Comparative absorption spectroscopy involving 4f-4f transitions to explore kinetics of complexation of Zn(II) with Er(III)-glutathione complex & compositional dependence of intensity parameters

Minaz A Gagnani¹, Ram S Shukla¹, Shreekala K Hari² & Sudhinda N Misra²

¹Central Salt & Marine Chemicals Research Institute, Bhavnagar, Gujarat 364 002
²Department of Chemistry, Bhavnagar University, Bhavnagar, Gujarat 364 002

Received 8 April 2002; revised 10 December 2002; accepted 14 February 2003

The kinetic and spectroscopic investigations on complexation of Zn(II) with Er₃(GSH)₂(H₂O)₁₁ (GSH = reduced glutathione) to form Er₃(GSH)₂Zn(H₂O)₆ complex 2 have been performed at 30 °C by following five, 4f-4f sensitive transitions of lanthanide Er(III), ¹¹¹₂ → ¹¹¹₂, ¹¹¹₂ → ¹¹¹₂, ¹¹¹₂ → ¹¹¹₂ and ¹¹¹₂ → ¹¹¹₂ in water as well as in equimolar mixture of DMF and water. Performances of all the five bands were found to be comparatively sensitive, on the basis of kinetic studies done by following the changes in the intensity (absorbance, molar absorptivity) and intensity parameters (oscillator strength P and Judd-Ofelt T₂ intensity). Kinetics showed first order dependence in terms of concentrations of Zn(II) and complex 1 on the rate of formation of complex 2. In order to support the kinetic and spectroscopic observations, complex 1 and 2 were synthesized also, and were characterized by C, H, N, S, and elemental analysis: UV/VIS, NMR and IR techniques. Kinetic, mechanistic and spectroscopic aspects of the complexation reaction are presented and discussed.

[Keywords: Kinetics of complexation, Complexation reaction, Spectroscopy of complexation, Lanthanide, UV/VIS, NMR, IR]

1 Introduction

The sensitivity of different 4f-4f transitions, reflected by the variation of their oscillator strengths and T₂ intensity parameters, towards minor changes in the immediate coordination environment around lanthanide (III), makes absorption intensity data analysis an excellent means of extracting information regarding the coordination characteristics (degree of outer and inner sphere coordination, relative binding capability of the binding sites of the ligand, incidence of covalence in hitherto predominantly ionic lanthanide-ligand bond) and varying binding nature of the ligands. Devlin et al., in their extensive studies on comparison of electric dipole intensity parameters for Nd(III), Ho(III) and Er(III) complexes, derived from structurally related ligands in aqueous medium, have shown that small chemical and structural changes due to the different binding capabilities of ligands could lead to substantial variation in the intensities of hypersensitive and some other 4f-4f transitions. The ligands used by them were quite similar and differed only in their central donor atom. Recently, there has been renewed interest in the absorption of 4f-4f transitions and their intensity analysis to probe the finer details of structure in complex lanthanide compounds. Unfortunately, most of the studies are devoted to crystalline lanthanide compounds, salts and coordination compounds. Paramagnetic lanthanides are involved in isomorphous substitution involving Ca(II) in biochemical reactions. Lanthanide compounds are proving as excellent catalysts in a number of stereo-selective, chemo-selective and regio-selective transformations. Multi-metal oxide ceramics containing lanthanides are excellent dielectric, ferroelectric, piezoelectric materials and their synthesis involving sol-gel techniques is well known. The authors are involved in using 4f-4f transition spectral quantitative analysis and correlation between the spectral parameters and the structural changes during sol-gel or lanthanide induced catalysis. The present work involves the application of quantitative 4f-4f intensity data analysis to probe the simultaneous tri-nuclear hetero-bimetallic complexation of chemically different metal ions with tripeptide glutathione biomolecule. Glutathione is a polydentate ligand,
offering as potential binding sites, two carboxylate, one amino, one sulphhydryl and two amide groups and its coordination chemistry serves as a model system for binding of endogenous metal ions by larger peptides and proteins.\textsuperscript{7,10} The d-d transition spectra have very extensively been used in kinetic and mechanistic studies but spectral changes in 4f-4f transitions have rarely been used for mechanistic and kinetic investigations.

Glutathione is involved in maintaining intracellular calcium ion homeostasis form, in studies with both intact cells, and subcellular organelle fractions exposed to toxins, which cause thiol depletion and subsequently, lead to disruption of intracellular Ca\textsuperscript{2+} homeostasis. Glutathione found in large amounts in animal tissues, plants and in microorganisms, undergoes complexation with intracellular Ca(II) and Zn(II) simultaneously, and most probably this hetero-bimetallic complexation may be responsible for many of the biological reactions, taking place intracellularly. Glutathione is also involved in a number of physiological and biochemical functions, both intracellular and extracellular and its coordination chemistry play an important role in understanding the functioning of this tripeptide. The Ca (II) ion and Zn (II) ions like glutathione, are present intracellularly and interact simultaneously, resulting in hetero-metal coordination of glutathione. The Er(III)-Zn(II) hetero-metallic complexation of glutathione in aqueous and in aquted organic solvent mimic to some extent the hetero-metal complexation of glutathione with Ca(II) and Zn(II) \textit{in vivo}. Biological fluid is a multimal-multiligand system, in which the effective concentrations of metal complexes formed \textit{in vivo} are interrelated and their mutual influence can be either antagonistic or stimulative.\textsuperscript{9} GSH has the sequence \ensuremath{\gamma}-L-glutamyl-L-cysteinyl glycine with eight potential donor sites. Some of the sites (like carboxylate) are strong complexing ligands for hard metal ions like Er(III) or Ca(II) and compete effectively with solvent (water) molecules for Ln(III) coordination. While sites like sulphhydryl group is the most suitable donor for soft metal ion like Zn (II), other donor sites are on the borderline and hence, may participate with either of type metal ion, if required for stable chelation. Probably for the first time, the kinetics of hetero-bimetallic complexation of glutathione (GSH) involving Er(III) and Zn(II) ion is being reported, using 4f-4f transition absorption spectrophotometric changes.

2 Experimental Details

Er(NO\textsubscript{3})\textsubscript{3} \cdot 6H\textsubscript{2}O (99.9 \text{ purity}) from Indian Rare Earths Alwaye, Zn(II) nitrate (Aldrich, USA) and ligand glutathione (GSH) of G R grade from SRL, India, were used without further purifications. All other chemicals used were of A R grade. All the solutions were prepared, using fresh, doubly-distilled water. GSH was kept at \textdegree{}C \textdegree{}C, in deep freezer, in nitrogen atmosphere, and always a fresh solution of GSH was prepared for experimental use. The spectro-photometric studies were done on a temperature controlled, Perkin Elmer Lambda 2 spectrophotometer with attached kinetics assembly. NMR and IR spectrum were recorded by using Bruker 400 MHz NMR and Perkin Elmer FT-IR spectrometers, respectively.

| Table 1—\textsuperscript{1}H NMR data for GSH, Er(III)-GSH and Er(III)-GSH-Zn(II) |
|-----------------|-----------------|-----------------|
| Proton peak     | Compound shift (\delta) |
| GSH             | Er(III)-GSH     | Er(III)-GSH-Zn(II) |
| Ha              | 3.98            | 4.37            | 4.39            |
| Hb              | 3.71            | 4.19            |                |
| Hc              | 3.90            | -               | -               |
| Hd              | 2.97            | 2.98            | 3.21            |
| He, Hf          | 2.91            | 2.64            |                |
|                 | 2.64            | 2.57            | 2.96            |

2.1 Synthesis of Er\textsubscript{5}(GSH)\textsubscript{2} (H\textsubscript{2}O)\textsubscript{4} (complex - 1)

The complex Er\textsubscript{5}(GSH)\textsubscript{2} (H\textsubscript{2}O)\textsubscript{4} was prepared by adding appropriate concentration of Er(NO\textsubscript{3})\textsubscript{3} and GSH in the solution of ethyl acetate-acetone mixture, which was continuously stirred for four hours at 30 °C. The complex was isolated as green crystals and was characterized by elemental analysis (C, H, N) and Pr), IR and \textsuperscript{1}H NMR spectra, which corresponded to stoichiometry: Er\textsubscript{5}(GSH)\textsubscript{2} (H\textsubscript{2}O)\textsubscript{4}. Karl Fischer titration determined the water contents in the complex.
2.2 Synthesis of Er₂(GSH)₂ Zn (H₂O)₆

The Er₂(GSH)₂(H₂O)₆ complex 1 was dissolved in ethanol-water (50:50 v/v) mixture and appropriate concentration of Zn(II) nitrate was added. The reaction mixture was thoroughly refluxed for 10 h in inert atmosphere (maintained by bubbling oxygen-free N₂ gas). The obtained microcrystalline green complex, characterized by elemental analysis, IR and ¹H NMR spectra, gave stoichiometry: Er₂(GSH)₂Zn (H₂O)₆.

Complex -1

Complex -2

P = T_J \omega_{0} \left| \left\langle \phi^{J} | \sum \left| \phi^{J'} \right\rangle \right|^2ight.

where \omega_{0} is the energy of absorption band \left\langle \phi^{J} | \sum \left| \phi^{J'} \right\rangle \right|^2 are the initial and final studies and U(J) represent unit tensor operators of the rank λ. T_J (J = 2,4,6) represents the Judd-Ofelt intensity parameters, which are basically phenomenological parameters, whose magnitude mainly depend on the chemical environment, and their variation provides significant information about structure and conformation of complexes.

Carnell has used T_J and Axe used Ω_λ parameters as intensity parameters. However, T_J, Ω_λ and Ω_α are interrelated as follows:

Ω_λ = \left( \frac{2J+1}{c} \right) \Omega_α

3 Results and Discussion

Er(III), the medium sized ions among the lanthanide series have been chosen specially because, these represent the ions with optimum ionic radii for effective isomorphous substitution of Ca(II) ion form biomolecules and to mimic the interaction between Ca(II) and metabolites taking place in vivo conditions intracellularly. The present study is aimed at, following the interaction of Ca²⁺ and Zn(II) with glutathione, seen through the simultaneous coordination of two, chemically different, metal ions Er(III) and Zn(II), with glutathione in aqueous and in aqurated organic solvent and via comparative absorption and absorption difference spectro-photometry as spectral probe. The study is most probably the maiden attempt to use versatile 4f-4f transition intensities to follow the kinetics of the rate of simultaneous coordination of lanthanide Er(III) and Zn(II) with glutathione. The study also proves that, the Judd-Ofelt theory on 4f-4f transition intensities is quite capable in investigating the kinetics of interaction between Ln(III) and biomolecules or biochemical reactions involving Ca(II) indirectly.

The present work deals with simultaneous complexation of Ln(III) [Ln(II) = Er(II)] and Zn(II) with naturally-occurring tripeptide glutathione reduced (GSH) just to mimic probable interaction of Ca²⁺ and Zn(II) with glutathione taking place...
intracellularly. The preliminary kinetic study of simultaneous complexation of a hard and soft metal ion to GSH has been investigated.

The shapes of 4f-4f bands and observed spectral patterns of these complexes have found to be quite similar to that shown by Er(III) aquo or Er(III) (haloacetate), H₂O complexes and Er(III)-GSH; Er(III)-GSH-Zn(II) complexes most probably can be ascribed to predominantly ionic mode of bonding of Ln(III) to the coordinating ligand.

The addition of Zn(II) to Er(III)-GSH appears to induce substantial changes in the immediate coordination environment around Er(III). It is found that, intensity parameters (Table 1) vary significantly with time which clearly suggested that, Ln(III) coordination environment appears to undergo significant changes in presence of GSH and Zn(II) with time of reaction. Both hypersensitive and pseudo-hypersensitive bands displayed significant changes in their oscillator strength with time, hence five bands for Er(III) were used for comparative rate measurement.

3.1 IR Spectral study

The infrared spectrum of glutathione (GSH) shows a stretching frequency due to sulphydryl group, occurring as a sharp, intense band around 2535 cm⁻¹. Addition of Er(III) to GSH clearly leads to deprotonation of carboxylic groups and in all probability, it induces the formation of very weak Er(III)-sulphur (GSH) bond. The IR spectra shows deprotonations of sulphydryl groups occurring even at pH-5.0, at which complexes are synthesized. The spectra in 800-200 cm⁻¹ region shows appearance of new bands, which can be ascribed to Er(III)-sulphur bonds. The addition of Zn(II) to Er(III)-GSH complexes enhances remarkably the deprotonation tendency. The intensity of sulphydryl group was considerably reduced in Er₂(GSH)₂(H₂O)₅ complex but, it was totally absent in Er₂(GSH)₂(Zn(H₂O))₆ complex as well as in Zn(II)-GSH complex. The ν, COO stretching frequency, occurring around -1715 cm⁻¹ in GSH shifts to 1630 cm⁻¹ in Er(III)-GSH and further, gets lower in Er(III)-GSH-Zn(II) complexes indicating strong interaction of carboxylic groups with Er(III) in these complexes.

3.2 ¹H NMR spectra

Structural formula of glutathione, is given in structure I as follows:

I Structural formula of glutathione

Corresponding data are given in Table 2. All the peaks for different protons show downfield shifts in complex 1 as compared to that found in GSH. The H₆ proton peak observed at δ 3.98 in GSH shifts to δ 4.37 in Er₂(GSH)₂(H₂O)₅. The triplet H₇ proton peaks centered at δ 3.83 in the ligand shift to δ 4.19 and H₈ proton peak also undergoes downfield shift, indicating weak interaction of Er(III)-sulphur. The H₅ and H₆ peaks are slightly broadened due to paramagnetic nature of Er(III).

In H₅ proton peak, still undergoes further downfield shift in hetero-bimetallic complex 2. Er₂(GSH)₂Zn(H₂O)₅ complex shows further downfield shifts in the H₅, H₆, H₇, H₈, and H₉ protons compared to that observed for Er₂(GSH)₂(H₂O)₅ complex. The ¹H NMR spectra of GSH, Er₂(GSH)₂(H₂O)₅ and Er₂(GSH)₂Zn(H₂O)₅ show clearly distinct changes which are also shown by IR and absorption spectral changes.

3.3 Compositional dependence of T₂ parameters

Devlin et al. have shown, from their systematic studies of Nd(III), Ho(III) and Er(III) complexes, derived from structurally related ligands in aqueous solution, and reported a relation between the magnitude and variation of intensity parameters (Ω₂) and the structural and compositional changes in these complexes. However, Reisfeld & Jorgensen as early as in 1977 discussed the relevance of structure and spectra correlation and showed the magnitude and variation of covalent character of the complexes with the change in the degree of covalency in the lanthanide ligand.
Tanabe et al. found $\Omega_6$ parameter sensitive to the overlap integral of $4f$ and $5d$ orbitals. This overlap integral is supposed to decrease when 6s electron density is large, because the radial integral dominates the $\Omega_6$ parameters. The parameters assumed to decrease with the increase in the 6s electron density. Tanabe et al. also showed negative correlation between $\Omega_6$ of Nd$^{3+}$ and Er$^{3+}$ and the 6s electron density. Tanabe et al., in latter publication concluded that, $\Omega_6$ parameters increase with increasing covalency, however, an opposite trend was observed for the $\Omega_4$ parameter. The variation of $\Omega_4$ and $\Omega_6$ was also related to the basicity of the rare earth sites.

Nageno et al. while working with Eu$^{3+}$ doped silicate glasses showed $\Omega_2$ parameter depending on the covalency of Eu-O band and structural changes around the Eu$^{3+}$ ion, whereas the $\Omega_2$ and $\Omega_4$ are only related to the covalency of the Eu-O band. These workers again showed that, $\Omega_2$, $\Omega_4$ are affected by the ionic packing ratio of the glass host. This ionic packing ratio is also related to the rigidity of the matrix. Other workers Uhlimann, Florez et al., and Saisndha & Ramakrishna gave different types of correlation for the $\Omega_2$ and $\Omega_4$ for different types of crystalline mixed oxides and glasses. Unfortunately, such correlation studies have been made on solid compounds or glasses and none of the study has so far been made to discuss the compositional dependence of intensity parameters in lanthanide complexes in solution. The authors are, therefore, trying to give some correlations between intensity parameters ($T_2; \lambda=2,4,6$) with the structural features of complexes.

Since $T_2$ parametric calculation, the authors have taken into consideration the contribution of all the $4f$-$4f$ bands, but have found the linear correlation with positive slope between $T_2$ and the oscillator strength of different $4f$-$4f$ bands. The authors have used the correlation for one complex.
system in different experimental conditions. In this, the main structure of the complex is retained while minor changes in the structure of the complexes are introduced due to the variation of solvent, $p$H of the medium and the progress of the hetero-bimetallic complexion of glutathione in presence of Er(III) and Zn(II) ion. These slopes indicate that, while the main structure of the complex is retained but with the progress of the hetero-metal complexion, the slope varies. The slopes for five transitions, $^4T_{1u}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4H_{11/2}$ and $^4G_{15/2}$ computed from Fig. 1 (A), (B) and (C) are (slopes $\times 10^3$): $0.47 < 1.78 < 2.73 < 3.03 < 5.82$ for $T_2' / T_2$, $0.31 < 1.29 < 1.91 < 2.67 < 3.17$ for $T_1 / T_1$ and $0.79 < 3.04 < 4.68 < 5.16 < 9.88$ for $T_1 / T_1$ respectively, and these order of the slopes are found
to be almost retained irrespective of $T_2^\prime/T_2^{\prime\prime}$, $T_1^\prime/T_1^{\prime\prime}$ and $T_2^\prime/T_2^{\prime\prime}$. It has also been attempted to correlate the nephelauxetic effect ($\beta$) with the variation of these ($T_2^\prime/T_2^{\prime\prime}$ ($T_1^\prime/T_1^{\prime\prime}$) slopes and the result will be communicated later.

Empirical ratio of Judd-Ofelt intensity parameters $T_2$ complex/$T_2$ aquo ion have shown that, the variation of $T_2$ parameters depend on the nature of ligand while $T_2$ showed metal dependence. The $T_2$ complex/$T_2$ aquo versus oscillator strength gives linear correlation with different slopes. Though the different transitions combinedly contribute towards the ($T_2$) parameters the different slopes show the relative sensitivities of different transitions and the relative contribution towards the magnitudes of these empirical phenomenological but relevant parameters. The plots of $T_1$ complex/$T_1$ aquo versus oscillator strength (Fig. 1) shows, as these slopes in the plots of $T_2^\prime/T_2^{\prime\prime}$ ($\lambda=2,4,6$) versus oscillator strengths of different $4f-4f$ bands, that the transition ${{1}^{1}S_{02}} \rightarrow {}^{4}F_{02}$, ${{1}^{1}S_{02}} \rightarrow {}^{4}G_{162}$ and ${{1}^{1}S_{02}} \rightarrow {}^{4}G_{162}$ transitions which do not obey $|\Delta J|$ selection rules, yet show significant sensitivity quite similar as that of hypersensitive ${{1}^{1}S_{02}} \rightarrow {}^{4}H_{152}$, ${{1}^{1}S_{02}} \rightarrow {}^{4}G_{162}$ transitions of Er(III), so the present paper studies our observation, ligand-mediated pseudo-hypersensitivity.$^{2,3,33}$

3.4 Comparative absorption spectra and kinetics

Both hypersensitive ${{1}^{1}S_{02}} \rightarrow {}^{4}H_{152}$ and ${{1}^{1}S_{02}} \rightarrow {}^{4}G_{162}$ and pseudo-hypersensitive transitions of Er(III) bands display significant changes during complexation, which can be seen from the spectral changes with time. The topmost curve in Fig. 2 represents the stage of apparent complexation of the reaction and no further changes were noted over the next few days. At this final stage, the spectrum matched very closely with that of the freshly prepared solution of the same concentration (0.02 mol dm$^{-3}$) of the isolated solid complex Er$_2$(GSH)$_2$Zn(H$_2$O)$_6$.

Devlin et al.$^{2,3}$ and Misra and coworkers$^{1,12,33}$ have shown that, most of the observed $4f-4f$ bands of Lanthanide(III) complexes have been very sensitive towards even minor changes in the immediate coordination environment around lanthanide(III) ions. Small changes in the binding mode of the ligand under different experimental conditions induced noticeable changes in the intensities of observed five, $4f-4f$ bands ${{1}^{1}S_{02}} \rightarrow {}^{4}G_{162}(378 \text{ nm})$, ${{1}^{1}S_{02}} \rightarrow {}^{4}F_{02}(487 \text{ nm})$, ${{1}^{1}S_{02}} \rightarrow {}^{3}H_{12}(522 \text{ nm})$, ${{1}^{1}S_{02}} \rightarrow {}^{4}F_{02}(652 \text{ nm})$ and ${{1}^{1}S_{02}} \rightarrow {}^{1}I_{10}(975 \text{ nm})$. The authors, therefore, used the absorption intensity changes in the observed five $4f$-$4f$ bands against time for present kinetics study. Series of kinetic experiments were conducted and for brevity, only one set of kinetic runs, covering all the five bands clearly (in four parts), showing changes in absorbance with time is given in Fig. 2.

Spectro-photometric experiments conducted by adding appropriate concentrations of Zn(NO$_3$)$_2$ with complex 1 revealed that, the said five $4f$-$4f$ transitions of Er(III) were sensitively changed with time and absorbance corresponding to all the five bands (378, 487, 522, 652 and 975 nm) increased significantly (Fig. 2). Detailed kinetic studies were performed by monitoring all these five bands for complexation of Zn(II) with complex 1 to form complex 2 [Er$_2$(GSH)$_2$Zn(H$_2$O)$_6$]. The observed rates ($k_{obs}$) were evaluated in terms of the concentration of complex 2, formed during the progress of the reaction. Isolated complex 2 was used to determine its concentration spectro-photometrically. Calibration curves prepared for concentration of complex 2, corresponding to all the five said bands were used to convert absorbance into concentrations, corresponding to each band and $k_{obs}$ were calculated from the plots of absorbance versus time. Rates ($k_{obs}$) were also calculated by plotting oscillator strength ($P$) versus time, for a set of kinetics condition; $[\text{Zn(NO}_3)\text{]}_2=1\times10^{-3}M$, Er$_2$(GSH)$_2$(H$_2$O)$_6$ = 2.5$\times$10$^{-5}$M and temperature = 30°C. Like spectro-photometric method, calibration curve was also prepared for oscillator strength for different suitable concentration of complex 2, and oscillator strength were converted into concentrations in order to get the rates. The $k_{obs}$ for this set of kinetic run, obtained from the plots of $P$ versus time were: $k_{obs}$ $\times$ 10$^6$ M$^{-1}$ min$^{-1}$ (nm) = 0.80 (378), 1.05 (487), 1.30 (522), 1.25 (652) and 1.24 (975). $k_{obs}$ calculated by this method are almost comparable with the values calculated by spectro-photometric method (Table 3).

A series of kinetic experiments conducted by varying initial concentration of complex 1 indicated that, the rates of complexation of complex 1 with Zn(II) to form complex 2, were linearly increased corresponding to all five transitions and kinetic performances of all the five transitions, were found
Table 2 — Observed and (computed)* values of oscillator strength ($P \times 10^5$) and Judd-Ofelt ($T_d \times 10^6$) parameters for Er(III) with GSH in presence of Zn(II) in DMF-H$_2$O (60:40) at different time intervals (1:1:1 system)

<table>
<thead>
<tr>
<th>Time</th>
<th>$P_{obs}(P_{cal})$</th>
<th>$P_{obs}(P_{cal})$</th>
<th>$P_{obs}(P_{cal})$</th>
<th>$P_{obs}(P_{cal})$</th>
<th>$P_{obs}(P_{cal})$</th>
<th>$\lambda=2$</th>
<th>$\lambda=4$</th>
<th>$\lambda=6$</th>
<th>$T_2/T_2^{\infty}$</th>
<th>$T_4/T_4^{\infty}$</th>
<th>$T_6/T_6^{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{4}I_{15/2} \rightarrow ^{4}I_{11/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}F_{9/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}H_{11/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}F_{7/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}G_{13/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}G_{13/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}G_{13/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}G_{13/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}G_{13/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}G_{13/2}$</td>
<td>$^{4}I_{15/2} \rightarrow ^{4}G_{13/2}$</td>
</tr>
<tr>
<td>0.00</td>
<td>(0.930)</td>
<td>(2.528)</td>
<td>(9.056)</td>
<td>(2.880)</td>
<td>(15.302)</td>
<td>(0.805)</td>
<td>(2.498)</td>
<td>(7.130)</td>
<td>(3.059)</td>
<td>(17.486)</td>
<td>(5.37)</td>
</tr>
<tr>
<td>0.25</td>
<td>(0.971)</td>
<td>(2.590)</td>
<td>(9.065)</td>
<td>(3.007)</td>
<td>(15.318)</td>
<td>(0.805)</td>
<td>(2.543)</td>
<td>(7.158)</td>
<td>(3.254)</td>
<td>(17.485)</td>
<td>(5.37)</td>
</tr>
<tr>
<td>0.50</td>
<td>(1.035)</td>
<td>(2.610)</td>
<td>(9.307)</td>
<td>(3.163)</td>
<td>(15.730)</td>
<td>(0.812)</td>
<td>(2.543)</td>
<td>(7.187)</td>
<td>(3.502)</td>
<td>(18.141)</td>
<td>(5.58)</td>
</tr>
<tr>
<td>0.75</td>
<td>(1.110)</td>
<td>(2.630)</td>
<td>(9.367)</td>
<td>(3.352)</td>
<td>(15.833)</td>
<td>(0.836)</td>
<td>(2.543)</td>
<td>(7.271)</td>
<td>(3.775)</td>
<td>(18.221)</td>
<td>(5.68)</td>
</tr>
<tr>
<td>1.00</td>
<td>(1.112)</td>
<td>(2.781)</td>
<td>(9.402)</td>
<td>(3.420)</td>
<td>(15.893)</td>
<td>(0.852)</td>
<td>(2.700)</td>
<td>(7.358)</td>
<td>(3.820)</td>
<td>(18.221)</td>
<td>(5.60)</td>
</tr>
<tr>
<td>2.00</td>
<td>(1.114)</td>
<td>(2.803)</td>
<td>(9.518)</td>
<td>(3.426)</td>
<td>(16.083)</td>
<td>(0.852)</td>
<td>(2.721)</td>
<td>(7.358)</td>
<td>(3.826)</td>
<td>(18.542)</td>
<td>(5.66)</td>
</tr>
<tr>
<td>3.00</td>
<td>(1.134)</td>
<td>(2.915)</td>
<td>(9.716)</td>
<td>(3.514)</td>
<td>(16.422)</td>
<td>(0.891)</td>
<td>(2.842)</td>
<td>(7.359)</td>
<td>(3.881)</td>
<td>(19.104)</td>
<td>(5.75)</td>
</tr>
<tr>
<td>4.00</td>
<td>(1.138)</td>
<td>(2.963)</td>
<td>(9.718)</td>
<td>(3.543)</td>
<td>(16.420)</td>
<td>(0.892)</td>
<td>(2.890)</td>
<td>(7.359)</td>
<td>(3.916)</td>
<td>(19.104)</td>
<td>(5.72)</td>
</tr>
<tr>
<td>5.00</td>
<td>(1.154)</td>
<td>(3.022)</td>
<td>(9.844)</td>
<td>(3.600)</td>
<td>(16.637)</td>
<td>(0.897)</td>
<td>(2.944)</td>
<td>(7.472)</td>
<td>(3.989)</td>
<td>(19.337)</td>
<td>(5.78)</td>
</tr>
<tr>
<td>6.00</td>
<td>(1.123)</td>
<td>(3.075)</td>
<td>(10.046)</td>
<td>(3.759)</td>
<td>(16.980)</td>
<td>(0.943)</td>
<td>(2.989)</td>
<td>(7.979)</td>
<td>(4.176)</td>
<td>(19.337)</td>
<td>(5.93)</td>
</tr>
<tr>
<td>8.00</td>
<td>(1.210)</td>
<td>(3.252)</td>
<td>(10.163)</td>
<td>(3.819)</td>
<td>(17.171)</td>
<td>(0.961)</td>
<td>(3.174)</td>
<td>(8.184)</td>
<td>(4.202)</td>
<td>(19.425)</td>
<td>(5.89)</td>
</tr>
<tr>
<td>10.0</td>
<td>(1.228)</td>
<td>(3.259)</td>
<td>(10.252)</td>
<td>(3.892)</td>
<td>(17.204)</td>
<td>(0.985)</td>
<td>(3.178)</td>
<td>(8.201)</td>
<td>(4.312)</td>
<td>(19.489)</td>
<td>(5.93)</td>
</tr>
</tbody>
</table>

* computed values are given in parenthesis.
to be competently significant. Kinetic results listed in Table 3, showed first-order dependence with respect to the concentration of complex 1 on the rate of formation of complex 2. On varying the initial concentration of Zn(II), keeping the concentration of complex 1 constant, the rate of complexation was found to be first-order dependent, in terms of concentration of Zn(II) also. Although all the five bands were found to be kinetically almost equally sensitive however, higher bands, viz 522 nm, 652 nm showed relatively more reactivity towards complexation, associated with higher rates.

Based on these observations the overall complexation is suggested to occur by interaction of one equivalent of Zn(II) with one equivalent of Er₂(GSH)₂(H₂O)₄, and the reaction is given as follows:

$$\text{Zn}^{2+} + \text{Er}^{3+} (\text{GSH})_2 (\text{H}_2\text{O})_4 \rightarrow \text{Er}^{3+} (\text{GSH})_2 \text{Zn} (\text{H}_2\text{O})_6$$

Based on kinetic and equilibrium conditions the rate law of the reaction is given by Eqs (2)-(3).

$$\frac{d[\text{Er}^{3+} (\text{GSH})_2 \text{Zn} (\text{H}_2\text{O})_6]}{dt} = k_{\text{obs}} = k \cdot [\text{Er}^{3+} (\text{GSH})_2 (\text{H}_2\text{O})_4] [\text{Zn}^{2+}]$$  \hspace{1cm} (2)

$$k = k_{\text{obs}}/[\text{Er}^{3+} (\text{GSH})_2 (\text{H}_2\text{O})_4] [\text{Zn}^{2+}]$$  \hspace{1cm} (3)

The overall second-order rate constants $k$ evaluated from Eq. (3) are listed in Table 3, and as expected, were found to be almost constant at each band. This constancy in second-order rate constants further supported that, an overall second-order kinetics is involved in this complexation reaction.

Acknowledgements

One of the authors (SNM) thanks the Department of Science and Technology, New Delhi, for generous research grant. Dr P K Ghosh, Director, and Mr A Tewari, Discipline Coordinator of Marine Algae & Marine Environment Discipline, CSMCRI, Bhavnagar are thankfully acknowledged for encouragement of the publication.

References


