

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Calculation of oscillator strength for praseodymium and praseodymium mixed with L-histidine in different solvents using 4f-4f transition spectra as Probe

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ABSTRACT

Spectrophotometric method can be used to evaluate the oscillator strength of coordination compounds whose absorption band lies in the region of UV/Visible region. The spectral behavior on complexation of praseodymium (III) and praseodymium (III) + L-histidine with widely different binding features which were an unusual sensitivity of some non hypersensitive transitions. These transitions were discussed to show wide variation of the oscillator strength only on minor changes in the immediate coordination around the praseodymium(III). The comparative oscillator strength ($f = 4.33 \times 10^{-9} [\int \epsilon \bar{\nu} d\bar{\nu}]$) involving 4f-4f transitions on praseodymium (III) in the absence and presence of L-histidine were carried out in different solvents, i.e., water and N, N-dimethyl formamide (DMF). The results were discussed and qualitatively in terms of oscillator strength of the 4f-4f intensities for metal ion and metal ion with ligand in different solvent, thus indicating that oscillator strength of metal ion with ligand was dominant.

Keywords: Lanthanoid ions; Oscillator Strength; 4f-4f transitions; comparative spectra; L-histidine; DMF.

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INTRODUCTION

Very little work has been reported in the field of lanthanoids, i.e., lanthanum to lutecium has been explored extensively in the last four decades but the importance of the role that lanthanoids play in several biochemical reactions and their utility as structural and functional probes in understanding structures conformation and characteristics of biomolecules [1-3]. Lanthanoid ions exhibit coordination number ranging from as low as three and as high as twelve. The geometry of the complex species is determined mainly by conformation, ligand donor group interactions and competitions of solvent molecules for the coordination sites of lanthanoid ions [4]. The unique similarity between the lanthanides and calcium in terms of size and the coordination preference for higher coordination numbers, the former has been used as probes in biochemical reactions and for structural studies of biomolecular compounds involving Ca (II) [5-8].

Interesting part of lanthanide chemistry is that the efficient shielding of the 4f shells by closed 5s² and 5p⁶ shells leads the trivalent lanthanide ions to exhibit unique spectroscopic properties. Since the 4f lie deep in the nucleus core, the ligand environment only weakly affects the lanthanide electron cloud which is small in magnitude. Therefore inter-configurational transitions are characterized by the weak perturbation results in spectral fine structure. The line width of the 4f-4f bands is considerably smaller than that observed for transition metal ions and the peak position of the spectral band reveals a part of 4fⁿ configuration. The significant information about the symmetry of the lanthanide site and the type of coordination polyhedron is provided by the crystal field splitting pattern. The existence of internal f-electron transition spectra in the accessible spectral region for most of the lanthanides and the sensitivity of their spectra to the coordination environment makes absorption spectrophotometry an extremely useful tool for lanthanide coordination chemistry particularly in solution both in aqueous and non- aqueous media [9-15].

In the present study, the properties of lanthanides are mainly focused on the comparative absorption spectrometry and the corresponding changes in oscillator strength of different 4f-4f transition spectra as probe in understanding the characteristics of Praseodymium and praseodymium with L-histidine in water and N, N-dimethyl formamide.

MATERIALS AND METHODS

Nd (NO)₃.6H₂O of 99.9% purity was purchased from CDH analytical reagent and L-histidine of 98.5% and N,N-Formamide of 99.8% were purchased from Merk-GR. The different solutions were prepared for Pr(III) with and without L-histidine in distilled water and N,N-dimethyl formamide. The weight measurements were done accurately by using a Mettler Balance, Model-TB-214 and spectra were observed by using UV/VIS spectrometer-119.

Spectrophotometric method can be used to evaluate the oscillator strength of coordination compounds whose absorption band lies in the region of UV/Visible region. The

theories and equations used to evaluate or calculate the oscillator strength are given as follows [16-17].

Oscillator Strength

The strength of electronic transition is generally expressed in terms of a quantity called "Oscillator Strength" represented by 'f'. It is defined as the ratio of the experimental transition probability to that of the ideal case of a harmonic oscillator, that is

$$f = \frac{\left[\int \epsilon \bar{\nu} d\bar{\nu} \right]_{\text{exp.}}}{\left[\int \epsilon \bar{\nu} d\bar{\nu} \right]_{\text{ideal}}} = \frac{\left[\int \epsilon \bar{\nu} d\bar{\nu} \right]}{2.31 \times 10^8}$$

or $f = 4.33 \times 10^{-9} \left[\int \epsilon \bar{\nu} d\bar{\nu} \right]$

For a one-electron transition, the ideal value of unity is obtained when all the molecules are transformed to the higher energy state i.e. when the transition probability is unity. The oscillator strength can also be expressed as

$$f = \frac{|R_{1,2}|^2_{\text{obs}}}{|R_{1,2}|^2_{\text{ideal}}}$$

i.e. $f = \frac{3hc \times 2.303 \times \int \epsilon \bar{\nu} d\bar{\nu}}{8\pi^3 N \bar{\nu}} \times \frac{8\pi^2 m c \bar{\nu}}{3c^2 h}$

$$= \frac{2.303 m c^2 \times \int \epsilon \bar{\nu} d\bar{\nu}}{\pi N C^2} = 4.33 \times 10^{-9} \int \epsilon \bar{\nu} d\bar{\nu}$$

$$f \approx 4.33 \times 10^{-9} \epsilon_{\text{max}} \Delta \bar{\nu}$$

Where ϵ_{max} = max. value of molar extinction co-efficient.

$\Delta \bar{\nu}$ = half band width

A transition is said to be fully allowed transition when $f_{1,2} = 1$. The observed oscillator strength for any given transition is seldom found to be unity. A certain degree of forbiddenness is introduced for each of the factors which cause deviations from the selection rules. The oscillator strength of a given transition can be conveniently expressed as the product of factors which reduce the value from that of a completely allowed transition.

Where f_m = forbiddenness due to spin multiplicity rule, 10^{-5} to 10^{-6} .
 f_o = forbiddenness due to overlap criterion, 10^{-2} to 10^{-4} .
 f_s = forbiddenness due to symmetry consideration, 10^{-1} to 10^{-3} .
 f_p = forbiddenness due to parity consideration, 10^{-1} to 10^{-2} .

Only when $f_m = f_o = f_s = f_p = 1$, that we get $f = 1$ and the transition is totally allowed.

RESULT AND DISCUSSION
Table 1: Spectral datas of Pr(NO₃)₃.6H₂O and Pr(III)+ L-Histidine in water and N,N-Dimethyl formamide

Solvents	Important 4f-4f transitions	λ_{\max} (nm) (nm)		$\epsilon_{\max}(\text{cm}^{-1}) \times 10^3$		$\lambda_1(\text{nm})$		$\lambda_2(\text{nm})$		$\nu_1(\text{cm}^{-1}) \times 10^3$		$\nu_2(\text{cm}^{-1}) \times 10^3$		$\Delta \nu (\text{cm}^{-1}) \times 10^3$	
		Pr(III)	Pr(III)+L-Histidine	Pr(III)	Pr(III)+L-Histidine	Pr(III)	Pr(III)+L-Histidine	Pr(III)	Pr(III)+L-Histidine	Pr(III)	Pr(III)+L-Histidine	Pr(III)	Pr(III)+L-Histidine	Pr(III)	Pr(III)+L-Histidine
Water	$^3\text{H} \rightarrow ^3\text{P}_2$	442.4	439.1	23.2	29.6	442.25	438.95	442.55	439.25	0.2261	0.2278	0.2259	0.2276	0.0002	0.0002
	$^3\text{H} \rightarrow ^3\text{P}_1$	465.5	465.5	10.4	9.6	465.35	465.31	465.65	465.7	0.2148	0.2149	0.2147	0.2147	0.0001	0.0002
	$^3\text{H} \rightarrow ^1\text{P}_0$	478.7	478.7	8	13.6	478.45	478.55	478.95	478.85	0.2090	0.2089	0.2088	0.2088	0.0002	0.0001
	$^3\text{H}_4 \rightarrow ^1\text{D}_2$	584.3	584.3	4	8.8	583.95	583.95	584.65	584.65	0.1712	0.1712	0.1710	0.1710	0.0002	0.0002
DMF	$^3\text{H}_4 \rightarrow ^3\text{P}_2$	442.4	445.7	31.2	28	442.25	445.55	442.55	445.85	0.2261	0.2244	0.2259	0.2242	0.0002	0.0002
	$^3\text{H}_4 \rightarrow ^3\text{P}_1$	468.8	465.5	6.4	8	468.68	465.35	468.92	465.65	0.2134	0.2149	0.2133	0.2147	0.0001	0.0002
	$^3\text{H}_4 \rightarrow ^1\text{P}_0$	485.3	482.0	4	5.6	484.8	481.9	485.8	482.1	0.2063	0.2075	0.2058	0.2074	0.0005	0.0001
	$^3\text{H}_4 \rightarrow ^1\text{D}_2$	590.9	494.2	8	8	590.58	593.8	591.22	594.6	0.1693	0.1684	0.16901	0.1681	0.0002	0.0003

Table 2: The calculated value of 'f' for Pr(III) and Pr(III) mixed with L- Histidine in different solvents.

Solvents	$^3\text{H}_4 \rightarrow ^3\text{P}_2$		$^3\text{H}_4 \rightarrow ^3\text{P}_1$		$^3\text{H}_4 \rightarrow ^1\text{P}_0$		$^3\text{H}_4 \rightarrow ^1\text{D}_2$	
	Pr(III)	Pr(III)+L-Histidine	Pr(III)	Pr(III)+L-Histidine	Pr(III)	Pr(III)+L-Histidine	Pr(III)	Pr(III)+L-Histidine
Water	0.0020	0.0025	0.00045	0.00083	0.00069	0.00058	0.00034	0.00076
DMF	0.0024	0.0027	0.00027	0.00069	0.00086	0.00024	0.00069	0.00010

The spectrum of the compound i.e., Pr(NO₃)₃.6H₂O in different solvents and also the spectrum of the complex i.e., Pr(NO₃)₃.6H₂O mixed with L-Histidine in different solvents were taken by VU-VIS spectrometer-119. Therefore, the following figures (i.e., Fig. 1(a) and Fig. 2(a) are the spectra of praseodymium(III) with ligand in different solvents, Fig. 1(b) and Fig. 2(b) are the spectra of praseodymium(III) in pure different solvents and Fig. 3(a & b) are the comparative spectra of praseodymium(III) in absence and presence of ligand in different solvents) are obtained and the experimental data are tabulated in Tables 1 & 2.

On complexation of Pr(III) and Pr(III) + L-Histidine with widely different binding features, we have an unusual sensitivity of some hypersensitive transitions like $^3\text{H}_4 \rightarrow ^3\text{P}_2$; $^3\text{H}_4 \rightarrow ^3\text{P}_1$; $^3\text{H}_4 \rightarrow ^1\text{P}_0$; and $^3\text{H}_4 \rightarrow ^1\text{D}_2$. These transitions are found to show wide variation of

the oscillator strength only on minor changes in the immediate coordination around the Pr(III), named as “ Ligand Mediated Pseudo hypersensitivity”, for such observation and referred these transitions as pseudohypersensitive [5,6]. The intensities of most of 4f-4f transition change slightly on complexation but the intensity of the non hypersensitive transition $^3H_4 \rightarrow ^3P_2$ of praseodymium(III) shows significant intensification and large variation with slight change in the immediate coordination environment around praseodymium(III) ion.

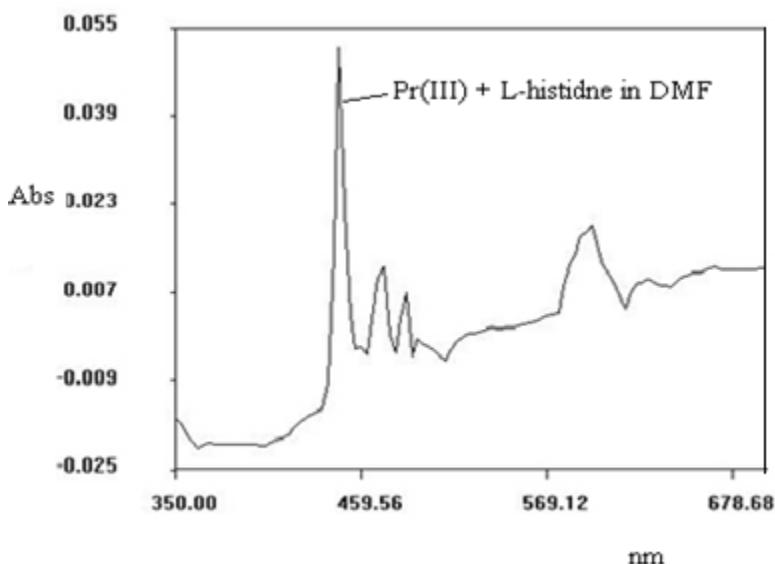


Fig.1(a). Spectra of Praseodymium(III)+ L-Histidine in N,N- dimethyl formamide

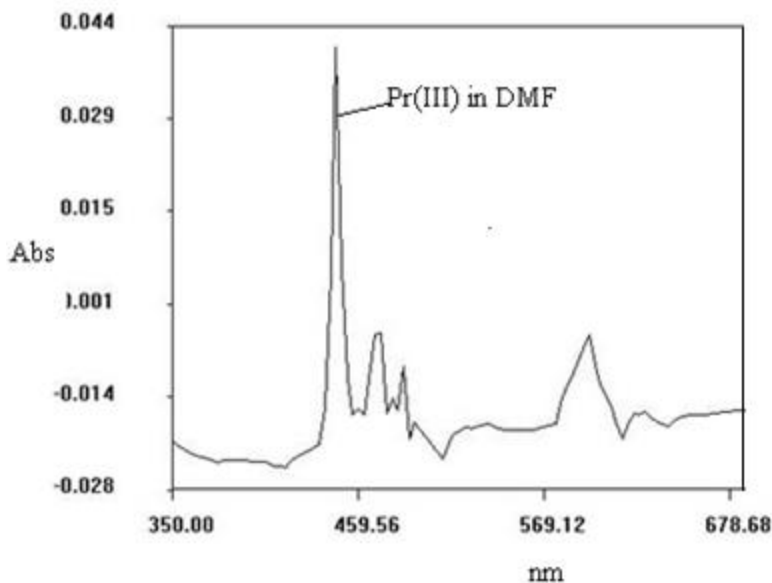


Fig.1(b). Spectra of Praseodymium(III) in N,N- dimethyl formamide

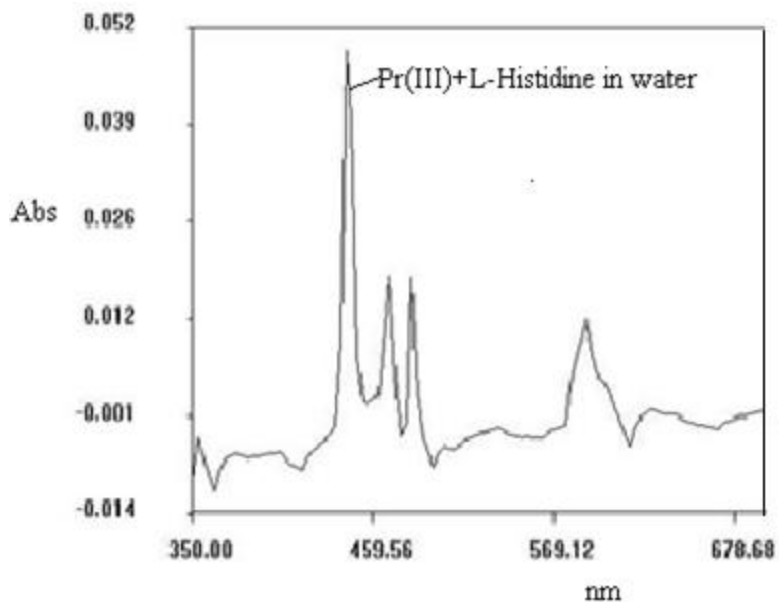


Fig.2(a). Spectra of Praseodymium(III) +L-Histidine in water

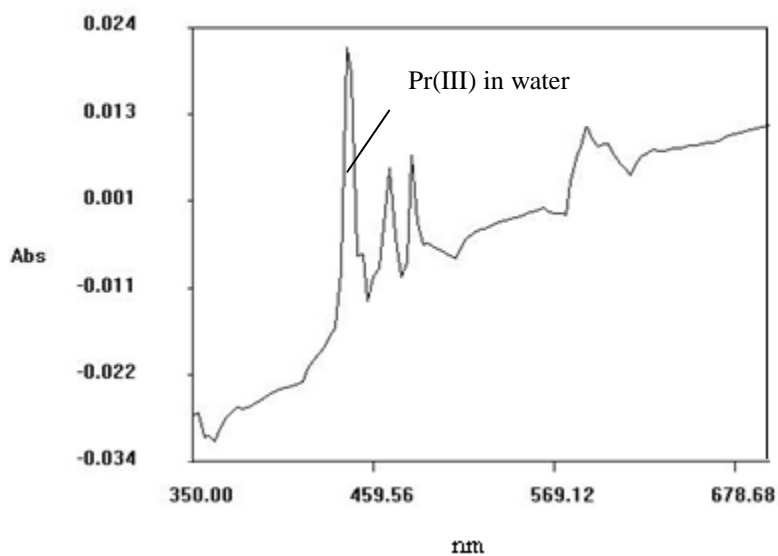


Fig.2(b). Spectra of Praseodymium(III) in water Comparison of spectra for Pr(III) and Pr (III) + L-histidine in different solvents

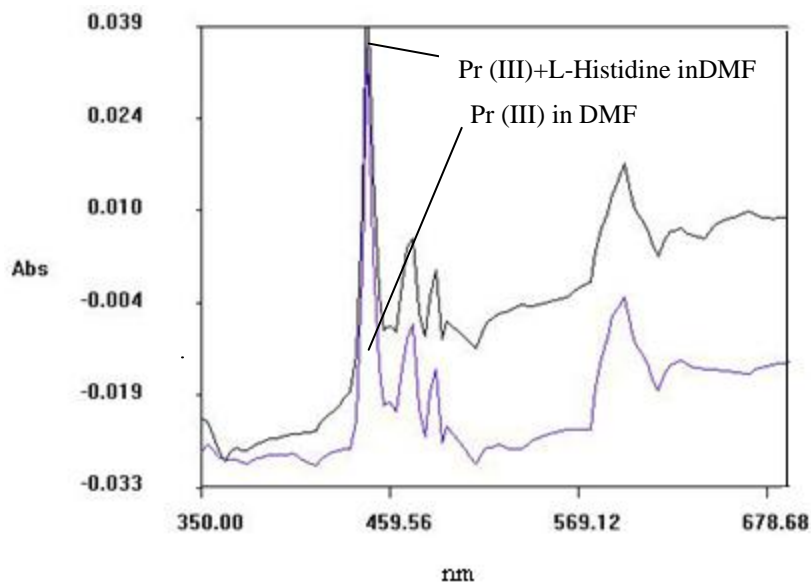


Fig.3(a). Comparison of Spectra for Praseodymium(III) and Praseodymium(III) +L- Histidine in N,N-Dimethyl formamide

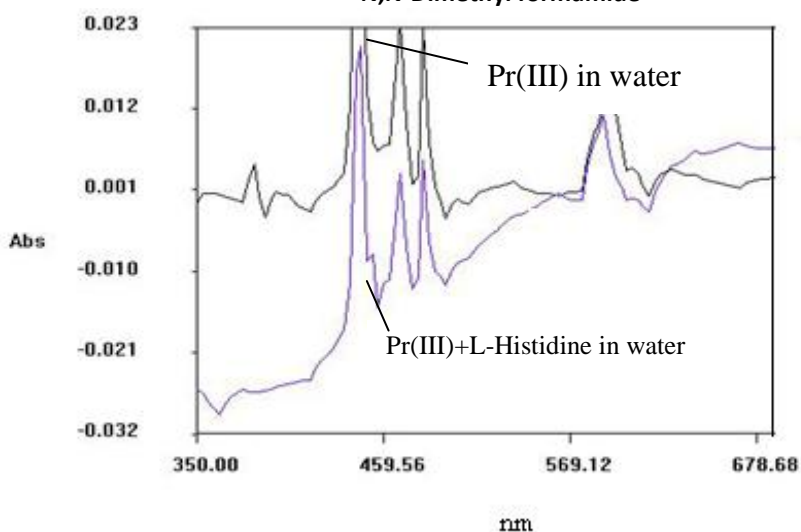


Fig.3 (b). Comparison of Spectra for Praseodymium(III) and Praseodymium(III) + L- Histidine in Water

From the comparative spectral analysis we conclude that the Pr(III) mixed with ligand i.e., L-histidine have more intense spectral line than that of Pr(III) without a ligand in different solvents like DMF and water. This is because the intensity of the complexes, formed with ligand implies that there is interaction of the ligand with the metal.

CONCLUSION

From the present investigation of the comparative absorption it has been observed that praseodymium(III) and praseodymium(III) mixed L-histidine, the intense peaks are observed

with praseodymium(III) + L-histidine in both solvents than praseodymium(III) in pure solvents, i.e., N,N-dimethyl formamide (DMF) and water. From Fig.1 (a) to Fig. 2(b), the spectra of the solvents, the intensity of the solvents are DMF > Water by observing the peak with their absorbance. The comparison of the oscillatory strength, it is found that there is increase in the oscillator strength when the ligand is added which shows that there is interaction of metal and ligand.

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