Ligand Dissociation in the Excited State of 2-Thenoyltrifluoroacetonato-europium(III) Ion in Aqueous Solution

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In the emission decay kinetics of Eu(III)–2-thenoyltrifluoroacetone (Htta) aqueous system, we found out a new quenching mechanism due to the tta$^-$ dissociation from Eu(tta)$^{2+}$ in the excited state. The mechanism well explained the double-exponential decay of the fluorescence observed in the Eu(III)-Htta system. The analysis of the decay curve observed at various temperatures gave the rate constants and thermodynamic parameters for the tta$^-$ dissociation from Eu(tta)$^{2+}$.

Eu(III) shows unique fluorescence; the emission wavelength is hardly influenced by ligands and sharp emission peaks appear at 595 nm ($^5D_0 \rightarrow {}^7F_1$) and 615 nm ($^5D_0 \rightarrow {}^7F_2$). Eu(III) is commonly used as fluorescent materials,[1] a tool for fluorescent immunoassay and a probe to know the microscopic environment around Eu(III).[2] Therefore, the fluorescence properties of Eu(III) have been extensively studied. The quenching mechanisms of Eu(III) have been also investigated and three kinds of path were established; the paths through the OH stretching vibration of water molecules binding to Eu(III), through the energy transfer and charge transfer to other compounds, and through photoreduction. In the present study, we propose a new quenching mechanism due to the ligand dissociation from the excited state of Eu(III) complex in the Eu(III)-Htta aqueous system. 2-Thenoyltrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione) is abbreviated as Htta.

Eu_2O_3 was purchased from Wako Pure Chemical Co. (99.9% purity). Water was distilled and purified with an ion-exchange system (Milli-Q Sp. Toc.). Other reagents were of analytical reagent grade. Eu_2O_3 was dissolved in diluted $HClO_4$ aqueous solution. In the Eu(III)-Htta aqueous system, the initial concentrations of Eu^{3+} and Htta were $5.0 \times 10^{-6} - 1.0 \times 10^{-4}$ M (1 M = 1 mol dm^{-3}), and $5.0 \times 10^{-6} - 1.0 \times 10^{-5}$ M respectively. The initial concentration of Eu^{3+} was not lower than that of Htta to produce only Eu(tta)$^{2+}$. The ionic strength, I, was fixed to 0.1 M with $NaClO_4$, and 1.0×10^{-3} M of acetate and HEPES (3-[4-(2-hydroxyethyl)-1-piperaziyl]propanesulfonic acid, pK_a 7.55) were used as a buffer to adjust pH to 4 – 6 and 6 – 7, respectively. Steady-state and time-resolved fluorescence measurements were carried out with a spectrofluorometer (model LS-50B, Perkin-Elmer). The sample temperature was controlled by circulation of thermostated water at 5 – 65 °C.

When the quenching process is only the path through the OH vibration of binding water molecules, a linear relationship between the reciprocal lifetime, i.e., rate constant, k, of solid Eu(III) compounds and the number of water molecules binding to Eu(III), n_w, is commonly known.[3] The relation can be written with modification as:

$$k = k_r + k_{OH}n_w \qquad (1).$$

The values of k_r and k_{OH} were reported as 667 and 952 s^{-1}, respectively. The quenching process through the OH vibration should be independent of temperature. This is clear from the fact that the reciprocal lifetime ($(9.1 \pm 0.2) \times 10^3$ s^{-1}) of Eu^{3+}aq did not depend on temperature, 25 – 65 ˚C. From the lifetime, n_w was calculated to be 8.8 ± 0.5. This agrees with the coordination number of Eu^{3+}aq of nine. The lifetime of $Eu(tta)_3$ in toluene was found to be 510 ± 4 μs, meaning that $Eu(tta)_3$ possessed 1.4 ± 0.5 water molecules. This is comparable to the crystal structure of $Eu(tta)_3(H_2O)_2$.[4] These mean that tta$^-$ molecules do not quench Eu(III) fluorescence in toluene and a solid state.

Eu^{3+} has very small absorption coefficient (< 1 M^{-1}cm^{-1}) at 350 nm, whereas Htta and tta$^-$ have larger absorption coefficients, about 10^4 M^{-1}cm^{-1}, at this wavelength. As for the Eu(tta)$^{2+}$ aqueous system, a light at 350 nm was used to excite. The tta$^-$ of Eu(tta)$^{2+}$ was first excited and followed by an intramolecular energy transfer to generate Eu(III) in the excited state.[5] In this system, the fluorescence gave a double-exponential decay as shown in Figure 1. Rate constants corresponding to the fast and slow decays were defined as $k_{obs,f}$ and $k_{obs,s}$, which were obtained to be 3.6×10^4 and 5.78×10^3 s^{-1}, respectively, in the figure case. The $k_{obs,f}$ value of 3.6×10^4 s^{-1} is about four times larger than the reciprocal lifetime of Eu^{3+}aq, indicating an alternative decay path other than the OH vibrational path. The tta$^-$ is not a quencher of Eu(III) and the emission of Eu(II) was not observed. Therefore, the larger rate

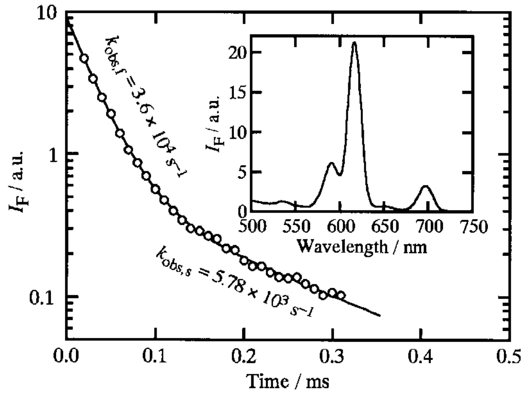

Figure 1. An example of double-exponential decay of fluorescence of Eu(tta)$^{2+}$ at 617 nm at 15 °C in aqueous system. Excitation at 350 nm; Eu^{3+}, 1.0×10^{-4} M; Htta, 1.0×10^{-5} M; pH, 6.13. Inserted figure is the steady-state fluorescence spectrum.

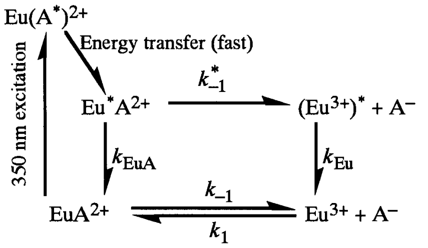

Figure 2. An overall reaction and deactivation scheme for EuA^{2+} and Eu^{3+} in the Eu(III)-Htta aqueous system.

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constants can not be explained by the previous mechanisms.

The lifetimes of Eu(III) complexes are much longer than those of common organic compounds. The reaction rate of Eu^{3+} ion is much faster than the decay rate of Eu(III) complexes. Therefore, the chemical reaction of Eu(III) in the excited state can affect the lifetime. We assume a new quenching mechanism due to the ligand dissociation process from EuA^{2+} in the excited state shown in Figure 2, where tta^- is abbreviated as A^-. According to this scheme, the $\mathrm{Eu}^*\mathrm{A}^{2+}$ concentration after the excitation at $t = 0$ can be expressed as:

$$[\mathrm{Eu}^*\mathrm{A}^{2+}] = [\mathrm{Eu}^*\mathrm{A}^{2+}]_\mathrm{i} e^{-k_2 t} \qquad (2),$$

where the subscript i means initial concentration, $k_2 = k^*_{-1} + k_{\mathrm{EuA}}$ (k^*_{-1} the rate constant for the ligand dissociation in the excited state, and $k_{\mathrm{EuA}} = k_\mathrm{r} + k_{\mathrm{OH}}n_\mathrm{w}$ for $\mathrm{Eu}^*\mathrm{A}^{2+}$). The $(\mathrm{Eu}^{3+})^*$ concentration is written as:

$$[(\mathrm{Eu}^{3+})^*] = \frac{k^*_{-1}[\mathrm{Eu}^*\mathrm{A}^{2+}]_\mathrm{i}}{k_2 - k_{\mathrm{Eu}}}(e^{-k_{\mathrm{Eu}}t} - e^{-k_2 t}) \qquad (3).$$

where k_{Eu} is the reciprocal lifetime of $(\mathrm{Eu}^{3+})^*$aq. Both $\mathrm{Eu}^*\mathrm{A}^{2+}$ and $(\mathrm{Eu}^{3+})^*$ show the emission specific to Eu(III), and therefore the fluorescence intensity at time t and wavelength λ, $I_\mathrm{F}(t,\lambda)$, can be expressed as:

$$I_\mathrm{F}(t,\lambda) = \alpha_{\mathrm{EuA}}(\lambda)[\mathrm{Eu}^*\mathrm{A}^{2+}] + \alpha_{\mathrm{Eu}}(\lambda)[(\mathrm{Eu}^{3+})^*] \qquad (4),$$

where $\alpha(\lambda)$ is the apparent emission efficiency at the wavelength. Equation 4 means that $I_\mathrm{F}(t,\lambda)$ will show a double-exponential decay possessing rate constants of k_2 and k_{Eu}.

By changing the Eu^{3+} and tta^- concentrations, pH, and temperature, k_{obs} values were obtained. The values did not depend on both concentrations and pH, supporting that any tta^- complexes, such as EuA_2^+ or dimers, other than EuA^{2+} did not exist. The $k_{\mathrm{obs,f}}$ value depends on $1/T$, as shown in Figure 3, indicating not the OH vibrational quenching but the chemical reaction.

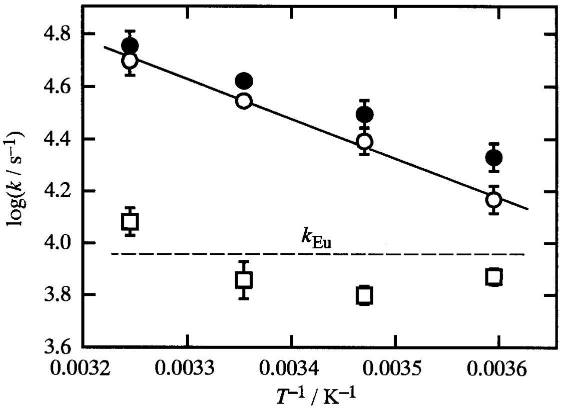

Figure 3. Dependence of the rate constants, $k_{\mathrm{obs,f}}$ (●), $k_{\mathrm{obs,s}}$ (□) and k^*_{-1} (○) on reciprocal temperature. The solid line means a regression curve, and the broken line indicates the k_{Eu} value.

Some rate constants of Eu(III) are estimated to be compared with the obtained rate constants. The n_w value should be seven for $\mathrm{Eu(tta)}^{2+}$ and k_{EuA} can be calculated to be 6.7×10^3 s^{-1} with eq 1. When the formation process of EuA^{2+} proceeds through the Eigen mechanism, the rate constant for the formation, k_1, can be expressed as $K_{\mathrm{os}}k_\mathrm{w}$, where K_{os} is the stability constant of an outer-sphere complex and k_w is the rate constant for the water molecule exchange. From the relationship between k_w and ionic radii for Gd^{3+} through Yb^{3+},[6,7] the k_w value of Eu^{3+} was estimated as 1.1×10^9 s^{-1}. By applying the Fuoss equation, K_{os} was calculated to be 5.3 M^{-1} at $I = 0.1$ M, 25 °C for the pair of Eu^{3+} and tta^-. The rate constant, k_1, for the formation of $\mathrm{Eu(tta)}^{2+}$ was obtained as 5.8×10^9 $\mathrm{M}^{-1}\mathrm{s}^{-1}$. The stability constant, β_1, of $\mathrm{Eu(tta)}^{2+}$ was reported as $10^{5.8}$ and $10^{4.5}$ M^{-1},[8,9] and thus k_{-1} was estimated to be 9.2×10^3 and 1.8×10^5 s^{-1}.

f-Orbitals are relatively deep inside an atom and interact only weakly with ligand orbitals. The excitation of Eu(III) occurs through the f-f transition, and thus the reaction characteristics in the excited state would be similar to those in the ground state. k^*_{-1} could be calculated as 3.5×10^4 s^{-1} at 25 °C from the averaged $k_{\mathrm{obs,f}}$ value at that temperature and k_{EuA}. This value is comparable to that in the ground state. The k^*_{-1} values at the other temperatures were obtained in a similar manner, and log k^*_{-1} was plotted against $1/T$ as shown in Figure 3. From this, $\Delta^\ddagger H$ and $\Delta^\ddagger S$ values could be calculated as 29 ± 1 kJ·mol^{-1} and -61 ± 5 J·K^{-1}·mol^{-1}, respectively, with Eyring equation. The obtained negative $\Delta^\ddagger S$ suggests that the transition state is associative, that is, water molecule(s) associates to $\mathrm{Eu}^*(\mathrm{tta})^{2+}$ and then tta^- is released. The exchange reactions of water molecules, one of the basic reactions of ligand substitution, for aquo complexes of some lanthanoids (Gd^{3+} through Yb^{3+}) are taken to be compared. Their transition states were reported to be also associative ($\Delta^\ddagger H > 0$, $\Delta^\ddagger S < 0$, $\Delta^\ddagger V < 0$),[7] showing the similarity of reaction mechanism to $\mathrm{Eu}^*(\mathrm{tta})^{2+}$.

The $k_{\mathrm{obs,s}}$ values do not depend on temperature. Their accuracy was relatively low due to the weak intensity of fluorescence at the longer time range (see Figure 1), but they roughly agree with the k_{Eu} value. These facts also support the scheme postulated in the present study. In our experiments, the equilibrium tta^- concentrations were lower than 1.6×10^{-6} M, which was calculated with the initial concentrations of Eu^{3+} and Htta, pH, pK_a of Htta (= 6.23)[10] and the stability constant of $\mathrm{Eu(tta)}^{2+}$. Under this condition, the formation rate of $\mathrm{Eu}^*(\mathrm{tta})^{2+}$ in the excited state would be slower than the quenching rate of $(\mathrm{Eu}^{3+})^*_{\mathrm{aq}}$ through the OH vibration, i.e., $k^*_1[\mathrm{tta}^-] < k_{\mathrm{Eu}}$. Therefore, the formation process of $\mathrm{Eu}^*(\mathrm{tta})^{2+}$ in the excited state was not included in the rate equations. The logarithmic value of stability constant, β_1, of Eu^{3+}–acetate complex was reported to be 1.76 ($I = 0.1$ M, 25 °C),[11] from which the concentration of Eu^{3+}–acetate complex was calculated to be negligibly low under the experimental conditions. This was also supported by the fact that the fluorescence characteristics of Eu(III)-Htta were not affected by the kind of buffer (acetate or HEPES).

This quenching mechanism of Eu(III) found in the present study can be applied to measure rate constants for chemical reactions of fluorescent metal ions like Eu^{3+}. It will be also used to analysis anomalous short lifetimes of fluorescent lanthanoids.

References and Notes

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