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Comparative study on the hydration states of Cm(III) and Eu(III) in solution and in cation exchange resin

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Abstract

The sorption behavior and hydration structure of Cm(III) and Eu(III) in the cation exchange resin–acid solution systems were studied by measurements of the distribution coefficient K_D and the inner-sphere hydration number N_{H_2O} of the ions in acid solution and in resin phase. The differences in the K_D and N_{H_2O} values for Cm(III) and Eu(III) above 5 M HCl are K_D(Eu)>K_D(Cm) and N_{H_2O}(Eu)>N_{H_2O}(Cm), while the N_{H_2O} of Cm(III) in the resin phase in 0.1–11 M HCl solution are approximately equal to those of Eu(III). The N_{H_2O} of Cm(III) in HNO_3 or $HClO_4$ solution and in the resin phase are similar to those of Eu(III), in agreement with the similarity in the K_D of the ions. The separation and sorption mechanisms of Cm(III) and Eu(III) are discussed from the K_D and N_{H_2O} values. © 1998 Elsevier Science S.A.

Keywords: Curium(III); Europium(III); Luminescence lifetime; Inner-sphere hydration number; Cation exchange resin; Acid solution

1. Introduction

Highly selective and efficient separation of trivalent actinides[An] from lanthanides[Ln] has been an important and rather difficult subject in the fields of inorganic chemistry and nuclear technology, because the two f-element series have similar range of ionic radii and show strong similarities in chemical behavior. Since the separation of An(III) from Ln(III) was first achieved by cation exchange from concentrated chloride media [1–3], many efforts have been devoted to develop An(III)/Ln(III) separations using ion exchange, solvent extraction, and other techniques [4,5]. For in-depth understanding of the separation mechanisms in the application of these techniques, it is necessary to identify and characterize at the molecular level the species sorbed on the ion exchange resin or extracted into the organic phase. In solvent extraction systems, many spectroscopic methods have allowed study of the extracted species. Since ion exchange resins are opaque to most spectroscopic investigations, experimental information on the sorbed species has been limited to techniques such as Mössbauer spectroscopy [6], electron spin resonance [7], neutron diffraction [8], etc.

The inner-sphere hydration number N_{H_2O} (i.e., the number of H_2O molecules in the first hydration sphere of a metal ion) provides significant information regarding the coordination environment of the chemical species in solution, in solid and at the interface. To establish a method for determining the N_{H_2O} of a metal ion from measurements of the luminescence lifetime, a correlation between the luminescence decay constant k_{obs} (the reciprocal of the excited state lifetime) and the N_{H_2O} of An(III) [An = Am, Cm] and Ln(III) [Ln = Nd, Sm, Eu, Tb, Dy] has been investigated [9–12]. From the measurements of the k_{obs} of Cm(III) and Eu(III) doped into lanthanum compounds, calibration relationships have been proposed by which the N_{H_2O} is related directly to the k_{obs} in H_2O. These can be utilized successfully to determine the N_{H_2O} of various species [9,13]. In the previous study [14], direct information on the hydration structure of Eu(III) exchanged on strongly and weakly acidic cation-exchange resins was provided by time-resolved laser-induced luminescence spectroscopy and the different mechanisms of the ion-exchange reactions were elucidated quantitatively.

In the present study, the luminescence method was applied to the hydration states of Cm(III) and Eu(III) in hydrochloric, nitric and perchloric acid solutions and in the cation exchange resin phases. The separation and sorption mechanisms of Cm(III) and Eu(III) were discussed by comparison of the hydration structure of the ions in the

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solutions and in the resin phases with the sorption behavior.

2. Experimental

^{244}Cm ($t_{1/2}=18.1$ years) supplied by C.E.A., France was purified from its daughter nuclide ^{240}Pu by passage through anion exchange resin (AG 1X8) with elution by 7 M HNO_3. The Cm fraction in effluent was fumed to dryness after addition of concentrated $HClO_4$. The residue obtained was dissolved in 0.01 M $HClO_4$ to yield the Cm(III) stock solution. The concentration of the Cm(III) stock solution was determined by α-ray spectrometry and liquid scintillation counting. Eu(III) stock solution in 0.01 M $HClO_4$ was prepared by dissolving an appropriate amount of Eu_2O_3 (Wako Pure Chem. Ind., Ltd.) in perchloric acid. AG 50WX8 (functional group, $R{-}SO_3^-$; matrix, styrene divinylbenzene; proton exchange capacity, 2.1 meq g^{-1}) purchased from Bio-Rad Lab., Inc. was used as the cation exchange resin. All other chemicals used were of analytical reagent grade and aqueous solutions were prepared from doubly distilled deionized water. The distribution of Cm(III) and Eu(III) between the solid and aqueous phases was measured using ^{244}Cm and ^{152}Eu tracers. From the radiometric analysis of aqueous phase, the distribution coefficient K_D(cm^3 g^{-1}) as defined by Eq. (1) was calculated

$$K_D = \frac{C_0 - C}{C} \cdot \frac{V}{M} \qquad (1)$$

where C_0 is the initial concentration of a metal ion in the aqueous phase; C, the equilibrium concentration of the metal ion in the aqueous phase; V, the volume of the aqueous phase (cm^3); M, the mass of the ion exchange resin (g).

The concentration of Cm(III) and Eu(III) in the samples was 6.3×10^{-7} M and 1.0×10^{-3} M, respectively, for the lifetime measurements. The luminescence lifetimes were measured using a 5 mm i.d. quartz cell by a XeCl excimer laser pumped dye laser apparatus described elsewhere [11,12]. The metal(III) ion in the samples was excited to the excited states of Cm ($^6I_{17/2,11/2}$, 397 nm) [15] and Eu ($^5L_6$, 394 nm) [16] by a pulsed laser beam. Subsequently, the emission from the lowest luminescent level to the groundstate manifold, i.e., $^6D_{7/2}\rightarrow{}^8S_{7/2}$ (596 nm) for Cm(III), $^5D_0\rightarrow{}^7F_1$ (592 nm) for Eu(III), was measured to obtain the luminescence lifetime. The luminescence decay curves observed in this work were fitted to single-exponential curves with correlation coefficients of 0.99–0.999.

3. Results and discussion

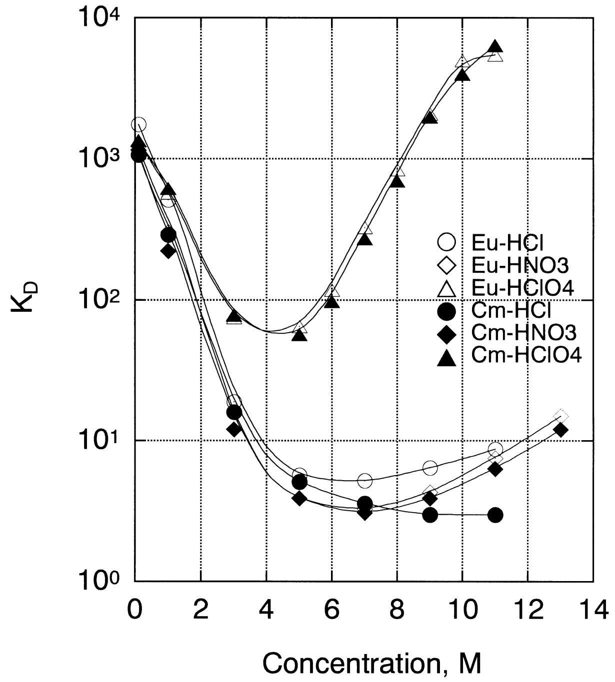

Fig. 1. Distribution coefficients K_D for Cm(III) and Eu(III) into AG 50WX8 resin as a function of hydrochloric, nitric or perchloric acid concentration.

The distribution coefficients K_D of Cm(III) and Eu(III) in the AG 50WX8 cation exchange resin–hydrochloric, nitric or perchloric acid solution systems are shown in Fig. 1. Up to about 5 M HCl there was very little difference in the sorption behavior of Cm(III) and Eu(III) and both ions behaved qualitatively in a similar manner to those in HNO_3 or $HClO_4$, indicating that below 5 M the dominant effect of HCl variation was the common ion effect caused by varying H^+ ion concentration. An appreciable divergence occurred above 5 M HCl, with K_D(Eu) increasing and K_D(Cm) continuing to decrease, which is quite similar to the behavior of An(III) and Ln(III) with Dowex 50 resin (similar to AG 50W) in the literature [2,3]. This difference in behavior has been assigned to stronger chloro complexing of An(III) than Ln(III) due to a greater extent of covalent bonding in the An(III) than Ln(III) [1,2]. The sorption behavior of Cm(III) and Eu(III) was not appreciably different in HNO_3 solutions. Up to about 5 M HNO_3 the K_D of the ions decreased with increasing HNO_3 concentration similarly to those in HCl. From 5 M to about 9 M HNO_3, the K_D for both ions into AG 50WX8 resin remained very low and essentially constant, $K_D=$ca. 3–4, and above 9 M they increased gradually. The K_D of Cm(III) and Eu(III) decreased with increase in $HClO_4$ concentration to about 4 to 5 M $HClO_4$ where minima appeared followed by marked increases at higher acidities [17,18]. This anomalous sorption behavior is not unique to Cm(III) or Eu(III) [18], and, although possible mechanisms have been discussed, no mechanism for the strong sorption in concentrated $HClO_4$ has been proven experimentally. It seems that the explanation of the behavior may not be the same for all metals and that more than one effect is involved; e.g., complexation, ion-pair formation, dehydration, resin swelling properties, etc.

The N_{H_2O} values of Cm(III) and Eu(III) in the acid solutions and in the cation exchange resin phases were measured to clarify the relationship between the sorption behavior and the hydration structure of the ions. Using Cm(III) and Eu(III) coprecipitated with lanthanum compounds of known hydration structure, we have reported the calibration relations of the $k_{obs}(ms^{-1})$ vs. N_{H_2O} for the ions [9,13].

$$N_{H_2O} = 0.65k_{obs}(Cm) - 0.88 \qquad (2)$$

$$N_{H_2O} = 1.07k_{obs}(Eu) - 0.62 \qquad (3)$$

If there is no contribution from the ligand to the deexcitation of the fluorescent excited state, the hydration of Cm(III) and Eu(III) in the different complexes can be obtained directly from the values of k_{obs} measured in H_2O. Since the validity of the correlations have been confirmed for the ions in various aqueous solutions [13,14], Eqs. (2) and (3) are used to determine the N_{H_2O} in this study. Fig. 2 shows the N_{H_2O} of Cm(III) and Eu(III) in acid solutions as a function of hydrochloric or nitric acid concentration. In agreement with the adsorption behavior of Cm(III) and Eu(III), there was very little difference in the hydration structure of Cm(III) and Eu(III) up to 5 M HCl, because of similar values of the stability constants for chloro complexation of Cm(III) and Eu(III), e.g., log β_1(Eu) = −0.28, log β_1(Cm) = −0.25 and log β_2(Eu) = log β_2(Cm) = −0.7 at 20°C and ionic strength 3.0 [19]. On the other hand, a marked divergence appeared in the N_{H_2O} at above 5 M HCl, i.e., $N_{H_2O}(Eu) > N_{H_2O}(Cm)$. This may result from the possible enhanced covalency in An–Cl bonding which results in formation of inner-sphere chloro complexation for Cm(III) while Eu(III) remains as an outer-sphere complex at higher HCl concentration (e.g., $[CmCl_2(H_2O)_7]^+$ and $[Eu(H_2O)_9]Cl_2^+$ as the main species in 11 M HCl). In 0.1–13 M HNO_3, the N_{H_2O} of Cm(III) and Eu(III) decreased similarly with increasing HNO_3 concentration, indicating inner-sphere complexation of both ions with the nitrate ion, with similar stability constants [19]. Approximately four H_2O molecules are removed from the first coordination sphere of the ions at 13 M HNO_3, suggesting the formation of $[M(NO_3)_2(H_2O)_5]^+$ with the nitrate ion functioning as a bidentate ligand. An anomalous concentration dependence on the N_{H_2O} was observed for Cm(III) and Eu(III) in $HClO_4$. The N_{H_2O} of both ions increased gradually with increasing $HClO_4$ concentration up to about 8–9 M where maxima occurred followed by marked decrease at higher acidities. Similar results were observed in the luminescence study of Ln(III) with the contradicting interpretations [20–23]. The mechanism of the increased quenching of Ln(III) could not be elucidated exactly by the luminescence study. Since the perchlorate ion cannot quench these cations, the concentrated perchlorate ion would perturb the hydration structure of Ln(III). For the nearly constant N_{H_2O} of Ln(III) in the perchlorate concentration below 7–9 M, our conclusion are consistent with the results from the studies of X-ray and neutron diffraction, extended X-ray absorption fine structure, etc. [24] as no evidence for inner sphere complexation by the perchlorate ion below 7–9 M $HClO_4$ has been found by the various measurement systems.

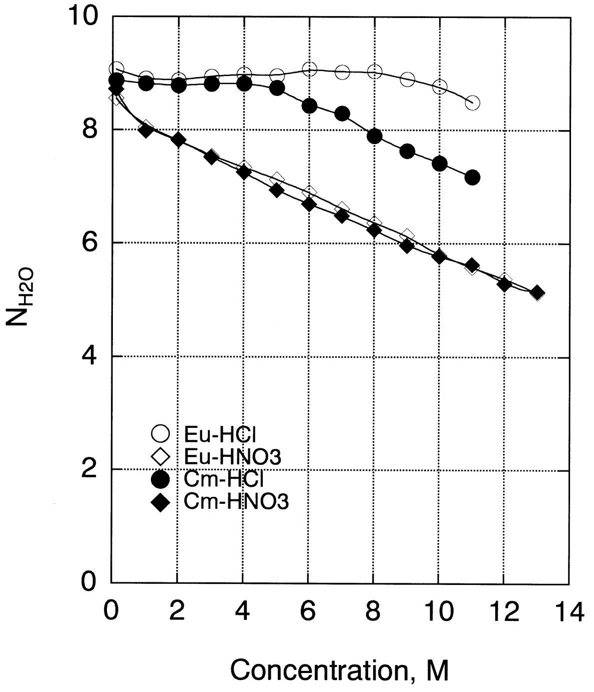

Fig. 2. Inner-sphere hydration numbers N_{H_2O} of Cm(III) and Eu(III) in acid solutions as a function of hydrochloric or nitric acid concentration.

Fig. 3 shows the N_{H_2O} of Cm(III) and Eu(III) in the AG 50WX8 resin phases as a function of hydrochloric or perchloric acid concentration. In contrast with the K_D and N_{H_2O} in HCl, almost no difference was found in the hydration structure of sorbed Cm(III) and Eu(III) even in higher HCl concentration and the N_{H_2O} of both ions decreased gradually with increasing HCl concentration from ca. 8 at 0.1 M to ca. 5 at 11 M. The decreasing tendency and values of the N_{H_2O} of sorbed Cm(III) and Eu(III) in HNO_3 were close to those in HCl, although the results were not shown in Fig. 3 since reproducible data could not be obtained because of the effect of decay products of HNO_3 in the resin by laser irradiation. In $HClO_4$, there was little difference in the hydration structure of Cm(III) and Eu(III) in the resin phases and the N_{H_2O} of the ions decreased rapidly with increasing $HClO_4$ concentration from ca. 8 at 0.1 M to ca. 4 or less at 8 M or above. In the previous study [14], from comparison of the N_{H_2O} of sorbed Eu(III) on AG 50WX8 resin with that of Eu(III) complexed with poly(4-styrenesulfonic) acid as linear polyelectrolyte analogue of the resin, it was shown that the cross-linked structure of the resin affected the

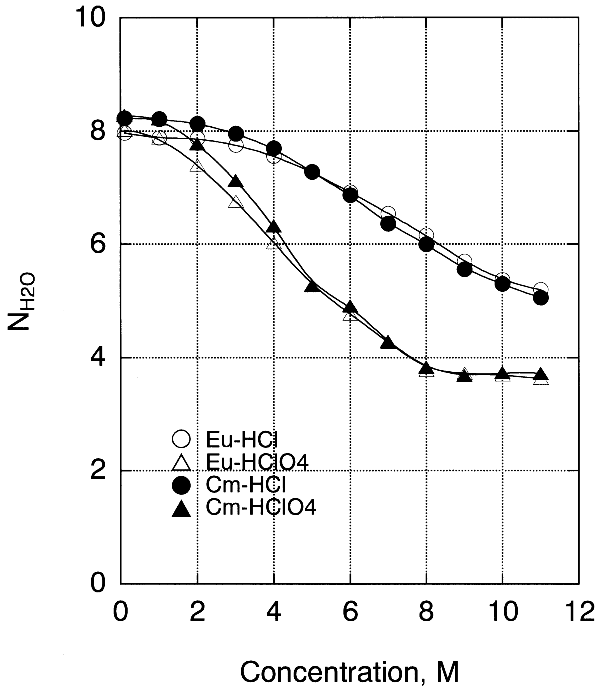

Fig. 3. Inner-sphere hydration numbers N_{H_2O} of Cm(III) and Eu(III) in the AG 50WX8 cation exchange resin phase as a function of hydrochloric or perchloric acid concentration: $V=0.5$ cm^3, $M=0.2$ g.

hydration structure of Eu(III) to some extent. The N_{H_2O}, ca. 7.5, of the sorbed Eu(III) in pH region [14] is in agreement with those of sorbed Cm(III) and Eu(III) at lower acid concentration within the uncertainty of ±0.5 H_2O molecules. The similarity in the N_{H_2O} for Cm(III) and Eu(III) in the resin phases in HCl or HNO_3 solutions suggests that both ions without chloride and nitrate ions are sorbed in the resin and that at higher HCl or HNO_3 concentration, which results in lower water content in the resin phase, about three sulfonate groups penetrate into the first hydration sphere of the ions. The ions in the resin in $HClO_4$ solution above 4 M release more, ca. 1.5–2.5 H_2O molecules, than those in the resin in HCl solution and this would be responsible for the anomalous sorption behavior of the ions at higher $HClO_4$ concentration. The difference in the N_{H_2O} between HCl and $HClO_4$ systems might be due to ion-pair formation of Cm(III) and Eu(III) with the perchlorate ion in the resin phase [17,25,26]

It has been well known that the separation of An(III) from Ln(III) can be performed by the cation exchange from concentrated chloride media but not from nitrate and perchlorate media. As mentioned above, the separation behavior of Cm(III) and Eu(III) in these media was well correlated with the hydration structure of the ions in the solutions, but is almost independent of that in the resin phases. The difference in the N_{H_2O} between both ions observed in concentrated HCl was not seen in concentrated HNO_3 and $HClO_4$. The present results on the hydration structure of An(III) and Ln(III) provides spectroscopic evidence that although the nitrate and perchlorate ions are strong bases which favor ionicity, the chloride ion is a softer donor and forms inner-sphere complexes with An(III) at lower chloride concentrations than do the analogous Ln(III) cations.

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