Pulse Radiolysis Study on Reactions of a Hydrated Electron with Europium(III)−Aminopolycarboxylate Complexes in Aqueous Perchlorate Media

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Pulse radiolysis of 1:1 complexes of europium(III)−aminopolycarboxylates was studied in aqueous perchlorate solutions to understand relations of the reduction rate of Eu(III) with hydration state and stability of the complex. The rate constant for the reaction of a hydrated electron (e_{aq}^-) with the complex was determined in the temperature range of 278.15 to 333.15 K and the ionic strength range of 0.05 to 1.0 mol kg^{-1}. The rate constant was linearly related not only with the residual hydration number of the complex representing the hydration state but also with the stability constant and redox potential as equilibrium constants. The reaction of e_{aq}^- with the complex was described by diffusive encounter and successive electron-transfer processes between e_{aq}^- and the complex. Gibbs free energy, enthalpy, and entropy of activation for the reaction were obtained from the effect of temperature on the rate constant, and the entropy term was found to be a dominant factor for the electron-transfer process after the diffusion process. These indicated that the entropy term, reflecting ionic interaction of Eu(III)−carboxylate groups and dehydration of aquo Eu(III) ion on the complexation, caused the difference in the rate constant between the complexes, and linear correlation between the rate constant and hydration number. The effect of ionic strength on the rate constant was examined by using the extended Debye−Hückel equation based on the specific ion interaction theory. Variation of the rate constant with the ionic strength was explained qualitatively by the diffusive encounter, characterized by the product of the expected charges, between e_{aq}^- and the complex. Ion interaction coefficients of e_{aq}^-, Eu(III), and activated complexes for the reaction were also discussed.

Introduction

Reduction−oxidation (redox) behavior of actinide and lanthanide ions in a solution is dependent on the oxidation states and chemical forms. The chemical form is characterized by hydration, solvation and complexation taking place in the coordination sphere of the ion. Elucidation of correlation between the redox reaction rate and coordination structure of the ion provides significant information on reaction systems involved in a wet-chemical process of nuclear technology and a migration process of the ion in geosphere and biosphere. To discuss the relation, experimental data on reaction kinetics and coordination chemistry of the ion are required to be correlated with each other systematically. However, since these investigations have so far been performed individually as mentioned below, no explanation for the relationship can be offered at the present time.

Reactions of trivalent actinide(III) (An: Am and Cm) and lanthanide(III) (Ln: Sm, Eu, Tm ,and Yb) ions with a radiolysis product of hydrated electron (e_{aq}^-) in aqueous solutions have been investigated by using a pulse radiolysis technique,[1−3] where the e_{aq}^- has a reduction potential of $E° = -2.87$ V (vs NHE) and reduces the trivalent ion to a divalent one. It was found that the reduction rates of aquo An(III) and Ln(III) ions decreased with decreasing the reduction potential $E°$ (III/II)[4] of the ions although there were differences in ionic radius and total coordination number between the ions. The formation process and spectroscopic property of the highly reactive divalent ion formed by the radiolysis and photolysis have been studied[5−8] from viewpoints of the application of divalent ions to H_2 generation as a reactant, and functional material and dosimeter (or actinometer) as a luminescent.

Coordination states of An(III) and Ln(III) ions and complexes have been investigated extensively in various inorganic and organic solutions by fluorescence spectroscopic methods. Hydration numbers, N_{H_2O}, in the first coordination sphere of An(III) and Ln(III) have been determined[9−11] by measurement of the fluorescence lifetimes using the time-resolved laser-induced fluorescence spectroscopy (TRLFS), because the photoexcited ion is quenched dominantly by electronic-vibrational energy transfer from the ions to O−H oscillators of solvating water molecules.[9,12]

To study the correlation between the redox reaction rate and the coordination structure of An(III) and Ln(III), 1:1 complexes of Eu(III)−aminopolycarboxylates are adopted for the following reasons. Eu is used as a typical element of luminescent probes for coordination chemistry of Ln(III), and its $E°$ (III/II) $= -0.35$ V for the aquo Eu(III) ion[4] allows the trivalent ion to be reduced easily by e_{aq}^- and by using an electrochemical method. Aminopolycarboxylic acids, of which carboxylate and amino groups as donor sites are capable to coordinate to Eu(III), are

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employed as chelating reagents. The residual N_{H_2O} of the complex was obtained in the previous work using TRLFS.[11] The stability constant, log β_1, of the complex and its thermodynamic parameters were determined and related with numbers, ΔN_{H_2O}, of solvating water molecules removed from the aquo ion.[13-15] In the present study, pulse radiolysis of the 1:1 complexes was conducted in aqueous perchlorate solutions, where variation of the rate constant, k_e, for the reaction of e_{aq}^- with the complex was observed with that of the N_{H_2O} across the aminopolycarboxylate series. The reaction mechanism was described on the basis of the relation between the k_e and N_{H_2O}, and discussed in terms of the effects of temperature and ionic strength on the k_e to clarify the correlation between the reduction rate of Eu(III) and the coordination structure of the complex.

Experimental Section

Reagents. Eu_2O_3 (Wako Pure Chem. Ind., Ltd.) was dissolved in $HClO_4$ and the solution was dried up to obtain the Eu(III) perchlorate salt. A stock solution of 0.5 mol dm^{-3} Eu(III) was prepared by dissolving the perchlorate salt in 1.0 mol dm^{-3} $HClO_4$ solution. Nine aminopolycarboxylic acids of nitrilotriacetic acid (NTA), *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid (HEDTA), ethylenediamine-*N*,*N*′-diacetic-*N*,*N*′-dipropionic acid (ENDADP), ethylenediaminetetraacetic acid (EDTA), 1,2-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetic acid (PDTA), *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (CDTA), diethylenetriaminepentaacetic acid (DTPA), glycoletherdiaminetetraacetic acid (EGTA), and triethylenetetraamine-*N*,*N*,*N*′,-*N*″,*N*‴,*N*‴-hexaacetic acid (TTHA) were used as received from Tokyo Kasei Kogyo Co., Ltd. Sample solutions of the aminopolycarboxylate complexes were prepared by mixing the Eu(III) and ligand stock solutions at concentration ratio of [L]/[Eu] = 1. The pH of the sample solution was adjusted by the addition of the standard NaOH or $HClO_4$ solutions. The pH for the preparation of 1:1 complexes of Eu(III)-ligands were 5.5 (without ligand), 4−5 (NTA), 4−6 (HEDTA), 5−7 (ENDADP), 4−6 (EDTA), 4−6 (PDTA), 4−6 (CDTA), 4−6 (DTPA), 4−6 (EGTA), and 6−7 (TTHA). Formation of the 1:1 complex was confirmed by the measurement of N_{H_2O} that was characteristic of the complex and constant in the pH range.[11] Initial concentration of Eu(III) was from 0.1 to 10 mmol dm^{-3}. Ionic strength, μ_m, of the sample solution was varied from 0.05 to 1.0 mol kg^{-3} by adding $NaClO_4$.

Apparatus. A spectrophotometric pulse radiolysis system was described elsewhere.[16] Electron pulses with a width of 8 ns, typical intensity of 30 nC pulse^{-1} and energy of 28 MeV from the L-band LINAC at Radiation Laboratory, ISIR, Osaka University, were used to irradiate the sample solution to observe transient intermediates in the wavelength range of 300−1000 nm and time range within 5 μs. Optical quartz cells with 10 or 20 mm path length were used as irradiation cells for the sample solution. Analyzing light from a Xe flash lamp passed through the cell coaxially in the beam direction of the electron pulses so that the optical path length was equal to the cell length. Although transient absorption of the divalent Eu(II) complex and the spectrum identified by two peaks of 260 and 320 nm[1] were observed in the time region shorter than 5 μs, absorption of e_{aq}^- was traced for the determination of the rate constant for the reaction of e_{aq}^- with the Eu(III) complex because of the higher molar absorption coefficient (19000 dm^3 mol^{-1} cm^{-1} at 720 nm) and the spectrum in the wide wavelength range from the UV to the near-IR region. The first-order decay curve of e_{aq}^- was fitted by the least-squares method to obtain the decay constant with experimental error less than 5%. Temperature control of the sample solution was made by a water jacket combined with a thermostat and a magnetic stirrer. The cell was covered with the jacket and a magnetic rotator in the cell stirred the solution. The sample solution was purged with Ar or N_2 gases, and the experiment was carried out at room temperature unless otherwise noted. The energy deposition was assumed to be proportional to the electron density of the solution and was corrected accordingly for estimation of formation yields of radiolysis products.

Results and Discussions

Homogeneous second-order reactions of e_{aq}^- within 5.0 μs after irradiation can be described as follows:

$$e_{aq}^- + H^+ \rightarrow H \quad \text{rate constant of } 2.3 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1\ 17} \tag{1}$$

$$e_{aq}^- + O_2 \rightarrow O_2^- \quad \text{rate constant of } 1.9 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1\ 17} \tag{2}$$

$$e_{aq}^- + L \rightarrow L^- \quad k_L \tag{3}$$

$$e_{aq}^- + [\text{Eu(III)L}(H_2O)_p]^{(3-l)+} \rightarrow [\text{Eu(II)L}(H_2O)_x]^{(2-l)+} \quad k_e \tag{4}$$

where L denotes the ligand molecule of aminopolycarboxylate, *l* number of negative charges originating mainly from deprotonated carboxylate groups of the ligand, and *p* (*x*) residual hydration number of Eu(III) (Eu(II)) complex. In deaerated solutions of pH > 4.0 and 0.1−10 mmol dm^{-3} Eu(III), reactions 1 and 2 were suppressed and became negligible in the present study. Self-decay of e_{aq}^-, composed of reactions of e_{aq}^- with e_{aq}^- and OH radical, was observed in the absence of Eu(III) and ligand at various pH and ionic strengths, and the decay curve was found to be of first-order (decay constant: k_0). Therefore, the decay constant, $k_{obs}(e_{aq}^-)$, for a pseudo-first-order decay of e_{aq}^- in the presence of the Eu(III) complex can be expressed in the equation

$$k_{obs}(e_{aq}^-) = k_0 + k_L[\text{ligand}] + k_e[\text{Eu(III)}] \tag{5}$$

The k_e for reaction 4 as a key reaction in the present study can be determined from the k_{obs} obtained in the absence and presence of Eu(III). The k_L for reaction 3 can be also determined from the k_{obs} obtained in the absence and presence of the ligand.

Relation between the Rate Constant for the Reaction of e_{aq}^- with the Eu(III) Complex and the Hydration Number of the Complex. Typical time-profiles of absorption of e_{aq}^- in deaerated solutions of 0.1 mmol dm^{-3} Eu(III) aquo ion and complexes are shown in Figure 1. The decay curve of e_{aq}^- was of first-order, and the decay rate was in the order of aquo ion > NTA complex > TTHA complex, corresponding to the order of hydration number, N_{H_2O}, of the aquo ion and complexes. Kimura and Kato[11] estimated dependences of the N_{H_2O} on pH and the concentration ratio ([L]/[Eu]). Assuming that one water molecule was removed from the aquo Eu(III) ion when one donor site of ligand was coordinated to Eu(III) during the inner-sphere complexation, the total coordination number, CN_T, of Eu(III) was calculated as the sum of the residual N_{H_2O} and ligand coordination number CN_L,[14]

$$CN_T = N_{H_2O} + CN_L \tag{6}$$

and the averaged value was 8.9 ± 0.4. The number of solvating

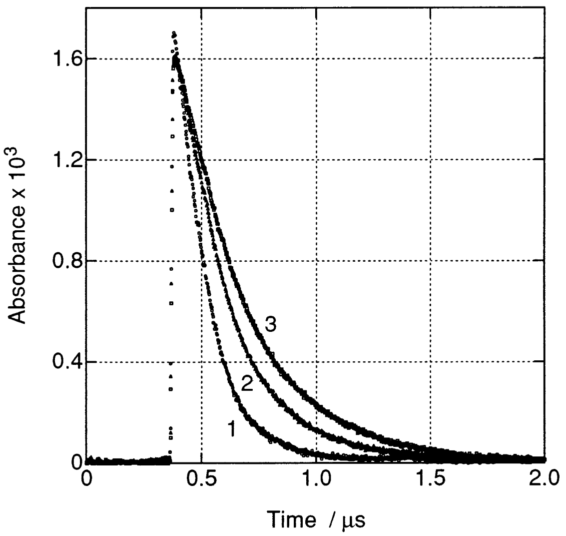

Figure 1. Time-profiles of absorption of e_{aq}^- in aqueous deaerated solutions of 0.1 mmol dm^{-3} Eu(III) aquo ion and complexes. $\lambda_{obs} = 500$ nm. Eu(III) aquo ion at pH 5.5 (1), and Eu(III) complexes with NTA at pH 4.3 (2), and TTHA at pH 6.1 (3).

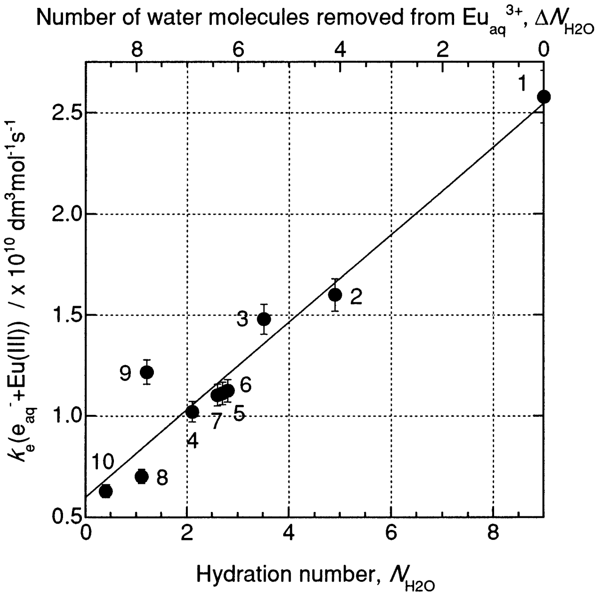

Figure 2. Rate constants for the reactions of e_{aq}^- with Eu(III) aquo ion and complexes in 0.1 mol dm^{-3} $NaClO_4$ solution. Eu(III) aquo ion at pH 5.5 (1) and Eu(III) complexes: NTA at pH 4.3 (2), HEDTA at pH 4.7 (3), ENDADP at pH 6.4 (4), EDTA at pH 5.9 (5), PDTA at pH 4.9 (6), CDTA at pH 5.6 (7), DTPA at pH 5.7 (8), EGTA at pH 4.9 (9), and TTHA at pH 6.1 at (10). $[Eu(III)]_0 = 0.1-5.0$ mmol dm^{-3}. Three independent data were averaged for each complex.

TABLE 1: Rate Constants for the Reactions of e_{aq}^- with 1:1 Complexes of Eu(III)−Aminopolycarboxylates in 0.1 mol dm^{-3} $NaClO_4$ Solution[a]

ligand	N_{H_2O}	$k_L \times 10^{-7}$	$k_e \times 10^{-10}$
aquo	9.0 ± 0.2		2.58 ± 0.13
NTA	4.9 ± 0.2	0.39 ± 0.03	1.60 ± 0.08
HEDTA	3.5 ± 0.2	17 ± 1	1.48 ± 0.07
ENDADP	2.1 ± 0.2	230 ± 16	1.02 ± 0.05
EDTA	2.7 ± 0.2	0.10 ± 0.007	1.11 ± 0.06
PDTA	2.8 ± 0.2	3.4 ± 0.2	1.13 ± 0.06
CDTA	2.6 ± 0.2	4.0 ± 0.3	1.11 ± 0.06
DTPA	1.1 ± 0.1	0.90 ± 0.06	0.70 ± 0.04
EGTA	1.2 ± 0.1	0.71 ± 0.05	1.22 ± 0.06
TTHA	0.4 ± 0.1	<0.01	0.63 ± 0.03

[a] Data were obtained at room temperature and pH shown in Figure 2. The k_L and k_e were in the unit of dm^3 mol^{-1} s^{-1}. The N_{H_2O} was obtained from the lifetime measurement of the sample solution using TRLFS.[11]

water molecules removed from the aquo ion, ΔN_{H_2O}, is defined to be equal to CN_L. It is worthwhile for the following discussion to summarize the N_{H_2O} [11] and number, $N(-CO_2H)$, of coordinated carboxylate groups in the 1:1 complex explicitly by parenthesis of (N_{H_2O}, $N(-CO_2H)$): NTA (4.7, 3), HEDTA (3.4, 3), ENDADP (3.3, 4), EDTA (2.8, 4), PDTA (2.8, 4), CDTA (2.6, 4), DTPA (1.1, 5), EGTA (1.2, 4), and TTHA (0.4, 6).

The rate constant, k_e, for the reaction of e_{aq}^- with the Eu(III) complex in 0.1 mol dm^{-3} $NaClO_4$ solution was determined from the decay constant, k_{obs}, of e_{aq}^- as shown in Figure 2. Table 1 summarizes the results of k_e and k_L. The N_{H_2O} values given in Table 1 were determined directly from the lifetime measurement of the sample solutions using TRLFS,[11] where there were a large discrepancy between the N_{H_2O} for ENDADP obtained in the present study and in the previous study.[11] For all the aminopolycarboxylates examined, the k_e was larger than the k_L. The k_e was not affected by pH as long as the 1:1 complex was dominantly formed in the solution, and found to decrease linearly with decreasing N_{H_2O} (or increasing ΔN_{H_2O}), i.e., in the order of NTA > HEDTA > ENDADP = EDTA = PDTA = CDTA > DTPA > TTHA except for EGTA. The k_e for the EGTA complex was close to that for the EDTA complex with the same $N(-CO_2H)$ rather than that for the DTPA complex with the same N_{H_2O}. The linear correlation between k_e and ΔN_{H_2O} was also represented as

$$(-\Delta k_e)/k_e^{aq} = (0.089 \pm 0.004)\ \Delta N_{H_2O} \qquad (7)$$

where k_e^{aq} is the rate constant for the aquo Eu(III) ion and $\Delta k_e = k_e - k_e^{aq}$. These indicate clearly that the reaction reflects the hydration state in the first coordination sphere of Eu(III).

Similar linearity appeared in the correlation between N_{H_2O} and the stability of the complex. In preliminary experiments,[3] the reduction wave of Eu(III) and the oxidation wave of Eu(II) were observed in 0.1 mol dm^{-3} $NaClO_4$ solution for the aquo ion and complexes of NTA, EDTA, DTPA, and TTHA by using cyclic voltammetry with a hanging mercury electrode,[18] where peak potentials of the reduction and oxidation waves (E_P^{red} and E_P^{ox}) were measured. The E_P^{red} was found to be from −0.326 (aquo) to −1.14 V vs NHE (TTHA), and the E_P^{ox} from −0.243 to −0.993 V. Both potentials decreased with decreasing N_{H_2O}, showing an almost linear relation between the potentials and N_{H_2O}. Stability constant, log β_1, for the 1:1 complex[15] increases linearly with decreasing N_{H_2O}. In a similar manner as the k_e, the log β_1 for the EGTA complex is close to that for the EDTA complex. Subsequently, the k_e has linear relations not only with N_{H_2O} but also with the equilibrium constants, although in general there is not such a linear relation between the rate constant for the one-way reaction and the equilibrium constant.

In the course of the reaction of e_{aq}^- with the Eu(III) complex, both reactants first diffuse in solution to encounter each other (diffusive encounter process) and then one-electron transfer from e_{aq}^- to Eu(III) takes place (electron-transfer process). The diffusion process is governed by a sum of the diffusion constants of e_{aq}^- and the complex in the solution as expected from the Smoluchowski-Debye equation for diffusion-controlled limits of reactions. The diffusion constants of e_{aq}^- and aquo Eu(III) ion are 4.96 × 10^{-5} and 0.62 × 10^{-5} cm^2 s^{-1}, respectively. The diffusion constant of the Eu(III) complex of TTHA largest in the complexes under interest was estimated from a peak current on the reduction wave of the complex,[3] and was at least a half smaller than that of the aquo ion. Accordingly, variation in the sum with a series of the complexes becomes negligible within an experimental error of the k_e. Therefore, the electron transfer process is considered dominantly to cause the difference in the k_e for the complexes. The electron-transfer process can be further separated into successive three processes: (a) expansion or dissociation of the bond between Eu(III) and the ligand, (b) formation of the activated complex of e_{aq}^- −Eu(III) to generate Eu(II), and (c) reorientation of the ligand and water molecules to form the Eu(II)−ligand complex. Processes (a) and (c) reflect orientation of the coordinated ligand and water molecules in the first coordination sphere of Eu and are expected to depend on N_{H_2O}. In the activated state (b) where the oxidation state of the Eu ion changes from +3 to +2, not only ionic radius but also CN_T of the Eu might change.

Effect of Temperature on the Reaction Kinetics of e_{aq}^- with the Eu(III) Complex. Activation parameters (Gibbs free energy, $\Delta G_e^‡$, enthalpy, $\Delta H_e^‡$, and entropy, $\Delta S_e^‡$) for the reaction are estimated from the effect of temperature on the k_e. According to Eyring et al.,[19] the k_e can be expressed on the basis of the transition-state theory as follows:

$$k_e = \kappa(k_bT/h)\exp(-\Delta G_e^‡/RT) = \kappa(k_bT/h)\exp(\Delta S_e^‡/R)\exp(-\Delta H_e^‡/RT) \quad (8)$$

where κ, k_b, h, and R denote the transmission coefficient, Boltzman constant, Planck constant, and molar gas constant, respectively. Preexponential factor (A) and activation energy (E_a) in the Arrhenius equation can be obtained as $A = \kappa(k_bT/h)\exp(\Delta S_e^‡/R)$ and $E_a = \Delta H_e^‡ + RT$, respectively. Figure 3a shows the Eyring plots of k_e for the Eu(III) aquo ion and complexes of NTA, EDTA, DTPA, and TTHA. Except for TTHA having an excess steric factor, slopes of the plots were in parallel irrespective of kinds of complexes, leading to constant values of $\Delta H_e^‡$ and E_a. The excess steric factor for the TTHA complex is considered to result from an excess of donor sites of TTHA over coordination sites of Eu(III), and lowers the $\Delta H_e^‡$ and E_a. Assuming $\kappa = 1$ regarded as adiabatic change for the reaction, the activation parameters were estimated from slopes and intercepts of the plots as listed in Table 2, and plotted against N_{H_2O} as shown in Figure 3b. Except for TTHA, the entropy term, $T\Delta S_e^‡$, increased with an increase of N_{H_2O} and the absolute value, $|T\Delta S_e^‡|$, became smaller. This indicates that the entropy term reflects steric factors such as geometrical configuration and reorientation of the ligand and water molecules in the first coordination sphere of Eu(III), and that the water molecules are more mobile for reorientation than the ligand molecules. The enthalpy term $\Delta H_e^‡$, reflecting bonding factors between the initial and activated states, was almost constant. On the other hand, $\Delta G_e^‡$ decreased with an increase of N_{H_2O} for all of the aquo ion and complexes. It can be noted that enthalpy and entropy changes causing the excess steric factor for the TTHA complex are compensated with each other. Since the absolute values show that $|T\Delta S_e^‡| > |\Delta H_e^‡|$, the entropy term is a dominant factor for the reaction, especially for the electron-transfer process, and brings about difference in the k_e for the aquo ion and complexes.

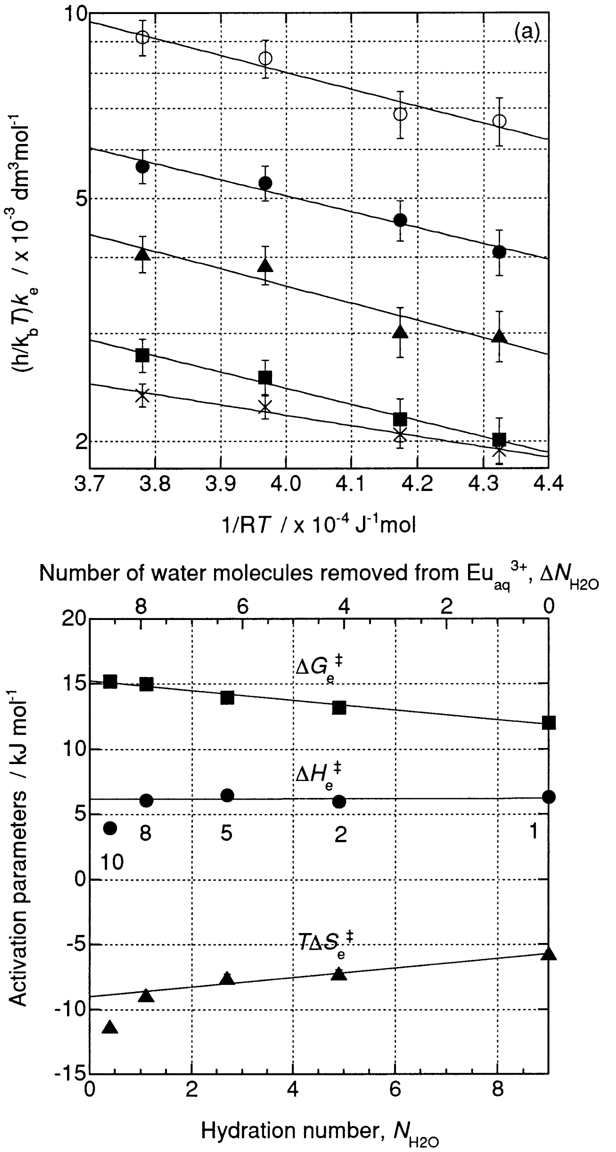

Figure 3. Eyring plots (a) and the activation parameters at 298.15 K (b) for the reactions of e_{aq}^- with Eu(III) aquo ion and complexes. Eu(III) aquo ion at pH 5.5 (○) and Eu(III) complexes: NTA at pH 4.3 (●), EDTA at pH 5.9 (▲), DTPA at pH 5.7 (■), and TTHA at pH 6.1 (×). $[Eu(III)]_0 = 5.0$ mmol dm^{-3}. Numbering in the figure is same as in Figure 2.

TABLE 2: Activation Parameters at 298.15 K for the Reactions of e_{aq}^- with 1:1 Complexes of Eu(III)−Aminopolycarboxylates[a]

ligand	$A \times 10^{-11}$	E_a	$\Delta G_e^‡$	$\Delta H_e^‡$	$-T\Delta S_e^‡$
aquo	17 ± 2	8.8 ± 0.5	12.1 ± 0.5	6.4 ± 0.4	5.7 ± 0.3
NTA	9.4 ± 0.9	8.5 ± 0.4	13.2 ± 0.4	6.0 ± 0.3	7.2 ± 0.3
EDTA	8.2 ± 0.8	8.9 ± 0.7	14.0 ± 0.6	6.5 ± 0.5	7.5 ± 0.2
DTPA	4.7 ± 0.6	8.6 ± 0.3	15.0 ± 0.4	6.1 ± 0.2	8.9 ± 0.3
TTHA	1.8 ± 0.2	6.4 ± 0.2	15.2 ± 0.6	4.0 ± 0.1	11.3 ± 0.3

[a] Data were obtained at pH shown in Figure 3. The A was in a unit of dm^3 mol^{-1} s^{-1}, and the E_a, $\Delta G_e^‡$, $\Delta H_e^‡$ and $-T\Delta S_e^‡$ in a unit of kJ mol^{-1}.

Such an entropy effect on the reaction and the relation between the entropy term and N_{H_2O} can be explained by thermodynamics of complexation. Free energy change ΔG_1(III) corresponding to log β_1 for the formation of Eu(III) complex is divided into free energy changes for two processes, i.e., ligand coordination to the aquo Eu(III) ion (ΔG_R) and subsequent dehydration of the aquo ion (ΔG_H). Although ΔG_H is much larger than ΔG_R, enthalpy and entropy changes for the dehydration are compensated with each other,[20] leading to the relation $\Delta G_1(III) \sim \Delta G_R$. Choppin et al.[14] found that entropy change ΔS_1(III) was a direct function of $N(-CO_2H)$ and pointed out that bonding of Eu(III)−carboxylate groups causes the dehydration of the aquo ion but not the bonding of Eu(III)−amino groups. Furthermore, from the k_e and log β_1 for the EGTA

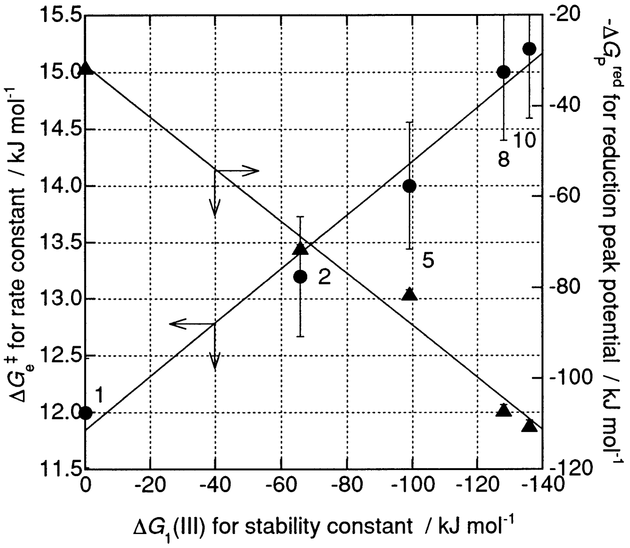

Figure 4. Linear free energy relationships of the activation free energy (●) and reduction peak potential (▲) as a function of the stability constant of Eu(III) complex. Numbering in the figure is same as in Figure 2.

complex, it is suggested that the ether oxygen of EGTA behaves as if its bonding with Eu(III) caused the dehydration of the aquo ion without affecting ΔG_1(III). These suggest that when any factors other than the entropy effect on the electron-transfer process cannot affect the reaction, k_e for any ligands with a specified ΔN_{H_2O} and $N(-CO_2H)$ is identical with that for a certain aminopolycarboxylate with the same ΔN_{H_2O} and $N(-CO_2H)$.

In addition, the following two relations can be deduced for the aminopolycarboxylate complexes when the thermodynamic constants mentioned above are combined with N_{H_2O}. First, concerning stability of the Eu(II) complex, the $\Delta G_e^\ddagger$ for reaction 4 can be expressed by activation free energy, $\Delta G_{e\ \mathrm{back}}^\ddagger$, for the backward reaction and reduction potential $E°$ (III/II), i.e.,

$$\Delta G_e^\ddagger = \Delta G_{e\ \mathrm{back}}^\ddagger - FE^0(\mathrm{III/II}) \qquad (9)$$

where F denotes the Faraday constant. The $\Delta G_{e\ \mathrm{back}}^\ddagger$ reflecting the reactivity of the Eu(II) complex is expected to have a linear relation with N_{H_2O}, because $E°$ (III/II) can be represented by linear combination of E_P^{red} and E_P^{ox} and results in a linear relation with N_{H_2O}. The stability constant of the Eu(II) complex corresponding to the free energy change ΔG_1(II) is also expected to have a linear relation with N_{H_2O} from the following relation between the reduction potentials and free energy changes:

$$F(E^0_{aq} - E^0_L) = \Delta G_1(\mathrm{III}) - \Delta G_1(\mathrm{II}) \qquad (10)$$

Second, linear free energy relationships (LFER) are established when the $\Delta G_e^\ddagger$, E_P^{red}, and $\log \beta_1$ are summarized. Figure 4 illustrates relations of the $\Delta G_e^\ddagger$ and E_P^{red} with $\log \beta_1$ expressed by their Gibbs free energy changes. It can be seen that the $\Delta G_e^\ddagger$ is much smaller and almost constant compared with the E_P^{red} and $\log \beta_1$. Such a relationship is also applicable to $\log \beta_1$ vs acid dissociation constants, ΣpK_a, of ligands for Sm(III) and Eu(III) complexes.[14]

Effect of Ionic Strength on the Reaction Kinetics of e_{aq}^- with the Eu(III) Complex. Effect of ionic strength on the k_e obtained by the pulse radiolysis technique may be helpful in estimating the unknown charge of a certain Eu(III) complex, which is complementary with N_{H_2O} determined by the fluorescence lifetime using TRLFS. The ionic strength is considered to affect the diffusive encounter process between e_{aq}^- and Eu(III) essentially. Since high concentrations of NaClO$_4$ (up to 1.0 mol dm^{-3}) and Eu(III) (5.0 mmol dm^{-3}) were used in the present study so that reaction 4 was dominant in the decay of e_{aq}^-, the effect of ionic strength on the k_e needs to be described by the extended Debye−Hückel equation (eq 11) based on the specific ion interaction theory.[21] The conventional Debye−Hückel term (the second term in eq 11) ($D = 0.509\ [\mu_m^{0.5}/(1 + 1.5\ \mu_m^{0.5})]$) accounts for electrostatic long-range interactions, and the correction term (the third term in eq 11) accounts for nonelectrostatic short-range interactions.

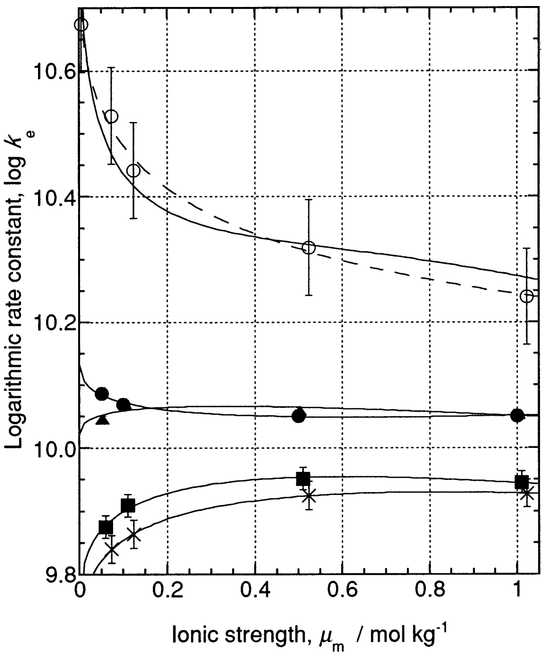

Figure 5. Effect of ionic strength on the reaction of e_{aq}^- with Eu(III) aquo ion and complexes. The logarithmic rate constant, log k_e, for Eu(III) aquo ion at pH 5.5 (○) and Eu(III) complexes: NTA at pH 4.5 (●), EDTA at pH 5.1 (▲), DTPA at pH 5.8 (■), and TTHA at pH 6.2 (×). $[\mathrm{Eu(III)}]_0 = 5.0$ mmol dm^{-3}. The solid lines were the curves fitted by the extended Debye−Hückel equation and the dashed line by the conventional one.

$$\log k_e = \log k_e^0 - \Delta z^2 D + \Delta\epsilon\, \mu_m \qquad (11)$$

$$\Delta z^2 = z(e_{aq}^-)^2 + z(\mathrm{Eu(III)})^2 - z(\text{activated complex})^2 \qquad (12)$$

$$\Delta\epsilon = \epsilon(e_{aq}^-,\mathrm{Na}^+) + \epsilon(\mathrm{Eu(III)}) - \epsilon(\text{activated complex}) \qquad (13)$$

where k_e^0 is the rate constant at infinite dilution. The difference of charges Δz^2 can be equivalent to $2(3 - l)$ from definition of the reaction 4, while the difference of ion interaction coefficients $\Delta\epsilon$ cannot be determined unequivocally for all of the Eu(III) aquo ion and complexes in the reactions. Therefore, the Δz^2 and $\Delta\epsilon$ were evaluated by fitting the experimental k_e to eq 11 with the two parameters.

Figure 5 shows the effect of ionic strength on the k_e for the aquo Eu(III) ion. The k_e, reflecting the reaction between the oppositely charged e_{aq}^- and aquo ion (Eu$_{aq}^{3+}$), decreased with increasing μ_m, and gave $\Delta z^2 = 5.3 \pm 0.4$ with $\Delta\epsilon$, which was dependent on μ_m and expressed as $0.47 - 0.89 \log \mu_m$. The Δz^2 was smaller than the theoretical value of $\Delta z^2 = 6.0$. On the other hand, Faraggi et al.[1] obtained the larger value of $\Delta z^2 = 11.6$ for the reactions of e_{aq}^- with aquo Eu(III), Sm(III), and Yb(III) ions at pH > 6.0 in the lower ionic strength range from

1.0×10^{-4} to 4×10^{-3} mol kg^{-1} by analyzing the data based on the conventional Debye−Hückel equation. They concluded that the trivalent ions in aqueous solution are dimers rather than monomers. However, no existence of such a dimer was suggested by the results of N_{H_2O} which was independent of μ_m and [Eu(III)] under the experimental conditions in the present study.

The effect of the ionic strength was also examined for Eu(III) complexes of NTA prepared at pH 4.5, EDTA at pH 5.1, DTPA at pH 5.8, and TTHA at pH 6.1 as shown in Figure 5. The k_e for the NTA and EDTA complexes was almost constant irrespectively of μ_m, and that for the DTPA and TTHA complexes increased with increasing μ_m. The Δz^2 and $\Delta\epsilon$ for the NTA, EDTA, DTPA, and TTHA complexes were evaluated as follows: the Δz^2 were 0.4 ± 0.1, 0.0 ± 0.2, -1.0 ± 0.4, and -1.2 ± 0.3, and the $\Delta\epsilon$ were 0.04 ± 0.02, -0.05 ± 0.06, -0.10 ± 0.03, and -0.08 ± 0.01, respectively. Furthermore, the pH dependence of the ionic strength effect for the EDTA complex was conducted in order to check whether the Δz^2 varied with pH or not. The result showed that the k_e at pH 3.0, 5.1, 7.1, 9.0, and 10.4 was almost independent of μ_m within the experimental error, so that the Δz^2 was constant despite formation of the ternary hydroxo complex at pH > 9.0. For the NTA, EDTA, DTPA, and TTHA complexes, the Δz^2 decreased with increasing $N(-CO_2H)$ (or decreasing residual N_{H_2O}), but was larger than the expected values of 0.0, −1.0, −2.0, and −3.0 when it was assumed that all the coordinated carboxylate groups were deprotonated.

In conclusion, the effect of ionic strength on the reaction for the Eu(III) aquo ion and complexes can be explained qualitatively by the diffusion encounter, characterized by the product of the expected charges, between e_{aq}^- and the Eu(III). However, deviation is present between the expected and experimentally determined Δz^2, so that validity of the pulse radiolysis technique for the estimation of the charge of Eu(III) complex cannot be discussed in detail at this time. The deviation results in acceleration of the k_e for the aquo ion and deceleration for the complexes. These suggest the necessity for further investigation to estimate the ion interaction coefficients individually and to subsequently determine their difference, giving difference between fittings using the extended and conventional Debye−Hückel equations at high salt concentration. The $\epsilon(e_{aq}^-,Na^+)$ for transient species of e_{aq}^- with Na^+, common in all the reactions with the ion and complexes, might be deduced from the effect of ionic strength on reactions such as $e_{aq}^- + Ag^+$ in which the activated complex has no charge. As a typical example, a coefficient, $\epsilon(e_{aq}^-,H^+)$, for e_{aq}^- with a different cation of H^+ can be estimated as $-0.06-0.20 \log \mu_m$ from $\epsilon(H^+,ClO_4^-) = 0.14$[22] and dependence of the rate constant for the reaction of e_{aq}^- with H^+ on [$HClO_4$] obtained by using a pulse radiolysis technique.[23] The ϵ(Eu(III)) are presumably close to values obtained for actinide cations and their anionic complexes,[22] ranging from ca. 0.5 to −0.3. It can be estimated from the effect of ionic strength on equilibria including the Eu(III) aquo ion and complexes. However, a separate treatment of the ϵ(activated complex) for the imaginary activated complex still remains unsolved.

Conclusion

When rate constant, k_e, for the reaction of e_{aq}^- the with 1:1 complex of Eu(III)−aminopolycarboxylate obtained by a pulse radiolysis technique was correlated with the residual hydration number, N_{H_2O}, of the complex determined by TRLFS, the k_e was related linearly with the N_{H_2O}. When the reaction was described by diffusive encounter and successive electron-transfer processes between e_{aq}^- and the complex, the linear relation between the k_e and N_{H_2O} was found to result from an entropy effect on the electron-transfer process that reflects steric factors such as geometrical configuration and reorientation of the ligand and water molecules in the first coordination sphere of Eu during the process, i.e., ionic interaction of Eu(III)−carboxylate groups and dehydration of the aquo Eu(III) ion on the inner-sphere complexation. These might be characteristic of the bonding nature between Eu(III), of which the 4f electrons have little contribution to the covalent bond, and aminopolycarboxylates, leading to their ionic interaction.

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