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Temperature Effect on the Association of Aqueous Europium and Sulfate Ions from Luminescence Decay Measurement

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The luminescence lifetime for $Eu_2(SO_4)_3$ and $EuCl_3$ in H_2O and D_2O has been measured at 0.01 and 0.001 mol dm^{-3} of Eu^{3+} and at various temperatures from 5 to 45 °C. The average number of water molecules coordinated to Eu^{3+} ion, q, is evaluated from the difference of the luminescence decay constants in the H_2O and D_2O solutions. By using the q value of 8.3 for aquaeuropium(III) ion in $EuCl_3$ solutions, q values for $Eu_2(SO_4)_3$ solutions were determined as a function of concentration and temperature. The average number of water molecules released from the primary hydration sphere by the inner-sphere complexation between Eu^{3+} and SO_4^{2-} ions is given as $\Delta q=8.3-q$, and Δq value increases with concentration and temperature. From the values of Δq and the known equilibrium constants on the overall complexation, it is revealed that for both the unis(sulfato) and bis(sulfato) complexation the ratio of inner-sphere complex to outer-sphere complex increases with temperature and that about one water molecule is released from the inner hydration sphere surrounding Eu^{3+} ion on the formation of an inner-sphere unis(sulfato) complex. The coordination state of the unis(sulfato) complex and the thermodynamic quantities for the equilibrium between outer- and inner-sphere complexes are discussed.

The ion-association is one of the most important problems in the chemistry of electrolyte solutions. In addition to conventional methods, modern techniques have been used to clarify this phenomenon. Ion complexes are classified into two types: inner- and outer-sphere complexes. It is rather difficult to identify them and, therefore, conflicting conclusions have frequently been reported. Some of the spectroscopic methods reflect not only inner-sphere interaction but also outer-sphere interaction. Thermodynamic data are useful for the examination of average characteristics of the complexes.

Recently, the luminescence decay measurement has been utilized in various fields as a method to investigate the coordination state of Eu^{3+} ion.[1—4] This method is based on the fact that the difference between the observed luminescence decay constants for H_2O and D_2O solutions is proportional to the number of inner-sphere water molecules surrouding Eu^{3+} ion. The information acquired by this method reflects only the inner-sphere interaction. In a previous work we showed the formation of an inner-sphere complex between Eu^{3+} and SO_4^{2-} ions by this method.[5] For revealing the details of ion-association in this system more quantitatively, the luminescence lifetime for H_2O and D_2O solutions of $Eu_2(SO_4)_3$ and $EuCl_3$ has been measured as a function of temperature. The combination of the present result with the known equilibrium constants for the overall complexation[6] will provide new information on the equilibrium between outer- and inner-sphere complexes.

Experimental

$EuCl_3 \cdot 6H_2O$ and $Eu_2(SO_4)_3 \cdot 8H_2O$ were prepared by dissolving Eu_2O_3 into HCl and H_2SO_4, respectively, as described previously.[5] Deuterated salts were obtained from hydrated salts by repeating D_2O addition and evaporation. D_2O of 99.95% grade(Merck) was used. A few modifications were made in the previous procedure and instrument for the lifetime measurement.[5] 1-Acetylnaphthalene was used as a photosensitizer instead of 2-acetylnaphthalene, because the fluorescence of the former was much weaker than that of the latter and so optical and electric interference due to the fluorescence from sensitizer reduced significantly. A transient memory(10 bits, Kawasaki Electronica TMR-10) was used. Data were analyzed by the least-squares method by means of a microcomputer system. Temperature was controlled by circulating thermostated water inside the cell holder.

Results and Discussion

Luminescence decay constants of Eu^{3+} ion in H_2O and D_2O, k^{H_2O} and k^{D_2O}, are related to the number of inner-sphere water molecules, q, as follows:[1—3,5]

$$\Delta k = k^{H_2O} - k^{D_2O} = A \cdot q, \tag{1}$$

Table 1. Luminescence Decay Constants(s^{-1})[a] for $EuCl_3$ and $Eu_2(SO_4)_3$ in H_2O and D_2O

[Eu^{3+}]	T	$EuCl_3$			$Eu_2(SO_4)_3$		
mol dm^{-3}	°C	k^{H_2O}	k^{D_2O}	Δk	k^{H_2O}	k^{D_2O}	Δk
0.001	5	8928	290	8638	8472	283	8189
	15	8951	313	8638	8471	306	8165
	25	8996	337	8659	8390	328	8062
	35	9077	367	8710	8373	356	8017
	45	9190	411	8779	8372	423	7949
0.01	5	8828	260	8567	8168	268	7900
	15	8940	266	8674	8173	281	7892
	25	9010	278	8732	8148	294	7854
	35	9100	292	8808	8109	312	7797
	45	9219	315	8904	8058	354	7704

a) ±20 for k^{H_2O} and ±5 for k^{D_2O}.

Table 2. Average Number of Water Molecules in the Primary Coordination Sphere, q, and Average Loss of Coodinated Water Molecules Caused by Inner-Sphere Complexation, Δq, and Fractions of Complexed Eu^{3+} Ions, f's, for $Eu_2(SO_4)_3$ Solutions

$[Eu_2(SO_4)_3]$ / mol dm^{-3}	T / °C	q[a)]	Δq[b)]	$f_{EuSO_4^+}$[c)]	$f_{Eu(SO_4)_2^-}$[c)]	$\Delta q/f$[d)]
5×10^{-4}	5	7.86	0.44	0.519	0.006	0.838
	15	7.84	0.46	0.577	0.010	0.783
	25	7.72	0.58	0.630	0.015	0.899
	35	7.64	0.66	0.682	0.022	0.937
	45	7.51	0.79	0.725	0.030	1.046
5×10^{-3}	5	7.65	0.65	0.719	0.046	0.849
	15	7.55	0.75	0.743	0.067	0.925
	25	7.46	0.84	0.756	0.091	0.991
	35	7.34	0.96	0.761	0.118	1.092
	45	7.18	1.12	0.756	0.149	1.237

a) Calculated by using the value of 8.3 as the hydration number of aquaeuropium(III) ion. b) $\Delta q = 8.3 - q$. c) Including both outer- and inner-sphere complexes. Estimated according to Ref. 6. d) $f = f_{EuSO_4^+} + f_{Eu(SO_4)_2^-}$.

Table 3. Formation Constants for Europium Unis(sulfato) Complex, K's, and Number of Water Molecules Released from the Primary Hydration Sphere by the Formation of One Inner-Sphere Complex, l, in the 5×10^{-4} mol dm^{-3} Solution of $Eu_2(SO_4)_3$

T / °C	K^T[a)] / mol^{-1} dm^3	$\mathring{a}$[b)] / Å	K^{out}[c)] / mol^{-1} dm^3	K^{io}[d)]	l[e)]
5	1132	6	266	3.25	1.10
15	1555		292	4.32	0.98
25	2129		323	5.59	1.08
35	3002		362	7.29	1.10
45	4171		407	10.2	1.19
5		7	155	6.30	0.98
15			168	8.25	0.89
25			172	11.3	1.08
35			204	13.7	1.03
45			226	17.4	1.15

a) Ref. 6.[10)] b) Distance of closest approach of ions which was assumed for the outer-sphere complex. c) Estimated by the Fuoss equation. d) Obtained by Eq. 2. e) Calculated by Eq. 6.

where A is the proportionality constant, which corresponds to the rate constant of nonradiative deactivation caused by one molecule of H_2O. Luminescence decay constants measured for $EuCl_3$ and $Eu_2(SO_4)_3$ in H_2O and D_2O are shown in Table 1. It shows that at different Eu^{3+} concentrations and temperatures Δk is smaller for $Eu_2(SO_4)_3$ than for $EuCl_3$ and that at both the concentrations Δk increases for $EuCl_3$ and decreases for $Eu_2(SO_4)_3$ with the rise of temperature. It has been known that inner-sphere complexes are not formed in $EuCl_3$ solutions under the present conditions and the inner coordination sphere surrounding Eu^{3+} ion is occupied solely by water molecules.[5,7,8)] The hydration number of aquaeuropium(III) ion has been determined to be 8.3 by X-ray diffraction for the $EuCl_3$ solution of 3.23 mol kg^{-1}.[7)] Apart from its absolute value, we reported previously by the luminescence lifetime measurement that the hydration number for $EuCl_3$ solutions is nearly constant over a wide range of concentration.[5)] We, therefore, use the q value of 8.3 for $EuCl_3$ solutions irrespective of concentration and temperature, and the values of A at each of conditions are obtained from Eq. 1. Subsequently, q values for $Eu_2(SO_4)_3$ solutions are determined by using these A values.[9)] The q values shown in Table 2 are smaller than 8.3, indicating that water molecules are partially removed from the primary hydration sphere of Eu^{3+} ion by the formation of inner-sphere sulfato complexes. As predicted from the chemical equilibrium, the value of q for 5×10^{-3} mol dm^{-3} is smaller than that for 5×10^{-4} mol dm^{-3} at respective temperatures.

Hale and Spedding investigated this system in detail by the UV absorption method.[6)] They suggested that their data were related to the equilibrium of overall complexation including both the outer-sphere and inner-sphere complexes. By using their data, we have calculated the fractions of unis(sulfato) and bis(sulfato) europium ions to total europium ions,[10)] fractions being denoted by $f_{EuSO_4^+}$ and $f_{Eu(SO_4)_2^-}$, respectively. On the other hand, the average loss of inner-sphere water molecules caused by the inner-sphere complexation is obtained from the relation, $\Delta q = 8.3 - q$. The values of f's and Δq are given in Table 2. The values of Δq and f's, and the ratio of Δq to the sum of fractions ($f_{EuSO_4^+} + f_{Eu(SO_4)_2^-}$) increase with the rise of temperature.

The temperature effect on the ion-association between various cations and the sulfate ion were studied by electrical conductivity and spectroscopic methods. The enthalpy change for the overall ion-association has a positive value in most cases.[11–14)] The enthalpy changes(ΔH) for formation of unis(sulfato) europium complex obtained by Hale and Spedding are 17.1 and 22.5 kJ mol^{-1} at 25 °C for the ionic strength of 0.045 mol kg^{-1} and infinite dilution, respectively.[6)] They also gave ΔH of 25.9 kJ mol^{-1} at 25 °C and the ionic strength of 0.045 mol kg^{-1} for the formation of bis(sulfato) complex.[6)]

We now consider the equlibrium between outer- and inner-sphere complexes by using the values of f's and Δq. The effect of temperature on the equilibrium can be expressed qualitatively by the value of $\Delta q/f$, where f denotes the sum of $f_{EuSO_4^+}$ and $f_{Eu(SO_4)_2^-}$. This

Table 4. Enthalpy and Entropy Changes[a] for Unis(sulfato) Complexation of Eu^{3+} Ion at 25 °C in the Infinite Dilution

$\mathring{a}$	ΔH^{out} [b]	ΔH^{io}	ΔS^{out} [b]	ΔS^{io}	ΔH^{T} [c]	ΔS^{T} [c]
6 Å	6.2	19.2	74.8	78.6	22.5	146.3
7 Å	5.3	18.7	67.2	82.8		

a) In $\mathrm{kJ\,mol^{-1}}$ and $J\,\mathrm{mol^{-1}\,K^{-1}}$ for ΔH and ΔS, respectively. b) By the Fuoss equation. c) Ref. 6.

value seems to be relevant to the ratio of inner-sphere complexes to the total complexes. The fact that the value of $\Delta q/f$ increases with temperature makes it conceivable to conclude that for both the unis(sulfato) and bis(sulfato) complexes the temperature elevation shifts the equilibrium between outer- and inner-sphere complexes toward the inner-sphere complex.

For the formation of the unis(sulfato) complex the following equations are derived.

$$K^{\mathrm{T}} = \frac{[\mathrm{EuSO_4^+}]_{\mathrm{out}}+[\mathrm{EuSO_4^+}]_{\mathrm{in}}}{[\mathrm{Eu^{3+}}][\mathrm{SO_4^{2-}}]} = K^{\mathrm{out}}(1+K^{\mathrm{io}}) \tag{2}$$

$$K^{\mathrm{out}} = \frac{[\mathrm{EuSO_4^+}]_{\mathrm{out}}}{[\mathrm{Eu^{3+}}][\mathrm{SO_4^{2-}}]} \tag{3}$$

$$K^{\mathrm{io}} = \frac{[\mathrm{EuSO_4^+}]_{\mathrm{in}}}{[\mathrm{EuSO_4^+}]_{\mathrm{out}}} \tag{4}$$

K^{out} can be estimated by the Fuoss equation,[15]

$$K = \frac{4\pi N_{\mathrm{A}}\mathring{a}^3 \mathrm{e}^b}{3000} \quad \text{and} \quad b = \frac{|z_i z_j| e^2}{\varepsilon k T \mathring{a}}, \tag{5}$$

where N_A=Avogadro's number, $\mathring{a}$=distance of closest approach of ions, ε=dielectric constant, k=Boltzmann constant, z=charge on the ion, and e=charge on the electron. Using the complex $[Eu(H_2O)SO_4]^+$, in which two ions are separated by one water molecule, as a model of the outer-sphere complex, we have calculated K^{out} at infinite dilution by Eq. 5 with two $\mathring{a}$ values of 6 Å and 7 Å.[16] K^{out} at the equilibrium ionic strength was evaluated by the Eq. 12 of Ref. 6, and K^{io} by Eq. 2 using calculated K^{out} and K^{T} given by Hale and Spedding.[10] On the other hand, in the $5\times10^{-4}\ \mathrm{mol\,dm^{-3}}$ solution, where the formation of the bis(sulfato) complex is almost negligible, K^{io} is correlated with Δq as follows:

$$K^{\mathrm{io}} = \frac{[\mathrm{EuSO_4^+}]_{\mathrm{in}}}{[\mathrm{EuSO_4^+}]_{\mathrm{out}}} = \frac{(1/l)\cdot\Delta q}{f_{\mathrm{EuSO_4^+}}-(1/l)\cdot\Delta q}, \tag{6}$$

where l represents the number of water molecules released from the inner hydration sphere by the inner-sphere coordination of sulfate ion to Eu^{3+} ion. The values of l calculated from Δq, $f_{\mathrm{EuSO_4^+}}$, and K^{io} by Eq. 6 are shown in Table 3 along with K^{T}, K^{out}, and K^{io} values.

The l values are close to 1, the result meaning that one water molecule is released from the inner hydration sphere on the formation of inner-sphere unis(sulfato) complex. If the average coordination number of Eu^{3+} ion is invariant in the aqua ion and the inner-sphere complex, the sulfate ion seems to act as a unidentate ligand. Further, it is postulated that aquaeuropium(III) ion exists as an equilibrium mixture of $[Eu(H_2O)_8]^{3+}$ and $[Eu(H_2O)_9]^{3+}$. The average hydration number of 8.3 assessed by X-ray diffraction indicates that the ratio of $[Eu(H_2O)_8]^{3+}$ to $[Eu(H_2O)_9]^{3+}$ is approximately 2.[7] The result that l is unity suggests that the inner-sphere complex $[Eu(H_2O)_7SO_4]^+$ is formed from a bidentate sulfate ion and an octaaqua europium(III) ion. Since the l values estimated are reasonable, dividing of K^{T} into K^{out} and K^{io} in Eq. 2, followed by application of the Fuoss equation, is considered to be appropriate.

Finally, it is interesting from the thermodynamic viewpoint to compare ΔH and ΔS corresponding to K^{out} and K^{io}. ΔH^{out} and ΔS^{out} at infinite dilution are calculated by the Fuoss equation. ΔH^{io} was calculated from ΔH^{T} and ΔH^{out} according to a relation based on Eq. 2, $\Delta H^{\mathrm{T}}=\Delta H^{\mathrm{out}}+[K^{\mathrm{io}}/(1+K^{\mathrm{io}})]\cdot\Delta H^{\mathrm{io}}$, and ΔS^{io} was obtained by $\Delta S^{\mathrm{io}}=\Delta H^{\mathrm{io}}/T+R\ln K^{\mathrm{io}}$. The results at 25 °C are listed in Table 4, together with Hale and Spedding's ΔH^{T} and ΔS^{T}. It indicates that the predominance of inner-sphere complex in this system is ascribed to the fairly large value of ΔS^{io}.

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9) We have assumed that the A value is dependent on temperature and concentration. It is probable that the hydration number of aquaeuropium(III) ion is dependent on these conditions and the A value is constant. However, the small difference caused by the two different treatments does not substantially influence on the following discussion.

10) The complex formation constants are calculated by using the equations in Ref. 6. For the unis(sulfato) complexation, the equation on the temperature dependence of k_1° and Eq. 12 with the value of D=0.6 were used. For the bis(sulfato) complexation, the values of K_2 and ΔH_2 at ionic

strength of 0.045 mol kg^{-1} and Eq. 12 with the value of D=0.3 were used. By repeating the calculation for Eq. 12, K's and f's were evaluated at respective concentrations and temperatures.

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