acid	(i)	DMF	22421	22.3	4913	0.2191
		(ii)	DMSO	22421	14.5	4931	0.2199
6.	Tartaric acid	(i)	DMF	22321	17.2	4904	0.2197
		(ii)	DMSO	22321	20.7	4896	0.2193

TABLE-2

COMPUTED VALUES OF THERMODYNAMIC PARAMETERS (A AND T.E.T)
FROM SPECTROSCOPIC DATA FOR HYPERSENSITIVE TRANSITION
IN Nd(III) ION SYSTEMS

S. No.	Ligand used	Solvent used		Energy	Oscillator strength $\rho \times 10^6$	Work funcition $(A \times 10^{15})$	T.E.T. $\times 10^{15}$
1.	Adipic acid	(i)	DMF	17241	26.4	3875	0.2248
		(ii)	DMSO	17176	27.6	3861	0.2248
2.	Ascorbic acid	(i)	DMF	17241	29.3	3871	0.2245
		(ii)	DMSO	17167	31.5	3853	0.2244
3.	Malonic acid	(i)	DMF	17167	33.1	3851	0.2243
		(ii)	DMSO	17226	30.7	3866	0.2244
4.	Succinic acid	(i)	DMF	17241	38.1	3857	0.2237
		(ii)	DMSO	17241	22.0	3883	0.2252
5.	Citric acid	(i)	DMF	17241	34.2	3864	0.2241
		(ii)	DMSO	17226	32.2	3864	0.2243
6.	Tartaric acid	(i)	DMF	17182	24.7	3866	0.2250
		(ii)	DMSO	17241	29.9	3870	0.2245

These values suggest that the magnitude of work function has been found to be $\sim 49 \times 10^{-13}$ cm^{-1} whereas T.E.T. to be $\sim 22 \times 10^{-17}$ in case of Pr(III) ion systems. The magnitudes of these parameters in case of Nd(III) ion system have been found to be $\sim 39 \times 10^{-13}$ cm and 22×10^{-17} cm respectively.

The computed values of partition function from the spectroscopic data of hypersensitive transitions in Pr(III) and Nd(III) ion systems have been reported in Table-3. When these values are compared with those of free or aquo ions then the ratio comes to be 1218.75 and 26.78.

TABLE-3

COMPUTED VALUES OF THERMODYNAMIC PARAMETERS (Q AND r_p)
FROM SPECTROSCOPIC DATA FOR THE HYPERSENSITIVE TRANSITIONS
OBSERVED IN VARIOUS SYSTEMS OF Pr(III) AND Nd(III) IONS.

Lanthanide ion	Engergy in cm^{-1}	Q	r_p
Pr(III) free ion	23161	0.0128×10^{-46}	
Pr(III) ion systems	22419 (average)	15.6000×10^{-46}	1218.75
Nd(III) aquo ion	17358	0.2301×10^{-35}	
Nd(III) ion systems	17237 (average)	6.1620×10^{-35}	26.78

The significance of thermodynamic parameters are well understood but their computation for the hypersensitive transitions and that too from spectroscopic data propose the microscopic behaviour of the f $\longleftrightarrow$ f transitions.

The present study finds that the microscopic behaviour of f $\longleftrightarrow$ f transitions with regard to T.E.T. for both Pr(III) and Nd(III) ion systems is almost same but the work function involved in Pr(III) ion systems is definitely greater in comparison to Nd(III) ion systems.

Similarly the value of partition function ratio has greater value in Pr(III) ion systems in comparison to Nd(III) ion systems.

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