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Luminescence Lifetimes of Aqueous Europium Chloride, Nitrate, Sulfate, and Perchlorate Solutions. Studies on the Nature of the Inner Coordination Sphere of the Europium(III) Ion[1]

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The luminescence lifetime of the europium(III) ion has been measured with high accuracy for aqueous chloride, nitrate, sulfate, and perchlorate solutions in a wide range of concentrations. The lifetime for chloride solutions shows a nearly constant value of ~110 μs from 10^{-4} M to ca. 1 M, and in more concentrated solutions it decreases slightly. This result indicates that the number of inner-sphere coordinated water molecules around a europium ion scarcely changes through a wide range of concentration. The inner-sphere complexation of Eu^{3+} with Cl^- is examined on the basis of the present result and those of other methods. The lifetimes for nitrate and sulfate solutions increase with increasing concentration by the formation of an inner-sphere complex, and the inner-sphere complex disappears at 10^{-3} M in the nitrate solution while it remains at 5×10^{-5} M in the sulfate solution. The lifetime for perchlorate solutions not exceeding 0.1 M is ~110 μs, and in higher concentrations it decreases remarkably with increasing concentration. This decrease of the lifetime is interpreted as an increase of the average hydration number of the Eu^{3+} aquo ion.

Introduction

It is well-known that the luminescent properties of europium(III) and terbium(III) ions in solution are sensitive to the environment of the first coordination sphere surrounding the ions.[2-7] Since for the first time Kropp and Windsor utilized the luminescence yield and lifetime for the study of ion association in Eu^{3+}– and Tb^{3+}–acetate systems,[7] the luminescence technique has become an important method for studies of solutions of Eu^{3+} and Tb^{3+} ions including determination of the hydration number of the aquo ion,[4] discrimination between inner-sphere and outer-sphere complex,[8,9] preferential solvation in mixed solvent,[4] and so on. The extensive work by Horrocks et al.[10-12] showed that the measurement of luminescence lifetimes in both H_2O and D_2O solutions is a useful method to determine quantitatively the number of water molecules coordinated to a Eu^{3+} ion or a Tb^{3+} ion in aqueous solutions. However, the hydration numbers of the aquo ions estimated by that method are fairly different from those estimated by X-ray diffraction.

The hydration number of the aquo ion of rare earths has been an interesting problem in solution chemistry.[13] On the basis of transport and thermodynamic data, it was pointed out that the hydration number changes from 9 for lighter rare-earth ions (La–Nd) to 8 for heavier rare-earth ions (Tb–Lu).[14,15] By means of X-ray diffraction on rare-earth-ion series, Habenschuss and Speeding[16-18] ascertained such a change of the hydration number directly, while other X-ray studies[19,20] gave a value of 8 for all ions of La, Nd, and Gd. A value of 8.5 was also obtained for Nd from neutron diffraction experiments.[22,23] According to the X-ray data by Habenschuss and Spedding, the hydration number is 8.3[18] for the Eu^{3+} ion in the middle region (Sm–Gd) and 8.2[16] for the Tb^{3+} ion in the heavier region. The values estimated by the luminescence method are 9[24] or 9.6[11] for the Eu^{3+} ion and 9[11] for the Tb^{3+} ion. To develop the luminescence method further, this disagreement should be examined in detail. In this study the luminescence lifetimes of aqueous europium chloride, nitrate, sulfate, and perchlorate solutions have been measured with higher accuracy than that in other workers' previous studies. The concentration range was widened to a higher level as employed in X-ray experiments and to a lower level for the purpose of elucidating the influence of the inner-sphere complexation.

Recently, a publication closely associated with our present work was presented.[25]

Experimental Section

$EuCl_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, and Eu_2O_3 were obtained from Mitsuwa Chemicals. $Eu(ClO_4)_3 \cdot 6D_2O$ and D_2O (99.95%) were obtained from Merck. $Eu(ClO_4)_3 \cdot 6H_2O$ was prepared by dissolving Eu_2O_3 into a slightly less than stoichiometric amount of perchloric acid and evaporating the filtrate in a vacuum desiccator. $Eu_2(SO_4)_3 \cdot 8H_2O$ was prepared by producing a precipitate by the addition of ethanol into the filtrate of $Eu_2(SO_4)_3$ similarly made from Eu_2O_3 and sulfuric acid. NaCl and $NaClO_4 \cdot H_2O$ were employed as additives of Cl^- and ClO_4^-. Ion-exchange water was used, and the concentration of the europium ion was determined by a chelate titration. The excitation of the europium ion was carried out by using a nitrogen laser (ca. 0.5 mJ/pulse) constructed in our laboratory and 2-acetonaphthone as a sensitizer. A 0.1 M acetonitrile solution of 2-acetonaphthone, which was dehydrated over molecular sieves, was added to sample solutions in 1% amounts. The influence of the addition of a small quantity of acetonitrile is considered to be negligible.[4] The luminescence from the $^5D_0 \rightarrow {}^7F_1$ transition at 592 nm was taken out

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Table I. Luminescence Lifetimes of Eu(III) in Aqueous Solutions of $EuCl_3$, $Eu(NO_3)_3$, and $Eu_2(SO_4)_3$

	τ^{H_2O}, μs	
R^a	$EuCl_3$	$Eu(NO_3)_3$
16	108.7 ± 0.2	133.2 ± 0.2
18	108.5 ± 0.1	
20	108.7 ± 0.1	129.4 ± 0.6
25	108.7 ± 0.1	127.5 ± 0.2

concn, mol L^{-1}	τ^{H_2O}, μs	concn, mol L^{-1}	τ^{H_2O}, μs
	$EuCl_3$		
0.84	110.0 ± 0.2	1×10^{-3}	110.6 ± 0.9
0.17	110.9 ± 0.2	5×10^{-4}	110.5 ± 0.5
0.054	110.9 ± 0.1	1×10^{-4}	111.3 ± 0.3
0.01	111.0 ± 0.2	0.01^b	109.1 ± 0.4
5×10^{-3}	110.7 ± 0.2		
	$Eu(NO_3)_3$		
1.5	124.4 ± 0.1	0.01	112.0 ± 0.2
1,0	121.7 ± 0.2	1×10^{-3}	110.1 ± 0.4
0.1	115.8 ± 0.1	1×10^{-4}	109.7 ± 0.3
	$Eu_2(SO_4)_3$		
0.034	123.7 ± 0.4	5×10^{-4}	118.1 ± 0.4
5×10^{-3}	121.3 ± 0.3	5×10^{-5}	112.9 ± 0.7

[a] Mole ratio of water to salt. [b] In the presence of 5 M NaCl.

Table II. Luminescence Lifetimes of Eu(III) in H_2O and D_2O Solutions of $Eu(ClO_4)_3$

R^a	τ^{H_2O}, μs	τ^{D_2O}, μs
16	92.7 ± 0.2	2260 ± 4
18	94.9 ± 0.2	
20	96.3 ± 0.1	2440 ± 16
25	98.8 ± 0.1	2652 ± 12
35	102.6 ± 0.2	3018 ± 4
50	105.2 ± 0.2	3260 ± 5

concn, mol L^{-1}	τ^{H_2O}, μs	concn, mol L^{-1}	τ^{D_2O}, μs
0.52	107.8 ± 0.3		
0.1	109.5 ± 0.1	~0.1	3947 ± 16
0.01	109.9 ± 0.1	~0.01	3913 ± 15
1×10^{-3}	109.4 ± 0.3		
1×10^{-4}	110.8 ± 0.7		

[a] Mole ratio of water to salt.

through a monochromator and recorded by a photomultiplier (Hamamatsu R374), a MR-50E transient memory (Kawasaki Electronica), and a TMC-700 averager (Kawasaki Electronica). The number of accumulated signals was 4096 for solutions above 10^{-3} M and 8192 for solutions of lower concentrations. Since a gradual decrease of the lifetime was observed when the irradiation to the dilute solutions was repeated further, new aliquots were always used on the measurement at low concentrations. The lifetime was determined by a least-squares method, and usually the values of four measurements were averaged. The preparation of D_2O solutions of $Eu(ClO_4)_3$ was carried out in a drybox. The addition and evaporation of D_2O was repeated to reduce residual H_2O until a gradual increase of the lifetime was scarcely observed.

Results and Discussion

In H_2O solution a decay rate constant (k^{H_2O}) is related to the number of inner-sphere coordinated water molecules (q) by eq 1[12] where k_r, k_n, and k_{H_2O} are rate constants of radiative

$$k^{H_2O} = k_r + k_n + qk_{H_2O} \tag{1}$$

decay, nonradiative decay not due to H_2O molecules, and nonradiative decay induced by one H_2O molecule, respectively. More strictly, the difference between k^{H_2O} and k^{D_2O} (a decay rate constant in D_2O solution) is utilized.[7,10–12]

$$\Delta k = k^{H_2O} - k^{D_2O} = q(k_{H_2O} - k_{D_2O}) \tag{2}$$

A value of $(k_{H_2O} - k_{D_2O})^{-1} = 1.05$ ms has been derived from experiments on a series of structurally well-defined crystalline solids.[11,12]

The luminescence method gives the value of q in the luminescent state ($^5D_0$), and hence the application of the obtained value to the ground state ($^7F_0$) is based on a hypothesis that the Eu^{3+} ion does not undergo changes in the inner coordination sphere between the two electronic states. Since observations of such changes between different electronic states, in fact, have been reported for a few rare-earth ions,[26,27] it should be noted that the present results may contain the inaccuracy due to the hypothesis.

Europium Chloride. Table I shows that the lifetime (τ^{H_2O}) for aqueous europium chloride solutions is a nearly constant value of ~110 μs from 10^{-4} M to ca. 1 M and decreases only slightly in higher concentrations. This result means that q scarcely changes through a wide range of concentration. The most comprehensible conclusion derived from the invariance of q is that the formation of an inner-sphere complex between Eu^{3+} and Cl^- is negligible even at a high concentration of $R = [H_2O]/[Eu^{3+}] = 16$ and the hydration number of the Eu^{3+} aquo ion is nearly constant from lower concentrations to higher concentrations. The absolute value of q cannot be estimated by the present results alone. If the hydration number of estimated by the present results alone. If the hydration number of 8.3, determined by the X-ray study for a $EuCl_3$ solution of 3.23 mol kg^{-1} ($R = 17.2$),[18] is valid, this value should hold true in a wide range of concentrations. Horrocks and Sudnick, on the basis of eq 2, obtained a value of $q = 9.6$ for the aquo ion in a $EuCl_3$ solution of 10^{-3} M.[11] As to the luminescence lifetime of the Eu^{3+} aquo ion in H_2O solution, a value of 103.6 μs used in that estimation is significantly smaller than ~110 μs in the present measurements and also 110 μs in their own recent experiments.[25] Taking into account this difference, together with the uncertainty of ±0.5 water molecule in eq 2,[11,12] we consider that the estimation of 9.6 may be too high by about 1 unit and the value of 8.3 estimated by the X-ray study is more probable. As mentioned later, the hydration number of the Eu^{3+} ion in the perchlorate solution depends on the concentration, and hence the use of the chloride solution is thought meaningful when the results obtained with different methods in various concentrations are compared.

Here, we should mention the inner-sphere interaction between Eu^{3+} and Cl^- because the formation of the inner-sphere complex has been suggested on the basis of changes in the excitation spectrum.[25] As shown in Table I, the lifetime is 109.1 μs under the conditions for $[Eu^{3+}] = 10^{-2}$ M and $[Cl^-] = 5$ M, similar to the experimental conditions in the excitation spectrum. This value, as well as the results for the concentration change of $EuCl_3$, also does not suggest the formation of inner-sphere complex. According to the formation constant ($K = 0.13$ M^{-1}) obtained from the excitation spectrum,[25] about 40% of the europium ions exist as the inner-sphere complex in this condition. If replacements of coordinated water molecules by the chloride ion occur, then the lifetime should increase to about 115 μs. The fact that q scarcely changes in the inner-sphere complexation between Eu^{3+} and Cl^- implies an increase of an average coordination number of a Eu^{3+} ion. On the other hand, it has been shown in the X-ray studies that no appreciable formation of the inner-sphere complex occurs even at a nearly saturated concentration for aqueous stoichiometric (no excess chloride) rare-earth chloride solutions.[16–21] This is contrast to the calculation from the excitation-spectrum data, which indicates that one-third of the europium ions exist as the inner-sphere complex in a $EuCl_3$

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Table III. Effect of Addition of $NaClO_4$ on the Luminescence Lifetimes of Eu(III) in Aqueous Solutions of $Eu(ClO_4)_3$ and $EuCl_3$

$[Eu(ClO_4)_3]$, mol kg^{-1}	$[NaClO_4]$, mol kg^{-1}	τ^{H_2O}, μs	$[Eu(ClO_4)_3]$, mol L^{-1}	$[NaClO_4]$, mol L^{-1}	τ^{H_2O}, μs	$[EuCl_3]$, mol kg^{-1}	$[NaClO_4]$, mol kg^{-1}	τ^{H_2O}, μs
0.55		107.8 ± 0.3	0.01		110.5 ± 0.5	0.83		109.1
0.52	3.8	103.0 ± 0.3	0.01	1.03	109.4 ± 0.3	0.80	2.09	107.0
0.44	11.8	96.0 ± 0.1	0.01	3.24	105.6 ± 0.1	0.77	2.14	105.7
0.10		109.5 ± 0.1	0.01	5.05	102.4 ± 0.2	0.73	6.19	103.2
0.099	0.66	109.1 ± 0.1	0.01	7.75	97.8 ± 0.1	0.66	11.1	98.8
0.095	2.65	106.2 ± 0.1						
0.092	4.55	104.2 ± 0.2						
0.089	6.15	102.3 ± 0.1						
0.085	8.28	100.2 ± 0.1						

solution of 3.23 mol kg^{-1}.[25] Further work is required to clarify the nature of the inner-sphere interaction in this system.

Europium Nitrate and Sulfate. The lifetime for nitrate solutions in Table I increases with increasing concentration, similar to results of previous workers,[9,25] suggesting that q decreases by the formation of inner-sphere complex. The high-accuracy measurement of the lifetime in this study reveals that a slight amount of the inner-sphere complex remains at 10^{-2} M and disappears at 10^{-3} M. A recent study by Marcantonatos et al. implies that these results for the luminescent state ($^5D_0$) are not applicable to the ground state ($^7F_0$). On the basis of spectroscopic measurements including a transient photokinetic method, they concluded that the inner-sphere complex between Eu^{3+} and NO_3^- is formed only in the $^5D_0$ state and the complex in the $^7F_0$ state is an outer-sphere type. However, their argument concerning the $^7F_0$ state is mainly based on thermodynamic data, and the possibility of coexistence of inner-and outer-sphere complexes is not taken into account. In light of diverse conclusions obtained for rare-earth nitrate complexes,[25,28-32] it seems impossible to exclude the existence of the inner-sphere complex in the ground state completely.

Many studies on the complexation between Eu^{3+} and SO_4^{2-} gave different conclusions about the character of the complex formed.[33] On the basis of thermodynamic data, Hale and Spedding suggested that the complex is predominantly an inner-sphere type.[33,34] The formation of the inner-sphere complex is shown directly by the lifetime data in Table I, and clearly the inner-sphere complex exists at a low concentration of 5×10^{-5} M. Using eq 2, we can calculate the average number (Δq) of inner-sphere coordinated water molecules removed by the complexation. Using $q = 8.3$ for the Eu^{3+} aquo ion, we obtain $\Delta q = 0.57 \pm 0.08$ and 0.78 ± 0.05 for $Eu_2(SO_4)_3$ solutions of 5×10^{-4} and 5×10^{-3} M, respectively.[35] On the other hand, fractions of the complexed europium ions at 15 °C (approximate temperature in this experiment) assessed by equations in ref 33 are 59% and 81% for the 5×10^{-4} and 5×10^{-3} M solutions, respectively.[36] These calculations show that the value of Δq is nearly equal to the fraction of the complexed europium ions at both concentrations. Since the ratio of inner-sphere to outer-sphere complex and the character of the anion (monodentate or bidentate) are not clear, for the present we cannot correlate this result directly with the nature of coordination of the inner-sphere complex.

Europium Perchlorate. As shown in Table II, the lifetime for H_2O solutions of $Eu(ClO_4)_3$ is a nearly constant value of ~110 μs up to 0.1 M and decreases remarkably in higher concentrations. This result, together with other recent studies,[9,25] excludes the formation of the inner-sphere complex. The anomalous trend observed in higher concentrations appears to suggest an increase of q. In order to examine the possibility of participation of k_n in this phenomenon, the lifetime for the D_2O solutions was measured. Though the decrease of the lifetime in higher concentrations is also observed for the D_2O solution (Table II), absolute changes in k^{D_2O} are much smaller than those in k^{H_2O} and so Δk increases significantly with increasing concentration.[37] This increase of Δk means that the average hydration number of the Eu^{3+} aquo ion increases in the concentrated perchlorate solutions. The addition of $NaClO_4$ to $Eu(ClO_4)_3$ or $EuCl_3$ solutions also decreases the lifetime as shown in Table III. Breen and Horrocks first reported this effect of high concentrations of ClO_4^- ion on the lifetime and indicated the change in the average hydration number of the Eu^{3+} aquo ion.[25] As they have mentioned, we also consider that the penetration of ClO_4^- ions into the second hydration sphere around a Eu^{3+} ion brings out the increase of the number of water molecules in the inner coordination sphere when the salt concentration or the total ClO_4^- concentration is increased. Using $q = 8.3$ for the Eu^{3+} aquo ion in the dilute solution, we obtain $q = 9.7$ for a $Eu(ClO_4)_3$ solution of $R = 16$. In a Raman study, Kanno and Hiraishi have presented a similar finding and a more detailed explanation for glassy $EuCl_3$ and $GdCl_3$ solutions at low temperatures.[38] Contrary to an expectation from that result, the decrease of the lifetime in higher concentrations is only slight for the $EuCl_3$ solution, as already described. On the basis of the measurement of the glass transition temperature, it has been postulated that main species of Gd^{3+} aquo ions is eight-coordinated for the chloride solution and nine-coordinated for the perchlorate solution.[39] That tendency is consistent with the present results for the europium ion, although this problem should be further examined from the viewpoints of the existence of the inner-sphere complex of $Eu^{3+}-Cl^-$ and the different effects of the two anions on the outer-sphere hydration structure around the europium ion.

Registry No. Eu(III), 22541-18-0; Cl^-, 16887-00-6; NO_3^-, 14797-55-8; SO_4^{2-}, 14808-79-8; ClO_4^-, 14797-73-0.

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(35) As the lifetime for the Eu^{3+} aquo ion we used 110.3 ± 0.5 μs, an average value of data for the chloride and perchlorate solutions below 0.1 M and the nitrate solutions of 10^{-3} and 10^{-4} M. For all D_2O solutions $k^{D_2O} = 253$ s^{-1} (a value for ~0.1 M $Eu(ClO_4)_3$ solution) was assumed.

(36) The calculation was performed by using two equations in ref 33; an equation of temperature dependence of k°_1 and an equation providing the dependence of K on the ionic strength.

(37) Since the influence of normal water remaining in the crystals of $Eu(ClO_4)_3 \cdot 6D_2O$ or entering into D_2O solutions during preparation is more significant in concentrated solutions, there may be some uncertainty in the obtained result.

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