Identification of Europium(III) Hydroxide Formation by Eu(III) Luminescence Spectroscopy

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A series of excitation spectra ($^7F_o \rightarrow {}^5D_o$ transition) of Eu(III) ion in aqueous solution ([Eu(III)] = 1.12×10^{-2} mol L^{-1}; pH 1.0 to 7.0) were obtained under CO_2 free atmosphere using a pulsed tunable dye laser system. The broad and low intensity spectra (peak maximum: 578.89 nm) showed that the trivalent ion (Eu^{3+}) underwent a low degree of hydrolysis at pH below 6.0. Eu(III) hydroxo complex formation seemed more significant at pH above 6.0, shown by the occurrence of intense new peak at 578.63 nm. The spectra of those solutions prepared in N_2 atmosphere showed no signs of the presence of interfering carbonate species. The Eu(III) hydroxo complex formation was not observed when complexation studies between Eu(III) ion and weak organic acids (e.g. glutarate and diglycolate) were conducted at pH 6.0 or below.

Introduction

Eu(III) excitation spectroscopy involving the $^7F_o \rightarrow {}^5D_o$ transition has been used as a luminescence probe of metal binding sites on biological materials such as *Datura innoxia* cell walls,[1,2] and naturally occurring complex material of environmental concern such as fulvic acid.[3] This method has also been widely used in the study of biomolecular structure of various proteins.[4] The principal advantage of this method is that $^7F_o \rightarrow {}^5D_o$ is a unique transition with both the ground and excited states that are nondegenerate, and the levels are not split by the ligand induced crystal field. Each peak may therefore be considered as representing each individual Eu(III) species, making this method suitable for their characterization in aqueous solutions.[5,6]

The Eu(III) speciation studies involving materials which are complex in nature (*i.e.* polyelectrolyte and heterogeneous system) are normally conducted in aqueous solution at different pH and experimental conditions. Eu(III) ions can become hydrolyzed, especially when working in aqueous media in neutral to basic range.[7] The Eu(III) hydroxo complex thus formed may cause difficulties in the probe of metal ion binding sites in macromolecules : The metal ion binding sites on proteins (e.g. oncomodulin or parvalbumin) are said to be pH dependent, but it is also possible that Eu(III) ion that is bound on such sites is simply competing with hydroxide ions.[4] A better understanding of the Eu(III) hydroxo complex formation may be obtained using Eu(III) luminescence spectroscopy, and such spectral data will be helpful in the characterization of metal binding sites.

The objective of this study is to obtain the $^7F_o \rightarrow {}^5D_o$ excitation spectra that are characteristic of the Eu(III) hydroxo complex formed in aqueous solution over a wide pH range. In addition, the formation of the Eu(III) hydroxo complex in solutions containing carbonate ions and weak organic acids (e.g. glutarate and diglycolate) was also investigated spectroscopically.

Experimental

Eu(III) luminescence spectroscopy used in this investigation consists of Nd : YAG (Spectron Laser System, SL-805G) pumped dye laser (SL-4000B) operating at 10 Hz and with a rhodamine 590 and 610 dye mixture having a spectral range of 573-593 nm (Exciton Laser Dye Catalog, 1989). The bandwidth of dye laser was 1.0 cm^{-1}, the laser pulse width was 10 ns, and the laser energy was kept slightly below 5 mJ. The focused laser beam was passed through a 1-cm quartz cell containing the sample of Eu(III) solutions. The luminescence from the cell was collected by a beam collimator set at right angle to the laser beam path, and was sent to a monochromator (HR250, JOBIN YVON) set at 616 nm with a beam path of 2.29 nm. With this setup, the luminescence from $^5D_o \rightarrow {}^7F_2$ was detected using PMT (DA-20, Attago Bussan Co.) followed by DC amplification.

The Eu(III) excitation spectra ($^7F_o \rightarrow {}^5D_o$) were acquired in ratio mode using two boxcar averagers (Model 4420, EG&G) and a signal processor (Model 4402, EG&G). The signal-to-noise ratio was enhanced by acquiring and averaging six and eight spectra. The excitation spectra of the Eu(III) ion and Eu(III) complexes were deconvoluted using a nonlinear least-squares regression routine: They were fitted with a sum of several peaks having Lorentzian-Gaussian function, $I \exp \{-2[(x - W)/L]^2\}/\{2(x - W)/L]^2 + 1\}$, where I, W, and L are the intensity, peak position, and linewidth respectively.[8]

Eu(III) ion solutions used in the investigation were prepared by dissolving $EuCl_3 \cdot 6H_2O$ (99.99%, Aldrich Co.) in double deionized water, under an inert gas (N_2) atmosphere, and pH was adjusted with 1.0 M HCl (Aldrich Co.) and 1.0 M NaOH (Baker Co, carbonate free). The Eu(III) concentration was measured by ICP-AES (JOBIN YVON, JY50P). The Eu(III)-carbonate solution was prepared at pH 8.0 by mixing sodium carbonate (Junsei Co.) with Eu(III) ion solution. The weak acids (glutaric acid; ODA: diglycolic acid) used as organic ligands were reagent-grade and were used without further purification.

Results and Discussion

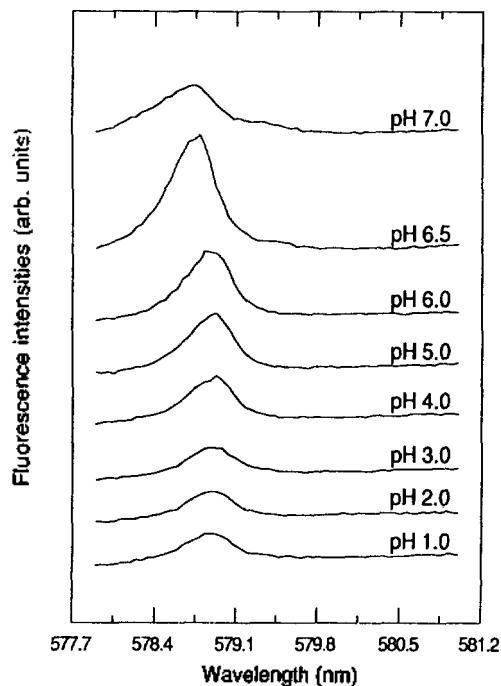A series of Eu(III) excitation spectra ($^7F_o \rightarrow {}^5D_o$) obtained

Figure 1. Excitation spectra of Eu^{3+} ion $(1.12 \times 10^{-2}$ mol $L^{-1})$ in aqueous solution measured in the pH range 1.0 to 7.0.

Figure 2. An example of the deconvoluted excitation spectrum of Eu(III)-carbonate system: $[Eu^{3+}] = 1.12 \times 10^{-2}$ mol L^{-1}; $[CO_3^{2-}]$ $= 1.0 \times 10^{-2}$ mol L^{-1}.

for the Eu^{3+} ion in aqueous solution in the pH range 1.0 to 7.0 is shown in Figure 1. The spectra obtained in the pH range 1.0 to 3.0 are quite similar showing the very low intensity peak (peak maxima: 578.89 ± 0.02 nm). This peak showed an increase in intensity as pH was further raised between 4.0 and 6.0, but at pH higher than 6.0, an increase in the intensity is accompanied by shift to shorter wavelength. The spectra shown in Figure 1 were further analyzed by spectral deconvolution using the parameters given in Table 1. The broad and low intensity peak centered around 578.89 nm observed in acidic media (pH 1.0-3.0) is the spectrum of aqueous Eu^{3+} ion. The gradual increasing in the intensity of this peak (pH 4.0-6.0) suggests the initiation of the formation of Eu(III) hydroxo complex when pH is raised to 6.0. The new and more intense peak observed that is centered around 578.63 nm (pH 6.5 spectrum in Figure 1) is probably due to the Eu(III) hydroxo complex formation, which is said to occur at pH greater than 6.0, forming in general mononuclear and polynuclear species.[7] At pH 7.0 and higher, the sharp decrease in intensity of the overall peak
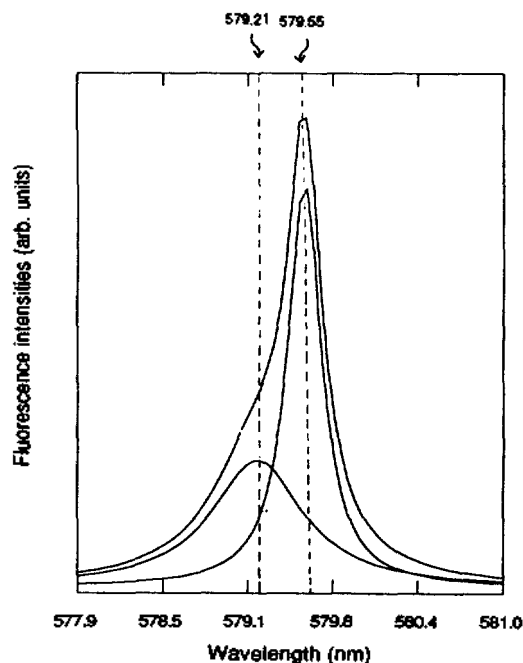
is caused by precipitate formation.

The appearance of new peak seen at higher pH range (pH>6.0) may also be caused by the presence of bicarbonate/carbonate formed from atmospheric carbon dioxide. A great care was taken to prepare the Eu^{3+} ion solutions free from atmospheric CO_2 gas. In spite of this, the possibilities of the Eu(III)-carbonate formation was tested by carrying out the spectral investigation on Eu(III)-carbonate systems at pH 8.0. An example of the excitation spectrum of Eu(III)-carbonate $([Eu(III)] = 1.12 \times 10^{-2}$ mol L^{-1}; $[CO_3^{2-}] = 1.0 \times 10^{-2}$ mol $L^{-1})$ is shown in Figure 2. The spectral deconvolution showed that this very intense peak is made up of two components (peak maxima: 579.21 nm and 579.55 nm) which has been described as due to the formation of the biscarbonate and triscarbonate complexes of Eu^{3+} ion.[3] This shows that when the carbonate complexes are formed, the resulting peak has higher intensity and is observed in the longer wavelength region of the spectrum compared to the aqueous Eu^{3+} ion. Therefore, it is most likely that the new peak (peak maxima: 578.63 nm) seen only at pH greater than 6.0 is

Table 1. Fitted parameters of excitation spectra of aqueous solution of Eu^{3+} ion in Figure 1

pH	1.0	2.0	3.0	4.0	5.0	6.0	6.5	7.0
first intensity†	–	–	–	–	–	0.00354	0.02019	0.00976
second intensity†	0.00552	0.00560	0.00568	0.00902	0.01177	0.01308	0.00979	–
first wavelength (nm)	–	–	–	–	–	578.63	578.63	578.68
second wavelength (nm)	578.88	578.89	578.89	578.89	578.87	578.90	578.88	–
first linewidth (nm)	–	–	–	–	–	0.49806	0.60145	0.88176
second linewidth (nm)	0.59697	0.56273	0.58036	0.59776	0.60087	0.54535	0.33694	–
baseline intensity†	−0.00086	−0.00092	−0.00081	−0.00080	−0.00072	−0.00036	0.00072	0.00089

†Arbitray units.

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578.00 579.12 579.52

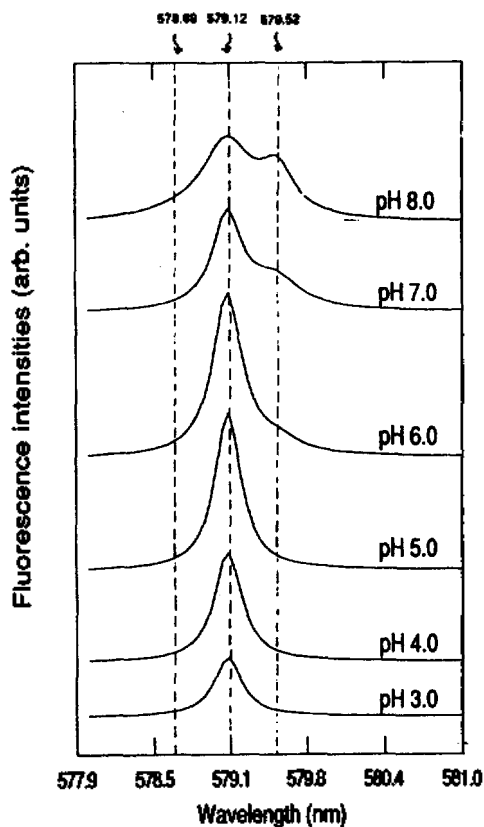**Figure 3.** A series of excitation spectra of the Eu(III)-diglycolate system measured over the pH range 3.0 to 8.0: [Eu³⁺]=1.12× 10⁻² mol L⁻¹; [ODA]=1.0×10⁻² mol L⁻¹.
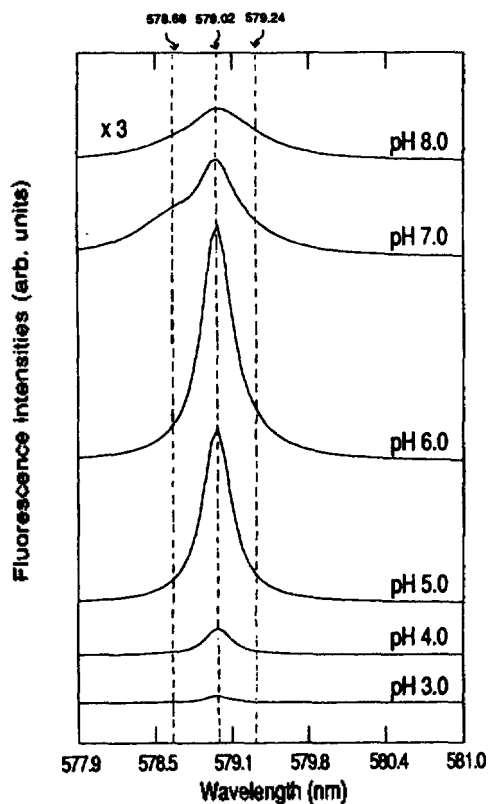
578.68 579.02 579.24

Figure 4. A series of excitation spectra of the Eu(III)-glutarate system measured over the pH range 3.0 to 8.0: [Eu³⁺]=1.12× 10⁻² mol L⁻¹; [glutarate]=1.0×10⁻² mol L⁻¹.

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Figure 5. The deconvoluted excitation spectra of Eu(III)-diglycolate in Figure 3.

due to the formation of Eu(III) hydroxo complex.

The hydrolysis is a serious concern in the study of the complexation between trivalent ions (e.g. Y^{3+}, Ln^{3+}, Eu^{3+}, and Ac^{3+}) and ligand systems that contain weak acid functional groups (e.g. carboxylate, phenolic OH): Trivalent lanthanide and actinide ions bind preferentially to negatively charged oxygen donors, such as carboxylate anion in aqueous media.[7] Therefore, the studies are carried out around pH 5.0-6.0 where carboxylic acids can become dissociated. To see if Eu(III) hydroxo complex is formed during the complexation between Eu^{3+} ion and weak organic acids, a series of excitation spectra were taken of the Eu(III)-diglycolate (ODA) and Eu(III)-glutarate systems, and they are shown in Figure 3 and 4 respectively. Both are dicarboxylic acid ligands, but ODA is stronger coordinating ligand because it has a neutral O donor. In the case of Eu(III)-ODA system (Figure 3), the main peak is observed at 579.12 nm (Eu(ODA)⁺), with a shoulder peak appearing at a longer wavelength of 579.52 nm (Eu(ODA)₂⁻) when pH is 6.0 or higher. Further analysis by spectral deconvolution, shown in Figure 5, reveals the absence of Eu(III) hydroxo complex formation (578. 63 nm) in the Eu(III)-ODA system except as a very small component when pH is raised to 8.0. In the Eu(III)-glutarate system (Figure 4), however, the main peak is observed at 579.02 nm : The peak maxima is shifted due to difference in their basicity. However, the shoulder peak that appears at higher pH is observed in the shorter wavelength region at 578.68 nm that corresponds to the hydroxide formation. The spectral deconvolution of the spectra in Figure 4 is
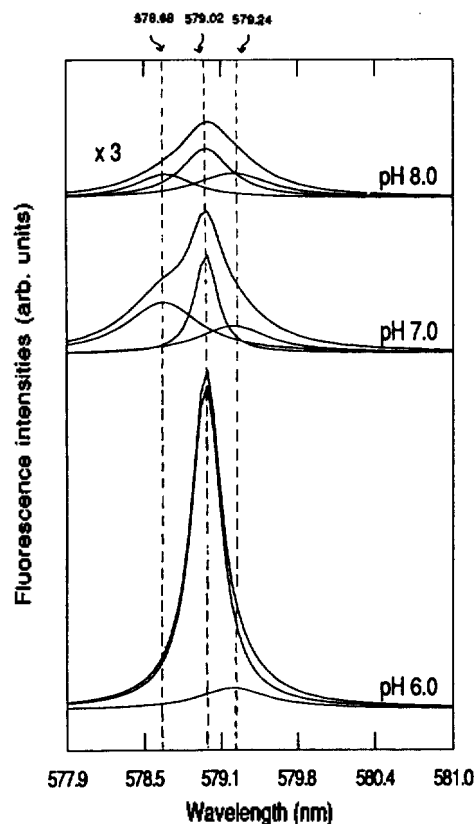
Figure 6. The deconvoluted excitation spectra of Eu(III)-gluta-rate in Figure 4.

shown in Figure 6. It reveals the main peak corresponding to Eu(glutarate)$^+$ with a small shoulder peak (Eu(glutarate)$_2^-$) at pH 6.0, but at a higher pH of 7.0, the shoulder peak at 578.68 nm can be seen clearly, revealing the occurrence

of Eu(III) hydroxo complex formation. At still higher pH of 8.0, all three peak components (Eu(glutarate)$^+$, Eu(glutarate)$_2^-$ and Eu(III)-hydroxo) can be seen in reduced intensities due to precipitation. It shows that the effect of hydrolysis is more pronounced in weakly complexing ligand systems.

Through this spectral investigation, it has been shown that Eu^{3+} ion hydrolyzes but slightly at pH below 6.0. The excitation peak at 578.63 nm at pH greater than 6.0 was identified as that due to the presence of Eu(III) hydroxo complexes. It was also shown that the formation of Eu(III) hydroxo complex poses less complication during complexation studies between trivalent metal ions and organic ligands, if the investigations are conducted at pH 6.0 or below.

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Kinetics and Mechanism of the Reactions of S-Phenyl Dithiobenzoates with Benzylamines in Acetonitrile

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Kinetic studies are carried out on the reaction of S-phenyl dithiobenzoates with benzylamines in acetonitrile at 30.0 °C. Small magnitude of ρ_X (β_X) as well as ρ_Z (β_Z) obtained suggests rate-limiting nucleophilic attack of the thiocarbonyl carbon. This is supported by the unusually small magnitude of ρ_{XY} and ρ_{YZ}, albeit their signs do not agree with those expected. Moreover, the inverse secondary kinetic isotope effects ($k_H/k_D < 1.0$) involving deuterated benzylamine nucleophiles are also in line with the proposed mechanism.

Introduction

The acyl transfer reactions involving amine nucleophiles

have been extensively studied due to their biological as well as synthetic relevance.[1] The acyl transfer reactions with a series of structurally similar amines are often found to ex-