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

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The saturated ligand environment produced by various ligands containing N, O donor atoms in 50% ethanol around Pr(III) ions, have been studied with respect to hypersensitive transitions 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. The thermodynamic parameters include thermodynamic efficiency and partition function of the transition.

INTRODUCTION

The study of hypersensitive transition plays an important role to establish the effect of ligand environment of 4f orbital[1-3]. 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 the thermodynamic treatment for the hypersensitive transition of the various systems, doped with Pr(III) ions.

The transition $^3H_4 \rightarrow {}^3P_2$ is said to be hypersensitive in case of Pr(III) ions. The thermodynamic treatment involves the determination of thermodynamic efficiency and partition function from spectroscopic data for the present systems. The thermodynamic parameters resulting from spectroscopic data also support the covalency in between lanthanide ion and surrounding ligands.

The present work includes systems of saturated solutions in 50% ethanol involving fifteen ligands. These include seven amino acids (L-cystine, L-leucine, L-threonine, L-proline, β-alanine, arginine and aspartic acid), four heterocyclic compounds, (indole, 4-aminoantipyrine, uracil and benzotriazole), two oximes (diacetyl monoxime and salicyl aldoxime) and two acids (benzilic acid and ascorbic acid).

These systems provide saturated ligand environment around Pr(III) ion. The solution spectra have been recorded for the various systems in the visible region (400–625 nm). The spectroscopic data (oscillator strengths and energy of transition) have been used to compute thermodynamic parameters. These parameters represent the microscopic behaviour of the hypersensitive transition.

EXPERIMENTAL

In the present study some saturated solution of various ligands have been prepared in 50% ethanol. To these solutions a constant amount (0.05 g) of $PrCl_3 \cdot 6H_2O$ has been added. Solution spectra of these systems have been recorded by using a standard spectrophotometer (Systronics-106) in the region 400–625 nm.

Calculation of thermodynamical parameters

(a) Thermodynamic efficiency of the transition (TET): By using the thermodynamic relations[1–3]:

$$A = E - TS \text{ and } S = -K \ln^* P$$

the following analogous relation may be obtained

$$A = E = 2.303\ KT \log P$$

where A = work function (in cm^{-1})
S = absolute entropy
E = energy absorbed for the transition (cm^{-1})
K = Boltzmann constant = 0.6945 cm^{-1}
P = oscillator strength of the transition or probability of the occurring transition
T = absolute Temp.

Thermodynamic efficiency of the transition (TET) may be expressed as:

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

(b) Partition function of the transition: The partition function (Q) of the electronic transition may be given as

$$Qe = g_i e^{-E/KT}$$

where $g_i = 2J + 1$ (*e.g.*, $g_i = 5$ for $^2P_2$), K = Boltzmann constant, T = absolute temperature

The ratio of partition function (r_p) may be expressed as:

$$r_p = \frac{Q(PET) \text{ for lanthanide ion systems}}{Q(PFT) \text{ for lanthanide aqua ion}}$$

RESULTS AND DISCUSSION

The computed values of the thermodynamic parameters like work function (A), thermodynamic efficiency (TET), partition function (Q) and ratio of partition function (r_p) for the hypersensitive transition from the spectroscopic data have been tabulated in Table-1.

*Since the value of P (oscillator strength) is always less than one, hence to get positive value of absolute entropy negative sign has been used for the relation.

TABLE-1
COMPUTED VALUES OF THERMODYNAMIC PARAMETERS FOR HYPERSENSITIVE TRANSITION IN Pr(III) SYSTEMS

Ligands + Pr^{3+}	Energy for hypersensitive transition (cm^{-1})	Oscillator strength $P_{obs} \times 10^6$	Work function $A \times 10^{12}$ ergs	TET	Partition function $Q \times 10^{47}$	Ratio of partition function (r_p)
Pr^{3+}-Aqua ion	22620	14.76	4.031	0.8975	3.608	–
L-Cystine	22321	33.30	4.006	0.9037	15.150	3.308
L-Leucine	22421	30.30	4.022	0.9033	9.376	2.598
L-Proline	22371	23.70	4.002	0.9008	11.920	3.303
L-Threonine	22523	17.60	4.062	0.9082	5.746	1.592
Aspartic acid	22421	23.30	4.011	0.9008	9.376	2.598
Arginine	22371	36.40	4.020	0.9048	11.920	3.303
β-Alanine	22422	23.90	4.012	0.9011	9.330	2.585
Indole	22422	27.70	4.018	0.9025	9.330	2.585
4-Amino-antipyrine	22472	25.60	4.025	0.9019	7.340	2.034
Uracil	22420	32.50	4.025	0.9039	9.421	2.611
1,2,3-Benzotriazole	22573	29.20	4.051	0.9036	4.521	1.253
Diacetyl monoxime	22522	33.40	4.046	0.9046	5.775	1.600
Salicylaldoxime	22422	23.90	4.012	0.9011	9.330	2.585
Benizilic acid	22371	23.80	4.002	0.9008	11.920	3.303
Ascorbic acid	22472	21.10	4.017	0.9001	7.340	2.034

T = 300 K, K = 0.6945 cm^{-1}

These values suggest that the magnitude of work function (A) has been found to be from 3.987×10^{-12} erg to 4.062×10^{-12} ergs per ion. The value of TET varies from 0.8975 to 0.9082. The values of partition function (Q) vary from 3.608×10^{-47} to 15.15×10^{-47}. The values of r_p vary from 1.253 to 4.208 for Pr(III) ion systems.

The significance of the thermodynamic parameters are well understood but their computation from spectroscopic data proposes the microscopic behaviour of the $f \leftrightarrow f$ transition.

The present study finds that the microscopic behaviour with regard to TET for Pr(III) ion systems is almost the same but there is a variation in partition function values.

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