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Journal of Alloys and Compounds 408–412 (2006) 1307–1311

Journal of ALLOYS AND COMPOUNDS

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Curium(III) species and the coordination states in concentrated LiCl-aqueous solutions studied by time-resolved laser-induced fluorescence spectroscopy

Makoto Arisaka*, Takaumi Kimura, Ryuji Nagaishi, Zenko Yoshida

Department of Materials Science, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-1195, Japan

Abstract

Study on Cm(III) species and the coordination states in concentrated LiCl-aqueous solutions were performed by using time-resolved laser-induced fluorescence spectroscopy. The inner-sphere hydration number, N_{H_2O} and average chloride coordination number, N_{Cl}, of Cm(III) were determined from the luminescence lifetimes and emission spectra, respectively. While the inner-sphere coordination sites of Cm(III) was fully occupied by water molecules in the C_{LiCl} range less than 4 M, the inner-sphere chloro complexation of Cm(III) was observed in the C_{LiCl} range more than 6 M. The total coordination number, defined as the sum of N_{H_2O} and N_{Cl}, was kept constant in the C_{LiCl} range up to 10 M, and then decreased gradually with an increase of C_{LiCl}. This indicates that one chloride ion excludes more than one water molecule through the inner-sphere chloro complexation in the extremely concentrated LiCl-aqueous solutions.

Keywords: Cm(III); Concentrated LiCl-aqueous solution; Inner-sphere hydration number; Average chloride coordination number; Time-resolved laser-induced fluorescence spectroscopy

1. Introduction

For safe treatment and disposal of high-level waste generated from the reprocessing of spent nuclear fuels, the partitioning and transmutation of minor actinides, MA, and long-lived fission products with accelerator-driven system were proposed instead of the deep geological disposal [1,2]. To attain the efficient transmutation of MA, it is important to remove lanthanides from MA because of large neutron capture cross-section of several lanthanides. However, it is difficult to separate trivalent actinides, An(III), from lanthanides, Ln(III), because of their similar chemical properties.

For in-depth understanding of the behavior of a metal ion in a separation system using ion exchange or solvent extraction method, it is indispensable to reveal the species and the coordination states of the metal ion in each phase, for example, total coordination number, solvation and/or hydration number, ligand coordination number and so on. Although the species and the coordination states of An(III) in an aqueous solution have been estimated indirectly by determination of the stability constant for the formed complex [3–5] using ion exchange or solvent exchange method, such indirect methods are unable to distinguish between inner-sphere and outer-sphere complexation. On the other hand, it is well known that the luminescence properties of Am(III) and Cm(III), as well as several Ln(III), are sensitive to the species and the coordination states of An(III) at the inner-sphere. Therefore, luminescence techniques have become important tools for studying the species and the coordination states of An(III) not only dissolved in an aqueous solution [6–11] but also sorbed on such solid–liquid interface as ion exchange resin [12–14].

Among the various media of interest, a chloride media is important since the successful separation of An(III) from Ln(III) was first achieved by cation exchange method using a concentrated HCl-aqueous solution as eluent [15]. In the present study, time-resolved laser-induced fluorescence spectroscopy (TRLFS) was employed to reveal the Cm(III)

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* Corresponding author. Tel.: +81 29 282 5788; fax: +81 29 282 6723.
E-mail address: arisaka@analchem.tokai.jaeri.go.jp (M. Arisaka).

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doi:10.1016/j.jallcom.2005.04.127

species and the coordination states in concentrated LiCl-aqueous solutions.

2. Experimental

2.1. Chemicals

A stock solution of Cm(III) was prepared in the same procedure as described in the Ref. [13]. All chemicals were of analytical reagent grade and were used without further purification. The samples were prepared by adding the Cm(III) stock solution with desired LiCl-aqueous solutions containing 0.01 M (mol/dm^3) HCl into a quartz tube cell of 5 mm in diameter. The final Cm(III) concentration of the sample solution was 1.2×10^{-5} M.

2.2. Time-resolved laser-induced fluorescence spectroscopy

Details on the experimental set-up were described previously [13]. Curium(III) in the samples was excited by a pulsed laser beam of 397 nm wavelength (5 Hz). The pulse power was approximately 4 mJ per pulse and the pulse width was approximately 15 ns. For the determination of the luminescence lifetime, τ_{obs}, of Cm(III), the emission light from the lowest luminescent level to the ground state of Cm(III), i.e. $^6D_{7/2} \rightarrow {}^8S_{7/2}$ transition, was measured at 594 nm. For the sample at LiCl concentration, $C_{LiCl} = 14$ M, the dependence of τ_{obs} on the emission wavelength was investigated in the wavelength range from 580 to 615 nm. To avoid the influence of the scattering light and the luminescence of the cell, the emission spectra were recorded under the following conditions: (i) delay time, 1 μs; (ii) gate width, 1 ms. The spectral resolution was 0.5 nm and the spectral range was 256 nm.

3. Results and discussion

3.1. Inner-sphere hydration number, N_{H_2O}, of Cm(III)

The N_{H_2O} of An(III) (An = Am, Cm), i.e. the number of water molecules bound to An(III) directly, is determined from the luminescence lifetime, τ_{obs}, of An(III) [6–8]. The method for determination of the N_{H_2O} of An(III) is based on the fact that electronic–vibrational energy transfer from the excited state of An(III) to the O–H vibrations of water molecules bound to An(III) is dominant in the de-excitation processes and the rate is proportional to the number of water molecules bound to An(III).

For Cm(III), the correlation between the N_{H_2O} and the τ_{obs} is obtained experimentally as following equation [8]:

$$N_{H_2O} = 6.12 \times 10^{-4} \times \left(\frac{1}{\tau_{obs}}\right) - 0.48 \qquad (1)$$

The luminescence decay curves of Cm(III) in a solution contains information about the kinetics of the complexation and dissociation. If the ligand and/or water exchange rate, k_{ex}, is fully high in comparison to the luminescence decay rate, k_{obs} ($1/\tau_{obs}$), of the excited Cm(III), differences in absorptivity at the excitation wavelength and in the k_{obs} of the different species are averaged since the species distribution is governed by the thermodynamic equilibrium. Therefore, the luminescence decay curve obeys a single-exponential decay law, and the τ_{obs} represents an average lifetime of all possible Cm(III) species present in the solution. On the other hand, if the k_{ex} is low in comparison to the k_{obs}, the differences described above are not averaged. Therefore, the luminescence decay curve obeys a multi-exponential decay law, and the τ_{obs} of each Cm(III) species are observed individually.

Since the emission peaks corresponding to each Cm(III) species present in the solution were observed individually as described later (see Section 3.2), the luminescence decay curves for the sample at $C_{LiCl} = 14$ M were investigated in the wavelength range from 580 to 615 nm to estimate the relative rate of the k_{ex} to k_{obs}. The decay curves measured in the whole wavelength range were fitted to single-exponential curves with correlation coefficients of 0.996–0.999, as shown in Fig. 1. No dependence of k_{obs} on the wavelength was observed. This indicates that the k_{ex} is fully high in comparison to the k_{obs} of the excited Cm(III). Therefore, the N_{H_2O} of Cm(III) was determined from the τ_{obs} measured at 594 nm wavelength for all samples using the Eq. (1).

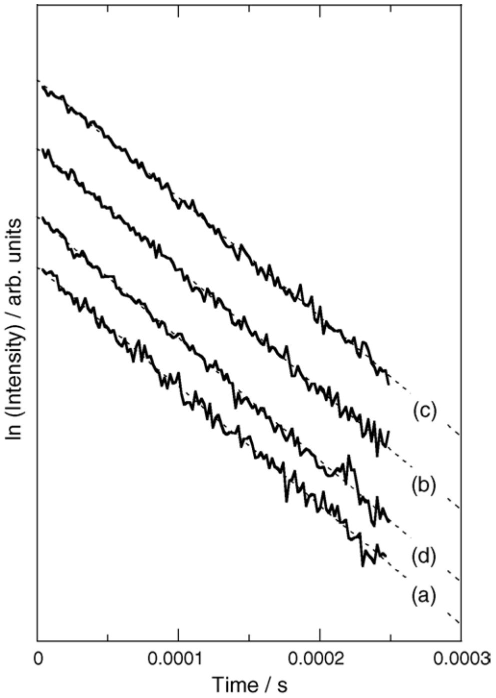

Fig. 1. Luminescence decay curves of Cm(III) at $C_{LiCl} = 14$ M excited by a pulsed laser beam of 397 nm wavelength: measured wavelength, 580 nm (a); 585 nm (b); 610 nm (c); 615 nm (d).

Table 1
Inner-sphere hydration number, N_{H_2O}, of Cm(III) in the LiCl-aqueous solutions

C_{LiCl} (M)	N_{H_2O}
0	8.3 ± 0.3
1	8.3 ± 0.3
4	8.1 ± 0.3
6	7.9 ± 0.3
8	7.4 ± 0.3
10	6.6 ± 0.3
12	5.4 ± 0.3
14	4.7 ± 0.3

The N_{H_2O} of Cm(III) at different C_{LiCl} are listed in Table 1. Up to 4 M, the N_{H_2O} are kept almost constant. This indicates that the inner-sphere coordination sites of Cm(III) are fully occupied by water molecules and the inner-sphere chloro complexation of Cm(III) can be neglected in this C_{LiCl} range. However, it does not always mean that Cm(III) exists as hydrated Cm^{3+} ion, and the formation of outer-sphere chloro complex of Cm(III) cannot be neglected. According to the stability constants for chloro complex of Cm(III), which were determined to be $\log \beta_1 = -0.25$ and $\log \beta_2 = -0.7$ at ionic strength 3 by solvent extraction method [3,5], the mole fractions of Cm(III) species in 3 M LiCl are estimated to be 0.22 of hydrated Cm^{3+}, 0.38 of mono-chloro complex, i.e. $CmCl^{2+}$ and 0.40 of di-chloro complex, i.e. $CmCl_2{}^{+}$. Therefore, Cm(III) interacts with chloride ion at the outer-sphere in this C_{LiCl} range. In the C_{LiCl} range from 6 to 14 M, the N_{H_2O} decreases with an increase of C_{LiCl}. Assuming that the total coordination number of Cm(III) does not change through the inner-sphere complexation with chloride ion in the whole C_{LiCl} range studied, the decrease of N_{H_2O} indicates the formation of the inner-sphere chloro complex of Cm(III). Moreover, it is expected from the result of N_{H_2O} at $C_{LiCl} = 14$ M that the mole fractions of tri-chloro complex, $CmCl_{3(aq)}$ and tetra-chloro complex, $CmCl_4{}^{-}$, are fairly high. Recently, the refined equation for the determination of N_{H_2O} of Eu(III) was presented by Supkowski and Horrocks taking account of the de-excitation by water molecules in the outer-sphere [16]. In the extremely concentrated LiCl-aqueous solutions, "free" water molecules would be insufficient for M(III) to form complete hydration sphere due to strong hydration of lithium ion, i.e. the water molecules in the outer-sphere decrease inevitably with an increase of C_{LiCl}. Although the dehydration due to the inner-sphere complexation was correlated to the enlargement of τ_{obs} of M(III), the decrease of water molecules in the outer-sphere would also cause the slight enlargement of τ_{obs} of M(III).

3.2. Mole fractions of Cm(III) species

Mole fractions of Cm(III) species have been determined from the emission spectrum in various inorganic salt aqueous solution [9–11]. The method for determination of the mole fractions of Cm(III) species is based on the fact that the emission peaks of inner-sphere complexes of Cm(III) with inorganic ligands are shifted several nanometers to the red side relative to that of hydrated Cm^{3+} ion.

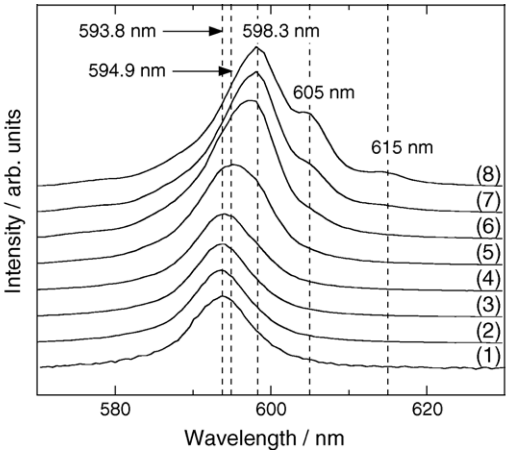

Fig. 2. Emission spectra of Cm(III) in the LiCl-aqueous solutions: C_{LiCl}, 0 M (1); 1 M (2); 4 M (3); 6 M (4); 8 M (5); 10 M (6); 12 M (7); 14 M (8).

The emission spectra of Cm(III) recorded at different C_{LiCl} are shown in Fig. 2. Up to 4 M, the emission spectra show no significant change in shape, intensity and peak position. Since the emission spectrum of Cm(III) is sensitive to the coordination states at the inner-sphere, it is evident from the results that the inner-sphere chloro coordination to Cm(III) is neglected in this C_{LiCl} range. This result is consistent with the result of N_{H_2O}. More than 6 M, a peak at about 598 nm wavelength in the emission spectra mainly grows with an increase of C_{LiCl}. The peak shift to the red side is attributed to the inner-sphere chloro complexation of Cm(III), and the peak at 594.9 nm and the peaks at 587 and 598.3 nm corresponding to $CmCl^{2+}$ and $CmCl_2{}^{+}$, respectively, were derived from a mixed spectrum by the peak deconvolution [9]. In the C_{LiCl} range from 10 to 14 M, the other peaks were observed at 577, 605 and 615 nm. The peaks at 577 and 605 nm and the peak at 615 nm would be attributed to $CmCl_{3(aq)}$ and $CmCl_4{}^{-}$, respectively.

In order to obtain the detail information about Cm(III) species present in the solution, the least squares fitting of emission spectra was performed using Lorentzian–Gaussian functions. An example of the fitting of the emission spectrum at $C_{LiCl} = 14$ M is shown in Fig. 3, together with the results of the wavelength dependence of N_{H_2O}. The mole fraction of each Cm(III) species was determined as a ratio of the sum of the area of emission peaks corresponding to each Cm(III) species to whole area due to ${}^6D_{7/2} \to {}^8S_{7/2}$ transition. The obtained mole fractions of Cm(III) are shown in Fig. 4 as a function of C_{LiCl}. The mole fraction of hydrated Cm^{3+} ion decreased rapidly in the C_{LiCl} range from 6 to 10 M due to the formation of inner-sphere chloro complexes, i.e. $CmCl^{2+}$ and $CmCl_2{}^{+}$. The $CmCl_{3(aq)}$ and $CmCl_4{}^{-}$ were found in the range of $C_{LiCl} \geq 8$ M and $C_{LiCl} \geq 10$ M, respectively. The mole fractions of Cm(III) species at $C_{LiCl} = 14$ M are determined to be 0 of hydrated Cm^{3+} ion, 0.25 of $CmCl^{2+}$, 0.46 of $CmCl_2{}^{+}$,

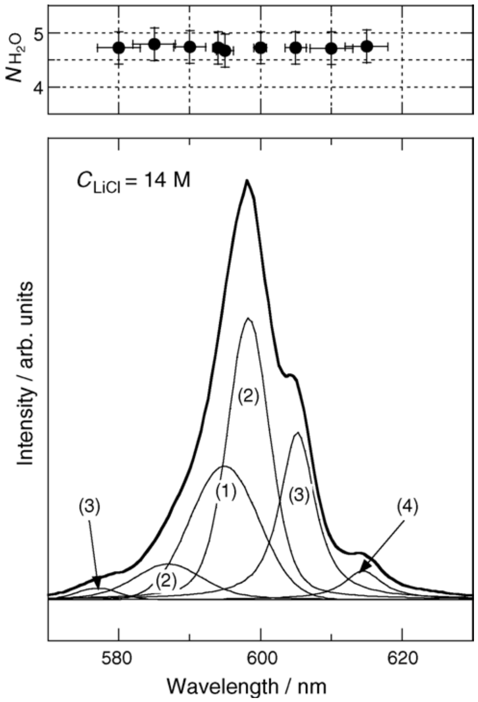

Fig. 3. An example of the fitting of the emission spectrum of Cm(III) at $C_{LiCl} = 14$ M: Cm(III) species, $CmCl^{2+}$ (1); $CmCl_2^+$ (2); $CmCl_{3(aq)}$ (3); $CmCl_4^-$ (4), and dependence of inner-sphere hydration number (N_{H_2O}) of Cm(III) on the emission wavelength.

0.24 of $CmCl_{3(aq)}$ and 0.05 of $CmCl_4^-$. It is not surprising that no existence of hydrated Cm^{3+} ion was observed since "free" water molecules would be insufficient for Cm(III) to form complete hydration sphere due to strong hydration of lithium ion. The average chloride coordination numbers, N_{Cl}, of Cm(III) were estimated on the basis of the mole fractions. The N_{Cl} at $C_{LiCl} = 14$ M was estimated to be 2.1. This result is not consistent with that expected from the decrease of N_{H_2O}.

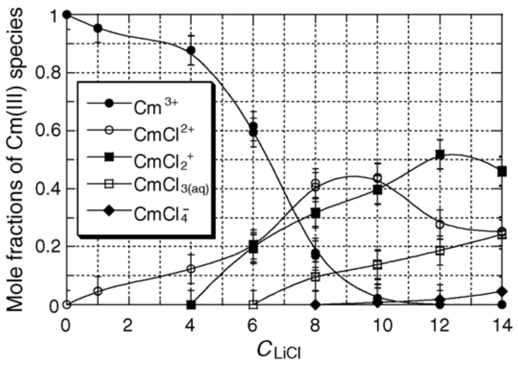

Fig. 4. Mole fractions of Cm(III) species determined by the least squares fitting of the emission spectra using Lorentzian–Gaussian functions.

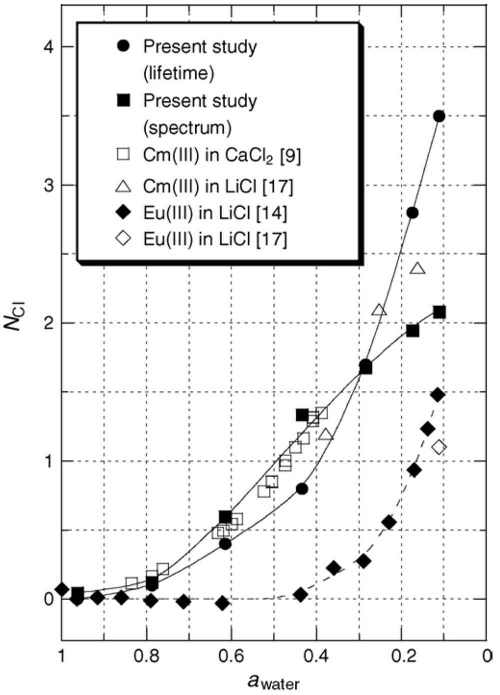

Fig. 5. Average chloride coordination number, N_{Cl}, of Cm(III) and Eu(III) as a function of water activity, a_{water}.

The N_{Cl} of Cm(III) are plotted in Fig. 5 together with the results of the previous study for Cm(III) [9,17] and Eu(III) [14,17] as a function of water activity, a_{water}, to place the data from two aqueous chloride solutions on a common scale. The N_{Cl} derived from the luminescence lifetime measurement is based on an assumption that the total coordination numbers of Cm(III) and Eu(III) do not change through the inner-sphere chloro complexation in the whole C_{LiCl} range studied. The results for Eu(III) are consistent with each other within experimental error even at $a_{water} = 0.11$ ($C_{LiCl} = 14$ M). This indicates that the total coordination number of Eu(III) is independent of C_{LiCl}. On the other hand, the result for Cm(III) based on the luminescence lifetime measurement is in disagreement with the other results in the a_{water} range less than 0.28, i.e. in the C_{LiCl} range higher than 10 M. The disagreement is too large to attribute to the overestimate of luminescence lifetime due to decrease of "free" water molecules around Cm(III), i.e. underestimate of N_{H_2O}. Therefore, the disagreement indicates that the total coordination number of Cm(III) decreases with a decrease of a_{water}, that is to say, one chloride ion excludes more than one water molecule bound to Cm(III) through the inner-sphere chloro complexation in the extremely concentrated LiCl-aqueous solutions. Such exclusion of some water molecules by one chloride ion for Cm(III) would be attributed to the stronger affinity to chloride ion of Cm(III) compared to that of Eu(III). The result that the interaction distance between Cm(III) and chloride ion is shorter than that between Eu(III) and chloride ion under the same chemical environment [17] supports the decrease of total coordination number of Cm(III).

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