QUANTITATIVE KINETIC TRANSITIONS PETROLOGICAL ANALYSIS TO PROBE THE KINETICS OF SIMULTANEOUS COMPLEXATION OF GUANINE WITH Pt(III) AND Au(III) IN PRESENCE OF Zn^{2+}/Mg^{2+} IN AQUEOUS AND AQUA ORGANIC SOLVENTS

THESIS SUBMITTED TO NAGALAND UNIVERSITY IN PARTIAL FULFILMENT FOR THE AWARD OF THE DEGREE OF **DOCTOR OF PHILOSOPHY IN CHEMISTRY**

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Certificate

This is to certify that the original works described in this accompanying thesis entitled, ***"QUANTITATIVE 4f-4f TRANSITION SPECTRAL ANALYSIS TO PROBE THE KINETICS OF SIMULTANEOUS COMPLEXATION OF GLUTATHIONE WITH Pr(III) AND Nd(III) IN PRESENCE OF Zn^{2+}/Mg^{2+} IN AQUEOUS AND AQUATED ORGANIC SOLVENTS"*** *has been carried out by* ***Miss Sumitra Chingangbam*** *under my direct guidance and supervision. This work is original and has not been submitted so far in part or full for any other degree or diploma of any other University/Institute.*

It is further certified that the candidate has fulfilled all the conditions necessary for the award of the degree of Doctor of Philosophy of Nagaland University.

16/11/06

Dr. (Mrs.) M. Indira Devi

I humblya nd affect ionate ly
dedicate t his wo rk
to my paren ts –
Ch. Ibo bi Singh & Ng. Asha Devi

- Sumitra Chingangbam

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Sumitra Ch.

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DECLARATION

I hereby declare that this thesis entitled, "***QUANTITATIVE 4f-4f TRANSITION SPECTRAL ANALYSIS TO PROBE THE KINETICS OF SIMULTANEOUS COMPLEXATION OF GLUTATHIONE WITH Pr(III) AND Nd(III) IN PRESENCE OF Zn^{2+}/Mg^{2+} IN AQUEOUS AND AQUATED ORGANIC SOLVENTS***" comprises the results of my own research work carried out in the Department of Chemistry, Nagaland University, Headquarters - Lumami, Mokokchung – 798 601, Nagalnd and that it is not substantially the same as any other thesis which has been submitted to this or any other University so far.

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Dated: 16/11/2006

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CONTENTS

SYMBOLS AND ABBREVIATIONS

Symbols :

A	Absorbance
$A(\Psi J,\Psi' J')$	Probability for spontaneous emission
A_{kp}	Crystal field cooefficient
A^{λ}_{tp}	Intensity parameter
$b^{1/2}$	Bonding parameter
c	Speed of light
C	Concentration
F_k	Slator-Condon parameter
g	Lande factor
T_λ	Intensity parameters (Judd-Ofelt parameter)
$U^{(\lambda)}$	Square reduced matrix element
β	Nephelauxetic parameter
δ	Covalency parameter
ε	Molar absorptivity
Ω_λ	Intensity parameter
ξ_{4f}	Lande spin orbit interaction parameter
Ψ	Wave function
$\Xi(k,\lambda)$	Radial integral
χ	Correction factor for medium effects
Ea	Activation energy
K	Rate constant

ABBREVIATIONS :

DC	Dynamic coupling
GSH	Glutathione reduced
GSSG	Glutathione oxidize
MeCN	Acetonitrile
DMF	Dimethyl formamide
MeOH	Methanol
NMR	Nuclear magnetic resonance
RMS	Root mean square
UV	Ultraviolet
LFSE	Ligand Filed Stabilization Energy
SC	Static Coupling
IR	Infra red
i.e.	That is

Perkin Elmer Lambda-35 UV-Visible Spectrophotometer

CHAPTER 1
Introduction

The term lanthanides are the very similar fourteen elements following lanthanum (La, atomic number 57) to Lutetium (Lu, atomic number 71), which resemble each other in their physical and chemical properties and are characterized by gradual filling up of electrons in the inner lying 4f-shell. The general electronic configuration of lanthanides is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. Since 4f-electrons are relatively less involved in binding, these highly electropositive elements have their prime oxidation number of +3.

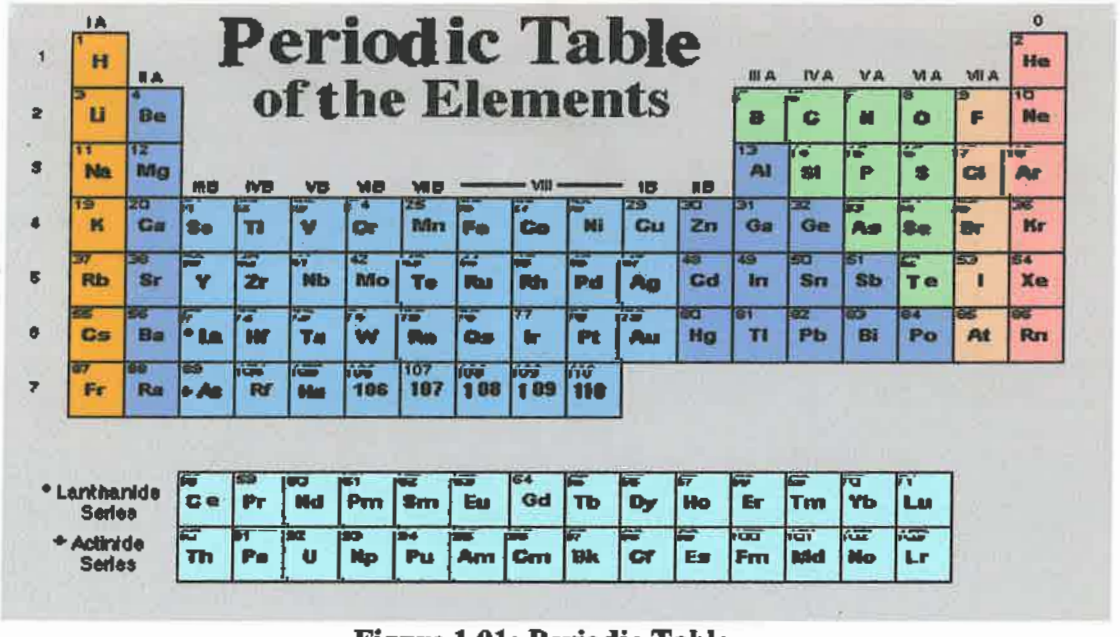

Figure 1.01: Periodic Table

In 1794, Johann Gadolin, a French chemists, while investigating a rare Swedish mineral, discovered a new element in impure form, believed to be a new element and to which he gave the name Ytterbia, from Ytterby, the village where the ore was found. The name, however, was soon shortened to Yttria. Owing to the close chemical similarities between the members of the lanthanide series, they resisted easy purification and separation from one another. Numerous misidentifications, false claims and counter claims are scattered through the pages of lanthanide chemical history. The following Table 1.01 gives a picture about the history of lanthanides.

Table 1.01 : Discovery of the lanthanides*

Lanthanide	Year	Discoverer	Origin of Name
Lanthanum	1839	Mosander	Lanthanum:Greek for "to lie hidden"
Cerium	1803	1.Berzelius and Hisinger 2.Klaproth	Ceres, an asteroid discovered in 1801
Praseodymium	1885	Von Welsbach	From Greek: prasios=green;dymium=twin
Neodymium	1885	Von Welsbach	From Greek:Neo=new;dymium=twin
Promethium	1947	1.Marinsky 2.Glenenin 3.Coryell	Prometheus, the greek God who stole fire from Heaven for men's use.
Samarium	1879	De Boisbaudran	From its ore, Samarskite, named after the Russian engineer Samarski
Europium	1889	Crookes	Europe
Gadolinium	1880	Marignac	After the finnish chemist Gadolin
Terbium	1843	Mosander	After the town of Ytterby in Sweden
Dysprosium	1886	De Boisbaudran	FromGreek: Dysprositors=hard to get at
Holmium	1879	1.Cleve 2.Soret	Holmia,Latinized version of Stockholm

Erbium	1843	Mosander	After the town of Ytterby in Sweden
Thulium	1878	Cleve	After Thule, the roman name for the northern most region of the inhabitable world.
Ytterbium	1878	Marignac	After the town of Ytterby in Sweden
Utecium	1908 1907	1.VonWelsbach 2.Urbain	Lutetia, Latin for Paris

* *Biochemistry of the Lanthanides by C.H. Evans, Plenum Press (New York and London) (1990), Chapter 1*

1.1 : General Feature of Lanthanides

Some properties of lanthanide including its electronic configuration, atomic radius and electrode potential are given below

Table 1.02 : Some properties of lanthanide atoms and ions

Atomic number	Name	Symbol	Electronic configuration	E^0(V)	Radius M^{3+}(Å)
57	Lanthanum	La	$5d^1 6s^2$	-2.37	1.17
58	Cerium	Ce	$4f^1 5d^1 6s^2$	-2.34	1.15
59	Praseodymium	Pr	$4f^3 6s^2$	-2.35	1.13
60	Neodymium	Nd	$4f^4 6s^2$	-2.32	1.12
61	Promethium	Pm	$4f^5 6s^2$	-2.29	1.11
62	Samarium	Sm	$4f^6 6s^2$	-2.30	1.10
63	Europium	Eu	$4f^7 6s^2$	-1.99	1.09
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	-2.29	1.08
65	Terbium	Tb	$4f^9 6s^2$	-2.30	1.06
66	Dysprosium	Dy	$4f^{10} 6s^2$	-2.29	1.05
67	Holmium	Ho	$4f^{11} 6s^2$	-2.33	1.04
68	Erbium	Er	$4f^{12} 6s^2$	-2.31	1.03
69	Thulium	Tm	$4f^{13} 6s^2$	-2.31	1.02
70	Ytterbium	Yb	$4f^{14} 6s^2$	-2.22	1.01
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	-2.30	1.00

An important feature of lanthanide elements is the occurrence of "lanthanide contraction", a steady decrease in ionic and atomic size with

increasing atomic number. The major cause of lanthanide contraction is the screening effect of the increasing nuclear charge by inner sphere 4f-electrons.

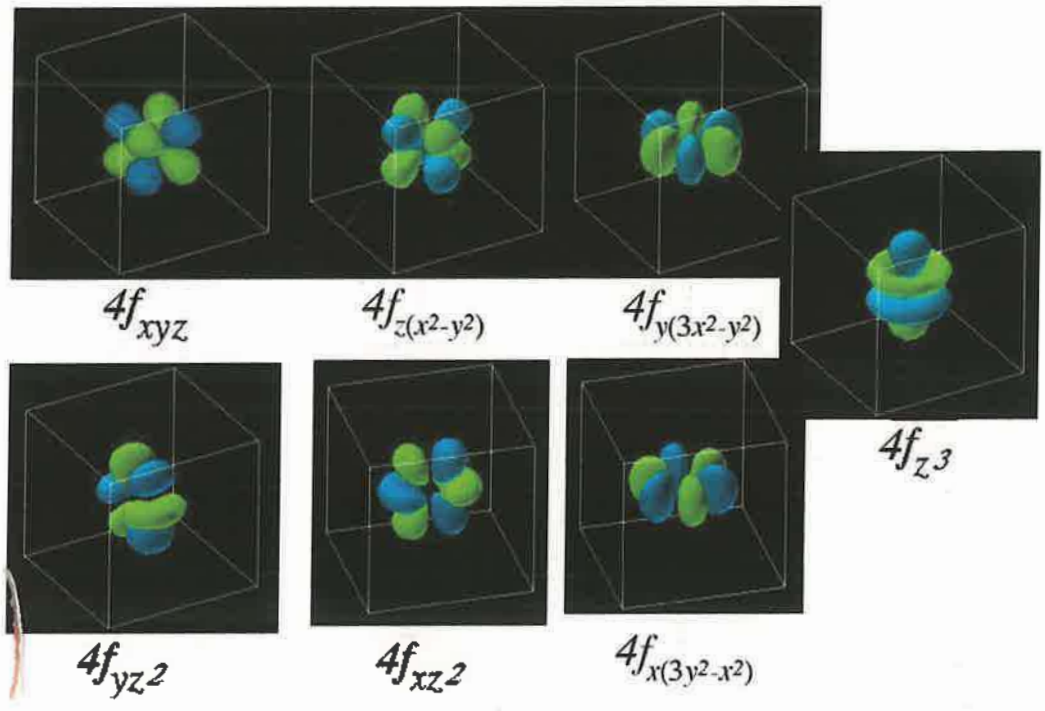

Figure 1.02 Shape of 4f-orbitals

The reduction in size from one lanthanide to the next makes their separation possible but the smallness and regularity of the reduction in size makes the separation difficult. By the time Ho^{3+} is reached, the radius has been sufficiently reduced to be almost identical with that of Y^{3+}, that is why with much lighter element is associated with heavier lanthanide. The total lanthanide contraction is of the similar magnitude to the expansion found in passing from the first to the second transitions series, which might therefore have been expected to occur from passing from second to third. This interaction of lanthanides in fact almost cancel this anticipated increase with the result, i.e. in

each group of transition elements the second and third member have almost similar sizes and properties[1-3].

According to Hard and Soft Acid Bases (HSAB) concept, lanthanides behave as typical hard acids and so its bonding preference is to fluorine (F) and oxygen (O) donor ligands. In the presence of water, complexes with nitrogen, sulphur and halogen (except fluorine) are not stable, but if these donor sites are a part of multidonor ligands these donor sites are involved in strong complexation with lanthanides.[4,5] The absence of extensive interaction with 4f-orbitals, minimizes ligand field stabilization energy (LFSE). Low LFSE reduces overall stability, but on the other hand provides a greater flexibility in geometry and coordination number because LFSE is not lost e.g. when an octahedral complex is transformed into trigonal prismatic or square anti prismatic geometry. Furthermore, the complexes tends to be labile in solution.

1.2 : The Biochemistry of Lanthanides and Actinides

In spite of the fact that f-block elements, the members of lanthanide and actinide transition series, have no known essential role in life processes[6], they no doubt pose some of the most fascinating, challenging and important chemical and biochemical problems of all inorganic elements of the periodic table. The reasons for this, primarily stem from the properties conferred by their outer electron configuration and associated energy levels coupled with their chemical toxicity which are low for lanthanides and with their radio toxicities which are a major problem for actinides.

The paramagnetic nature of lanthanides is responsible for higher magnetic moment due to number of unpaired electrons in 4*f* orbitals. This makes them of great practical value for their application in Nuclear Magnetic Resonance Spectroscopy (NMR) as well Nuclear Magnetic Resonance Imaging (MRI). Gadolinium(III) complexes especially with polyamino-polycarboxylic acids, make good contrast enhancing agent because of their high magnetic moment coupled with good relaxation efficiencies. Dysprosium and Thulium chelates have been proved excellent SHIFT REAGENTS in following compartmentalization of sodium during onslaught of *Ischaemia*. Other important biological and biochemical applications are as follows:

(i) Lanthanides can be used as heavy atom 'STAINS' in electron microscopy or x-ray diffractions studies.

(ii) Thermodynamic properties of metal ion binding site, e.g. for Calcium(II) can be elucidated through competition or exchange reactions with lanthanide ions. This is most important because calcium, one of the most important and ubiquitous of essential elements, has very few properties, which can be used to PROBE its Biochemistry *in situ*. The lanthanide(III) ions, make almost BIOMIMETIC agent for Ca(II) [Table 1 .03]

Table 1.03 : Comparison of calcium and lanthanide ion characteristics

Property	Ca(II)	Ln(II)
Coordination number	6 - 12 reported 6 or 7 favored	6 – 12 reported 8 or 9 observed
Coordination geometry	Highly flexible	Highly flexible
Preference for donor sites	O > N > S	O > N > S
Ionic radii (A^0)	1.00 – 1.18 (CN 6-9)	0.86 – 1.22 (CN 6-9)
Type of Bonding	Electrostatic	Electrostatic
Hydration number	Six	8 or 9
Water exchange rate constant (s^{-1})	~ 5 x 10^8	~5 x 10^7
Crystal field stabilization	None	Negligible
Spectroscopic behavior	Spectroscopic silence	Abundance of spectroscopic signals both optical and magnetic
Stability of complexes	Weak complexes	Strong complexes

(iii) Kinetic properties of biochemical reaction involving metal ions, can likewise be investigated and mechanistic information gained.

(iv) Fine structural features of biological systems may be researched and defined using NMR, ESR and 4f-4f transition spectra and energy transfer leading to fluorescence.

(v) Further applications include *in vivo* targeting and localization in tumors using appropriate lanthanide ion complexes.[7]

1.2.1 : Biochemistry in Body Compartments

After entry into the body by whatever route, transport of lanthanide or actinides, secondary disposition sites is mainly via the plasma in blood stream. Within body compartment it is convenient to consider the f-element as being

placed between the three (or perhaps four) fractions which are in equilibrium with one another and which are responsible for transport and intracellular uptake. We take iron as important essential elements to illustrate this concept. Iron is partitioned between fractions, which exist in a labile and thermodynamic equilibrium with one another. There is a fourth fraction in which the metal is bound inertly and which is also exchangeable with the other three fractions. This latter fraction can be thought as storage compartment.

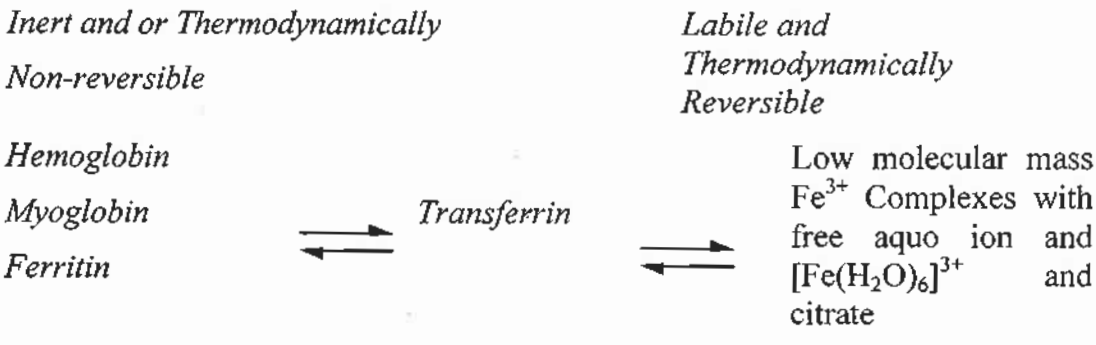

Figure 1.03 : Inert and labile forms of metal ions in vivo

With respect to metal transport, it is the three labile compartments, which are of interest. Transferrin, the protein which is responsible for transporting iron in and out of cells via receptor mediated endocytosis, appears to play a major role in f-clement transport within the blood stream.[7-8] Transferrin is a glycoprotein (molecular mass 80k Da) containing 800 amino acid residues. The protein is bilobular with one metal binding site in each lobe. These metal bindings are designated as N- and C- terminal sites. In addition to binding and transporting Fe^{3+} ions, transferrin is also responsible for binding lanthanides and actinides *in vivo*.

The protein also binds to both lanthanide and actinides. Comparative studies *in vitro* and *in vivo* have shown the binding of lanthanides.[9-11] UV difference spectroscopy and other studies *in vitro* with Pu(IV), Th(IV) and a number of trivalent lanthanides have very clearly demonstrated that, like iron, two lanthanide or actinide metal atoms are bound per transferrin molecule.[12]

Data on the formation constants for actinide and lanthanide complexes with transferrin is very sparse. Harris[13] however reported conditional values of equilibrium formation constants of Nd(III) and Sm(III) transferrin complexes, using absorption difference and comparative absorption spectra. However the data published on conditional stability constants of human serum transferrin with lanthanides and actinides have important implications with regard to actinide/lanthanide distribution within the human body. It has been shown that in binding to human serum transferrin, the f-elements are participating in certain aspects of iron transport pathways *in vivo*. However, no plutonium e.g. is found within RBC following incorporation and there is no unequivocal evidence that plutonium and the other actinides or lanthanides are transported into the cell via "Transferrin-Receptor Mediated Endocytosis", This is the PUZZLING aspect of f-element transferrin chemistry and biochemistry and it requires much more study. A number of explanations can be advanced which may explain the apparent dichotomy of f-elements binding to transferrin and the imperfect participation in the iron metabolic pathway. Duffied and Taylor[14] investigated absorption spectral studies and shown the line details of Pu(IV) and Th(IV)

binding to transferrin very similar to that of Fe(III). One molecule of transferrin bind two moles of Pu(IV) in a specific fashion implying that Pu(IV) binds at same sites as Fe(III). The same is true for Th(IV). Fe(III) binding to transferrin requires stabilization with a synergistic anion, carbonate or bicarbonate. Binding of Pu(IV) and Th(IV) also requires synergistic anion.

Differences in Fe(III)-transferrin and lanthanide/actinide transferrin may be due to changes in the conformation upon metal ion binding and the conformational changes are very critical regarding subsequent binding of metal transferrin complexes to cell surface receptor, prior to internalization by Receptor Mediated Endocytosis.[15] The interactions of various lanthanides with a very wide range of proteins have been reviewed in depth by Evans (1990). The range of proteins which have been investigated is large and includes enzymes such as *Trypsins, Elastase, Collagenase, Amylase, Nuclease, ATPase, Phospholipase—A_2 and Acetyicholinesterase,* the contractile proteins *Actins, Myosin* and molecular oxygen carriers such as *Haemocyanin.* These studies have shown that the major ligand for Ln(III) ion is the carboxyl group with additional coordination through carboxyl or hydroxylic oxygen. Often lanthanides occupy Ca^{2+} binding sites. However, Ln^{3+} ions may also bind to sites of proteins, which are not known to bind Ca^{2+} or any other metal. Because of their higher charge to volume ratio, Ln^{3+} ions usually have higher affinity for proteins than Ca^{2+}. The affinities of different lanthanides vary widely but in general they increase with decreasing hydration of sequestered lanthanide ion and with increasing cationic

charge of binding site. In addition to protein study the Ln^{3+} binding to other types of biomolecules *in vitro* can also provide valuable structural and other information. The biomolecules include *Nucleic acid, Phospholipids, Phospholipid membrane, Porphyrins, Vitamin* B_{12} *and high-density Lipoproteins.*

The most important aspect of lanthanide binding to biomolecule is the fact that these MIMIC interaction of these biomolecules with radioactive actinides. Increasing use of nuclear reactor, radioactive isotopes, nuclear medicines, the medicinally compatible Ln(III) interaction has been extremely useful in exploring biochemistry and biological chemistry of actinides.[16-18]

1.3 : Glutathione

1.3.1 :Function of Glutathione

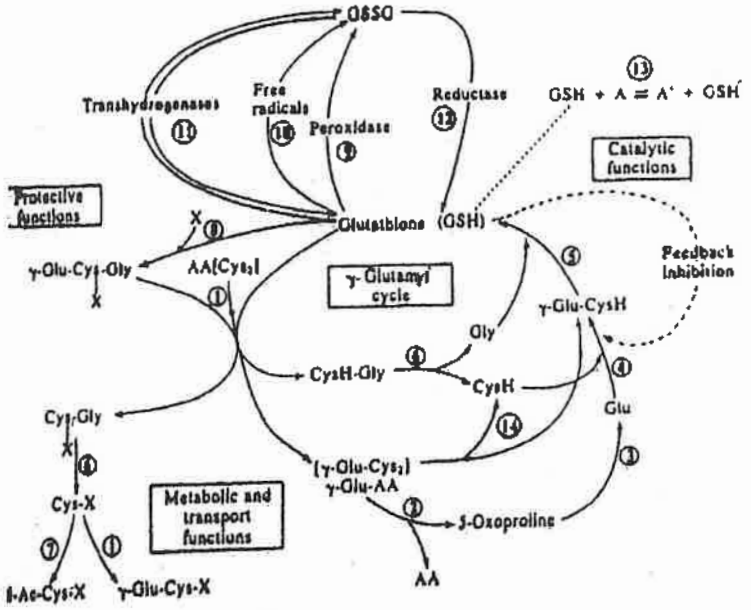

Figure 1.04 : Overview of the metabolism and function of glutathione

Most, but not all, cells contain glutathione. This molecule, which has been conserved through evolution, is adopted to perform many diverse functions. Glutathione is synthesized within the cells and exerts many of its functions intracellularly. Transport of glutathione out of the cell seems to be associated with cell membrane functions such as transport and protection. In higher animals and human. cellular transport of glutathione is related to the transport of amino acid sulphur to other cell : Figure 1.04 summarise information available about the metabolism of glutathione and indicates the biochemical path ways that seems to be connected with the several functions of glutathione. These include cellular protection (against reactive organic oxygen compounds, other toxic compounds of exogenous and endogenous origin, free radicals) catalysis, metabolism and transport.

The multifunctional properties of glutathione are perhaps most dramatically reflected by continually increasing interest in this molecule by investigation of such divers subjects as organic chemical mechanism enzymology, molecular biology, intermediatory, agriculture toxicology, aging and still many other fields.Intracellular total glutathione consists of greater than 99.5% glutathione, the small amounts of glutathione disulphide present may be an artifact. Glutathione is the major transport form. Table 1.04 shows the different glutathione levels in different body fluids.

Table 1.04 : Glutathione levels in different body fluids :

Body Organ	Total	% Glutathione
Rat :		
Hepatic vein plasma	26.0±4.2 μM	~80
Aortic plasma	14.5±2.7 μM	~80
Renal vein plasma	2.6±0.6 μM	~80
Inferior vena cava plasma	8.1±2.0μM	~70
Arterial plasma (no anesthesia)	25-35 μM	~85
Bile	2.4 mM	~80-90
Pancreatic juice	0	-
Mouse :		
Arterial blood plasma	25-35 μM	~85
Urine (after AT-125)	25-30 mM	30-70
Human lymphoid cells	0.12-3.4 nM	> 90

The cellular export of glutathione serves to protect cell membranes against oxidative and other types of damage by maintaining essential thiol groups or other components of the membrane. Export of glutathione also provides a mechanism for reducing compounds in the immediate environment of the cell membrane. Such export facilitates the transport of certain compounds especially disulphides.

Depletion of cellular glutathione has been of great importance as an experimental tool in investigations on mechanism and functions of tripeptide.

(i) Depletion of glutathione via inhibition of γ-gluatamylcysteine synthatase.

(ii) Depletion of glutathione by the use of oxidising agent.

(iii) Depletion of glutathione by the use of the compounds such as diamide.

(iv) Depletion of glutathione by the use of compounds that react with glutathione (diethyl maleate, 1-chloro-2,4-dinitrobenzene).

(v) The decreasing cellular level of glutathione by inhibiting glutathione synthetase level.

(vi) Depletion of glutathione by administration of buthionine sulphoximine has considerable member of effect on metabolic activity.

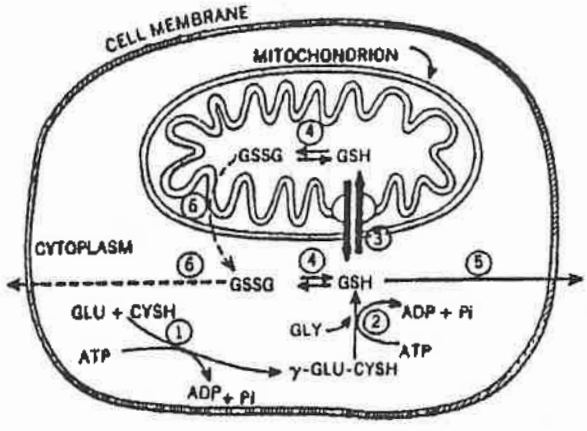

Figure 1.05 : Scheme for synthesis and transport of glutathione in mitochondria and cytoplasm

After administration of buthionine sulphoximine, the level of glutathione in liver and kidney is significantly affected. Figure 1.05 clearly demonstrates the synthesis of glutathione and its transport in mitochondria and cytoplasm. Reversible conversion of glutathione disulphide occurs in both mitochondria

and cytoplasm, but the synthesis of glutathione occurs only in cytoplasm. Glutathione, rather the glutathione disulphide, is probably the major transport form, since glutathione is the predominant intra-cellular form. Transport of glutathione-disulphide, which may be formed in mitochondria that are under severe oxidative stress, serves as a mechanism for protection. The observed rapid labeling of mitochondrial glutathione after administration of isotopically labeled cysteine is in the accord with the view that there is an exchange carrier in the mitochondrial membrane, that is, accessible to both mitochondrial and cytoplasmic glutathione. Glutathione is essential for mitochondrial function. The net efflux of glutathione from mitochondria is very slow. This suggest that, this transport mechanism functions in a manner that conserves mitochondrial glutathione during periods of cytoplasmic glutathione depletion, which may be produced by nutritional factors and also by phenomenon associated with oxidation and the presence of toxic compounds.[82]

1.3.2 : Metal Complex of Glutathione

Glutathione is a polydentate ligand, offering as potential binding sites of two carboxylate oxygen, an amino nitrogen, a sulphydryl group and two amide groups.[83] The structure of glutathione is such that all its potential binding sites cannot be simultaneously coordinated to the same metal ion, and therefore the coordination chemistry of glutathione is characterized by the formation of protonated and polynuclear complexes. The coordination chemistry of glutathione is very important and is of great interest as a model system. For the

binding of metal ion by larger peptides and proteins and because metal-glutathione complexes are involved in the toxicology of several metals. Glutathione present in the cellular system at a relatively high concentration and generally it is the most abundant non protein thiol. Because of high affinity of a sulphur for many heavy metals glutathione is involved in their uptake and excretion.[84,85] And naturally their complexation can explain very well their inter-cellular competition. The complex of several heavy metals by glutathione in intact erythrocytes has been detected directly and noninvasively by ^{1}H NMR spectroscopy.[86-87]

1.3.3 : Acid-Base Chemistry of Glutathione

The acid-base chemistry of glutathione at the molecular level is described by eight microscopic constant as shown in the scheme (Figure 1.06)

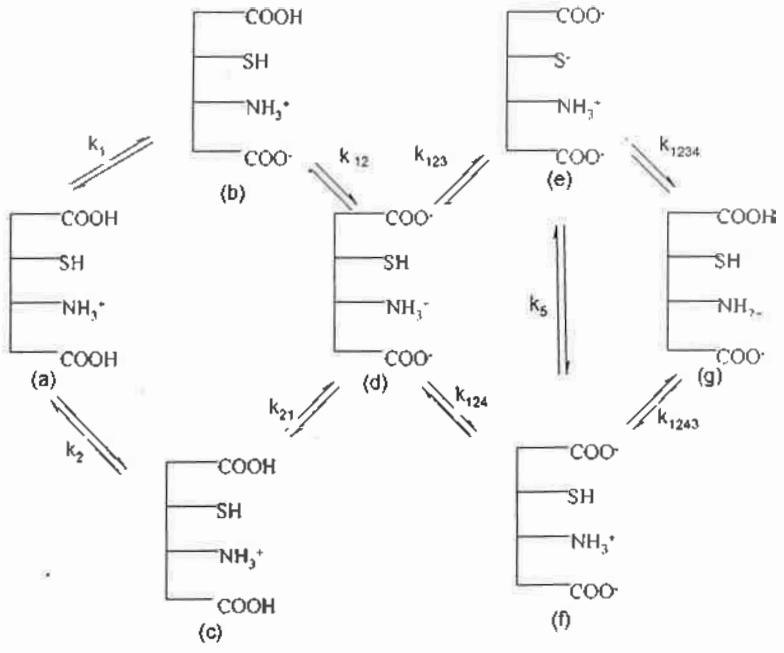

Figure 1.06 : Macroscopic acid dissociation scheme for glutathione

$$Ki = \frac{[H^+] \times [H_{4-i}L]}{[H_{5-i}L]}$$

Proton NMR data indicate that two carboxylic acid groups ionize simultaneously over the pH 0.5-6.0 while sulphydryl and ammonium groups ionize simultaneously over the pH range 7-12.[88] The value of microscopic constants for sulphydryl ammonium group is highly affected by the nature of solvent. Increase in the acetonitrile content in the aquated organic solvent dielectric constant decreases, this has dramatic effect on the on the relative activity of sulphydryl and ammonium group (decrease in the K_a value from 1.6 to 0.4)[89].

Table 1.05 : Microscopic acid dissociation constant of GSH

pK_1		2.19[b]					
pK_2		3.22					
pK_{12}		3.45					
pK_{21}		2.42					
pK_{123}	8.92[a]	8.97	8.93[c]	8.88[d]	9.15[d]	9.47[d]	9.64[d]
pK_{124}	9.20	9.17	9.16	9.09	9.26	9.20	9.28
pK_{1234}	9.44	9.35	9.53	9.21	9.53	9.56	9.71
pK_{1243}	9.16	9.08	9.31	9.13	9.46	9.82	10.07
K_5	1.9	1.6	1.7	1.6	1.3	0.5	0.4

[a] Determined by pH titration; I=0.16, 25 °C

[b] Determined by ^{1}H NMR; I=0.2-0.5, 25°C

[c] Determined by pH titration; I=0.15, 25°C

[d] Determined by spectrophotometric titration; I=0.10, 25°C

The K_{124}, K_{1234} pathways, which involves the more highly charged zwitter-ionic intermediate as acetonitrile content increases. This change in the acid base chemistry with decreasing dielectric constant is of great interest in view of the hydrophobic regions of low dielectric constant in protein. Therefore our study of complexation of glutathione with one, two or three different metal ion simultaneously investigated in different mixed solvents (DMF-H_2O, Dioxane-H_2O and Acetonitrile-H_2O) of different stoichiometry, will be important and relevant in understanding hetero metal complexation of large proteins involving endogenous metal ions.

The thesis presents the quantitative absorption spectral analysis with absorption difference, comparative absorption spectroscopy involving 4f-4f transitions as PROBE in understanding the coordination and binding characteristics of Glutathione reduced (GSH) with hard metal ions Pr(III) and Nd(III) and a soft metal ion Mg(II)/Zn(II) in process of simultaneous coordination in different pH, i.e. pH3, pH4, pH5 and pH6 . Since such hetero-bimetallic complexation of GSH involving Pr(III)/Nd(III) and Mg(II)/Zn(II) MIMICS the *in vitro* hetero bimetallic simultaneous complexation of these sulphur containing peptides with Mg(II) and Zn(II) occurring both intra and extracellularly. All the effectivity of such effort made in present thesis opens up new vistas of structure and spectra correlation which pave way to make 4f-4f transition spectroscopy on very effective tool in following the progress of several biochemical reaction involving most essential metal ions like Mg^{2+} and

Zn^{2+} ions. The thesis also report the kinetics for the complexation of Pr(III):GSH and Nd(III):GSH with Zn(II) in DMF medium at different temperatures (303K, 308K, 313K and 318K) and activation energy of the complexations are calculated following Arrhenius rate equations.

1.4 : Chemical Kinetics

Chemical kinetics is defined as the branch of the chemistry which deals with the study of rate of the chemical reactions and their mechanism. It is a positive quantity that expresses the concentration of a reactants or product changes with time during the course of reaction. During the progress of a reaction, the concentration of the reactants gradually decreases, while those of the products increases as the time increases. For the hypothetical reaction,

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate of the reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

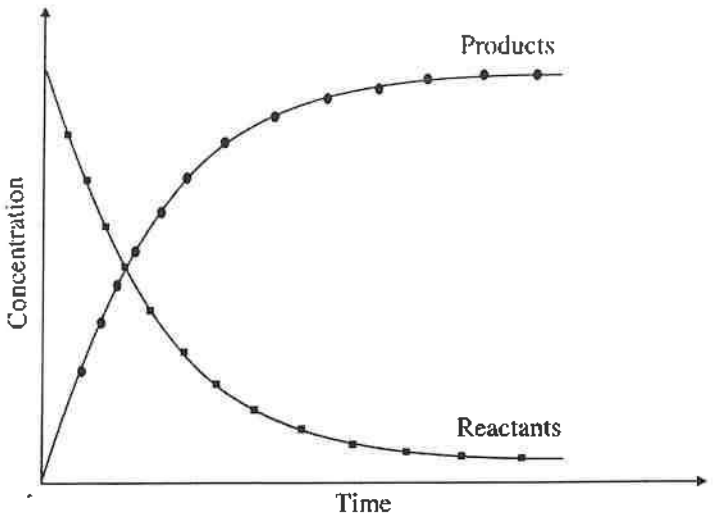

Figure 1.07 : Change of concentration of reactants and products with time of a chemical reaction

1.4.1 : Factors affecting the rate of a reaction

The rate of a reaction depend upon the following factors :

a) Concentration of the reactants,

b) Temperature,

c) Presence of catalysts

d) Nature of the reactants,

e) Surface area of the reactants and

f) Exposure to radiation.

a) Concentration of the reactants :

The rate of a chemical reaction is directly proportional to the concentration of the reactants. The increase in concentration of the reactants increases the no. of particles in a given volume thereby increasing the effective collision rate of the molecules. The higher frequency of collision results in a higher rate of reaction.

b) Temperature :

The rate of a reaction changes with change in temperature drastically. It has been observe that the rate of a reaction increases 2 to 3 times for every 10 degree rise in temperature. This is due to increase in number of molecules which cross over the activation energy (Ea) by increase in the effective number of collision with increasing temperature.

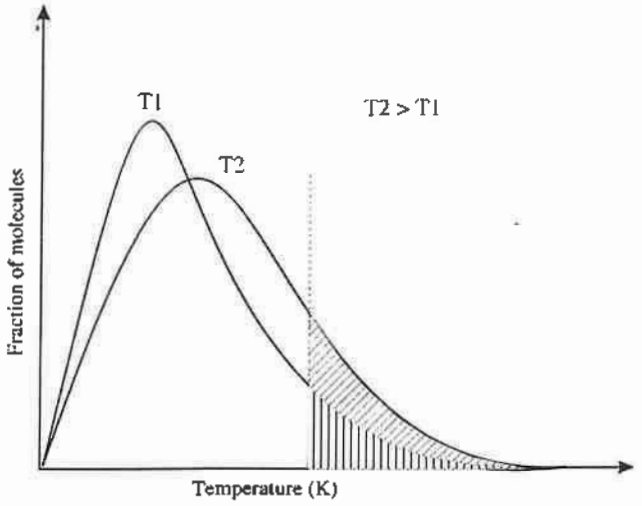

Figure 1.08 : Effect of temperature on the rate of reaction

c) Presence of catalyst :

A catalyst is a substance which changes the rate of a reaction without undergoing any chemical change by itself. It has been observed that many reactions are made to proceed at an increased rate by the presence of certain catalyst. This is due to lowering of the value of activation energy (Ea) in the presence of a catalyst.

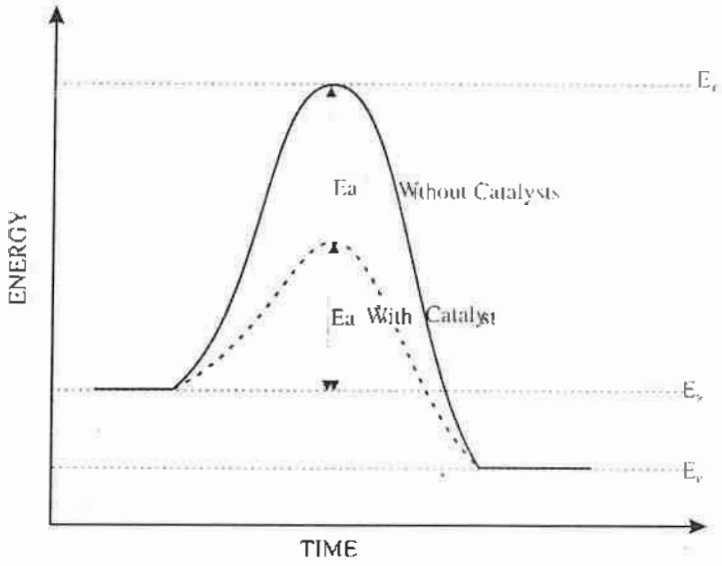

Figure1.09 : Effect of catalyst on the rate of reaction

d) Nature of the reactants:

Reactions involving polar and ionic substances excluding the proton-transfer reactions are usually very fast. On the other hand, the reactions in which bonds are rearranged or electron transferred are slow. Oxidation-reduction reactions which involve electrons transferred are also slow as compared to the ionic reactions.

e) Surface area of the reactants :

In case of heterogenous reactions, the rate of a reaction is proportional to the surface area. With increase in surface area (i.e., with the decrease in the particle size of reactants) the rate of reaction also increases.

Example : i) Wood chips burn rapidly than a log of wood.

ii) Coal dust burns brilliantly in air than a lump of it.

f) Exposure to radiation : In some cases, the rate of a chemical reaction is considerably increased by the use of certain radiations. The photons of these

radiations having frequencies (ν) possess sufficient energies (E = hν) to break certain bonds in reactants.

Example : Reaction of hydrogen and chlorine takes place very slowly in the absence of light. However, in the presence of light, the reaction takes place very rapidly.

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

1.4.2 : Dependence of reaction rate on concentration

When a chemical reaction proceeds, the reactants get converted into the products. As a result, the concentration of reactants decreases while that of products increases. A quantitative relationship between the rate of a reaction and the molar concentration of the reacting substances was given by two Norwegian chemists, Guldberg and Waage in 1867. This relationship is known as Laws of Mass Action. According to this law :

> "At a given temperature the rate of a chemical reaction is directly proportional to the molar concentrations of the reactants with each concentration term raised to the power equal to the stoichiometric coefficient possessed by it at the balance chemical equation."

For the hypothetical reaction,

$$aA + bB \rightarrow \text{Products}$$

$$\text{Rate} \propto [A]^a [B]^b$$

$$\text{Rate} = k [A]^a [B]^b$$

Where, [A] and [B] are the molar concentrations of the reactants and 'k' is a proportionality constant known as velocity constant or specific rate constant.

The above expression is known as rate law or rate equation. It may be defined as,

> "the mathematical expression which denotes the experimentally observed rate of a reaction in terms of the concentrations of the reacting species which influence the rate of the reaction."

1.4.3 : Activation energy vs temperature

Over a narrow range of temperature, the activation energy is found to be nearly constant. So, over a narrow range of temperature, the activation energy is temperature independent. However, precise measurements over a wide temperature range, the activation energy is found to increase with the lowering, ie., at lower temperature the activation energy tends to increase.

1.4.4 : Concept of activation energy (E_a)

Arrhenius proposed the concept of activation energy (E_a) in 1897. According to Arrhenius, the conversion of the reactant into products is not down the slope process (process taking place of its own). Instead, the reacting molecules must cross an energy- barrier before they get converted to products. The energy-barrier is an imaginary high energy state between the reactants and products. The energy which corresponds to the top of the energy barrier is called threshold energy,(E_T). It is the minimum energy which the reacting molecules should acquire before they are able to react. The reacting molecules having energy more or equal to the threshold energy (at the top of the energy barrier) is called the activated molecules.

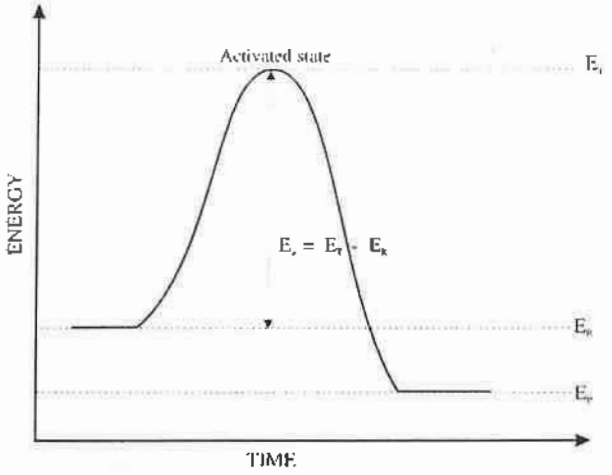

Figure 1.10 :The concept of activation energy

The additional energy which the reacting molecules must acquire over their average energy in order to react is called the activation energy. Thus,

Activation energy = Threshold energy – Average energy of the reactant molecules

Or, $E_a = E_T - E_R$

Where, Ea is the activation energy of the reaction; E_T is the threshold energy and E_R is the average energy of the reactant molecules.

1.4.5 : Activation energy and the rate of the reaction

Depending upon the magnitude of the activation energy, the following three cases are possible :

i) When the activation energy (E_a) is small, the reaction is fast.

ii) When the activation energy (E_a) is large, the reaction is slow.

iii) When the activation energy (E_a) is zero (0), the reaction is very very fast or instantaneous.

1.4.6 : Arrhenius rate equation

On the basis of the concept of the activation energy. Arrhenius described the temperature dependence of the rate constant (k) by the equation,

$$k = Ae^{-\frac{E_a}{RT}} \qquad (1.1)$$

This equation is known as Arrhenius rate equation.

Where, A is called frequency factor. The factor $\exp(-E_a/RT)$ is a measure of the probability for the occurrence of a molecule in the activated state.

The above equation (1) can be written as

$$\ln k = \ln A - \frac{E_a}{RT}$$

or, $$2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$$

or, $$\log k = \log A - \frac{E_a}{2.303RT} \qquad (1.2)$$

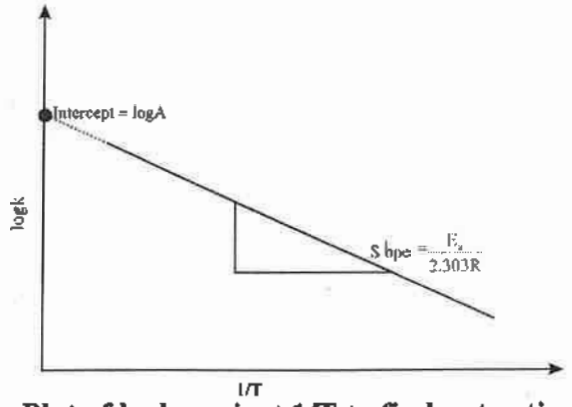

Figure 1.11 : Plot of logk against 1/T to find out activation energy

Thus, a plot of logk against 1/T should give a straight line with negative slope, in which

$$\text{Slope} = \frac{E_a}{2.303R} \text{ and Intercept} = \log A \qquad (1.3)$$

1.5 Spectroscopic Features of Lanthanides :

The trivalent lanthanide ions have unique spectroscopic properties. Since *4f* shell is effectively shielded by closed 5s and 5p shells, the ligand environment has only a weak influence on the electronic cloud of lanthanide ion. Although weak, this perturbation is responsible for the spectral fine structure. The line width of the bands is small and its peak position reveals the electronic structure (of a part) of the $4f^n$ configuration. The crystal field splitting gives information about the symmetry of the rare earth site and about the shape of the coordination polyhedron.[21]

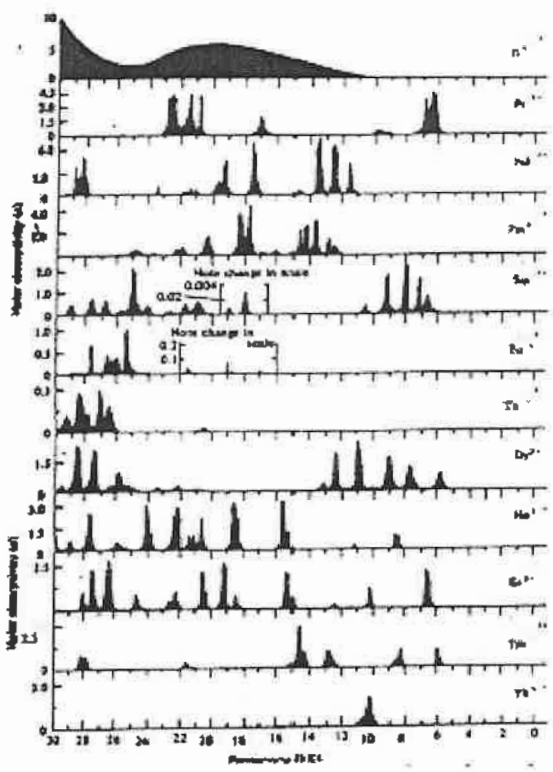

Figure 1.12 Absorption spectra of Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+} in dilute acid solution

Absorption and luminescence spectroscopy are important techniques in the study of lanthanide system as they allow determining the natural frequencies of lanthanide. The absorption spectra of lanthanide doped single crystals of lanthanide compounds show group of narrow lines in solution or in glasses, however the lines within group broaden to one absorption band, these bands have to be ascribed to electronic to electronic transition inside the *4f* shell. Each group or band corresponds to the transition

between $^{2S+1}L_j$ free ion levels (or J-manifolds). They are not accompanied by a change in configuration and hence named as Intra-configurationally Transition. Three mechanisms must be considered for the interpretation of the observed transitions[22].

(i) Magnetic-Dipole Transitions
(ii) Induced Electric Dipole Transitions
(iii) Electric Quadrupole Transition.

1.5.1 Magnetic Dipole Transition

The magnetic dipole transition is caused by the interaction of spectroscopic active ion with magnetic field component of the light through a magnetic dipole. Magnetic dipole radiations can also be considered as rotational displacement of charge. Because the sense of rotation is not reversed under inversion through a point (or inversion centre) a magnetic dipole transition has even parity. Therefore a magnetic dipole operator possesses even transformation properties between states of equal parity (or intra-configurational transition).

1.5.2 Induced Electric Dipole Transition

The majority of observed optical transition of lanthanides is *Induced Electric Dipole Transition.,* which have consequence of interaction of spectroscopically active ion/the lanthanide ion with the *Electric Filed* vector through an electric dipole. The creations of electric dipole suppose a linear movement of charge, and such transition has odd parity. The electric dipole operator has therefore odd transformation properties under inversion with

respect to an inversion centre. Intra configurational electric dipole transitions are forbidden by the Laporte Selection rules. The induced electric dipole transitions are described in details in Judd[23] and Ofelt[24] theory.

1.5.3 Electric Quadrupole Transition

The electric quadrupole transition arises from the displacement that has a quadrupole nature. An electric quadrupole consists of four point charges with overall zero charge and zero dipole moment. It may visualized as two dipoles arranges in a way to annul each other's dipole moment. An electric quadrupole has even parity. Electric quadrupole transitions are much weaker than magnetic dipole, which in turn are weaker than induced electric dipole transitions. However *hypersensitive transitions* are considered as pseudoquadrupole transitions as these transitions obey the selection rules of quadrupole transitions.

1.6 Selection Rules

Selection rules are only valid in strict conditions and can be relaxed under circumstances. The selection rules for ΔL and ΔS are only applicable for Russel Saunders Coupling Scheme. These selection rules are relaxed in intermediate coupling scheme, because in this scheme L and S are not good numbers. Since J remains a good quantum number in the intermediate coupling scheme, the selection rules on ΔJ are harder to break down, it can be relaxed only by J-mixing, which is a weak effect. The selection rules on ΔM depend on

point group symmetry of the rare earth site.[25] The selection rules for magnetic dipole and induced electric dipole transitions are given in Table 1.06

Table 1.06 : Selection rules for magnetic dipole and induced electric dipole transitions:

Magnetic Dipole Transition (MD)	Induced Electric Dipole Transition (ED)
$\Delta\tau=\Delta S=\Delta L=0$	$\Delta L=\pm l$, $\Delta\tau=0$, $\Delta S=0$, $\lvert\Delta L\rvert\leq 6$
$\Delta J=0, \pm 1$ but $0\leftrightarrow 0$ is forbidden	$\lvert\Delta J\rvert\leq 6$; $\lvert\Delta L\rvert=2,4,6$ if $J = 0$ and $J' = 0$
$M' - M = -P$, where $P = \pm 1$	$M' - M = -(q+p)$

A well known example of the breakdown of selection rules of the Judd-Ofelt theory is the occurrence of $^7F_0 \rightarrow {}^5D_0$ and $^5D_0 \rightarrow {}^7F_0$ transitions in some Eu(III) complexes.[26-29] The $^7F_0 \leftrightarrow {}^5D_0$ transitions are forbidden by the selection rules, as ΔJ $(0\leftrightarrow 0)$ is forbidden. The breakdown of closure approximation in Judd-Ofelt can be explained to this exceptional behaviour was ascribed by Tanaka et al[30,31]. Wybourne[32] has shown that the second order matrix element $U^{(\lambda)}$ is zero, ,so that no intensity can come from this mechanism. Wybourne proposed a mechanism in which spin selection rule is relaxed by scalar third order contribution involving spin-orbit interaction acting within higher lying perturbing states. This model was later developed further by Burdick.[33-36]

1.7 Intensity Parameterization of Transition between Crystal Field Levels

1.7.1 Static Coupling(SC) Model for Line Transition

The induced electric dipole matrix elements between two states B and B′ of the f^n configuration can be written as :

$$\begin{aligned}\langle B|\hat{m}_p^{(1)}|B'\rangle &= \langle B|-e\hat{D}_p^{(1)}|B'\rangle \\ &= -e\sum_M\sum_M aMa'M'\sum_{T,S,L}\sum_{T'S'L'} h(TSL)h'T'S'L' \\ &\times\sum_{k,q}\sum_{\lambda=even} A_{kq}\Xi(k,\lambda)(-1)^{(q+p)+(J-M)+(S+L'+J+\lambda)} \\ &\times\begin{pmatrix} 1 & \lambda & k \\ p-q & -p & q\end{pmatrix}\begin{pmatrix} J & \lambda & J' \\ -M & q+p & M'\end{pmatrix}\begin{pmatrix} L & \lambda & L' \\ J' & S & J\end{pmatrix} \\ &\times(2\lambda+1)[(2J+1)(2J'+1)]^{1/2}\langle f^N\|\hat{U}^{(\lambda\lambda)}\|f^N T'S'L'\rangle\end{aligned} \tag{1.4}$$

The matrix element in above equation (4) is valid for transitions between two crystal field levels. Because of the radial integrals, the calculation of matrix elements is very tedious and can in fact be done by using some approximations. Axe[37] treated the quantities $A_{kq} \equiv (k, \lambda)$ in equation in equation (4) as adjustable parameter with λ is equal to 2, 4 and 6 and k is restricted to the values of $\lambda \pm 1$. The values of q are determined by crystal field symmetry constraints and lie between 0 and ±k. Porchner and Caro[38] introduced notation $B_{\lambda kq}$ for the intensity parameters.

$$B_{\lambda kq} = A_{kq} \equiv (k,\lambda) \tag{1.5}$$

All the quantities of equation (4) are not included in $B_{\lambda kq}$ parameters and are taken together in a coefficient $\alpha_{\lambda kq}$. When the coefficient $\alpha_{\lambda kq}$ of intensity parameters $B_{\lambda kq}$ have been calculated and when the experimental dipole

strength has been corrected for the magnetic dipole contribution, the $B_{\lambda kq}$ parameters can be determined by a fitting procedure. For a crystal field transition ($B \leftarrow \alpha$) a quadrate can be constructed.

$$\frac{1}{\chi_{ED}}\left[D_{exp} - \chi_{MD} D_{MD}\right] = \left[\sum_{\lambda kq} \alpha_{\lambda kq}^{p\alpha\alpha} B_{\lambda kq}\right] \qquad (1.6)$$

or

$$D_{exp}^{0} = \left[\sum_{\lambda kq} \alpha_{\lambda kq}^{p\alpha\beta} B_{\lambda kq}\right]^{2} \qquad (1.7)$$

Where D_{exp}^{0} is the experimental dipole strength for the magnetic dipole contribution and p is the polarization number. The symbol α and β stands for ground and excited state respectively. In general one has to write down such an equation for each of the M transitions for which a value of the experimental dipole strength is available and $M \geq N$ (N is the number of intensity parameters). The parameters are determined by finding the minimum of a function, which consists of sum of M nonlinear quadratic functions in N variables. The equations to be solved are of the form :

$$\sum_{M} \left| \sum_{\lambda kq} \left[\sum_{\lambda kq} \alpha_{\lambda kq}^{p\alpha\beta} B_{\lambda kq} \right]^{2} - D_{exp}^{0} = 0 \right. \qquad (1.8)$$

The optimised phenomenological intensity parameters depend to a large extent on starting values chosen for those parameters, because the minimisation procedure stops at the first local minimum.

Intensity parameterisation of spectral transitions between crystal field levels for lanthanide doped single crystal have been reported for $LaAlO_3 : Pr^{3+}$(Delsart and Gorller-Walrand et al)[39,40], $LaF_3 : Pr^{3+}$, $Pr_2Mg_3(NO_3)_{12}.24H_20$ (Gorller-Walrand et al)[41], $LiYF_4 : Nd^{3+}$ (Gorller – Walrand et al)[42], $LiYF_4 : Eu^{3+}$ (Fluyt et al)[43], $Na_5Eu(MoO_4)_3$ and $Na_5Eu(WO_4)_3$ (Holsa et al)[44].

The parameterisation scheme given by Judd-Ofelt for J-multiplate transition intensities in terms of T_λ parameters is general and is limited by the assumption of one electron one photon interaction. The parameterisation scheme is independent of the nature of metal ligand interaction. The parameterisation scheme of Axe of describing the intensities of crystal field transition is not general in terms of its applicability. In addition to one electron and one photon assumption, the parameterisation scheme required that the superposition approximation is valid which requires all metal-ligand pair wise interactions to be cylindrically symmetric and independent.[45] The super-position approximation poses problems for lanthanide systems with polyatomic ligands with highly anisotropic charge distribution.

1.7.2 Reid-Richardson Intensity Model

Reid – Richardson[46-50] developed a parameterisation scheme, which is very similar to that given by Newman et al.[45] They pointed out that the intensity parameters can be interpreted and calculated in terms of two intensity mechanism namely STATIC COUPLING (SC) and DYNAMIC COUPLING(DC). In both SC and DC models the interactions are considered

purely electrostatic and thus an overlap between the change distributions between the ligand and central metal ion is neglected. In SC coupling model the electronic configuration of the lanthanide ion is perturbed by the ligands and the ligands produced a static potential of odd parity around lanthanide ion, so the 4f states of mixed parity are formed. Transitions between these states can be polarised isotropically by the Ln^{3+} ion. The basic assumption in the Static Coupling Model is however that the ligands are not perturbed by the radiation field of the incident light. The intermediate perturbing wave functions are fully localized on the lanthanide ion. Judd-Ofelt theory is an example of Static Coupling model.

1.7.3 Dynamic Coupling (DC) Model

In DC model the change in the distribution of the ligand charges under the influence of radiation field of light is taken into account. The electric dipole component of the light induces transient dipoles on the ligands, which in turn induce 4f-4f transitions in lanthanide ions. These are two possibilities, (1) isotropic polarisability and (2) anisotropic polarisability. In the former the ligands are isotropic and ligand-ligand polarisation is cylindrically symmetric and independent. In case of the anisotropic polarisability the ligand are anisotropic.(BO_3^{-3}, NO_3^-, ODA, GSH) and thus lanthanide-ligands interactions cannot be considered cylindrically symmetric. The perturbing wave functions in DC mechanism are localised on ligands. Reid-Richardson used a combination of DC and SC mechanism and made *'ab initio'* calculation of intensity

parameters in such a way that an easy differentiation between SC and DC mechanism can be made. Their intensity parameters A^{λ}_{tp}, the $t=\lambda$ parameter reflect the lanthanide ligand pair wise interactions, which are not cylindrically ellipsoids. These extra parameters are symmetry allowed in all point groups except $C_{\infty v}$.

The static coupling scheme gives rise to A^{λ}_{tp} parameters with λ =2,4,6 are with $t= \lambda \pm 1$ and employing Reid-Richardson's SC and DC models, parametric calculations were made successfully by Burdick et al[51,52] and Chertanov et al.[53] The agreement between the experimental and calculated oscillator strength (P) of transitions between the ground state and $^{2S+1}L_j$ manifolds is good, but the relative intensities of crystal field transitions are still not well produced. Placing the samples in a magnetic field induces optical activity. The differential absorption of left and right circularly polarised light in a longitudinal magnetic field can be measured. In the longitudinal magnetic field, the magnetic lines are parallel to the light beam. This technique is known as MCD (Magnetic Circular Dichroism), which is based upon Zeeman Effect. The simulation of MCD spectrum and calculation of MCD signals do not require more parameters than crystal field and intensity parameters extracted from absorption spectrum.[54,55]

1.7.4 Carnall's $\mathfrak{I}_{\lambda}$ Intensity Parameters and Ω_{λ} Intensity Parameters

These are very commonly used in solution spectral analysis studies. Carnall et al[61] used new parameter T_{λ} and thus described Oscillator Strength as:

$$P_{exp} = \sum_{\lambda=2,4,6} \Im_\lambda \frac{\bar{\nu}_0}{2J+1} \left| \langle f^N \Psi J \| f^N \Psi' J' \rangle \right|^2 \qquad (1.9)$$

The parameter $\Im_\lambda$ (Carnall et al) is related to Judd-Ofelt (T_λ) parameter through

$$\Im_\lambda = (2J+1)cT_\lambda \qquad (1.10)$$

This is essentially only an extraction of $(2J+1)^{-1}$ weighing factor out of the T_λ parameter. The factor c (the speed of light) is used to convert frequency ν_0 into the wane number $\bar{\nu}_0$ ($\nu_0 = c\bar{\nu}_0$). Workers studying absorption spectra of lanthanide complexes in solution[56-60] still universally use these spectral parameters T_λ and $\Im_\lambda$. The parameter Ω_λ is introduced by Axe which is related to $\Im_\lambda$ by

$$\Omega_\lambda = \left(\frac{8\pi^2 mc}{3h} \chi_{ED} \right)^{-1} \Im_\lambda \qquad (1.11)$$

$$\text{or } \Omega_\lambda = \left(1.085 \times 10^{11} \chi_{ED}\right)^{-1} \Im_\lambda \qquad (1.12)$$

The χ_{ED} is the correction factor included in the $\Im_\lambda$ parameters but not in Ω_λ parameters. Similarly Ω_λ parameters are also related to $A^I_{t,p}$ parameters as follows:

$$\Omega_\lambda = \frac{1}{2\lambda+1} \sum_{t,p} \left| A^\lambda_{t,p} \right|^2 \qquad (1.13)$$

1.8 Standard Least Square Fit Procedure

The standard least square method minimizes the absolute differences between experimental and calculated values. This method is much simpler than Chi-square fit method, but has the disadvantage that a small discrepancy in a

large experimental value has the same influence as a large error in small experimental value. Hence the magnitude of T_λ or Ω_λ parameters depend largely on the relative magnitude of the Oscillator Strength of transitions used in the fit. However, the parameter set is able to predict both small and large Oscillator Strength.

$$\Delta^{exp} = \frac{(2J+1)D_{exp}}{e^2\chi_{ED}} \tag{1.14}$$

then,

$$\Delta^{exp} = \Omega_2 U^{(2)} + \Omega_4 U^{(4)} + \Omega_6 U^{(6)} \tag{1.15}$$

The same thing can be used for writing down such an equation for each spectral transition resulting in a system of equation for n transitions.

$$\begin{aligned}
\Delta_1^{exp} &= \Omega_2 U_1^{(2)} + \Omega_4 U_1^{(4)} + \Omega_6 U_1^{(6)} \\
\Delta_2^{exp} &= \Omega_2 U_2^{(2)} + \Omega_4 U_2^{(4)} + \Omega_6 U_2^{(6)} \\
\Delta_3^{exp} &= \Omega_2 U_3^{(2)} + \Omega_4 U_3^{(4)} + \Omega_6 U_3^{(6)} \\
&\cdots\cdots\cdots\cdots \\
&\cdots\cdots\cdots\cdots \\
\Delta_n^{exp} &= \Omega_2 U_n^{(2)} + \Omega_4 U_n^{(4)} + \Omega_6 U_n^{(6)}
\end{aligned} \tag{1.16}$$

We want to find a good estimate for the parameter set (Ω_2', Ω_4',Ω_6') or (T_2', T_4', T_6') The set of equation (16) is of form:

$$Y_1 = a_1X_{11} + a_2X_{12} + a_3X_{13} + \ldots\ldots\ldots\ldots + a_kX_{1k}$$

$$Y_2 = a_1X_{21} + a_2X_{22} + a_3X_{23} + \ldots\ldots\ldots\ldots + a_kX_{2k}$$

$$Y_3 = a_1X_{31} + a_2X_{32} + a_3X_{33} + \ldots\ldots\ldots\ldots + a_kX_{3k}$$

..... (1.17)

$$Y_n = a_1X_{n1} + a_2X_{n2} + a_3X_{n3} + \ldots\ldots\ldots\ldots + a_kX_{nk}$$

The Y_i is the values of the observations and X_{ik} is coefficients and a_i is the unknown parameters. The observational model is a general linear model, because the dependent variable Y_i, is described as a function of several independent variables X_{ik}. The function is a linear function (there are no terms of degree higher than 1). The matrix method is used to solve the problem. The equation (17) can be written in terms of the response random vector containing the response values of n observations:

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ . \\ . \\ y_n \end{bmatrix} \qquad (1.18)$$

the model parameter vector

$$a = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ . \\ . \\ a_n \end{bmatrix} \qquad (1.19)$$

the vector of errors associated with n observations :

$$E = \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ . \\ . \\ \varepsilon_n \end{bmatrix} \tag{1.20}$$

and the n X k design matrix

$$X = \begin{bmatrix} x_{11} & x_{12} & x_{13} & \cdots & x_{1k} \\ x_{21} & x_{22} & x_{23} & \cdots & x_{2k} \\ x_{31} & x_{32} & x_{33} & \cdots & x_{3K} \\ . & . & . & & . \\ . & . & . & \cdots & . \\ x_{n1} & x_{n2} & x_{n3} & \cdots & x_{nk} \end{bmatrix} \tag{1.21}$$

The matrix representation for any set of observation $Y_1, Y_2, Y_3, \cdots Y_n$ becomes

$$Y = Xa + E \tag{1.22}$$

Let the matrix

$$\hat{a} = \begin{bmatrix} \hat{a}_1 \\ \hat{a}_2 \\ \hat{a}_3 \\ . \\ . \\ \hat{a}_n \end{bmatrix} \tag{1.23}$$

Equation (230) represents the matrix of the least square estimates for the parameters of the general linear model. The matrix can be calculated as follows:

$$\hat{a} = (\chi^T X)^{-1} X^T Y \tag{1.24}$$

Where χ^T is the transpose of X. The matrix χ is an n X k matrix. X^T is a k x n matrix and $\chi^T X$ is a K x K matrix with $n \geq k$. The matrix solution gives the set of parameter estimates d_1, d_2 .....d_k in general linear model that minimizes $\sum_i (y_i - \bar{y}_i)^2$ for the data collected.

After the parameter estimates (T_2, T_4, T_6 or Ω_2, Ω_4, Ω_6) have been obtained D'_{ED} or P'_{ED} can be calculated

$$P'_{ED} = e^2(\Omega_2 U_i^{(2)} + \Omega_4 U_i^{(4)} + \Omega_6 U_i^{(6)} \qquad (1.25)$$

$$RMS = \left[\frac{\text{Sum of square of deviation}}{\text{Number of observation} - \text{Number of parameters}}\right]^{1/2} \qquad (1.26)$$

1.9 Chi-Square Method

If one wants to weigh each value of dipole strength or Oscillator Strength by its own uncertainty, the Chi-Square method has to be chosen as the minimizing quantity and well explained by Caird et al[61], Seeber et a1[62] and Auzel et al.[63] This method minimizes the relative difference between the experimental and calculated values rather than their absolute differences. The uncertainty in the measured intensity of each transition is often difficult to estimate. Goldner and Auzel[63] take a constant fraction of the experimental Oscillator Strength for the uncertainty. The RMS of this method is independent of the number or magnitude of the included transition. The Chi-square method is analogous to the matrix calculation presented for the standard least square method except that the design matrix X is now given as:

$$X = \begin{bmatrix} \frac{x_{11}}{\sigma_1} & \frac{x_{12}}{\sigma_1} & \cdots & \frac{x_{1k}}{\sigma_1} \\ \frac{x_{21}}{\sigma_2} & \frac{x_{22}}{\sigma_2} & \cdots & \frac{x_{2k}}{\sigma_2} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{x_{n1}}{\sigma_n} & \frac{x_{n1}}{\sigma_n} & \cdots & \frac{x_{nk}}{\sigma_n} \end{bmatrix} \qquad (1.27)$$

And the vector Y with the observation is now given by:

$$Y = \begin{bmatrix} \frac{y_1}{\sigma_1} \\ \frac{Y_2}{\sigma_2} \\ \cdot \\ \cdot \\ \frac{y_n}{\sigma_n} \end{bmatrix} \qquad (1.28)$$

The fit is applied to the quantities P/σ_i where σ is the uncertainty in the experimental Oscillator Strength (P_{exp}). The error of a parameter is given by square root of the respective diagonal matrix elements of the matrix $(X^T X)^{-1}$.

Judd-Ofelt theory though is quite commanding yet for Pr^{3+},this theory does not seem work well. Difficulties are experienced if one tries to fit both the $^3H_4 \rightarrow {}^3F_3, {}^3F_4$ and $^3H_4 \rightarrow {}^3P_{2,1,0}$ transition groups with the same set of T_λ intensity parameter. Instead of determining parameter set with the inclusion of all the transitions the $^3H_4 \rightarrow {}^3F_3, {}^3F_4$ transitions can be excluded. A number of authors preferred to exclude $^3H_4 \rightarrow {}^3P_2$ transition.[64] Eyal et al[65-66] and Quimby[67] have included Ω_3 and Ω_5 parameters in the intensities of 4f - 4f transitions of

Pr^{3+} while Florez et al[68] also included odd intensity parameters and also include $^3H_4 \rightarrow {}^1I_6$ transition in the fitting procedure.

It should be mentioned that the hypersensitive transition for Pr^{3+}, $^3H_4 \rightarrow {}^3F_2$ has to be included in the fit of Pr^{3+}, because otherwise a negative value of T_2 will be found which has no relevance. Extraction of reliable Ω_2 parameter is often a problem for Pr^{3+}, because $^3H_4 \rightarrow {}^3F_2$ transition is situated in infrared spectral region and thus cannot be observed in aqueous and in aquated organic solvent in absorption spectrum in UV-Visible region. In order to obtain more reliable intensity parameters Quimby and Miniscalo[69] introduced a modified Judd-Ofelt theory in which luminescence branching ratios are included in the fit. We have found that by including T_5 and T_3 parameters and by including $^3H_4 \rightarrow {}^1I_6$ transition. Oscillator Strengths for computing purposes improves the closeness between the observed and calculated oscillator strength of 4f – 4f transition.

1.10 Hypersensitivity

The environment does not affect the intensities of the induced dipole transitions in lanthanides significantly. The dipole strength of particular transition of the lanthanide(III) ion in different matrices does not vary more than a factor two or three. However, a few transitions are very sensitive to the environment and these are much more intense in lanthanides complex, than that for lanthanide (III) aquo ion complex.[70-72]

The high sensitivity of spectral intensities for ligand environment as a general phenomenon was first noticed by Moeller et al[73-75] for β-diketonate and EDTA complexes of Nd^{3+}, Ho^{3+} and Er^{3+} much before the advent of Judd-Ofelt Theory. Jorgensen and Judd have called such transitions HYPERSENSITIVE and these transitions obeyed selection rules $|\Delta S|=0$; $|\Delta L|\leq 2$; $|\Delta J|\leq 2$ and these rules are the same as the selection rules for pure quadrupole transitions. But calculations have revealed that the intensities to have a quadrupole character, therefore, hypersensitive transitions have been called pseudoquadrupole in character.[76-77] Karraker[78] has investigated the hypersensitive transitions of Nd^{3+}, Ho^{3+} and Er^{3+} and considered the absorption spectra of six, seven and eight coordinated β-diketonates in nonaqueous media to determine effect of coordination number on the intensity and fine structure of the spectra. The β - diketonate ligands were chosen because all of them bind to lanthanides (III) in bidentate manner involving two oxygen donor atoms yielding six member chelate ring. Thus the two main variables were coordination number and geometry of the bonded ligands. Solvents chosen were with low polarity to reduced the solvent effect to the crystal field splitting of the lanthanide ion. His excellent study showed that the hypersensitive transitions showed differences that were characteristic, for the coordination and symmetry of the lanthanide ion. The conclusion was based on following findings:

i) There is a difference between the appearance of the absorption bands for hypersensitive transitions between six, seven and eight coordinated lanthanide ion;

ii) Addition of unidentate ligand to solution of six or seven coordinated complexes results in changing the spectra to spectra resembling those of seven or eight coordinated complexes.

iii) The removal of water from the solution of hydrated complexes results in changing the spectra to spectra resembling the spectra of lower coordination lanthanide;

iv) There is a correlation between the intensities of hypersensitive transition and coordination number of lanthanide.

In his latter paper Karraker[79] investigated the effect of strong aqueous chloride on perchlorate solution on hypersensitive transitions. The change in the shape of the band was considered diagnostic marker for the change in the coordination number of lanthanides.

Chopin et al[80] have made excellent contribution into the absorption spectral intensities of lanthanide complexes in solutions. While systematically analyzing Ln(III) complexes with Poly (amino carboxylic) acids they have suggested different sequence for oscillator strength of hypersensitive transitions for Nd^{3+} and Ho^{3+}. The chelates order of oscillator strength was

EDTA>HEDTA>DTPA>DCTA>NTA..... for Nd(III)

HEDTA>DTPA>NTA>EDTA>DCTA.....for Ho(III)

However these workers could not give any explanation for different behaviour of Nd^{3+} and Ho^{3+}. Fellow and Choppin[80] and Choppin[81], however found a good correlation between the oscillator strength and sum of the ligand pK_a for dibasic acid. These workers made three generalizations concerning intensity of hypersensitive transitions :

i) An increasing basic character of coordination ligand results in increasing ligand absorption intensity;

ii) Decreasing metal ligand bond distance results in intensity enhancement; and

iii) The greater is the number of more basic ligand greater is the degree if enhanced intensity.

During our solution spectral studies on Pr(III), Nd(III) and Er(III) complexes with variety of ligands we also have made a number of generalizations. The alkoxides and bimetallic alkoxides of lanthanides in nonpolar solvents like benzene gave quite intense 4f-4f bands and the intensities of both hypersensitive as well as some of the non-hypersensitive (not obeying $|\Delta J|$ selection rules) transitions are affected very significantly by the bulkiness of the alkoxy ligands.

The primary < secondary < tertiary alkoxides group,

n-butanol < isobutanol < secondary butanol < tertiary butanol,

n-pentanol < secondary pentanol < tertiary pentanol < neo pentanol

The branched alkyl group also were responsible for the lowering of the molecular complexity of metal alkoxides irrespective of lanthanide (III) ion. The solvent effect of these alkoxides was also quite prominent. The polar solvents like DMF, DMSO enhanced the intensities of the both hypersensitive and pseudohypersensitive transitions again irrespective of the nature of metal.

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CHAPTER 2
Review on lanthanides : Biological activity and coordination phenomena

Lanthanide coordination chemistry in solution is of great importance with the increase use of lanthanide as probes in the exploration of the structural functions of biomolecular reactions.[1]. This is particularly due to their ability to replace Ca(II) ions in a specific manner.[2] Lanthanides have no known inherent biological function but only trace amounts have been detected in whole body analysis.[3] Lanthanide salts were first investigated in clinical trials for antimicrobial, anticoagulant and other pharmacological properties in the early part of the century.[4-6]

Misra et al[7] had proposed a modified method for the evaluation of spectral parameters (i.e, energy interaction, spin-orbital interaction, bonding, nephelauxetic, oscillator strength and Judd-Ofelt parameters) of 4f - 4f transitions in Pr (III) and Nd(III) complexes. Misra and Somerer[8] had studied the ligand mediated pseudohypersensitivity of the $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and

$^3H_4 \rightarrow {}^1D_2$ transitions of Pr(III) complexes in solution media. They had reported that such transitions exhibit substantial intensification as well as a wide variation of oscillator strength by employing absorption difference, comparative absorption spectrophotometry and quantitative analysis of 4f-4f spectra of Pr(III) complexes with ligands possessing varying structural features and binding capabilities. These transitions cannot be considered hypersensitive as they do not follow the selection rule. They had also considered the solution spectra of 173 species and reported the high sensitivity of the Pr(III) transitions, viz:- $^3H_4 \rightarrow {}^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ and they had termed the unique sensitivity of such transitions as 'Ligand Mediated Pseudohypersensitivity'. K. Binnemans[9] discussed the reliability and sensitivity of Judd-Ofelt intensity parameter T_λ (λ=2,4,6) by comparing experimental absorption spectra with simulated spectra.

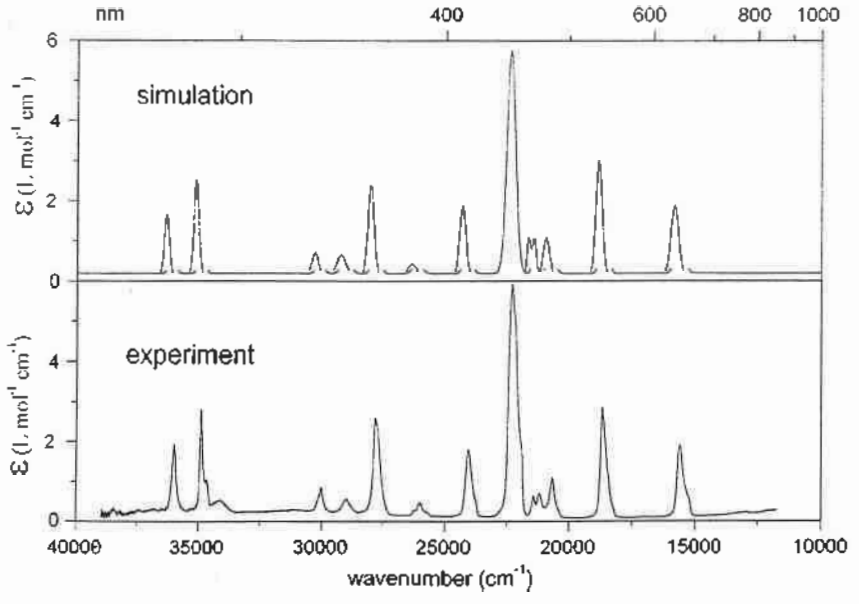

Figure 2.01 : Experimental and simulated absorption spectrum of ZBLAN:Ho^{3+} glass at ambient temperature

Misra et al[10] had studied about the preparation and characterization of some praseodymium haloacetates and investigation of their electronic spectra in different non-aqueous solvents (DMF, DMSO, CH_3OH and their equimolar mixtures). It has been reported that the absorption spectra of praseodymium monohaloacetates when recorded in non-aqueous polar solvents like CH_3OH, DMF and DMSO and in their equimolar mixtures showed significant changes in the intensities of the absorption bands. The intensification of the bands had been interpreted in terms of increased interaction of the 4f-orbitals with ligand orbitals. They had also reported that praseodymium monohaloacetates form complexes with aprotic dipolar solvents DMF and DMSO and complex formation is responsible for intensification of the bands in these media. In general, they had found that the increase in the intensity was greatest with DMF and least for methanol. The intensity (oscillator strength, P) data with DMF and DMSO were quite similar which can be correlated with greater ligating strengths of DMF and DMSO as compared to that of methanol.

Jerico et al[11] had studied the behaviour of the phenomenological 4f-4f intensity parameters in compounds of the Nd^{3+} ion with Amino Acids (glyceine, L-aspartic acid, L-glutamic acid, L-histidine, DL-malic acid and Aspartame) in aqueous solution, as a function of the pK values and partial charges on the oxygen of the carboxylate groups of these molecules. They had reported that the intensity

of the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^4G_{7/2}$ transitions increases as the pH increases up to approximately 5.4 value. For pH values above 5.5, the Nd^{3+} ion hydrolyses. Among the T_λ parameters, in general, T_2 is the most sensitive to the coordination geometry and the characteristics of the ligands. They had also examined the behaviour of T_2 with the ligands pK and found that T_2 has varied linearly with P^k_1 provided the monocarboxylic and dicarboxylic species were considered separately. They had also examined the behaviour of T_2 with the average value $\langle P^k \rangle = (P^k_1 + P^k_2)/2$, since at pH ~ 5 both carboxylic groups are expected to be equally deprotonated. In this case, T_2 has increased with $\langle P^k \rangle$, but not linearly. Tater et al[12] had studied electronic spectral studies on Nd^{3+} doped sulphoanilide system. It also provides useful information regarding metal-ligand interaction and change in symmetry around lanthanide ion. Misra et al [13] had studied about the interactions of praseodymium and neodymium with nucleosides and nucleotides in different stoichiometry in water and water-DMF mixtures by employing absorption difference and comparative absorption spectrophotometry. These studies indicated that the binding of the nucleotide is through phosphate oxygen in a bidentate manner and the complexes undergo substantial ionisatioin in aqueous medium, thereby supporting the observed weak 4f-4f bands and lower values for Nephelauxetic effect (β), bonding parameter ($b^{1/2}$) and percent covalency (δ) parameters derived from coulombic and spin-orbit interaction parameters.

Ryan and Jorgensen[14] had studied the absorption spectra of octahedral lanthanide hexalides particularly about Ce (IV), Sm (III), Eu (III), Tm (III) and Yb (III) hexalides. They had found that the apparent optical electronegativities are somewhat higher than for the analogous halide complexes in ethanolic solution. Misra et al [15] had investigated about the synthesis and electronic spectral studies of mixed soaps, chloride mixed soaps and alkoxide mixed soaps of Pr (III) and Nd (III). As expected the values of F_k and ξ_{4f} for the Pr (III) and Nd (III) complexes are lower than the corresponding parameters of free ions. It is quite evident that ternary mixed trisoaps of the type M (OOCR) (OOCR′) (OOCR″) exhibit maximum nephelauxetic effect and lowest F_2 value. The chloride mixed disoaps have lowest nephelauxetic effect which is quite understandable in the presence of electronegative Cl^- ion bonded strongly to hard lanthanide metal ion. The isopropoxide mixed disoaps and t-butoxide mixed disoaps have the values of nephelauxetic effect ($1-\beta$) and mixing coefficient ($b^{1/2}$) which are intermediate between those of the comparatively covalent ternary mixed trisoaps M (OOCR) (OOCR′) (OOCR″) and comparatively ionic chloride mixed disoaps. In case of Pr (III) compounds, the negative values of T_2 parameter are of little significance while in case of Nd (III) compounds, the T_2 parameters are of great significance.

Misra[16] had done studies on Pr (III) and fluorouracil, fluorocystosine, fluoroadinine, fluorothymine, fluorouridine, fluorocytidine, fluoroadenosine and fluorothymidine systems at pH ~ 5.5 and in different stoichiometries in 80% DMF

by employing absorption difference and comparative absorption spectrophotometric technique. Magnitudes of spectral parameters and their variation have provided information on the binding mode of these biomolecules in terms of outer and inner sphere complexation, degree of covalency and extent of 4f-orbital involvement. The analysis of the isolated solid complexes had suggested octa- and nona-coordination for Pr(III) in fluorinated nucleic bases and fluorinated nucleoside complexes. Joseph et al[17] had reported about the absorption spectral studies on the interaction of adenine, adenosine, adenosine 5'-mono-adenosine 5'-di- and adenosine 5'- triphosphates with Pr(III) in different stoichiometries and at varying hydrogen ion concentrations. The sharp bands in the spectra had been analysed by Gaussian Curve analysis and various spectral parameters have been computed using partial and multiple regression methods. The studies of the crystalline complexes of the type: Pr (nucleotide)$_2$ (H_2O) (where nucleotide = AMP, ADP & ATP) indicate that the binding of the nucleotide is through phosphoric oxygen. Henrie et al[18] had shown that the low magnitudes of oscillator strengths indicate outer sphere complexation while high values indicate inner sphere complexation. For the present complexes T_2, T_4 and T_6 parameters have low values, indicating thereby the predominance of outer sphere complexation.

Misra et al [19] had recorded absorption spectral intensity data in a series of structurally related Pr (III) and Nd (III) complexes with nitrogen, phosphorous, arsenic, bismuth and oxygen donor ligands (L) [L-being triphenylamine (TPA),

triphenylphosphine (TPP), triphenylphosphineoxide (TPPO), triphenylarsine (TPAs) and triphenyl bismuthine (TPBi)] in DMF, methanol and acetonitrile. The significant variation in the intensities of certain absorption bands and perturbation on f-f transition intensities which are clearly apparent in Judd-Ofelt. (T_λ) parameters computed for the different complexes under different experimental conditions are caused by the different ligands and solvents. The relative sensitivities of the 4f-4f transitions and (T_λ) parameters and the specific correlation between relative intensities, ligand structures and nature of Ln(III)-ligand interaction are shown by the variation of oscillator strengths of different 4f-4f transitions and the computed values of Judd-Ofelt electric dipole intensity (T_λ) parameters. Indira[20] had one studies involving 4f-4f transition of Nd (III) and different diols (butane1, 4-diol, butene1, 4-diol and butyne1, 4diol) by employing intensity difference and comparative absorption spectrophotometric technique in DMF and Methanol as well as in equimolar mixtures of DMF+CH_3CN, DMF+CH_3OH, DMF+dioxane, CH_3OH+CH_3CN and CH_3CN+dioxane. The involvement of π-electron density of diols in complexation with Nd (III) are revealed from the correlations made from the plot of Oscillator strength (Pobs) against T_λ parameters. The absorption spectral bands of Nd (III)-diols in DMF solvent clearly show that the presence of single, double and triple bonds in diols affect the energiés and oscillator strength of these 4f-4f bands. It has been found

that the sequence of the three diols in complexation is butane diol <butene diol <butyne diol.

Lakshman and Buddhudu[21] had calculated the values of the Slater-Condon (F_2, F_4, F_6), Racah (E^1, E^2, E^3) and Lande (ξ_{4f}) coefficients, the Nephelauxetic ratio (β), the bonding parameter (β) and the Judd-Ofelt Intesity (T_λ) parameters from the reported absorption spectra of Pr^{3+}, Nd^{3+} and Er^{3+} ions in an aprotic solvent $SeOCl_2$ acidified with antimony pentachloride. They had suggested that the nature of bonding is covalent in the laser liquid (for Pr^{3+}, Nd^{3+} and Er^{3+} ions). Peacock[22] had studied the sensitivity of completed Judd-Ofelt parameters to the particular transitions used. It appears to be necessary to associate a separate value of T_2 with each hypersensitive transition. Hussain et al [23] had reported about the optical absorption and NMR studies of trivalent lanthanide complexes with 2,2′-bipyridine (bpy). The paramagnetic and intramolecular shift ratio have been recorded and analysed and suggested that the paramagnetic shift is predominantly dipolar in origin. They had also studied the electronic spectra Pr, Nd, Ho, Er and Dy complexes in different solvents viz, MeOH, pyridine, DMSO and DMF) and revealed that the chemical environment around the lanthanide ion has great impact on f-f transitions and any change in the environment results in modifications of the spectra. They had also determined the oscillator strength for the hypersensitive and non-hypersensitive transitions. It has been found that the largest increase in the oscillator strength is found in pyridine and this could be related to the ligand

polarization effect and the smallest increase in the oscillator strength in DMSO. It has been found that the values of $b^{1/2}$ and δ are highest for pyridine, which follows that it is the strongest ligand in a nephelauxetic sense and the complexes in this solvent show largest covalency.

Khan and Iftikhar[24] had studied the interaction of trivalent lanthanide thiocynates and 2, 2'-bipyridyl in ethanol and this results in the formation of the complexes viz; $[Ln\ (bpy)_n\ (SCN)_3\ (H_2O)]_y$ where Ln stands for La (n=3, x=1, y=0), Pr (n=3, x=y=0), Nd (n=3, x=0, y=1), Sm, Eu (n=2, x=1, y=0), Dy, Er (n=2, x=2, y=1), Ho and Yb (n=2, x=2, y=0). It has been found that the complexes are non-electrolyte in methanol and the three triocynates are inside the first co-ordination sphere, the La-complex is ten-coordinate, the Sm and the Eu complexes are eight-coordinate while others are nine-coordinate. They had also analysed the chemical shifts and the paramagnetic shifts are found to be predominantly dipolar in nature. The Pr, Nd, Sm and Eu are isostructural in methanol. Khan et al[25] had done absorption spectroscopic studies on the mixed ligand complexes of Pr (III) and Nd (III) with 2,2'-bipyridyl and thiocyanate in pyridine, DMSO, DMF and methanol. They had calculated the oscillator strengths for the hypersensitive and non-hypersensitive transitions and had compared with 1,10-phenanthroline complexes and shown that bipyridyl is a weaker ligand than phenanthroline for these ions. It has also been found that pyridine is the most effective ligand in promoting 4f-4f intensity. Indira[26] carried out comparison of electric-dipole

intensity parameters for a series of structurally related Nd(III) complexes with ureas and thioureas in non-aqueous media. Fields and Rajnak[27] had correlated the experimentally determined band intensities in the solution absorption spectra of the trivalent lanthanides with a theoretical expression derived by Judd. The spectra were measured in a single medium, dilute acid solution, and, in most cases, in the range ≈ 6000-50,000 cm^{-1}. They had also discovered the variation of the intensity parameters.

Gunnlaugsson et al [28] had reported about the synthesis, structural and biological evaluation of Gly, Ala based lanthanide macrocyclic conjugates as supramolecular ribonuclease mimics. Zhang et al[29] had done hydrothermal synthesis and crystal structures of three novel lanthanide coordination polymers with glutarate and 1, 10-phenanthroline. They had prepared the first series of lanthanide coordination polymers with glutarate (glu) and 1, 10-phenanthroline (phen), $[Nd_2 (glu)_3 (phen)Cl]_n$1, [Tb (glu) (phen)$Cl]_n$2 and [Ho (glu) (phen)$Cl]_n$ 3 by hydrothermal reaction and they are two different conformations for glutarate ligands, the gauche- and anti-forms. Nd (III) ions are bridged by glutarate ligands in three modes to form 2D layer structure. Phen ligand coordinate to Nd (III) ions in chelating mode and protrude from the polymeric layer in two different directions. There exists two types of π-π interactions between two adjacent layers. In complex 2, Tb (III) ions are connected by glutarate ligands into 1D chain structure. Phen ligands coordinate to Tb (III) ions in chelating mode and locate at

both sides of the chain. It has been found that the C-H...O, C-H...Cl weak hydrogen bonds and π-π slacking interactions between chains result in 3D supramolecular structure. They have found that complex 3 is isostructural with complex 2 by single-crystal x-ray diffraction analysis. Subhan et al[30] had reported the simultaneous observation of low temperature 4f-4f and 3d-3d emission spectra in a series of Cr (III) (ox) Ln (III) assembly.

Wang et al [31] had studied the complexation of trivalent lanthanides with aromatic (mellitic, pyromellitic, hemimellitic, trimellitc, trimesic, phtalic, isopthalic, terephthalic and benzoic) carboxylic acids by employing luminescence and absorption spectroscopic methods. They had also found that both the luminescence spectra and decay constants under the conditions of this study, mellitate, pyromellitate, hemimellitate, trimellitate, trimesate and terephthalate form 1:1 complexes while phthalate, isophthalate, benzoate form 1:1 and 1:2 complexes. The carboxylate ligands with adjacent carboxylates group are bidentate and replace two water molecules upon complexation. It has also found that benzoate and terephthalate are unindented while isophthalate and trimesate replace approximately 1.5 H_2O molecules, suggesting greater binding capability of these ligands due to the contribution from the non-binding carboxylate groups. They had also proposed that ligand polarisability along with other factors are responsible for the variation in oscillator strength in these complexes. Wang and Xie [32] had reported about synthesis and crystal structure of a novel praseodymium

complex with β-alanine: $\{[Pr_2(alanine)_6\ (H_2O)_4]\ [(ClO_4)_6\ H_2O]\}_n$. The structure of this complex comprises of two kinds of polymer chains, both with dimeric repeat units. In each dimeric unit, two praseodymium ions are connected by four carboxyl groups from β -alanine, two using simple bridges and two using tridentate bridges. A symmetry centre exists in each dimeric unit. The other two carboxyl groups link the units to each other by simple bridges. With two coordination water molecules for each central ion, the praseodymium ions are nine-coordinated, forming distorted, monocapped, square antiprism polyhedrons. They had also reported that β-alanine-praseodymium complex exhibits significant differences in both composition and structure than α–alanine lanthanide complex, usually with the core formula $[Ln\ (\alpha\text{ -alanine})_4\ (H_2O)_8]^{6+}$. Since the β -alanine ligand is more slender than α -alanine, it is expected that β -alanine forms more compact structural complexes than α -alanine.

Misra [33] had studied the absorption spectral intensity data for multiplet to multiplet electronic transitions in a series of structurally related Nd (III) complexes of the type, $Nd(diket)_3(N)_2$ (where diket is 1-phenyl-1,3-butanedione benzoylacetone, bzac), 1,3- diphenyl- 1,3-propanedione (dibenzoylmethane, dbm) and 4,4,4-trifluoro-L-(2-thienyl)-1,3-butenedione(theonyltrifluoroacetone, ttfa) and $(N)_2$ stands for two molecules of unidentate nitrogen ligands : pyridine, 2-chloro-, 2-bromo-, 2-acetyl-, 3-acetyl-, 4-acetyl-pyridine or one mole of bidentate

2,2`-bipyridine or O-phenanthroline) which have been recorded in MeOH, DMF, acetonitrile and isopropanol. They had also suggested specific correlations between the relative intensities, ligand structure and nature of Nd (III) –ligand interaction by studying the variation of oscillator strengths of different 4f-4f transitions and computed values of electric dipole intensity and Judd-Ofelt parameters(T_λ). Zhao et al [34] had reported the synthesis of lanthanide complexes with L-isoleucine : X-ray crystal structure of $[Nd_2(I\text{-}leu)_4(H_2O)_8][ClO_4]_6$. They had synthesized two lanthanide complexes, $Ln_2(I\text{-}leu)_4(ClO_4).8H_2O$ in aqueous solution (where Ln = Nd or Er, I-leu = L-isoleucine). They had determined the crystal structure of the Nd – complex by X-ray diffraction. The complex is a binuclear complex, each neodymium ion is coordinated by four carboxylic oxygen atoms from four L-isoleucine and four oxygen atoms from water, forming a square antiprism coordination polyhedron. They had also reported that the crystal structure of the isoleucine complex has some similarities with those of alanine and phenylalanine complexes. For example, they are all dimeric molecules, eight-coordinated and have a C_2 symmetry axis.

Inomata et al[35] had reported the synthesis and crystal structure of lanthanide metal complexes with N,N-bis(2-hydroxyethyl)glycine and they are characterized by means of IR spectra, magnetic susceptibility, thermal analysis and powder X-ray analysis. They had reported that this complexes appear as two types : $[M(bheg)_2]Cl.3H_2O$ and $M(bheg)_2(CH_3COO)(H_2O)_4$ (M : La, Ce, Nd).

They had determined the crystal and molecular structure of $[La(bheg)_2]Cl.3H_2O$ by a single crystal X-ray diffraction method. The central lanthanum atom is nine – coordinated with a face – centered trigonal prism geometry. The structure of this complex consists of a one - dimensional polymer bridged by carboxylato oxygen atoms. This complex has two types of carboxyl groups : one works as a bidentate ligand and bridges to two lanthanum atoms in anti – anti type. There are six intramolecular and twelve intermolecular hydrogen bond. The complex molecules are connected to each other in three dimensions by these intermolecular H – bonds. Zou et al[36] had studied the synthesis and structure of carboxylate-bridged polynuclear Copper (II):Lanthanum(III) ring : $[La(H_2O)_5\ (CuL)_2][CuL].8H_2O$. They had prepared the complex, $[La(H_2O)_5(CuL)_2]\ [CuL].8H_2O$ by the reaction of the Na[CuL] (where L = Schiff base derived from 5-bromosalicylaldehyde and glycylglycine) with $LaCl_3.nH_2O$. The structure of the title complex is such that it contains ring like hexanuclear $[La_2(H_2O)_{10}(CuL)_4]^{2+}$ cation.

Gheorghe et al[37] had reported new binuclear model compounds for the study of the 4f-4f exchange interaction. Zhang and Wang[38] had studied and investigated and measured the absorption spectrum of Neodymium (III) (Nd^{3+}) doped in poly(methylmethacrylate). They had found that the nephelauxetic effect in the spectrum had been compared to other spectra of Nd^{3+} doped in various matrices. By using the Taylor series expansion which is based on the assumption that the energy separation between J levels of the $4f^n$ configuration is a function of F_2, F_4,

F_6 and ξ_{4f}, they had calculated the Slater- Condon parameters (F_2, F_4, F_6) and Lande parameter. They had reported that the nephelauxetic parameter can be related to the covalency factor by

$$b^{1/2} = \left[\frac{1-\beta}{2}\right]^{1/2}$$

indicating that as β decreases, $b^{1/2}$ increases, the 4f–ligands mixing increases, the degree of covalency increases and the nephelauxetic effect exhibits a corresponding increase. Costes, Novitchi, Lebrun[39] had reported the synthesis and characterization of new heterodinuclear (4f, 4f') lanthanide complexes. They had synthesized heterodinuclear complex from the reaction of 3-ethoxysalicylaldehyde and tris (2-amino ethyl) amine in which the La ions are coordinated in the inner N_4O_3 and the outer sites. Introduction of the second lanthanide ion as a trifluroacetate salt yields heterodinuclear entities which are soluble enough to be characterized by electrospray mass spectrometry techniques. Bukietynska and Choppin[40] had investigated the environmental effects of nitrate, sulfate and α-picolinate anions on f-f transitions of lanthanide ions in aqueous solution.

Zinner and Brito[41] had reported about the synthesis and properties of complexes between lanthanide trifluoroacetates and 2-picolline-N-oxide (2-PicNO). They had described the complexes of lanthanide trifluroacetates with 2-piotine-N-oxide (2-PicNO) with composition Ln $(CF_3COO)_3$. 2 (2-Pic-NO). they were characterized by elemental analysis, electrolytic conductance measurements,

x-ray powder patterns, IR and absorption (neodymium) and emission (europium) spectra. They had grouped the compounds in 3 isomorphous series: (a) La, Pr (b) Nd, Sm and (c) Eu, Lu, Y. They behave as non-electrolytes in CH_3CN. They had suggested two types of coordination of the anion and coordination of 2-PicNO through the oxygen. Electrostatic interaction has been indicated from the absorption spectra. Benetollo et al[42] had reported about the coordination chemistry of lanthanides with Cryptands: An x-ray and spectroscopic study of the complex, $Nd_2(NO_3)_6[C_{18}H_{36}O_6N_2].H_2O$. They had synthesized the complex $Nd_2(NO_3)_6[C_{18}H_{36}O_6N_2].H_2O$ by reacting neodymium nitrate hexahydrate with the cryptand <222> in methanol. They were analysed by single crystal x-ray diffraction. They had reported that the compound contains the cations $[Nd<222>(NO_3)]^{2+}$ and the anions $[Nd(NO_3)_5.H_2O]^{2-}$ and is isostructural with the samarium analogue.

Bukietynska and Mondry[43] had investigated the spectral properties of Nd^{3+} - EDTA solutions at different Nd^{3+} EDTA concentrations within a broad pH region. In order to investigate the formation and the type of bonding in the Nd^{3+} - EDTA species, the analysis of the oscillator strength values of the 'hypersensitive' $^4G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition and of the Judd-Ofelt intensity parameters. They had suggested a relatively complete model of the Nd^{3+} - EDTA coordination by the correlation of these results with NMR and kinetic data. Kamenskaya and Mikheev[44] had also investigated about the coordination compounds of divalent

lanthanides with crown ethers. Santos et al[45] had reported about the crystal structures of Neodymium and Holmium Trifluoromethane sulfonate Enneahydrated. Fox et al[46] had studied about praseodymium nitrate and neodymium nitrate complexation with organophosphorus reagents in supercritical carbon-dioxide solvent. Mehta et al[47] had explored heterobimetallic complexation of lysozyme (HEW) with hard metal ions Pr (III)/Nd (III) and soft metal ion Zn (II) using absorption difference and comparative absorption spectroscopy involving 4f-4f transitions in aquated organic solvents. They had correlated the changes in the oscillator strengths of different 4f-4f bands and experimentally determined Judd-Ofelt (T_λ) parameters with the binding of lysozyme with the two chemically different metal ions Pr (III)/Nd (III) and Zn (II) in different aquated organic solvent. They had recorded the comparative absorption spectra of Pr (III)/Nd (III) in aqueous and aquated organic solvents at pH 0.6, 1.4, 2.0, 4.0 and 6.0 and they had calculated intensity parameters from the observed 4f-4f bands using partial and multiple regression analysis (Misra et al, 1980, 1992, 1993, 1994 and 1997). They had investigated and reported that the binding of lysozyme and Pr (III)/Nd (III) is stronger in acidic medium i.e, pH less than one, but no significant change is observed upto pH 6.0. When pH increases from 0.6 to 6.0, the intensity data shows some hypochromacity in the observed 4f-4f bands of Pr (III) and Nd (III). They had also reported that in 50 : 50 DMF – water, the change in the oscillator strength values were meager while noticeable effect was seen

when solvent solvent was 70 : 30 DMF – water. Not only this they had also reported that similar observations were found in aquated acetonitrile, aquated methanol and aquated dioxane. From these, they had concluded that solvent effect are more marked on the complexation as compared to the effect of pH (0.6 to 6.0).

Issa et al[48] had described the synthesis and structural elucidation of some lanthanide – thioschiff base complexes. The structures of the complexes had been characterized by elemental analysis, IR, ^{1}NMR and thermal analysis. The results indicate the formation of 1 : 2 (M : L) complexes with the general formula $(ML_2.H_2O.X)2H_2O$ where M = trivalent Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er and Yb; HL (or H_2L) = thioschiff base and X = ClO_4- or Cl^- ion. They had proposed C.N's 6 and 8 for the lanthanides in these complexes. Takahashi and Ishiguro[49] had reported about the inner-sphere and outer-sphere complexes of Yttrium (III), Lanthanum (III), Neodymium (III), Terbium (III) and Thulium (III) with halide ions in N, N-dimethylformamide. Habenschuss and Spedding[50] had studied about the coordination (hydration) of rare earth ions in aqueous chloride solutions from X-ray diffraction in $SmCl_3$, $EuCl_3$ and series behavior. They had investigated and reported that inner sphere water coordination of the ions in aqueous solutions decreases from 9 to 8 due to the decreasing rare earth ionic radii. The ions La^{3+} through Nd^{3+} are nine coordinated, those between Nd^{3+} and Tb^{3+} are transitional between nine and eight, and those from Tb^{3+} to Lu^{3+} are eight coordinated.

Kumar and Rao[51] had reported studies on some rare-earth metal complexes: Ten- and six- coordinated complexes of an unsymmetrical amino acid derivative. They had synthesized and characterized 2, 4-Dihydroxy benzaldehyde (N-benZoyl) glycyl hydrazone, H_3dhbbgh. They had also synthesized rare earth metal complexes of the empirical formulae, [Ln (H_3dhbbgh)$_2$ Cl_2]Cl.nH_2O and [Ln (dhbbgh) (H_2O)$_2$], where Ln = La (III), Pr (III), Nd (III), Sm (III), Eu (III), Gd (III), Tb (III), Dy (III) and Y (III) and they are characterized by elemental analyses, molar conductances, magnetic susceptibilities, electronicx, IR and NMR spectral studies. They had calculated various bonding parameters (β, $b^{1/2}$, δ% and η) from the electronic spectra of Pr (III), Nd (III), Sm (III) and Dy (III) complexes had suggested that there is a weak covalent bond between the metal and ligand. The experimental values and the theoretical values of the oscillator strength and the Judd-Ofelt Intensity parameters (T_λ = 2, 4, 6) are in good agreement. They had proposed C.N's ten and six for the Ln (III) ions in the adduct and deprotonated complexes respectively on the basis of the spectral profiles of the hypersensitive transitions ($^4I_{9/2} \rightarrow {}^4G_{3/2}$, $^4G_{7/2}$). Srivastava et al[50] had studied about the lanthanide complexes of 4-(N-Acetyl)-amino antipyrine. They had synthesized a series of new complexes of lanthanide (III0 chlorides and bromides with 4-(N-acetyl) amine antipyrine (NAAA) and they are characterized by various physicochemical techniques. They had reported that the C.N. of lanthanide (III) in these complexes is seven.

Wong[53] had reported about the configuration interaction of the Pr^{3+} ion. Misra et al[54] had studied about the neodymium (III)-substituted bismuyh titanate thin film generation using metal alkoxo, acyloxo a β -diketonato precursors employing a sol-gel route and using 4f-4f transition spectra as probes to explore kinetic performance. Lebret et al [55] had reported about single crystal and for IR analysis of some lanthanide thiophosphates. Binnemans et al[56] had investigated about the relabililty of Judd-Ofelt Intensity parameters by graphical simulation of the absorption spectrum. Malta et al[57] had studied the intensity parameters of 4f-4f transitions in the Eu (dipivaloylmethanate)$_3$ 1, 10-phenanthroline complex. Chen and his co-workers[58] had investigated about the spectro scopic properties of Nd^{3+} ions in $La_2 (WO_4)_3$ crystal. Devlin et al[59] had reported model calculations of 4f-4f intensity parameters for a series of tris (terdentate) Er (III) complexes. They had calculated the intensity which are based on an electrostastic intensity model for lanthanide 4f-4f electric-dipole transitions by considering the static coupling (point-charge crystal field) and dynamic coupling (ligand polarization) intensity mechanisms. They had compared the intensity parameters obtained from the model calculations to those derived from empirical intensity data and correlations are made between the relative intensity properties exhibited by the various systems and their respective structural features. They had drawn conclusions regarding the relative contributions made by the static coupling Vs. dynamic coupling mechanisms to the T_λ ($\lambda = 2, 4, 6$) intensity parameters.

Verma et al [60] had studied and calculated electronic spectral parameters, viz, Judd-Ofelt (T_λ), Racah (E_k), Slater Condon (F_k), Lande (ξ_{4f}) and bonding parameters (β, $b^{1/2}$, δ and η) for the saturated solution of fifteen ligands having N and O donor atom, doped with Nd (III) ion. They had also observed the change in symmetry around Nd (III) ion and covalency in M-L interaction. Wang et al[61] had reported the lanthanide coordination with α-Amino Acids under near physiological pH conditions: Polymetallic complexes containing the cube-like $[Ln_4 (\mu_3\text{-}OH)_4]^{8+}$ cluster core. Wang et al[62] had reported about spectroscopic study of lanthanide (III) complexes with aliphatic dicarboxylic acids. Tang et al[63] had studied about the synthesis and characterization of mixed-ligand 1, 3-dithiole-2-thione-4, 5-dithiole and 1, 10-phenanthroline complexes of lanthanide chloride and their iodinated materials. Gelinsky et al [64] had studied zinc complexation of glutathione and glutathione-derived peptides. Khan, Saxena and Iftikhar[65] had reported mixed ligand lanthanide complexes. Interaction of trivalent lanthanides with 1,10-phenanathroline and thiocyanate in alcohol. Khan and Iftikhar[66] had studied mixed-ligand lanthanide complexes. Absorption spectra and hypersensitivity in the complexes of Pr^{3+}, Nd^{3+}, Ho^{3+}, Er^{3+} in non-aqueous solvents (pyridine, DMSO, DMF and methanol). They had determined the oscillator strengths for the hypersensitive and non-hypersensitive transitions and variations in the oscillator strengths and band shapes with respect to solvent type is rationalized in terms of ligand (solvent) structures and ligand co-ordination

properties. Pyridine has been found to be most effective in promoting 4f-4f intensity and is the strongest ligand in a nephelauxetic sense among the solvents studied.

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CHAPTER 3
Aims and objectives

Dimensions to lanthanide coordination chemistry in solution becomes a new age with the increase use of lanthanides as PROBES in the exploration of the structural function of biomolecular reactions. Specially due to its ability to replace Ca(II) ions in a specific manner. In this dissertation we are going to exploit the binding characteristics of trivalent lanthanides especially Pr(III) and Nd(III) with glutathione reduced (GSH) in presence and absence of Zn(II)/Mg(II) in different aquated organic solvent at different pH (pH 3, pH 4, pH 5 and pH 6). The kinetics for the complexation of Pr(III):GSH and Nd(III):GSH complexation with Zn(II) at different temperatures at DMF medium is carried out and from the kinetic data at different temperatures the activation energy (Ea) of the complexations are determined. All the studies are going to carry out by the spectral analysis of 4f-4f transitions at different environment. Some of the important procedures for the study are given below :

a) to calculate the values of the energy interaction parameters like Slater Condon (F_k, K=2,4,6), Lande spin orbit coupling (ξ_{4f}), Nephelauxetic effect (β), bonding parameter ($b^{1/2}$), Racah parameter (E^K, K=2,4,6) and covalency parameter (δ) to discussed

the binding of Pr(III)/Nd(III) with GSH in presence and absence of Zn(II)/Mg(II) at different pH, i.e. pH 3, pH 4, pH 5 and pH 6 at different aquated organic solvents like dioxane, CH_3OH, CH_3CN and DMF and their equimolar mixtures.

b) To calculate intensity parameters like oscillator strengths (P) and Judd-Ofelt electric dipole intensity parameters T_λ, (λ=2,4,6) to discusse the bonding of Pr(III)/Nd(III) with GSH in presence and absence of Zn(II)/Mg(II) at different pH, i.e. pH 3, pH 4, pH 5 and pH 6 at different aquated organic solvents like dioxane, CH_3OH, CH_3CN and DMF and their equimolar mixtures.

c) To discuss the kinetics for the complexation of Pr(III):GSH and Nd(III):GSH with Zn(II) at DMF medium at different temperatures like 303K (30°C), 308K (35°C), 313 (40°C) and 318 (45°C), and calculation of activation energy (E_a) for the complexation from the plot of logk against 1/T (using Arrhenius rate equation).

CHAPTER NO. 4

Spectral analysis of 4f-4f transitions of Pr(III):GSH complexation in presence and absence of Zn(II)/Mg(II) at different pH

4.1 Introduction:

In this chapter, the absorption difference and comparative absorption spectroscopy involving 4f-4f transitions of heterobimetallic complexation of glutathione reduced (GSH) with Pr(III) and Zn(II)/Mg(II) are explored in aqueous and aquated organic solvents like CH_3OH, CH_3CN, DMF and Dioxane and their equimolar mixtures at different pH, i.e.pH3, pH4, pH5 and pH6. The variation in the values of energy interaction parameters like Slater Condon (F_k, K=2,4,6), Lande spin orbit coupling constant (ξ_{4f}), Nephelauxetic effect (β), bonding parameter ($b^{1/2}$), Racah parameter (E^K, K=2,4,6) and covalency parameter (δ) are calculated to explain the nature of complexation of Pr(III) with glutathione reduced (GSH) in presence and absence of Zn(II)/Mg(II) at different pH. In addition to this, values of experimentally calculated oscillator strengths (P) and calculated values of Judd- Ofelt electric

dipole intensity parameters, T_λ (λ =2,4,6) are calculated for different 4f-4f transitions in different solvents at different pH. The changes in their values suggest the specific correlation between relative intensities ligand structures and nature of interaction of Pr(III) with GSH in the presence and absence of Zn(II)/Mg(II). The oscillator strengths of certain 4f-4f transitions in the Ln(III) complexes exhibit significant sensitivity to the ligand environment and are found to be more intensified when the ions are in complexation than that they are in the corresponding free ions.

The ligand we choose, glutathione reduced (GSH) is a naturally occurring tripeptide with γ-L-glutamyl-L-cysteinyl glycine.[1] It has eight potential binding sites , viz. two carboxylic acid groups, an amino group, a sulphydryl group and two peptide linkages. Glutathione reduced (GSH) has several important functions in human metabolism, especially in Ca(II) ion homeostasis.[2-4] The coordination chemistry of GSH is of great importance due to its excellent model system for the binding of metal ions. During its interaction all potential binding sites cannot be simultaneously coordinated to the same metal ion. According to HSAB (Hard and Soft Acids and Bases), during complexation, Mg(II) prefers hard donor sites like carboxyl and carbonyl groups, while Zn(II) prefers soft donor sites like sulphydryl group (-SH). Ca(II)/Mg(II) ion, being diamagnetic, is spectroscopically silent towards optical and magnetic spectral techniques. So, the isomorphous substitution of Ca(II) by Ln(III) can provide a very useful supplement to understand the

interaction of GSH with Ca(II)/Mg(II) in presence and absence of Zn(II), since Ln(III) ions are paramagnetic and spectroscopically active. So, comparative and differential absorption spectral study involving 4f-4f transitions is one of the most effective techniques to reveal the interaction of biologically active ligands with Ln(III).[5]

4.2 Experimental

Praseodymium(III) nitrate of 99.9% purity was purchased from CDH, Mumbai and Glutathione reduced (GSH) from SRL Pvt. Ltd., Mumbai are used for synthesis and spectral analysis. Glutathione reduced (GSH) is kept below 3^0C and fresh solution of 0.01M was prepared for spectral study. The Pr(III):GSH complex is synthesized by mixing and constant stirring of Pr(III) nitrate (0.002m) with 0.004 M glutathione in ethylacetate-acetone mixture and yields greenish crystalline complex after 8-10 days. It is separated out from the liquor. The crystal obtained is washed with acetone and dried in desiccators over P_4O_{10}. The analysis of the complex gave the stoichiometry $[Pr_2(GSH)_2(H_2O)_4]$.

For the preparation of Pr(III):GSH:Zn(II) complex, Zn(II) nitrate (0.001M) and glutathione reduced (0.002 M) in ethyl acetate- acetone mixture at pH-6. Greenish crystalline complex is formed after 8-10 days and washed over P_4O_{10} in a desiccator. The analysis of the complex gave the stoichiometry, $[Pr_2(GSH)_2Zn(H_2O)_6]$. The absorption spectra are recorded on Perkin Elmer Lambda-35 UV-Visible spectrophotometer upgraded with high resolution of 0.5

nm band width and expansion of scale in the region 350nm to 900nm at different pH, i.e. pH3, pH4, pH5 and pH6. The temperature of all the observation is maintained at 298K by using water circulating HAAKE DC 10 thermostat. The metal contents in the complexes were estimated by complexometric titration with EDTA.

4.3 Methods :

The energy E_{so} arising from the most important magnetic interactions, which are spin orbit interactions may be written as

$$E_{so} = A_{so}.\xi_{4f} \qquad (4.1)$$

Where A_{so} is the angular part of spin orbit interaction and ξ_{4f} is the radial integral and is known as Lande parameter.

The Slator-Condon (F_K, K = 2,4,6) and Lande parameter (ξ_{4f}) of praseodymium complex may be evaluated by expressing energy as Taylor series expansion. In the first order, energy E_j of the j^{th} level is given by Wang[6-7] as

$$E_j(F_k,\xi_{4f}) = E_{oj}(F_k^o,\xi_{4f}^o) + \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k}\Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}}\Delta\xi_{4f} \qquad (4.2)$$

Where E_{oj} is the zero order energy of the j^{th} level. The values of F_K and ξ_{4f} are given by

$$F_k = F_k^o + \Delta F_k \qquad (4.3)$$

$$\xi_{4f} = \xi_{4f}^o + \Delta\xi_{4f} \qquad (4.4)$$

The differences between the observed E_j-value and the zero order values, ΔE_j is evaluated by

$$\Delta E_j = \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f} \qquad (4.5)$$

By using the zero order energy and partial derivatives of Pr(III) ion given by Wong (Table 4.1), the above equation (4.5) can be solved by least square fit technique and the values of ΔF_2 and $\Delta \xi_{4f}$ can be found out by using equation (4.3). The values of F_4 and F_6 are calculated by the relations,

$$\frac{F_4}{F_2} = 0.13805 \quad \text{and} \quad \frac{F_6}{F_2} = 0.0151 \qquad (4.6)$$

Table 4.1 : The Zero-order energies and partial derivatives* with respect to F_K and ξ_{4f} parameters for Pr(III)

Level	E_{oj} [(a)]	$\frac{\delta E_j}{\delta F_2}$	$\frac{\delta E_j}{\delta F_4}$	$\frac{\delta E_j}{\delta F_6}$	$\frac{\delta E_j}{\delta \xi_{4f}}$
$^1D_2$	16972	45.97	-37.63	510	2.906
$^3P_0$	20412	70.17	81.17	-1253	1.905
$^3P_1$	20990	70.07	80.66	-1278	3.974
$^3P_2$	22220	67.56	68.42	-1077	5.029

(a) $F_2^0 = 305.000\ cm^{-1}$ $F_4^0 = 51.880\ cm^{-1}$

$F_6^0 = 5.321\ cm^{-1}$ $\xi_{4f}^0 = 730.50\ cm^{-1}$

* E.Y. Wong, *J. Chem. Phys.*, 36 (1963) 976.

The result of complexation on the spectra is the red shift of all the electronic transitions, the red shift is due to the expansion of the metal orbital radius resulting in the decrease of the inter-electronic repulsion parameters (Slater-Condon, F_k's or Racah, E_k). This phenomenon is known as Nephelauxetic effect, which measures the change in F_k with respect to free ion and expressed by a Nephelauxetic ratio 'β', which is defined as:

$$\beta_1 = \frac{F_k^o}{F_k^f}; \beta_2 = \frac{\xi_{4f}^o}{\xi_{4f}^f}$$

$$\text{and} \quad \beta = \left[\frac{\beta_1 + \beta_2}{2}\right] \tag{4.7}$$

Where F_k^o and F_k^f refers to parameters in complex and free ion respectively. There is ample evidence to the fact that 4f-orbitals do participate in chemical bonding. The amount of mixing of 4f-orbitals does participate in chemical bonding. The amount of mixing of 4f-orbital and ligand orbital can be given by another bonding parameter '$b^{1/2}$', which is related to Nephelauxetic effect (β) and is given as :

$$b^{\frac{1}{2}} = \left[\frac{1-\beta}{2}\right]^{\frac{1}{2}} \tag{4.8}$$

Sinha[8] introduced another parameter known as the percentage covalency parameter, which is defined as:

$$\delta\% = \left[\frac{1-\beta}{\beta}\right] \times 100 \tag{4.9}$$

The intensity of the absorption band is measured by the oscillator strength (P), which is directly proportional to the area under the absorption curve. It can be expressed in terms of molar extinction (ε_m), energy of the transition in wave number ($\bar{\nu}$) and the refractive index (η) of the medium by the relationship

$$P = 4.31\times10^{-9}\left[\frac{9\eta}{\left(\eta^2+\eta\right)^2}\right]\int\varepsilon_{max}(\bar{\nu})d\bar{\nu} \qquad (4.10)$$

where ε_{max} = molar extinction coefficient

$\bar{\nu}$ = energy of the transition in wave number

η = the refractive index of the medium

The experimental values of oscillator strength (P_{exp}) of the absorption bands were calculated by performing Gaussian curve analysis of the curves.

The oscillator strength (P_{exp}) can be found out from the equation,

$$P = 4.60\times10^{-9}\times\varepsilon_m\times\Delta\nu_{1/2} \qquad (4.11)$$

where the molar extinction co-efficient ε_m is given by the equation

$$\varepsilon_m = \frac{\text{Absorbance}}{\text{Concentration}\times l}$$

where l = path length of the cell in cm = 1 cm

The electronic transition of trivalent lanthanides can be electric dipole, magnetic dipole electric quadrupole character. Some transitions have appreciable contributions from more than one mode of electric dipole transition, which in pure f^n configurations are strictly parity forbidden. However, a weak induced electric dipole transition can occur as a result of interaction of central metal ion with the

surrounding ligand field. Judd[9] observed that the oscillator strength of an induced electric dipole transition was related to the energy of transition ($\bar{\nu}$), square of the matrix element of unit tensor operator, $U^{(\lambda)}$ connection initial $<f^n\psi J|$ and $|f^n\psi'J'>$ through three phenomenological parameters T_λ (λ=2,4,6). These parameters are related to the radial wave function of the state, refractive index of the media and the ligand field parameters that characterize the environmental field.

$$P = \sum T_\lambda \bar{\nu} \left\langle f^n \psi J \| U^{(\lambda)} \| f^n \psi' J' \right\rangle \tag{4.12}$$

These three parameters T_2, T_4 and T_6 are related to the redial wave function of the perturbing configuration and after including weighing factor $(2J + 1)^{-1}$ the equation can be written as :

$$P = \sum T_\lambda \left\langle f^n \psi J \| U^{(\lambda)} \| f^n \psi' J' \right\rangle^2 (2J+1)^{-1} \tag{4.13}$$

For calculating matrix element $U^{(\lambda)}$ the eigen vectors were of the form,

$$f^n \psi J = \sum_{\alpha SL} \varepsilon^{\alpha SL} \, | f^n \alpha SLJ \tag{4.14}$$

and can be calculated by diagonalizing the complete energy matrices. Details of the computation involved have been dealt with separately for praseodymium and neodymium systems.

The observed oscillator strength (P_{obs}) of the transition energies were expressed in terms of parameters defined by Judd and Ofelt known as the T_2, T_4 and T_6 parameters which are given by the following equation,

$$\frac{P_{obs}}{Y} = \left[(U^2)\right]^2 T_2 + \left[(U^4)\right]^2 T_4 + \left[(U^6)\right]^2 T_6 \tag{4.15}$$

For Pr(III) $^3H_4 \rightarrow {}^3F_3$ transition occurring around 5200cm^{-1} shows hypersensitivity, however, the $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$ transitions also have been found minor changes in the immediate coordination environment around Pr(III), though these transitions cannot be regarded as hypersensitive as these do not obey selection rules.

Table 4.2 : Matrix elements* $U^{(\lambda)}$ for Pr(III) aquo

Levels	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$
$^1D_2$	0.0026	0.0170	0.0520
$^3P_0$	0	0.1728	0
$^3P_1$	0	0.1707	0
$^3P_2$	0	0.0362	0.1355

* W.T. Carnall, P.R. Fields and K. Rajnak, J. Chem. Phys., 49 (1968) 4424.

4.4 Results and Discussions

a. IR-Spectral Analysis

Preliminary infrared spectral studies have been made to find out the important structural features of Pr(III):GSH complexes. The spectra are quite complicated because of the presence of several functional groups and hence to extract any quantitative information regarding the complexes will be misleading.

Two important information which could provide by our IR spectra :

(i) regarding the changes taking place in the sulphydryl (-SH) group of the biomolecule, when it undergoes complexation, and

(ii) the carboxylic group attachment to lanthanide.

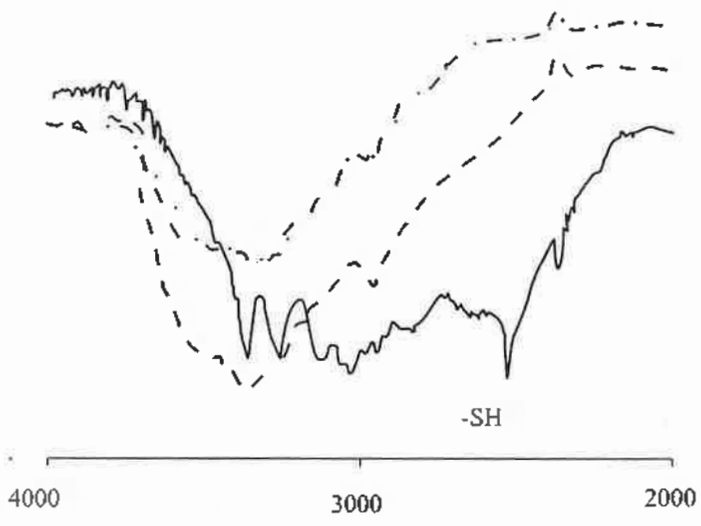

Figure 4.1(a) Comparative IR spectra of GSH ———— , Pr(III):GSH – – – – and Pr(III):GSH:Zn –·–·–·– in the range 4000-2000cm^{-1}

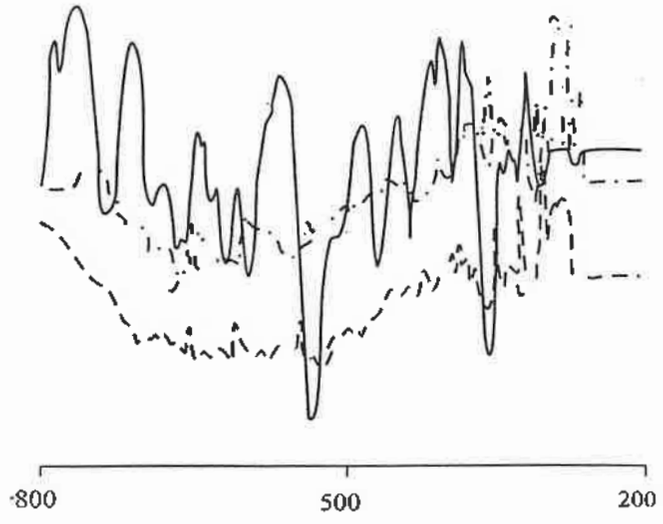

Figure 4.1(b) Comparative IR spectra of GSH ———— , Pr(III):GSH – – – – and Pr(III):GSH:Zn –·–·–·– in the range 800-200cm^{-1}

The IR spectrum of the glutathione (GSH) shows a stretching frequency due to sulphydryl (-SH) group occurring as a sharp intense band around 2523 cm^{-1} the addition of Pr(III) to glutathione clearly leads to its deprotonation, in all probability, it induces the formation of lanthanide(III) - sulphur bond. This looks little but surprising in view of the hardness of the Ln (III) ion which generally do not prefer sulphur for coordination, but the IR spectra (Figure 4.1a) shows that without doubt deprotonation of sulphydryl group occurs even at pH 5.00 at which the complexes are being synthesized.

The IR spectra in the 800 — 200 cm^{-1} region (Figure 4.1b) show the appearance of new bands, and some of these can be ascribed to Pr - S. The addition of Mg(II) or Zn(II) to lanthanide(III) : GSH complex enhances the deprotonation tendency. The Mg(II)- or Zn(II) - S bands can be expected in the region 800 - 200 cm^{-1} which we could not resolve. The carboxylic group frequencies as well as carbonyl group frequencies are highly sensitive when the complex has metal ion like lanthanide(III). This is clearly visible in the IR spectrum. The carbonyl (CO) stretching frequency occurring at 1715 cm^{-1} in the ligand (GSH) spectrum is shifted to the lower field at around 1680 cm^{-1} in Ln(III) : GSH complex and showing a shift at 1675 cm^{-1} and 1630 cm^{-1} in Ln(III): GSH: Zn(II) complex, indicating the involvement of CO group in binding with the lanthanide ion.

b. HNMR – Spectral Analysis

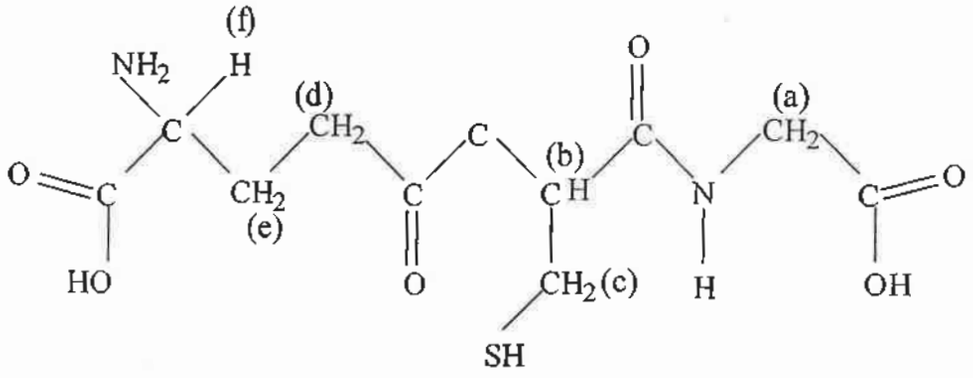

Figure 4.2(a) : Structural formula of glutathione

The ^1H spectrum of the Pr(III) : GSH complex [Figure 4.2(a)] gives evidence of the interaction of glutathione (GSH) with Pr(III) ion. Table 4.3 clearly shows the shifts in the proton peaks. All the peaks are showing a down field shift in the Pr(III) : GSH complexes. The H(a) proton peak observed at $\delta_{3.98}$ in the ligand (GSH) spectrum is shifted to $\delta_{4.37}$ in the complex. The triplet H(b) proton [Figure 4.2(b)] peaks centered at $\delta_{3.83}$ in the ligand to shifted to $\delta_{4.19}$. Interestingly H(c) proton peak also shows a down field shift which indicates the weak interaction of sulphur with Pr(III) ion. Similarly other proton peaks of the complex are also showing down field shift the H(e) and H(f) proton peaks are slightly broadened due to the paramagnetic nature of the complex. In the ^1H spectrum of the Pr(III):GSH:Zn complex, the H(a) proton peak is shifted from 4.00 ppm to 4.32 ppm. The peak is slightly broadened and can be accounted for 3H, which indicates that the CH proton (b) is merged with these protons. The doublet H(c) proton peaks observed at 2.97 ppm and 2.91

ppm in the ligand spectrum are shifted to 3.21 ppm and 3.15 ppm in the Pr(III):GSH:Zn(II) complex [Figure4.2(b)] with a coupling constant of 6.35 Hz. This shows that the presence of Zn(II) strengthens the binding of S with the metal ion. The H(d) protons centered at 2.96 ppm are not appeared as well resolved triplet as in the glutathione spectrum, but it shows a downfield shift by 0.7 ppm. H(e) and H(f) protons appeared as broad singlet at 2.64 ppm. with a downfield shift by 0.57 ppm. The H(e) and H(f) proton peaks observed at 2.20 ppm in the GSH is shifted to 2.42 ppm. in Pr(III):GSH complex with a downfield shift by 0.22 ppm. While H(e) and H(f) proton peaks observed at 2.64 ppm in the Pr(III):GSH:Zn(II) complex showing a downfield shift by 0.44 ppm. This increase in the value gives evidence of the involvement of Zn(II) in complexation with glutathione (GSH) and Pr(III) ion.

Table 4.3 : ^{1}H NMR δppm for protons of GSH in different complexation states

Compound	a	b	C	D	e and f
GSH	3.98	3.77	2.97	2.64	2.20
		3.83	2.91	2.57	
		3.90		2.49	
Ln(III):GSH	4.37	4.19	2.98	2.84	2.61
				3.12	2.42
Ln(III):GSH:Zn	4.32		3.21	2.96	2.64
			3.15		

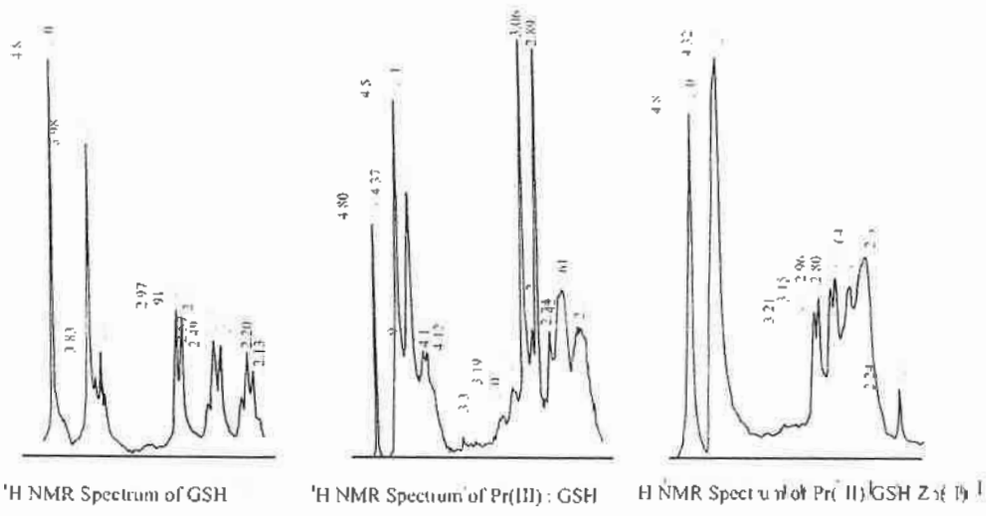

Figure 4.2 (b) : 1H NMR Spectra of GSH in different complexation state

c). Comparative absorption spectral analysis of 4f-4f transition of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) by employing energy interaction parameter at different solvents and different pH (pH 3, pH 4, pH 5 and pH6)

Figures 4.3, 4.4 , 4.5 and 4.6 give the comparative absorption spectra of Pr(III), Pr(III):GSH , Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in acetonitrile (CH_3CN) at pH3. Similarly Figures 4.7 to 4.18 give the their comparative absorption spectra in DMF, dioxane and methanol (CH_3OH) at pH 4, pH5 and pH 6 respectively. Figure 4.19 shows the comparative absorption spectra of Pr(III):GSH:Zn(II) in different solvents like CH_3CN, DMF, dioxane and CH_3OH at pH 6. Figure 4.20 gives the comparative absorption spectra of Pr(III):GSH:Zn(II) complex at different pHs, i.e. pH 3, pH 4, pH5 and pH 6. From the Figures 4.3 to 4.18, we can reveal that there is a red shift as GSH is

added to Pr(III) and further longer wave length is observed on addition of Zn(II). Tables 4.2, 4.3, 4.4 and 4.5 shows the variation of the magnitude of energy interaction parameters like Slater Condon (F_K), Lande factor (ξ_{4f}), Racah energy (E^K), Nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency parameter (δ) for Pr(III), Pr(III):GSH Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in aqueous and different aquated organic solvents at different pH, i.e. pH 3, pH 4, pH 5 and pH 6. There is a slight decrease in the values of F_K, ξ_{4f} and E^K as the complexation goes on which lead to increase in the values of Nephelauxetic ratio (β) and so in bonding parameter ($b^{1/2}$) & percent covalency parameter (δ).

For spectral studies on the structures of co-ordination compounds of lanthanides in solution, the evidence of the relationship between the Nephelauxetic band shift and the structure is of special interest. Jorgensen and Ryan[10] noticed the dependence of Nephelauxetic effect (β) on the co-ordination number. It was suggested that shortening in the metal ligand distance occurs with decrease in the co-ordination number. Langhlin and Conway[11] studied the absorption spectra of Pr(III) ion in the iso-structural crystals $CeCl_3$, $NdCl_3$, $SmCl_3$ and $GdCl_3$ and they concluded that with identical structures of complexes (C.N. = 9 and D_{3h} symmetry), there exits a linear relationship between wave no. of $^3H_4 \longrightarrow {}^3P_{0,1,2}$ transitions in the spectra of Pr^{3+} and distance between praseodymium and ligand, R(Ln-O) [R(Ln-O) is the mean Ln-Oxygen distance in the complexes with ligands coordinated via oxygen

atom]. It was observed that increase in the value of R increases the band shift towards the short wave region. Yatsimirskii and Davidenko[12,13] pointed out a close linear correlation between R(Ln-O) and wave number of some f-f transitions in the absorption spectra of some praseodymium and neodymium complexes having different co-ordination number and symmetries. To interpret the correlation and analysis of the relationship between Nephelauxetic effect and geometry, energy parameters have been derived and evaluated for complex compound using the angular overlap model, the value of 'n' is proportional to the Nephelauxetic effect as

$$n = \left[\frac{\left(1-\beta^{1/2}\right)}{\beta^{1/2}}\right] \tag{4.16}$$

It may also be expressed as

$$n = \frac{H_L^2}{\left(H_M - H_L\right)^2}.\left(S^*R\right)^2 N \tag{4.17}$$

where N is the co-ordination number, H_M and H_L are coulomb integrals of atomic orbital; S is the overlap integral; R is the radius of the orbit. For compounds with ligand coordinated through identical donor atoms, the term of equation (4.17) is a constant and it becomes

$$n = \text{constant}.\left(S^*R\right)^2 N \tag{4.18}$$

The above equation (4.18) represents the Nephelauxetic effect as a function of two variable, S*R and N which vary with changes in lanthanides-ligand distance in opposite directions. However any variation in the value of R leads to

a larger change in $(S^*R)^2$ compared to that in N. As a result, the Nephelauxetic effect (β) increases when the co-ordination number decreases. The Ln-O distance shortens in spite of the addition nature of β and decrease in the number of the co-ordinating ligand. The variation in the value of E^K (K = 2,4,6); corresponds to that in the value of F_K, since they are inter-related. Misra et al[14-15] observed a general decrease in the values of F_K, E^K and ξ_{4f} parameters as compared to the corresponding parameters of the free ion.

The $^3H_4 \rightarrow {}^3P_0$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_2$ and $^3H_4 \rightarrow {}^1D_2$ transitions of Pr(III) do not obey selection rules but they have found to show substantial sensitivity reflected through wide variation of oscillator strengths and energies with even minor changes in the immediate coordination environment around it even in the presence of structurally related ligand[16-17] and they are termed as ligand mediated pseudohypersensitive or pseudohypersensitive transitions. Due to extremely fast water exchange rate and very small crystal field stabilization energy the conversion from one-geometry to another is very convenient and facile. Karraker[18] showed that the shape, energy and oscillator strength of hypersensitive or pseudohypersensitive transitions can be correlated with coordination number and diagnostic of immediate coordination environment around lanthanides ions. The addition of GSH in Pr(III) resulted in a marginal red shift of 4f-4f transition bands and the addition of Mg(II) give a very small longer wavelength shift and the further addition of Zn(II) to Pr(III):GSH gave further shift towards the longer wavelength . This shows the stimulated effect of

Zn(II) towards the complexation of Pr(III) with GSH. The identical spectral pattern of the complex with that of Pr(III) aquo suggest that the Pr(III) and Zn(II) bind to different coordinating sites of this multidentate ligand. Table 4.4 to 4.7 gives the computed values of Slator Condon (F_k), Racah (E^k) and Lande (ξ_{4f}), Nephelauxetic parameter (β), bonding parameter($b^{1/2}$) and covalency parameter (δ) of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in aqueous and aquated organic solvents at different pH. Table 4.8 – 4.11 gives the computed and observed values of energies for the various transition bands and root mean square deviation (R.M.S.) showing the correctness of the various energy parameters. One can clearly see that the variation of solvent nature and composition has significant effect on the energy parameters of the different 4f-4f transition bands.

d) Comparative absorption spectral analysis of 4f-4f transition of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) by employing intensity parameter like oscillator strengths (P) and Judd-Ofelt parameter, T_λ (λ=2,4,6) at different solvent and different pH (pH 3, pH 4, pH 5 and pH6)

The calculation of the band intensities is based upon the theoretical treatment derived by Judd[9] and Ofelt[19]. A consideration of the mechanisms by which intra-f-electron transitions may occur shows that the intensities of the observed bands can be adequately accounted for two processes. In a few cases, the

transitions occur wholly or partially by a magnetic-dipole mechanism. Such transitions follow the selection rule $\Delta J \leq 1$, $\Delta L=0$, $\Delta S=0$ and $\Delta l =0$ in the Russell-Saunders coupling scheme, which is adopted. Given the eigenvectors of the states involved, the magnetic-dipole intensities may be readily calculated.[20] The second and principal mechanism treats the transitions as being essentially (forced or induced) electric dipole in character. Both Judd and Ofelt were concerned with developing expressions for the intensity which arises via the later mechanism.

$$P = \sum_{\lambda=2,4,6} T_\lambda \sigma (f^N \psi J \| U^{(\lambda)} \| f^N \psi' J')^2 \qquad (4.19)$$

where P is the oscillator strength corresponding to the induced electric dipole transition $\psi J \rightarrow \psi' J'$ at energy σ (cm^{-1}) and $U^{(\lambda)}$ is a tensor operator of rank λ.The three quantities T_λ (λ =2,4,6) are related to the radial parts of the $4f^N$ wave functions, the wave functions of perturbing configurations of which the nearest is $4f^{N-1}5d$, the refractive index of the medium, and the ligand-field parameters which characterize the environment of the ion. While 'i' principle values of T_λ could be calculated, we have treated these quantities as parameters to be determined from experimental oscillator strengths.

The measured intensity of an absorption band is related to the probability (P) for the absorption of radiant energy (oscillator strength) by the expression

$$P = \frac{2303mc^2}{N\pi e^2} \int \varepsilon_i(\sigma) d\sigma$$

or,
$$P = 4.318 \times 10^{-9} \int \varepsilon_i(\sigma) d\sigma \qquad (4.20)$$

where ε is the molar absorptivity at the energy σ (cm^{-1}) and other symbols have their usual meaning. It will be noted that in 'i' a factor involving the index of refraction of the medium was improperly written as part of the experimental P, whereas it should only occur within the expression for T_λ.

Interest in the intensities of lanthanides 4f-4f transition spectra can be said to have begun with a paper by Vleck.[21] In which, it was not known whether the sharp lines in the spectra of trivalent lanthanides were due to intra – $4f^N$ transition or $4f^{N-1} \rightarrow 5d$ transition. Hoogschagen et al[22-23] made an accurate estimation of the absolute intensities of the lanthanides. A compilation of the oscillator strength of the lanthanide aquo ions was published in 1948.[24] The transition levels and the matrix elements used for the intensity analysis of Pr(III) complexes is given by Carnall.[25]

The calculated oscillator strengths were determined using the equation

$$\frac{P_{obs}}{\nu} = \left[U^{(2)}\right]T_2 + \left[U^{(4)}\right]T_4 + \left[U^{(6)}\right]T_6 \qquad (4.21)$$

For composite bands, the sum of the matrix elements of individual transitions were used to determine the calculated oscillator strengths.

The spectra of lanthanide are composed of clearly special groups of sharp lines, similar to atomic spectra. The groups of lines are normal. These spectra arises from transitions among levels of f^N configuration. The usual (2J+1) fold degeneracy terms of such configurations are reduced to some extent by the action of crystal field. However, the energy levels of rare earth ions in solid state are determined largely by spin orbit interaction, which has a larger magnitude than that

of the influence of crystal field. Contrary to this, in transition elements, the contribution of the crystal field is more than that of the spin-orbit interaction. The 4f-electrons of lanthanides are more or less protected from the influence of lattice by the polarisation of $5s^2$ and $5p^6$closed shells. The crystal field splitting effect in the lanthanide ions is small, 200-300cm^{-1} at the most cases.

Judd[9] assigned the hypersensitivity to the changes in symmetry of the environment of a lanthanide ion. Hypersensitivity is observed in the absorption spectra of the lanthanide trihalides in the gaseous state having D_{nh} symmetry.[26] Jorgenson and Judd[27] considered the problem of hypersensitivity and concluded that all such transition obeyed selection rules. These are the transitions whose intensities are determined by the values of T_λ.

The 4f-4f transitions, $^3H_4 \rightarrow {}^1D_2$, $^3H_4 \rightarrow {}^3P_0$, $^3H_4 \rightarrow {}^3P_1$, and $^3H_4 \rightarrow {}^3P_2$ of Pr(III) do not obey selection rule and so they are considered non-hypersensitive transitions. But, they are found to be quite sensitive towards even minor changes in the coordination environment.[28-30] Such transitions are termed as pseudohypersensitive transitions. Karraker[31-33] studied the hypersensitive transition correlate with the coordination number of lanthanide ions. It is very challenging to note that Judd-Ofelt theory is not applicable so well to the complex of Pr(III) as to those of other lanthanides due to difficulty experienced in fitting both $^3H_4 \rightarrow {}^3F_4$ and $^3H_4 \rightarrow {}^3F_2$ transition with the same phenomenological parameter. In most of the cases the value of T_2-parameters comes out as negative which provides no meaning. Since only $^3H_4 \rightarrow {}^3F_2$ transition has significant $U^{(2)}$ matrix element, but it has not been included in the data set of any of the complexes as it is beyond the

range of UV region. The pseudohypersensitivities of $^3H_4 \rightarrow {}^1D_2$ and $^3H_4 \rightarrow {}^3P_2$ transitions of Pr(III) in heteropolymolybdates and polytungstates are quite clearly shown by Peacock.[34]

Carnall[35] and Weber[36] give a common theory to explain the anomalous behaviour of Pr(III). According to them, the approximation configuration which are degenerate and of much higher energy than that of the intra f – f transition which is not valid. The effect of pH is responsible for the degree of protonation and deprotonation of different coordinating sites of GSH. The bonding of GSH is affected significantly by degree of deportation of the coordinating sites and therefore pH will have significant effect on Pr(III):GSH binding, which is clearly reflected through significant variation in intensity parameters.

The binding of Pr(III):GSH brings about changes in the energies of various 4f-4f transition bands. Since interaction of Pr(III) with GSH is generally predominant with carboxylic groups of GSH, the bonding between Pr(III):GSH is basically electrostatic in nature. Since lanthanides are hard metal ions their preference will be for hard donor sites like oxygen atoms. Therefore, energy and Nephelauxetic changes are not apparently significant The absorption spectral study at pH 3.0 indicates the deprotonation of glutamyl residue of GSH. Pr(III) being a hard metal ion, has a tendency to coordinate, preferentially with –COOH group. Hence Pr(III) interacts with glutamyl residue in acidic medium, of GSH. One more carboxylic (Glycilic) group and sulphydryl (-SH) group from glycine and cysteinyl residue gets deprotonated at pH 4.0 and 6.0 respectively .

Misra[37-42] studied the high sensitivity of $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^2D_1$ transitions of Pr(III) and other transitions of Nd(III) chelates in their complexes with ligands having widely different binding characteristics. They have found that the nature of the coordinating sites, chelating power of the ligand, denticity of the ligand and nature as well as the geometry of the complex species induced unusual sensitivity to this pseudohypersensitive transitions.

In Tables 4.12 to 4.15 the absolute values of observed oscillator strengths, computed values of Judd-Ofelt parameters (T_2,T_4,T_6) and calculated values of oscillator strength of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in different solvents and different pH, i.e. pH3, pH4, pH5 and pH6 are given. We analyse the changes in the absolute values of oscillator strengths and Judd-Ofelt electric dipole intensity parameters (T_2,T_4,T_6) at different pH (pH3, pH4, pH5 and pH6) and different solvents. This clearly suggest a significant change when Pr(III) interacts with GSH in the solution and further changes when Mg(II) and Zn(II) ions are added. Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in different solvent and different pH clearly show that the addition of GSH to Pr(III) results in significant enhancement in the oscillator strength of different 4f-4f transition (Figures 4.3 to 4.12). As a result, we have observed noticeable increase in the magnitude of Judd-Ofelt (T_λ) parameters. This suggest the binding of the tripeptide GSH to Pr(III) in presence and absence of Zn(II)/Mg(II) in solution. Such increase in the values of oscillator strengths and T_λ-parameter is more when Zn(II)/Mg(II) is added to the solution of Pr(III):GSH. The increase in sharp in the case of Zn(II)

and less in the case of Mg(II). This is due to the involvement of Zn(II) to other ligating site of GSH like sulphydryl group as being soft – metal ion.

The pH of the medium play a big role for the degree of protonation and deportonation of different coordinating sites of GSH. So, it plays significant effect on Pr(III) and GSH binding in presence and absence of Zn(II)/Mg(II), which is clearly reflected through significant variation in oscillator strength (P) and T_λ parameters. In Figure 4.20 the comparative absorption spectra of Pr(III):GSH:Zn(II) in aquated DMF in different pH, i.e. pH 3, pH 4, pH5 and pH 6 are given. From the figures and table we can conclude that the complexation is most favoured in pH 6.

The absorption spectral study at lower pH 3.0, indicates the deprotonation of glutamyl residue of GSH. Pr(III) being hard metal ion, extracts with glutamyl residue of GSH in acidic medium. One more carboxylic group of glycine and sulphydryl (-SH) group from cysteinyl residue get deprotonated at pH 4 and pH 6 respectively. So, the binding of Zn(II)/Mg(II) with Pr(III):GSH complex is more favoured in the case of pH 6. This is vividly seen from the distinct variation of the value of oscillator strengths and T_λ value at higher pH-value from lower pH value. The optimum pH for stable species of Pr(III):GSH with Zn(II)/Mg(II) is found at pH 6.

The effect of solvent on complexation is quite significant. DMF appears to induce the maximum intensification on the complexation of Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) complexes and least in the case of methanol. This is due to its strong nitrogen donor capacity which can enter the

coordination sphere by replacing one of the water groups. Methanol is a very weak donor, which in some cases does coordinate and otherwise not. All these are clearly seen from the comparative absorption spectra of Pr(III):GSH:Zn(II) at different solvents like DMF, CH_3CN, CH_3OH and dioxane at pH 6.0 in Figure 4.19.

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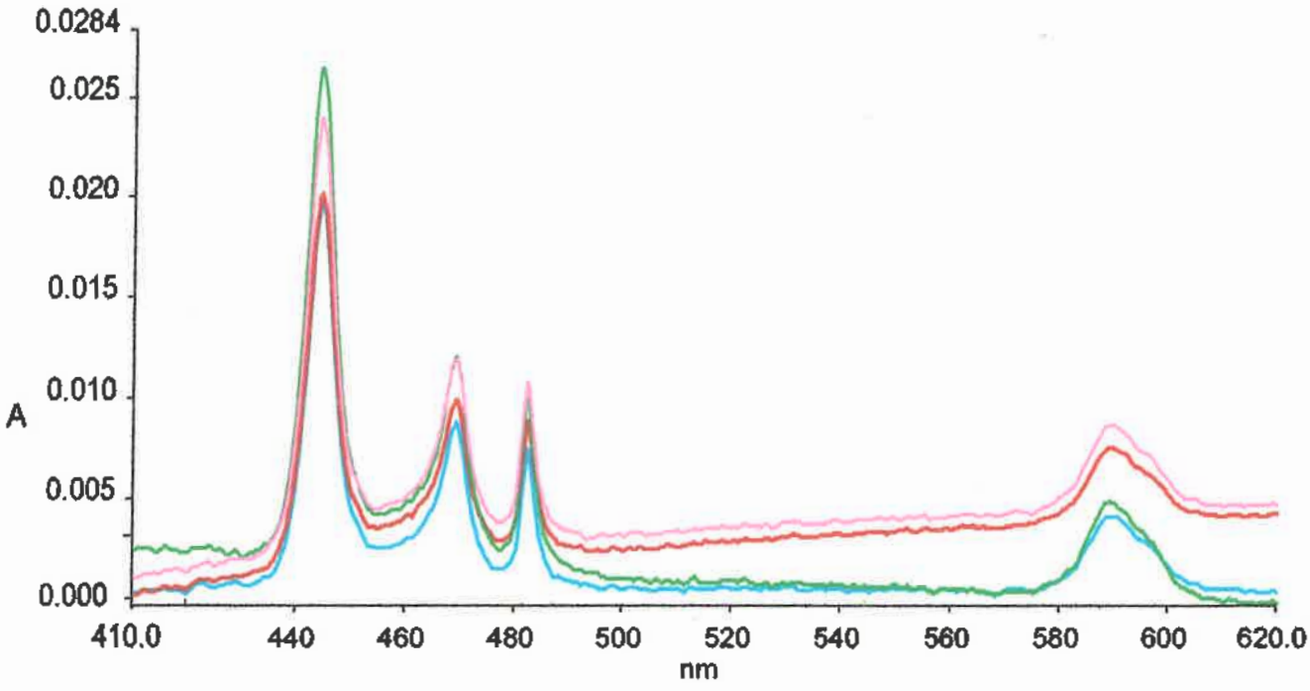

Figure 4.3 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in CH_3CN at pH-3

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

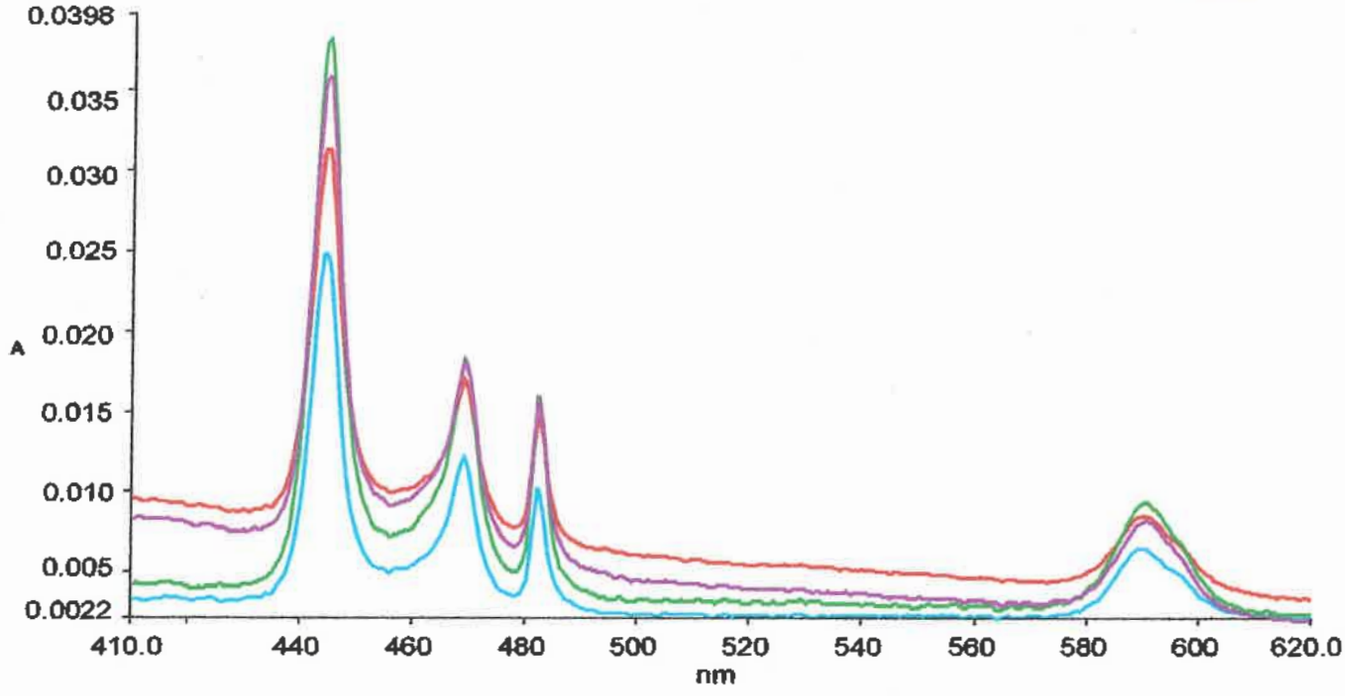

Figure 4.4 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in DMF at pH-3

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

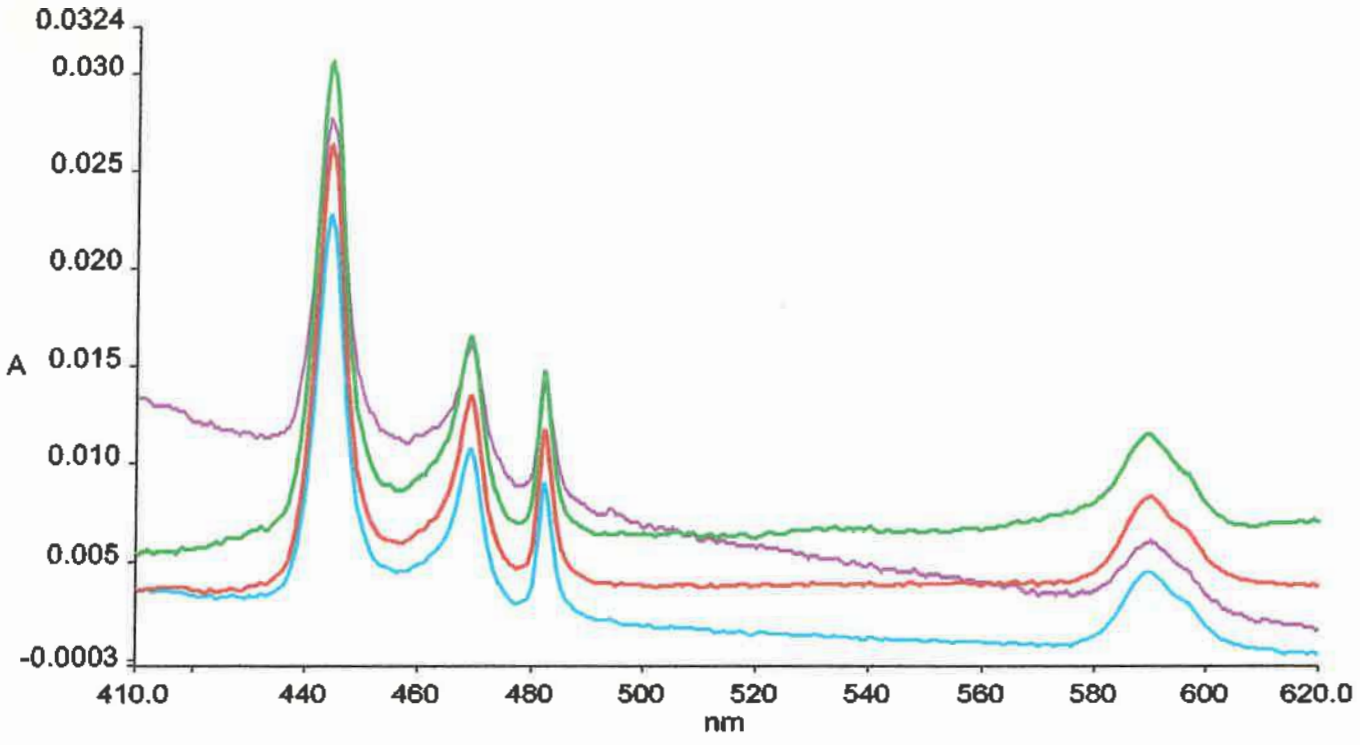

Figure 4.5 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in Dioxane at pH - 3

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

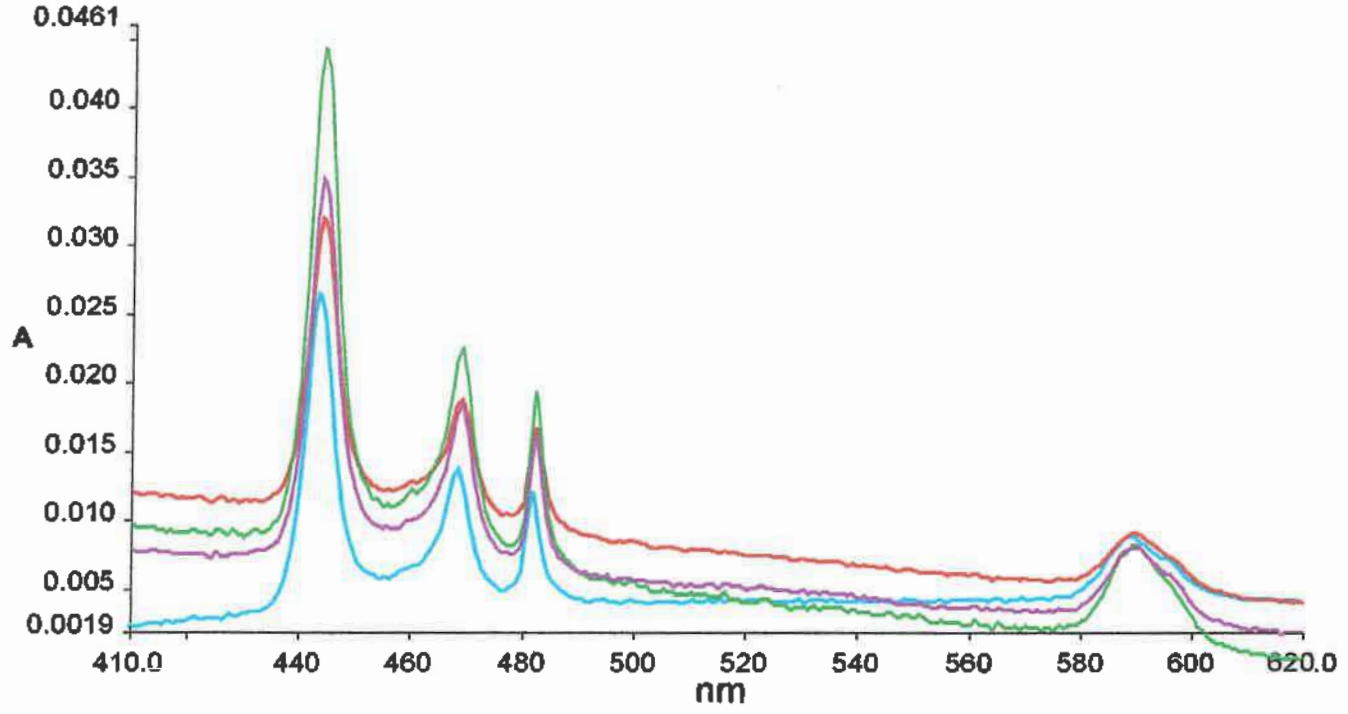

Figure 4.6 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in CH_3OH at pH-3

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

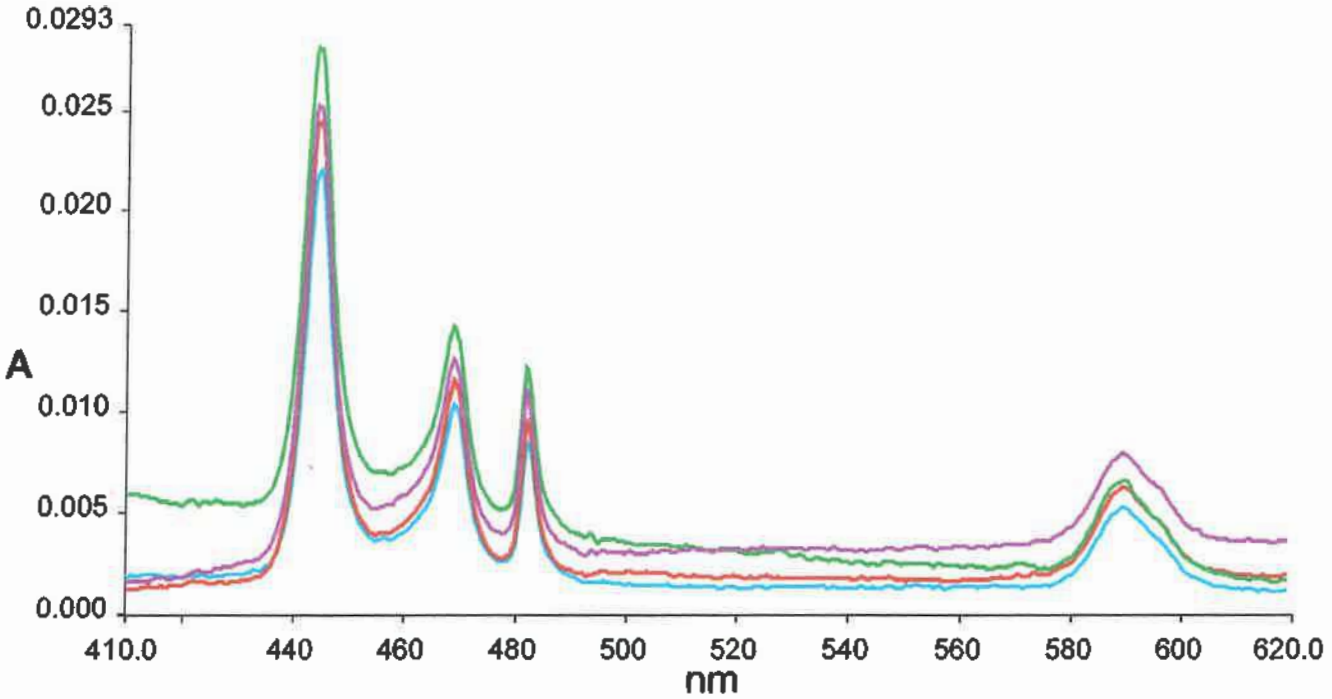

Figure 4.7 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in CH_3CN at pH-4

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

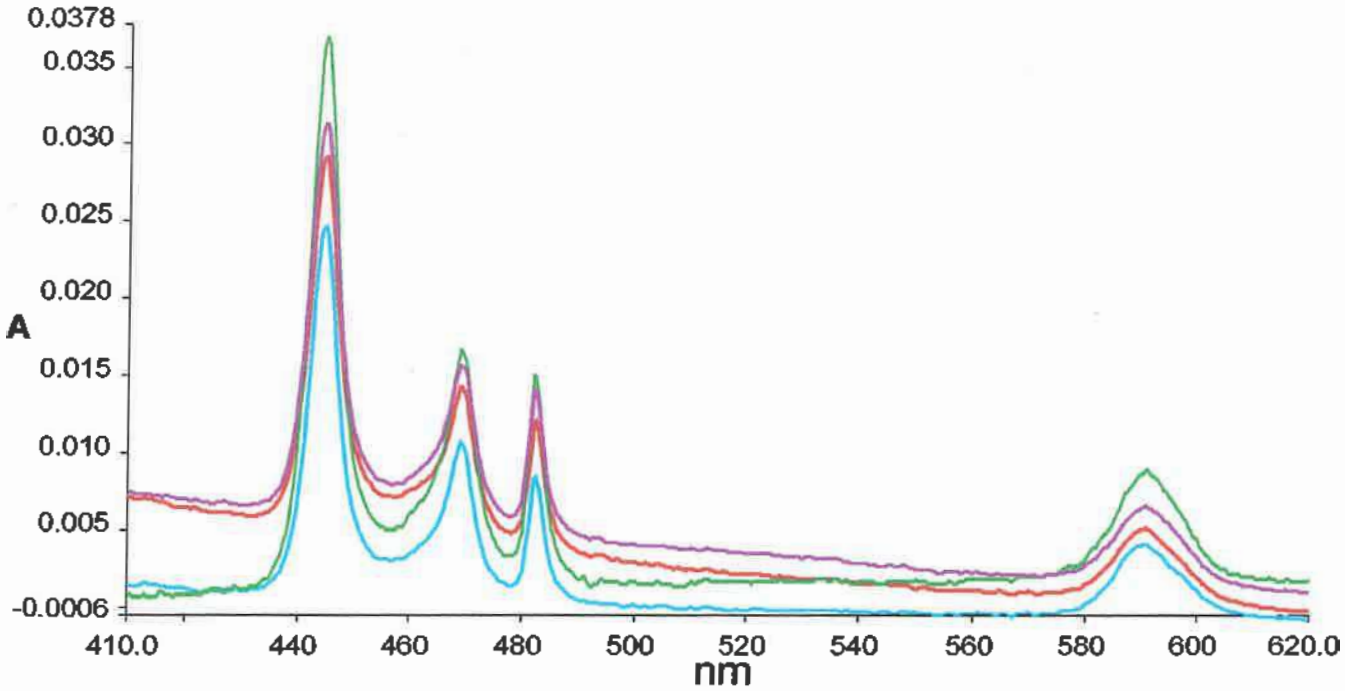

Figure 4.8 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in DMF at pH-4

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

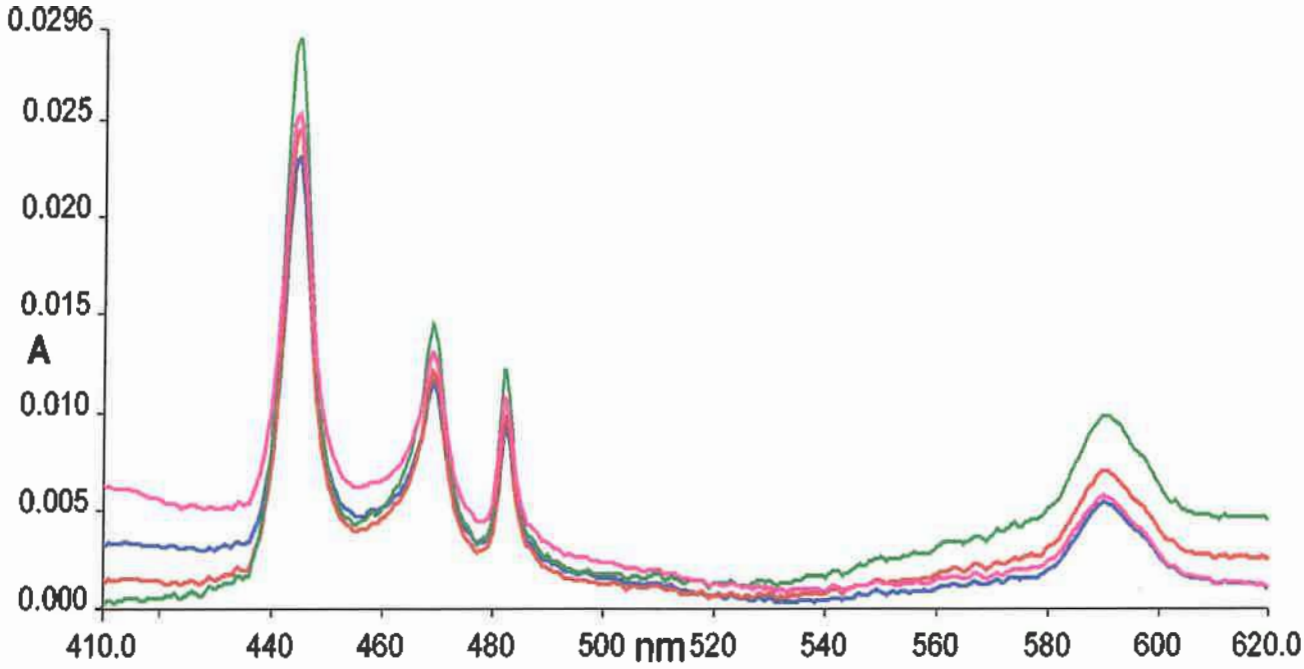

Figure 4.9 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in Dioxane at pH-4

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

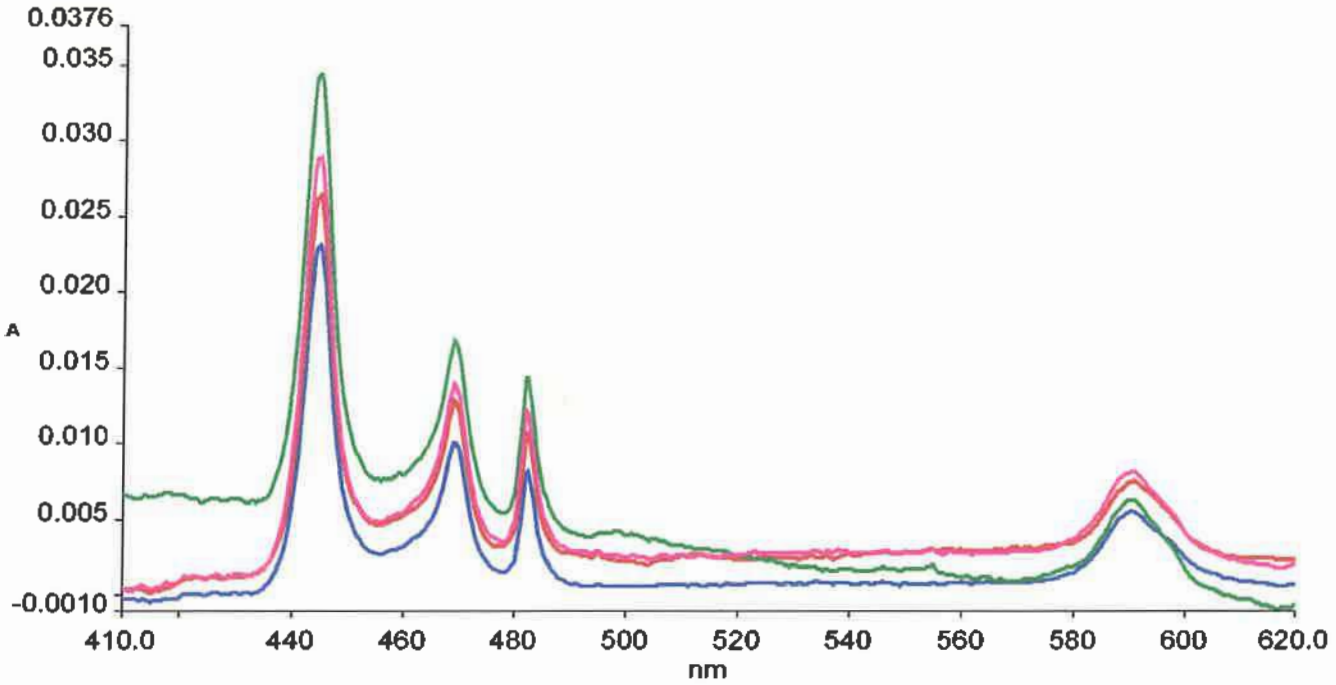

Figure 4.10 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in CH_3OH at pH-4

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

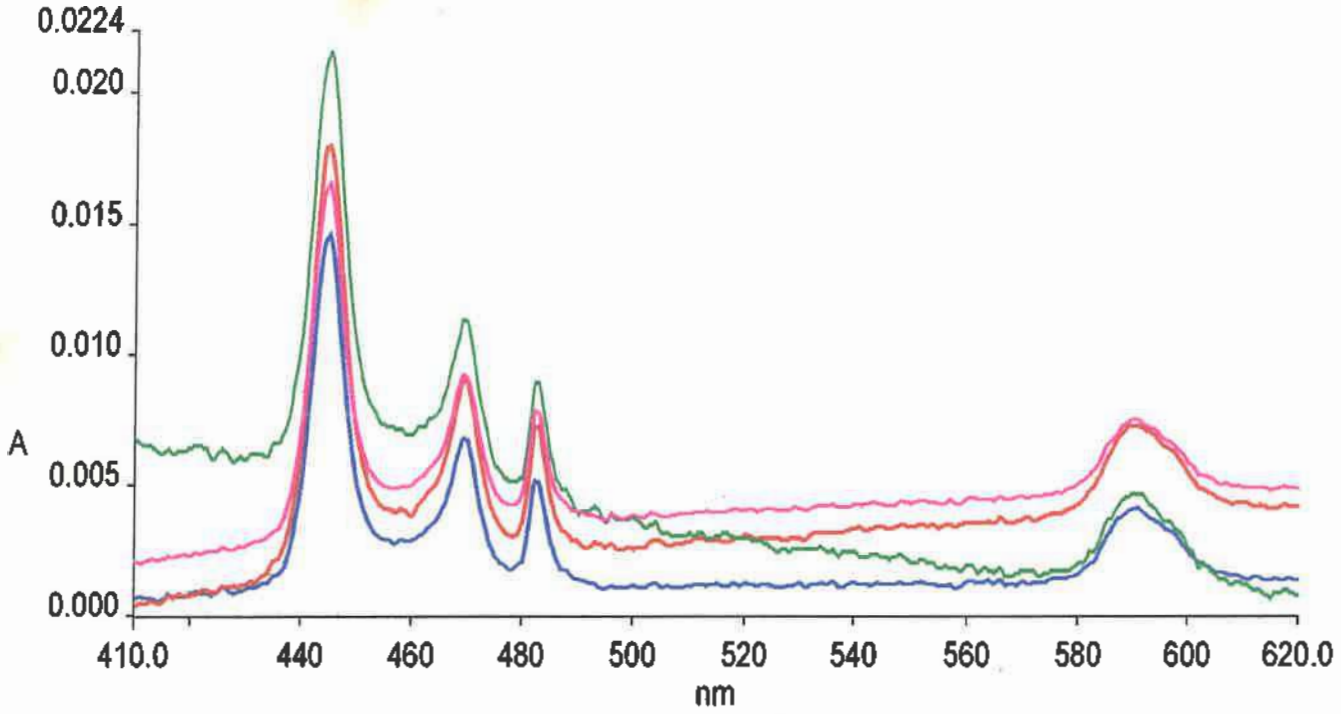

Figure 4.11 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in CH_3CN at pH-5

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

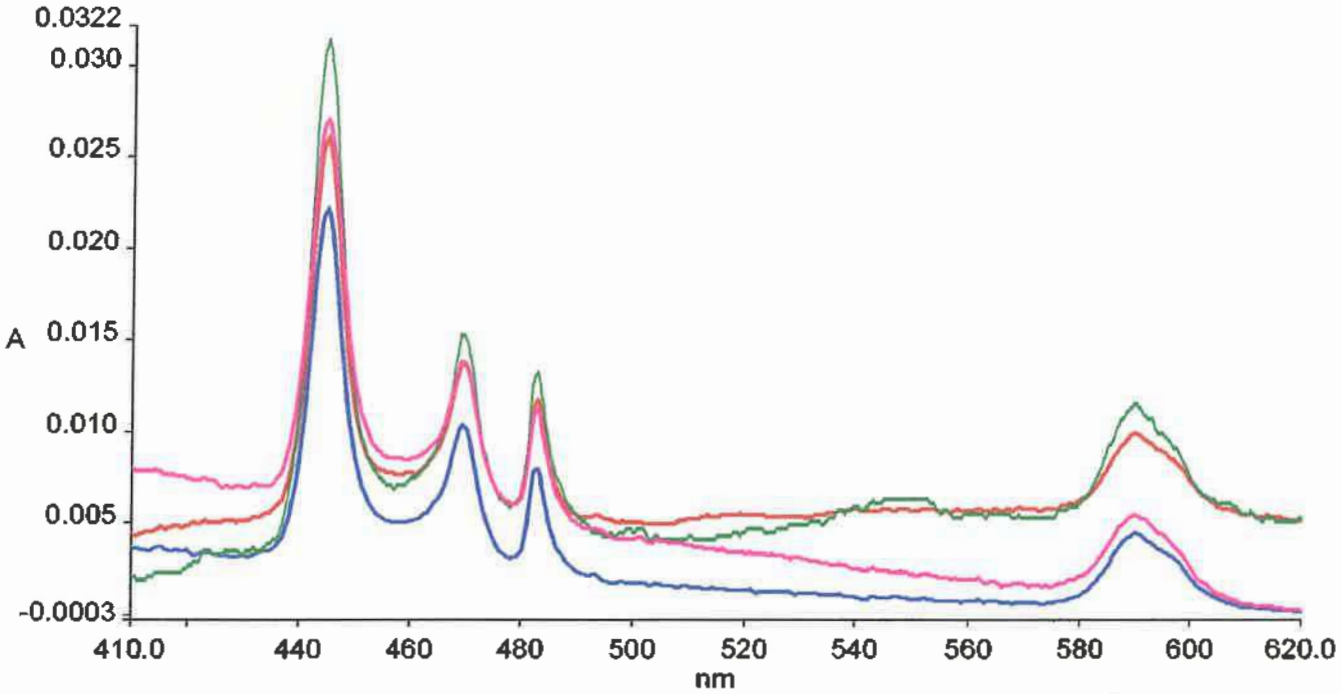

Figure 4.12 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in DMF at pH - 5

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

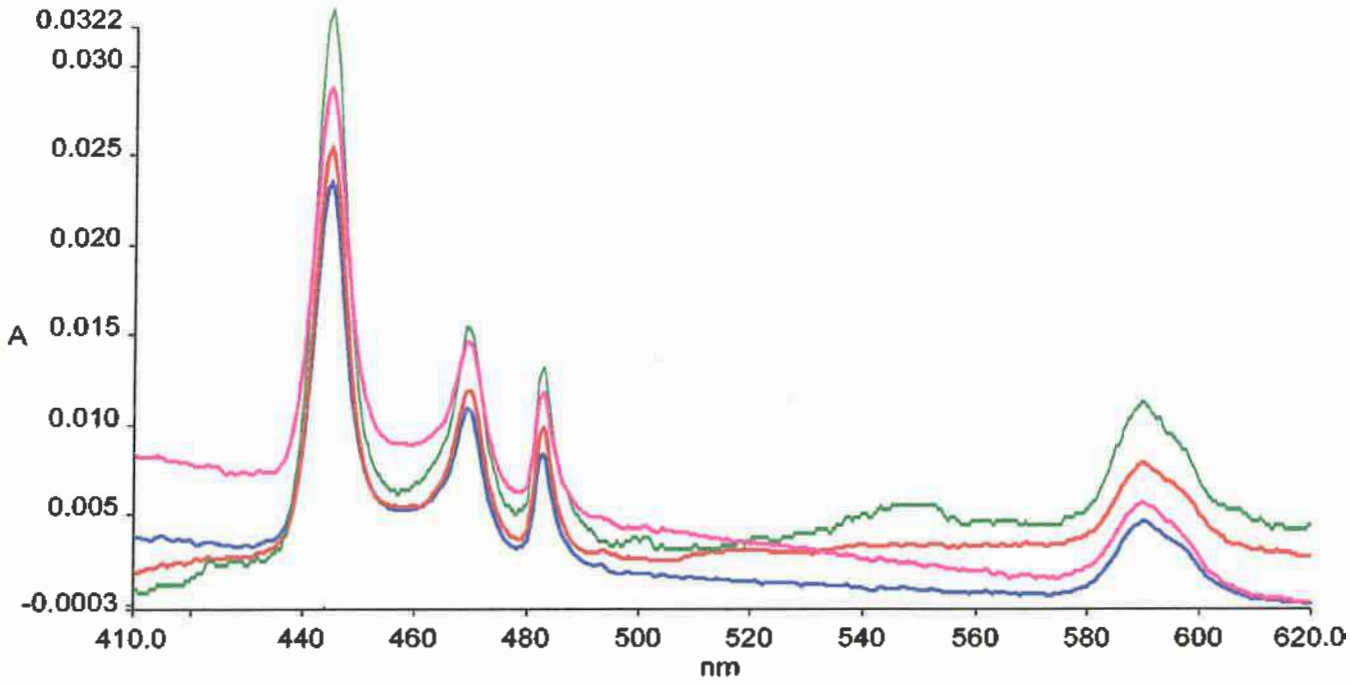

Figure 4.13 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in dioxane at pH - 5

Pr(III) :
Pr(III):GSH :
Pr(III):GSH:Mg(II) :
Pr(III):GSH:Zn(II) :

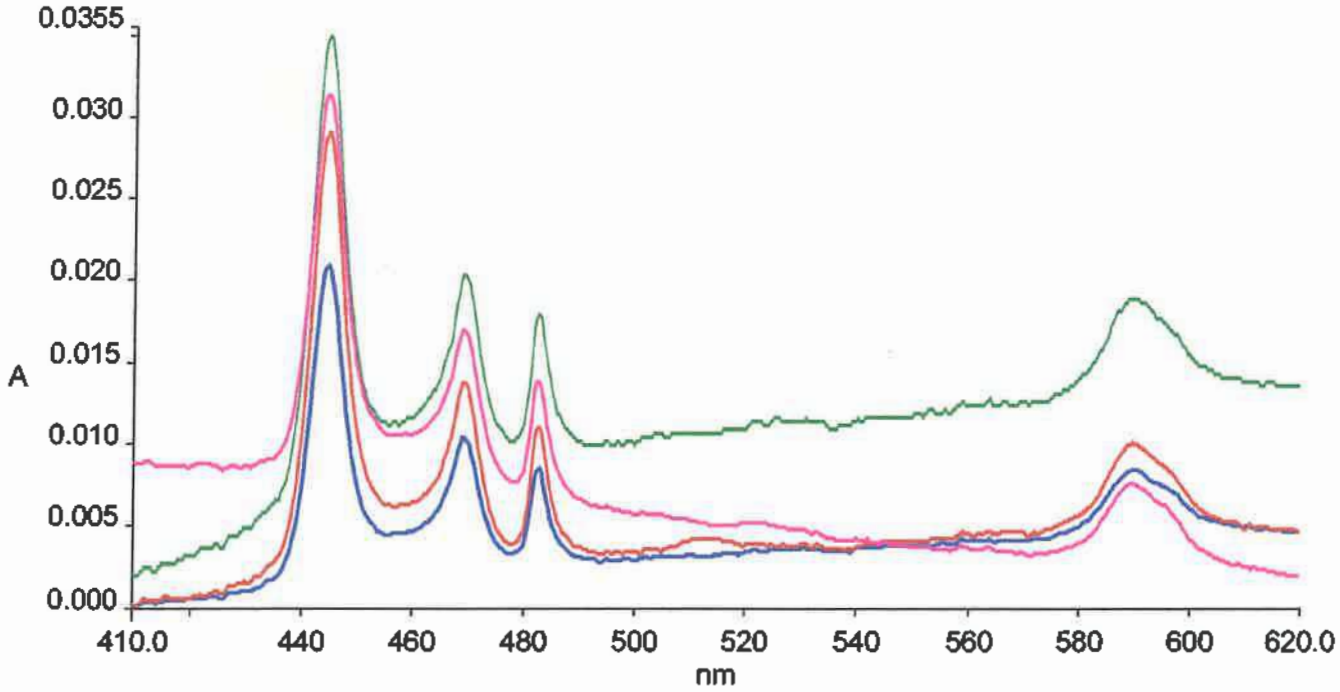

Figure 4.14 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in CH_3OH at pH-5

Pr(III) :
Pr(III):GSH :
Pr(III):GSH:Mg(II) :
Pr(III):GSH:Zn(II) :

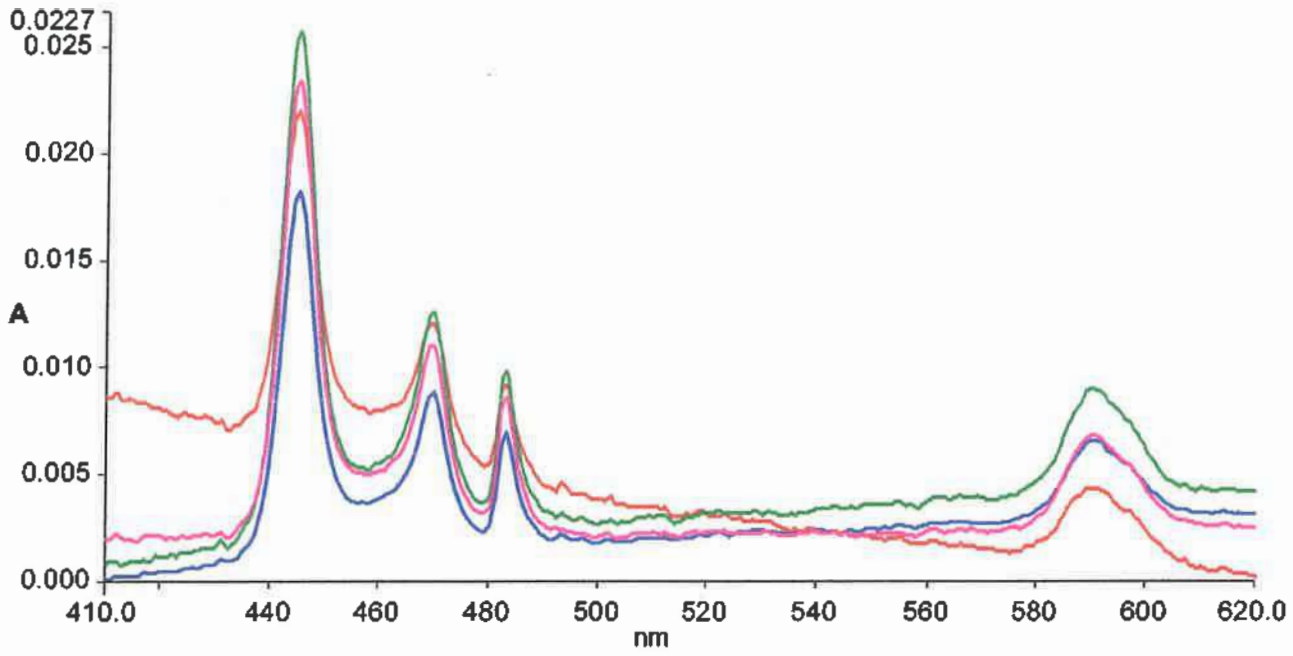

Figure 4.15 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in CH_3CN at pH - 6

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

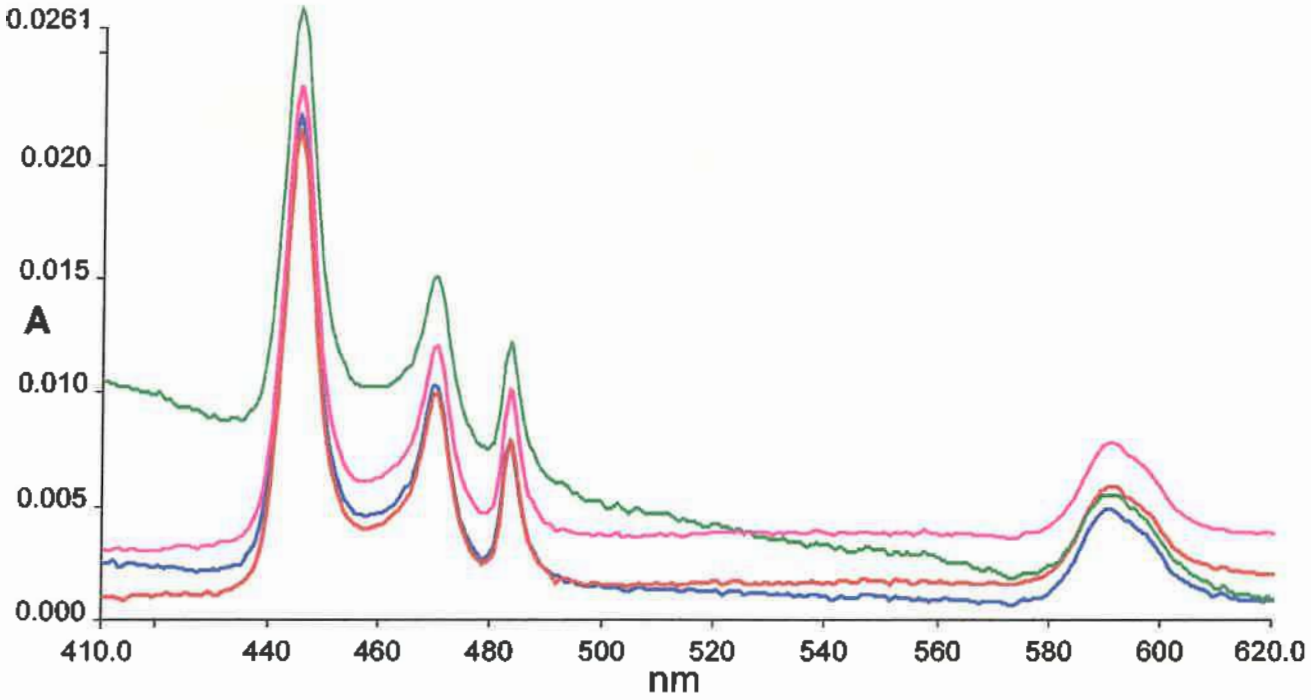

Figure 4.16 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in DMF at pH - 6

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

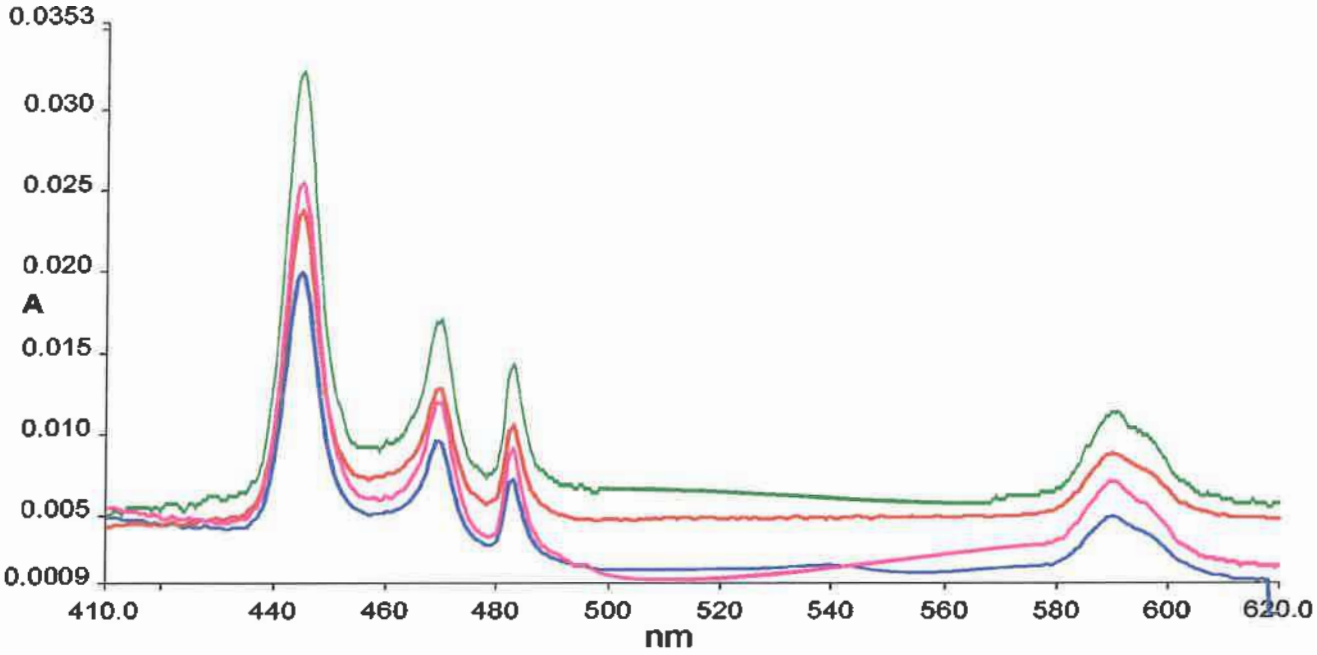

Figure 4.17 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in dioxane at pH - 6

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

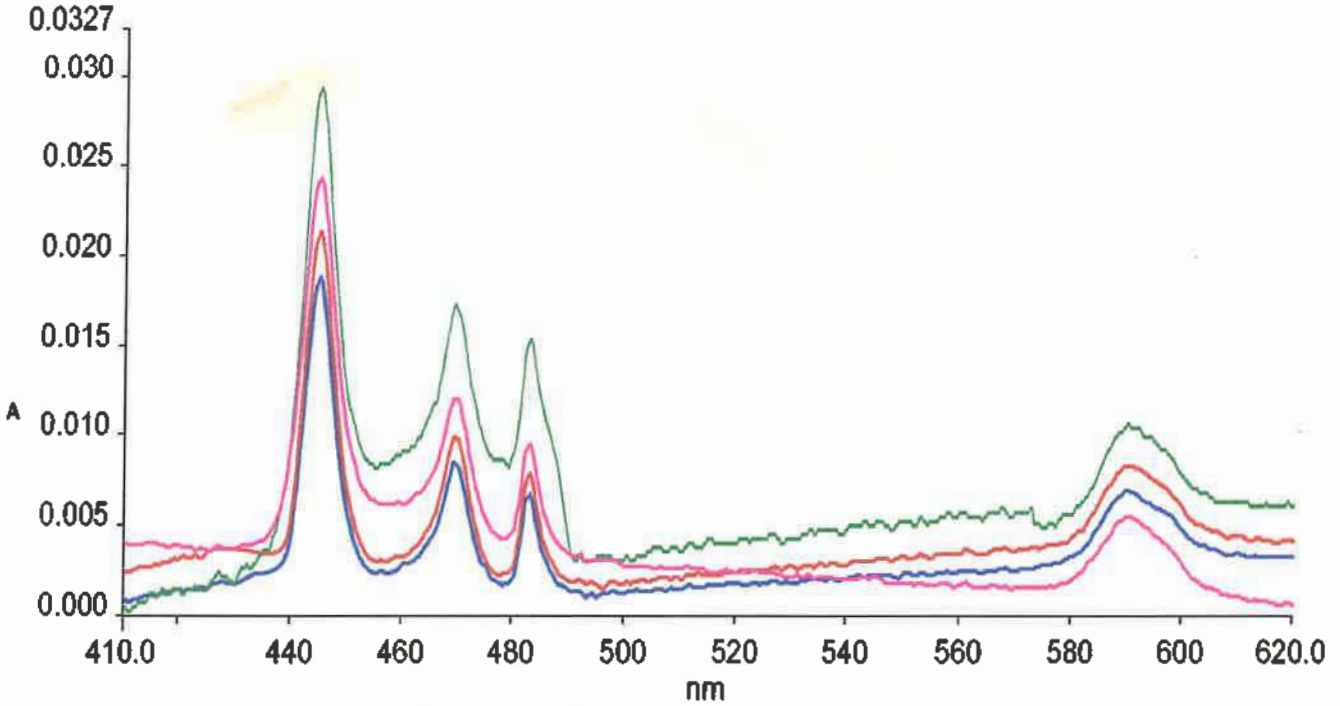

Figure 4.18 Comparative absorption spectra of Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in CH_3OH at pH-6

Pr(III) : Pr(III):GSH :

Pr(III):GSH:Mg(II) : Pr(III):GSH:Zn(II) :

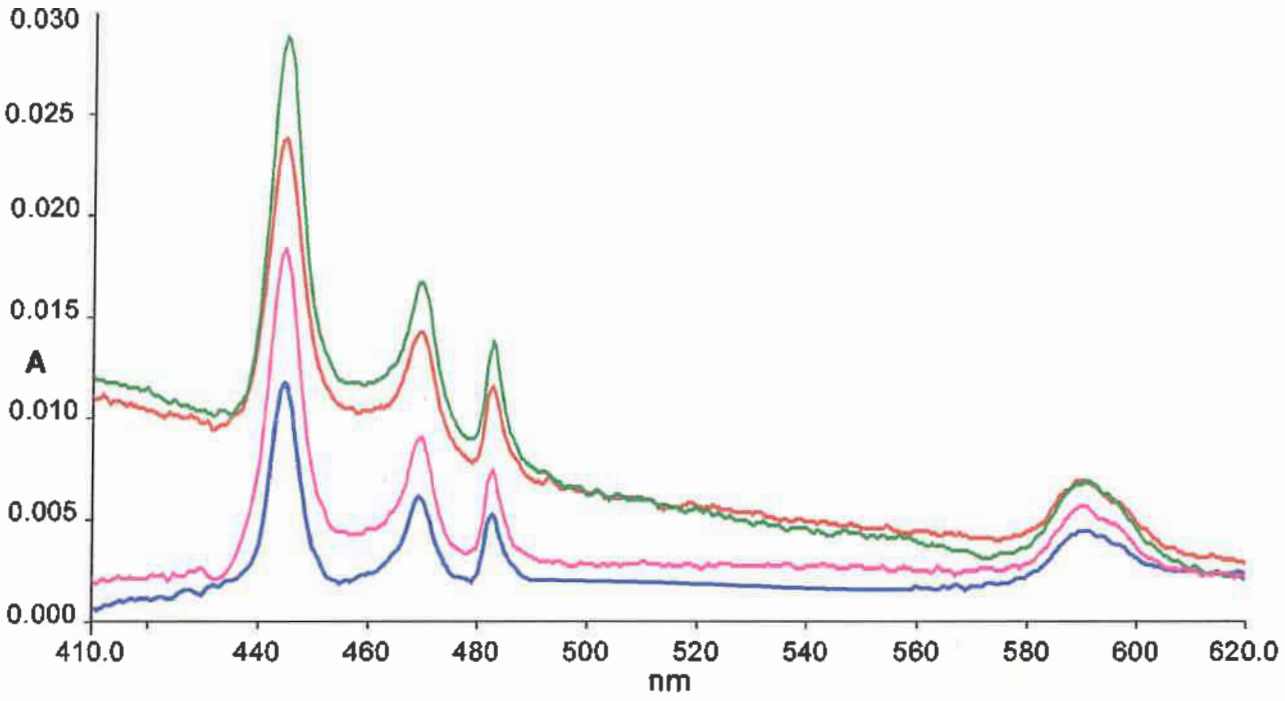

Figure 4.19 Comparative absorption spectra of Pr(III):GSH:Zn(II) in different solvents at pH - 6

Methanol : Acetonitrile :

Dioxane : DMF :

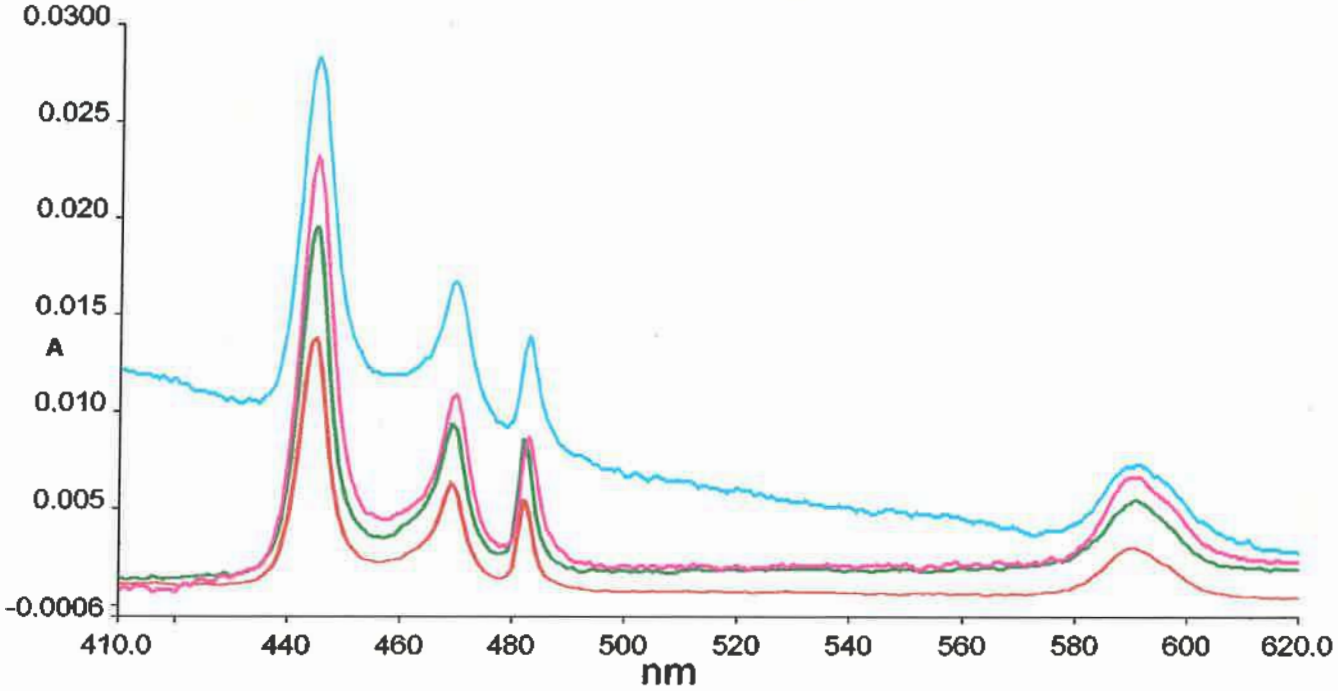

Figure 4.20 Comparative absorption spectra of Pr(III):GSH:Zn(II) in DMF at Different pHs

PH - 3 : PH - 5 :

PH - 4 : PH - 6 :

Table 4.4 : Computed value of energy interaction Slater Condon F_k (cm^{-1}), Spin orbit interaction ξ_{4f} (cm^{-1}), Racah energy E^K (cm^{-1}), Nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency (δ) parameters of Pr(III), Pr(III):GSH (1:1), Pr(III):GSH:Mg(II) (1:1:1) and Pr(III):GSH:Zn(II) (1:1:1) systems in aqueous and different aquated organic solvents(50:50) at pH=3 and 298K are given below :

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
1. CH_3CN										
Pr(III)	309.1868	42.6842	4.6687	722.4906	3510.7080	23.7576	586.6717	0.9468	0.1630	5.6156
Pr(III):GSH	309.1774	42.6819	4.6686	722.4497	3510.6020	237568	586.6539	0.9468	0.1631	5.6203
Pr(III):GSH:Mg(II)	309.1696	42.6809	4.6685	722.4255	3510.512	23.7562	586.6390	0.9468	0.1632	5.6234
Pr(III):GSH:Zn(II)	309.1473	42.6778	4.6681	722.4591	3510.2600	23.7545	586.5967	0.9468	0.1632	5.6245
2. DMF										
Pr(III)	309.0868	42.6694	4.6672	721.5003	3509.5730	23.7499	586.4819	0.9460	0.1643	5.7076
Pr(III):GSH	309.0503	42.6644	4.6667	721.2606	3509.1580	23.7471	586.4126	0.9458	0.1646	5.7319
Pr(III):GSH:Mg(II)	309.0295	42.6615	4.6663	720.9412	3508.9220	23.7455	586.3732	0.9455	0.1650	5.7598
Pr(III):GSH:Zn(II)	308.9701	42.6533	4.6654	721.1192	3508.2470	23.7409	586.2604	0.9456	0.1650	5.7559
3. Dioxane										
Pr(III)	309.1618	42.6798	4.6683	722.4318	3510.4240	23.7556	586.6241	0.9468	0.1632	5.6242
Pr(III):GSH	309.1415	42.6770	4.668	722.3118	3510.1940	23.7541	586.5858	0.9466	0.1633	5.6367
Pr(III):GSH:Mg(II)	309.1308	42.6755	4.6679	722.1599	3510.0720	23.7533	586.5654	0.9465	0.1635	5.6500
Pr(III):GSH:Zn(II)	309.0771	42.6681	4.6671	722.1616	3509.4630	23.7491	586.4636	0.9464	0.1636	5.6586
4. CH_3OH										
Pr(III)	309.1904	42.6837	4.6688	722.5815	3510.7490	23.7578	586.6785	0.9469	0.1629	5.6081
Pr(III):GSH	309.1825	42.6826	4.6687	722.5599	3510.6590	23.7572	586.6635	0.9469	0.1630	5.6110
Pr(III):GSH:Mg(II)	309.1075	42.6723	4.6675	722.6085	3509.8080	23.7515	586.5212	0.9468	0.1631	5.6195

Pr(III):GSH:Zn(II)	309.0376	42.6626	4.6665	722.5609	3509.0140	23.7461	586.3886	0.9467	0.1633	5.6346
5. CH_3CN + DMF										
Pr(III)	309.1614	42.6797	4.6683	722.3155	3510.4200	23.7556	586.6235	0.9467	0.1633	5.6331
Pr(III):GSH	309.1370	42.6764	4.6680	722.1230	3510.1430	23.7537	586.5772	0.9465	0.1635	5.6518
Pr(III):GSH:Mg(II)	309.1064	42.6721	4.6675	722.1057	3509.7950	23.7514	586.5190	0.9464	0.1636	5.6581
Pr(III):GSH:Zn(II)	309.0305	42.6617	4.6664	722.0054	3508.9330	23.7456	586.3750	0.9463	0.1639	5.6782
6. CH_3CN:Dioxane										
Pr(III)	309.1532	42.6786	4.6682	722.1235	3510.3260	23.7550	586.6079	0.9465	0.1635	5.6491
Pr(III):GSH	309.0968	42.6708	4.6674	722.1799	3509.6870	23.7507	586.5009	0.9465	0.1636	5.6540
Pr(III):GSH:Mg(II)	309.0672	42.6667	4.6669	722.1083	3509.3500	23.7484	586.4446	0.9464	0.1637	5.6643
Pr(III):GSH:Zn(II)	308.9135	42.6455	4.6646	722.4971	3507.6050	23.7366	586.1531	0.9464	0.1637	5.6597
7. DMF : Dioxane										
Pr(III)	309.1219	42.6743	4.6677	722.0259	3509.9720	23.7526	586.5486	0.9464	0.1637	5.6617
Pr(III):GSH	309.0830	42.6689	4.6672	721.7743	3509.5300	23.7496	586.4748	0.9462	0.1640	5.6873
Pr(III):GSH:Mg(II)	309.0283	42.6614	4.6663	721.5342	3508.9098	23.7454	586.3709	0.9459	0.1644	5.7146
Pr(III):GSH:Zn(II)	308.9130	42.6454	4.6646	721.5644	3507.5990	23.7365	586.1522	0.9458	0.1646	5.7311
8. CH_3OH + CH_3CN										
Pr(III)	309.1539	42.6787	4.6682	722.0024	3510.3340	23.7550	586.6029	0.9464	0.1636	5.6583
Pr(III):GSH	309.0649	42.6664	4.6669	722.4288	3509.3240	23.7482	586.4403	0.9466	0.1634	5.6402
Pr(III):GSH:Mg(II)	309.0807	42.6686	4.6671	722.1069	3509.5030	23.7494	586.4703	0.9464	0.1637	5.6622
Pr(III):GSH:Zn(II)	309.0199	42.6602	4.6662	722.0146	3508.8130	23.7447	586.3549	0.9463	0.1639	5.6792
9. CH_3OH+DMF										
Pr(III)	309.1438	42.6773	4.6681	722.2325	3510.2190	23.7543	586.5900	0.9466	0.1634	5.6423
Pr(III):GSH	309.1194	42.6739	4.6677	722.0470	3509.9430	23.7524	586.5438	0.9464	0.1637	5.6605
Pr(III):GSH:Mg(II)	308.9857	42.6555	4.6657	721.0687	3508.4240	23.7421	586.2900	0.9456	0.1650	5.7572

Pr(III):GSH:Zn(II)	308.9781	42.6544	4.6656	721.7072	3508.3380	23.7415	586.2757	0.9460	0.1643	5.7096
10. CH_3OH + Dioxane										
Pr(III)	309.1648	42.6802	4.6684	722.3130	3510.4580	23.7559	586.6299	0.9467	0.1633	5.6328
Pr(III):GSH	309.1525	42.6785	4.6682	722.2290	3510.3180	23.7549	586.6065	0.9466	0.1634	5.6412
5.6533Pr(III):GSH:Mg(II)	309.0875	42.6695	4.6672	722.0999	3509.5800	23.7499	586.4832	0.9464	0.1637	5.6617
Pr(III):GSH:Zn(II)	309.0242	42.6608	4.6663	722.1413	3508.8610	23.7451	586.3630	0.9464	0.1638	5.6688
11. Water										
Pr(III)	309.2485	42.6918	4.6697	722.5340	3511.4090	23.7623	586.7888	0.9469	0.1629	5.6022
Pr(III):GSH	309.2367	42.6901	4.6695	722.4649	3511.2750	23.7614	586.7663	0.9469	0.1630	5.6094
5.6533Pr(III):GSH:Mg(II)	309.2246	42.6885	4.6693	722.4741	3511.1370	23.7605	586.7433	0.9469	0.1630	5.6107
Pr(III):GSH:Zn(II)	309.1920	42.6840	4.6688	722.4578	3510.7670	23.7580	586.6815	0.9468	0.1631	5.6173

Table 4.5 : Computed value of energy interaction Slater Condon F_k (cm^{-1}), Spin orbit interaction ξ_{4f} (cm^{-1}), Racah energy E^K (cm^{-1}), Nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency (δ) parameters of Pr(III), Pr(III):GSH (1:1), Pr(III):GSH:Mg(II) (1:1:1) and Pr(III):GSH:Zn(II) (1:1:1) systems in aqueous and different aquated organic solvents(50:50) at pH=4 and 298K are given below :

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
1. CH_3CN										
Pr(III)	309.0344	42.6622	4.6664	721.1262	3508.9780	23.7459	586.3825	0.9457	0.1648	5.7448
Pr(III):GSH	309.0094	42.6587	4.6660	721.2076	3508.6930	23.7439	586.3350	0.9457	0.1648	5.7427
Pr(III):GSH: Mg(II)	313.1204	43.2263	4.7281	692.5450	3555.3720	24.0598	594.1354	0.9321	0.1843	7.2861
Pr(III):GSH:Zn(II)	308.9153	42.6458	4.6646	721.0182	3507.6250	23.7367	586.1564	0.9454	0.1652	5.7726
2. DMF										
Pr(III)	308.9553	42.6513	4.6652	720.6349	3508.0790	23.7398	586.2323	0.9452	0.1655	5.7954
Pr(III):GSH	308.9423	42.6495	4.6650	720.6133	3507.9320	23.7388	586.2078	0.99452	0.1655	5.7991
Pr(III):GSH:Mg(II)	308.8986	42.6435	4.6644	720.3871	3507.4360	23.7354	586.1248	0.9460	0.1659	5.8237
Pr(III):GSH:Zn(II)	308.8655	42.6389	4.6639	720.3102	3507.0600	23.7329	586.0620	0.9449	0.1660	5.8350
3. Dioxane										
Pr(III)	308.9964	42.6570	4.6658	721.3854	3508.5460	23.7429	586.3104	0.9458	0.1646	5.7312
Pr(III):GSH	308.9883	42.6558	4.6657	721.3931	3508.4550	23.7423	586.2951	0.9458	0.1646	5.7319
Pr(III):GSH:Mg(II)	308.9795	42.6546	4.6656	721.4219	3508.3540	23.7416	586.2783	0.9458	0.1646	5.7312
Pr(III):GSH:Zn(II)	309.0288	42.6614	4.6663	722.4818	3508.9140	23.7454	586.3719	0.9466	0.1634	5.6421
4. CH_3OH										
Pr(III)	308.9919	42.6563	4.6658	720.7278	3508.4940	23.7426	586.3018	0.9453	0.1653	5.7823
Pr(III):GSH	308.9919	42.6563	4.6658	720.7278	3508.4940	23.7416	586.2761	0.9452	0.1655	5.7924
Pr(III):GSH: Mg(II)	308.9631	42.6524	4.6653	720.5909	3508.1680	23.7404	586.2473	0.9452	0.1655	5.7975

Pr(III):GSH:Zn(II)	308.9087	42.6448	4.6645	720.6706	3507.5500	23.7362	586.1439	0.9452	0.1656	5.8003
5 . CH_3CN + DMF										
Pr(III)	308.7965	42.6294	4.6628	722.4115	3506.2760	23.7276	585.9311	0.9462	0.1640	5.6854
Pr(III) GSH	308.7397	42.6215	4.6620	722.3372	3505.6310	23.7232	585.8232	0.9461	0.1642	5.7004
Pr(III):GSH:Mg(II)	308.7021	42.6163	4.6614	722.3021	3505.2040	23.7203	585.7519	0.9460	0.1643	5.7092
Pr(III):GSH:Zn(II)	308.6782	42.6130	4.6610	722.0649	3504.9330	23.7185	585.7067	0.9458	0.1646	5.7312
6 . CH_3 CN+Dioxane										
Pr(III)	309.0568	42.6653	4.6668	721.8173	3509.2310	23.7476	586.4249	0.9462	0.1640	5.6883
Pr(III):GSH	309.0262	42.6611	4.6663	721.5729	3508 8840	23.7452	586.3669	0.9460	0.1644	5.7120
Pr(III):GSH: Mg(II)	308 9922	42 6564	4.6658	721.7032	3508.4990	23.7426	586.3025	0.9460	0.1643	5.7075
Pr(III):GSH:Zn(II)	308.9525	42.6509	4 .6652	721.4927	3508.0470	23.7396	586.2271	0.9460	0.1643	5.7075
7 .DMF + Dioxane										
Pr(III)	309.0103	42.6589	4.6661	721.1907	3508.7030	23.7440	586.3367	0.9457	0.1648	5.7438
Pr(III):GSH	308.9918	42.6563	4.6658	721.1761	3508 4930	23.7426	586.3016	0.9456	0.1649	5.7480
Pr(III):GSH: Mg(II)	308.9698	42.6533	4.6654	721.1296	3 508.2440	23.7409	586.2598	0.9456	0.1650	5.7551
Pr(III):GSH:Zn(II)	308.9238	42.6469	4.6648	721.0628	3507 7220	23.7374	586.1727	0.9455	0.1651	5.7677
8. CH_3 OH+Dioxane										
Pr(III)	309.0438	42.6635	4.6666	721.4194	3509.0840	23.7466	586.4003	0.9459	0.1645	5.7208
Pr(III):GSH	309.0268	42.6612	4.6663	721.3656	3508 8920	23.7453	586.3681	0.9458	0.1646	5.7277
Pr(III):GSH:Mg(II)	309.0041	42.6580	4.6660	721.3143	3508.6330	23.7435	586.3250	0.9458	0.1647	5.7354
Pr(III):GSH Zn(II)	308.9850	42.6554	4.6657	721.6026	3508.4160	23.7421	586.2886	0.9459	0.1644	5.7164
9 . CH_3OH+DMF										
Pr(III)	309.0511	42.6645	4.6667	721.2996	3509.1670	23.7471	586.4142	0.9458	0.1646	5.7288
Pr(III)GSH	309.0380	42.6627	4.6665	721 788	3509 0180	23.7461	586.3893	0.9458	0.1646	5.7325
Pr(III):GSH:Mg(II)	309.0157	42.6596	4.6661	721.2214	3508.7650	23 7444	586.3470	0.9457	0.1648	5.7406

Pr(III)GSH :Zn(II)	308.9849	42.6554	4.6657	721.1275	3508.4160	23.7421	586.2886	0.9456	0.1649	5.7528
10. CH_3OH+CH_3CN										
Pr(III)	309.10	42.6721	4.66675	721.6064	3509.7930	23.7514	586.5188	0.9461	0.1642	5.6963
Pr(III)GSH	309.0883	42.6696	4.6672	721.6066	3509.5890	23.7500	586.4847	0.9461	0.1642	5.6992
Pr(III):GSH:Mg(II)	309.0764	42.6680	4.6671	721.5212	3509.4540	23.7491	586.4622	0.9460	0.1643	5.7077
Pr(III):GSH:Zn(II)	309.0495	42.6643	4.6666	721.4911	3509.1490	23.7470	586.4111	0.9459	0.1644	5.7144
11. Water										
Pr(III)	309.0894	42.6698	4.6673	721.7225	509.6020	23.7501	586.4869	0.9462	0.1641	5.6902
Pr(III)GSH	309.0721	42.6674	4.6670	721.7350	3509.4050	23.7488	586.4569	0.9461	0.1641	5.6921
Pr(III):GSH:Mg(II)	309.0551	42.6651	4.6667	721.7606	3509.2120	23.7474	586.4217	0.9461	0.1641	5.6929
Pr(III)GSH :Zn(II)	309.0044	42.6581	4.6660	721.7427	3508.6370	23.7436	586.3256	0.9461	0.1642	5.7025

Table 4.6 Computed value of energy interaction Slater Condon F_k (cm^{-1}), Spin orbit interaction ξ_{4f} (cm^{-1}), Racah energy E^K (cm^{-1}), Nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency (δ) parameters of Pr(III), Pr(III):GSH (1:1), Pr(III):GSH:Mg(II) (1:1:1) and Pr(III):GSH:Zn(II) (1:1:1) systems in aqueous and different aquated organic solvents(50:50) at pH =5 and 298K are given below :

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
1. CH_3CN										
Pr(III)	308.8684	42.6393	4.6639	721.0256	3507.0930	23.7331	586.0674	0.9454	0.1653	5.7797
Pr(III):GSH	315.2827	43.5248	4.7608	710.5672	3579.9240	24.2260	598.2383	0.9476	0.1619	5.5313
Pr(III):GSH:Mg(II)	308.8822	42.6412	4.6641	721.6876	3507.2500	23.7342	586.0937	0.9458	0.1646	5.7267
Pr(III):GSH.Zn(II)	308.7718	42.6259	4.6625	720.3729	3505.9960	23.7257	585.8842	0.9448	0.1662	5.8455
2. DMF										
Pr(III)	308.7603	42.6244	4.6623	721.9941	3505.8660	23.7248	585.8625	0.9459	0.1645	5.7232
Pr(III):GSH	308.6608	42.6106	4.6608	721.9697	3504.7360	23.7172	585.6736	0.9457	0.1648	5.7414
Pr(III):GSH:Mg(II)	308.5884	42.6006	4.6597	721.6351	3503.9140	23.7116	585.5362	0.9454	0.1653	5.7788
Pr(III):GSH:Zn(II)	308.5566	42.5962	4.6592	721.5332	3503.5520	23.7091	585.4758	0.9453	0.1655	5.7918
3. Dioxane										
Pr(III)	308.8204	42.6327	4.6632	722.1250	3506.5480	23.7294	585.9765	0.9460	0.1643	5.7034
Pr(III):GSH	308.7463	42.6224	4.6621	722.2688	3505.7070	23.7237	585.8359	0.9460	0.1643	5.7045
Pr(III):GSH:Mg(II)	308.7193	42.6187	4.6617	722.2582	3505.4000	23.7216	585.7846	0.9460	0.1643	5.7097
Pr(III):GSH:Zn(II)	308.6618	42.6108	4.6608	722.3185	3504.7470	23.7171	585.6755	0.9459	0.1644	5.7145
4. CH_3OH										
Pr(III)	308.8505	42.6368	4.6636	722.2092	3506.8890	23.7317	586.0334	0.9461	0.1641	5.6920
Pr(III):GSH	308.8254	42.6334	4.6633	722.1508	3506.6050	23.7298	585.9860	0.9461	0.1642	5.7006
Pr(III):GSH:Mg(II)	308.8109	42.6313	4.6630	722.1298	3506.4390	23.7287	585.9583	0.9460	0.1643	5.7046

Pr(III):GSH:Zn(II)	308.7839	42.6276	4.6626	722.0975	3506.1330	23.7266	585.9072	0.9460	0.1644	5.7115
5. CH_3CN + DMF										
Pr(III)	308.8835	42.6414	4.6641	722.1729	3507.2650	23.7343	586.0963	0.9462	0.1641	5.6894
Pr(III):GSH	308.7862	42.6279	4.6627	722.4078	3506.1600	23.7268	585.9116	0.9462	0.1640	5.6873
Pr(III):GSH.Mg(II)	308.7441	42.6221	4.6620	722.4117	3505.6820	23.7236	585.8317	0.9461	0.1641	5.6939
Pr(III):GSH:Zn(II)	308.7139	42.6180	4.6616	722.2582	3505.3390	23.7212	585.7744	0.9460	0.1643	5.7106
6. CH_3CN Dioxane										
Pr(III)	308.8475	42.6364	4.6636	722.1951	3506.8550	23.7315	586.0278	0.9461	0.1641	5.6936
Pr(III):GSH	308.8167	42.6321	4.6631	722.2090	3506.5060	23.7291	585.9694	0.9461	0.1642	5.6976
Pr(III):GSH: Mg(II)	308.8049	42.6305	4.6630	722.1401	3506.3720	23.7282	585.9470	0.9460	0.1643	5.7048
Pr(III):GSH:Zn(II)	308.7743	42.6263	4.6625	722.1535	3506.0240	23.7259	585.8890	0.9460	0.1643	5.7087
7. CH_3OH +CH_3CN										
Pr(III)	308.8908	42.6424	4.6643	722.1053	3507.3470	23.7348	586.1100	0.9461	0.1641	5.6934
Pr(III):GSH	308.8796	42.6408	4.6641	722.0275	3507.2190	23.7340	586.0887	0.9461	0.1642	5.7012
Pr(III):GSH:Mg(II)	308.8445	42.6360	4.6636	721.8997	3506.8210	23.7313	586.0221	0.9459	0.1644	5.7167
Pr(III):GSH:Zn(II)	308.7840	42.6276	4.6626	721.8519	3506.1340	23.7266	585.9073	0.9458	0.1646	5.7302
8. CH_3OH+Dioxane										
Pr(III)	308.8911	42.6424	4.6643	722.3938	3507.3500	23.7348	586.1105	0.9463	0.1638	5.6713
Pr(III):GSH	308.8361	42.6348	4.6634	722.6336	3506.7250	23.7306	586.0061	0.9464	0.1637	5.6619
Pr(III):GSH.Mg(II)	308.8350	42.6347	4.6634	722.7214	3506.7130	23.7305	586.0040	0.9465	0.1636	5.6554
Pr(III):GSH:Zn(II)										
9. CH_3OH+DMF										
Pr(III)	308.8090	42.6311	4.6630	721.9271	3506.4180	23.7285	585.9547	0.9459	0.1645	5.7204
Pr(III) GSH	308.7143	42.6180	4.6616	722.3434	3505.3430	23.7213	585.7751	0.9460	0.1643	5.7040
Pr(III):GSH:Mg(II)	308.6733	42.6124	4.6610	722.1676	3504.8770	23.7181	585.6973	0.9459	0.1645	5.7242

Pr(III):GSH:Zn(II)	308.6237	42.6055	4.6602	721.9136	3504.3140	23.7143	585.6031	0.9456	0.1649	5.7517
10. DMF+ Dioxane										
Pr(III)	308.6031	42.2446	4.6231	721.9418	3505.6640	23.2468	585.6256	0.9596	0.1656	5.7324
Pr(III):GSH	308.6082	42.1065	4.6082	721.6976	3504.3602	23.1742	585.7365	0.9574	0.1684	5.7145
Pr(III):GSH:Mg(II)	308.8845	42.0067	4.5974	721.3514	3503.1405	23.1156	585.3624	0.9545	0.1635	5.7884
Pr(III):GSH:Zn(II)	308.5667	42.9628	4.5925	721.3321	3503.5206	23.0911	585.7582	0.9532	0.1652	5.7128
11. Water										
Pr(III)	309.0491	42.6642	4.6666	721.8217	3509.1450	23.7470	586.4104	0.9462	0.1641	5.6892
Pr(III):GSH	309.0326	42.6619	4.6664	721.7665	3508.9570	.7475	586.3790	0.9461	0.1642	5.6961
Pr(III):GSH:Mg(II)	308.9397	42.6491	4.6650	720.7789	3507.9030	23.7386	586.2028	0.9453	0.1654	5.7869
Pr(III):GSH:Zn(II)	308.9020	42.6439	4.6644	720.7589	3507.4750	23.7357	586.1313	0.9452	0.1655	5.7946

Table 4.7 Computed value of energy interaction Slater Condon F_k (cm^{-1}), Spin orbit interaction ξ_{4f} (cm^{-1}), Racah energy E^K (cm^{-1}), Nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency (δ) parameters of Pr(III), Pr(III):GSH (1:1), Pr(III):GSH:Mg(II) (1:1:1) and Pr(III):GSH:Zn(II) (1:1:1) systems in aqueous and different aquated organic solvents(50:50) at pH=6and 298K are given below :

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
1. CH_3CN										
Pr(III)	308.7618	42.6246	4.6623	722.1035	3505.8820	23.7249	585.8652	0.9459	0.1644	5.7146
Pr(III):GSH	308.7499	42.6229	4.6621	722.1072	3505.7470	23.7240	585.8427	0.9459	0.1644	5.7146
Pr(III):GSH: Mg(II)	308.7392	42.6214	4.6620	722.0399	3505.6260	23.7232	585.8223	0.9459	0.1645	5.7232
Pr(III):GSH:Zn(II)	308.7159	42.6182	4.6616	722.0460	3505.3610	23.7214	585.7781	0.9458	0.1646	5.7265
2. DMF										
Pr(III)	308.6907	42.6147	4.6612	722.6774	3505.0750	23.7194	585.7303	0.9462	0.1640	5.6823
Pr(III):GSH	308.6396	42.6077	4.6605	722.6100	3504.4950	23.7155	585.6334	0.9461	0.1641	5.6958
Pr(III):GSH:Mg(II)	308.6093	42.6035	4.6600	722.4354	3504.1510	23.7132	585.5759	0.9459	0.1644	5.7141
Pr(III):GSH:Zn(II)	308.5869	42.6004	4.6597	722.3949	3503.8970	23.7115	585.5334	0.9459	0.1645	5.7209
3 . Dioxane										
Pr(III)	308.8126	42.6316	4.6631	722.5525	3506.4590	23.7288	585.9615	0.9463	0.1638	5.6720
Pr(III):GSH	308.7693	42.6256	4.6624	722.7118	3505.9680	23.7255	585.8795	0.9464	0.1638	5.6669
Pr(III):GSH:Mg(II)	308.7487	42.6228	4.6621	722.4535	3505.7330	23.7239	585.8403	0.9462	0.1641	5.6900
Pr(III):GSH: Zn(II)	308.6969	42.6156	4.6613	722.2922	3505.1450	23.7199	585.7420	0.9460	0.1644	5.7108
4. CH_3OH										
Pr(III)	308.8163	42.6321	4.6631	722.3795	3506.5020	23.7291	585.9688	0.9462	0.1641	5.6900

Pr(III):GSH	308.7614	42.6245	4.6623	722.5276	3505.8780	23.7249	585.8646	0.9462	0.1640	5.6822
Pr(III):GSH: Mg(II)	308.7385	42.6213	4.6620	722.3857	3505.6170	23.7231	585.8209	0.9461	0.1642	5.6968
Pr(III):GSH:Zn(II)	308.6938	42.6152	4.6613	722.3337	3505.1100	23.7197	585.7362	0.9460	0.1643	5.7081
5. CH_3CN + DMF										
Pr(III)	308.7154	42.6182	4.6616	722.4501	3505.3560	23.7213	585.7772	0.9461	0.1641	5.6957
Pr(III):GSH	308.6985	42.6158	4.6613	722.3865	3505.1640	23.7201	585.7452	0.9460	0.1642	5.7033
Pr(III):GSH:Mg(II)	308.6674	42.6115	4.6609	722.1633	3504.8110	23.7177	585.6862	0.9458	0.1646	5.7255
Pr(III):GSH:Zn(II)	308.6297	42.6063	4.6603	722.1552	3504.3820	23.7148	585.6146	0.9458	0.1646	5.7323
6. CH_3CN:Dioxane										
Pr(III)	308.8751	42.6402	4.6640	723.2736	3507.1690	23.7336	586.0802	0.9469	0.1629	5.6067
Pr(III):GSH	308.8427	42.6357	4.6635	723.3055	3506.8010	23.7311	586.0187	0.9469	0.1630	5.6095
Pr(III):GSH: Mg(II)	308.8296	42.6339	4.6633	723.2893	3506.6520	23.7301	585.9938	0.9469	0.1630	5.6129
Pr(III):GSH.Zn(II)	308.7889	42.6283	4.6627	723.1679	3506.1900	23.7270	585.9166	0.9467	0.1632	5.6288
7 .CH_3OH +CH_3CN										
Pr(III)	308.8170	42.6322	4.6631	723.0751	3506.5100	23.7292	585.9700	0.9467	0.1633	5.6313
Pr(III):GSH	308.7963	42.6293	4.6628	723.0482	3506.3740	23.7276	585.9306	0.9466	0.1633	5.6368
Pr(III):GSH:Mg(II)	308.7829	42.6275	4.6626	723.0308	3506.1220	23.7265	585.9052	0.9466	0.1634	5.6403
Pr(III):GSH:Zn(II)	308.7409	42.6217	4.6620	723.0308	3506.1220	23.7265	585.9052	0.9466	0.1634	5.6403
8. CH_3OH+ Dioxane										
Pr(III)	308.7872	42.6281	4.6627	721.8752	3506.1700	23.7269	585.9134	0.9458	0.1646	5.7279
Pr(III):GSH	308.7638	42.6248	4.6623	721.8094	3505.9050	23.7251	585.8690	0.9457	0.1647	5.7369
Pr(III):GSH:Mg(II)	308.7190	42.6187	4.6617	721.7911	3505.3960	23.7216	585.7841	0.9457	0.1648	5.7455
Pr(III):GSH:Zn(II)	308.6827	42.6137	4.6611	721.8021	3504.9850	23.7188	585.7152	0.9456	0.1649	5.7506
9. CH_3OH +DMF				722.						
Pr(III)	308.7681	42.6254	4.6624	9301	3505.9540	23.7254	585.8772	0.9465	0.1635	5.6504

Pr(III):GSH	308.7250	42.6195	4.6617	722.9087	3505.4640	23.7221	585.7954	0.9464	0.1636	5.6591
Pr(III):GSH:Mg(II)	308.7116	42.6176	4.6615	722.8958	3505.3120	23.7211	585.7700	0.9464	0.1637	5.6622
Pr(III):GSH:Zn(II)	308.6743	42.6125	4.6610	722.8088	3504.8890	23.7182	585.6993	0.9463	0.1639	5.6750
10. DMF+ Dioxane										
Pr(III)	308.8911	42.6424	4.6643	722.3938	3507.3500	23.7348	586.1105	0.9463	0.1638	5.6713
Pr(III):GSH	308.8361	42.6348	4.6634	722.6336	3506.7250	23.7306	586.0061	0.9464	0.1637	5.6619
Pr(III):GSH:Mg(II)	308.8350	42.6347	4.6634	722.7214	3506.7130	23.7305	586.0040	0.9465	0.1636	5.6554
Pr(III):GSH:Zn(II)	308.8911	42.6424	4.6643	722.3938	3507.3500	23.7348	586.1105	0.9463	0.1638	5.6713
11. Water										
Pr(III)	309.0282	42.6613	4.6663	722.0153	3508.9070	23.7454	586.3707	0.9463	0.1639	5.6778
Pr(III):GSH	309.0106	42.6589	4.6661	722.0285	3508.7070	23.7440	586.3372	0.9463	0.1639	5.6797
Pr(III):GSH:Mg(II)	308.9926	42.6564	4.6658	722.0286	3508.5030	23.7426	586.3032	0.9462	0.1640	5.6826
Pr(III):GSH:Zn(II)	308.9468	42.6501	4.6651	722.0643	3507.9830	23.7391	586.2162	0.9462	0.1640	5.6874

Table 4.8 : Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for Pr(III), Pr(III):GSH (1:1), Pr(III):GSH:Mg(II) (1:1:1) and Pr(III):GSH:Zn(II) (1:1:1) in aqueous and different aquated organic solvents(50:50) at pH – 3 and 298K

System	$^3H_4$		$^3P_2$		$^3H_4$		$^3P_1$		$^3H_4$		$^3P_0$		$^3H_4$		$^1D_2$		R.M.S
	Eobs		Ecal		Eobs		Ecal		Eobs		Ecal		Eobs		Ecal		
1. CH_3CN																	
Pr(III)	22511	.37	22462.58		21327.87		21251.54				20746.46		20746.46		6971	.88	7141 19	00 00
Pr(III):GSH	22510.86		22461.74		2 326.96		21250.72				20746.03		20689.79		6970.72		7140.64	00.32
Pr(III):GSH: Mg (II):GSH	22509.85		22461.09		21326.05		21 250.07				20745. 60		20689.20		6970.44		7140.2 1	00.19
Pr(III):GSH:Zn	22509.34		22459. 75		21325.14		21 248.65				20743.88		20687.70		6969 .00		7139.29	00.58
2. DMF																	
Pr(III)	22506	18	22450.85		21321	.05	12	240.60			20744. 74		2068	1.63	6946.28		7 133.72	10.36
Pr(III):GSH	22496.68		22447.17		21320.60			21237.08			20743.02		20678.61		6943.41		7131.34	10.56
Pr(III):GSH:Mg	22490.61		22444.16		2 B 19.69			21234.36			20743.02		20676.54		6938.82		7129.46	12.03
Pr(III):GSH:Zn	22487.58		2244 1.04		21317.87		2123	0.90			20737 .85		20674. 71		6937.38		7127.24	11.83
3. DXN																	
Pr(III)	22512.89		22460.59		21 325.60		2	1249.55			207451 7		20688.66		6967 .85		7 139.87	1 82
Pr(III):GSH	22510.36		22458.62		21324.69			21247.66			20744.31		20687 01		6964.97		71 38.59	102.52
Pr(III):GSH:Mg	22508.84		22457.13		21324.23			21246. 30			20744.31		20685.97		6961.80		7137.66	03.77
Pr(III):GSH:Zn	22504.78		22453. 52		21322.42		21	242.55			20740.43		2 0682 2		6958.35		135.20	04.49
4. CH_3OH																	
Pr(III)	22517.96		22463.28		21329.24		21	2521 5			20746.46		20690.96		6969.00		7141.62	02.24
Pr(III):GSH	22517.45		22462.63		21 328.33			21251.51			20746.03		20690.36		6968.42		7141.1 9	02.29
Pr(III):GSH:Mg	22516.44		22457.82		21329.24			21246.45			20740.43		20685 19		6959.21		7137.89	06.38
Pr(III):GSH:Zn	22509.85		22452. 86		21324.23			21241.37			20735.70		20680.20		6956 94		7134.54	06.01
5. CH_3CN:DMF																	
Pr(III)	22508.84		22459.98		21 325.14			21249.06			20745.60		20688.41		6968.42		713 9.52	00.89
Pr(III):GSH	22503.26		22457.37		21323.33		21	246.59			20744.74		20686.34		6966 12		7137 .84	01.11
Pr(III):GSH:Mg	22500.73		22455.21		21322.87			21244.37			20742.58		20684 15		6963.53		7136.38	01.89
Pr(III):GSH:Zn	22499 2		22449.58		21 13 9.69		21	238.66			2073 7.85		20678.63		6954.32		7132.60	05.26
6. CH_3CN:DXN																	
Pr(III)	225 11.37		22458.46		2 1327.87		21	247 72			20746.03		20687 .47		6960.08		7138.58	05.49
Pr(III):GSH	22508.84		22454.94		21 326 5		21	244.00			20741.72		20683.63		6956 05		71 36 15	06.68
Pr(III):GSH:Mg	225063		22452.58		21324.23		21	24 1.64			20740.00		20681.41		6953 75		71 34.58	07 05
Pr(III):GSH:Zn	22503.26		22444.15		21312.42		2	1232.42			207 2.54		20671 7.3		6950.30		7128.65	05.90
7. DMF Dioxane																	
Pr(III)	22507.32		22455.86		21324.69		2	1246 5			20744.31		20685.09		6958.64		71 36.86	06 17
Pr(III):GSH	22498.20		2245 1.97		1322.87		21	24 1.42			20742.58		2068 .88		6955.47		7134.34	05.41
Pr(III):GSH:Mg	22494.66		22447.06		2131 9.23			2123 6.63			20740.00		20677.59		6948.00		713113	07.84
Pr(III):GSH:Zn	22488 99		2243 9.43		21311.06			21228. 68			20731.83		20669.55		6942.26		7125.91	08.18
8. CH_3OH : CH_3CN																	
Pr(III)	22515.42		22457 .90		21327 .87		2	1247.29			20746.89		20687 79		6955.19		71 38.26	08.25
Pr(III):GSH	22511.88		22454.03		21326.96			21242.75			20738.28		20681.86		6954.32		7135.41	07.72
Pr(III):GSH:Mg	22506.30		22453.48		21 326.5			21242.58			20740.86		20682.35		6954.04		7135.20	07.33
Pr(III):GSH:Zn	22500.22		22448.91		21 322.42			21237.95			20736.99		20677.91		6950.59		7132.13	07.49
9. CH_3OH:DMF																	
Pr(III)	22508.33		22458.38		21 326.05			21247.50			20744.74		20687.02		6964. 11		713 8.46	02.95
Pr(III):GSH	2250 1.74		22455.80		1322.42			21245.06			20743.88		20684.96		6963 82		7136.81	1.85
Pr(III):GSH:Mg	22497 70		22441 .84		2131969			21231.79			20739.57		20673.71		6930.79		7127.81	16.19
Pr(III):GSH:Zn	22488.08		22444.54		2 1309.24		21	233.80			20735 70		20674.39		6955.47		71 29.32	01.94
10. CH_3OH : Dioxane																	
Pr(III)	2251	3.90	22460.20		21326.05		12	249.29			20746.03		20688.65		6964.97		713 9.66	03.18
Pr(III):GSH	225	2.38	22458.95		21 324.69			21248.1 0			20745.60		2068 .62		16963 53		7138.85	03.47
Pr(III):GSH:Mg	22 10	86	22453.90		21 322.87		21	243.03			2074172		20682.81		6954.32		7135.49	07.13
Pr(III):GSH:Zn	22504.78		22449.84		131 8.33		12	238 86			20736.99		20678.45		6953.46		132. 70	05.95
11. Water																	
Pr(III)	225 2	00	22466.97		12 332.88		12	256.04			20750.76		20694.94		6971.59		144. 15	03 13
Pr(III):GSH	22.520.49		22465.82		2 133 1.51		21	254.93			20750.33		20693.98		6969.86		17 143.4	02.65
Pr(III):GSH:Mg	22520.49		22465 05		2130.60		2	1254 12			20749.47		20693. 5		16969 00		7142. 88	02 87
Pr(III):GSH:Zn	225 19.48		22462.76		21 328.33		2	125 .77			20747 .32		20690.83		6966 4		7141.33	103 .52

Table 4.9 : Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for Pr(III), Pr(III): GSH (1:1), Pr(III)GSH :Mg(II) (1 :1:1)and Pr(III):GSH:Zn(II) (1:1:1) in a queous and different aquaed or ganicsolv ents(50:50) at pH – 4 and 298K

S ystem	$^3H_4\rightarrow$	$^3P_2$	$^3H_4\rightarrow$	$^3P_1$	$^3H_4\rightarrow$	$^3P_0$	$^3H_4\rightarrow$	$^1D_2$	R.M.S.
	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	
1. CH_3CN									
Pr(III)	22492.13	22445.42	21316.51	21235.44	20742.58	20677.24	16944.27	17130.22	109.09
Pr(III):GSH	22491.62	21234.01	21315.14	21234.01	20740.43	20675.64	16943. 70	17129.31	108.96
Pr(III):GSH :Mg	22490.10	22577.74	21312.87	21408.16	21179.71	20909.50	16943.12	17235.00	209.14
Pr(III):GSH:Zn	22485.05	22463.83	21307.88	21226.66	20734.84	20668.67	16936.23	171 24.43	110.36
2. DMF									
Pr(III)	22491.12	22437.61	21316.51	21227.94	20739.57	20670.75	16924.48	17125.16	118.02
Pr(III):GSH	22486.56	22436.62	21313.33	21226.95	20738.71	20669.80	16927.35	17124.50	115.73
Pr(III):GSH:Mg	22484.54	22432.53	21307.42	21222.99	20738.99	20666.30	16922.19	17121.83	116.93
Pr(III):GSH:Zn	22483.53	22429.91	21301.52	21220.36	20735.27	20663.83	16920.76	17120.08	116.51
3. DXN									
Pr(III)	22487.68	22444.16	21319.42	21233.81	20738.24	20675.06	16945.10	17129.23	108.53
Pr(III):GSH	22487.47	22443.65	21319.10	21233.27	20737.64	20674.51	16944.50	171 28.88	108.71
Pr(III):GSH:Mg	22487.37	22443.20	21319.05	21232.77	20736. 86	20673 .95	16943 .95	171 28.55	108.90
Pr(III):GSH:Zn	22487.17	22451.86	2131 8.69	21240.44	20734.76	20679.43	16971.88	17133.90	95.77
4. CH_3OH									
Pr(III)	2249 1.12	22440.54	21314.69	21230.87	2074 1.72	20673.49	16932.51	17127.11	114.14
Pr(III):GSH	22489.60	22439.11	21313.78	21229.52	20741 .29	20672.35	16930.21	17126.19	114.90
Pr(III):GSH:Mg	22488.59	2243 7.92	2131 1.96	21228.32	20740.43	2067 1.21	16929.35	17125.39	114.88
Pr(III):GSH:Zn	22484.54	22434.64	2309.24	21224.82	20736.13	20667 .55	16927.92	17123.12	114.48
5. CH_3CN:DMF									
Pr(III)	22486.56	22435.81	21304.70	21223.88	20719.38	20662.99	16948. 58	17123.02	103.34
Pr(III):GSH	2248252	22431.60	21296.53	21219.60	20715.94	20658.86	16941.43	17120.19	102.00
Pr(III):GSH:Mg	22481 .00	22428.88	21297.89	21216.82	20713.37	20656.16	16941 .69	17118.36	104.61
Pr(III):GSH:Zn	22476.96	22426.08	21293.81	21214.21	2071 2.94	20654.03	16939.11	17116.58	104.75
6. CH_3CN:DXN									
Pr(III)	22491.12	22450.41	21 317.42	21239.75	20740.43	20680.12	16960.94	17133.26	101.27
Pr(III):GSH	22490.61	22447.12	21216.96	21 236.64	20739.57	20677.51	16952.60	17131.14	104.97
Pr(III): GSH:Mg	22490. 6	22445.48	21315.60	21234.78	20736.56	20675.38	16951.45	17129.96	105.09
Pr(III):GSH:Zn	22484.54	22441.73	21310.15	21231.15	20734.84	20672.19	16949.44	17127.52	104.54
7. DMF :Dioxane									
Pr(III)	22488.59	22444.12	2315.60	21234.00	20740.43	20675.66	16945.13	17129.30	108.11
Pr(III):GSH	22486.06	22442.79	2131 4.69	21232.65	20739.14	20674.34	16944.56	17128.41	107.94
Pr(III):GSH:Mg	22484.54	22441.07	21312.87	21230.92	20737.85	20672 71	16942.84	17127.26	108.24
Pr(III):GSH:Zn	22479.99	2243763	2131 151	21227.44	2073 4.84	20669.36	16939.11	17124.96	109.19
8. CH_3OH : CH_3CN									
Pr(III)	22491.62	22452.69	21324.69	21242.38	20744.74	2068319	16958.35	17134.92	103.99
Pr(III):GSH	22490.10	22451.48	21323.78	21241.12	20743.45	20681.93	16957.49	17134.09	104.04
Pr(III):GSH:Mg	22488.59	22450.25	213 23.33	21239.95	20743.02	20680.94	16955.47	17133.30	104.76
Pr(III):GSH:Zn	22486.56	22448.28	21321.05	21237.95	20741.29	2067899	16954.04	17131.97	104.78
9. CH_3OH DMF									
Pr(III)	22491.62	22452.69	21324.69	21242.38	20744.74	20683.19	16958.35	17134.92	103.99
Pr(III):GSH	22490.10	22451.48	21323.78	21241.12	20743.45	20681.93	16957.49	17134.09	104.04
Pr(III):GSH:Mg	22486.06	2244464	21318.33	21234.51	20740.43	20676 11	16946.28	1712 9.64	107.82
Pr(III):GSH:Zn	22483.03	22442.09	21316.51	21231.98	20738.71	20673.77	16943.41	17127.95	108.51
10. CH_3OH : Dioxane									
Pr(III)	22496.18	22447.54	21320.14	21237.26	20741.72	20678.46	16946.28	17131.51	109.02
Pr(III):GSH	22494.66	22446.12	21317.42	21235.86	20740.86	20677.16	16945.71	17130.57	108.67
Pr(III):GSH:Mg	22494. 15	22444.32	2316.05	21234.06	20739.57	20675.47	16942.84	17129.38	109.67
Pr(III):GSH:Zn	22506.30	2244.48	21311.51	21233.87	20737.42	20674.67	16941.11	17129.33	110.92
11. Water									
Pr(III)	2249719	22452.14	21328.78	3241.66	20743.02	20682.23	16952.03	17134.48	107.94
Pr(III):GSH	22496.18	2245103	21 327.87	21240.50	2074.72	2068.04	1695.16	17133.72	108.03
Pr(III):GSH:Mg	22495.67	22450.01	2 1326.51	21239.41	20740.43	20679.89	16950.59	17133.01	107.95
Pr(III):GSH:Zn	22492.63	22446.50	21322.87	21235.79	20736.99	20676.31	16947.72	17130.63	108.23

Table 4.10 : Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for Pr(III), Pr(III):GSH (1:1), Pr(III):GSH:Mg(II) (1:1:1) and Pr(III):GSH:Zn(II) (1:1:1) in aqueous and different aquated organic solvents(50:50) at pH – 5 and 298K

System	$^3H_4 \rightarrow$	$^3P_2$	$^3H_4 \rightarrow$	$^3P_1$	$^3H_4 \rightarrow$	$^3P_0$	$^3H_4 \rightarrow$	$^1D_2$	R.M.S.
	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	
1. CH_3CN									
Pr(III)	22488.08	22433.70	21 303.34	21223.41	20731.83	20665.40	16931.07	17122.30	112.17
Pr(III):GSH	22495.16	22814.46	22303.01	21631.29	21195.87	21095.56	16927.06	17386.77	440.04
Pr(III):GSH:Mg	22486.56	22437.96	21313.78	21227.01	20728.82	20667.63	16939. 96	17124. 86	109.34
Pr(III):GSH:Zn	22482.02	22423. 89	21309.69	21214.04	20727.97	20657.37	16904.74	17115.96	124.62
2. DMF									
Pr(III)	22484.04	22431.27	21304.25	21219.69	20718.95	20659.86	16937.38	17120.15	108.23
Pr(III):GSH	22478.98	22424.43	21299.25	21212.62	20712.08	20652.63	16929.93	17115.50	110.06
Pr(III):GSH:Mg	22475.45	22417.85	21 297.92	21206.21	20709.08	20646.91	16923.34	17111.20	110.85
Pr(III):GSH:Zn	22472.42	22415. 19	21 285.20	21 203.58	20707.36	20644.48	16920.76	17109.44	111.23
3. DXN									
Pr(III)	22484.54	22435 .99	21 306.97	21224.42	20722.38	20664.13	16945.99	17123.29	104.88
Pr(III):GSH	22484.04	22431.71	21297.44	21219.79	20716.80	20659.20	16945.42	171 20.30	1 03.28
Pr(III):GSH:Mg	22483.53	22429.83	21 293.81	21217.86	20715.09	20657.28	16944.27	17119.03	103.12
Pr(III):GSH:Zn	22481.00	22426.25	21 289.73	21214.07	20710.79	20653.36	16941.97	17116. 56	103.08
4. CH_3OH									
Pr(III)	22490.90	22438.44	21311.51	21226.86	20724.10	20666.39	16945.13	17124.91	106.64
Pr(III):GSH	22489.09	22436.46	21 306.52	21224.87	20722.81	20664.53	16944.56	17123.59	105.93
Pr(III):GSH:Mg	22488.59	22435.37	21304. 70	21223.76	20721.95	20663.46	16943.70	17122.86	105.95
Pr(III):GSH:Zn	22486.06	2243 3.38	21 301.98	21221.75	20720.24	20661.51	1 6942.84	17121.53	10 5.58
5. CH_3OH : DMF									
Pr(III)	22488.59	22440.50	2 1308.33	21229.03	20726.68	20668.65	16952.03	171 26.33	102.90
Pr(III):GSH	22485.05	22435.1 0	21 306.97	21223.14	20718.52	20662.27	16946.57	17122.54	1 04.46
Pr(III):GSH:Mg	22483.03	22432.28	21305.61	21220.21	20715.51	20659.32	16943.12	17120.62	105.51
Pr(III):GSH:Zn	22481.00	22429.46	21 302.88	21217.48	20714.23	20656.91	16939.11	17118.78	106.67
6. CH_3OH : DXN									
Pr(III)	22487.58	22438.17	213 05.61	21 226.59	20724.10	20666.16	16950.02	17124. 73	103. 16
Pr(III):GSH	22486.56	22436.16	21 302.43	21224.49	20721 .95	20664.02	16948.87	17123.36	102.98
Pr(III):GSH:Mg	22486.06	2243 5.02	21301.07	21223.39	20721.52	20663.06	16947.14	171 22.62	103 .50
Pr(III):GSH:Zn	22485.05	2243 3.02	21 298.35	21221.30	20719.38	20660.95	1 6945.71	17121.25	1 03.53
7. DMF : Dioxane									
Pr(III)	2249 1.62	22452.69	2 1324.69	21 242.38	20744.74	20683. 19	16958.35	171 34.92	103.99
Pr(III):GSH	22490.1 0	2245 .48	21 323.78	21241.12	20743.45	2068 1.93	1 6957.49	17134.09	104.04
Pr(III):GSH:Mg	22488.59	22450.25	21323.33	21239.95	20743.02	20680.94	16955.47	17133.30	104.76
Pr(III):GSH:Zn	22486.56	22448.28	21 321.05	21237.95	20741 .29	20678.99	16954.04	17131.97	104.78
8. CH_3OH : CH_3CN									
Pr(III)	22490.61	22440.65	2131 0.60	21229.27	20727 .54	20669.03	16948.87	17126.46	104.97
Pr(III):GSH	2248 8.59	22439.50	21309.69	21228.17	20727.11	20668.09	16947.72	1712 5.72	105.15
Pr(III):GSH:Mg	22488.08	22436.48	21307.42	21225.21	20725.39	20665.38	16942.26	17123.74	107.19
Pr(III):GSH:Zn	22484.04	22432.16	21 300.16	21220.78	20721 .52	20661.05	16940.54	17120.82	106.24
9. CH_3OH DMF									
Pr(III)	22488.59	22434.22	2 1306.52	21222.82	20722.81	20663.94	16938.24	17122.19	1 08.83
Pr(III):GSH	22483.53	22429.92	21305 .61	21217.85	20713.80	20657. 09	16937.38	17119.04	108.16
Pr(III):GSH:Mg	2248 8.51	22426.27	21 297.89	21214.28	2071 2.08	20653.88	16934.80	1711 6.65	1 0782
Pr(III):GSH:Zn	22478.98	2242 1.63	21295.1 7	2 120979	20709.94	20649.91	16926.49	17113.63	110.91
10. CH_3OH Dioxane									
Pr(III)	22488.59	22442.12	21313. 78	2123 0.43	20725.82	20669.60	16953.75	17127.32	102.95
Pr(III):GSH	22486.56	22439 .61	213 12.42	21227 .53	20720.67	20666.19	16953 .18	17125.48	1 0255
Pr(III):GSH:Mg	22486.06	22439.97	21 309.24	2 122780	20720.24	20666.28	16957.20	17125.69	100.07
Pr(III):GSH:Zn	2248 1 .00	22435.72	2 1308.33	21223 .01	20716.37	20661.73	16950.30	17 122.51	1 02.49
11. Water									
Pr(III)	22499.72	22449.92	21312.87	21 239.23	20740.43	20679.60	16957 .49	171 32.92	102.93
Pr(III):GSH	22498.20	22448. 52	2131 1.06	21237.86	20739.57	20678.33	1 6956.34	171 32.00	1 03.00
Pr(III):GSH:Mg	22496.68	22437.28	21308. 79	2122 7.43	20738.28	20669.93	1 6926.77	17 124.86	1 6.25
Pr(III):GSH:Zn	22493.1 4	22434.63	21 306.06	21224. 70	20735.70	20667.25	16925.34	171 23.07	116. 00

Table 4.11 : Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for Pr(III), Pr(III):GSH (1:1), Pr(III):GSH:Mg(II) (1:1:1) and Pr(III):GSH:Zn(II) (1:1:1) in aqueous and different aquated organic solvents(50:50) at pH – 6 and 298K

System	$^3H_4 \rightarrow$	$^3P_2$	$^3H_4 \rightarrow$	$^3P_1$	$^3H_4 \rightarrow$	$^3P_0$	$^3H_4 \rightarrow$	$^1D_2$	R.M.S.
	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	
1. CH_3CN									
Pr(III)	22488.08	22431.92	21296.99	21220.22	20718.95	20659.97	16941.97	17120.53	105.30
Pr(III):GSH	22487.07	22431.14	21296.08	21219.40	20718.09	20659.14	16941.69	17119.99	105.21
Pr(III):GSH:Mg	22485.05	22430.07	21294.72	21218.38	20717.66	20658.26	16941.11	17119.31	105.04
Pr(III):GSH:Zn	22483.03	22428.53	21293.81	21216.78	20715.94	20656.64	16939.96	17118.25	105.13
2. DMF									
Pr(III)	22479.99	22430.00	21302.43	21217.52	20710.37	20656.07	16945.13	17118.93	103.52
Pr(III):GSH	22476.96	22426.21	21293.81	21213.67	20707.36	20652.36	16944.56	17116.38	101.92
Pr(III):GSH:Mg	22472.92	22423.29	21291.54	21210.86	20706.08	20649.90	16941.11	17114.48	102.70
Pr(III):GSH:Zn	22472.42	22421.57	21289.28	21209.13	20704.79	20648.26	16939.11	17113.34	103.15
3. DXN									
Pr(III)	22487.58	22437.61	21304.70	21225.56	20719.81	20664.39	16952.89	17124.17	101.45
Pr(III):GSH	22486.06	22435.49	21302.88	21223.17	20715.94	20661.66	16952.31	17122.64	101.08
Pr(III):GSH:Mg	22485.55	22432.79	21300.16	21220.69	20715.94	20659.71	16946.57	17120.94	103.28
Pr(III):GSH:Zn	22483.03	22428.48	21292.45	21216.42	20713.37	20655.77	16943.12	17118.09	103.31
4. CH_3OH									
Pr(III)	22485.05	22436.99	21309.69	21225.14	20720.67	20664.32	16948.29	17123.84	104.22
Pr(III):GSH	22482.02	22434.03	21308.79	21221.88	20715.94	20660.75	16946.28	17121.75	104.51
Pr(III):GSH:Mg	22480.50	22431.76	21306.97	21219.71	20715.09	20658.87	16942.55	17120.28	105.76
Pr(III):GSH:Zn	22474.94	22428.49	21304.70	21216.37	20712.08	20655.64	16940.54	17118.07	105.67
5. CH_3CN:DMF									
Pr(III)	22486.06	22430.53	21306.97	21218.35	20713.37	20657.38	16937.10	17119.40	108.75
Pr(III):GSH	22485.05	22429.07	21306.06	21216.91	20712.51	20656.07	16934.80	17118.44	109.54
Pr(III):GSH:Mg	22481.00	22425.85	21298.35	21213.85	20711.65	20653.46	16933.94	17116.37	108.22
Pr(III):GSH:Zn	22479.99	22423.26	21296.53	21211.17	20709.08	20650.80	16930.50	17114.61	109.31
6. CH_3CN:DXN									
Pr(III)	22488.59	22445.46	21309.69	21232.81	20720.24	20670.15	16971.59	17129.14	93.68
Pr(III):GSH	22484.54	22443.43	21308.79	21230.67	20717.66	20667.94	16971.01	17127.74	93.31
Pr(III):GSH:Mg	22483.53	22442.46	21308.33	21229.69	20716.80	20666.99	16969.86	17127.09	93.64
Pr(III):GSH:Zn	22479.99	22439.10	21302.88	21226.35	20714.66	20663.90	16967.85	17124.87	93.22
7. DMF : Dioxane									
Pr(III)	22488.59	22434.22	21306.52	21222.82	20722.81	20662.94	16938.24	17122.19	108.83
Pr(III):GSH	22483.53	22429.92	21305.61	21217.85	20713.80	20657.09	16937.38	17119.04	108.16
Pr(III):GSH:Mg	22481.51	22426.27	21297.89	21214.28	20712.08	20653.88	16934.80	17116.65	107.82
Pr(III):GSH:Zn	22478.98	22421.63	21295.17	21209.79	20709.94	20649.91	16926.49	17113.63	110.91
8. CH_3OH : CH_3CN									
Pr(III)	22486.06	22440.54	21306.52	21227.95	20717.23	20665.70	16963.53	17125.89	96.52
Pr(III):GSH	22484.54	22439.00	21304.25	21226.39	20715.94	20664.19	16962.66	17124.86	96.33
Pr(III):GSH:Mg	22483.03	22438.01	21302.88	21225.38	20715.09	20663.21	16962.38	17124.19	96.06
Pr(III):GSH:Zn	22481.00	22434.18	21296.08	21221.66	20713.37	20659.89	16958.64	17121.69	96.41
9. CH_3OH : DMF									
Pr(III)	22486.06	22432.49	21304.70	21221.09	20721.52	20661.32	16937.10	17121.03	108.76
Pr(III):GSH	22484.54	22430.57	21302.88	21219.19	20720.24	20659.55	16934.80	17119.77	109.33
Pr(III):GSH:Mg	22481.00	22427.46	21298.35	21215.98	20717.23	20656.38	16933.65	17117.66	108.64
Pr(III):GSH:Zn	22479.99	22425.06	21296.53	21213.48	20714.66	20653.85	16930.79	17116.02	109.46
10. CH_3OH : Dioxane									
Pr(III)	22486.56	22436.50	21304.70	21223.95	20714.66	20661.99	16954.90	17123.22	100.17
Pr(III):GSH	22483.53	22433.48	21303.79	21220.84	20711.65	20658.92	16951.16	17121.18	101.33
Pr(III):GSH:Mg	22483.03	22432.51	21302.88	21219.85	20710.79	20657.96	16950.02	17120.52	101.63
Pr(III):GSH:Zn	22481.51	22429.56	21301.07	21216.90	20708.65	20655.18	16945.42	17118.56	103.22
11. Water									
Pr(III)	22497.19	22449.47	21312.42	21238.54	20737.85	20678.49	16960.36	17132.52	101.11
Pr(III):GSH	22496.18	22448.35	21311.06	21237.36	20736.56	20677.28	16959.79	17131.75	101.00
Pr(III):GSH:Mg	22494.66	22447.14	21310.15	21236.10	20735.27	20676.02	16958.93	17130.92	101.04
Pr(III):GSH:Zn	22491.12	22444.22	21307.42	21233.03	20731.83	20672.88	16957.49	17128.92	100.75

Table 4.12 : Experimental values of oscillator strength (P x 10^6) (observed and calculated) and Judd-Ofelt parameter (T_λ x 10^{10}) cm^{-1} for Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) complexes in different aquated organic solvents at pH 3 and 298K

Sytem	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. CH_3CN											
Pr(IIII	0.8754	0.8754	0.3892	0.5621	0.7465	0.5709	3.1291	3.1291	-8.5797	1.5681	9.8394
Pr(III) :GSH	0.9202	0.9202	0.4088	0.5914	0.7860	0.6006	3.2489	3.2489	-6.4838	1.6498	10.2098
Pr(III) : GSH : Mg(II)	0.9659	0.9659	0.4209	0.6031	0.7976	0.6125	3.1369	3.1369	11.2974	1.6822	9.8386
Pr(III):GSH: Zn(II)	0.9903	0.9903	0.4195	0.6041	0.8009	0.6134	3.1579	3.1579	15.3466	1.6849	9.9002
2. Dioxane											
Pr(IIII	0.5566	0.5566	0.5733	0.6044	0.6454	0.6138	2.5737	2.5737	-44.5426	1.6861	7.9864
Pr(III) :GSH	0.6312	0.6312	0.4355	0.6066	0.7897	0.6160	2.8463	2.8463	-80.8040	1.6921	8.8796
Pr(III) : GSH :Mg(II)	0.7274	0.7274	0.4679	0.7024	0.9513	0.7132	3.5963	3.1996	-47.0844	1.9594	9.9649
Pr(III) : GSH :Zn(II)	0.7894	0.7894	0.5093	0.7244	0.9539	0.7356	3.5963	3.5963	-59.2524	2.0206	11.2508
3. DMF											
Pr(IIII	0.6176	0.6176	0.3918	0.5459	0.7107	0.5543	2.7538	2.7538	-42.3365	1.5227	8.6220
Pr(III) :GSH	0.6077	0.6077	0.3948	0.5586	0.7336	0.5672	3.1254	3.1254	-68.9790	1.5227	8.6220
Pr(III) : GSH:Mg(II)	0.7037	0.7037	0.4570	0.6500	0.8559	0.6600	3.1811	3.1811	-51.0522	1.8134	9.9539
Pr(III) : GSH : Zn(II)	0.8055	0.8055	0.4512	0.6264	0.8138	0.6360	3.3069	3.3069	-36.1076	1.7474	10.3844
4. CH_3OH											
Pr(IIII	0.4214	0.4214	0.3661	0.4727	0.5884	0.4801	2.4373	2.4373	-65.8177	1.3186	7.6357
Pr(III) :GSH	0.5237	0.5237	0.3952	0.5000	0.6152	0.5086	2.7196	2.7190	99.2080	1.3971	0.5181
Pr(III) : GSH:Mg(II)	0.5244	0.52444	0.3808	0.4995	0.6279	0.5073	2.6391	2.6391	-55.6982	1.3934	8.2768
Pr(III) : GSH : Zn(II)	0.5058	0.5058	0.3895	0.5055	0.6310	0.5132	2.6459	2.6459	-60.4543	1.4095	8.2957

5. Dioxane+CH_3CN											
Pr(III)	0.5963	0.5963	0.3538	0.4983	0.6513	0.5049	2.5753	2.5753	-35.2774	1.3868	8.0723
Pr(III) :GSH	0.6192	0.6192	0.3749	0.5273	0.6902	0.5355	2.6514	2.6514	-35.1697	1.4708	8.3003
Pr(III) :GSH Mg(II)	0.7103	0.7103	0.3875	0.5386	0.7004	0.5470	2.5840	2.5840	-10.1250	1.5023	8.0698
Pr(III) : GSH : Zn(II)	0.6935	0.6935	0.3733	0.5294	0.6962	0.5377	2.5740	2.5740	-13.2616	1.4767	8.0446
6. DMF+ Dioxane											
Pr(III)	0.6183	0.6183	0.3455	0.4830	0.6302	0.4905	2.5851	2.5851	-30.9118	1.3476	8.1164
Pr(III) :GSH	0.6097	0.6097	0.3515	0.4904	0.6391	0.4980	2.5817	2.5817	-32.7068	1.3683	8.1032
Pr(III) :GSH:Mg(II)	0.7563	0.7563	0.4071	0.6003	0.8058	0.6096	2.4997	2.4997	5.6078	1.6748	7.7536
Pr(III) :GSH :Zn(II)	0.6667	0.6667	0.3493	0.5074	0.6758	0.5152	2.5214	2.5215	-15.8335	1.4156	7.8935
7. CH_3OH+DMF											
Pr(III)	0.7630	0.7630	0.3853	0.5394	0.7056	0.5488	2.6414	2.6414	-2.0257	1.5075	8.2579
Pr(III) :GSH	0.7849	0.7849	0.3911	0.5619	0.7439	0.5705	2.6942	2.6942	-0.6643	1.5675	8.4176
Pr(III) : GSH:Mg(II)	0.7986	0.7986	0.3146	0.5287	0.7543	0.5369	2.5987	2.5987	9.1357	1.4750	8.1306
Pr(III) :GSH :Zn(II)	0.8687	0.8687	0.3960	0.5774	0.7705	0.5863	2.7176	2.7176	16.7818	1.6108	8.4842
8. DMF+CH_3CN											
Pr(III)	0.7378	0.7378	0.3857	0.5546	0.7347	0.5632	2.7172	2.7172	-12.7957	1.5471	8.4957
Pr(III) :GSH	0.7961	0.7961	0.3697	0.5549	0.7515	0.5634	2.7498	2.7498	-1.7890	1.5480	8.6046
Pr(III) :GSH:Mg(II)	0.7885	0.7885	0.3988	0.5684	0.7493	0.5771	2.7508	2.7508	-3.4056	1.5855	8.5988

Pr(III) : GSH : Zn(II)	0 .8221	0.8221	0.4237	0.6124	0.8135	0.6219	2.7757	2.7757	2.3603	1.7085	8.6483
9. CH_3OH+Dioxane											
Pr(III)	0.7400	0.7400	0.3645	0.5236	0.6933	0.5313	2.4675	2.4675	4.2511	1.4606	7.6983
Pr(III) :GSH	0.7479	0.7479	0.3735	0.5494	0.7366	0.5579	2.4887	2.4887	4.5695	1.5326	7.7491
Pr(III) : GSH:Mg(II)	0.8094	0.8094	0.3732	0.5553	0.7488	0.5639	2.4847	2.4847	18.8669	1.5489	7.7311
Pr(III) :GSH :Zn(II)	0.8988	0.8988	0.3898	0.5732	0.7684	0.5821	2.5544	2.5544	34.4843	1.5989	7.9458
10. CH_3O H+CH_3CN											
Pr(III)	0.6921	0.6921	0.3570	0.4953	0.6434	0.5030	2.5327	2.5327	-10.6821	1.3815	7.9326
Pr(III) :GSH	0.7262	0.7262	0.3649	0.5064	0.6580	0.5143	2.5508	2.5508	-4.1833	1.4125	7.9836
Pr(III) :GSH:Mg(II)	0.7398	0.7398	0.3671	0.5041	0.6510	0.5119	2.5349	2.5349	-0.1516	1.4060	7.9334
Pr(III) :GSH :Zn(II)	0.7794	0.7794	0.3830	0.5499	0.7280	0.5585	2.5776	2.5776	5.9954	1.5338	8.0383
11. Water											
Pr(III)	0.6365	0.6365	0.3444	0.6215	0.9126	0.6312	2.3522	2.3522	-11.9331	1.7333	7.2467
Pr(III) :GSH	0.6791	0.6791	0.3184	0.5821	0.8593	0.5914	2.2429	2.2429	4.9737	1.6235	6.9166
Pr(III) :GSH : Mg(II)	0.6854	0.6854	0.3491	0.6538	0.9734	0.6640	2.3625	2.3625	-1.5373	1.8231	7.2546
Pr(III):GSH: Zn(II)	0.7476	0.7476	0.3495	0.6168	0.8981	0.6266	2.1903	2.1903	23.8835	1.7199	6.7173

Table 4.13 : Experimental values of oscillator strength ($P \times 10^6$) (observed and calculated) and Judd-Ofelt parameter ($T_\lambda \times 10^{10}$) cm^{-1} for Pr(III), Pr(III):GSH, Pr(III): GSH:Mg(II) and Pr(III):GSH:Zn(II) complexes in different aquated organic solvents at pH 4 and 298K

Sytem	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. CH_3CN											
Pr(IIII	0.7580	0.7580	0.3828	0.5931	0.8158	1.6023	2.9925	2.9925	-26.3257	1.6552	9.3775
Pr(III) :GSH	0.8231	0.8231	0.3981	0.6151	0.8487	0.6245	3.1401	3.1401	-21.3010	1.7162	9.8442
Pr(III) :GSH : Mg(II)	0.8528	0.8528	0.4065	0.6670	0.9215	0.6627	3.1893	3.1893	-17.8633	1.8207	9.9759
Pr(III):GSH: Zn(II)	0.9825	0.9825	0.5345	0.8558	1.1953	0 8690	3.3751	3.3751	-1.0969	2.3876	10.4325
2. Dioxane											
Pr(IIII	0.7144	0.7144	0.3636	0.5406	0.7288	0.5490	2.6820	2.6820	-15.6881	1.5086	8.3988
Pr(III):GSH	0.7785	0.7785	0.3737	0.5496	0.7366	0 5580	2.7491	2.7491	-5.5850	1.5334	8.6127
Pr(III) :GSH :Mg(II)	0.8742	0.8742	0.3986	0.5834	0.7800	0.5924	2.7950	2.7950	12.9908	1.6276	8.7368
Pr(III) :GSH :Zn(II)	0.9070	0.9070	0.4154	0.5826	0.7613	0.5915	2.8877	2.8877	14.3969	1.6254	9 0422
3 DMF											
Pr(IIII	0.5784	0.5784	0 3947	0.5478	0.7117	0.5562	2.8836	2.8836	-59.6194	1 5286	9.0535
Pr(III) :GSH	0.5992	0.5992	0.4120	0.5866	0.7728	0 5955	3.1978	3.1978	75 7020	1.6368	10.0577
Pr(III) :GSH: Mg(II)	0.6125	0.6125	0.4365	0.6075	0.7901	0.6166	3.1061	3.1061	-66.7223	1.6948	9.7424
Pr(III) :GSH : Zn(II)	0.6622	0 6622	0.4581	0.6794	0.9142	0.6896	3.2563	3.2563	-66 7223	1.6948	9.7424
4. CH_3OH											
Pr(IIII	0.5673	0.5673	0.3138	0.4345	0.5637	0.4411	2.5202	2.5202	-37.9961	1.2124	7.9464
Pr(III):GSH	0.6055	0.6055	0.3247	0.4476	0.5792	0.4544	2.5917	2.5917	-34.0330	1.2658	8.1712
Pr(III): GSH :Mg(II)	0.6143	0.6341	0.4509	0.5035	0.5647	0.5112	2.5781	2.5781	-31.2741	1.4048	8.0837
Pr(III): GSH : Zn(II)	0.4964	0.4964	0.3242	0.4648	0.6147	0.4719	2.6341	2.6341	-61.6286	1.2968	8.2953

5. Dioxane+CH_3CN											
Pr(III)	0.5815	0.5815	0.3193	0.5280	0.7499	0.5360	2.5815	2.5815	-39.3121	1.4734	8.0771
Pr(III) :GSH	0.6174	0.6174	0.3068	0.5190	0.7424	0.5270	2.5178	2.5178	-26 8955	1.4482	7.8750
Pr(III) :GSH:Mg(II)	0.6261	0.6261	0.3174	0.5465	0.7874	0.5548	2.5970	2.5970	-30.1535	1.5246	8.1130
Pr(III) :GSH :Zn(II)	0.6640	0.6640	0.3391	0.5776	0.8587	0.5865	2.6693	2.6693	-30.1535	1.5246	8.1130
6. DMF + Dioxane											
Pr(III)	0.5695	0.5695	0.3705	0.4965	0.6320	0.5041	2.7025	2.7025	-49.7684	1.3854	8.4987
Pr(III) :GSH	0.5770	0.5770	0.3710	0.5020	0.6426	0.5096	2564 5	2.5645	-39.0590	1.4007	8.0427
Pr(III) :GSH :Mg(II)	0.5971	0.5971	0.3755	0.5233	0.6818	0.5309	2.5609 2	5609	-34.1596	1.4604	8.0140
Pr(III) :GSH :Zn(II)	0.6248	0.6248	0.3711	0.5209	0.6809	0.5288	2.5280	2.5280	-25.7385	1.4533	7.9092
7. CH_3OH+DMF											
Pr(III)	0.7630	0.7630	0.3708	0.5212	0.6819	0.5292	2.4608	2.4608	9.8992	1.4543	7.6867
Pr(III) :GSH	0.7943	0.7943	0.3727	0.4475	0.5304	0.4544	2.4931	2.4931	15.1052	1.2487	7.8489
Pr(III) :GSH:Mg(II)	0.8516	0.8516	0.3726	0.5415	0.7211	0.5497	2.4903	2.4903	2 8.1106	1.5106	7.7694
Pr(III) :GSH :Zn(II)	0.8583	0.8583	0.3967	0.6814	0.9810	0.6919	2.5234	2.5234	2 6.9733	1.9010	7.7735
8. DMF+CH_3CN											
Pr(III)	0.5213	0.5213	0.2899	0.3823	0.4822	0.3883	2.4641	2.4641	-44.7641	1.0678	7.8041
Pr(III) :GSH	0.7549	0.4549	0.2834	0.3783	0.4806	0.3842	2.4098	2.4098	11.5785	1.0569	7.6280
Pr(III) :GSH :Mg(II)	0.5486	0.5486	0.2968	0.3942	0.4994	0.4004	2.7174	2.7174	-55.1180	1.1015	8.6264

Pr(III) : GSH : Zn(II)	0.6815	0.6815	0.3218	0.4076	0 5009	0 4138	2.4136	2.4136	-5.2769	1.1385	7.6206
9. CH_3OH+ Dioxane											
Pr(III)	0.7425	0 7425	0.3857	0.5588	0.7433	0.5675	2.8580	2.8580	-20 8606	1.5593	8 9594
Pr(III) :GSH	0.7590	0.7590	0.3847	0.5758	0.7787	0.5847	2.9391	2.9391	-22.5207	1.6065	9.2134
Pr(III) : GSH :Mg(II)	0.8582	0.8582	0.4216	0.6284	0.8480	0.6380	3.2087	3.2087	-17.7993	1.7530	10.0567
Pr(III) : GSH : Zn(II)	0.8967	0.8967	0.4180	0.6219	0.8385	0.6315	3.0430	3 0430-	1.8132	1.7349	9.5187
10. CH_3OH+CH_3CN											
Pr(III)	0.5220	0.5220	0.4738	0.5318	0.5988	0.5399	2.6517	2.6517	-57.3377	1.4837	8.3045
Pr(III) :GSH	0.6034	0.6034	0.3831	0.5173	0.6616	0.5253	2.7819	2.7819	-47.3842	1.4431	8.7403
Pr(III) : GSH Mg(II)	1.1187	1.1187	0.3726	0.5415	0.7211	0.5497	2.4903	2.4903	28.1106	1 5106	7.7694
Pr(III) : GSH : Zn(II)	0.6710	0.6710	.3854	0.5157	0.6558	0.5236	2.7652	2.7652	-30.9337	1.4384	8.6856
11. Water											
Pr(III)	0 3556	0.3556	0.3461	0.3855	0.4314	0.3914	2.6550	2.6550	-94.8017	1.0754	8.0
Pr(III) : GSH	0.4935	0.4935	0.3503	0.4006	0.4588	0.4076	2.5773	2.5773	-58.4638	1.1198	8 1558
Pr(III) : GSH : Mg(II)	0.7081	0 7081	0.3904	0.5313	0.6826	0.5395	2.7520	2.7520	-21.5583	1.4819	8.6291
Pr(III): GSH : Zn(II)	0.5981	0.5981	0.3688	0.4976	0 6360	0 5052	2.5982	5982	-36.3335	1 3879	8.1496

Table 4.14 : Experimental values of oscillator strength ($P \times 10^6$) (observed and calculated) and Judd-Ofelt parameter($T_\lambda \times 10^{10}$) cm^{-1} for Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) complexes in different aquated organic solvents at pH 5 and 298K

Sytem	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. CH_3CN											
Pr(IIII	0.7470	0.7470	0.3263	0.4535	0.5894	0.4603	3.0042	3.0042	-29.0008	1.2653	9 5210
Pr(III) :GSH	0.8261	0.8261	0.3593	0 4936	0.6527	0.5131	3.1862	3.1862	22 9760	1.3477	10 093 0
Pr(III) : GSH : Mg(II)	0.8302	0.8302	0.3487	0.5034	0.6684	0.5113	3 159 6	3 1596	-205 740	1.4053	9.9944
Pr(III):GSH: Zn(II)	0 9321	0.3321	0.4049	0.5477	0 7014	0.5563	3.4169	3.4169	-14.0867	1.5292	10.8079
2. Dioxane											
Pr(IIII	0.5574	0.5574	0.3253	0.4686	0.6215	0.4760	2.8451	2.8451	-61.7661	1.3088	8.9888
Pr(III) :GSH	0.6338	0 6338	0.3583	0.5123	0.6770	0.5205	2.7959	2.7959	-413 179	1.4315	8 7968
Pr(III) : GSH :Mg(II)	0.6423	0.6423	0.3459	0.4908	0.6456	0.4985	2.9341	2.9341	-48.4535	1.3713	9.2682
Pr(III) : GSH :Zn(II)	0.8280	0.8280	0.4608	0 6653	0.8835	0.6758	3.4514	3.4514	-40.8352	1.8592	10.8355
3. DMF											
Pr(IIII	0.6352	0.6352	0.2993	0.43 75	0 5850	0.4446	2.2535	2.2535	-5.1811	1.2220	7.0683
Pr(III) :GSH	0 6500	0 6500	0.3089	0.4698	0 6406	0.4772	2.2877	2.2877	-4 .2206	1.3120	7.1569
Pr(III) : GSH:Mg(II)	0.6782	0.6782	0.3079	0.4672	0.6364	0.4746	2.3385	2.3385	-1.2184	1.3045	7.3242
Pr(III) : GSH : Zn(II)	1.0067	1.0067	0.5269	0.7590	1.0065	0 7708	3 3984	3.3984	2.7801	2.1197	10 5875
4. CH_3OH											
Pr(IIII	0.6778	0.6778	0.32333	0.4380	0.5614	0.4449	2.7312	2.7312	-26 9078	1.2232	8.6377
Pr(III) :GSH	0.7033	0.7033	0.3585	0.4994	0.6503	0 5072	2.9179	2.9179	33 6354	1.3952	9.2048
Pr(III) : GSH:Mg(II)	0.7998	0 7998	0.4013	0 5820	0.7007	0 5912	3.0696	3.0696	21 9767	1 6256	9 6416
Pr(III) : GSH : Zn(II)	0 8105	0 8105	0.3972	0 5432	0.7001	0.5518	3.2158	3.2158	2 9 017 6	1.5 172	10.1507

5 . Dioxane+CH_3CN											
Pr(III)	0.5876	0.5876	0.3219	0.4274	0.5441	0.4364	2.4542	2.4542	-29.1878	1.1933	7.7351
Pr(III) :GSH	0.5866	0.5866	0.3255	0 4354	0.5540	0.4423	2.3864	2.3864	-24. 9738	1.2162	7.7351
Pr(III) :GSH :Mg(II)	0.6098	0.6098	0.3246	0.3874	0.4574	0.3936	2.3773	2.3773	-18.9555	1.0822	7.5147
Pr(III) :GSH :Zn(II)	0.8815	0.8815	0.5328	0 7100	0.9014	0.7214	1.4914	1.4914	99.7581	1.9832	4. 3654
6 . DMF+Dioxane											
Pr(III)	0.6839	0.6839	0.3117	0.4365	0.5699	0.4432	2 3806	2.3806	-2.5929	1.2187	7.4861
Pr(III) :GSH	0 6893	0 6893	0.3212	0.4456	02.5786	0.4526	2.4383	2.4383	0.4237	1.2441	7.3930
Pr(III) : GSH:Mg(II)	0.7296	0 7296	0.3201	0.4547	0 5986	0.4619	2.3629	2 3629	8 9920	1.2697	7.4153
Pr(III) :GSH :Zn(II)	0.7486	0.7486	0.3528	0.4727	0.6019	0.4799	2.4065	2.4065	0.3887	1.3200	7.5464
7 . CH_3OH+DMF											
Pr(III)	0 7322	0.7322	0.3330	0.4522	0.5803	0.4593	2 5442	2.5442	-2.2352	1.2627	8.0119
Pr(III) :GSH	0.7429	0.7429	0.3366	0 4394	0 5510	0.4465	2.4613	2.4613	5.7240	1.2277	7.7511
Pr(III) :GSH :Mg(II)	0.7707	0.7707	0.3382	0.4680	0 6072	0.4753	2.4425	2.4425	3.1137	1.3074	7.6688
Pr(III) :GSH :Zn(II)	0.8015	0.8015	0.3865	0.5224	0.6689	0.5308	2.5130	2.5130	15.4214	1.4594	7.8579
8 DMF +CH_3CN											
Pr(III)	0.7737	0 7737	03476	0 4738	0.6096	0.4814	2.5491	2.5491	6.6964	1.3230	8 0119
Pr(III) :GSH	0 7860	0.7860	0.3724	0 5057	0.6492	0.5138	2.6826	2.6826	0.5457	1.4123	8.4270
Pr(III) :G SH:Mg(II)	0.8589	0.8589	0.3885	0.5349	0.6951	0.5434	2.8099	2.8099	8.6601	1.4938	8.8224

Pr(III) : GSH : Zn(II)	0.8801	0.8801	0.3901	0.5351	0.6913	0.5439	2.7942	2 7942	8.6790	1.4949	9.4303
9. CH_3OH+Dioxane											
Pr(III)	0 5464	0.5464	0.2951	0.3960	0.5047	0.4022	2.4574	2.4574	-38.6335	1.1059	7.7694
Pr(III) :GSH	0.5147	0.5147	0.3009	0.3967	0 5003	0.4030	2.4906	2.4906	-48 0079	1.1081	7.8781
Pr(III) : GSH:Mg(II)	0.5915	0.5915	0.3093	0.3993	0.4970	0.4056	2.4719	2.4719	-29.3486	1.1152	7.8150
Pr(III) : GSH : Zn(II)	0.6289	0.6289	0.3581	0.4506	0.5514	0.4575	2.7413	2.7413	-38.7502	1.2584	8.6613
10. CH_3OH+CH_3CN											
Pr(III)	0.7425	0.7425	0.3857	0.5588	0.7433	0.5675	2.8580	2.8580	-20.8606	1.5593	8.9594
Pr(III) :GSH	0 7590	0 7590	0.3847	0.5758	0 7787	0.5847	2.9391	2.9391	-22.5207	1.6065	9.2134
Pr(III) : GSH:Mg(II)	0.8582	0 8582	0.4216	0.6284	0.8480	0.6380	3.2087	3.2087	-17.7993	1.7530	10.0567
Pr(III) : GSH : Zn(II)	0 8967	0.8967	0.4180	0.6219	0.8385	0.6315	3.0430	3.0430-	1 8132	1.7349	9 5187
11 Water											
Pr(III)	0.2352	0.2352	0 3064	0.4529	0 6083	0.4596	2.4126	2.4126	-106.4536	1.2639	7.5768
Pr(III) : GSH : Zn(II)	0.2585	0.2585	0 3024	0.4577	0.6222	0.4646	2.3668	2.3668	-98.1424	1.2770	7.4224
Pr(III) : GSH : Mg(II)	0.7323	0.7323	0.2457	0.4492	0.6625	0.4560	2.6539	2.6539	-9.3155	1.2531	8.3672
Pr(III):GSH:	0.7442	0.7442	0.3182	0.5033	0 6990	0.5110	2.3492	2.3492	13.1303	1.4042	7.3287

Table 4.15 : Experimental values of oscillator strength ($P \times 10^6$) (observed and calculated) and Judd-Ofelt parameter ($T_\lambda \times 10^{10}$) cm^{-1} for Pr(III), Pr(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) complexes in different aquated organic solvents at pH 6 and 298K

Sytem	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. CH_3CN											
Pr(IIII	0.5676	0.5676	0.3189	0.4423	0.5745	0.4491	2.8364	2.8364	-58.7608	1.2354	8.9783
Pr(III) :GSH	0.5708	0.5708	0.3458	0.4575	0.5780	0.4646	2.9866	2.9866	-66.2605	1.2783	9.4616
Pr(III) :GSH : Mg(II)	0.7914	0.7914	0.4567	0.5268	0.6059	0.5348	2.5713	2.5713	8.8804	1.4712	8.0466
Pr(III):GSH: Zn(II)	0.3453	0.3453	0.4631	0.5279	0.6018	0.5360	2.9650	2.9650	-118.0910	1.4742	9.3355
2. Dioxane											
Pr(IIII	0.7515	0.7515	0.3169	0.4143	0.5199	0.4209	2.7174	2.7174	-9.2402	1.1576	8.6120
Pr(III):GSH	0.7464	0.7464	0.3288	0.4789	0.6391	0.4865	2.7688	2.7688	-13.5970	1.3384	8.7334
Pr(III) :GSH :Mg(II)	0.7463	0.7463	0.3696	0.5328	0.7069	0.5412	3.1517	3.1517	-39.3015	1.4840	9.9523
Pr(III): GSH : Zn(II)	0.7914	0.7914	0.3897	0.5639	0.7013	0.5731	3.3215	3.3215	--39.9853	1.5760	10.4862
3. DMF											
Pr(IIII	0.4611	0.4611	0.2706	0.3900	0.5175	0.3962	2.5877	2.5877	-66.5240	1.0893	8.2015
Pr(III) :GSH	0.5156	0.5156	0.3017	0.3995	0.5050	0.4057	2.6524	2.6524	-58.4776	1.1161	8.4076
Pr(III) :GSH :Mg(II)	0.5461	0.5461	0.3178	0.4496	0.5906	0.4567	2.9346	2.9346	-39.3015	1.4840	9.9523
Pr(III) :GSH : Zn(II)	0.5671	0.5671	0.3298	0.4705	0.6215	0.4777	2.9831	2.9831	-68.6192	1.3144	9.4396
4. CH_3OH											
Pr(IIII	0.6822	0.6822	0.3416	0.4588	0.5851	0.4661	2.2901	2.2901	2.9513	1.2813	7.1743
Pr(III) :GSH	0.7574	0.7574	0.3918	0.4643	0.6185	0.4717	2.3659	2.3659	15.0217	1.2969	7.4199
Pr(III) : GSH:Mg(II)	0.7400	0.7400	0.3230	0.4803	0.6476	0.4878	2.3516	2.3516	11.9952	1.3414	7.3589
Pr(III) :GSH : Zn(II)	0.8016	0.8016	0.3548	0.5213	0.6990	0.5298	2.5136	2.5136	15.1833	1.4563	7.8617
5. Dioxane+CH_3CN											

Pr(III)	0.5922	0.5922	0.3319	0.4666	0.6108	1.4740	2.5500	2.5500	-34.4635	1.3031	8.0211
Pr(III) :GSH	0.6113	0.6113	0.3354	0.4764	0.6270	0.4838	2.6165	2.6165	-34.5560	1.3310	8.2345
Pr(III) : GSH:Mg(II)	0.6363	0.6363	0.3420	0.4645	0.6065	0.4770	2.5191	2.5191	-22.3778	1.3119	7.9192
Pr(III) : GSH : Zn(II)	0.6921	0.6921	0.3816	0.5170	0.6625	0.5250	2.8413	2.8413	-31.0631	1.4441	8.9404
6. DMF+Dioxane											
Pr(III)	0.5335	0.5335	0.3106	0.4152	0.5280	0.4217	2.2662	2.2662	-29.1855	1.597	7.1272
Pr(III) :GSH	0.5011	0.5011	0.3230	0.4380	0.5619	0.4450	2.5035	2.5035	-52.2439	1.2235	7.8903
Pr(III) : GSH:Mg(II)	0.5467	0.5467	0.3295	0.4372	0.5537	0.4442	2.6442	2.6442	-50.9856	1.2213	8.3528
Pr(III) : GSH : Zn(II)	0.7013	0.7013	0.3841	0.4824	0.5901	0.4902	2.9013	2.9013	-32.9876	1.3475	9.1648
7. CH_3OH+DMF											
Pr(III)	0.7545	0.7545	0.3316	0.4701	0.6183	0.4776	2.4456	2.4456	8.9411	1.3131	7.6771
Pr(III) :GSH	0.7620	0.7620	0.3313	0.4895	0.6581	0.4973	2.5176	2.5176	5.8088	1.3676	7.8981
Pr(III) : GSH:Mg(II)	0.8080	0.8080	0.3615	0.5253	0.6997	0.5334	2.3524	2.3524	27.1783	1.4671	7.3293
Pr(III) : GSH : Zn(II)	0.8215	0.8215	0.3871	0.5463	0.7165	0.5548	2.7016	2.7016	7.1977	1.5262	8.4603
8. DMF+CH_3CN											
Pr(III)	0.7508	0.7508	0.3797	0.5166	0.6637	0.5247	2.6820	2.6820	-7.2792	1.4426	8.4171
Pr(III) :GSH	0.7709	0.7709	0.3645	0.5296	0.7056	0.5379	2.7418	2.7418	-6.7135	1.4797	8.6061
Pr(III) : GSH:Mg(II)	0.7955	0.7955	0.3785	0.5235	0.6791	0.5318	2.6470	2.6470	5.2190	1.4627	8.2988
Pr(III) : GSH : Zn(II)	0.8014	0.8014	0.3952	0.5544	0.7245	0.5629	2.7513	2.7513	-0.4558	1.5484	8.6171

9. CH_3OH+Dioxane											
Pr(III)	0.7293	0.7293	0.3315	0.4525	0.5826	0.4597	2.4517	2.4517	3.0549	1.2641	7.7088
Pr(III) :GSH	0.6679	0.6679	0.3451	0.4637	0.5917	0.455712	2.5603	2.5603	-18.0851	1.2956	8.0579
Pr(III) : GSH:Mg(II)	0.8069	0.8069	0.3629	0.4957	0.6385	0.5051	2.8164	2.8164	12.2293	1.3850	8.0930
Pr(III) : GSH : Zn(II)	0.8225	0.8225	0.3915	0.4972	0.6125	0.5051	2.8164	2.8164	-0.0758	1.3892	8.8739
10. CH_3OH+CH_3CN											
Pr(III)	0.5335	0.5335	0.3106	0.4152	0.5280	0.4217	2.2662	2.2662	-29.1855	1.597	7.1272
Pr(III) :GSH	0.5011	0.5011	0.3230	0.4380	0.5619	0.4450	2.5035	2.5035	-52.2439	1.2235	7.8903
Pr(III) : GSH:Mg(II)	0.5467	0.5467	0.3295	0.4372	0.5537	0.4442	2.6442	2.6442	-50.9856	1.2213	8.3528
Pr(III) : GSH : Zn(II)	0.7013	0.7013	0.3841	0.4824	0.5901	0.4902	2.9013	2.9013	-32.9876	1.3475	9.1648
11. Water											
Pr(III)	0.6513	0.6513	0.3012	0.4321	0.5716	0.4387	2.4455	2.4455	-14.1674	1.2061	7.7019
Pr(III) :GSH	0.7202	0.7202	0.2914	0.4411	0.5997	0.4478	2.3197	2.3197	9.6935	1.2309	7.2812
Pr(III) : GSH : Mg(II)	1.1727	1.1727	0.4639	0.4806	0.5050	0.4881	2.7081	2.7081	86.5272	1.3409	8.5228
Pr(III):GSH: Zn(II)	0.7808	0.7808	0.2856	0.4454	0.6144	0.4522	2.2652	2.2652	26.9840	1.2426	7.0969

CHAPTER NO. 5

Spectral analysis of 4f-4f transitions of complexation of Nd(III) with glutathione reduced (GSH) in presence and absence of Zn(II)/Mg(II) at different pH

5.1 Introduction

Lanthanides have extensive applications in the field of industries, agriculture, medicines and biomolecular reactions. So, it has become more important to understand the behaviours of lanthanides in biological system.[1,2] Hence, lanthanide coordination chemistry in solution state is of great importance with the increase use of the lanthanides as probes in the exploration of the structural functions of biomolecular reactions. This is particularly due to their ability to replace Ca(II) ion in a specific manner.[3]

In this chapter, the absorption difference and comparative absorption spectroscopy involving 4f-4f transitions of heterobimetallic complexation of glutathione reduced (GSH) with Nd(III) in presence and absence of Zn(II)/Mg(II) has been carried out in aqueous and aquated organic solvents like CH_3OH, CH_3CN, DMF and dioxane and their equimolar mixtures at different pH, i.e. pH 3, pH 4, pH 5 and pH 6. The variation in the energy interaction parameters like Slator-Condons (F_K, K=2,4,6), Lande spin-orbit

coupling constant (ξ_{4f}), Nephelauxetic effect (β), bonding parameter ($b^{1/2}$) and covalency parameter (δ) are calculated to explain the nature of complexation at different pH. The value of oscillator strengths (P) and Judd-Ofelt electric dipole intensity parameters T_λ,(λ =2,4,6) for different 4f-4f transitions in different solvents and different pH are also calculated. The changes in their values suggested the specific correlation between ligand structures and nature of interaction of Nd(III) with GSH in presence and absence of Zn(II)/Mg(II).

The ligand we choose, glutathione reduced (GSH) is a naturally occurring tripeptide with γ-L-glutamyl-L-cysteinyl glycine.[4] It has eight potential binding sites, viz. two carboxylic acid groups, an amino group, a sulphydryl group and two peptide linkages. The coordination chemistry of GSH is of great importance due to its excellent model system for the binding of metal ions. During its interaction all potential binding sites cannot be simultaneously coordinated to the same metal ion. According to HSAB concept, during complexation, Mg(II) ion prefers hard donor sites like carboxyl and carbonyl groups, while Zn(II) ion prefers soft donor sites like sulphydryl group (-SH). Ca(II)/Mg(II) ions being diamagnetic, is spectroscopically silent towards optical and magnetic spectral techniques. So, the isomorphous substitution of Ca(II) by Ln(III) can provide a very useful supplement to understand the interaction of GSH with Ca(II)/Mg(II) in presence and absence of Zn(II), since Ln(III) ions are paramagnetic and spectroscopically active. So, comparative and differential absorption spectral study involving 4f-4f transitions is one of the

most effective techniques to study the interaction of biologically active ligands with Ln(III).[5]

5.2 Experimental

Neodymium(III) nitrate of 99.9% purity was purchased from CDH, Mumbai and Glutathione reduced (GSH) from SRL Pvt. Ltd., Mumbai are used for synthesis and spectral analysis. Glutathione reduced (GSH) is kept below 3^0C and fresh solution of 0.01M was prepared for spectral study. The Nd(III):GSH complex is synthesized by mixing and constant stirring of Nd(III) nitrate (0.002 M) with 0.004 M glutathione reduced in ethylacetate-acetone mixture and yields pinkish crystalline complex after 8-10 days. It is separated out from the liquor. The crystal obtained is washed with acetone and dried in desiccators over P_4O_{10}. The analysis of the complex gave the stoichiometry $[Nd_2(GSH)_2(H_2O)_4]$.

For the preparation of Nd(III):GSH:Zn(II) complex, Nd(III) nitrate (0.001M), Zn(II) nitrate (0.001M) and glutathione reduced (0.002 M) in ethyl acetate- acetone mixture at pH-6. Pinkish crystalline complex is formed after 8-10 days and dried over P_4O_{10} in a desiccator. The analysis of the complex gave the stoichiometry, $[Nd_2(GSH)_2Zn(H_2O)_6]$. The absorption spectra are recorded on Perkin Elmer Lambda-35 UV-Visible spectrophotometer upgraded with high resolution of 0.5 nm band width and expansion of scale in the region 350nm to 900nm at different pH, i.e. pH3, pH4, pH5 and pH6. The temperature of all the observation is maintained at 298K by using water circulating HAAKE DC 10

thermostat. The metal contents in the complexes were estimated by complexometric titration with EDTA.

5.3 Methods

The energy E_{so} arising from the most important magnetic interactions, which are spin orbit interactions may be written as

$$E_{so} = A_{so}.\xi_{4f} \qquad (5.1)$$

where A_{so} is the angular part of spin orbit interaction and ξ_{4f} is the radial integral part and is known as Lande spin orbit coupling constant.

The Slator-Condon (F_K, K=2,4,6) and Lande parameter (ξ_{4f}) of neodymium complex may be evaluated by expressing energy as Taylor series expansion. In the first order, energy E_j of the j^{th} level is given by Wang[9-10] as

$$E_j(F_k, \xi_{4f}) = E_{oj}(F_k^o, \xi_{4f}^o) + \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k}\Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}}\Delta\xi_{4f} \qquad (5.2)$$

Where E_{oj} is the zero order energy of the j^{th} level. The values of F_K and ξ_{4f} are given by

$$F_k = F_k^o + \Delta F_k \qquad (5.3)$$

$$\xi_{4f} = \xi_{4f}^o + \Delta\xi_{4f}$$

The differences between the observed E_j-value and the zero order values, ΔE_j is evaluated by

$$\Delta E_j = \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k}\Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}}\Delta\xi_{4f} \qquad (5.4)$$

By using the zero order energy and partial derivatives of Nd(III) ion given by Wong (Table 5.1), the above equation (5.4) can be solved by least square fit technique and the values of F_2, F_4, F_6 and ξ_{4f} can be found out by solving equation (5.3).

Table 5.1: The zero order energies and partial derivatives* with respect to F_4 and ξ_{4f} parameters for Nd(III)

Energy Level	E_{oj} (a)	$\delta E_j/\delta F_2$	$\delta E_j/\delta F_4$	$\delta E_j/\delta F_6$	$\delta E_j/\delta \xi_{4f}$
$^4F_{3/2}$	11523.34	35.27	39.50	-588.9	1.02
$^4F_{5/2}$	12606.77	34.93	39.36	-631.4	2.58
$^4F_{7/2}$	13453.73	35.02	41.04	-602.5	3.24
$^4G_{5/2}$	17357.56	54.98	63.01	-991.2	1.29
$^4G_{7/2}$	19288.93	41.95	101.66	-620.8	4.13

(a) $F_2^\circ = 331.567\ cm^{-1}$ $F_4^\circ = 49.057\ cm^{-1}$

$F_6^\circ = 5.170\ cm^{-1}$ $\xi_{4f}^\circ = 906.00\ cm^{-1}$

**E.Y. Wong, J. Chem. Phys. 35(1961)544*

The result of complexation on the spectra is the red shift of all the electronic transitions, the red shift is due to the expansion of the metal orbital radius resulting in the decrease of the inter-electronic repulsion parameters (Slater-Condon, F_k's). This phenomenon is known as Nephelauxetic effect, which measures the change in F_k with respect to free ion and expressed by a Nephelauxetic ratio 'β', which is defined as:

$$\beta_1 = \frac{F_k^c}{F_k^f}; \beta_2 = \frac{\xi_{4f}^c}{\xi_{4f}^f}$$

and $$\beta = \left[\frac{\beta_1 + \beta_2}{2}\right] \qquad (5.5)$$

Where F_k^o and F_k^f refers to parameters in complex and free ion respectively.

There is ample evidence to the fact that 4f-orbitals do participate in chemical bonding. The amount of mixing of 4f-orbitals does participate in chemical bonding. The amount of mixing of 4f-orbital and ligand orbital can be given by another bonding parameter '$b^{1/2}$', which is related to Nephelauxetic effect and is given as

$$b^{\frac{1}{2}} = \left[\frac{1-\beta}{2}\right]^{\frac{1}{2}} \qquad (5.6)$$

Sinha[11] introduced another parameter known as the covalency parameter, which is defined as:

$$\delta\% = \left[\frac{1-\beta}{\beta}\right] \times 100 \qquad (5.7)$$

The intensity of the absorption band is measured by the oscillator strength (P), which is directly proportional to the area under the absorption curve. It can be expressed in terms of molar extinction (ε_m), energy of the transition in wave number ($\bar{\nu}$) and the refractive index (η) of the medium by the relationship

$$P = 4.31 \times 10^{-9} \left[\frac{9\eta}{\left(\eta^2 + \eta\right)^2}\right] \int \varepsilon_{max}(\bar{\nu}) d\bar{\nu} \qquad (5.8)$$

where ε_{max} = molar extinction coefficient

$\bar{\nu}$ = energy of the transition in wave number

η = the refractive index of the medium

The experimental values of oscillator strength (P_{exp}) of the absorption bands were calculated by performing Gaussian curve analysis of the curves.

The oscillator strength (P_{exp}) can be found out from the equation,

$$P = 4.60 \times 10^{-9} \times \varepsilon_m \times \Delta\nu_{1/2} \qquad (5.9)$$

where the molar extinction co-efficient ε_m is given by the equation

$$\varepsilon_m = \frac{\text{Absorbance}}{\text{Concentration} \times l}$$

where l = path length of the cell in cm

The electronic transition of trivalent lanthanides can be electric dipole, magnetic dipole and electric quadrupole transitions. Some transitions have appreciable contributions from more than one mode of electric dipole transition, which in pure f^n configurations are strictly parity forbidden. However, a weak induced electric dipole transition can occur as a result of interaction of central metal ion with the surrounding ligand field. Judd[12] observed that the oscillator strength of an induced electric dipole transition was related to the energy of transition ($\bar{\nu}$), square of the matrix element of unit tensor operator, $U^{(\lambda)}$ connection initial $<f^n\psi J|$ and $|f^n\psi'J'>$ through three phenomenological parameters T_λ (λ=2,4,6). These parameters are related to the radial wave function of the state, refractive index of the media and the ligand field parameters that characterize the environmental field.

$$P = \sum T_\lambda \bar{v} \left\langle f^n \psi J \left\| U^{(\lambda)} \right\| f^n \psi' J' \right\rangle \qquad (5.10)$$

These three parameters T_2, T_4 and T_6 are related to the redial wave function of the perturbing configuration and after including weighing factor $(2J + 1)^{-1}$ the equation can be written as :

$$P = \sum T_\lambda \left\langle f^n \psi J \left\| U^{(\lambda)} \right\| f^n \psi' J' \right\rangle^2 (2J+1)^{-1} \qquad (5.11)$$

For calculating matrix element $U^{(\lambda)}$, the eigen vectors were of the form

$$f^n \psi J = \sum_{\alpha SL} \varepsilon^{\alpha SL} \mid f^n \alpha SLJ \qquad (5.12)$$

and can be calculated by diagonalizing the complete energy matrices. Details of the computation involved have been dealt with separately for praseodymium and neodymium systems.

The observed oscillator strength (P_{obs}) of the transition energies were expressed in terms of parameters defined by Judd and Ofelt known as the T_2, T_4 and T_6 parameters which are given by the following equation,

$$\frac{P_{obs}}{Y} = \left[(U^2)\right]^2 T_2 + \left[(U^4)\right]^2 T_4 + \left[(U^6)\right]^2 T_6 \qquad (5.13)$$

The absorption spectra of neodymium shows ten resolvable bands, eight of which are composites of several multiple to multiple transition manifolds. Out of these ten bands, only five most intense bands were used in energy and intensity analysis. These five bands are $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$ and $^4I_{9/2} \rightarrow {}^4F_{3/2}$, out of these the hypersensitive transition is $^4I_{9/2} \rightarrow {}^4G_{5/2}$ and the rest are pseudo-hypersensitive transitions, which are also regarded as very sensitive towards even minor coordination changes around central metal ions.

Table 5.2 : Matrix elements, $U^{(\lambda)}$ for Nd(III) aquo

Energy Level	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$
$^4F_{3/2}$	0	0.2299	0.0547
$^4F_{5/2}$	0.0009	0.2361	0.3973
$^4H_{9/2}$	0.0092	0.0076	0.1196
$^4F_{7/2}$	0.0010	0.0420	0.4249
$^4S_{3/2}$	0	0.027	0.2354
$^4G_{5/2}$	0.8968	0.4091	0.0355
$^2G_{7/2}$	0.0755	0.1848	0.0316
$^4G_{7/2}$	0.0551	0.1569	0.0547
$^4G_{9/2}$	0.0046	0.0611	0.0407
$^4K_{13/2}$	0.0068	0.0002	0.0313

W.T. carnall, P.R. Fields and B.G.Wybourne, J.Chem. Phys.42(II)(1965)3797.

5.4 Results and Discussions:

a) IR-Spectral Analysis :

Preliminary infrared spectral studies have been made to find out the important structural features of Nd(III):GSH complexes. The spectra are quite complicated because of the presence of several functional groups.

Two important information which could provide by our IR spectra :

(i) regarding the changes taking place in the sulphydryl (-SH) group of the biomolecule, when it undergoes complexation, and

(ii) the carboxylic group attachment to lanthanide.

Figure 5.1(a) Comparative IR Spectra of GSH ———— , Nd(III):GSH – – – – and Nd(III):GSH:Zn –·–·–·– in the range 4000-2000cm^{-1}.

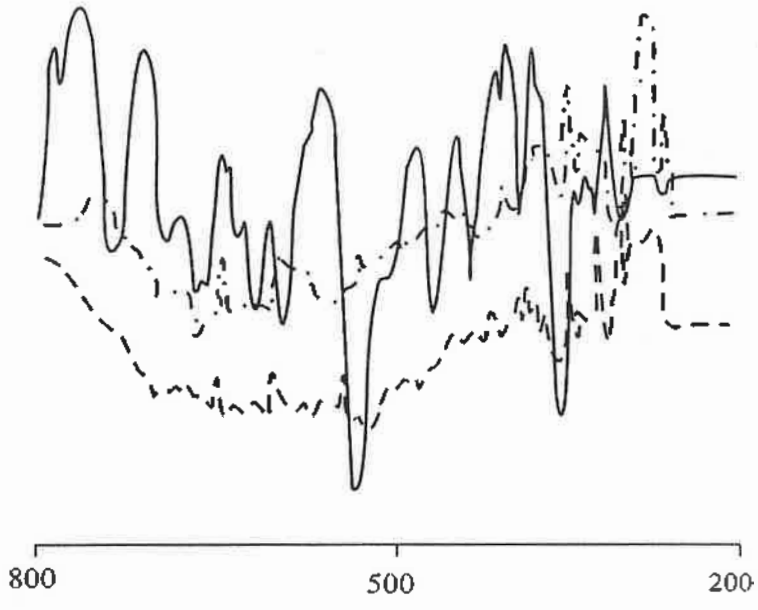

Figure 5.1(b) Comparative IR Spectra of GSH ———— , Nd(III):GSH – – – – and Nd(III):GSH:Zn –·–·–·– in the range 800-200cm^{-1}

The IR spectrum of the glutathione (GSH) shows a stretching frequency due to sulphydryl (-SH) group occurring as a sharp intense band around 2523 cm^{-1} the addition of Nd(III) to glutathione clearly leads to its deprotonation, in all probability, it induces the formation of Nd(III) - S bond. This looks little but surprising in view of the hardness of the Nd(III) ion which generally do not prefer sulphur for coordination, but the IR spectra [Figure 5.1(a)] shows that without doubt deprotonation of sulphydryl group occurs even at pH 5.00 at which the complexes are being synthesized.

The IR spectra in the 800-200 cm^{-1} region [Figure 5.1(b)] show the appearance of new bands, and some of these can be ascribed to Nd(III)-S. The addition of Mg(II) or Zn(II) to Nd(III):GSH complex enhances the deprotonation tendency and the Mg(II)- or Zn(II) - S bands can be expected in the region 800 - 200 cm^{-1} which we could not resolve. The carboxylic group frequencies as well as carbonyl group frequencies are highly sensitive when the complex has metal ion like lanthanide(III). This is clearly visible in the IR spectrum. The carbonyl (C=O) stretching frequency occurring at 1715 cm^{-1} in the ligand (GSH) spectrum is shifted to the lower field at around 1680 cm^{-1} in Nd(III):GSH complex and showing a shift at 1675 cm^{-1} and 1630 cm^{-1} in Nd(III): GSH: Zn(II) complex, indicating the involvement of C=O group in binding with the lanthanide ion.

4.3.2 HNMR – Spectral Analysis :

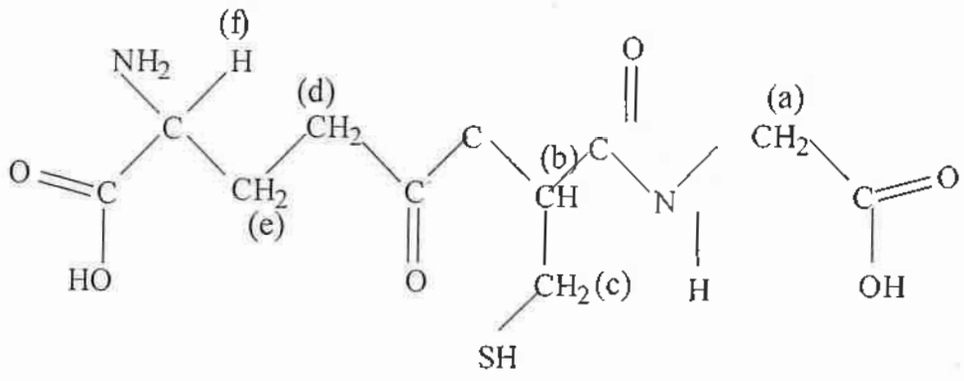

Figure 5.2 (a) Structural Formula of Glutathione

The ^{1}H spectrum of the Nd(III):GSH complex [Figure 5.2(b)] gives evidence of the interaction of glutathione (GSH) with Nd(III) ion. Table 5.3 clearly shows the shifts in the proton peaks. All the peaks are showing a down field shift in the Nd(III):GSH complexes. The H(a) proton peak observed at $\delta_{3\,98}$ in the ligand (GSH) spectrum is shifted to $\delta_{4\,37}$ in the complex. The triplet H(b) proton [Figure 5.2 (b)] peaks centered at $\delta_{3\,83}$ in the ligand to shifted to $\delta_{4.19}$. Interestingly H(c) proton peak also shows a down field shift which indicates the weak interaction of sulphur with Nd(III) ion. Similarly other proton peaks of the complex are also showing down field shift the H(e) and H(f) proton peaks are slightly broaden due to the paramagnetic nature of the complex. In the ^{1}H spectrum of the Nd(III)-GSH-Zn(II) complex, the H(a) proton peak is shifted from 4.00 ppm to 4.32 ppm. The peak is slightly broadened and can be accounted for 3H, which indicates that the CH proton (b) is merged with these protons. The doublet H(c) proton peaks observed at 2.97

ppm and 2.91 ppm in the ligand spectrum are shifted to 3.21 ppm and 3.15 ppm in the Nd(III):GSH:Zn(II) complex [Figure 5.2(b)] with a coupling constant of 6.35 Hz. This shows that the presence of Zn(II) strengthen the binding of S with the metal ion. The H(d) protons centered at 2.96 ppm are not appeared as well resolved triplet as in the glutathione spectrum, but it shows a downfield shift by 0.7 ppm. H(e) and H(f) protons appeared as broad singlet at 2.64 ppm. with a downfield shift by 0.57 ppm. The H(e) and H(f) proton peaks observed at 2.20 ppm. in the GSH is shifted to 2.42 ppm. in Nd(III):GSH complex with a downfield shift by 0.22 ppm. While H(e) and H(f) proton peaks observed at 2.64 ppm. in the Nd(III):GSH:Zn(II) complex showing a downfield shift by 0.44 ppm. This increase in the value gives evidence of the involvement of Zn(II) in complexation with glutathione (GSH) and Nd(III) ion.

Table 5.4 ^{1}H NMR δppm for protons of GSH in different complexation states:

Compound	a	B	c	D	e and f
GSH	3.98	3.77	2.97	2.64	2.20
		3.83	2.91	2.57	
		3.90		2.49	
Nd(III):GSH	4.37	4.19	2.98	2.84	2.61
				3.12	2.42
Nd(III):GSH:Zn	4.32		3.21	2.96	2.64
			3.15		

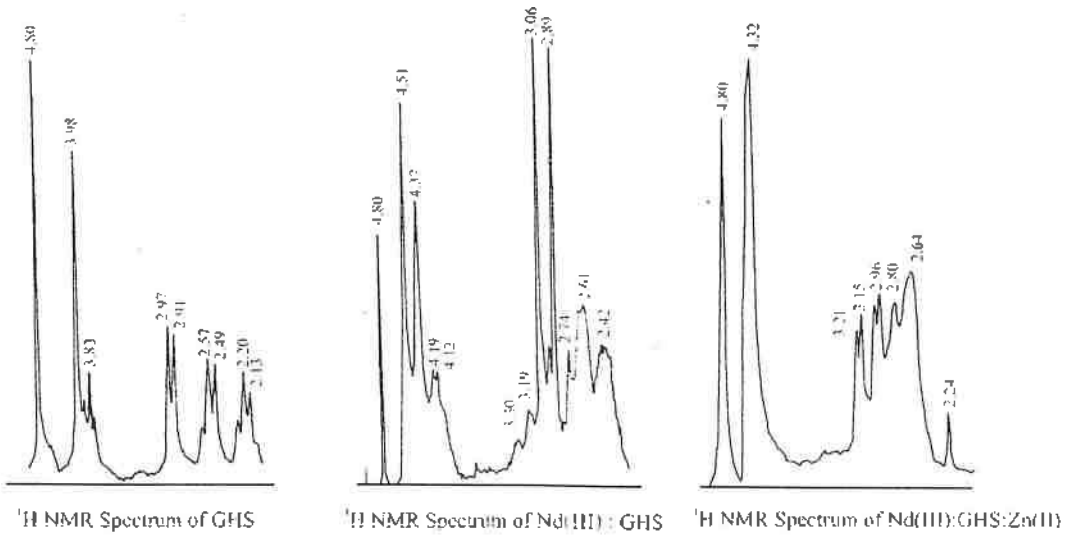

Figure 5.2 (b) : ^{1}H NMR Spectra of GSH in different complexation state

c) Comparative absorption spectral analysis of 4f-4f transition of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) by employing energy interaction parameter at different aquated organic solvent and different pH

Figures 5.3, 5.4, 5.5 and 5.6 gives comparativeabsorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3CN, DMF, dioxane and CH_3OH at pH 3. Similarly Figures 5.7 to 5.18 gives their spectra at different solvents in CH_3CN, DMF, dioxane and CH_3OH at pH 4, pH 5 and pH 6 respectively. Figure 5.19 shows the comparative absorption spectra of Nd(III):GSH:Zn(II) in different solvents like CH_3CN, DMF, dioxane and CH_3OH at pH 6. Figure 5.20 gives the comparative absorption spectra of Nd(III):GSH:Zn(II) complex at different pH, i.e. pH 3, pH 4, pH5 and pH 6. From the Figures 5.3 to 5.18, we can reveal that there is a red shift as GSH is added to Pr(III) and further longer wave length is observed on addition of

Zn(II).,From all the figures we can reveal that there is a red shift as GSH is added to Nd(III) and further longer wave length is observed on addition of Zn(II). Table 5.4 to 5.7 shows the variation of the magnitude of energy interaction parameters like Slater Condon (F_K), Lande factor (ξ_{4f}), Racah energy (E^K), Nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency parameter(δ) for Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in aqueous and different aquated organic solvents at different pH, i.e. pH 3, pH 4, pH 5 and pH 6. There is a slight decrease in the values of F_K and ξ_{4f} as the complexation goes on, which lead to increase in the values of Nephelauxetic ratio (β) and so in bonding parameter ($b^{1/2}$) and covalency parameter (δ).

For spectral studies on the structures of co-ordination compounds of lanthanides in solution, the evidence of the relationship between the Nephelauxetic band shift and the structure is of special interest. Jorgensen and Ryan[13] noticed the dependence of Nephelauxetic effect on the co-ordination number. It was suggested that shortening in the metal ligand distance occurs with decrease in the co-ordination number. Yatsimirskii and Davidenko[14-15] pointed out a close linear correlation between R(Ln-O) and wave number of some f-f transitions in the absorption spectra of some praseodymium and neodymium complexes having different co-ordination number and symmetries. To interpret the correlation and analysis of the relationship between Nephelauxetic effect and geometry, energy parameters have been derived and

evaluated for complex compound using the angular overlap model, the value of 'n' is proportional to the Nephelauxetic effect as

$$n = \left[\frac{\left(1-\beta^{1/2}\right)}{\beta^{1/2}}\right] \tag{5.14}$$

It may also be expressed as

$$n = \frac{H_L^2}{\left(H_M - H_L\right)^2}.\left(S^*R\right)^2 N \tag{5.15}$$

where N is the co-ordination number, H_M and H_L are coulomb integrals of atomic orbital; S is the overlap integral; R is the radius of the orbit. For compounds with ligand coordinated through identical donor atoms, the term of equation (5.15) is a constant and it becomes

$$n = \text{constant}.\left(S^*R\right)^2 N \tag{5.16}$$

The above equation (5.16) represents the Nephelauxetic effect as a function of two variable. S*R and N which vary with changes in lanthanides-ligand distance in opposite directions. However any variation in the value of R leads to a larger change in $(S^*R)^2$ compared to that in N. As a result, the Nephelauxetic effect increases when the co-ordination number decreases. The Ln – O distance shortens in spite of the enhancing nature of β and decrease in the number of the co-ordinating ligand. Misra et al[16-17] [18-19] observed a general decrease in the values of F_K and ξ_{4f} parameters as compared to the corresponding parameters of the free ion.

In absorption spectra of Nd(III) ion ten 4f-4f transition bands have been observed, out of which only five bands are resolved. They are $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$ and $^4I_{9/2} \rightarrow {}^4F_{3/2}$. Out of these, only $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition obeys selection rule and show vide variation in energy and intensity parameter with even minor changes in the coordination environment around the central metal ion. Such transition is called hypersensitive transition. Other transitions, i.e. $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$ and $^4I_{9/2} \rightarrow {}^4F_{3/2}$ also show some slight changes in their physical parameters with the change in their coordination environment and they are called pseudohypersensitive transitions.[18,19] Due to extremely fast water exchange rate and very small crystal field stabilization energy the conversion from one-geometry to another is very convenient and facile. Karraker[20] showed that the shape, energy and oscillator strength of hypersensitive or pseudohypersensitive transitions can be correlated with coordination number and diagnostic of immediate coordination environment around lanthanides ions. The comparative absorption spectra of Nd(III) ion, Nd(III):GSH (in 1:1 molar ratio), Nd(III):GSH:Mg(II) (in 1:1:1 molar ratio), and Nd(III):GSH:Zn(II) (in 1:1:1 molar ratio) in different aqueous and aquated organic solvents (50%) are given in Figures 5.3 to 5.18. The addition of GSH in Nd(III) resulted in a marginal red shift of 4f-4f transition bands and the further addition of Zn(II) to Nd(III):GSH gave further shift towards the longer wavelength. This shows the stimulated effect of Zn(II) towards the complexation of Nd(III) with GSH. The identical spectral pattern of

the complex with that of Nd(III) aquo suggest that the Nd(III) and Zn(II) bind to different coordinating sites of this multidentate ligand. Tables 5.4 to 5.4 gives the computed values of Slator Condon (F_k) and Lande spin orbit coupling constant (ξ_{4f}), Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and covalency(δ) of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in aqueous and aquated organic solvents at different pH. Tables 5.8 to 5.11 give the computed and observed values of energies for the various transition bands and root mean square deviation (R.M.S.) showing the correctness of the various energy parameters. One can clearly see that the variation of solvent nature and composition has significant effect on the energy parameters of the different 4f-4f transition bands.

d) Comparative absorption spectral analysis of 4f-4f transition of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) by employing intensity parameter like oscillator strengths (P) and Judd-Ofelt parameter, T_λ (λ=2,4,6) at different aquated organic solvents and different pH

The calculation of the band intensities is based upon the theoretical treatment derived by Judd[12] and Ofelt[21]. A consideration of the mechanisms by which the observation of intra-f-electron transitions may occur shows that the intensities of the observed bands can be adequately accounted for two processes. In a few cases, the transitions occur wholly or partially by a magnetic-dipole mechanism. Such transitions follow the selection rule $\Delta J \leq 1$,

$\Delta L=0$, $\Delta S=0$ and $\Delta l=0$ in the Russell-Saunders coupling scheme which is adopted. With the eigenvectors of the states involved, the magnetic-dipole intensities may be readily calculated.[22] The second and principal mechanism treats the transitions as being essentially (forced or induced) electric dipole in character. Both Judd and Ofelt were concerned to developed expressions for the intensity which arises via the later mechanism.

$$P = \sum_{\lambda=2,4,6} T_\lambda \sigma (f^N \psi J \| U^{(\lambda)} \| f^N \psi' J')^2 \qquad (5.17)$$

where P is the oscillator strength corresponding to the induced electric dipole transition $\psi J \rightarrow \psi' J'$ at energy σ (cm^{-1}) and $U^{(\lambda)}$ is a tensor operator of rank λ.The three quantities T_λ (λ =2,4,6) are related to the radial parts of the $4f^N$ wave functions, the wave functions of perturbing configurations of which the nearest is $4f^{N-1}5d$, the refractive index of the medium, and the ligand-field parameters which characterize the environment of the ion. While principle values of T_λ could be calculated, we have treated these quantities as parameters to be determined from experimental oscillator strengths.

The measured intensity of an absorption band is related to the probability (P) for the absorption of radiant energy (oscillator strength) by the expression

$$P = \frac{2303mc^2}{N\pi e^2} \int \varepsilon_i(\sigma) d\sigma$$

or,
$$P = 4.318 \times 10^{-9} \int \varepsilon_i(\sigma) d\sigma \qquad (5.18)$$

where ε is the molar absorptivity at the energy σ (cm^{-1}) and other symbols have their usual meaning. It will be noted that in 'i' a factor involving the index of refraction of the medium was improperly written as part of the experimental P, whereas it should only occur within the expression for T_λ.

Hoogschagen et al[23,24] made an accurate estimation of the absolute intensities of the lanthanides. He published a compilation of the oscillator strength of the lanthanide aquo ions in 1948.[25]

The spectra of lanthanide are composed of clearly special groups of sharp lines, similar to atomic spectra. The groups of lines are normal. These spectra are arises from transitions among levels of f^N configuration. The usual (2J+1) fold degeneracy terms of such configurations are reduced to some extent by the action of crystal field. However, the energy levels of rare earth ions in solid state are determined largely by spin orbit interaction, which has a larger magnitude than that of the influence of crystal field. Contrary to this, in transition elements, the contribution of the crystal field is more than that of the spin-orbit interaction. The 4f-electrons of lanthanides are more or less protected from the influence of lattice by the polarisation of $5s^2$ and $5p^6$closed shells. The crystal field splitting effect in the lanthanide ions is small, 200-300cm^{-1} at the most cases.

Judd[12] assigned the hypersensitivity to the changes in symmetry of the environment of a lanthanide ion. Hypersensitivity is observed in the absorption spectra of the lanthanide trihalides in the gaseous state having D_{nh} symmetry.[26]

Jorgenson and Judd[27] considered the problem of hypersensitivity and concluded that all such transition obeyed selection rules. These are the transitions whose intensities are determined by the values of T_λ.

The effect of pH is responsible for the degree of protonation and deprotonation of different coordinating sites of GSH. The bonding of GSH is affected significantly by degree of deportation of the coordinating sites and therefore pH will have significant effect on Nd(III):GSH binding, which is clearly reflected through significant variation in intensity parameters.

The interaction of Nd(III) with GSH is generally predominant with carboxylic groups of GSH, the bonding between Nd(III):GSH is basically electrostatic in nature. Since lanthanides are hard metal ions their preference will be for hard donor sites like oxygen atoms. Therefore, energy and Nephelauxetic changes are not apparently significant The absorption spectral study at pH 3.0 indicates the deprotonation of glutamyl residue of GSH. Nd(III) being a hard metal ion, has a tendency to coordinate, preferentially with –COOH group. Hence Nd(III) interacts with glutamyl residue in acidic medium, of GSH. One more carboxylic (Glycilic) group and sulphydryl (-SH) group from glycine and cysteinyl residue gets deprotonated at pH 4.0 and 6.0 respectively .

Misra[28-29] studied the high sensitivity of are $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$ and $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transitions of Nd(III) chelates in their complexes with ligands having widely different binding characteristics. They

have found that the nature of the coordinating sites, chelating power of the ligand, denticity of the ligand and nature as well as the geometry of the complex species induced unusual sensitivity to this pseudohypersensitive transitions.

Tables 5.12 to 5.15 gives the observed (P_{obs}) and calculated (P_{cal}) values of oscillator strengths and Judd-Ofelt electric dipole intensity parameters , T_λ, (λ=2,4,6) of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in different aquated organic solvents and at different pH (pH3, pH4, pH5 and pH6). In all tables the absolute values of observed oscillator strengths, computed values of Judd-Ofelt parameters (T_2, T_4, T_6) and calculated values of oscillator strength of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) complexes are given. This clearly suggest a significant change in the value of oscillator strengths and T_λ - parameter when Nd(III) interacts with GSH in the solution. The change is more more proounced when Zn(II) is added to the reaction mixture. Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in DMF clearly show that the addition of GSH to Nd(III) results in significant enhancement in the oscillator strength of different 4f-4f transition (Figure 5.19). As a result, we have observed noticeable increase in the magnitude of Judd-Ofelt (T_λ) parameters. This suggest the binding of the tripeptide GSH to Nd(III) in solution. Such increase in the values of oscillator strengths and T_λ-parameter is more when Zn(II) is added to the solution of

Nd(III):GSH. This is due to the involvement of Zn(II) to other ligating site of GSH like sulphydryl group as being soft – metal ion.

The pH of the medium play a big role for the degree of protonation and deportonation of different coordinating sites of GSH. So, it plays significant effect on Nd(III) and GSH binding in presence and absence of Zn(II), which is clearly reflected through significant variation in oscillator strength (P) and T_λ parameters. In Figure 5.20 the comparative absorption spectra of Nd(III):GSH:Zn(II) in aquated DMF in different pH, i.e. pH 3.0, pH 4.0, pH5.0 and pH 6.0 is given. The absorption spectral study at lower pH, (pH 3) indicates the deprotonation of glutamyl residue of GSH. Nd(III) being hard metal ion, extracts with glutamyl residue of GSH in acidic medium. One more carboxylic group of glycine and sulphydryl (-SH) group from cysteinyl residue get deprotonated at pH 4.0 and pH 6.0 respectively. So, the binding of Zn(II) with Nd(III):GSH complex is more favoured in the case of pH 6.0. This is vividly seen from the distinct variation of the value of oscillator strengths and T_λ value at higher pH-value from lower pH value. The optimum pH for stable species of Nd(III):GSH with Zn(II) is found at pH 6.0.

The effect of solvent on complexation is quite significant. DMF appears to induce the maximum intensification on the complexation of Nd(III):GSH and Nd(III):GSH:Zn(II) complex and least in the case of methanol. This is due to its strong oxygen donor capacity which can enter the coordination sphere by replacing one of the water groups. Methanol is a very weak donor, which in

some cases does coordinate and otherwise not. All these are clearly seen from the comparative absorption spectra of Nd(III):GSH:Zn(II) at different solvents like DMF, CH_3CN, CH_3OH and dioxane at pH 6.0 in Figure 5.20..

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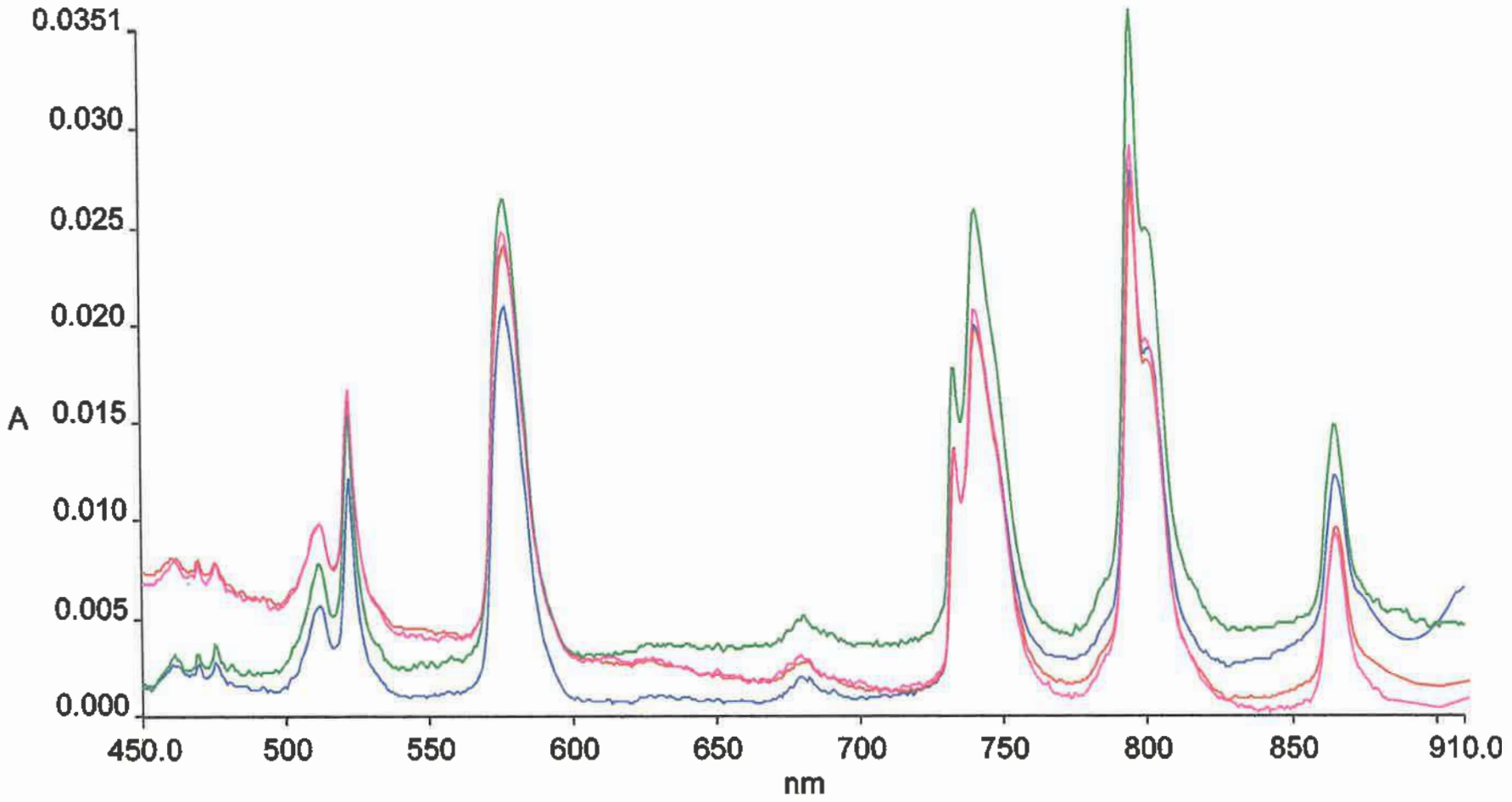

Figure 5.3 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3CN at pH-3

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

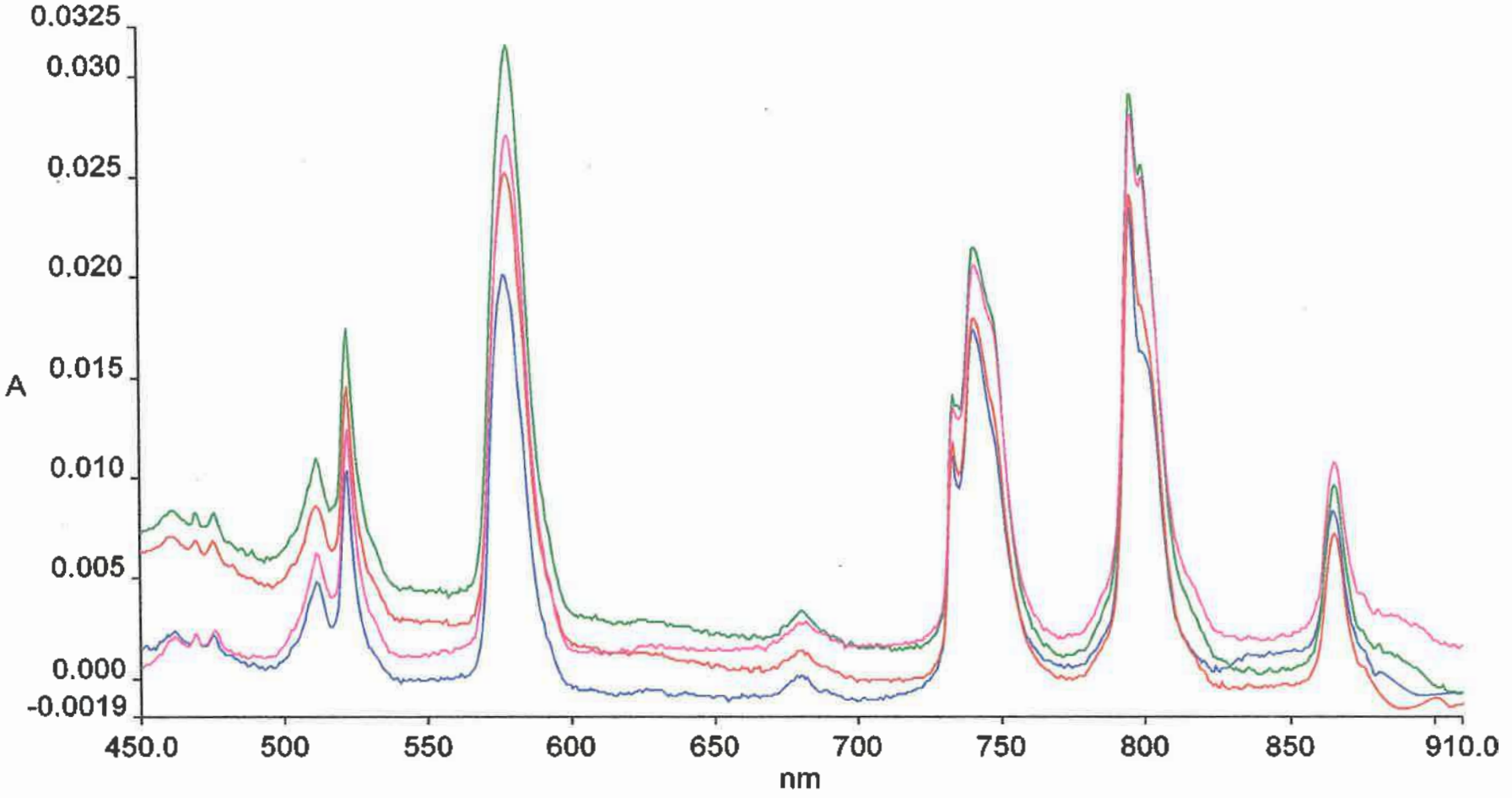

Figure 5.4 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in DMF at pH-3

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

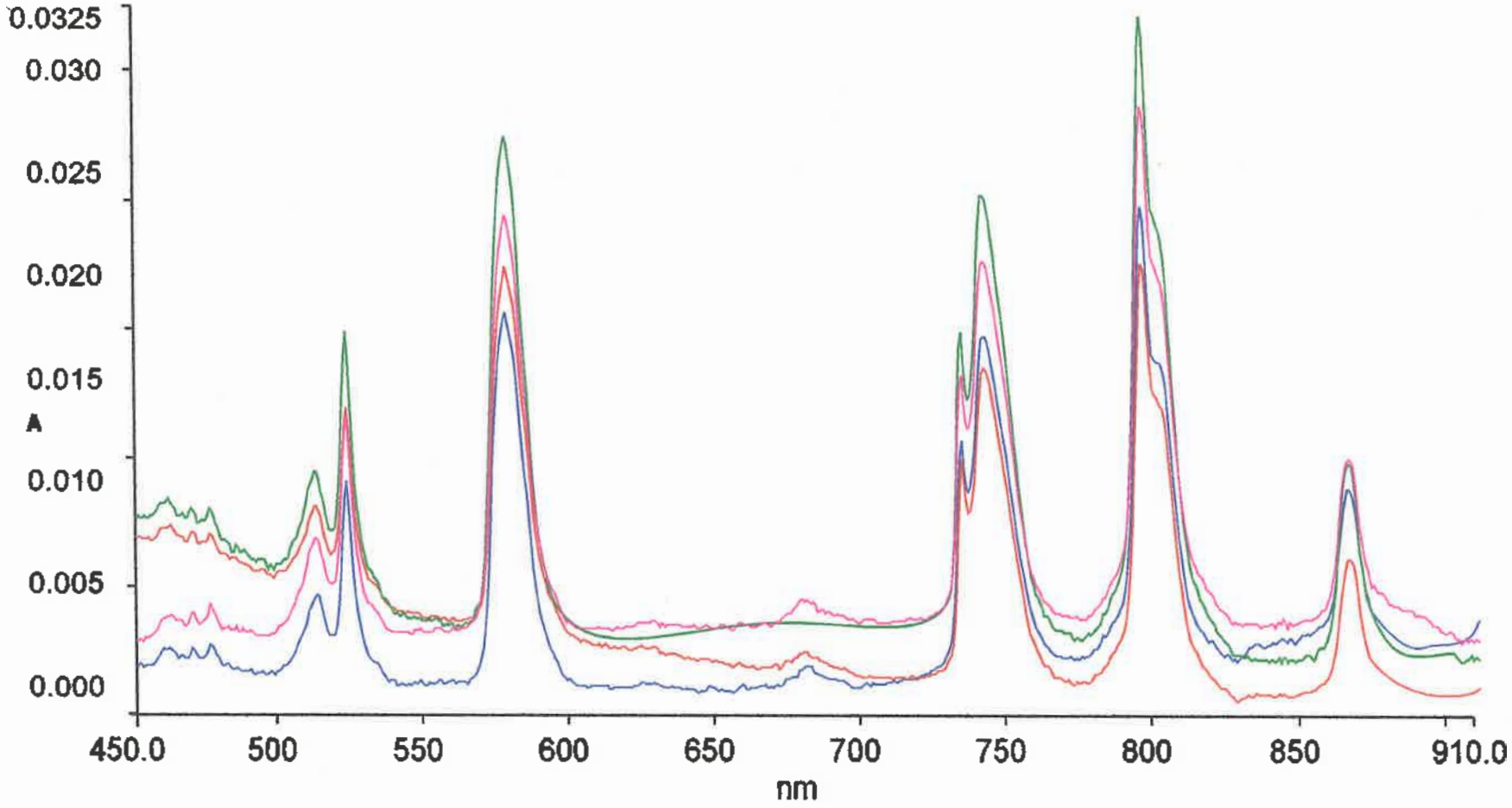

Figure 5.5 : Comparative absorption spectra of Nd (III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in dioxane at pH-3

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

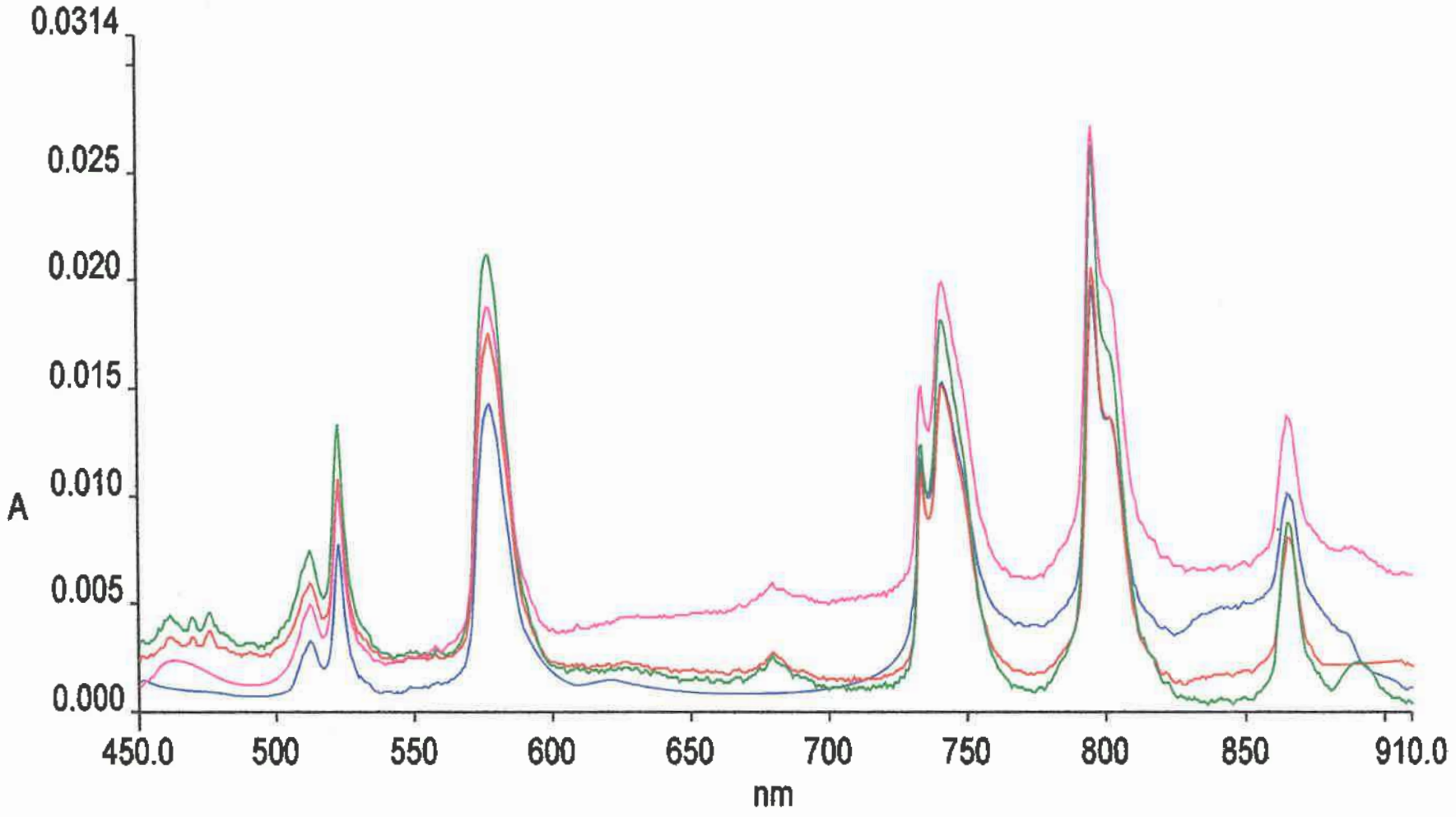

Figure 5.6 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3OH at pH-3

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

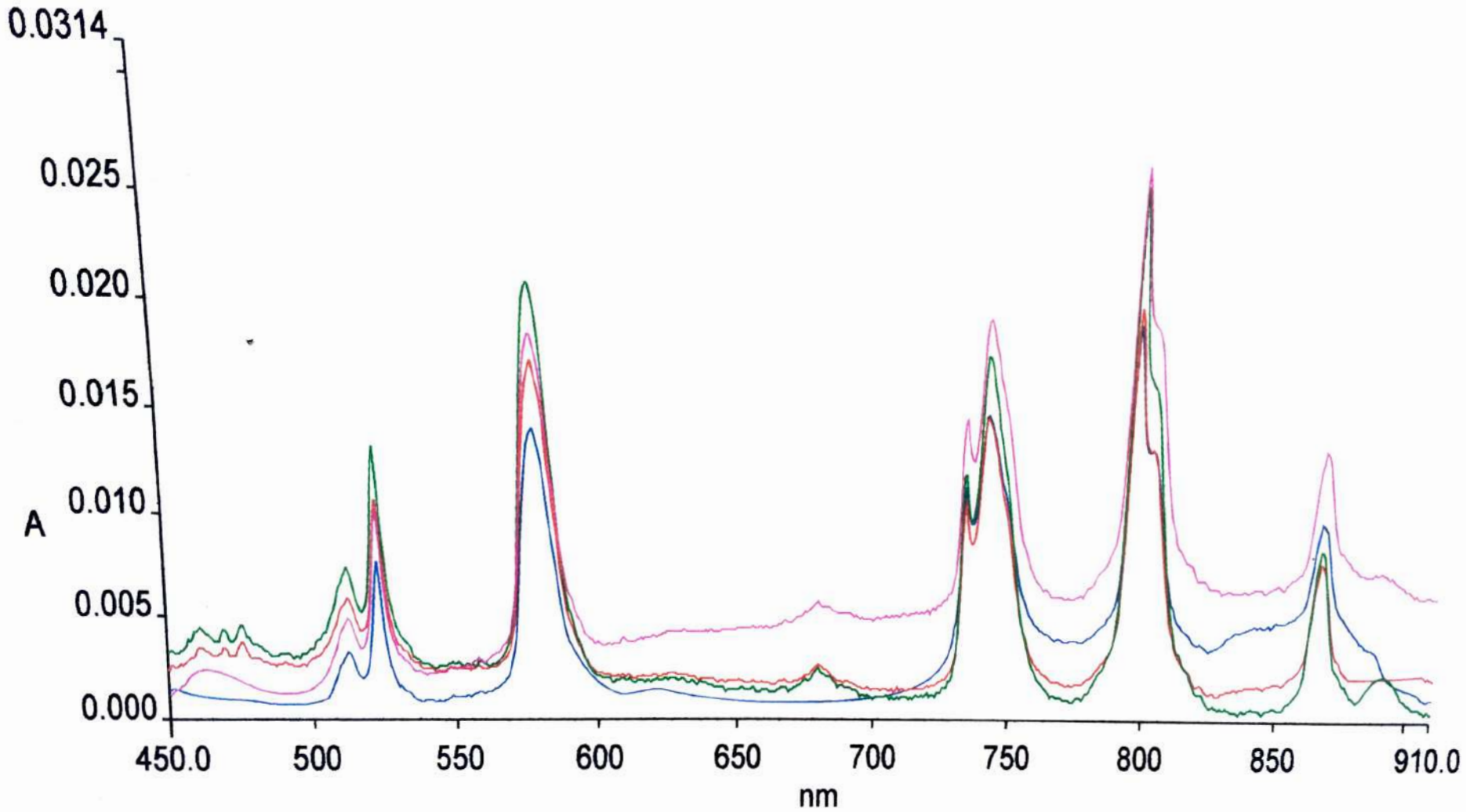

Figure 5.6 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3OH at pH-3

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

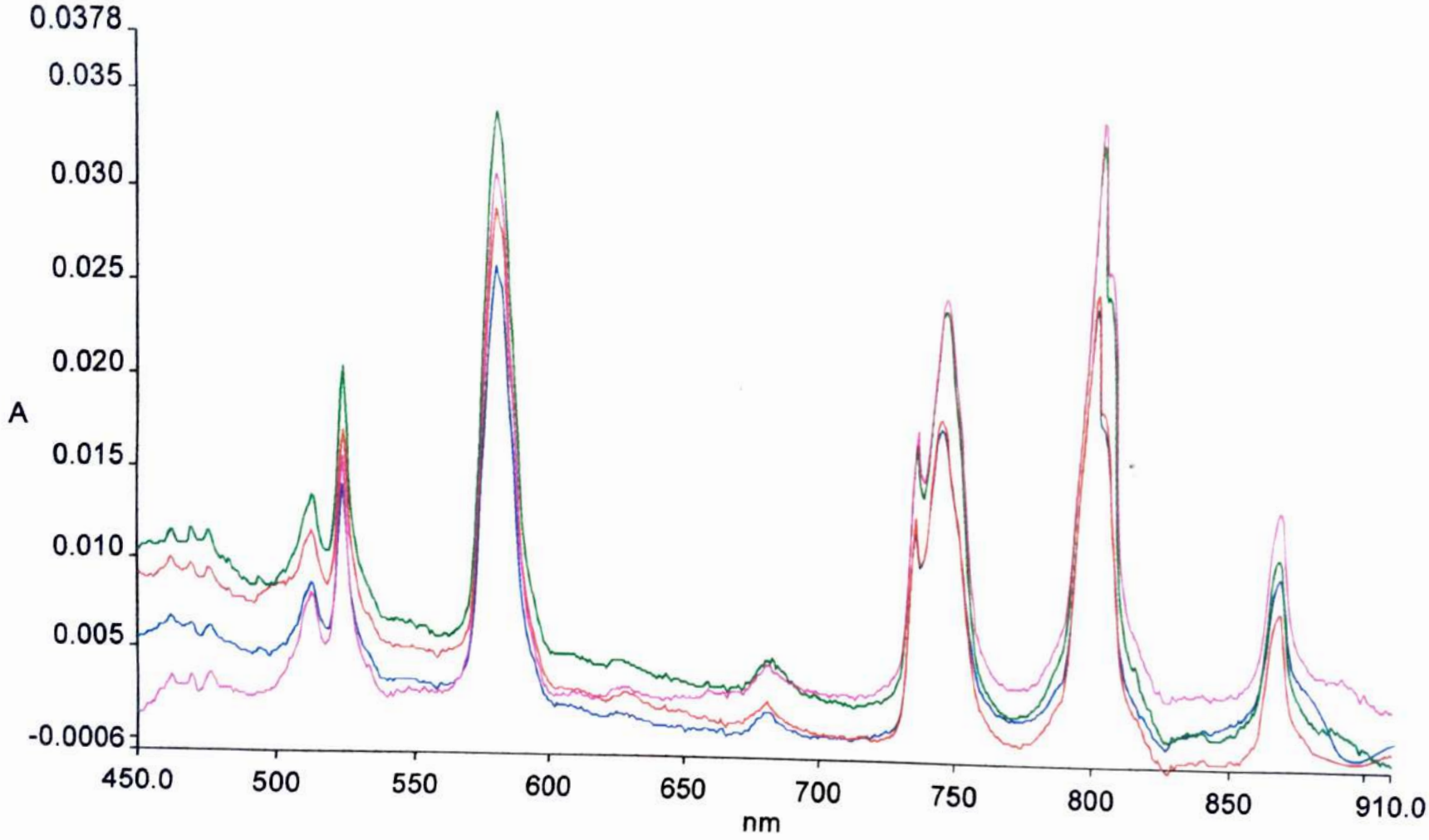

Figure 5.7 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3CN at pH-4

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

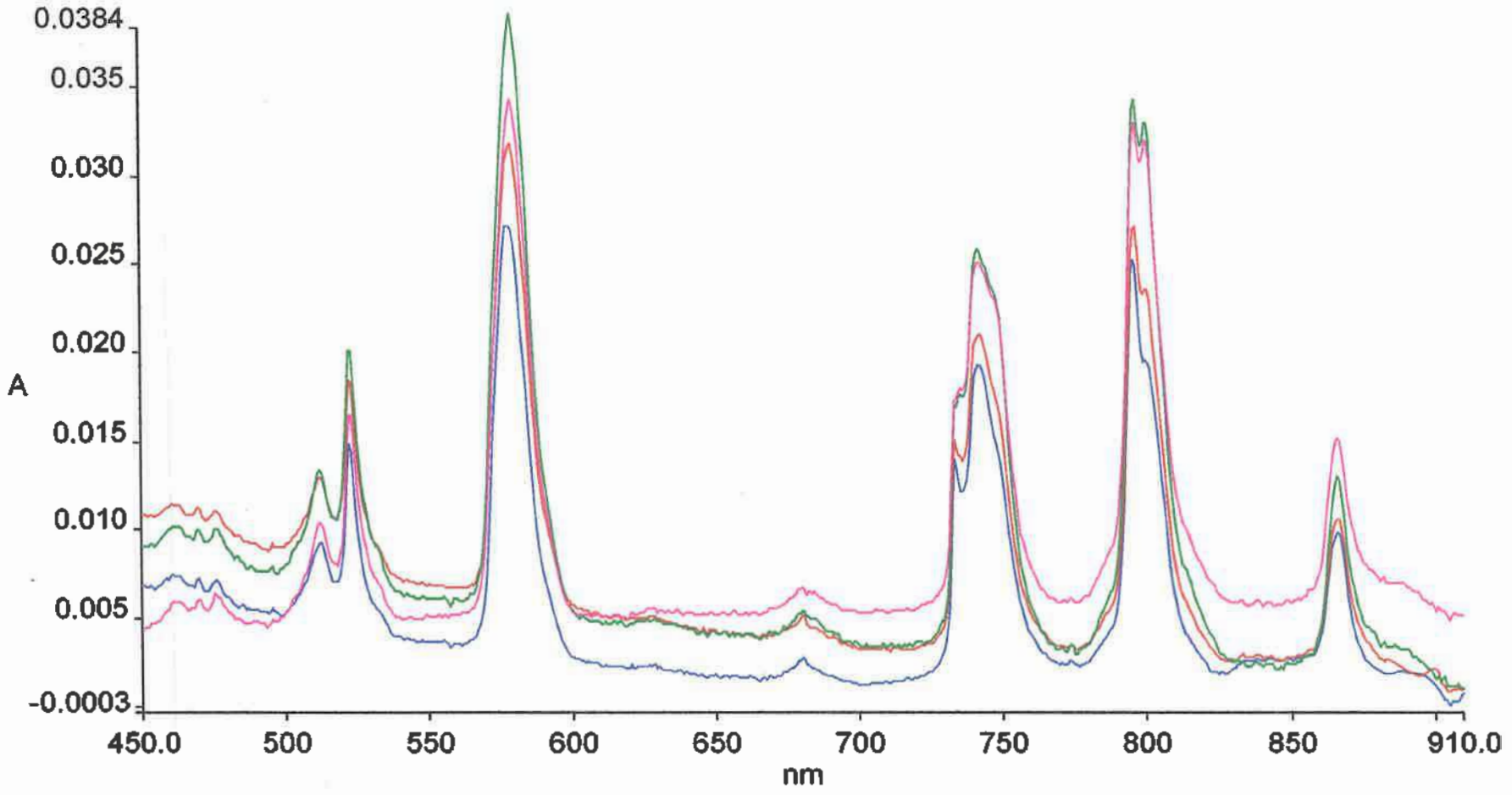

Figure 5.8 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in DMF at pH-4

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

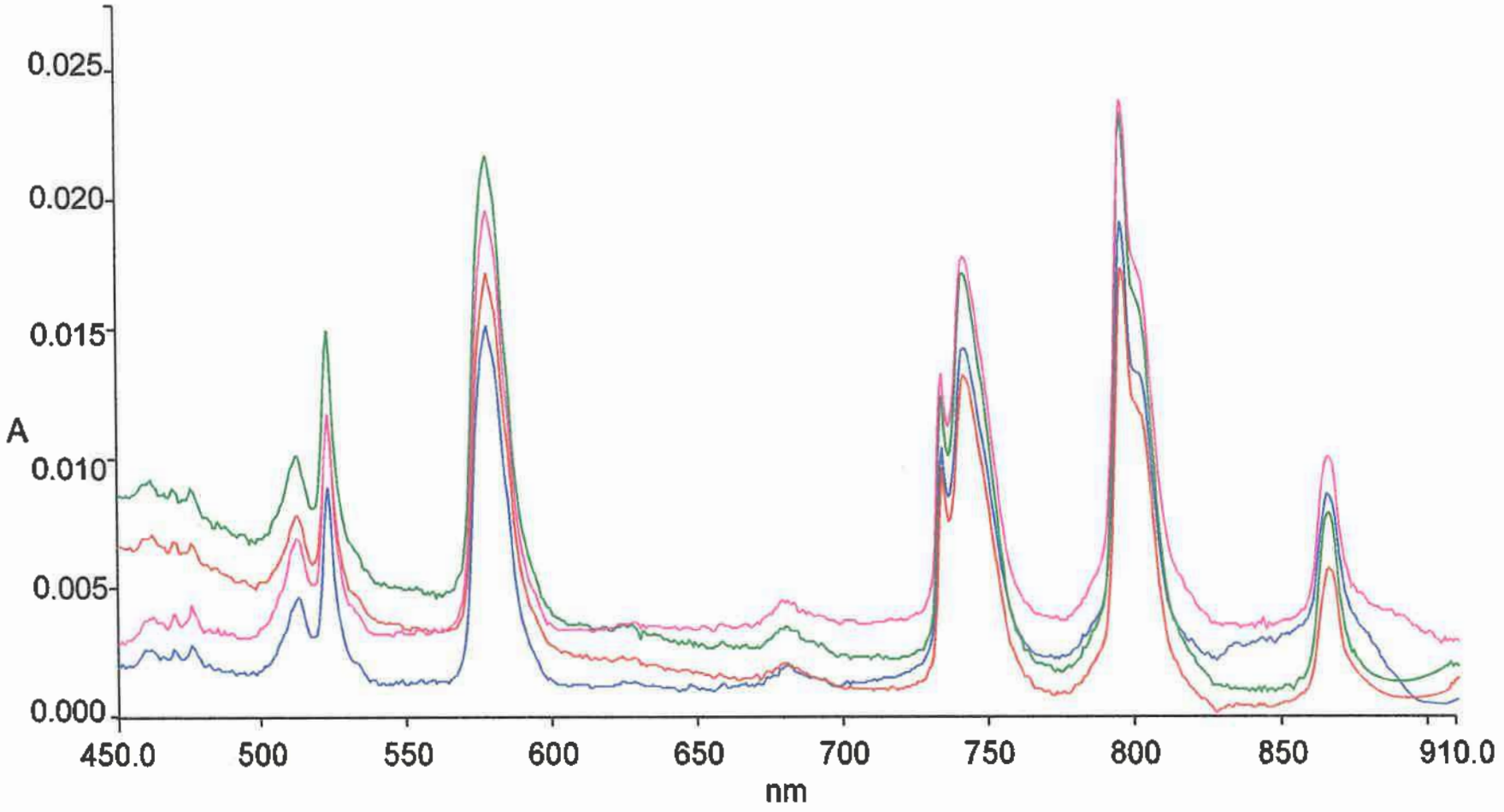

Figure 5.9 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in dioxane at pH-4

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

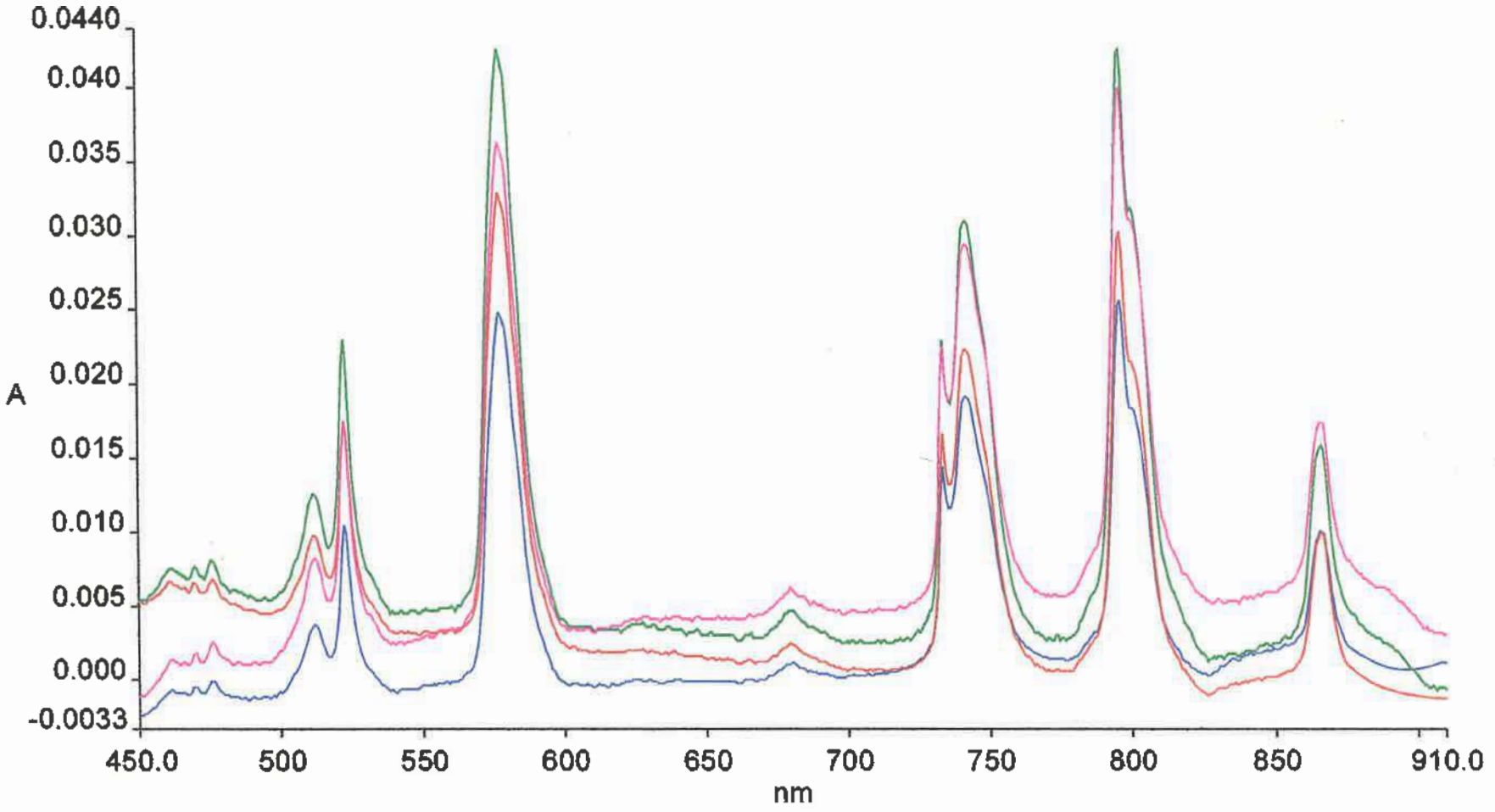

Figure 5.10 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3OH at pH-4

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

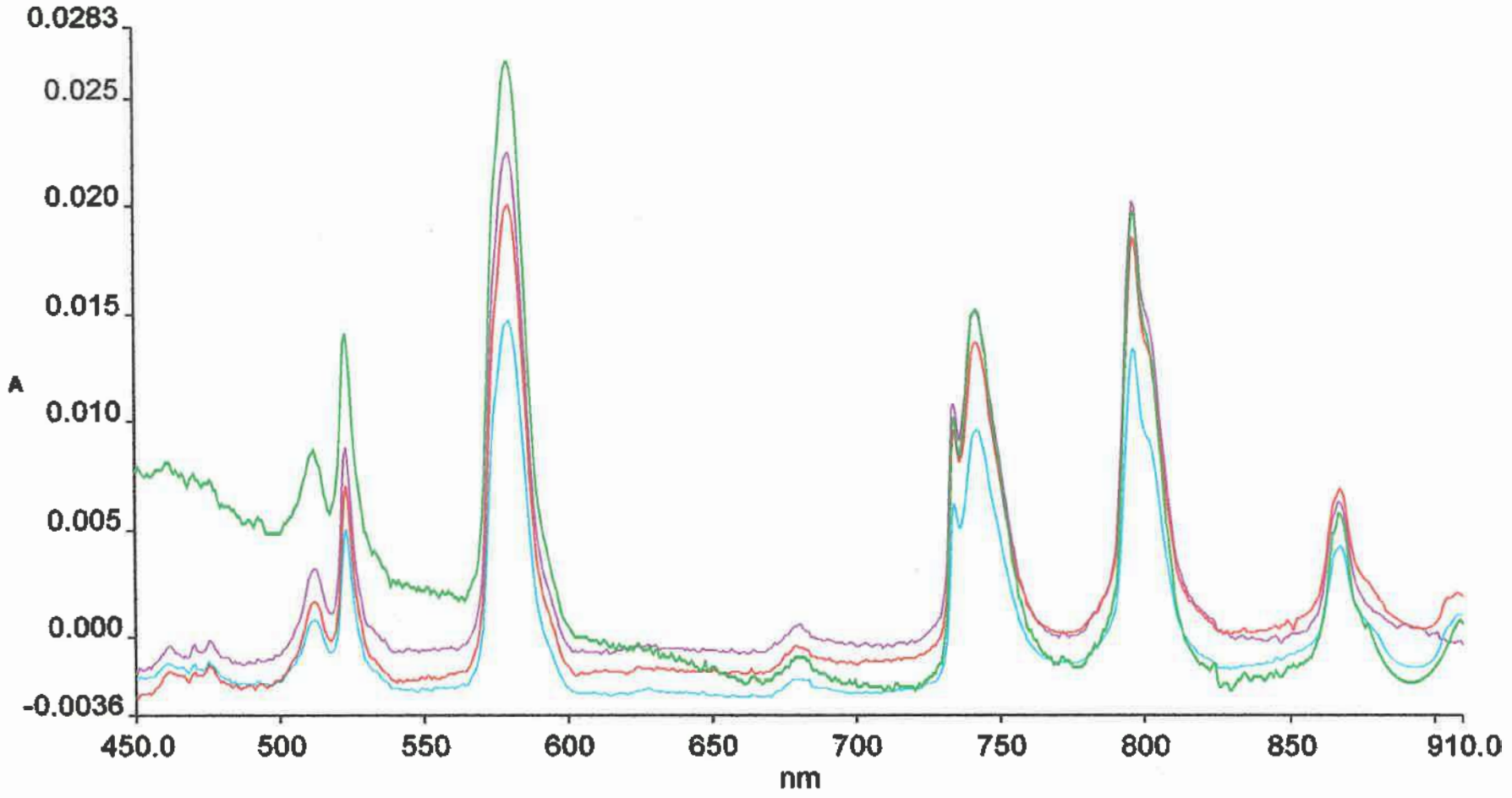

Figure 5.11: Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3CN at pH - 5

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

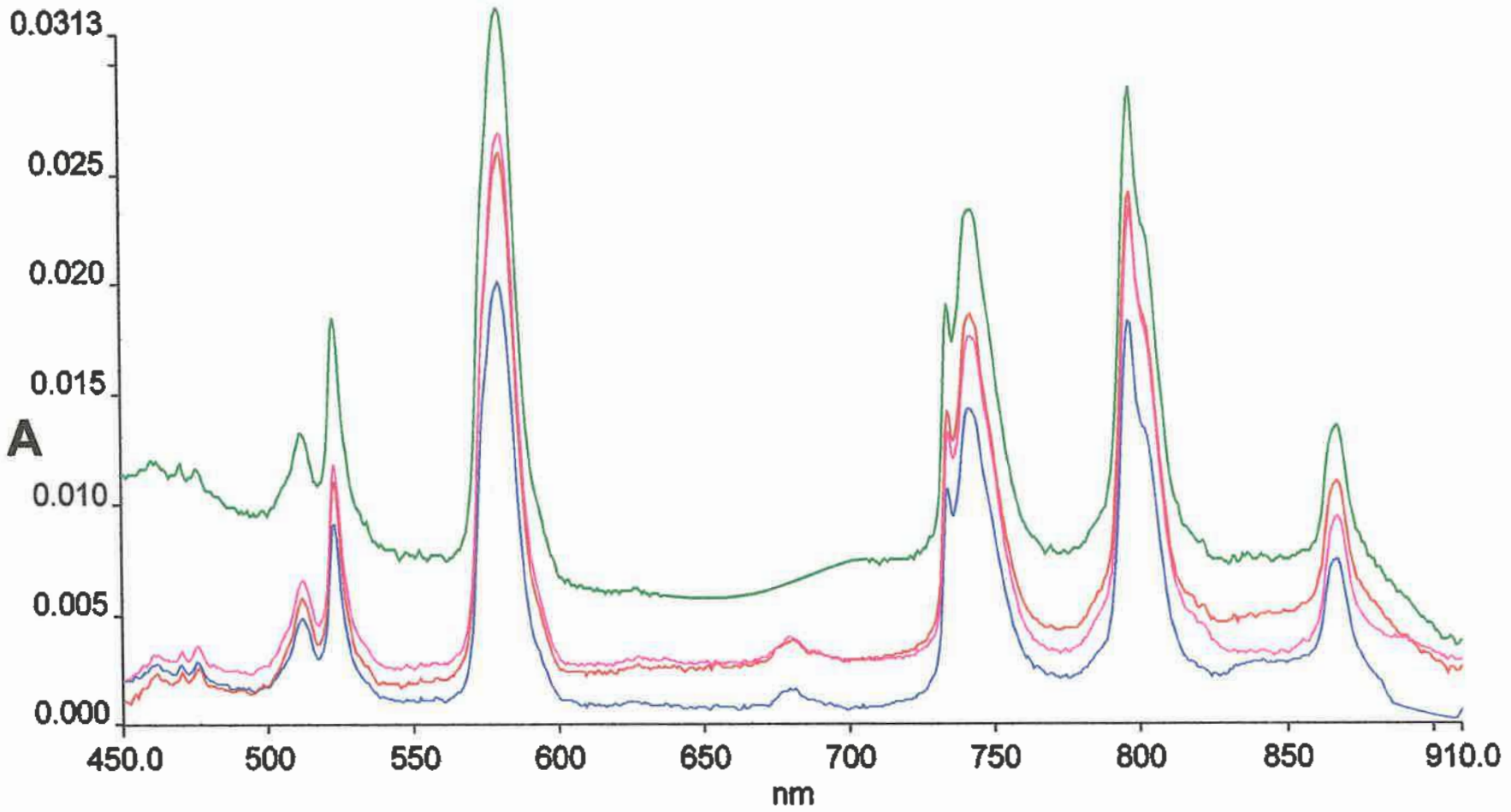

Figure 5.12 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in DMF at pH - 5

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

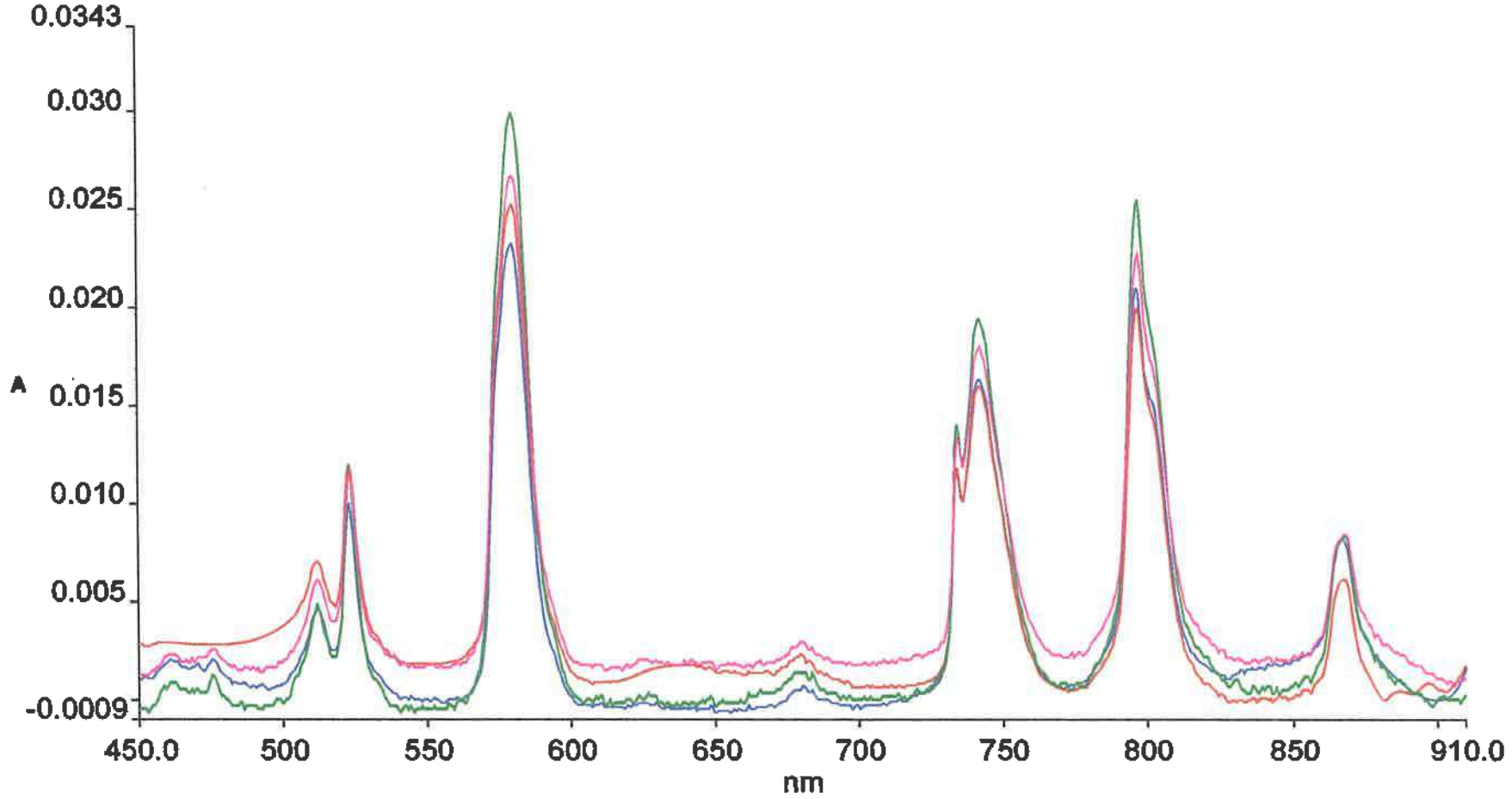

Figure 5.13 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in dioxane at pH - 5

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

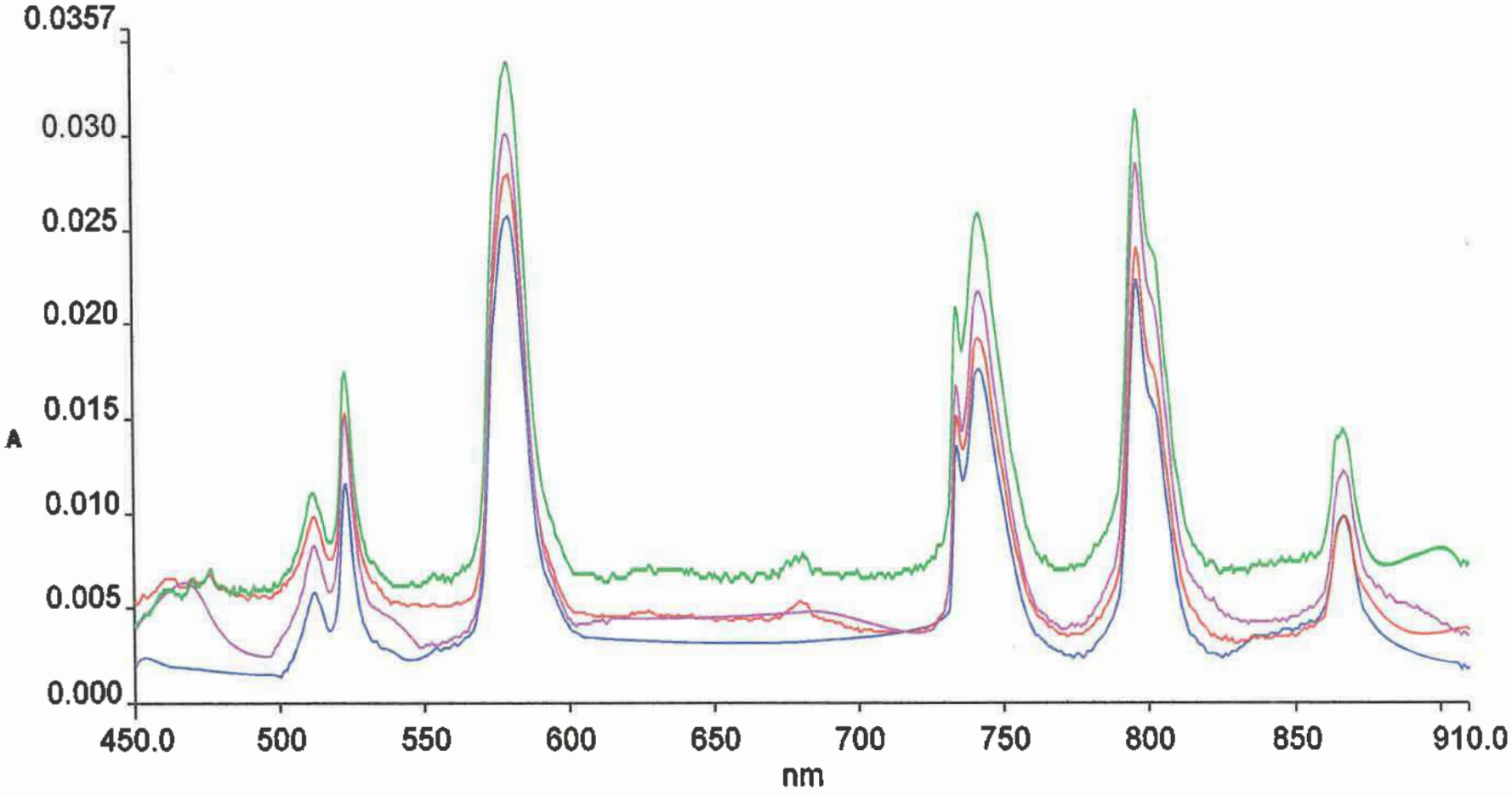

Figure 5.14: Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3OH at pH - 5

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

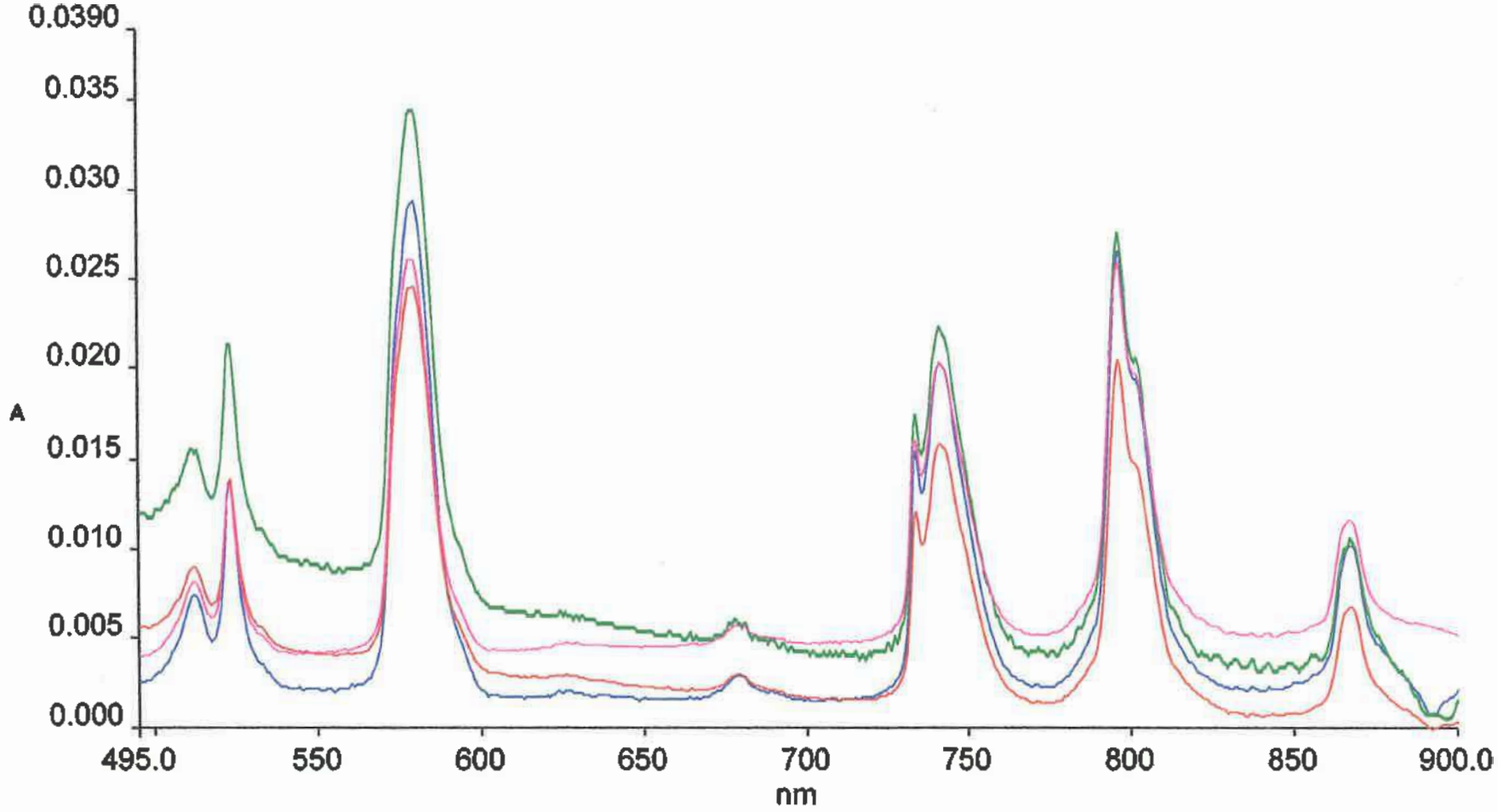

Figure 5.15 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3CN at pH - 6

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

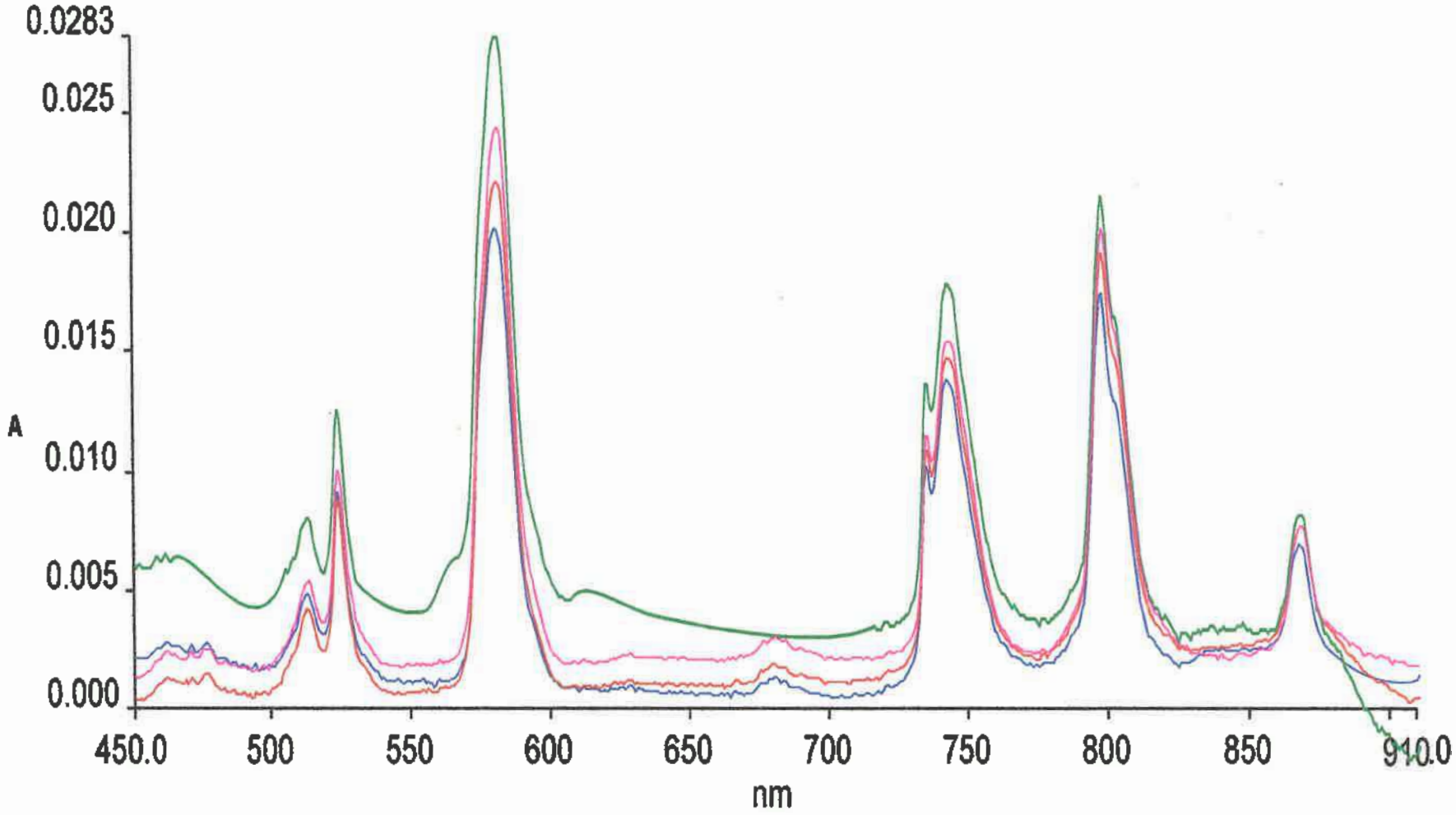

Figure 5.16: Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in DMF at pH - 6

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

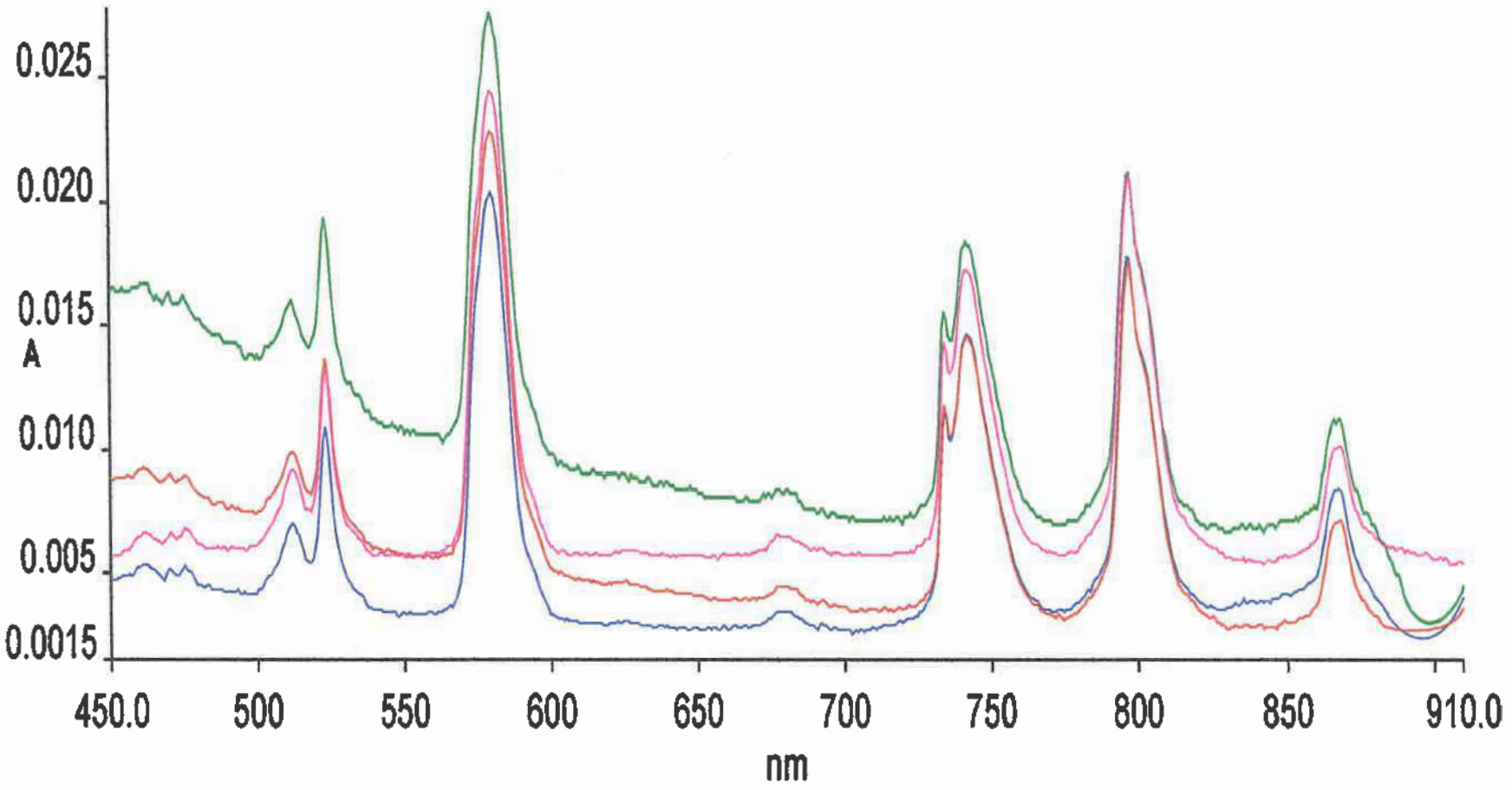

Figure 5.17: Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in DIOXANE at pH -6

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

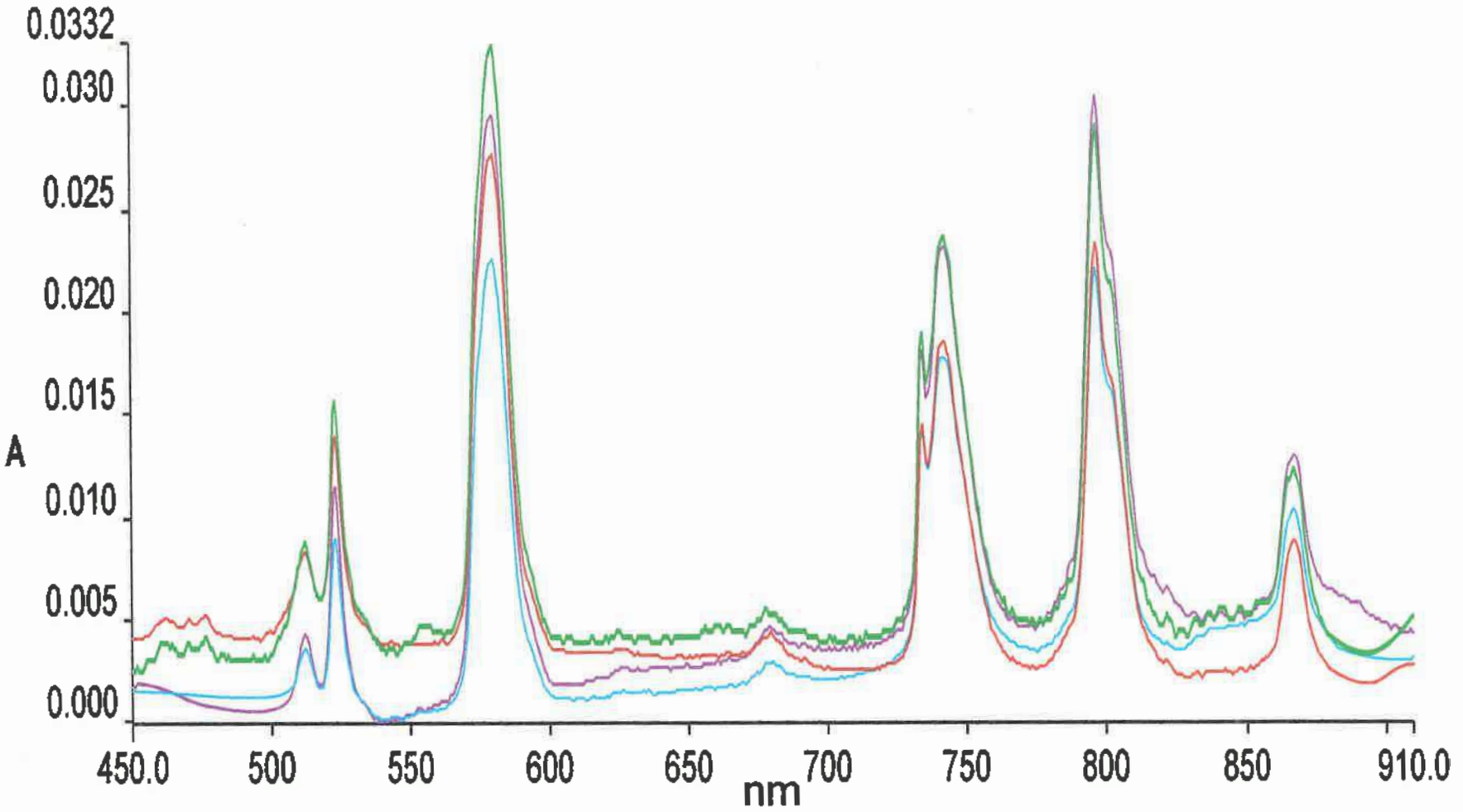

Figure 5.18 : Comparative absorption spectra of Nd(III), Nd(III):GSH, Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) in CH_3OH at pH - 6

Nd(III) : Nd(III):GSH : Nd(III):GSH:Mg(II) : Nd(III):GSH:Zn(II) :

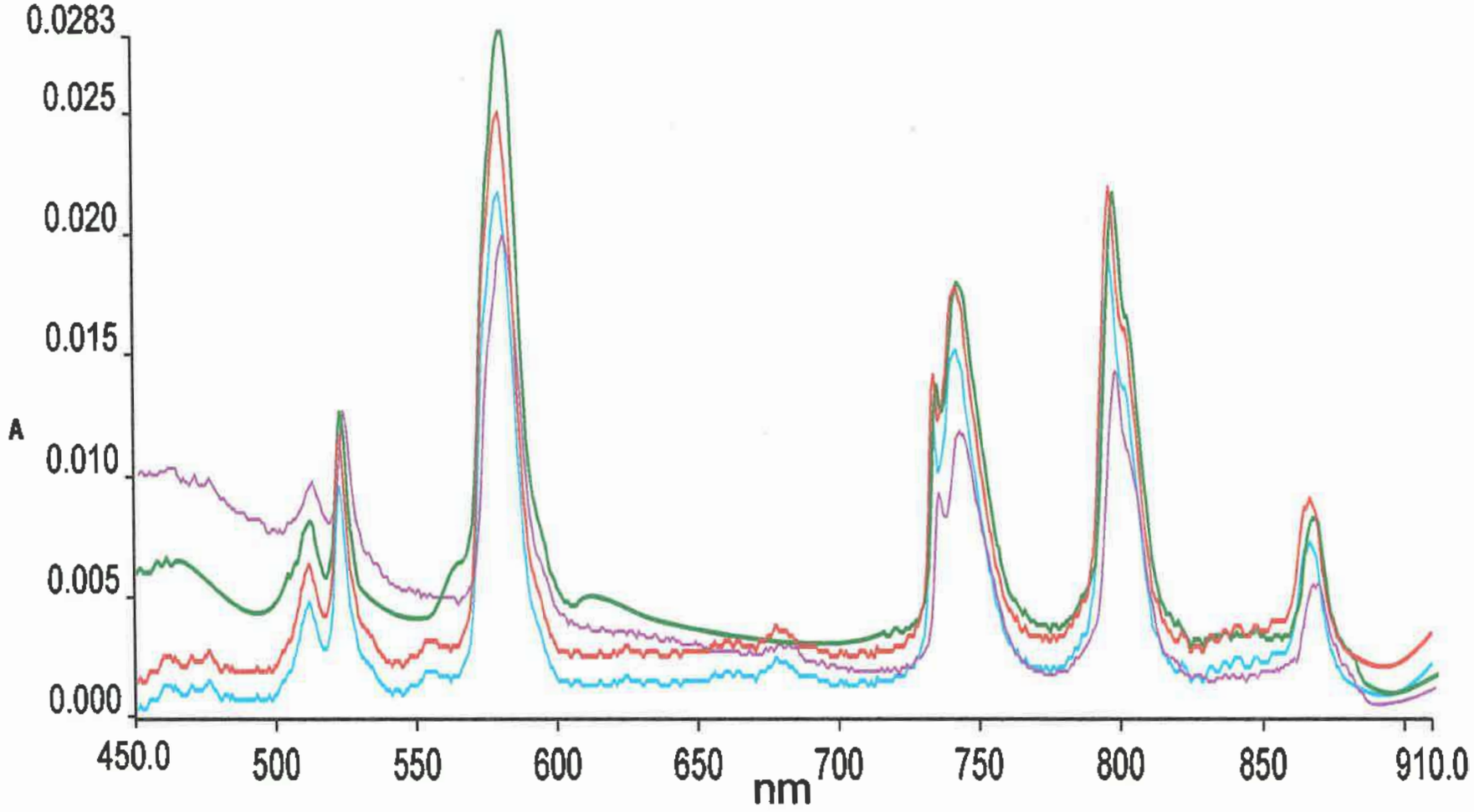

Figure 5.19 : Comparative absorption spectra of Nd(III):GSH:Zn(II) at different solvents at pH - 6

Methanol : Acetonitrile : Dioxane : DMF :

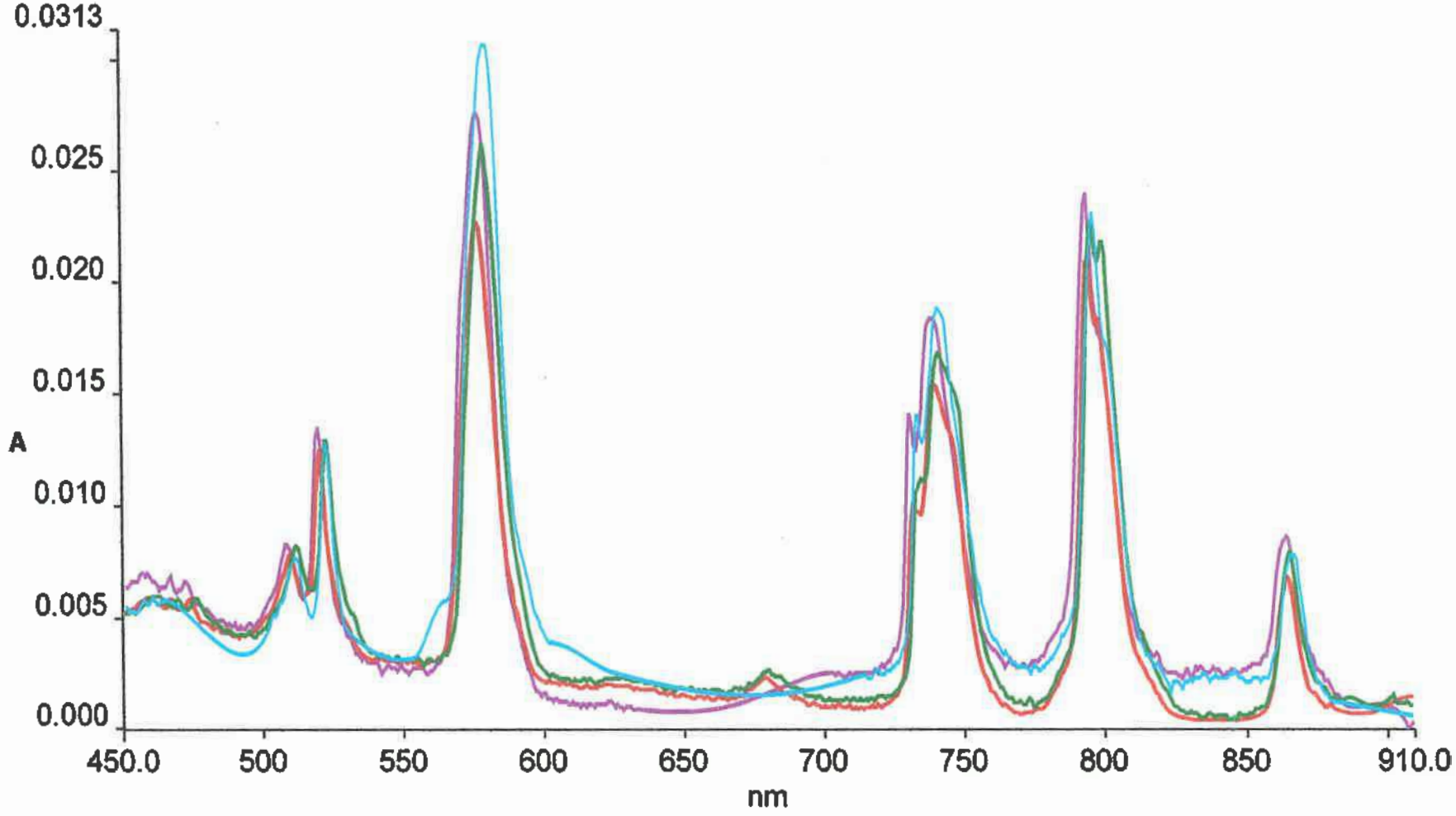

Figure 5.20 : Comparative absorption spectra of Nd(III):GSH:Zn(II) in DMF at different pH

pH-3 :
pH-4 :
pH-5 :
pH-6 :

Table 5.4 : Computed values of energy interaction Slater Condon $F_K(cm^{-1})$, Lande spin orbit interaction $\xi_{4f}(cm^{-1})$. Nephelauxetic ration (β), bonding ($b^{1/2}$) and covalency (δ) parameters for Nd(III), Nd(III):GSH Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) system In different aquated organic solvents at pH-3 :

	System	F_2	F_4	F_6	ξ_{4f}	β	$b^{1/2}$	δ
1.	MeOH							
	Nd(III)	331.6087	48.6207	5.1393	908.3562	0.9989	0.0240	0.1151
	Nd(III):GSH	331.5958	48.6232	5.1420	908.8895	0.9992	0.0196	0.0769
	Nd(III):GSH:Mg(II)	331.6218	48.6337	5.1338	907.0101	0.9980	0.0318	0.2024
	Nd(III):GSH:Zn(II)	331.6267	48.6377	5.1385	907.7365	0.9985	0.0269	0.1454
2.	CH_3CN							
	Nd(III)	331.6522	48.6077	5.1370	907.8004	0.9984	0.0279	0.1558
	Nd(III):GSH	331.5983	48.6273	5.1440	909.1415	0.9995	0.0166	0.0549
	Nd(III):GSH:Mg(II)	331.3254	48.6301	5.1462	909.14.35	0.9997	0.0169	0.1654
	Nd(III)GSH :Zn(II)	331.6802	48.6326	5.1315	906.1237	0.9974	0.0358	0.2566
3.	DMF							
	Nd(III)	331.7068	48.6291	5.1434	908.1003	0.9989	0.0233	0.1085
	Nd(III):GSH	331.5515	48.6365	5.1619	912.5778	1.00019	0.0311	0.1928
	Nd(III):GSH:Mg(II)	331.4440	48.6603	5.1720	914.8400	1.0035	0.0420	0.3522
	Nd(III):GSH:Zn(II)	331.5056	48.6243	5.1694	914.5226	1.0032	0.0399	0.3172
4.	Dioxane							
	Nd(III)	330.6810	48.6843	5.2136	928.1988	1.0119	0.0773	1.1803
	Nd(III):GSH	330.5907	48.6585	5.2227	931.0369	1.0137	0.0827	1.3486
	Nd(III):GSH:Mg(II)	330.4668	48.6919	5.2343	933.5148	1 0155	0.0879	1.5229
	Nd(III):GSH:Zn(II)	330.4302	48.5889	5.2612	940.4126	1 0198	0.0994	1.9388
5.	DMF+Dioxane							
	Nd(III)	331.5451	48.6439	5.1471	909.8497	1.0000	0.0038	0.0028
	Nd(III):GSH	331.4508	48.6252	5.1589	913.0865	1 0020	0.0318	0.2023
	Nd(III):GSH:Mg(II)	331.4561	48.6325	5.1624	913.0215	1.0125	0.0319	0.2123
	Nd(III):GSH:Zn(II)	331.4861	48.6350	5.1662	913.1235	1.0251	0.0325	0.2145
6.	MeOH+Dioxane							
	N d(III)	33.5421	48.682	5.1532	909.7123	0.9875	0.0061	0.0135
	Nd(III):GSH	331.5309	48.6515	5.1462	909.6647	0.9999	0.0084	0.0141
	N d(I I)GSH:M g(I)	331.5425	48.6465	5.1493	910.1951	1.0002	0.0109	0.0239
	Nd(III):GSH:Zn(II)	331.5844	48.6302	5.1435	909.1259	0.9994	0.0169	0.0569

7.	CH_3CN+Dioxane							
	Nd(III)	331.5542	48.6445	5.1457	909.5084	0.9997	0.0113	0.0255
	Nd(III):GSH	331.5037	48.6612	5.1457	909.5084	0.9997	0.0113	0.0255
	Nd(III):GSH:Mg(II)	331.5877	48.6235	5.1447	909.4436	0.9996	0.0137	0.0378
	Nd(III):GSH:Zn(II)	331.5778	48.6452	5.1425	908.7317	0.9992	0.0197	0.0773
8.	CH_3CN+ CH_3OH							
	Nd(III)	331.5808	48.6059	5.1434	909.5818	0.9996	0.0142	0.0406
	Nd(III):GSH	331.5553	48.6316	5.1465	909.8735	0.9999	0.0059	0.0070
	Nd(III):GSH:Mg(II)	331.6420	48.6230	5.1323	906.7588	0.9978	0.0334	0.2238
	Nd(III):GSH:Zn(II)	331.5946	48.6248	5.1429	909.0169	0.9993	0.0182	0.0663
9	CH_3OH + Dioxane							
	Nd(III)	331.5646	48.6214	5.1460	909.9055	0.9999	0.0070	0.0098
	Nd(III):GSH	331.4926	48.6230	5.1542	911.9287	1.0012	0.0250	0.1248
	Nd(III):GSH:Mg(II)	331.4187	48.5945	5.1759	916.9623	1.0046	0.0479	0.4572
	Nd(III):GSH:Zn(II)	331.4239	48.5942	5.1741	916.6042	1.0043	0.0466	0.4321
10	CH_3CN+ DMF							
	Nd(III)	331.5565	48.6491	5.1467	909.5795	0.9998	0.0091	0.0166
	Nd(III):GSH	331.5576	48.6234	5.1534	911.2412	1.0009	0.0210	0.0880
	Nd(III):GSH:Mg(II)	331.5172	48.6341	5.1631	913.1177	1.0022	0.0335	0.2238
	Nd(III):GSH:Zn(II)	331.4985	48.6349	5.1650	913.6042	1.0026	0.0358	0.2562
11	Water							
	Nd(III)	331.6644	48.6462	5.1308	905.8776	0.9973	0.0366	0.2685
	Nd(III):GSH	331.7579	48.6513	5.1147	902.1276	0.9948	0.0510	0.5229
	Nd(III):GSH:Mg(II)	331.7101	48.6275	5.1346	906.5186	0.9978	0.0335	0.2247
	Nd(III):GSH:Zn(II)	331.8631	48.6274	5.1067	900.2420	0.9935	0.0571	0.6571

Table 5.5 : Computed values of energy interaction Slater Condon $F_K(cm^{-1})$, Lande spin orbit interaction $\xi_{4f}(cm^{-1})$. Nephelauxetic ration (β), bonding ($b^{1/2}$) and covalency (δ) parameters for Nd(III), Nd(III):GSH Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) system in different aquated organic solvents at pH-4

	System	F_2	F_4	F_6	ξ_{4f}	β	$\beta^{1/2}$	δ
1.	MeOH							
	Nd(III)	331.2737	48.7145	5.1594	912.9972	1.0022	0.0332	0.2205
	Nd(III):GSH	331.2938	48.7053	5.1589	912.9141	1.0021	0.0326	0.2123
	Nd(III):GSH:Mg(II)	331.2969	48.7244	5.1623	913.1184	1.0024	0.0347	0.2408
	Nd(III):GSH:Zn(II)	331.3218	48.7181	5.1573	912.1511	1.0017	0.0292	0.1708
2.	CH_3CN							
	Nd(III)	331.2451	48.7498	5.1645	913.4741	1.0027	0.0370	0.2734
	Nd(III):GSH	331.3194	48.7150	5.1628	913.1844	1.0024	0.0350	0.2439
	Nd(III):GSH:Mg(II)	331.4160	48.7043	5.1545	911.1252	1.0011	0.0230	0.1055
	Nd(III):GSH:Zn(II)	331.4218	48.7070	5.1543	910.9858	1.0010	0.0222	0.0983
3.	DMF							
	Nd(III)	331.1650	48.7448	5.1686	9149895	1.0037	0.0427	0.3641
	Nd(III):GSH	330.9457	48.7876	5.1981	921.3239	1.0081	0.0638	0.8070
	Nd(III):GSH:Mg(II)	330.9203	48.7409	5.1973	922.2668	1.0085	0.0650	0.8388
	Nd(III):GSH:Zn(II)	331.5056	48.6243	5.1694	914.5226	1.0032	0.0399	0.3172
4.	Dioxane							
	Nd(III)	331.2788	48.7544	5.1613	912.5536	1.0022	0.0329	0.2159
	Nd(III):GSH	331.1891	48.8134	5.1665	913.1428	1.0028	0.0375	0.2804
	Nd(III):GSH:Mg(II)	331.2703	48.7712	5.1657	913.0993	1.0027	0.0365	0.2653
	Nd(III):GSH:Zn(II)	331.3215	48.7292	5.1628	912.9185	1.0023	0.0343	0.2343
5.	DMF+Dioxane							
	Nd(III)	331.1662	48.7835	5.1692	914.3702	1.0034	0.0416	0.3450
	Nd(III):GSH	331.0710	48.7442	5.1921	920.0090	1.0071	0.0597	0.7083
	Nd(III):GSH:Mg(II)	331.0005	48.7791	5.2018	921.6740	1.0084	0.0650	0.8375
	Nd(III):GSH:Zn(II)	331.0000	48.7235	5.2001	920.21	1.0089	0.0714	0.912
6.	MeOH+Dioxane							
	Nd(III)	331.1909	48.7705	5.1629	913.2821	1.0026	0.0362	0.2621
	Nd(III):GSH	331.1928	48.7789	5.1667	913.7828	1.0031	0.0391	0.3047
	Nd(III):GSH:Mg(II)	331.2685	48.7528	5.1630	912.9797	1.0024	0.0350	0.2438
	Nd(III):GSH:Zn(II)	331.2978	48.7346	5.1610	912.7154	1.0022	0.0331	0.2181

7.	CH_3CN+Dioxane							
	Nd(III)	331.1754	48.7598	5.1945	915.8421	1.0021	0.0352	0.3546
	Nd(III):GSH	331.1661	48.7541	5.1738	915.7181	1.0043	0.0461	0.4236
	Nd(III):GSH:Mg(II)	331.0974	48.7760	5.1920	919.1661	1.0068	0.0582	0.6740
	Nd(III):GSH:Zn(II)	331.2779	48.7261	5.1628	913.3561	1.0086	0.0658	0.7552
8.	CH_3CN+ CH_3OH							
	Nd(III)	331.2972	48.7516	5.1626	9126779	0.0337	1.0023	0.2268
	Nd(III):GSH	332.2290	49.1892	5.1875	901.2831	0.9987	0.0251	0.1260
	Nd(III):GSH:Mg(II)	331.4391	48.5885	5.1525	912.7056	1.0015	0.0272	0.1478
	Nd(III):GSH:Zn(II)	331.3438	48.7809	5.1600	911.2842	1.0015	0.0278	0.1540
9	CH_3OH + Dioxane							
	Nd(III)	331.2199	48.7461	5.1694	914.6422	1.0035	0.0420	0.3507
	Nd(III):GSH	331.0523	48.7740	5.1942	919.9847	1.0073	0.0603	0.7225
	Nd(III):GSH:Mg(II)	338.6394	42.8444	4.6307	863.7469	0.9417	0.1707	6.1859
	Nd(III):GSH:Zn(II)	331.1024	48.7166	5.1922	920.2515	1.0072	0.0600	0.7149
10	CH_3CN+ DMF							
	Nd(III)	331.0932	48.7562	5.1718	915.9656	1.0043	0.0464	0.4280
	Nd(III):GSH	331.0627	48.7406	5.1919	920.0972	1.0072	0.0598	0.5106
	Nd(III):GSH:Mg(II)	331.0521	48.7364	5.1846	920.0025	1.0012	0.0598	0.6124
	Nd(III):GSH:Zn(II)	331.0821	48.7112	5.1895	920.0687	1.0070	0.0601	0.6926
11	Water							
	Nd(III)	331.2994	48.8177	5.1603	911.0415	1.0015	0.0276	0.1521
	Nd(III):GSH	331.3643	48.8008	5.1530	909.4952	1.0004	0.0143	0.0407
	Nd(III):GSH:Mg(II)	330.8044	48.6164	5.1964	925.3852	1.0097	0.0695	0.9578
	Nd(III):GSH:Zn(II)	331.6518	48.6689	5.1341	906.1651	0.9977	0.0342	0.2346

Table 5.6 Computed values of energy interaction Slater Condon $F_K(cm^{-1})$, Lande spin orbit interaction $\xi_{4f}(cm^{-1})$. Nephelauxetic ration (β), bonding $(b^{1/2})$ and covalency (δ) parameters for Nd(III), Nd(III):GSH Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) system in different aquated organic solvents at pH-5

	System	F_2	F_4	F_6	ξ_{4f}	β	$\beta^{1/2}$	δ
1.	MeOH							
	Nd(III)	330.7694	48.6305	5.2103	927.8676	1.0115	0.0759	1.1387
	Nd(III):GSH	330.7335	48.5903	5.2142	929.5812	1.0124	0.0788	1.2281
	Nd(III):GSH:Mg(II)	330.4262	48.8652	5.2369	931.1916	1.0148	0.0861	1.4618
	Nd(III):GSH:Zn(II)	330.7536	48.6727	5.2152	928.0988	1.0119	0.0773	1.1798
2.	CH_3CN							
	Nd(III)	331.4160	48.7043	5.1545	911.1252	1.0011	0.0230	0.1055
	Nd(III):GSH	330.6445	48.6157	5.2199	930.8789	1.0134	0.0818	1.3200
	Nd(III):GSH: Mg(II)	330.5984	48.7120	5.2219	929.8454	1.0132	0.0812	1.3001
	Nd(III):GSH:Zn(II)	330.5984	48.7120	5.2219	929.8454	1.0132	0.0812	1.3001
3.	DMF							
	Nd(III)	330.7885	48.6483	5.2238	929.7684	1.0131	0.0808	1.2902
	Nd(III):GSH	330.5549	48.7042	5.2321	932.1942	1.0148	0.0859	1.4538
	Nd(III):GSH:Mg(II)	330.4899	48.6536	5.2399	935.0741	1.0164	0.0905	1.6124
	Nd(III):GSH :Zn(II)	330.6359	48.6353	5.2332	932.9951	1.0150	0.0867	1.4813
4.	Dioxane							
	Nd(III)	330.6555	48.6429	5.2176	929.8878	1.0129	0.0802	1.2691
	Nd(III):GSH	330.5851	48.6692	5.2210	930.6020	1.0134	0.0819	1.3234
	Nd(III):GSH :Mg(II)	330.4549	48.7016	5.2314	932.9165	1.0151	0.0868	1.4844
	Nd(III):GSH:Zn(II)	330.5811	48.6794	5.2173	929.7805	1.0129	0.0802	1.2707
5.	DMF+Dioxane							
	Nd(III)	330.7081	48.6113	5.2195	930.3652	1.0131	0.0809	1.2927
	Nd(III):GSH	330.5630	48.6167	5.2269	932.8215	1.0146	0.0855	1.4426
	Nd(III):GSH: Mg(II)	330.5014	48.5948	5.2382	935.7558	1.0165	0.0909	1.6247
	Nd(III):GSH :Zn(II)	330.5765	48.6154	5.2250	932.3787	1.0143	0.0847	1.4130
6.	MeOH+Dioxane							
	Nd(III)	330.7870	48.6191	5.2115	928.1273	1.0117	0.0764	1.1536
	Nd(III):GSH	330.5400	48.6719	5.2200	930.7290	1.0134	0.0820	1.3255
	Nd(III):GSH:Mg(II)	330.6798	48.5991	5.2160	930.1915	1.0128	0.0801	1.2670
	Nd(III):GSH:Zn(II)	330.5347	48.7139	5.2252	930.9396	1.0139	0.0832	1.3669

7.	CH_3CN+Dioxane							
	Nd(III)	330.6943	48.5679	5.2176	930.9323	1.0132	0.0812	1.3022
	Nd(III):GSH	330.5990	48.5744	5.2213	932.2717	1.0140	0.0837	1.3831
	Nd(III):GSH:Mg(II)	330.5466	48.5729	5.2261	933.6024	1.0149	0.0863	1.4666
	Nd(III):GSH:Zn(II)	330.5980	48.5648	5.2220	932.5912	1.0142	0.0842	1.3994
8.	CH_3CN+CH_3OH							
	Nd(III)	330.6489	48.6403	5.2207	930.5280	1.0133	0.0815	1.3119
	Nd(III):GSH	330.5273	48.6813	5.2256	931.6740	1.0142	0.0842	1.3966
	Nd(III):GSH:Mg(II)	330.7743	48.5665	5.2140	929.6437	1.0124	0.0787	1.2251
	Nd(III):GSH:Zn(II)	330.6740	48.5610	5.2178	931.2744	1.0134	0.0817	1.3181
9	CH_3OH + Dioxane							
	Nd(III)	330.6039	48.6837	5.2152	929.1519	1.0125	0.0790	1.2328
	Nd(III):GSH	330.4329	48.7102	5.2251	931.8513	1.0143	0.0845	1.4094
	Nd(III):GSH:Mg(II)	330.4331	48.7331	5.2316	932.5992	1.0150	0.0866	1.4773
	Nd(III):GSH:Zn(II)	330.3490	48.7792	5.2273	931.6773	1.0145	0.0850	1.4256
10	CH_3CN+DMF							
	Nd(III)	330.7402	48.6240	5.2185	929.6761	1.0127	0.0798	1.2581
	Nd(III):GSH	330.6259	48.6767	5.2251	930.8519	1.0137	0.0828	1.3542
	Nd(III):GSH:Mg(II)	330.6943	48.6512	5.2218	930.1520	1.0132	0.0812	1.3010
	Nd(III):GSH:Zn(II)	330.5265	48.7292	5.2280	931.2197	1.0141	0.0841	1.3952
11	Water							
	Nd(III)	330.8038	48.6163	5.1964	925.3909	1.0097	0.0695	0.9580
	Nd(III):GSH	330.9336	48.6844	5.1899	921.74	0.0625	1.0078	0.7749
	Nd(III):GSH:Mg(II)	331.4118	48.6892	5.1612	912.6228	1.0020	0.0320	0.2038
	Nd(III):GSH:Zn(II)	331.2029	48.6896	5.1668	915.3735	1.0036	0.0427	0.3626

Table 5.7 : Computed values of energy interaction Slater Condon $F_K(cm^{-1})$, Lande spin orbit interaction ξ_{4f} (cm^{-1}). Nephelauxetic ration (β), bonding $(b^{1/2})$ and covalency (δ) parameters for Nd(III), Nd(III):GSH Nd(III):GSH:Mg(II) and Nd(III):GSH:Zn(II) system in different aquated organic solvents at pH-4

	System	F_2	F_4	F_6	ξ_{4f}	β	$\beta^{1/2}$	δ
1.	MeOH							
	$N_{d(III)}$	330.7609	48.6720	5.2138	927.8067	1.0117	0.0766	1.1599
	$N_{d(III)}$:GSH	330.6872	48.6745	5.2159	928.7291	1.0123	0.0784	1.2131
	$N_{d(III)}$:GSH:Mg(II)	330.7361	48.6977	5.2213	928.8512	1.0126	0.0795	1.2470
	$N_{d(III)}$:GSH:Zn(II)	330.6995	48.6681	5.2151	928.6176	1.0122	0.0780	1.2033
2.	CH_3CN							
	$N_{d(III)}$	330.7458	48.5917	5.2146	929.5372	1.0124	0.0789	1.2283
	$N_{d(III)}$:GSH	330.7920	48.5842	5.2111	928.6610	1.0118	0.0769	1.1697
	$N_{d(III)}$:GSH:$M_{g(II)}$	330.7349	48.6978	5.2213	928.8632	1.0126	0.0795	1.2477
	$N_{d(III)}$:GSH:Zn(II)	330.7000	48.6684	5.2151	928.6136	1.0122	0.0780	1.2032
3.	DMF							
	Nd(III)	330.6247	48.6182	5.2158	930.2941	1.0129	0.0804	1.2754
	Nd(III):GSH	330.4981	48.6033	5.2370	935.4049	1.0163	0.0903	1.6048
	Nd(III):GSH:Mg(II)	330.4051	48.5873	5.2448	937.8569	1.0178	0.0944	1.7501
	Nd(III):GSH:Zn(II)	330.4752	48.6360	5.2314	934.0305	1.0155	0.0880	1.5235
4.	Dioxane							
	$N_{d(III)}$	330.5286	48.6706	5.2249	931.7363	1.0141	0.0841	1.3942
	$N_{d(III)}$:GSH	330.5206	48.6185	5.2284	933.3743	1.0150	0.0865	1.4753
	$N_{d(III)}$:GSH:Mg(II)	330.5699	48.5746	5.2231	932.8448	1.0144	0.0848	1.4184
	Nd(III):GSH:Zn(II)	330.6054	48.5707	5.2229	932.5751	1.0142	0.0844	1.4037
5.	DMF+Dioxane							
	$N_{d(III)}$	330.5527	48.6047	5.2209	932.0490	1.0140	0.0836	1.3778
	$N_{d(III)}$:GSH	330.3978	48.6614	5.2301	933.9219	1.0154	0.0878	1.5180
	$N_{d(III)}$:GSH:Mg(II)	330.4522	48.6043	5.2332	935.0793	1.0160	0.0894	1.5735
	$N_{d(III)}$:GSH:Zn(II)	331.3409	49.1975	5.2613	921.7487	1.0120	0.0775	1.1855
6.	MeOH+Dioxane							
	Nd(III)	330.6376	48.6008	5.2136	930.1155	1.0127	0.0797	1.2539
	Nd(III):GSH	330.6721	48.5753	5.2134	930.2624	1.0127	0.0797	1.2544
	Nd(III):GSH:Mg(II)	330.5648	48.5795	5.2207	932.3635	1.0141	0.0838	1.3863
	Nd(III):GSH:Zn(II)	330.5961	48.5730	5.2142	931.0741	1.0131	0.0810	1.2959

7.	CH_3CN+Dioxane							
	Nd(III)	330.5276	48.6193	5.2228	932.3100	1.0142	0.0843	1.4013
	Nd(III):GSH	329.8729	48.9987	5.2518	935.9557	1.0181	0.0952	1.7798
	Nd(III):GSH:Mg(II)	330.4459	48.5654	5.2317	935.5561	1.0161	0.0896	1.5812
	Nd(III):GSH:Zn(II)	330.4051	48.5773	5.2331	935.9304	1.0163	0.0904	1.6076
8.	CH_3CN+ CH_3OH							
	Nd(III)	330.6345	48.5463	5.2183	931.9560	1.0137	0.0827	1.3493
	Nd(III):GSH	330.6345	48.5463	5.2183	931.9560	1.0137	0.0827	1.3493
	Nd(III):GSH:Mg(II)	330.6254	48.5713	5.2184	931.5873	1.0136	0.0823	1.3378
	Nd(III):GSH:Zn(II)	330.5592	48.5824	5.2273	933.5355	1.0149	0.0864	1.4706
9	CH_3OH + DMF							
	Nd(III)	330.6296	48.6086	5.2170	930.6418	1.0131	0.0810	1.2951
	Nd(III):GSH	329.9386	49.0295	5.2512	934.7563	1.0176	0.0937	1.7273
	Nd(III):GSH:Mg(II)	330.5157	48.6227	5.2301	933.6573	1.0152	0.0872	1.4969
	Nd(III):GSH:Zn(II)	330.5759	48.5926	5.2221	932.2883	1.0141	0.0840	1.3915
10	CH_3CN+ DMF							
	Nd(III)	330.7171	48.5673	5.2194	931.0775	1.0133	0.0817	1.3166
	Nd(III):GSH	330.6301	48.6202	5.2259	931.9973	1.0142	0.0842	1.3996
	N d(III)GSH: Mg(II)	330.7258	48.6186	5.2234	930.7823	1.0135	0.0821	1.3308
	Nd(III):GSH:Zn(II)	330.4868	48.5528	5.2240	934.0737	1.0150	0.0865	1.4757
11	Water							
	Nd(III)	330.9045	48.6545	5.2059	925.5397	1.0102	0.0716	1.0136
	N d(III)GSH	331.0602	48.7359	5.1909	920.0230	1.0071	0.0594	0.7018
	Nd(III)GSH :Mg(II)	331.2299	48.7470	5.1760	915.7390	1.0043	0.0466	0.4325
	Nd(III):GSH:Zn(II)	331.1933	48.7679	5.1762	915.6858	1.0044	0.468	0.4357

Table 5.8 : Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for Nd(III), Nd(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in aqueous and different aquated organic solvents at pH-3

Sytem	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		RMS
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
1.CH_3OH											
Nd(III)	19156.35	19175.10	17334.93	17365.81	13504.57	13463.40	12580.20	12616.50	11558.82	11528.05	32.45
Nd(III):GSH	19156.35	19175.38	17363.33	17363.33	13504.94	13463.19	12578.93	12615.86	11557.49	11526.68	29.73
Nd(III):GSH:Mg(II)	19157.09	19174.82	17345.75	17371.06	13506.76	13464.02	12584.63	12617.58	11557.35	11529.90	30.40
Nd(III):GSH:Zn(II)	19158.19	19175.54	17340.94	17367.89	13504.02	13463.22	12580.52	12616.72	11556.55	11529.21	30.82
2. CH_3CN											
Nd(III)	19157.46	19174.78	17340.04	17369.02	13506.76	13464.02	12580.99	12617.58	11556.95	11529.90	31.74
Nd(III):GSH	19157.46	19175.68	17335.23	17362.03	13504.21	13463.04	12580.04	12615.47	11552.81	11525.99	30.72
Nd(III):GSH:Mg(II)	19157.56	19175.23	17336.25	17365.23	13504.24	13462.54	12581.05	12646.57	11552.57	11545.68	38.03
Nd(III):GSH:Zn(II)	19159.29	19174.96	17349.97	17375.39	13505.85	13463.89	12582.73	12618.67	11558.42	11533.39	30.23
3. DMF											
Nd(III)	19162.60	19176.51	17328.32	17367.41	13505.85	13463.93	12582.73	12617.77	11558.42	11529.21	33.35
Nd(III):GSH	19156.72	19177.73	17305.23	17346.73	13503.29	13462.13	12577.67	12611.77	11553.08	11517.65	35.43
Nd(III):GSH:Mg(II)	19157.09	19178.70	17295.95	17335.21	13498.92	13460.57	12575.93	12608.40	11550.54	11511.16	34.88
Nd(III):GSH:Zn(II)	19157.46	19177.95	17294.75	17338.54	13503.66	13461.81	12576.09	12575.93	11550.54	11513.15	33.13
4.Dioxane											
Nd(III)	19128.50	19178.85	17257.74	17270.81	13486.18	13453.08	12552.56	12590.91	11530.17	11474.35	40.96
Nd(III):GSH	19124.85	19178.18	17257.69	17258.88	13483.81	13452.58	12553.82	12588.33	11523.92	11467.7	40.43
Nd(III):GSH:Mg(II)	19123.38	19179.38	17244.65	17245.82	13479.45	13450.62	12550.99	12584.35	11512.78	11460.31	39.58
Nd(III):GSH:Zn(II)	19123.75	19179.13	17244.35	17219.52	13487.27	13451.23	12552.25	12579.81	11468.29	11446.12	35.31
5. DMF+Dioxane											

Nd(III)	19155.99	19176.13	17328.32	17357.99	13502.75	13462.28	12577.35	12614.14	11556.02	11523.66	32.63
Nd(III):GSH	19152.69	19176.32	17312.42	17344.12	13502.38	13461.60	12574.98	12611.02	11551.48	11515.96	34.02
Nd(III):GSH :Mg(II)	19153.42	19176.52	17314.52	17355.23	13502.38	13461.65	12575.02	12611.02	11551.5	11516.96	35.61
Nd(III):GSH:Zn(II)	19154.23	19155.23	17315.25	17354.12	13501.23	13486.21	12576.02	12612.35	11552.2	11514.23	30.00
6. CH_3OH+Dioxane											
Nd(III)	19153.12	19153.12	17330.15	17354.2	13494.55	13495.21	12576.51	12615.3	11556.23	11514.62	27.62
Nd(III):GSH	19155.62	19176.1	17331.32	17358.34	13501.47	13462.04	12577.67	12614.03	11555.35	11523.8	31.69
Nd(III):GSH :Mg(II)	19156.72	19176.38	17330.12	17356.33	13502.38	13462.12	12577.83	12613.68	11551.75	11522.76	31.05
Nd(III):GSH:Zn(II)	19156.72	19175.61	17335.83	17361.88	13504.39	13462.89	12578.77	12615.35	11553.61	11525.87	31.19
7. CH_3CN+Dioxane											
Nd(III)	19156.35	19176.03	17332.22	17359.46	13502.57	13462.35	12578.14	12614.47	11554.68	11524.48	31.56
Nd(III)GSH	19154.89	19176.32	17329.82	17345.21	13501.11	13461.63	12575.77	12613.38	11556.15	11522.77	30.93
Nd(III):GSH:Mg(II)	19156.35	19175.66	17328.92	17360.91	13506.03	13463.07	12577.04	12615.52	11557.49	11525.31	33.94
Nd(III)GS H:Zn(II)	19156.72	19175.88	17333.43	17363.00	13503.11	13462.63	125 8.30	12615.35	11558.16	11526.44	32.43
8. CH_3OH + CH_3CN											
Nd(III)	19155.25	19174.94	17333.43	17360.86	13505.12	13463.32	12579.88	12615.52	11553.35	11525.31	31.44
Nd(III)GSH	19155.99	19175.78	17331.92	17358.39	13503.29	13462.57	12578.62	12614.44	11552.68	11523.91	31.18
Nd(III):GSH:Mg(II)	19157.09	19174.5	1735 3.28	17372.69	13505.67	13463.72	12580.83	12618.07	11554.28	11531.82	29.43
Nd(III)GSH :Zn(II)	19157.09	19175.43	17337.93	17353.28	13503.48	13505.67	12581.15	12580.83	11551.61	11554.28	10.81
9. CH_3OH +DMF											
Nd(III)	19155.62	19175.55	17329.82	17358.78	13504.75	13462.86	12577.98	12614.75	11554.42	11524.15	32.43
Nd(III):GSH	19153.79	19176.00	17320.81	17349.47	13503.66	13462.06	12575.77	12612.38	11551.08	11518.94	32.92
Nd(III)GSH :Mg(II)	19152.69	19177.32	17283.10	17328.59	13504.21	13461.54	12573.71	12607.97	11549.08	11507.57	38.45
Nd(III):GSH:Zn(II)	19152.69	19177.13	17285.79	17330.15	13503.48	13461.62	12574.98	12608.33	11548.94	11508.42	37.61
10. CH_3CN+DMF											
Nd(III)	19157.09	19176.26	17331.62	17358.97	13501.29	13462.25	12579.57	12614.28	11553.61	11524.22	30.69

Nd(III):GSH	19157.09	19176.39	17321.72	17352.90	13504.02	13462.57	12578.62	12613.36	11550.54	11520.98	32.07
Nd(III):GSH:Mg(II)	19129.60	19178.24	17241.97	17262.68	13490.18	13454.37	12556.19	12590.32	11522.73	11470.15	40.02
Nd(III):GSH:Zn(II)	19157.09	19177.63	17302.54	17341.92	13500.74	13461.63	12578.62	12610.51	11550.28	11514.93	33.97
11. Water											
Nd(III)	19159.29	19175.09	17352.98	17375.74	13502.02	13463.51	12584.31	12618.45	11557.09	11533.52	28.18
Nd(III):GSH	19161.13	19174.01	17376.50	17392.28	13502.75	13464.52	12587.64	12622.37	11560.16	11542.64	26.04
Nd(III):GSH:Mg(II)	19161.13	19175.39	17351.77	17374.12	13508.58	13464.13	12580.20	12618.55	11553.08	11532.80	30.2
Nd(III):GSH:Zn(II)	19163.70	19173.19	17389.19	17402.08	13506.58	13465.95	12590.49	12625.31	11558.69	11548.21	25.41

Table 5.9 : Computed and Obse rved values of Energies(cm^{-1}) and R.M.S. values for Nd(III), Nd(III):GSH, Pr(III):GSH:Mg(II) and Pr(III) :GSH:Zn(II) in aqueous and d iffe ent aqu ated organic solvents at pH – 4

Sytem	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		RMS
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
1 .CH_3OH											
Nd(III)	19149.38	19177.27	17327.42	17339.37	13490.73	13458.45	12573.40	12607.78	11546.14	11512.83	29.17
Nd(III):GSH	19149.75	19177.13	17327.42	17340.22	13492.18	13458.79	12573.40	12608.20	11546.14	11513.37	29.37
Nd(III):GSH:Mg(II)	19151.95	19177.98	17328.32	17338.59	13490.36	13458.34	12574.50	12607.48	11542.01	11512.48	27.45
Nd(III):GSH :Zn(II)	19151.58	19177.47	17329.52	17343 .24	13491.09	13458.81	12574.98	12608.75	11547.21	11515.05	28.55
2. CH_3CN											
Nd(III)	19151.22	19178.50	17328.92	17335.63	13487.81	13457.40	12572.92	12606.21	11540.95	11510.73	27.33
Nd(III):GSH	19152.69	19177.95	17329.52	17338.85	13492.54	13458.67	12573.87	12607.77	11540.02	11512.69	27.45
Nd(III):GSH:Mg(II)	19154.89	19155.25	17331.02	17331.02	13494.73	13494.73	12576.24	12576.24	11548.54	11549.08	00.29
Nd(III):GS H:Zn(II)	19154.89	19177.50	17331.02	17348.97	13494.73	13459.89	12576.24	12610.60	11548.54	11518.41	28.76
3. DMF											
Nd(III)	19147.55	19178.31	17319.62	17328.74	13486.54	13456.79	12570.71	12604.50	11542.68	11506.81	29.47
Nd(III):GSH	19144.62	19181.30	17277.13	17298.31	13479.09	13453.62	12565.02	12596.89	11540.15	11488.84	34.9
Nd(III):GSH:Mg(II)	19140.22	19179.88	17271.46	17295.99	13483.27	13454.35	12562.34	12596.45	11542.95	11488.55	37.77
Nd(III):GSH :Zn(II)	19157.46	19177.95	17294.75	17338.54	13503.66	13461.81	12576.09	12609.98	11550.54	11513.15	36.43
4.Dioxane											
Nd(III)	19152.32	19178.55	17327.12	17339.72	13487.09	13457.69	12574.66	12607.19	11546.41	11513.03	27.87
Nd(III):GSH	19152.32	19179.97	17327.12	17334.10	13480.36	13455.74	12573.56	12604.61	11544.01	11509.73	26.68
Nd(III):GSH :Mg(II)	19153.79	19149.75	17324.42	17336.65	13486.18	13457.20	12574.03	12604.11	11544.01	11511.35	24.40
Nd(III):GSH:Zn(II)	19153.42	19178.36	17326.82	17339.49	13491.27	13458.45	12574.03	12607.70	11543.08	11513.04	27.91

5. DMF+Dioxane											
Nd(III)	19149.75	19179.38	17321.12	17329.90	13484.36	13456.08	12569.92	12604.11	11544.01	11507.42	29.20
Nd(III):GSH	19147.18	19180.44	17279.81	17306.71	13485.27	13455.57	12567.24	12599.29	11542.41	11494.74	34.67
Nd(III):GSH:Mg(II)	19147.60	19181.91	17273.80	17297.61	13482.70	13454.12	12564.10	12596.41	11537.60	11489.65	34.36
Nd(III):GSH:Zn(II)	19148.53	19152.23	17282.53	17298.23	13485.99	13456.23	12565.48	12586.23	11538.55	11542.06	17.83
6. CH_3OH+Dioxane											
Nd(III)	19149.02	19178.51	17326.52	17335.26	13484.54	13456.67	12571.97	12605.62	11546.68	11510.37	28.89
Nd(III):GSH	19150.74	19179.15	17326.82	17332.76	13485.27	13456.41	12570.71	12604.91	11542.41	11509.03	28.14
Nd(III):GSH:Mg(II)	19151.97	19178.64	17324.42	17337.90	13487.63	13457.61	12573.56	12606.78	11546.41	11512.02	28.57
Nd(III):GSH:Zn(II)	19151.95	19178.17	17325.62	17340.00	13490.18	13458.24	12573.40	12607.67	11546.94	11513.24	29.07
7. CH_3CN+Dioxane											
Nd(III)	19150.48	19156.54	17324.72	17335.23	13448.73	13456.12	12570.87	12573.21	11539.88	11541.23	6.467
Nd(III):GSH	19149.38	19179.11	17317.22	17325.23	13486.18	13456.47	12570.71	12603.53	11538.28	11504.92	28.36
Nd(III):GSH:Mg(II)	19150.48	19181.37	17288.48	17309.20	13484.36	13455.14	12567.24	12599.37	11538.42	11496.14	31.8
Nd(III):GSH:Zn(II)	19150.85	19178.00	17324.42	17337	13491.09	13458.19	12572.13	12607.16	11545.21	11511.81	29.4
8. CH_3OH + CH_3CN											
Nd(III)	19153.42	19178.74	17326.82	17339.44	13488.00	13457.85	12574.82	12607.23	11544.68	11512.93	27.45
Nd(III):GSH	19228.18	19199.82	17327.42	17378.89	13493.64	13456.54	12574.35	12611.90	11546.54	11536.82	35.59
Nd(III):GSH:Mg(II)	19149.02	19174.50	17323.52	17347.01	13504.57	13462.30	12575.29	12612.22	11548.68	11517.47	32.64
Nd(III):GSH:Zn(II)	19156.72	19179.56	17329.22	17344.66	13486.54	13457.75	12576.09	12608.08	11548.28	11515.87	27.07
9. CH_3OH +DMF											
Nd(III)	19150.48	19178.83	17321.12	17330.63	13489.45	13457.18	12569.76	12605.08	11541.08	11507.98	29.25
Nd(III):GSH	19148.29	19181.29	17280.71	17305.48	13483.45	13454.82	12565.97	12598.45	11541.61	11494.02	34.18
Nd(III):GSH:Mg(II)	19146.82	19144.32	17273.84	17314.97	13490.18	13499.46	12490.18	12540.77	11540.02	11541.87	29.48
Nd(III):GSH:Zn(II)	19146.82	19180.02	17274.14	17307.02	13489.82	13456.38	12565.18	12599.97	11545.48	11495.02	37.57
10. CH_3CN+DMF											

Nd(III)	19144.98	19178.49	17313.02	17323.59	13484.54	13455.97	12568.34	12602.93	11544.94	11503.83	31.42
Nd(III):GSH	19146.45	19180.26	17280.11	17306.41	13485.81	13455.58	12566.44	12599.26	11542.55	11494.56	35.01
Nd(III):GSH:Mg(II)	19146.54	19182.35	17295.23	17304.56	13486.23	13456.28	12564.56	12602.32	11543.21	11495.46	34.56
Nd(III):GSH:Zn(II)	19144.98	19179.43	17275.93	17307.93	13488.72	13456.39	12565.97	12600.20	11546.94	11495.44	37.63
11. Water											
Nd(III)	19156.72	19180.20	17332.82	17340.04	13482.36	13456.70	12575.93	12607.11	11547.74	11515.28	25.64
Nd(III):GSH	19157.46	19179.39	17340.04	17351.67	13484.90	13457.71	12577.35	12609.38	11550.54	11519.67	25.82
Nd(III):GSH:Mg(II)	19127.04	19175.80	17259.53	17286.67	13489.82	13455.82	12559.19	12596.11	11544.68	11483.24	43.38
Nd(III):GSH:Zn(II)	19160.39	19175.98	17354.18	17373.52	13503.48	13462.91	12579.88	12617.52	11554.95	11532.29	28.96

Table 5.10 Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for Nd(III), Nd(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in aqueous and different aquated organic solvents at pH – 5

Sytem	$^4I_{9/2}\rightarrow{}^4G_{7/2}$		$^4I_{9/2}\rightarrow{}^4G_{5/2}$		$^4I_{9/2}\rightarrow{}^4F_{7/2}$		$^4I_{9/2}\rightarrow{}^4F_{5/2}$		$^4I_{9/2}\rightarrow{}^4F_{3/2}$		RMS
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
1.CH_3OH											
Nd(III)	19129.60	19177.40	17249.41	17275.09	13486.36	13454.86	12561.39	12593.09	11533.89	11476.93	40.46
Nd(III):GSH	19126.68	19176.49	17248.81	17268.97	13489.27	13455.18	12560.13	12592.24	11526.45	11473.55	39.70
Nd(III):GSH:Mg(II)	19129.24	19184.07	17252.38	17248.91	13482.18	13447.21	12528.50	12582.11	11524.59	11461.81	47.02
Nd(III):GSH:Zn(II)	19132.17	19178.94	17246.73	17272.31	13483.27	13453.83	12560.76	12591.70	11532.70	11475.38	39.88
2. CH_3CN											
Nd(III)	19154.89	19177.50	17331.02	17348.97	13494.73	13459.89	12576.24	12610.60	11548.54	11518.41	28.76
Nd(III):GSH	19124.85	19177.13	17247.92	17247.65	13486.90	13453.85	12556.66	12589.85	11522.33	11469.35	39.33
Nd(III)GSH :Mg(II)	19128.14	19179.51	17249.41	17261.93	13478.36	13451.67	12556.19	12588.13	11525.92	11469.33	39.32
Nd(III):GSH:Zn(II)	19128.14	19179.51	17249.41	17261.93	13478.36	13451.67	12556.19	12588.13	11525.92	11469.33	39.32
3. DMF											
Nd(III)	19134.36	19179.51	17243.46	17266.38	13490.36	13454.31	12556.35	12590.87	11523.53	11472.32	39.19
Nd(III)GSH	19127.41	19180.21	17236.63	17251.88	13480.72	13451.23	12551.78	12585.87	11522.73	11463.83	41.28
Nd(III):GSH:Mg(II)	19122.65	19179.39	17220.00	17241.10	13484.36	13451.51	12548.31	12584.12	11522.20	11457.88	45.08
Nd(III)GSH:Zn(II)	19127.41	19179.23	17227.71	17251.94	13490.73	13453.18	12549.10	12587.36	11524.06	11464.13	44.13
4.Dioxane											
Nd(III)	19126.31	19177.68	17247.92	17264.95	13483.99	13453.51	12558.08	12590.18	11526.98	11471.15	40.01
Nd(III)GSH	19124.85	19178.24	17246.43	17260.29	13481.45	13452.39	12555.40	12588.45	11526.31	11468.43	40.82
Nd(III):GSH:Mg(II)	19122.65	19179.20	17249.11	17247.90	13478.72	13450.42	12550.36	12584.62	11514.24	11461.38	39.92
Nd(III):GSH:Zn(II)	19124.48	19178.03	17252.38	17263.35	13480.18	13452.25	12555.87	12588.95	11527.38	11470.05	40.37

5. DMF+Dioxane											
Nd(III)	19127.41	19177.49	17243.76	17264.62	13489.45	13454.48	12556.66	12590.83	11542.92	11471.14	45.80
Nd(III):GSH	19121.56	19177.47	17234.25	17252.78	13488.54	13453.09	12549.89	12587.62	11525.65	11464.36	44.51
Nd(III):GSH:Mg(II)	19119.73	19177.76	17217.33	17240.59	13487.81	13452.73	12549.89	12585.03	11521.53	11457.66	45.72
N d(III):GSH:Zn(II)	19121.92	19177.29	17238.70	17254.79	13488.54	13453.25	12550.83	12588.12	11524.46	11465.48	43.45
6. CH_3OH+Dioxane											
Nd(III)	19130.34	19177.29	17260.72	17274.46	13491.63	13455.11	12557.45	12593.15	11524.19	11476.64	38.11
N d(III)GSH	19122.65	19177.81	17252.09	17259.21	13480.54	13451.98	12554.30	12588.00	11523.92	11467.71	40.51
Nd(III)GSH.Mg(II)	19124.85	19176.51	17253.57	17265.52	13490.00	13454.52	12556.03	12591.11	11522.33	11471.45	39.72
Nd(III):GSH:Zn(II)	19125.58	19179.48	17249.71	17256.64	13479.81	13451.04	12551.15	12586.70	11522.99	11466.31	40.64
7. CH_3CN+Dioxane											
Nd(III)	19124.12	19176.02	17245.84	17263.74	13491.82	13455.20	12557.13	12591.31	11523.39	11470.64	40.76
Nd(III):GSH	19120.09	19175.94	17243.16	17257.02	13492.36	13454.26	12550.99	12589.38	11522.99	11466.75	43.36
Nd(III):GSH:Mg(II)	19118.27	19176.08	17239.09	17250.96	13493.09	13453.76	12547.68	12587.87	11520.60	11463.35	44.55
N d(III):GSH:Zn(II)	19119.73	19175.77	17242.57	17256.01	13493.09	13454.41	12550.99	12589.31	11521.67	11466.21	43.27
8. CH_3OH + CH_3CN											
Nd(III)	19126.70	19177.88	17246.70	17262.22	17246.40	13453.40	13483.50	12589.57	12558.90	11469.66	1810
Nd(III):GSH	19123.80	19178.62	17244.40	17254.70	13478.70	13451.56	12555.20	12586.78	11522.50	11465.25	40.31
Nd(III):GSH:Mg(II)	19127.40	19179.14	17252.10	17269.94	13494.00	13455.93	12558.60	12592.98	11523.00	11474.20	40.02
Nd(III):GSH:Zn(II)	19122.70	19175.73	17244.70	17262.40	13492.20	13455.17	12556.20	12591.06	11523.70	11469.86	41.50
9. CH_3OH +DMF											
N d(III)	19125.20	19178.12	17248.20	17266.13	13479.10	13452.45	12557.50	12589.62	11533.20	11471.61	41.61
N d(III)GSH	19120.50	19178.64	17239.90	17252.07	13471.30	13450.33	12556.80	12585.40	11528.00	11463.55	42.28
Nd(III):GSH:Mg(II)	19122.70	19180.06	17226.50	17248.09	13470.40	13449.81	12555.40	12584.16	11531.80	11461.42	44.63
Nd(III):GSH:Zn(II)	19120.50	19180.07	17238.70	17249.43	13463.10	13448.35	12556.50	12583.36	11531.10	11461.86	43.35
10. CH_3CN+DMF											

Nd(III)	19129.60	19177.92	17244.95	17267.33	13488.18	13454.52	12558.71	12591.33	11526.71	11472.69	39.88
Nd(III):GSH	19128.14	19179.20	17243.76	17259.26	13483.27	13452.46	12554.61	12588.23	11523.79	11468.00	40.10
Nd(III):GSH:Mg(II)	19129.60	19178.65	17244.06	17263.82	13484.90	13453.55	12558.24	12589.92	11524.99	11470.66	39.33
Nd(III):GSH:Zn(II)	19126.68	19180.14	17243.16	17254.79	13476.18	13450.63	12553.82	12586.00	11524.46	11465.29	40.45
11. Water											
Nd(III)	19127.00	19175.79	17259.50	17286.65	13489.80	13455.82	12559.20	12596.10	11544.70	11483.23	43.39
Nd(III):GSH	19136.60	19177.59	17286.10	17299.95	13488.40	13455.62	12562.20	12598.30	11537.50	11490.71	35.89
Nd(III):GSH:Mg(II)	19154.90	19177.86	17327.10	17343.15	13500.90	13459.98	12569.80	12609.53	11543.80	11515.29	31.15
Nd(III):GSH:Zn(II)	19145.70	19177.01	17314.80	17329.66	13492.70	13458.20	12569.50	12605.80	11545.20	11507.43	32.05

Table 5.11 : Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for Nd(III), Nd(III):GSH, Pr(III):GSH:Mg(II) and Pr(III):GSH:Zn(II) in aqueous and different aquated organic solvents at pH – 6

Sytem	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		RMS
	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}	
1.CH_3OH											
Nd(III)	19132.20	19178.82	17247.90	17273.65	13483.30	13453.94	12561.10	12592.04	11533.50	11476.12	39.87
Nd(III):GSH	19129.20	19178.54	17248.80	17268.96	13481.50	13453.24	12559.70	12590.67	11530.60	11473.38	39.68
Nd(III):GSH:Mg(II)	19134.40	19180.06	17249.70	17267.85	13481.50	13453.00	12560.60	12590.16	11524.10	11472.93	36.66
Nd(III):GSH:Zn(II)	19129.20	19178.41	17246.10	17269.82	13481.80	13453.49	12560.30	12591.03	11533.00	11473.89	40.56
2. CH_3CN											
Nd(III)	19127.41	19176.68	17248.22	17269.21	13490.00	13455.24	12559.66	12592.31	11526.58	11473.72	39.84
Nd(III):GSH	19128.5	19176.43	17250.9	17273.65	13491.63	13455.84	12560.45	12593.43	11528.57	11476.24	39.80
Nd(III):GSH:Mg(II)	19134.36	19180.06	17249.71	17267.78	13481.45	13452.99	12560.60	12590.13	11524.06	11472.89	36.65
Nd(III):GSH:Zn(II)	19129.24	19178.42	17246.14	17269.83	13481.81	13453.49	12560.29	12591.03	11532.96	11473.89	40.54
3. DMF											
Nd(III)	19122.29	19176.71	17244.06	17264.07	13488.54	13453.85	12552.41	12590.36	11532.56	11470.59	44.38
Nd(III):GSH	19119.73	19177.81	17221.78	17241.71	13488.36	13452.57	12548.31	12585.13	11521.00	11458.25	45.49
Nd(III):GSH:Mg(II)	19116.07	19177.56	17217.04	17231.02	13488.00	13451.90	12546.11	12582.65	11513.44	11452.24	45.52
Nd(III):GSH:Zn(II)	19118.63	19177.95	17219.71	17246.27	13484.72	13452.02	12547.84	12585.59	11532.70	11460.61	48.82
4.Dioxane											
Nd(III)	19123.02	19178.28	17245.54	17254.87	13480.72	13451.80	12553.67	12587.00	11522.33	11465.35	40.83
Nd(III):GSH	19120.46	19177.25	17244.35	17249.82	13487.45	13452.59	12549.89	12586.71	11515.96	11462.64	41.64
Nd(III):GSH:Mg(II)	19119.00	19175.94	17243.16	17254.31	13492.91	13453.98	12548.94	12588.67	11521.14	11465.21	43.79
Nd(III):GSH:Zn(II)	19120.82	19176.04	17244.65	17255.86	13492.54	13454.31	12551.78	12589.18	11519.02	11466.15	42.02

5. DMF+Dioxane											
Nd(III)	19119.36	19176.37	17240.79	17256.42	13486.90	13453.37	12552.56	12588.59	11526.85	11466.28	43.78
Nd(III):GSH	19116.80	19177.70	17238.11	17244.84	13479.63	13450.83	12549.23	12584.48	11521.67	11459.59	44.00
Nd(III):GSH:Mg(II)	19116.80	19177.02	17230.98	17242.63	13487.63	13452.26	12547.05	12585.14	11519.54	11458.59	45.12
Nd(III):GSH:Zn(II)	19199.02	19202.11	17237.52	17283.83	13477.63	13447.61	12550.20	12587.40	11522.86	11483.23	34.67
6. CH_3OH+Dioxane											
Nd(III)	19121.92	19176.07	17244.35	17265.57	13486.54	13454.30	12557.29	12591.01	11532.16	11471.44	43.00
Nd(III):GSH	19121.92	19175.67	17244.35	17266.27	13492.18	13455.07	12554.14	12591.73	11531.76	11471.93	44.13
Nd(III):GSH:Mg(II)	19118.63	19175.77	17240.79	17256.15	13488.91	13453.92	12553.04	12588.99	11525.12	11466.18	43.57
Nd(III):GSH:Zn(II)	19118.27	19175.13	17241.97	17262.24	13488.72	13454.49	12554.93	12590.61	11531.90	11469.54	44.67
7. CH_3CN+Dioxane											
Nd(III)	19119.73	19176.71	17243.16	17254.44	13483.45	13452.80	12554.77	12587.78	11522.73	11465.13	41.76
Nd(III):GSH	19114.98	19184.85	17239.60	17218.27	13433.46	13439.79	12551.78	12570.91	11514.37	11443.65	46.36
Nd(III):GSH:Mg(II)	19114.61	19175.70	17238.11	17241.93	13489.09	13452.89	12549.10	12585.57	11512.38	11458.20	43.18
Nd(III):GSH:Zn(II)	19113.52	19175.86	17238.70	17239.51	13487.81	13452.31	12547.68	12584.68	11511.32	11456.78	43.57
8. CH_3OH + CH_3CN											
Nd(III)	19120.09	19175.10	17244.65	17259.71	13492.18	13455.11	12555.72	12590.56	11522.06	11468.30	41.79
Nd(III):GSH	19120.09	19175.10	17244.65	17259.71	13492.18	13455.11	12555.72	12590.56	11522.06	11468.30	41.79
Nd(III):GSH:Mg(II)	19121.19	19175.66	17249.11	17260.18	13490.18	13454.54	12555.72	12590.19	11520.34	11468.52	40.58
Nd(III):GSH:Zn(II)	19120.09	19176.54	17234.84	17250.94	13488.36	13453.63	12553.51	12587.73	11520.74	11463.37	42.69
9. CH_3OH +DMF											
Nd(III)	19122.65	19176.59	17244.06	17232.17	13487.45	13432.38	12555.24	12552.88	11529.11	11522.99	35.00
Nd(III):GSH	19119.36	19186.15	17232.17	17222.87	13432.38	13439.80	12552.88	12571.71	11522.99	11446.31	46.56
Nd(III):GSH:Mg(II)	19120.46	19177.59	17234.84	17248.51	13486.54	13452.49	12549.89	12586.37	11521.27	11461.93	43.50
Nd(III):GSH:Zn(II)	19120.09	19176.37	17236.33	17256.09	13487.63	13453.75	12553.82	12588.81	11527.38	11466.18	43.99
10. CH_3CN+DMF											

Nd(III)	19125.58	19176.38	17243.76	17263.34	13492.91	13455.35	12556.98	12591.30	11522.60	11470.50	40.66
Nd(III):GSH	19125.21	19177.87	17241.68	17256.63	13490.18	13453.53	12551.30	12588.62	11521.27	11466.63	41.76
Nd(III):GSH:Mg(II)	19129.60	19178.24	17241.97	17262.68	13490.18	13454.37	12556.19	12590.32	11522.73	11470.15	40.02
Nd(III):GSH:Zn(II)	19114.61	19174.78	17241.97	17249.10	13486.72	13453.64	12555.09	12587.53	11516.76	11462.16	41.95
11. Water											
Nd(III)	19135.83	19178.63	17250.00	17285.40	13492.54	13455.70	12557.29	12595.54	11543.08	11482.87	43.66
Nd(III):GSH	19145.72	19179.95	17294.46	17306.82	13492.73	13455.63	12558.55	12599.40	11535.36	11494.77	34.69
Nd(III):GSH:Mg(II)	19151.58	19179.80	17306.43	17326.16	13493.64	13457.17	12564.24	12604.16	11545.61	11505.64	33.78
Nd(III):GSH:Zn(II)	19151.58	19179.99	17316.92	17325.11	13490.18	13456.40	12565.66	12603.39	11538.15	11504.94	30.14

Table 5.12 : Observed and calculated values of oscillator strengths (P x 10^6) and Judd-Ofelt parameters T_λ, (x 10^{10}) for Nd(III) : GSH, Nd(III):GSH:Mg(II) an Nd(III):GSH:Zn(II) at different aquated organic solvents at 298K and pH- 3

System	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. CH_3OH													
Nd(III)	0.7061	0.6052	2.8070	2.5181	2.4593	1.3997	1.8741	2.0632	0.3197	0.2359	1.4096	0.1089	4.1883
Nd(III):GSH	0.7446	0.6926	2.9630	2.8825	2.4883	1.4617	1.9458	2.1498	0.3406	0.2523	1.492	0.1760	4.2415
Nd(III):GSH:Mg(II)	0.7536	0.6978	3.1606	3.1681	2.5608	2.4886	2.079	2.2445	0.3895	0.3106	1.5062	0.1941	4.3913
Nd(III):GSH:Zn(II)	0.7967	0.7112	3.2658	3.1706	2.6739	2.5001	2.1571	2.2542	0.3958	0.4048	1.6808	0.2683	4.5268
2. CH_3CN													
Nd(III)	0.7459	0.6989	3.2964	3.3045	2.6675	2.7495	2.1349	2.2879	0.4001	0.2955	1.9479	0.2273	4.7890
Nd(III):GSH	0.7460	0.6924	3.3244	3.3273	2.8514	2.7417	2.1931	2.2936	0.4006	0.2895	1.9687	0.2339	4.7247
Nd(III):GSH:Mg(II)	0.7556	0.6935	3.3560	3.3756	2.8546	2.7514	2.2056	2.3168	0.4059	0.3145	1.9725	0.2568	4.7345
Nd(III):GSH:Zn(II)	0.7658	0.7143	3.9125	3.9153	2.7624	2.8961	2.2277	2.3251	0.4618	0.3271	2.6279	0.2763	4.8301
3. DMF													
Nd(III)	0.7714	0.7269	4.2719	4.2855	2.7291	2.6554	1.9763	2.1832	0.3197	0.2364	1.0511	0.1733	4.4676
Nd(III):GSH	0.7785	0.7751	4.5877	4.5912	2.8088	2.8729	2.055	2.2003	0.3359	0.2406	2.4041	0.1636	4.4947
Nd(III):GSH:Mg(II)	0.8006	0.7901	4.6953	4.6048	2.8511	2.9705	2.2017	2.3566	0.3521	0.3554	2.5358	0.2225	4.6380
Nd(III):GSH:Zn(II)	0.8117	0.8034	4.8713	4.9745	2.9958	3.0058	2.1557	2.2827	0.3833	0.3909	2.5869	0.2555	4.7300
4. Dioxane													
Nd(III)	0.7261	0.6052	2.8070	2.6181	2.5593	1.4197	1.8741	2.0632	0.3197	0.2359	1.5123	0.1159	4.1035
Nd(III):GSH	0.7246	0.6926	2.8630	2.8925	2.5883	1.4217	1.9458	2.1498	0.3406	0.2523	1.5320	0.1860	4.1926

Nd(III):GSH:Mg(II)	0.7556	0.6978	3.9106	3.0281	2.6108	2.4986	2.079	2.2445	0.3895	0.3106	1.5462	0.1941	4.2561
Nd(III):GSH:Zn(II)	0.8012	0.8112	3.9658	3.1706	2.6739	2.5045	2.1571	2.2542	0.3958	0.4048	1.6808	0.2253	4.5621
5. DMF + dioxane													
Nd(III)	0.8467	0.7197	3.4075	3.4145	2.5701	2.5691	2.2701	2.2764	0.2854	0.3235	1.949	0.1573	4.4577
Nd(III):GSH	0.7709	0.6981	3.7108	3.7147	2.6460	2.5361	2.0829	2.2103	0.3589	0.2810	2.2142	0.1654	4.4144
Nd(III):GSH:Mg(II)	0.9290	0.8501	4.1714	4.1758	2.7840	2.6455	2.2493	2.4095	0.5031	0.4010	2.3187	0.4239	4.5664
Nd(III):GSH:Zn(II)	0.8361	0.7367	3.9042	3.9097	2.6831	2.5773	2.1410	2.2649	0.3703	0.3044	2.3075	0.8541	4.6810
6. CH_3OH + Dioxane													
Nd(III)	0.8012	0.6061	3.0918	3.1025	2.7079	2.5186	1.9252	2.1477	0.3413	0.2286	1.9069	0.0876	4.1048
Nd(III):GSH	0.7031	0.6379	3.3125	3.3161	2.6497	2.5199	2.0162	2.1659	0.3454	0.2470	2.0127	0.1169	4.3993
Nd(III):GSH:Mg(II)	0.7623	0.6706	3.1844	3.1895	2.5706	2.4845	2.0821	2.1834	0.3441	0.2937	2.1454	0.1787	4.3184
Nd(III):GSH:Zn(II)	0.7433	0.4955	3.2104	3.2241	2.6102	2.6025	2.0653	2.0841	0.0259	0.0952	2.2278	0.4370	4.6031
7. CH_3CN + Dioxane													
Nd(III)	0.7101	0.5990	3.1084	3.1145	2.7098	2.5087	1.9000	2.1324	0.3702	0.2209	1.927	0.2127	4.0092
Nd(III):GSH	0.6840	0.6438	3.4555	3.4577	2.7143	2.5476	1.9905	2.1810	0.3807	0.2409	2.1181	0.1523	4.1509
Nd(III):GSH:Mg(II)	0.6676	0.6653	3.3022	3.3023	2.4958	2.4031	2.0083	2.1133	0.3703	0.2864	2.9211	0.1846	4.1747
Nd(III):GSH:Zn(II)	0.7468	0.6471	3.1123	3.1178	2.5047	2.3933	1.9712	2.1014	0.3522	0.2812	2.8098	0.6683	4.2603
8. CH_3OH + CH_3CN													
Nd(III)	0.8103	0.6208	3.0626	3.0730	2.5834	2.43	1.9216	2.1031	0.335	0.2534	1.1339	0.0540	4.2357
Nd(III):GSH	0.6497	0.6494	3.2947	3.2947	2.6593	2.5381	2.0542	2.1916	0.3699	0.2594	1.1796	0.0769	4.2266
Nd(III):GSH:Mg(II)	0.7721	0.6839	3.1416	3.1464	2.5193	2.4256	2.0499	2.1597	0.3745	0.3162	1.2688	0.1899	4.2040
Nd(III):GSH:Zn(II)	0.7540	0.6458	3.0901	3.0960	2.6526	2.5276	2.0489	2.1949	0.3515	0.2708	1.2696	0.1981	4.4038

9. CH_3OH + DMF													
Nd(III)	0.6253	0.5792	3.1555	3.1581	2.5505	2.4125	1.8840	2.0422	0.3156	0.2039	1.9729	0.1369	4.2231
Nd(III):GSH	0.7054	0.6721	3.6099	3.6116	2.6864	2.5613	2.0653	2.2084	0.3627	0.2588	2.1886	0.1883	4.4675
Nd(III):GSH:Mg(II)	0.8822	0.7850	4.0725	4.0779	2.7339	2.6537	2.2594	2.3542	0.3811	0.3379	2.3677	0.2778	4.6017
Nd(III):GSH:Zn(II)	0.7819	0.6567	3.8660	3.8729	2.7748	2.7471	2.2660	2.3025	0.1951	0.2083	2.4724	0.3613	4.8178
10. CH_3CN + DMF													
Nd(III)	0.5718	0.7775	3.3995	3.3881	1.5608	1.7467	1.9877	1.7686	0.3445	0.4508	1.6085	0.1071	3.9425
Nd(III):GSH	0.7878	0.6813	3.4155	3.4214	2.6740	2.5232	2.0297	2.2049	0.3900	0.2853	2.0151	0.1299	4.3897
Nd(III):GSH:Mg(II)	0.9345	0.8733	5.1436	5.1470	2.7464	2.6332	2.2244	2.3550	0.4398	0.3555	3.0309	0.2569	4.5614
Nd(III):GSH:Zn(II)	0.9291	0.7403	3.6388	3.6492	2.7491	2.6136	2.1508	2.3121	0.3900	0.3245	3.1071	0.3425	4.5971
11. Water													
Nd(III)	0.7164	0.6450	2.9071	2.9111	2.3899	2.3228	1.9868	2.0658	0.3387	0.2994	1.6345	0.1282	4.0282
Nd(III):GSH	0.3589	0.6152	2.8239	2.8096	2.5189	2.4927	2.1415	2.1608	0.3647	0.2619	1.6531	0.1484	4.3457
Nd(III):GSH:Mg(II)	0.6965	0.6966	3.6417	3.6417	3.1198	2.961	2.3283	2.5082	0.3971	0.2523	2.2642	0.1830	5.1814
Nd(III):GSH:Zn(II)	0.7340	0.6694	2.5002	2.5037	2.5182	2.478	2.1789	2.2271	0.3601	0.3433	2.312	0.2713	5.2881

Table 5.13 Observed and calculated values of oscillator strengths (P x 10^6) and Judd-Ofelt parameters T_λ, (x 10^{10}) for Nd(III) : GSH, Nd(III):GSH:Mg(II) an Nd(III):GSH:Zn(II) at different aquated organic solvents at 298K and pH - 4

System	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. CH_3OH													
Nd(III)	0.9697	0.7086	4.2812	4.2957	2.9007	2.6845	2.0297	2.2853	0.3557	0.2388	2.0780	0.1183	4.3985
Nd(III):GSH	0.9988	0.8698	5.0075	5.0146	3.3107	3.1445	2.5248	2.7184	0.4353	0.3234	2.0896	0.1871	5.4866
Nd(III):GSH:Mg(II)	1.1757	0.8462	3.7172	3.7354	3.3117	3.1312	2.5559	2.7739	0.455	0.3916	2.1055	0.1916	5.4397
Nd(III):GSH:Zn(II)	0.9948	0.8645	4.6277	4.635	3.2562	3.0953	2.5179	2.7056	0.4557	0.349	2.7544	0.2322	5.6901
2. CH_3CN													
Nd(III)	0.6788	0.6815	3.8698	3.8697	2.7474	2.5628	1.9939	2.2031	0.4191	0.2499	2.1692	0.1237	4.2785
Nd(III):GSH	0.6087	0.6584	3.6467	3.6439	2.5973	2.491	2.0264	2.1449	0.3592	0.247	2.2199	0.1439	4.3501
Nd(III):GSH:Mg(II)	0.8168	0.717	3.669	3.6744	2.699	2.576	2.118	2.2614	0.3825	0.301	2.2559	0.1676	4.4808
Nd(III):GSH:Zn(II)	0.6246	0.6621	3.5291	3.5271	2.5579	2.4681	2.0407	2.1409	0.3548	0.2614	3.1169	0.3394	4.6034
3. DMF													
Nd(III)	0.7494	0.6534	4.1531	4.1583	2.8239	2.6505	2.0146	2.2151	0.3208	0.1922	2.6679	0.2837	4.1571
Nd(III):GSH	0.721	0.6911	4.3297	4.3314	2.8114	2.6667	2.0868	2.252	0.3406	0.2178	2.7435	0.3921	4.2785
Nd(III):GSH:Mg(II)	1.0219	0.8089	4.6137	4.6254	2.9007	2.7377	2.2067	2.4001	0.4004	0.3171	2.7697	0.3611	4.5662
Nd(III):GSH:Zn(II)	0.8125	0.7476	4.1731	4.1767	2.7312	2.6144	2.1478	2.2827	0.3804	0.2938	2.9016	0.4246	4.7483
4. Dioxane													

Nd(III)	0.735	0.7405	4.2186	4.2182	2.9383	2.8099	2.2653	2.4107	0.3877	0.2688	2.0916	0.1366	4.0126
Nd(III):GSH	0.563	0.6148	3.549	3.546	2.4298	2.3281	1.8823	1.9956	0.3288	0.22	2.1848	0.1404	4.1733
Nd(III):GSH:Mg(II)	0.6651	0.5767	3.0907	3.0955	2.0871	1.9947	1.6479	1.7563	0.2949	0.2378	2.2229	0.2705	4.4697
Nd(III):GSH:Zn(II)	0.5375	0.5245	2.8326	2.8334	1.8832	1.8172	1.5224	1.5978	0.2709	0.2147	2.6723	0.2857	4.6605
5. DMF + dioxane													
Nd(III)	0.6099	0.5277	3.8881	3.8927	2.7645	2.6378	1.9494	2.0964	0.1683	0.078	2.6945	0.1193	4.1785
Nd(III):GSH	0.646	0.6889	4.1009	4.0984	2.6906	2.5637	2.052	2.1941	0.3695	0.2405	2.7405	0.1606	4.2842
Nd(III):GSH:Mg(II)	0.8657	0.7963	4.0235	4.0273	2.7773	2.6586	2.2364	2.3738	0.4397	0.3527	2.74513	0.2322	4.6123
Nd(III):GSH:Zn(II)	0.7187	0.7744	4.2388	4.2357	2.5706	2.4757	2.1052	2.2105	0.4322	0.3285	2.7651	0.2569	4.5931
6. CH_3OH + Dioxane													
Nd(III)	0.8502	0.6876	3.9857	3.9946	2.7006	2.5235	1.9664	2.1738	0.3622	0.2506	2.4442	0.1051	4.4509
Nd(III):GSH	0.6727	0.6485	4.003	4.0043	3.1033	2.8246	2.0243	2.3413	0.4315	0.1846	2.6025	0.2873	4.4715
Nd(III):GSH:Mg(II)	0.8077	0.7295	3.7138	3.7181	2.5432	2.4302	2.0392	2.1706	0.4015	0.3224	2.7298	0.2916	4.5145
Nd(III):GSH:Zn(II)	0.8039	0.7441	4.0698	4.0731	2.5686	2.4296	2.0002	2.1603	0.4209	0.3124	3.2753	0.3737	4.9158
7. CH_3CN + Dioxane													
Nd(III)	0.7445	0.6752	4.0344	4.0383	2.9306	2.7045	2.0236	2.2828	0.4048	0.2199	2.1481	0.2997	4.143
Nd(III):GSH	0.5843	0.6457	3.6506	3.6471	2.769	2.572	1.9671	2.188	0.4255	0.2269	2.2689	0.2166	4.2045
Nd(III):GSH:Mg(II)	0.7626	0.7083	3.9196	3.9226	2.4925	2.391	1.9894	2.1066	0.3632	0.2873	2.3228	0.3934	4.5585
Nd(III):GSH:Zn(II)	0.9302	0.7306	3.8802	3.8913	2.6692	2.5561	2.1101	2.2464	0.3432	0.3014	2.9931	0.4778	4.9459
8. CH_3OH + CH_3CN													
Nd(III)	0.7473	0.6938	3.8759	3.8788	2.5817	2.4343	1.9568	2.1261	0.3903	0.2723	2.2206	0.0170	4.2402
Nd(III):GSH	0.719	0.6800	3.6712	3.6734	2.735	2.566	2.0208	2.2139	0.4016	0.2594	2.2327	0.0885	4.4791

Nd(III):GSH:Mg(II)	0.9364	0.9552	3.9328	3.9871	3.1255	2.9671	2.5327	2.7521	0.3456	0.503	2.5436	0.0887	5.0986
Nd(III):GSH:Zn(II)	0.9619	0.7308	3.9866	3.991	2.7377	2.5649	2.0476	2.2469	0.4262	0.2934	2.8518	0.1427	6.4660
9. CH_3OH + DMF													
Nd(III)	0.6474	0.6034	3.8423	3.8447	2.7279	2.5581	1.9268	2.1211	0.31	0.1686	1.1955	0.4352	2.5003
Nd(III):GSH	0.8921	0.9356	3.5446	3.5422	1.3174	1.5961	2.1319	1.8142	0.3784	0.6192	1.4012	0.7121	2.6132
Nd(III):GSH:Mg(II)	0.9195	0.8575	3.1371	3.1406	2.8507	2.866	2.8507	2.8348	0.4335	0.4665	1.5656	0.8836	4.9388
Nd(III):GSH:Zn(II)	0.8282	0.7916	4.5041	4.5061	2.8853	2.7565	2.2555	2.4028	0.412	0.3058	2.7144	0.9093	5.0017
10. CH_3CN + DMF													
Nd(III)	0.6799	0.602	3.1211	3.0254	2.4615	2.3108	1.7762	1.9501	0.3011	0.1876	2.4209	0.2576	4.0529
Nd(III):GSH	0.7278	0.6712	3.2244	3.1276	2.4904	2.3568	1.8837	2.0375	0.3172	0.2427	2.4654	0.3642	4.1135
Nd(III):GSH:Mg(II)	0.74	0.7120	3.7251	3.3251	2.5132	2.4152	1.8852	2.0254	0.3251	0.2501	2.5671	0.3760	4.2707
Nd(III):GSH:Zn(II)	0.7753	0.7170	3.9542	3.9575	2.7573	2.5863	1.9570	2.0398	0.3493	0.3024	2.7081	0.4056	4.9642
11. Water													
Nd(III)	0.7302	0.925	4.9246	4.9138	3.3517	3.2452	2.7405	2.8535	0.5388	0.3816	2.1950	0.0934	3.6488
Nd(III):GSH	0.655	0.7169	3.8819	3.8785	2.6389	2.5481	2.1289	2.2294	0.3903	0.2883	2.2049	0.1297	3.8387
Nd(III):GSH:Mg(II)	0.7906	0.6916	3.8844	3.8899	2.1909	2.1099	1.8000	1.8957	0.3374	0.294	2.2596	0.2389	3.8521
Nd(III):GSH:Zn(II)	0.8048	0.7321	3.5118	3.5158	2.6123	2.5099	2.1226	2.2416	0.4052	0.3341	2.5185	0.2534	4.0478

Table 5.14 Observed and calculated values of oscillator strengths (P x 10^6) and Judd-Ofelt parameters T_λ, (x 10^{10}) for Nd(III) : GSH, Nd(III):GSH:Mg(II) an Nd(III):GSH:Zn(II) at different aquated organic solvents at 298K and pH – 5

System	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. CH_3OH													
Nd(III)	0.8482	0.8321	4.1485	4.2103	2.2282	2.1356	1.4786	1.4523	0.3245	0.4001	2.2655	0.2074	3.0033
Nd(III):GSH	0.8463	0.8787	4.1613	4.1467	2.2357	2.0264	1.8362	1.6722	0.3438	0.4117	2.4644	0.2096	3.7885
Nd(III):GSH:Mg(II)	0.8629	0.8712	4.1815	4.1544	2.2552	3.3724	1.9039	2.0123	0.3495	0.4207	2.5346	0.2925	3.8561
Nd(III):GSH:Zn(II)	0.8712	0.8812	4.2130	4.2287	2.4609	3.899	1.9714	2.0759	0.8692	0.4538	2.672	0.3014	4.4577
2. CH_3CN													
Nd(III)	0.8568	0.8073	4.1669	4.3103	2.4990	3.0801	2.1180	2.5061	0.3825	0.3384	2.1559	0.0676	2.4808
Nd(III):GSH	0.8593	0.8409	4.1733	4.2467	2.5251	2.0296	2.5348	2.7621	0.4217	0.3500	2.5246	0.1266	3.9071
Nd(III):GSH:Mg(II)	0.8651	0.8810	4.1905	4.3544	2.5330	2.4407	2.6284	2.2014	0.4357	0.3432	2.6206	0.1683	4.5026
Nd(III):GSH:Zn(II)	0.8894	0.8921	4.2516	4.3287	2.5572	2.9319	2.7775	2.683	0.4657	0.3709	2.6506	0.1909	4.4807
3. DMF													
Nd(III)	0.8598	0.8123	4.4498	4.8051	2.6234	3.1142	2.1864	2.5354	0.2848	0.378	2.7209	0.0405	4.0018
Nd(III):GSH	0.8758	0.8421	4.7709	5.1256	2.7371	3.1683	2.9051	2.7691	0.3068	0.275	2.9321	0.0833	4.0652
Nd(III):GSH:Mg(II)	0.8881	0.8856	5.6551	6.0435	2.8351	3.2225	3.3074	3.2936	0.3284	0.4243	3.3486	0.1899	4.7158
Nd(III):GSH:Zn(II)	0.9334	0.8923	6.5432	6.4688	3.1291	3.4438	3.4103	3.3017	0.4212	0.593	3.6256	0.2015	4.9655

4. Dioxane													
Nd(III)	0.8348	0.5372	4.2731	3.2294	2.4475	2.0008	1.8689	1.6362	0.3355	0.2023	2.6011	0.2143	3.0375
Nd(III):GSH	0.62	0.4486	3.8828	3.5292	2.1088	1.743	1.6483	1.5408	0.2807	0.1733	2.798	0.2187	3.5309
Nd(III):GSH:Mg(II)	0.6735	0.8874	3.4074	4.0528	1.738	1.948	1.3961	1.7943	0.2651	0.2903	2.8128	0.2251	3.8769
Nd(III):GSH:Zn(II)	0.4289	0.3074	2.8703	2.551	1.4814	1.2294	1.1588	1.0737	0.2081	0.1186	2.9694	0.2276	4.0062
5. DMF + dioxane													
Nd(III)	0.8025	0.6516	4.4024	5.7078	3.2282	5.3128	1.8077	2.8884	0.2968	0.0476	3.1337	1.0508	4.0911
Nd(III):GSH	0.7864	0.5721	0.6449	0.6824	3.1719	2.7889	0.8487	1.0497	0.3078	0.0686	3.246	0.949	4.1183
Nd(III):GSH:Mg(II)	0.9511	1.9365	5.0962	8.9684	2.6231	4.1141	1.9988	3.8992	0.3507	0.5262	3.1309	0.0095	4.1258
Nd(III):GSH:Zn(II)	0.3853	0.1398	2.9047	1.6777	1.5838	1.0549	1.109	0.6975	0.1834	0.0435	1.9022	0.2782	4.6118
6. Metnaol+Dioxane													
Nd(III)	0.8161	0.5525	4.2752	3.5853	2.5594	2.3209	1.7951	1.8003	0.3046	0.168	2.7224	0.262	4.1701
Nd(III):GSH	0.65	0.7168	4.7552	5.2763	1.2609	0.7413	1.9148	1.739	0.3567	0.5867	2.3738	1.298	2.491
Nd(III):GSH:Mg(II)	0.8244	1.0819	4.4418	5.9982	2.2792	3.0273	1.913	3.5138	0.1644	0.164	2.7965	0.1688	3.9673
Nd(III):GSH:Zn(II)	0.5018	0.2224	3.2952	2.4748	1.7064	1.1766	1.0515	0.7119	0.2059	0.0511	2.1857	0.3496	2.709
7. CAN + Dioxane													
Nd(III)	0.8414	0.6911	4.3318	4.2352	2.5747	2.6677	1.7758	1.8781	0.3691	0.5069	2.7024	0.1295	4.1265
Nd(III):GSH	0.7569	0.6554	4.8523	5.4381	2.5471	2.3469	1.8478	2.1305	0.3929	0.2583	3.0065	0.0687	4.1381
Nd(III):GSH:Mg(II)	0.7899	0.9489	4.9082	7.7647	2.2512	2.9025	1.7761	2.843	0.3328	0.3599	2.9879	0.0899	3.7354
Nd(III):GSH:Zn(II)	0.6092	0.3594	3.1051	2.0388	1.6681	1.0857	1.1824	0.855	0.2397	0.1063	1.9162	0.021	2.6824
8. Methanol + ACN													
Nd(III)	0.8742	0.7731	4.2808	3.7406	2.3557	2.3348	1.8089	1.9931	0.3237	0.2555	2.5892	0.0688	3.8789
Nd(III):GSH	0.6345	0.3029	4.3698	4.4734	2.5116	2.1456	0.939	0.7863	0.3609	-0.031	3.1298	0.962	3.6003
Nd(III):GSH:Mg(II)	0.697	0.8366	4.5888	6.9151	2.3776	3.3819	1.8695	3.1186	0.3643	0.4257	2.7883	0.0448	3.9516
Nd(III):GSH:Zn(II)	0.5999	0.312	3.043	2.0932	1.597	0.9795	1.1916	0.786	0.2233	0.1003	1.8574	0.0253	2.6053

9. Methanol + DMF													
Nd(III)	0.7991	0.7628	4.5752	4.5699	2.5464	2.558	1.8255	1.9656	0.299	0.159	2.9177	0.2648	4.1851
Nd(III):GSH	0.8463	0.6821	4.8859	5.2322	2.4921	2.3465	1.86	2.0147	0.1725	0.0849	3.2054	0.4496	4.2231
Nd(III):GSH:Mg(II)	0.6473	0.74	4.935	6.6347	2.5172	3.1099	2.0641	3.1032	0.3898	0.4422	2.9969	0.0536	4.2566
Nd(III):GSH:Zn(II)	0.6792	0.5578	3.668	2.9583	1.9767	1.5343	1.4253	1.211	0.2492	0.126	2.3055	0.1229	3.2334
10. ACN + DMF													
Nd(III)	0.613	0.5035	4.8424	4.7508	0.9555	1.0389	1.8561	1.8903	0.1753	0.0021	3.4632	1.1456	4.8871
Nd(III):GSH	0.9275	1.187	4.6491	4.4715	2.5928	2.1461	1.9965	2.3342	0.4012	0.7117	2.769	0.1632	4.2458
Nd(III):GSH:Mg(II)	0.914	1.2632	5.0682	8.2711	2.7573	4.0837	2.2259	74.113	0.4175	0.5766	3.0152	0.1804	4.5983
Nd(III):GSH:Zn(II)	0.6168	0.112	3.1075	1.9932	1.7874	0.7897	0.0706	0.0252	0.2445	-0.087	2.4452	1.1084	2.1853
11. Water													
Nd(III)	0.7906	0.5982	3.8844	2.9787	2.1909	1.6759	1.8	1.5329	0.3374	0.2372	2.2596	0.2389	3.6521
Nd(III):GSH	0.7225	0.6288	3.7506	3.6176	2.3417	2.3954	1.8777	2.0789	0.3718	0.3201	2.1893	0.1697	3.888
Nd(III):GSH:Mg(II)	1.0554	1.0291	3.9306	4.3756	2.2654	2.1777	2.0423	2.1723	0.1712	0.137	2.306	0.1731	3.9626
Nd(III):GSH:Zn(II)	0.7278	0.6804	3.5455	3.5482	2.3768	2.2776	1.9112	2.0255	0.3701	0.2942	2.0518	0.1685	3.9512

Table 5.15 Observed and calculated values of oscillator strengths (P x 10^6) and Judd-Ofelt parameters T_λ, (x 10^{10}) for Nd(III) : GSH, Nd(III):GSH:Mg(II) an Nd(III):GSH:Zn(II) at different aquated organic solvents at 298K and pH – 6

System	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. CH_3OH													
Nd(III)	0.8594	0.6890	4.5456	4.555	2.5249	2.3812	1.8657	2.0355	0.3000	0.2214	2.4511	0.2562	4.365
Nd(III):GSH	0.8372	0.7157	4.3948	4.4016	2.3609	2.2543	1.86	1.9858	0.3308	0.2710	2.6495	0.2594	4.3803
Nd(III):GSH:Mg(II)	0.8532	0.7598	4.5976	4.6027	2.5103	2.426	2.0363	2.1355	0.3378	0.2897	2.7675	0.2894	4.4501
Nd(III):GSH:Zn(II)	0.5836	0.4146	2.7280	2.7373	1.5033	1.4055	1.0886	1.2062	0.1728	0.1357	3.1059	0.3012	4.4567
2. CH_3CN													
Nd(III)	0.9390	0.8381	4.9713	4.9770	2.8253	2.6945	2.2218	2.3741	0.4140	0.3259	2.9794	0.2157	4.6822
Nd(III):GSH	0.8595	0.8407	4.9304	4.9314	2.7855	2.6933	2.2739	2.3791	0.4104	0.3322	2.9383	0.1404	4.6774
Nd(III):GSH:Mg(II)	0.8532	0.7598	4.5976	4.6028	2.5103	2.426	2.0362	2.1355	0.3378	0.2897	2.9676	0.2893	4.722
Nd(III):GSH:Zn(II)	0.5840	0.4147	2.7280	2.7374	1.5030	1.4053	1.0886	1.2062	0.1728	0.1358	3.2057	0.3724	4.6563
3. DMF													
Nd(III)	0.7803	0.6198	4.4696	4.4784	2.5357	2.3533	1.7361	1.9492	0.2724	0.1555	2.9138	0.3982	4.1385
Nd(III):GSH	0.9256	0.7551	5.0838	5.0931	2.5753	2.4416	1.9464	2.1046	0.3173	0.2480	3.1645	0.4016	4.2604
Nd(III):GSH:Mg(II)	0.9898	0.8318	5.2734	5.2822	2.5335	2.4299	2.0378	2.1615	0.3627	0.3169	3.1654	0.4148	4.6133
Nd(III):GSH:Zn(II)	0.4454	0.3906	2.9616	2.9646	1.5749	1.4637	1.0766	1.2047	0.1732	0.0887	3.2448	0.4486	4.8776
4. Dioxane													

Nd(III)	0.7626	0.6819	4.4088	4.4133	2.5187	2.3598	1.8393	2.0226	0.3456	0.2257	3.0494	0.3297	3.1262
Nd(III):GSH	0.6492	0.6831	4.3655	4.3637	2.2799	2.1949	1.8173	1.9121	0.3313	0.2435	3.0156	0.4103	3.8228
Nd(III):GSH:Mg(II)	0.1763	0.9649	0.8498	0.7696	4.5738	4.674	4.5738	4.4212	1.8611	1.5004	3.0391	0.4126	4.0102
Nd(III):GSH:Zn(II)	0.6492	0.6481	0.2955	0.2954	2.4747	1.9531	1.3298	1.8262	1.0093	0.6048	3.1001	0.4364	4.5189
5. DMF + dioxane													
Nd(III)	0.8908	0.7000	4.8201	4.8306	2.6971	2.5051	1.8867	2.1118	0.3200	0.2038	3.0763	0.2760	4.2915
Nd(III):GSH	0.9867	0.1692	4.8693	4.5196	2.4934	2.7468	1.7995	2.1785	0.3584	18332	3.0842	0.2850	4.3120
Nd(III):GSH:Mg(II)	0.9890	0.8265	5.3610	5.3700	2.4808	2.3803	1.9957	2.116	0.3506	0.3091	3.1273	0.3185	4.3275
Nd(III):GSH:Zn(II)	0.2827	0.3676	2.7469	2.7421	1.5488	1.4456	1.0700	1.1835	0.2001	0.0801	3.1818	0.3644	4.3503
6. CH_3OH + Dioxane													
Nd(III)	0.7916	0.6852	4.4921	4.498	2.3295	2.2019	1.7619	1.9108	0.3193	0.2357	2.7678	0.0245	3.8383
Nd(III):GSH	0.7719	0.7467	4.6458	4.6471	2.272	2.1852	1.8513	1.9506	0.3634	0.2920	2.7637	0.2005	3.7854
Nd(III):GSH:Mg(II)	0.8002	0.6860	4.6675	4.6739	2.2744	2.1795	1.7710	1.8831	0.2766	0.2253	2.8971	0.0541	3.8013
Nd(III):GSH:Zn(II)	0.6453	0.6732	3.5040	3.5024	1.9344	2.0173	1.9344	1.8394	0.2426	0.3096	1.9726	0.3391	3.4815
7. CH_3CN + Dioxane													
Nd(III)	0.9318	0.7351	5.0130	5.0239	2.8100	2.5847	1.9271	2.1903	0.3659	0.2211	3.1803	0.2427	4.528
Nd(III):GSH	0.7927	0.6754	4.9363	4.9427	2.8491	2.601	1.8658	2.1525	0.3518	0.1611	3.2363	0.4851	4.5972
Nd(III):GSH:Mg(II)	1.0673	1.0016	6.2880	6.2916	2.7816	2.6887	2.3366	2.4444	0.4700	0.4056	3.6907	0.4284	4.6399
Nd(III):GSH:Zn(II)	1.1626	0.8725	6.4632	6.4793	3.0478	2.9753	2.4041	2.4979	0.2088	0.2321	4.1509	0.3648	5.2179
8. CH_3OH + CH_3CN													
Nd(III)	0.8222	0.6694	4.3591	4.3675	2.3637	2.2202	1.7470	1.9156	0.3105	0.2268	2.7007	0.0655	3.8729
Nd(III):GSH	0.8222	0.6694	4.3591	4.3675	2.3637	2.2202	1.7470	1.9156	0.3105	0.2268	2.7007	0.0655	3.8729
Nd(III):GSH:Mg(II)	0.8117	0.8065	4.9988	4.9991	2.4107	2.2973	1.9369	2.0654	0.4230	0.3214	2.9522	0.2678	3.9745

Nd(III):GSH:Zn(II)	0.5048	0.4026	2.7670	2.7727	1.3189	1.2632	1.0249	1.0921	0.1504	0.1311	1.7199	0.0289	2.2029
9. CH_3OH + DMF													
Nd(III)	0.7958	0.6070	4.2172	4.2276	2.3630	2.2113	1.6764	1.8559	0.2511	0.1709	2.7071	0.3182	3.8797
Nd(III):GSH	0.7589	0.7645	6.1447	6.1444	2.5717	2.4151	1.8532	2.031	0.3281	0.1831	3.2039	0.3209	4.454
Nd(III):GSH:Mg(II)	0.6689	0.7912	5.1488	5.1420	2.3614	2.3209	2.0146	2.0554	0.367	0.2925	3.2010	0.3456	4.5286
Nd(III):GSH:Zn(II)	0.6343	0.4273	2.8783	2.8897	1.4850	1.3804	1.0634	1.1902	0.1718	0.1401	3.2944	0.3445	4.6088
10. CH_3CN + DMF													
Nd(III)	0.7469	0.5005	4.1877	4.2014	2.6517	2.5464	1.8509	1.9802	0.0531	0.0330	2.9722	0.3528	4.5287
Nd(III):GSH	0.8886	0.7553	4.7549	4.7623	2.5940	2.452	1.9692	2.1354	0.3600	0.2716	3.0065	0.3697	4.2699
Nd(III):GSH:Mg(II)	0.9336	0.8233	5.1286	5.1346	2.7388	2.6168	2.1511	2.2936	0.3816	0.3044	3.1103	0.3761	4.5514
Nd(III):GSH:Zn(II)	0.4509	0.3516	2.4526	2.4581	1.4269	1.3186	0.9739	1.1006	0.1634	0.0954	3.2851	0.4109	4.6163
11. Water													
Nd(III)	0.8404	0.7176	4.2251	4.2319	2.3398	2.2362	1.8628	1.9850	0.3435	0.2868	2.5101	0.1579	3.8792
Nd(III):GSH	0.7500	0.6919	3.8724	3.8756	2.3125	2.2257	1.8759	1.9765	0.3473	0.2861	2.5729	0.1602	3.8611
Nd(III):GSH:Mg(II)	0.6223	0.5569	1.8798	1.8834	2.3814	2.3272	1.9835	2.0475	0.3079	0.2786	2.6138	0.1865	4.248
Nd(III):GSH:Zn(II)	0.7260	0.6414	3.0745	3.0792	2.3921	2.3009	1.9271	2.0338	0.3414	0.2843	2.7696	0.2205	4.4981

CHAPTER NO. 6

Kinetics for the complexation of Pr(III):GSH and Nd(III):GSH with Zn(II) in DMF medium at different temperatures and calculation of activation energies

6.1 Introduction

In transition metal ions the absorption spectra involving d-d transitions have used for following the kinetics of the chemical reaction leading to the development of mechanism of chemical and biochemical reactions. In lanthanide however rarely absorption spectra involving 4f-4f transition are used for mechanistic studies for the kinetic reactions involving lanthanide ions and coordination ligand including biomolecules. In this chapter we are going to investigate the kinetics for the complexation of Pr(III) :GSH and Nd(III):GSH with Zn(II) in DMF medium in different temperatures viz., 303K (30^0C), 308K (35^0C), 313K (40^0C) and 318 (45^0C). from the values of rate of the reactions at different temperatures the activation energies of the twp complexes determined. and calculation of activation energies (E_a's) of the complexations. The rates of the complexation of Pr(III):GSH and Nd(III):GSH with Zn(II) have been measured by using two different methods i.e., comparative absorption and absorption different spectroscopy using 4f-4f transitions by monitoring the changes of absorbance and oscillator strengths of multiplet to multiplet electronic transitions, $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$ transitions of Pr(III) ion and $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$ and $^4I_{9/2} \rightarrow {}^4F_{3/2}$ of Nd(III) ion. The activation energy of the complexation of Pr(III):GSH with

Zn(II) and Nd(III):GSH with Zn(II) have been explored from the data of rates at different temperatures by following Arrhenius rate equation.

6.2 Experimental

Praseodymium(III)nitrate hexadydrate and Neodymium(III) nitrate hexahydrate of 99.9% purity was purchased from CDH, Mumbai and Glutathione reduced (GSH) from SRL Pvt. Ltd., Mumbai are used for synthesis and kinetic studies. Glutathione reduced (GSH) is kept below 3^0C and fresh solution of 0.01M was prepared for spectral study. The Pr(III)/Nd(III):GSH complex is synthesized by mixing and constant stirring of Pr(III)/Nd(III) nitrate (0.002 M) with 0.004 M glutathione reduced in ethylacetate-acetone mixture and yields pinkish crystalline complex after 8-10 days. It is separated out from the liquor. The crystal obtained is washed with acetone and dried in desiccators over P_4O_{10}. The analysis of the complex gave the stoichiometry $[Pr_2(GSH)_2Zn(H_2O)_6]$ and $[Nd_2(GSH)_2Zn(H_2O)_6]$.

For the preparation of Pr(III):GSH:Zn(II) and Nd(III):GSH:Zn(II) complex, Pr(III)/Nd(III) nitrate (0.001M), Zn(II) nitrate (0.001M) and glutathione reduced (0.002 M) in ethyl acetate- acetone mixture at pH-6. Pinkish crystalline complex is formed after 8-10 days and dried over P_4O_{10} in a desiccators. The analysis of the complex gave the stoichiometry, $[Pr_2(GSH)_2Zn(H_2O)_6]$ and $[Nd_2(GSH)_2Zn(H_2O)_6]$.

For the kinetic studies, equimolar concentration of Pr(III)/Nd(III) (nitrate) and GSH were added and the resultant mixture was stirred for sufficient time in inert atmosphere, created by maintaining a constant flush of oxygen free nitrogen to form the complex in solution. Stock solution of Zn(II) was prepared by adding an appropriate quantity of $Zn(NO_3)_2$ in deareated double distilled water. On Mixing the two solution, the increase in absorbance and oscillator strength of all the 4f-4f transition bands were observed. The solvent used DMF, is of A/R grade from E. Merck. All the spectra are recorded on a temperature controlled Perkin Elmer Lambda-35 UV-Visible Spectrophotometer with attached kinetic assembly in the range 350-910 nm at different temperatures

i.e.303K (30^0C), 308K (35^0C), 313K (40^0C) and 318K (45^0C). The temperatures of all the observation is maintained by using water circulating HAAKE DC 10 thermostat.

6.3 Methods

The calculation of the band intensities is based upon the theoretical treatment derived by Judd[1] and Ofelt[2]. They considered the transitions are essentially electric dipole in character and the oscillator strength corresponding to the induced electric dipole transition $\Psi J \rightarrow \Psi' J'$ as given by

$$P = \sum_{\lambda=2,4,6} T_\lambda \sigma (f^N \psi J \| U^{(\lambda)} \| f^N \psi' J')^2 \qquad (6.1)$$

Where $U^{(\lambda)}$ is matrix element of rank λ. The three quantities T_2, T_4 and T_6 are related to the radial parts of the $4f^N$ wave functions, the wave functions of perturbing configurations of which the nearest is $4f^{N-1}5d$.

The measured intensity of an absorption band is related to the probability (P) for the absorption of radiant energy (oscillator strength) by the expression:

$$P = \frac{2303mc^2}{N\pi e^2} \int \varepsilon_i(\sigma) d\sigma$$

or

$$P = 4.318 \times 10^{-9} \int \varepsilon_i(\sigma) d\sigma \qquad (6.2)$$

Where ε is the molar absorptivity at the energy σ (cm^{-1}) and other symbols have their usual meaning. From these values the value of T_2, T_4 and T_6 are calculated by using

$$\frac{P_{obs}}{\nu} = \left[\left(U^2\right)\right]^2 T_2 + \left[\left(U^4\right)\right]^2 T_4 + \left[\left(U^6\right)\right]^2 T_6 \qquad (3)$$

where $U^{(\lambda)}$ are the matrix elements of Pr(III) and Nd(III) system given by Carnall.[3] The activation energy for the complexation of Pr(III):GSH with Zn(II) in DMF is calculated from the plot of log k (k=rate constant) against 1/T by using Arrhenius rate equation.[4]

$$\log k = \log A - \frac{Ea}{2.303R} \frac{1}{T} \qquad (4)$$

Where, A is the frequency factor. From the slope the activation energy (Ea) is calculated as

$$E_a = \text{Slope} \times 2.303 \times R \qquad (5)$$

Where R is gas universal gas constant.

6.4 Results and Discussion

Figure 6.1 and Figure 6.5 shows the time scan absorption spectra of the formation of the complexes, $[Pr_2(GSH)_2Zn(H_2O)_6]$ and $[Nd_2(GSH)_2\ Zn(H_2O)_6]$ respectively at 303K. Figures 6.2, 6.3 and 6.4 give the time scan comparative absorption spectra of the complexation of Pr(III):GSH with Zn(II) at DMF medium in different temperatures - 308K, 313K and 318K respectively. Similarly Figures 6.6, 6.7 and 6.8 give the time scan comparative absorption spectra of the complexation of Nd(III):GSH with Zn(II) at DMF medium in different temperatures-308K, 313K and 318K respectively. From the figures it is seen that there is increase of absorbance and intensity with time. Both hypersensitive and pseudohypersensitive transitions of Pr(III) and Nd(III) display significant changes during complexation, which can be seen from the spectral changes with time (Figure 6.1 to 6.8) The top most curve in all the figures represent the stage of apparent completion of the complexation and no further changes were noted over the next few days. At this stage, the spectrum matched very closely with that of the freshly prepared solution of the same concentration of the isolated solid complexes, $[Pr_2(GSH)_2Zn(H_2O)_6]$ and $[Nd_2(GSH)_2\ Zn\ (H_2O)_6]$. In most of the studies on structural correlation with 4f-4f spectral bands, the hypersensitive bands has been used as marker band and the 4f-4f bands other than hypersensitive were shown almost insensitive or only very slightly sensitive to the coordination environment changes and therefore been ignored.[4-6]

On other hand, we observed that the bands other than hypersensitive bands can acquire sensitivity due to the binding characteristics of the coordinating ligand, change of denticity, nature of the donor sites as well as nature of Ln(III) – ligand bond and nature of complex species do induced significant intensity to the non-hypersensitive 4f-4f bands. Such transitions are known as pseudohypersensitive transitions. Therefore we suggested that the

changes in the oscillator strengths of both hypersensitive and pseudohypersensitive transitions should be considered for spectra structural correlation in Ln(III) complexes with coordination ligands including biomolecules.

Tables 6.1 to 6.4 give the values of observed (Pobs) and calculated (Pcal) values of oscillator strengths and calculated values of Judd-Ofelt intensity parameter, T_λ, (λ = 2,4,6) for complexation of Pr(III):GSH with Zn(II) in DMF at different temperatures, viz., 303K, 308K, 313K and 318K respectively. Tables 6.5 to 6.8 give the values of observed (Pobs) and calculated (Pcal) values of oscillator strengths and calculated values of Judd-Ofelt intensity parameter, T_λ, (λ = 2,4,6) for complexation of Nd(III):GSH with Zn(II) in DMF at different temperatures, viz., 303K, 308K, 313K and 318K respectively. The rate constants for the complexation at different temperatures were evaluated from the plots of absorbance and oscillator strength versus time. The observed rate constant (Kobs) calculated by both methods were found to be almost identical indicating that the rate of complexations are comparable and very significant for hypersensitive and pseudohypersensitive transitions. From these tables we can conclude that the rates of complexation of Pr(III)/Nd(III):GSH with Zn(II) for form complexes, $[Pr_2(GSH)_2Zn(H_2O)_6]$ and $[Nd_2(GSH)_2Zn(H_2O)_6]$ were linearly increases on increasing time.

A series of kinetic experiments were also performed by varying the initial concentration of Ln(III):GSH at constant temperature (303K) and constant concentration of Zn(II) for studying the effect of concentration of Ln(III):GSH on the rate of the formation of the $[Pr_2(GSH)_2Zn(H_2O)_6]$ and $[Nd_2(GSH)_2Zn(H_2O)_6]$. From the study it is found that the rate of the formation depends on concentration of Ln(III):GSh linearly i.e. first order with respect to [Ln(III):GSH]. Similar results were obtained on varying the initial

concentrations of the Zn(II) keeping the concentration of Ln(III):GSH fixed and the rates comes out first order dependence on concentration of Zn(II). Hence the complexation was found to be of second order. Based on the observations the it can be conclude that one equivalent of Zn(II) interact with one equivalent of $Pr_2(GSH)_2(H_2O)_4$ and $Nd_2(GSH)_2(H_2O)_4$ and the reaction may be given as:

$$Ln_2(GSH)_2(H_2O)_4 + Zn(II) \xrightarrow{k} Ln_2(GSH)_2Zn(H_2O)_6$$

The rate law is

$$\text{Rate} = k[Ln_2(GSH)_2(H_2O)_4][Zn(II)]$$

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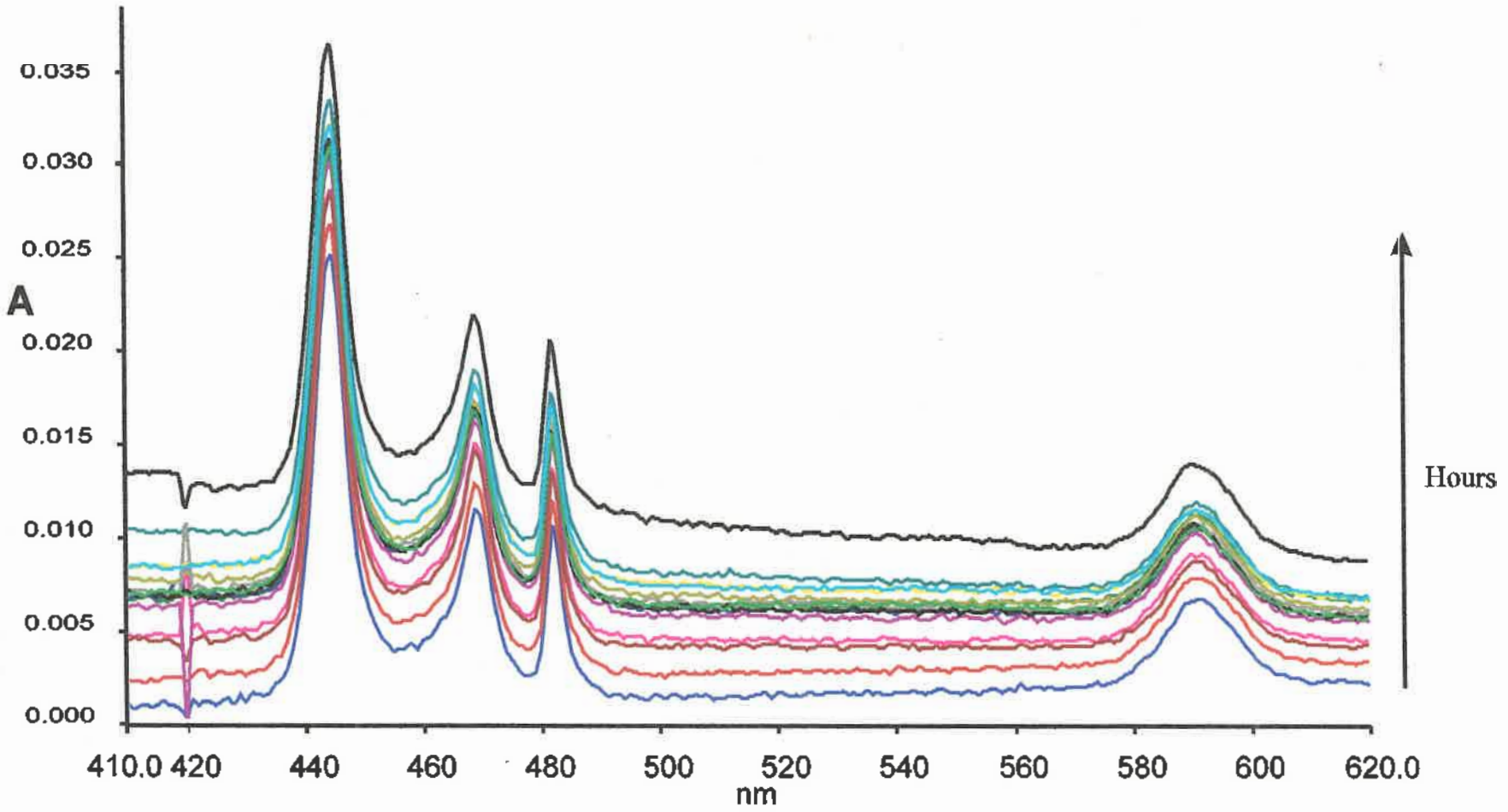

Figure 6.1 : Comparative absorption spectra of Pr(II)I:GSH complexation with Zn(II) in DMF at 303K (30^{0}C) and at different times (hour)

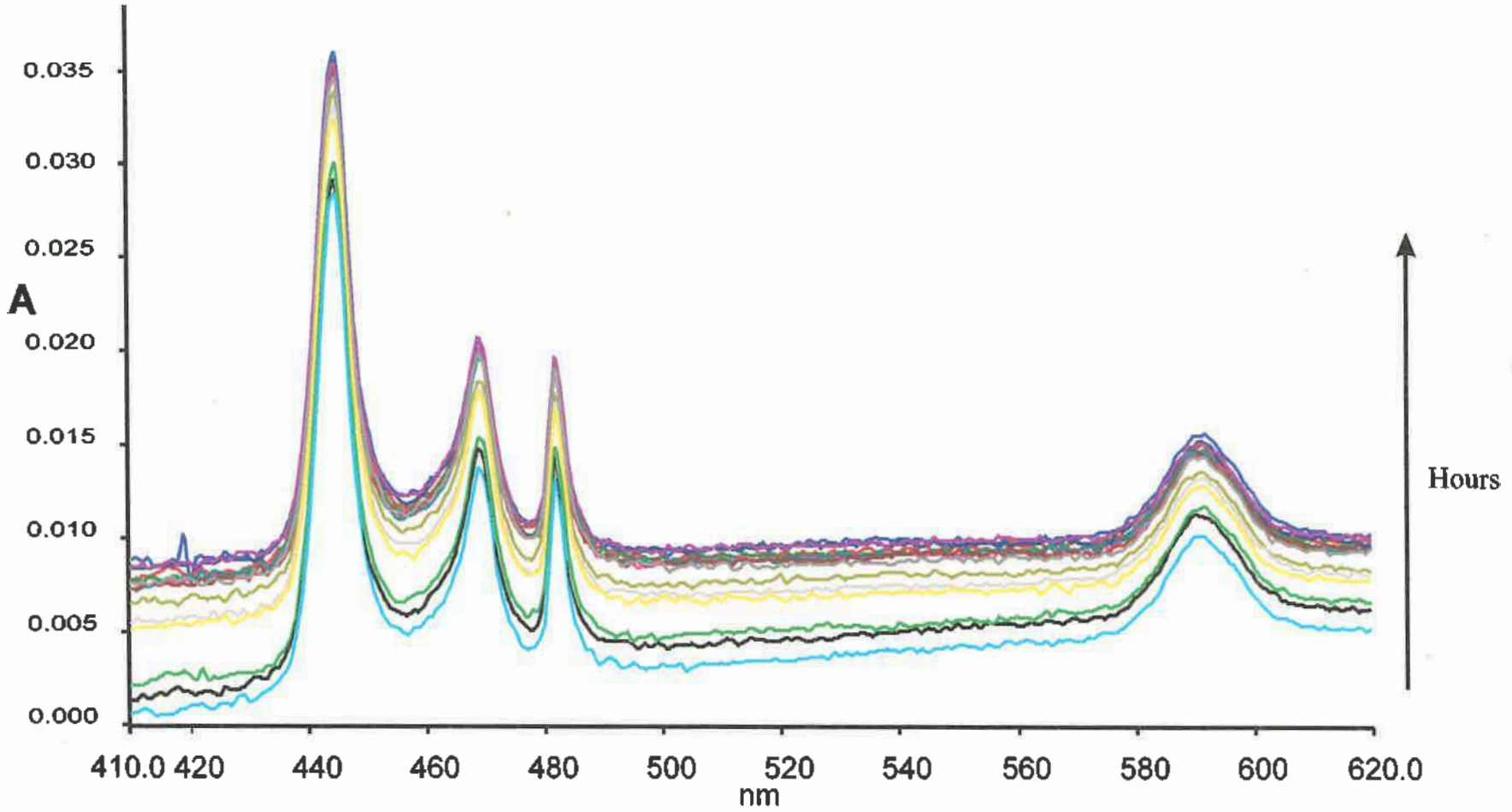

Figure 6.2 : Comparative absorption spectra of Pr(II)I:GSH complexation with Zn(II) in DMF at 308K (35°C)and at different times (hour)

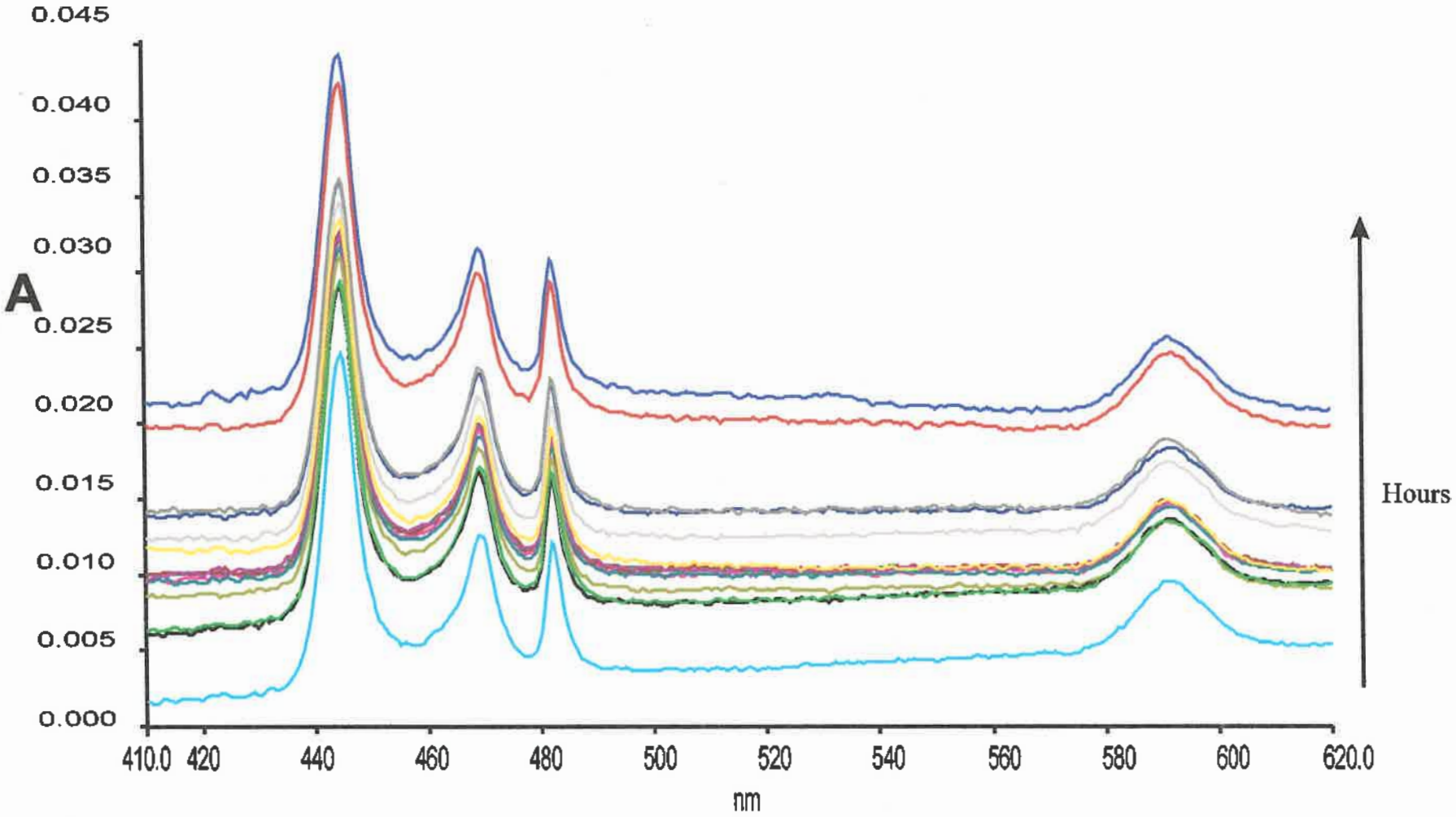

Figure 6.3 : Comparative absorption spectra of Pr(III):GSH complexation with Zn(II) in DMF at 313K (40°C) and different times (hour)

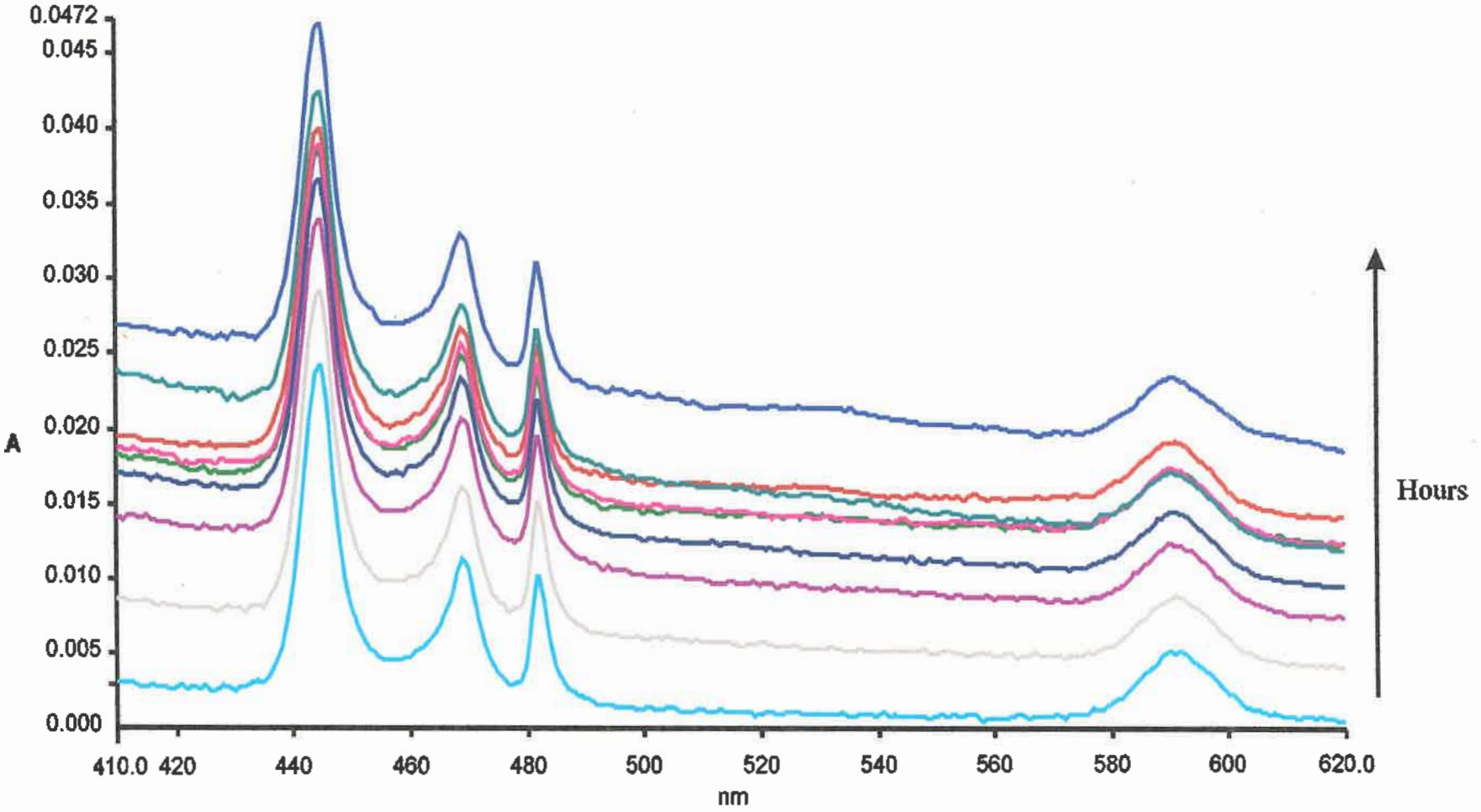

Figure 6.4 : Comparative absorption spectra of Pr(III):GSH complexation with Zn(II) in DMF at 318K (45°C)and at different times (hour)

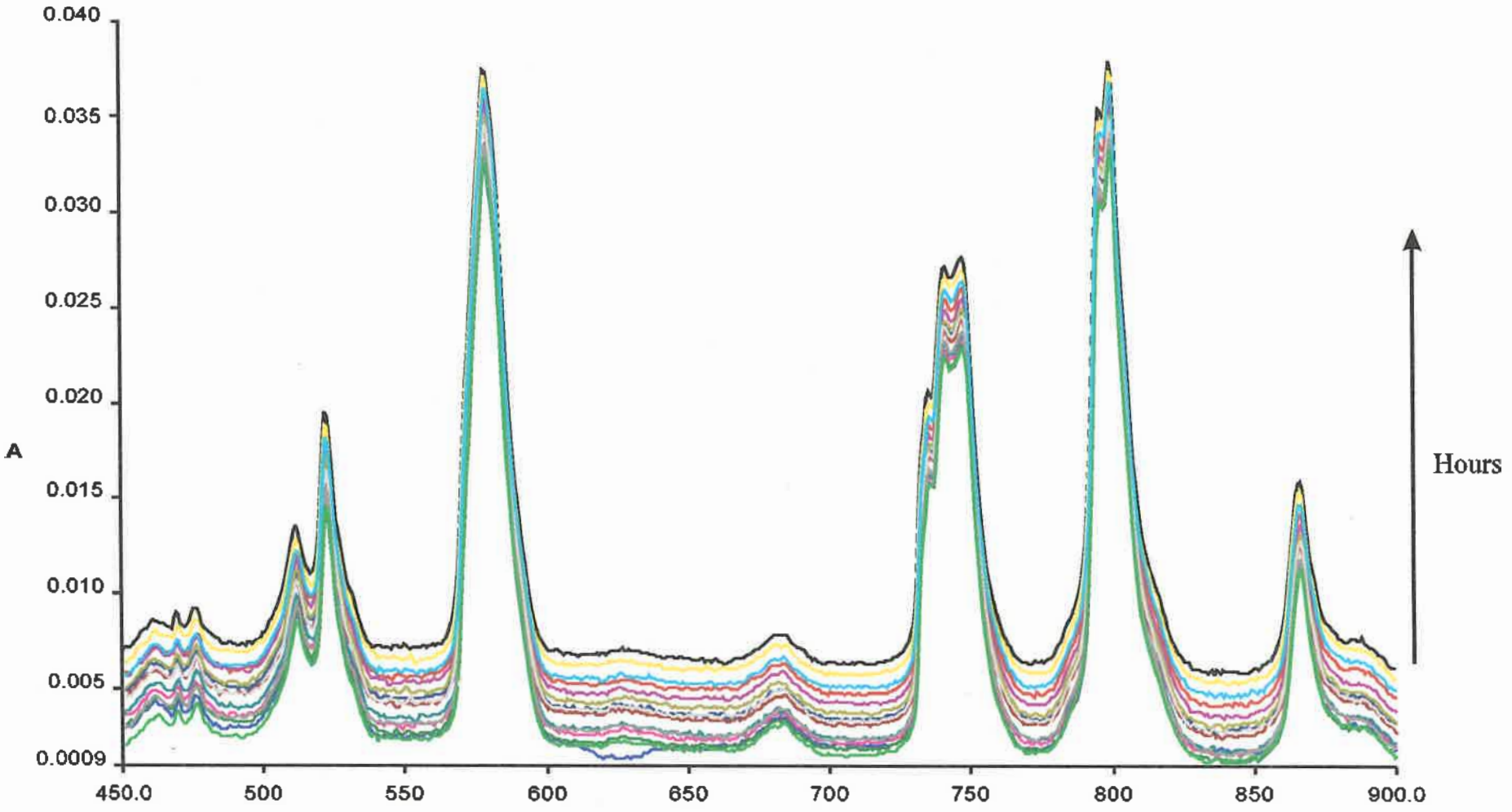

Figure 6.5 : Comparative absorption spectra of Nd(III):GSH complexation with Zn(II) in DMF at 303K (30^{0}C)and at different times (hour)

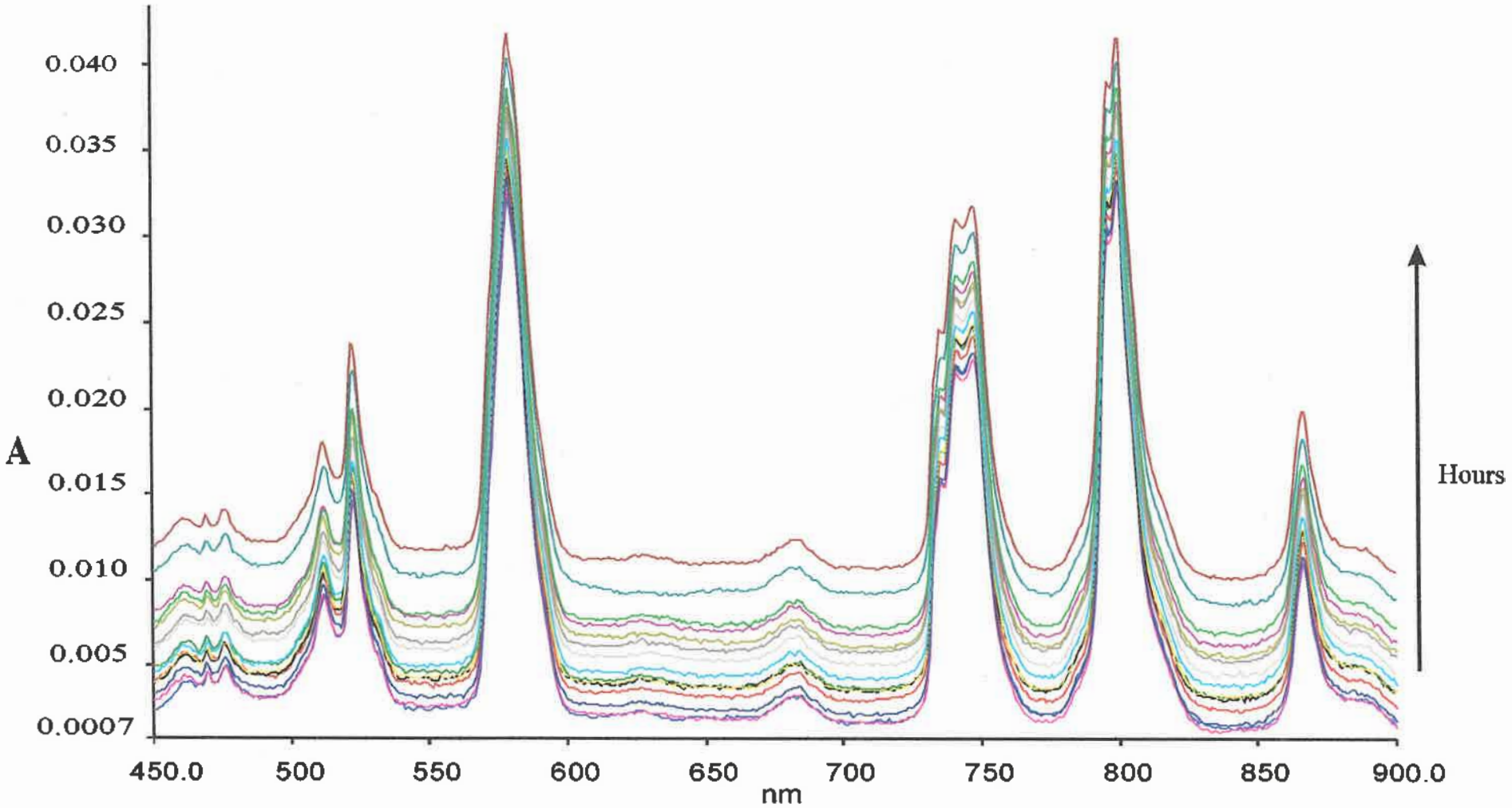

Figure 6.6 : Comparative absorption spectra of Nd(III):GSH complexation with Zn(II) in DMF at 308K (35°C)and at different times (hour)

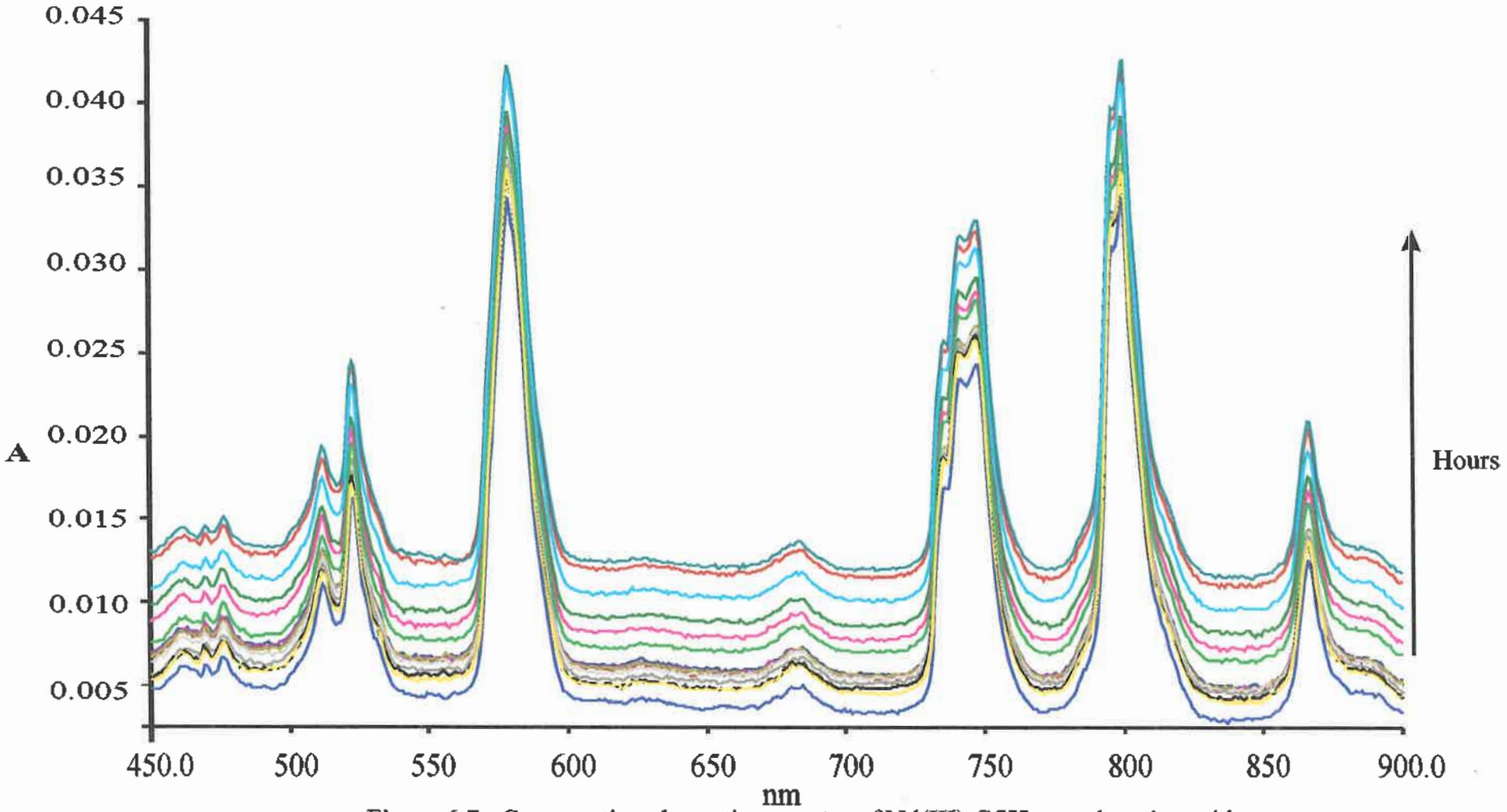

Figure 6.7 : Comparative absorption spectra of Nd(III):GSH complexation with Zn(II) in DMF at 313K (40°C)and at different times (hour)

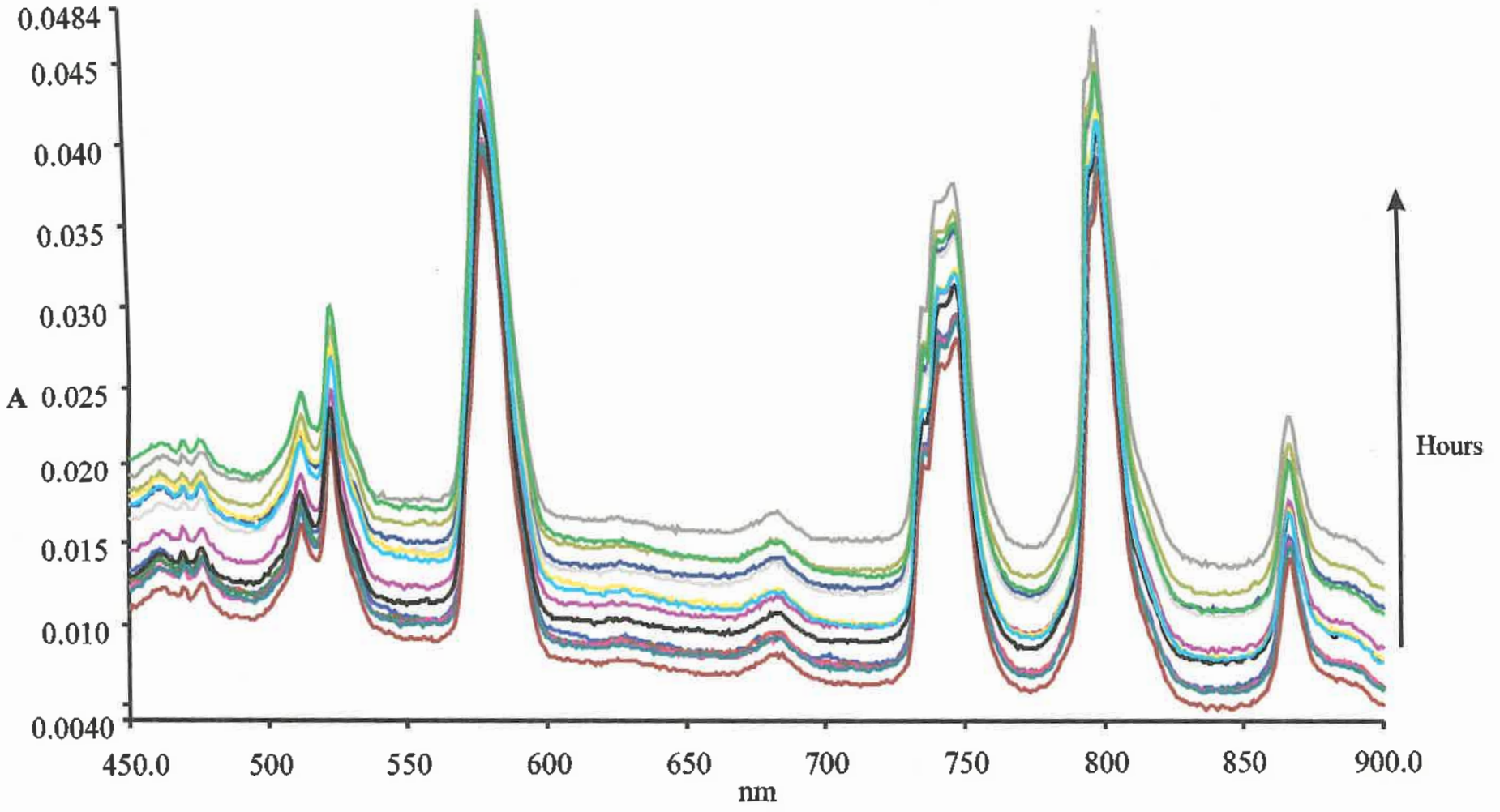

Figure 6.8 : Comparative absorption spectra of Nd(III):GSH complexation with Zn(II) in DMF at 318K (45^{0}C)and at different times(hour)

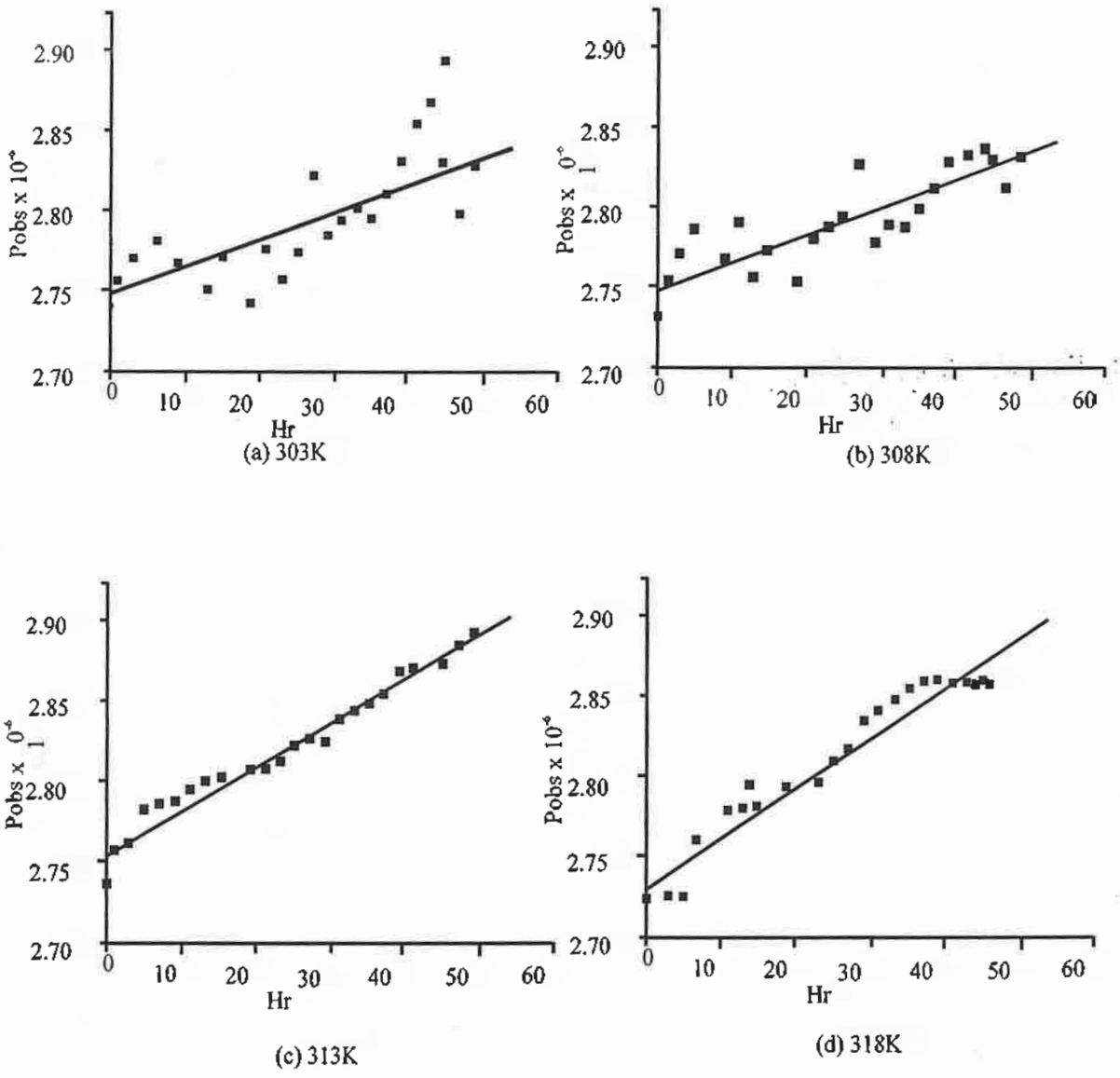

Figure 6.9 : Plot of oscillator strengths (Pobs) versus time (hr) for $^3H_4 \rightarrow {}^3P_2$ transition of Pr(III):GSH complexation with Zn(II) at DMF at different temperatures (a) 303K, (b) 308K, (c) 313K and (d) 318K

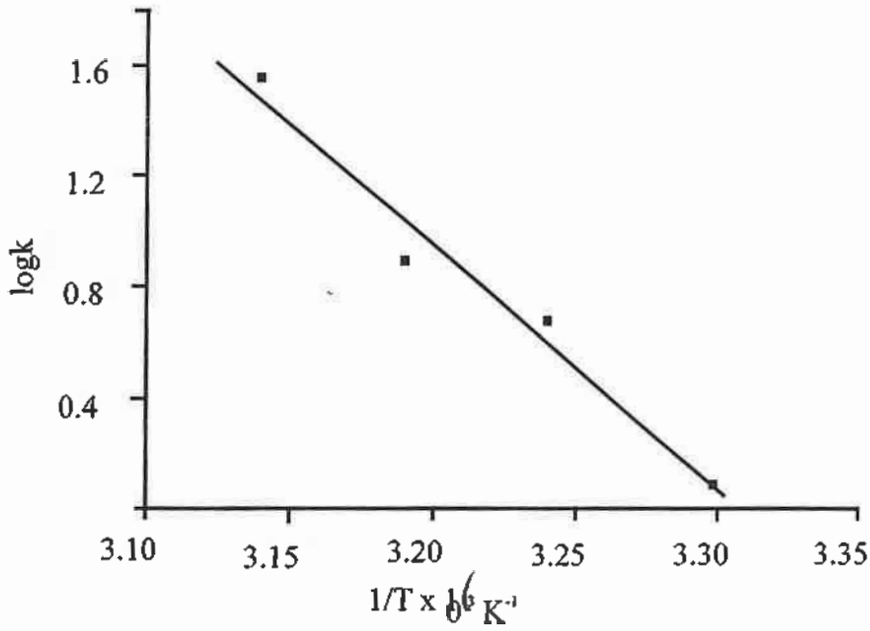

Figure 6.10 : Plot of logk versus 1/T for the complexation of Pr(III):GSH and Zn(II) in DMF medium

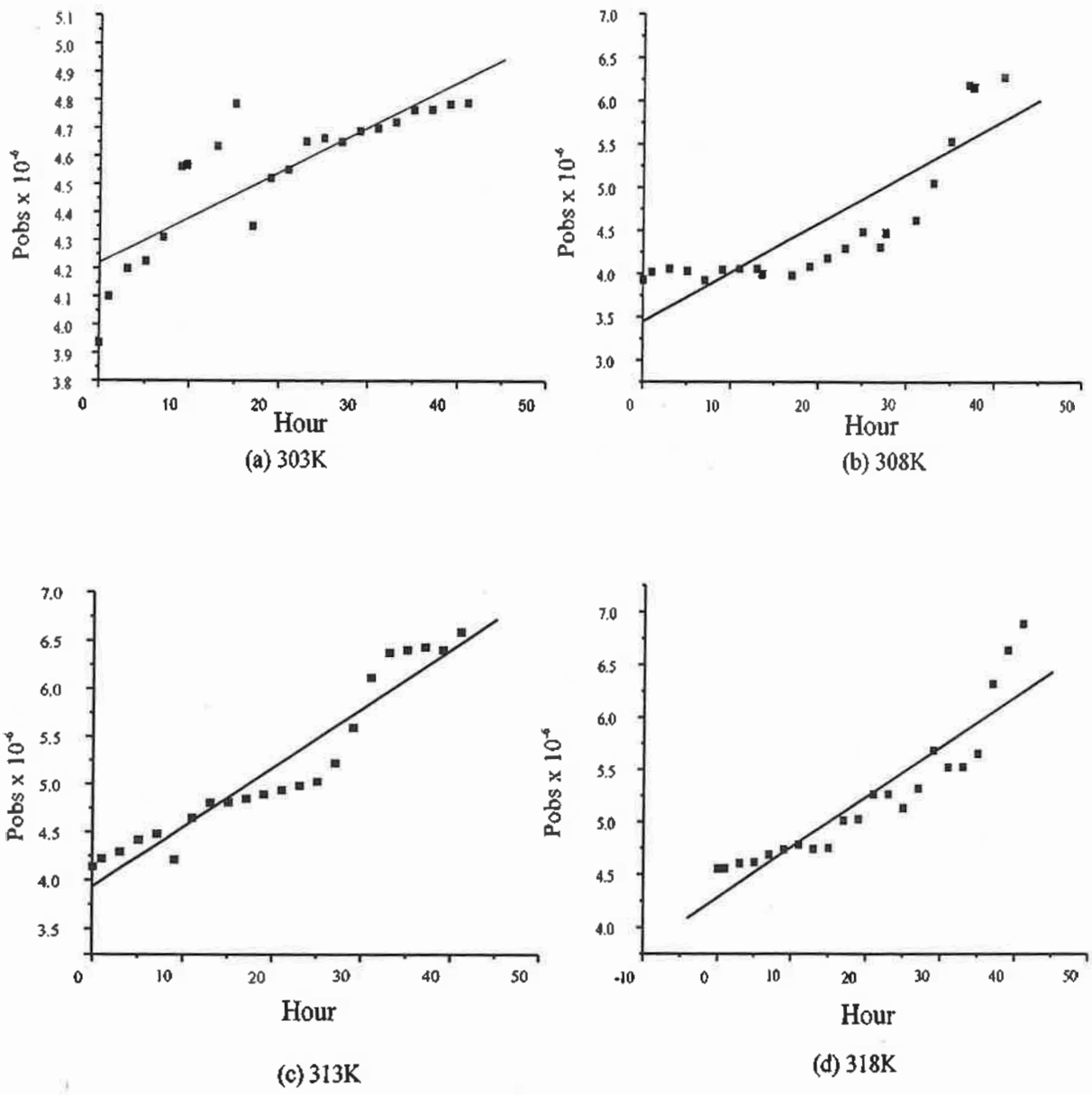

Figure 6.11 : Plot of oscillator strengths (Pobs) versus time (hr) for $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd(III):GSH complexation with Zn(II) at DMF at different temperatures (a) 303K, (b) 308K, (c) 313K and (d) 318K ⇌

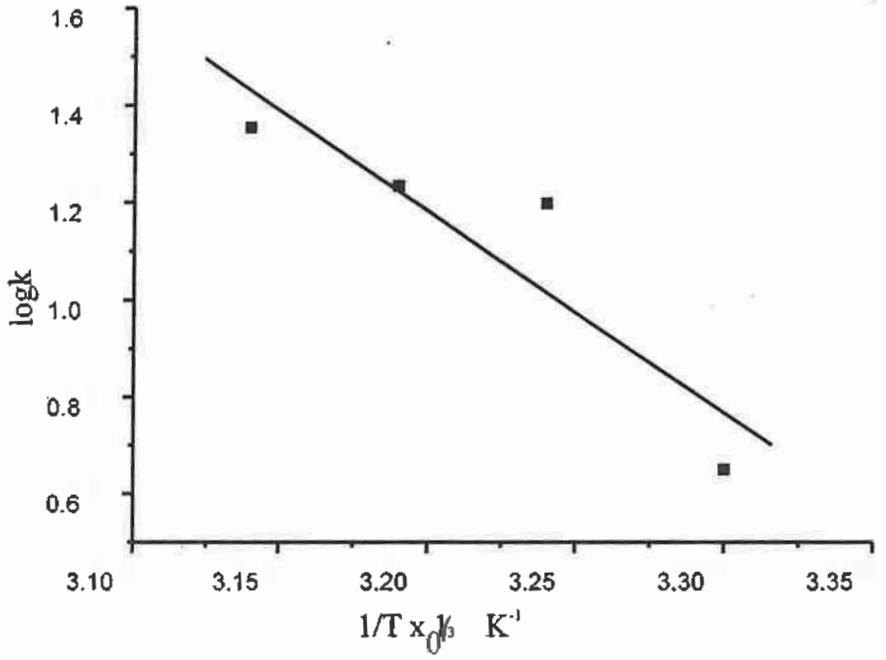

Figure 6.12 : Plot of logk versus 1/T for the complexation of Pr(III):GSH and Zn(II) in DMF medium

Table 6.1: Observed and calculated oscillator strengths (P X 10^6), and Judd-Ofelt intensity parameter (T_λ, λ=2,4,6 X 10^{10})cm^{-1} parameters for Pr(III):GSH:Zn(II) complex at 303K (30^OC) at different time (hr)

Time (hrs)	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
0	.2919	.2919	0.0788	0.0628	0.0462	0.0619	0.0685	0.0685	-3.7974	0.1727	0.9119
1	0.2896	0.2896	0.0772	0.0612	0.0445	0.0603	0.0716	0.0716	-2.9602	0.1682	0.9056
3	0.0716	0.0716	0.0772	0.0612	0.0445	0.0603	0.0716	0.01716	11.3505	0.1682	0.1901
5	0.2966	0.2966	0.0833	0.0659	0.0478	0.0644	0.0799	0.0799	-1.5368	0.1812	0.9252
7	0.2912	0.2912	0.1003	0.0745	0.0480	0.0734	0.0839	0.0839	-0.3341	0.2048	0.9012
9	0.3016	0.3016	0.0818	0.0639	0.0453	0.0629	0.0741	0.0741	-3.1886	0.1756	0.9431
11	0.2950	0.2950	0.0838	0.0648	0.0451	0.0638	0.0777	0.0777	-1.9194	0.1781	0.9206
13	0.2960	0.2960	0.1210	0.0834	0.0451	0.0822	0.0777	0.0777	-2.0461	0.2292	0.9103
15	0.2890	0.2890	0.0790	0.0637	0.0477	0.0628	0.0742	0.0742	-2.2891	0.1751	0.9019
17	0.3016	0.3016	0.0818	0.0639	0.0453	0.0629	0.0741	0.0741	-3.1886	0.1756	0.9431
19	0.2903	0.2903	0.0798	0.0631	0.0458	0.0622	0.0566	0.0566	-6.3863	0.1735	0.9066
21	0.2991	0.2991	0.0758	0.0609	0.0454	0.0600	0.0721	0.0721	-3.4473	0.1675	0.9370
23	0.2918	0.2918	0.0796	0.0639	0.0475	0.0630	0.0785	0.0785	-1.5222	0.1757	0.9109
25	0.2920	0.2920	0.0798	0.0636	0.0468	0.0627	0.0834	0.0834	-0.4059	0.1750	0.9118
27	0.2875	0.2875	0.0466	0.0488	0.0423	0.0441	0.0834	0.0834	-0.0629	0.1230	0 9107
29	0.2821	0.2821	0.1194	0.0816	0.0431	0.0804	0.0866	0.0866	0.9193	0.2242	0.8660

31	0.2994	0.2994	0.1470	0.0964	0.0452	0.0950	0.0742	0.0742	-3.1075	0.2659	0.9118
33	0.3207	0.3207	0.0599	0.0514	0.0423	0.0507	0.0531	0.0531	-9.1539	0.1414	1.0949
35	0.3232	0.3232	0.0626	0.0533	0.0434	0.0525	0.0599	0.0599	-77967	0.1466	1.0217
37	0.3244	0.3244	0.0645	0.0538	0.0425	0.0530	0.0573	0.0573	-8.4329	0.1479	1.0254
39	0.3220	0.3220	0.0591	0.0511	0.0425	0.0504	0.0594	0.0594	-7.8050	0.1405	1.0194
41	0.3254	0.3254	0.0626	0.0526	0.0419	0.0518	0.0674	0.0674	-6.2297	0.1445	1.0292
43	0.3107	0.3107	0.0747	0.0591	0.0428	0.0582	0.0779	0.0779	-2.8988	0.1624	0.9766
45	0.3019	0.3019	0.0736	0.0593	0.0443	0.0584	0.0680	0.0680	-4.5390	0.1630	0.9474
47	0.2953	0.2953	0.0795	0.0627	0.0453	0.0618	0.0801	0.0801	-1.4050	0.1725	0.9233
49	0.2956	0.2956	0.0801	0.0631	0.0454	0.0622	0.0828	0.0828	-0.7616	0.1734	0.9240

Table 6.2 : Observed and calculated oscillator strengths (P X 10^6), and Judd-Ofelt intensity parameter (T_λ, λ=2,4,6 X 10^{10})cm^{-1} parameters for Pr(III):GSH:Zn(II) complex at 308K (35°C) at different time

Time (hrs)	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
0	2.2011	2.2011	0.3220	0.3786	0.4287	0.3730	0.7871	0.7871	33.4428	1.0405	6.9473
1	2.7568	2.7568	0.8321	0.6605	0.4925	0.6654	0.7058	0.7058	-22.6177	1.8156	8.5638
3	0.6402	0.6402	0.1805	0.3391	0.4903	0.3341	0.8003	0.8003	138.4799	0.9319	1.8526
5	2.7867	2.7867	0.7889	0.6233	0.4510	0.6142	0.7580	0.7580	-12.4753	1.7135	8.6902
7	2.8156	2.8156	0.8554	0.6588	0.4555	0.6492	0.8062	0.8062	-3.9752	1.8111	8.7580
9	2.7678	2.7678	0.8418	0.6520	0.4554	0.6424	0.8479	0.8479	8.8951	1.7922	8.6057
11	2.8059	2.8059	0.8494	0.6581	0.4599	0.6483	0.3596	0.3596	-104.6175	1.8087	8.7272
13	2.7510	2.7510	0.3251	0.3989	0.4657	0.3930	0.8578	0.8578	13.1237	1.0963	8.7363
15	2.7720	2.7720	0.8184	0.6359	0.4469	0.6269	0.7697	0.7697	-8.9865	1.7487	8.6319
17	2.8699	2.8699	0.9017	0.6353	0.3636	0.6261	0.7096	0.7096	-28.9248	1.7464	8.9514
19	2.7373	2.7373	0.7589	0.6131	0.4604	0.6040	1.3618	1.3618	128.2075	1.6851	8.5352
21	2.7737	2.7737	0.8436	0.6508	0.4512	0.6412	0.8428	0.8428	7.6298	1.7888	8.6264
23	2.7439	2.7439	0.5524	0.4103	0.2643	0.4043	0.7411	0.7411	-13.2265	1.1280	8.7053
25	2.7333	2.7333	0.8625	0.6652	0.4611	0.6556	0.7965	0.7965	-0.3136	1.8290	8.4841
27	2.8263	2.8263	0.8712	0.7015	0.5240	0.6911	0.7947	0.7947	-7.0571	1.9280	8.7616

29	2.7728	2.7728	0.8733	0.5472	0.2176	0.5385	0.8261	0.8261	3.9949	1.5041	8.6983
31	2.7586	2.7586	0.8808	0.5585	0.2326	0.5502	0.7530	0.7530	-11.8063	1.5349	8.6451
33	2..7826	2..7826	0.8199	0.6527	0.4783	0.6431	0.9042	0.9042	20.6265	1.7940	8.6532
35	2.7928	2.7928	0.8437	0.6540	0.4573	0.6442	0.8159	0.8159	-0.0825	1.7973	8.6885
37	3.0390	3.0390	0.5366	0.4641	0.3859	0.4573	0.4592	0.4592	-96.5181	1.2757	9.6343
39	3.0579	3.0579	0.5746	0.4851	0.3897	0.4779	0.4463	0.4463	-100.9675	1.3332	9.6816
41	3.1825	3.1825	0.3197	0.3795	0.4328	0.3739	0.6050	0.6050	-72.8386	1.0430	10.1675
43	3.1649	3.1649	0.7114	0.5759	0.4341	0.5677	0.8287	0.8287	-21.3954	1.5836	9.9648
45	2.8955	2.8955	0.8209	0.5943	0.3624	0.5856	0.7317	0.7317	-25.9343	1.6337	9.0678
47	2.7968	2.7968	0.6542	0.5657	0.4701	0.5573	0.8127	0.8127	-0.5285	1.5548	8.7655
49	2.8264	2.8264	0.8610	0.6644	0.4611	0.6548	0.7974	0.7974	-6.7196	1.8268	8.7905

Table 6.3 : Observed and calculated oscillator strengths (P X 10^6), and Judd-Ofelt intensity parameter (T_λ, λ=2,4,6 X 10^{10})cm^{-1} parameters for Pr(III):GSH:Zn(II) complex at 313K (40^0C) at different time

Time (hrs)	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
0	2.8581	2.8581	0.8207	0.6436	0.4598	0.6344	0.9478	0.9478	25.7575	1.7695	8.9065
1	2.8269	2.8269	0.8756	0.6888	0.4730	0.6678	0.8935	0.8935	15.6170	1.8630	8.7804
3	2.7019	2.7019	0.8049	0.5125	0.2169	0.5049	0.9122	0.9122	28.6126	1.4084	8.4927
5	2.7587	2.7587	0.7825	0.6137	0.4384	0.6047	0.8103	0.8103	1.3459	1.6870	8.6033
7	2.6725	2.6725	0.7830	0.6170	0.4445	0.6082	0.8400	0.8400	13.4654	1.6967	8.3196
9	2.7640	2.7640	0.8320	0.6462	0.4538	0.6370	0.7998	0.7998	-2.0111	1.7769	8.5975
11	2.7464	2.7464	0.7858	0.6297	0.4667	0.6205	0.7762	0.7762	-5.6554	1.7308	8.5519
13	2.7574	2.7574	0.7833	0.5999	0.4103	0.5910	0.8064	0.8064	0.4397	1.6486	8.6101
15	2.7130	2.7130	0.7942	0.6265	0.4521	0.6173	0.7818	0.7818	-2.6095	1.7220	8.4450
17	2.7640	2.7640	0.8320	0.6462	0.4538	0.6370	0.7998	0.7998	-2.0111	1.7769	8.5975
19	2.7849	2.7849	0.7829	0.6176	0.4456	0.6085	0.8778	0.8778	14.9155	1.6975	14.9155
21	2.7732	2.7732	0.7831	0.6240	0.4581	0.6149	0.9048	0.9048	21.5085	1.7153	8.6880
23	2.7637	2.7637	0.8259	0.6423	0.4518	0.6327	0.7620	0.7620	-10.2086	1.7651	8.6001
25	2.1219	2.1219	0.8787	0.6741	0.4629	0.6646	0.8205	0.8205	45.2458	1.8539	6.4700
27	2.8782	2.8782	0.8277	0.6360	0.4378	0.6268	0.8433	0.8433	0.6828	1.7484	8.9793

29	2.7077	2.7077	0.7996	0.6325	0.4586	0.6233	0.7792	0.7792	-2.8712	1.7389	8.4229
31	2.6783	2.6783	0.8561	0.6428	0.4233	0.6335	0.9156	0.9156	30.1622	1.7672	8.3194
33	1.0039	1.0039	0.8560	0.6588	0.4549	0.6493	0.7951	0.7951	112.6217	1.8112	2.8117
35	2.6530	2.6530	0.8125	0.6440	0.4685	0.6346	0.7349	0.7349	-9.2747	1.7703	8.2361
37	2.6536	2.6536	0.9438	0.7052	0.4592	0.6940	0.8303	0.8303	12.2756	1.9389	8.1911
39	2.7831	2.7831	0.8898	0.6807	0.4650	0.6711	0.7692	0.7692	-9.8316	1.8722	8.6354
41	2.7717	2.7717	0.9246	0.6970	0.4624	0.6867	0.7165	0.7165	-21.3508	1.9157	8.5855
43	2.7831	2.7831	0.8898	0.6807	0.4650	0.6711	0.7692	0.7692	-9.8316	1.8722	8.6354
45	2.8502	2.8502	0.7368	0.5965	0.4496	0.5878	0.7375	0.7375	-21.4847	1.6398	8.9186
47	2.7538	2.7538	0.8279	0.6506	0.4665	0.6412	0.8664	0.8664	14.1684	1.7886	8.5621
49	2.8701	2.8701	0.8373	0.6539	0.4636	0.6443	0.9356	0.9356	21.9044	1.7974	8.9407

Table 6.4 : Observed and calculated oscillator strengths (P X 10^6), and Judd-Ofelt intensity parameter (T_λ, λ=2,4,6 X 10^{10})cm^{-1} parameters for Pr(III):GSH:Zn(II) complex at 318K (45°C) at different time

Time (hrs)	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
0	2.9061	2.9061	0.6398	0.4812	0.3179	0.4741	0.7391	0.7391	-24.0841	1.3227	9.1705
1	2.9853	2.9853	0.7210	0.5853	0.4430	0.5768	0.6402	0.6402	-52.2382	1.6089	9.3675
3	2.8699	2.8699	0.9017	0.6353	0.3636	0.6261	0.7096	0.7096	-28.9248	1.7464	8.9514
5	2.9129	2.9129	0.9155	0.6765	0.4310	0.6665	0.7740	0.7740	-17.7641	1.8593	9.0632
7	3.0652	3.0652	0.6429	0.5292	0.4068	0.5182	0.6309	0.6309	-59.6954	1.4455	9.6740
9	2.8699	2.8699	0.9017	0.6353	0.3636	0.6261	0.7096	0.7096	-28.9248	1.7464	8.9514
11	3.1501	3.1501	0.7190	0.5598	0.3947	0.5516	0.6774	0.6774	-54.7377	1.5386	9.9273
13	2.6912	2.6912	1.8009	1.1115	0.4161	1.0956	0.7122	0.7122	-18.6917	3.0561	80.170
15	2.7967	2.7967	0.6990	0.5560	0.4069	0.5478	0.7244	0.7244	-20.7631	1.5281	8.7720
17	2.8699	2.8699	0.9017	0.6353	0.3636	0.6261	0.7096	0.7096	-28.9256	1.7464	8.9514
19	2.7616	2.7616	0.6562	0.5478	0.4331	0.5399	0.7663	0.7663	-8.8713	1.5061	8.6634
21	2.8699	2.8699	0.9017	0.6353	0.3636	0.6261	0.7096	0.7096	-28.9248	1.7464	8.9514
23	3.4978	3.4978	0.4389	0.4023	0.3604	0.3964	0.5322	0.5322	-110.1641	1.1059	11.1861
25	3.4994	3.4994	0.4139	0.3331	0.2485	0.3281	0.4341	0.4341	-132.2597	0.9153	11.2397
27	3.5086	3.5086	0.4397	0.4169	0.3883	0.4108	0.4305	0.4305	-133.8538	1.1458	11.2109

29	2.8347	2.8347	0.7435	0.5945	0.4389	0.5857	0.8837	0.8837	13.1582	1.6340	8.8680
31	2.8435	2.8435	0.7529	0.6265	0.4928	0.6173	0.7601	0.7601	-15.9233	1.7220	8.8734
33	2.8820	2.8820	0.7810	0.6084	0.4293	0.5994	0.8326	0.8326	-1.9653	1.6721	9.0122
35	2.8571	2.8571	0.7227	0.5857	0.4421	0.5770	0.8796	0.8796	10.2724	1.6096	8.9472
37	2.8803	2.8803	0.7701	0.6142	0.4515	0.6051	0.5832	0.5832	-58.7084	1.6881	9.0032
39	2.8407	2.8407	0.7379	0.5894	0.4345	0.5808	0.7492	0.7492	-17.8816	1.6202	8.8930
41	2.8978	2.8978	0.7308	0.5822	0.4273	0.5737	0.7883	0.7883	-12.9157	1.6003	9.0845
43	2.9048	2.9048	0.7467	0.5909	0.4286	0.5821	0.7908	0.7908	-12.8649	1.6239	9.1016
45	2.9067	2.9067	0.7344	0.5842	0.4277	0.5757	0.7725	0.7725	-17.1403	1.6060	9.1111
47	2.8385	2.8385	0.7642	0.6210	0.4707	0.6118	0.7761	0.7761	-12.2307	1.7067	8.8619
49	2.8748	2.8748	0.7853	0.6202	0.4483	0.6110	0.7976	0.7976	-9.7309	1.7045	8.9816

Table 6.5 : Observed and calculated oscillator strengths (P X 10^6), and Judd-Ofelt intensity parameter (T_λ, λ=2,4,6 X 10^{10})cm^{-1} parameters for Nd:GSH:Zn(III) Complex at DMF at 303K(30^0C) at different time (hr)

Time (hr)	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{9/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		T_2	T_4	T_6
	Posb	Pcal	Posb	Pcal	Posb	Pcal	Posb	Pcal	Pobs	Pcal			
0	2.153	4.5940	3.9356	4.3074	6.3205	2.218	4.2463	6.4917	0.7308	5.0448	2.2089	4.213	16.9691
1	2.2132	1.2000	4.1004	4.1564	5.5192	5.1295	4.0070	4.4907	0.6273	0.5806	2.3065	0.442	10.1 $_{01}$3
3	2.3921	1.4364	4.1989	4.2517	6.2219	6.05	5.1274	5.3614	0.6182	0.7539	2.1794	3.192	10.0183
5	2.6832	1.7783	4.2256	4.8961	7.261	7.1853	6.3291	6.4517	0.7757	0.9842	2.3338	7.216	12.5805
7	3.0587	2.0892	4.3102	5.2763	8.1371	8.2379	7.5478	7.4726	0.8172	1.2082	2.3205	11.355	14.6915
9	3.0628	2.0344	4.5621	5.3999	8.2236	8.2828	7.4642	7.4386	0.7649	1.1356	2.5315	8.350	14.7625
11	3.2085	2.2366	4.5871	5.8052	8.8017	8.9554	8.2176	8.0824	0.8292	1.2693	2.6426	10.647	15.3605
13	3.3356	2.1527	4.6351	6.0498	9.218	9.1415	7.9749	8.1097	0.8543	1.1476	3.0361	5.147	16.1677
15	3.5912	2.3295	4.7865	6.3865	9.8092	9.7561	8.5802	8.6916	0.9252	1.2643	3.1262	7.015	17.7881
17	3.0836	2.2344	4.351	5.658	8.5684	8.8087	8.2276	7.989	0.8079	1.2899	2.4945	12.05	15 $_{.644}$7
19	2.7908	1.7027	4.5214	5.1195	8.5006	8.2476	6.7666	7.0979	0.703	0.8051	2.9234	4.248	14.3701
21	2.2651	1.4845	4.5521	4.3132	6.2488	6.1705	5.3699	5.4905	0.624	0.7921	2.1677	4.147	10.0346
23	2.1195	1.3332	4.6521	3.6142	5.7661	5.6108	4.7885	4.9967	0.6257	0.7247	1.7649	3.941	10.2308
25	2.4853	4.536	4.6642	4.3225	6.3205	2.243	16.463	6.4522	0.7308	4.9821	1.107	182.6	21.6511
27	2.4257	1.2366	4.6512	4.1661	5.5192	5.1137	4.0070	4.5157	0.6273	0.6201	2.2416	2.036	13.6671
29	2.2117	1.4052	4.689	4.2435	6.2219	6.0633	5.1274	5.3402	0.6182	0.7203	2.2339	1.841	10.3851
31	2.1455	1.6856	4.6995	4.8715	7.261	7.2252	6.3291	6.3884	0.7757	0.8842	2.4981	3.184	12.6772
33	1.3021	1.7883	4.721	5.1959	8.1371	8.3697	7.5478	7.2639	0.8172	0.8815	2.8542	1.814	14.2671
35	1.1963	1.7128	4.7654	5.3145	8.2236	8.4223	7.4642	7.2175	0.7649	0.7887	3.0998	5.630	14.5958
37	1.1221	1.8775	4.7665	5.7098	8.8017	9.1117	8.2176	7.8349	0.8292	0.8819	3.2779	4.986	16.652
39	1.0046	1.7527	4.7854	5.9431	9.218	9.3169	7.9749	7.8324	0.8543	0.7151	3.7441	12.29	16.9471
41	0.9181	1.8697	4.7899	6.2642	9.8092	9.9562	8.5802	8.3748	0.9252	0.7676	3.9407	13.019	17.2816

Table 6.6 : Observed and calculated oscillator strengths (P X 10^6), and Judd-Ofelt intensity parameter (T_λ, λ=2,4,6 X 10^{10})cm^{-1} parameters for Nd:GSH:Zn(III) Complex at DMF at 308 K(35^{0}C) at different time (hr)

Time (hr)	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		T2	T4	T6
	Posb	Pcal	Posb	Pcal	Posb	Pcal	Posb	Pcal	Pobs	Pcal			
0	2.14434	0.7815	3.9275	4.4028	1.0221	0.6271	0.6271	1.131	0.6279	0.6838	2.1007	23.7069	8.6895
1	2.23132	0.7463	4.0199	4.5019	0.7547	0.4046	0.4761	0.934	0.5215	0.6563	1.2574	23.5971	4.7855
3	2.13132	0.7483	4.0573	4.4936	0.7556	0.4142	0.4991	0.9431	0.5470	0.6582	1.3323	23.6282	4.9509
5	2.29788	0.7641	4.0314	4.5161	0.8046	0.4352	0.4905	0.9722	0.5397	0.6717	1.399	24.0644	5.2778
7	2.38984	0.8093	3.9223	3.6096	0.8421	0.4722	0.5536	1.0378	0.5647	0.7110	1.4309	25.4239	5.7942
9	2.48299	0.8546	4.0458	4.7057	0.8833	0.4952	0.5856	1.0925	0.6062	0.7500	1.4672	26.8276	6.0586
11	2.73157	0.973	4.0568	4.864	1.0088	0.5706	0.6850	1.2539	0.7211	0.8590	2.2519	30.7067	7.0037
13	2.60001	0.8743	4.0584	4.8437	0.9376	0.5562	0.6420	1.1452	0.5762	0.7561	0.6079	26.8046	7.1316
15	2.77601	0.9568	4.0595	4.8369	0.9939	0.5926	0.7251	1.2545	0.6515	0.8418	2.1026	29.9566	7.4642
17	2.78866	0.9855	3.9817	4.0012	1.0931	0.642	0.7215	1.3071	0.7174	0.8572	1.246	30.3369	8.2927
19	2.0401	0.7214	4.0838	4.5108	0.9342	0.5811	0.5763	1.0309	0.5346	0.6156	0.2703	21.2719	8.1153
21	1.78586	0.6751	4.1811	4.3424	0.7250	0.4197	0.4916	0.8833	0.5297	0.5907	1.1247	21.003	5.3063
23	1.56934	0.5503	4.2975	4.1337	0.5876	0.3149	0.3474	0.6985	0.4181	0.4809	0.6823	17.2096	3.8377
25	2.14434	0.7816	4.4875	4.4027	1.0221	0.6272	0.6271	1.1309	0.6279	0.6838	2.1007	23.7054	8.6899
27	2.23132	0.7462	4.3099	4.5019	0.7547	0.4046	0.4761	0.9339	0.5215	0.6565	1.2558	23.596	4.7847
29	2.13132	0.7484	4.5373	4.4936	0.7556	0.4141	0.4991	0.9431	0.5470	0.6581	1.3351	23.6333	4.9487
31	2.29788	0.764	4.6214	4.5161	0.8046	0.4352	0.4905	0.9722	0.5397	0.6718	1.3974	24.0634	5.2772
33	2.38984	0.8095	5.0523	5.6096	0.8421	0.4723	0.5536	1.0377	0.5647	0.7108	1.4303	25.4118	5.7962
35	2.48299	0.8545	5.5358	6.7057	0.8833	0.4951	0.5856	1.0926	0.6062	0.7501	1.4657	26.8287	6.058
37	2.73157	0.9728	6.1868	6.864	1.0088	0.5706	0.6850	1.2541	0.7211	0.8591	2.2529	30.7146	7.0022
39	2.60001	0.8742	6.7484	6.8437	0.9376	0.5561	0.6420	1.1452	0.5762	0.7561	0.6106	26.8058	7.1313
41	2.77601	0.9566	6.7365	6.8369	0.9939	0.5925	0.7251	1.2547	0.6515	0.8420	2.1027	29.9601	7.4628

Table 6.7 : Observed and calculated oscillator strengths (P X 10^6), and Judd-Ofelt intensity parameter (T_λ, λ=2,4,6 X 10^{10})cm^{-1} parameters for Nd:GSH:Zn(III) Complex at DMF at 313K(40^0C) at different time (hr)

Time	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{9/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		T2	T4	T6
(hr)	Posb	Pcal	Posb	Pcal	Posb	Pcal	Posb	Pcal	Pobs	Pcal			
0	2.9443	1.0387	4.1553	4.9606	1.2228	0.7606	0.84405	1.4461	0.7464	0.90771	2.2419	31.7744	10.2399
1	2.8198	0.9807	4.2386	4.8402	1.0842	0.7104	0.86163	1.3606	0.6363	0.85835	2.2186	30.0819	9.523
3	2.6076	0.9553	4.3098	4.7011	1.0185	0.66	0.83513	1.3092	0.6665	0.84496	2.9496	29.7837	8.6673
5	2.6316	0.9369	4.4329	4.7265	1.073	0.6913	0.80836	1.3105	0.6508	0.82092	2.3278	28.7244	9.323
7	3.0685	1.1379	4.4957	4.1023	1.353	0.9334	1.1028	1.6575	0.7821	0.99063	2.5562	34.241	13.0354
9	4.4332	1.6563	4.2293	4.1464	2.0548	1.3959	1.57016	2.431	1.183	1.43111	2.9384	49.2589	19.6836
11	4.3952	1.674	4.664	4.2143	2.187	1.5248	1.67127	2.5334	1.2072	1.43512	2.4057	48.8524	21.9872
13	4.4234	1.672	4.8215	5.1734	2.167	1.4828	1.61685	2.5053	1.222	1.43887	2.7968	49.1904	21.2211
15	4.3589	1.6533	4.8283	5.1277	2.1127	1.4578	1.61874	2.4722	1.1945	1.42429	2.8647	48.7349	20.8245
17	4.3265	1.6261	4.8657	5.9348	2.0368	1.3999	1.58534	2.418	1.1693	1.41425	3.9992	48.5858	19.822
19	3.9561	1.5115	4.9127	4.8278	1.9511	1.3645	1.51966	2.2849	1.0901	1.30275	2.7831	44.426	19.6075
21	3.7439	1.4263	4.9557	5.5837	1.8032	1.2655	1.44201	2.1465	1.0184	1.23696	3.3391	42.3189	18.0772
23	3.3605	1.283	5.0011	5.3019	1.5293	1.0445	1.23285	1.8676	0.9285	1.12201	3.423	38.8253	14.5377
25	2.9443	1.0387	5.0453	5.9606	1.2228	0.7607	0.84405	1.4461	0.7464	0.90771	2.2401	31.7718	10.2397
27	2.8198	0.9806	5.2386	5.8402	1.0842	0.7104	0.86163	1.3606	0.6363	0.85838	2.2184	30.0831	9.5235
29	2.6076	0.9553	5.6098	5.7011	1.0185	0.66	0.83513	1.3092	0.6665	0.84496	2.9483	29.7834	8.6686
31	2.6316	0.9367	6.1329	5.7265	1.073	0.6913	0.80836	1.3107	0.6508	0.82108	2.3256	28.7285	9.3201
33	3.0685	1.1382	6.3957	5.1023	1.353	0.9335	1.1028	1.6573	0.7821	0.99033	2.5532	34.2229	13.0363
35	4.4332	1.6556	6.423	6.1465	2.0548	1.3956	1.57016	2.4315	1.183	1.43178	2.9439	49.2866	19.6735
37	4.3952	1.6737	6.4524	6.2143	2.187	1.5246	1.67127	2.5339	1.2072	1.43522	2.4026	48.8569	21.9853
39	4.4234	1.6718	6.4215	6.1734	2.167	1.4828	1.61685	2.5055	1.222	1.43909	2.7939	49.1947	21.2176
41	4.3589	1.6527	6.6083	6.1278	2.1127	1.4577	1.61874	2.4724	1.1945	1.4248	2.861	48.7407	20.8222

Table 6.8 : Observed and calculated oscillator strengths (P X 10^6), and Judd-Ofelt intensity parameter (T_λ, λ=2,4,6 X 10^{10})cm^{-1} parameters for Nd:GSH:Zn(III) Complex at DMF at 318 K(45°C) at different time (hr)

Time (hr)	$^4I_{9/2} \rightarrow {}^4G_{7/2}$		$^4I_{9/2} \rightarrow {}^4G_{5/2}$		$^4I_{9/2} \rightarrow {}^4F_{7/2}$		$^4I_{9/2} \rightarrow {}^4F_{9/2}$		$^4I_{9/2} \rightarrow {}^4F_{3/2}$		T2	T4	T6
	Posb	Pcal	Posb	Pcal	Posb	Pcal	Posb	Pcal	Pobs	Pcal			
0	7.1473	2.3912	4.5534	4.8163	2.3891	1.5121	1.9547	3.1434	1.43	2.08731	3.4607	74.0834	19.273
1	6.6908	2.2961	4.5564	4.5792	2.3708	1.5313	1.9441	3.0756	1.4203	2.00024	3.4418	70.6272	19.9523
3	6.7886	2.2844	4.6050	4.5338	2.2601	1.4618	1.9287	3.0176	1.3446	1.99562	3.7562	70.7667	18.7171
5	6.7997	2.2869	4.6147	4.5139	2.3422	1.4882	1.8878	3.0405	1.3954	1.99797	3.8846	70.7373	19.1849
7	6.7012	2.2434	4.6873	4.4537	2.2206	1.4302	1.8838	2.9622	1.317	1.96246	3.7166	69.6277	18.2773
9	6.8510	2.3034	4.7364	4.5076	2.2993	1.4833	1.9429	3.0537	1.3681	2.01615	4.2475	71.4602	19.0274
11	6.9341	2.3942	4.7831	4.6839	2.3664	1.526	2.0252	3.1635	1.4737	2.09705	4.4685	74.3996	19.488
13	6.6693	2.3051	4.7415	4.5926	2.35	1.5396	1.992	3.0891	1.4107	2.00784	3.4868	70.9058	20.0679
15	6.9063	2.3564	4.7513	4.6927	2.4534	1.6133	2.047	3.1853	1.4226	2.0494	3.4811	72.1998	21.2409
17	6.5288	2.2497	5.0124	4.438	2.2871	1.4839	1.9212	3.0068	1.3875	1.96617	3.8251	69.5354	19.2269
19	6.3278	2.1797	5.0268	4.31	2.2195	1.4475	1.8737	2.9185	1.3362	1.90272	3.5832	67.2359	18.8139
21	6.0361	2.0348	5.2649	4.022	2.0308	1.2955	1.6889	2.6862	1.2258	1.78108	3.5025	63.1796	16.5437
23	12.825	4.768	5.2674	9.4024	5.2358	3.6461	4.5862	6.7181	3.1084	4.12536	6.7685	143.6015	49.9317
25	7.1473	2.3917	5.1334	5.8161	2.389	1.5124	1.9547	3.1431	1.43	2.08665	3.4448	74.0493	19.2831
27	6.6908	2.2957	5.3214	5.5793	2.3708	1.5312	1.9441	3.0757	1.4203	2.00077	3.449	70.6487	19.9458
29	6.7886	2.2841	5.6850	5.5339	2.2601	1.4617	1.9287	3.0179	1.3446	1.99583	3.7548	70.7755	18.7134
31	6.7997	2.2866	5.5247	5.514	2.3422	1.4881	1.8878	3.0407	1.3954	1.99839	3.8823	70.7479	19.1791
33	6.7011	2.2436	5.5263	5.4536	2.2206	1.4303	1.8838	2.9619	1.317	1.96232	3.7167	69.6167	18.274
35	6.8510	2.3025	5.6544	6.5078	2.2993	1.4828	1.9429	3.0544	1.3681	2.01727	4.261	71.5129	19.011
37	6.9341	2.393	6.3211	6.6841	2.3664	1.5256	2.0252	3.1641	1.4737	2.09855	4.4771	74.4384	19.4759
39	6.6693	2.3051	6.6415	6.5926	2.35	1.5396	1.992	3.0891	1.4107	2.00773	3.4849	70.9011	20.071
41	6.9063	2.3555	6.8913	6.6928	2.4534	1.6129	2.047	3.1861	1.4226	2.05049	3.4847	72.2306	21.228

Table 6.9 . Values of rate c onstantof k ($MolL^{-1}s^{-1}$) for log k for thecomplexation of Pr(III):GSH and Zn(II) at di fferenttemp eratures and activation en ergy, Ea

Temp (K)	Rate Constant Mol $L^{-1}hr^{-1}$	Rate Constant (k) Mol $L^{-1}s^{-1}$	logk	1/T, K^{-1} ($x10^3$)	Activation Energy Ea (kJ)
303	0.0004	1.2139	0.0842	3.30	166.99
308	0.0017	4.7780	0.6790	3.24	
313	0.0028	7.6944	0.8862	3.19	
318	0.0130	36.0000	1.5563	3.14	

Table 6.10 . Values of rate c onstantof k ($MolL^{-1}s^{-1}$) for log k for the complexation of Nd(III):GSH and Zn(II) at di fferenttemp eratures and acti vation energy, Ea

Temp (K)	Rate Constant(k) Mol $L^{-1}hr^{-1}$	Rate Constant (k) Mol $L^{-1}s^{-1}$	logk	1/T, K^{-1} ($x10^3$)	Activation Energy (kJ)
303	0.0161	4.47	0.6503	3.30 Ea	79.38
308	0.0569	15.80	1.1987	3.24	
313	0.0619	17.19	1.2353	3.19	
318	0.0815	22.64	1.3549	3.14	

CHAPTER 7
S ummary an dconclusio n

The biological fluids are basically multimetal-multiligand system with abundance of organic and inorganic species present in micro, sub-micro and mili-molar concentration with fluctuating lipophilicity and lipophobicity in widely divergent physiological pH. These multidimensional characteristics of the biological fluids provide platforms for a number of TEMPLATE synthesis, homogeneously catalyzed transformations, redox reactions, influx and efflux of ionic and molecular species both intra- and extra- cellularly. Thus these immensely important biological fluids are essentially multimetal- multiligand systems, where a number of endogenous metal ions compete with the coordinating sites of multidentate macromolecular metabolites and multidonor sites also experience strong competition for different metal sites. Thus the binding of metal to a particular donor site of the biomolecules depends upon a number of factors like donor capability, structure, conformation, orientation, physiological pH, presence of similar type of metal ions and their relative abundance. It is considered therefore worthwhile to study the simultaneous coordination of two or three different metal ions with a multidentate biological

molecule with immense biological relevance. We have chosen a very important polypeptide glutathione reduced (GSH) which in its reduced form is a tripeptide with active carboxylate groups, a sulphydryl group and peptide groups, which has total eight potential donor binding sites for endogenous metal ion complexation.

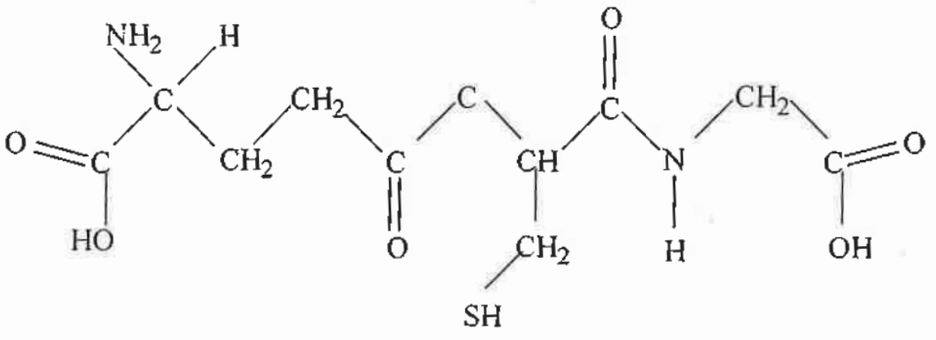

Figure 6.01 Structural Formula of Glutathione

The coordination chemistry of glutathione, not only is of interest as it serves as an indicator for the chemistry of thiol-sulphide interchange reactions, as well as in understanding toxicology of several metals, but it is equally relevant in understanding large number of biological functions.

Quantitative absorption spectral analysis involving 4f—4f transition absorption difference and comparative absorption difference spectroscopy has been used by us as PROBE to follow the simultaneous coordination of two or three chemically different metals in tri-nuclear simultaneous coordination of glutathione reduced GSH in aqueous and in aquated organic solvents at different pH is an attempt to MIMIC the *in vivo* complexation of the

GLUTATHIONE (GSH) with endogenous metal ions like Ca(II) and Zn(II). We also study the kinetics for the complexation of Pr(III)/Nd(III): GSH with Zn(II) at aquated DMF medium at different temperatures (303K, 308K, 313K and 318K). Glutathione has been chosen because of easy availability in pure form the molecule is of immense biological relevance and it is a very good ligand for simultaneous complexation by both hard metal ions [Mg(II) and Ln(III)) and soft metal (Zn(II), Cd(II) and Cu(II)] ions. It is an excellent multi-dentate ligand for metal ions offering eight potential binding sites two carboxylate oxygen, one amino nitrogen, a sulphydryl group and two amine groups. The structure of glutathione is such that all its potential binding sites cannot be coordinated to the same metal ions and therefore the coordination chemistry of this multidentate biomolecule is characterized by the formation of protonated and polynuclear species.

The 4f electrons of lanthanides yield three types of transitions:

i) Internal 4f— 4f transitions, which give, rise to sharp narrow bands of comparatively weak intensities such transitions are Laporte-forbidden in nature.

ii) Allowed $4f^n$- $4f^{n+1}$ (n -1)d which are relatively broad and intense.

iii) Broad and often very intense $4f^n$ - λ^{-1} f^{n+1}electron transfer bands generally occurring in the ultraviolet region (λ^{-1} represents a hole in the orbital concentrated mainly on ligands).

The presence of internal 4f electron transition spectra in the accessible spectral region for the most of the lanthanides and the sensitivities of such transitions towards immediate coordination environment, makes quantitative absorption spectroscopy involving 4f-4f transitions a powerful tool in the investigation of coordination chemistry and biochemistry of lanthanides specially in solutions.The ground state for Nd^{3+} ion is $^4I_{9/2}$ and Pr(III) is $^3H_4$. Since coulombic and spin orbit coupling represent major interaction between equivalent 4f electrons, the second order configuration interaction should be included for highly accurate spectral work. To do this one requires the inclusion of higher energy configurations into ground state configuration via electrostatic repulsion terms. For the atom with N-electrons, and the Ze nuclear charge, the non-relativistic Hamiltonian can be written as,

$$H = \sum_{i=1}^{N} \frac{Pi^2}{2m} - \sum_{i=1}^{N} \frac{Ze^2}{r_i} + \sum_{K}^{N} \frac{Pe^2}{r_{ij}}$$

Where the first term represents the kinetic energy of all the electrons, the second term represents the nuclear electrical field and the third term describes the repulsive coulombic potential between pairs of electrons.

The central field Hamiltonian,

$$H_{CF} = \sum_{i=1}^{N} \frac{Pi^2}{2m} + U_{(ri)}$$

The energy levels are found to be highly degenerate, however by the inclusion of covalency and perturbing effect, the degeneracy may be lifted. The important perturbation of f electrons can be evaluated as:

$$H - H_{CF} = \sum_{i=1}^{N} \left[\frac{Ze^2}{2m} - U_{(ri)} \right] + \sum_{i<1}^{N} \frac{e^2}{r_{ij}}$$

The energy levels of electrostatic interactions are generally written in terms of Slater integrals.

$$F^k = e^2 \int_0^a \frac{r_<^K}{r_<^{K+1}} \left[R_{4f}(r_i) R'_{jf} R_{4f}(r_j) \right]^2 dr_i dr_j$$

Where r< and r> are the smaller and larger radius r_i and r_j, k and R must be even and $k \leq 2l$

The area under the absorption band is a better measure of the intensity of the absorption band than the molar absorptivity at the peak maximum, because it is the same for the resolved, partly resolved or even unresolved hand. The area under the curve determined by integrating

the peak, which is equivalent to the calculation of the integral.

$$\int \varepsilon(\bar{\nu}) d\bar{\nu}$$

where $\bar{\nu}$ is the wave number

The integrated molar absorptivity can be seen as the sum of $\varepsilon(\bar{\nu})$ values over whole absorption band, instead of molar absorptivity, the dipole strength D or the Oscillator strengths P are reported. The molar absorptivity $\varepsilon(\bar{\nu})$ at a wave number $\bar{\nu}$ is related to the dipole strength by.

$$\varepsilon(\bar{\nu}) = \frac{8\pi^2}{hc} \cdot \frac{N_A}{2303} \int f(\bar{\nu}) \nu\nu$$

$$\varepsilon(\nu) = \frac{8\pi^2}{hc} \cdot \frac{N_A}{2303} \int f(\bar{\nu}) \bar{\nu} D'$$

where

N_A — Avogadro number = 6.02214 x 10^{23} $f(\bar{\nu})$ — line shape function

h — Planck Constant = 6.625 54 x 1 0^{-27} ergs D' — Dipole strength

c — Velocity of light = 2.997925 x 10^{10} cm/s

The oscillator strength P of a 4f — 4f transition can be given by,

$$P = \frac{8\pi^2 m_e c^2}{he^2} \cdot \frac{2303hc}{8\pi^2 N_A} \int \varepsilon(\bar{\nu}) d\bar{\nu}$$

$$= \frac{2303 m_e c^2}{N_A \pi e^2} \int \varepsilon(\bar{\nu}) d\bar{\nu}$$

$$P = \frac{2.303 \times (9.10904 \times 10^{-28}) \times (2.997925 \times 10^{10})^2}{(6.02214 \times 10^{23}) \times 3.14159 \times (4.803 \times 10^{-10})^2} \int \varepsilon(\bar{\nu}) d\bar{\nu}$$

$$P = 4.32 \times 10^{-9} \int \varepsilon(\bar{\nu}) d\bar{\nu}$$

Above is the simplest representation of oscillator strength. The oscillator strength of the induced electric dipole transition is related to the energy of

transition (σ) square of the matrix element of unit tensor operator $U^{(\lambda)}$, connecting initial $\langle f^N \psi J$ and final $|f^N \psi' J'$ through three phenomenological parameters T_λ or $\Im_\lambda$ (λ =2, 4, 6). These parameters are related to the radial wave function of the state, and the ligand field parameters that characterize the environmental field (Carnall et al 1965).

$$P = \sum_{\lambda=2,4,6} \Im_\lambda \sigma \left\langle f^N \psi J \middle\| U^{(\lambda)} \middle\| f^N \psi' J' \right\rangle^2$$

Judd used T,. parameters instead 3,, used by Carnall et al,

$$T_\lambda = \Im_\lambda (2J+1)^{-1}$$
$$P = \sum_{\lambda=2,4,6} T_\lambda \left\langle f^N \psi J \middle\| U^{(\lambda)} \middle\| f^N \psi' J' \right\rangle^2 (2J+1)^{-1}$$

For calculating matrix elements U the eigen vectors were of the form,

$$f^N \psi = \sum_{\alpha SL} \xi^{\alpha SL} |\alpha^{SLJ}$$

and can be calculated by diagonalizing the complete energy matrices.

In order to define energy interaction parameters, we have to calculate four terms F_2, F_4, F_6 and ξ_{4f}, since we have been using five main multiplet to multiplet transition manifolds for our calculation and therefore the above four terms can be solved using following equation.

$$E_{oj} = \sum_{k=2,4,6} \frac{\delta E_j}{\delta F_k} \Delta F_k + \frac{\delta E_j}{\delta \xi_{4f}} \Delta \xi_{4f}$$

By considering F_k's and ξ_{4f} as empirical parameters derived from least square fit of the experimental energy levels of Nd(III) ion, which is either free of complexed. Solutions of the equations taking into account the reported values given by Wong, for F_2^0, F_4^0, F_6^0 and ξ_{4f}^0 gave parameters for Slater Condon integrals. In our complexes, we expected the metal ion radius expanded and thus lowering the values F_k and ξ_{4f} parameter than the values F_k^0 and ξ_{4f}^0. This would give β value less than unity (i.e. nephelauxetic effect 1-β) and values of bonding parameter (b) positive, we have used partial and multiple regression method and the values for zero order energies, and the partial derivatives (Wong's values) and computed F_k (k = 2, 4, 6) and ξ_{4f} parameters and determined values for β, b and δ all nephelauxetic bonding and covalency parameters.

$$E_{obs} = E_{oj} + \frac{\delta E_j}{\delta F_2}\Delta F_2 + \frac{\delta E_j}{\delta F_4}\Delta F_4 + \frac{\delta E_j}{\delta F_6}\Delta F_6 + \frac{\delta E_j}{\delta \xi_{4f}}\Delta \xi_{4f}$$

Dividing the above equation by we get

$$\frac{E_{ob} - E_{oj}}{\delta E_j/\delta\delta_2} = F_2 + \frac{\delta E_j/\delta\delta_4}{\delta E_j/\delta\delta_2}\Delta F_4 + \frac{\delta E_j/\delta\delta F}{\delta E_j/\delta\delta_2}\Delta F_6 + \frac{\delta E_j/\delta\delta_{4f}}{\delta E_j/\delta\delta_2}\Delta \xi_{4f}$$

We evaluate four intensity parameters P, T_2, T_4, T_6 and four energy interaction parameters F_2, F_4, F_6 and ξ_{4f} by employing partial multiplet regression method using least square fit procedure (discussed in detail in chapters 2).

The $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd^{3+} is universally acceptable as HYPERSENSITIVE. Birnbaum and coworkers utilized significant changes in

the shape of intensity and oscillator strength of hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd(lII) as a spectral probe in exploring the binding of Nd(III) with bovine serum albumin by employing absorption difference spectrophotometry involving 4f — 4f transitions. This transition showed marked variation and extreme sensitivity towards even minor coordination changes around Nd(III). Bukietynska and Mondry used oscillator strength of hypersensitive transition as a MARKER band and the magnitude and variation of Judd - Ofelt electric dipole intensity parameters (Tx) in diagnosing the involvement of amino carboxylic group in the inner sphere of coordination.

The transitions other than the hypersensitive transition were generally considered to be almost insensitive and hence of little relevance. During the course of our studies involving spectra of Pr(III) and Nd(III), we have found that the complexes formed by variety of ligands with widely different binding characteristics induced substantial sensitivity to the nonhypersensitive transitions (earlier considered insensitive). The transitions $^3H_4 \rightarrow {}^3P_2, {}^3P_1, {}^1D_2$ in Pr(III) and $^4I_{9/2} \rightarrow {}^4G_{7/2}, {}^4G_{7/2}$ of Nd(III) are such transitions which do not follow selection rules and as such cannot he considered as hypersensitive transition. but showed wide variation of their oscillator strength and high sensitivity by the complexes of Nd(lII) formed by even structurally related ligands. We have given the name 'Ligand Mediated Pseudohypersensitivity' (LMP) for such observations and referred these nonhypersensitive transitions as pseudohypersensitive. In the present thesis, we have used absorption difference

and comparative absorption spectrophotometry as probe in extracting information regarding the binding modes of glutathione reduced (GSH) in different solvents towards Ln(III), in presence and absence of soft metal ions like Zinc(II).

From both the studies of energy interaction parameters and intensity parameter (Judd-Ofelt parameter, T_λ, λ=2,4,6) at different pH (pH3, pH4, pH5 and pH6), it is found that maximum intensification is found in pH6 and from the data at different solvents it is found that maxium intensification and red-shift is found in DMF (dimethyl formamide) and least in methanol. This is due to the maxium participation of N-donating site of DMF in complexation. From the kinetic studies for the formation of $Ln_2(GSH)_2Zn(H_2O)_6$, it is found that the order of the complexation with relate to the concentration of Ln(III):GSH is one and with relate to the concentration of Zn(II) is also one. So the complexation of Ln(III):GSH with Zn(II) is second order reactions. From the rate data of the complexation at different temperatures (303K, 308K, 313K and 318K), the activation energy for the formation of complexes, $Pr_2(GSH)_2Zn(H_2O)_6$ and $Pr_2(GSH)_2Zn(H_2O)_6$ are calculated.

APPENDIX

a) Abstract Published in Seminars/Symposium/ Conferences :

1. "Twenty First Conference of Indian Council of Chemists" Rani Durgavati University, Jabalpur (M.P.), October 24-26, 2002.
2. "International Symposium on Spectroscopy, Structure and Dynamics", December 12-13, 2002, Indian Association for the Cultivation of Science, Jadavpur.
3. "6th CRSI National Symposium", I.I. T., Kanpur, February 6-8,2004.
4. "Recent Trends in Organic Chemistry and Natural Product Chemistry" - organized by the Department of Chemistry, Manipur University and co-sponsored by the Council of Scientific and Industrial research (CSIR), New Delhi and North-East Council (NEC) during march 29-30, 2004.
5. "XII National Conference on Surfactants, Emulsion and Bio-colloids" held at Department of Chemistry, Manipur University, Canchipur, Imphal, India during November 09-11, 2005.
6. "6th International Conference on f-Elements", Wroclaw, Poland, September 4-9, 2006, organized by Institute of Low Temperature and Structure Research, Polish Academy of Sciences and Faculty of Chemistry, University of Wroclaw.

b) List of Publications :

1. Comparison of energy interaction parameters for the complexation of Pr(III) with glutathione reduced(GSH) in absence and presence of Zn(II) in aqueous and aquated organic solvents using *4f-4f* transition spectra as PROBE

   Th. David Singh, **Ch. Sumitra,** N. Yaiphaba, H. Debecca Devi, M. Indira Devi and N. Rajmuhon Singh
   Spectrochimica Acta, **61(6)**(2005)1219.

2. Spectral study of the complexation of Nd(III) with glutathione reduced (GSH) in the presence and absence of Zn(II) in aquated organic solvents

   Th David Singh, **Ch Sumitra,** N. Rajmuhon Singh and M. Indira Devi

Journal of Chemical Sciences,**116(6)** (2004)303.

3. Simultaneous interaction of two dissimilar metal ions praseodymium(III) and a soft metal ion Zn(II) or a hard metal ion Ca(II) with tripeptide glutathione (reduced) in different aquated organic solvents : An absorption spectral study"

   Th. David Singh, N. Mohondas Singh, N. Yaiphaba, H. Debecca Devi, **Ch. Sumitra.**, T. Kriyananda, M. Indira Devi and N. Rajmuhon Singh

   Chem. & Environ. Res, **12(3&4)**(2003)295

4. An absorption spectral study of 4f-4f transitions for the interaction of Pr(III) with different amino acids in aqueous and aquated organic solvents

   H. Debecca Devi, Th. David Singh, N. Yaiphaba, **Ch. Sumitra** , M. Indira Devi and N. Rajmuhon Singh

   Asian Journal of Chemistry,**16(1)** (2004)412

5. Comparison of electric –dipole intensity parameter for a series of structurally related Pr(III) complexes with ureas and thioureas in non-aqueous media

   Th. David Singh, **Ch. Sumitra**, N. Rajmuhon Singh and M. Indira Devi, *Asian Journal of Chemistry,* **17(3)** (2005) 1435.

6. Calculation of electric dipole intensity parameter to explore some of the interaction between hard metal ions Pr(III) and Nd(III) with π-electron density of butane-1,4 and butyne-1,4-diols in non-aqueous solutions : An absorption spectral study

   Th. David Singh, **Ch. Sumitra**, G.C. Bag, M. Indira Devi and N. Rajmuhon Singh, *Spectrochimica Acta,* , **63**(2006)154.

7. Calculation of electric dipole intensity parameters of 4f-4f transitions of Pr(III) and glutathione reduced (GSH) complex in presence and absence of Zn(II)

   Ch. Sumitra, Th. David Singh, M. Indira Devi and N. Rajmuhon Singh

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