

TRLFS Study on Eu(III) Carbonate Complexation under Aerobic Conditions

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1. Introduction

Speciation is essential to obtain the thermodynamic data which are used for the nuclear repository safety assessment. Time-resolved laser fluorescence spectroscopy (TRLFS) is one of the most established tools for speciation of lanthanides and actinides especially in aqueous solution.

There are a few thermodynamic data on europium carbonate in aqueous solution. Europium carbonate solid state study gives comparable information about europium speciation in aqueous solution. In this study, pH of prepared solutions was titrated under normal atmospheric condition. Fluorescence lifetime of the Eu(III) carbonate complex was measured by TRLFS.

2. Experiment and Results

2.1 Experiment

A stock solution was prepared by dissolution of 10^{-4} M EuCl_3 (Aldrich, Powder, 99.9+%) in 10^{-2} M HClO_4 (Riedel-de Haen). The pH of each sample was titrated from 3 to 11 by adding K_2CO_3 (Aldrich, Powder, 99.995%). For equilibration, all of solutions were left exposed to atmosphere ($P_{\text{CO}_2}=10^{-3.5}$) for more than 1 week.

Fluorescence measurements were performed at 25°C . This temperature was maintained with tempered water circulation flowing between copper cuvette holder and water bath. A quartz cuvette (Hellma) was used and the samples were stirred to avoid the fluorescence intensity decrease due to poly-europium precipitation process. A 355 nm laser pulse from Nd:YAG laser (Continuum Surelite Laser, 20 Hz, 6 ns pulse width) with 5 mJ per pulse was used to excite europium ion in the sample. The fluorescence was collected by optic fiber bundle which transmits the light into a single grating polychromator and then into ICCD (Andor Technology, CCD Head DH734). The ICCD camera was triggered by Q-switch signal from the laser for synchronization. Delay time varied from $10\mu\text{s}$ to $800\mu\text{s}$ with a delay time interval of 10 or $20\mu\text{s}$. Lifetime of precipitated samples was measured during magnetic stirring.

2.2 Results

As can be seen from the previous fluorescence data [1,2], it is well known that Eu^{3+} ions hydrated with 9 water molecules give around $110\mu\text{s}$ lifetime at room temperature. If one CO_3^{2-} ion binds to a europium, the

lifetime of $^4\text{D}_0$ state of europium then increases to around $170\mu\text{s}$. This lifetime gives 6 or 7 water molecules around europium ion in the first hydration sphere according to Horrocks' equation [1].

In the present study, the samples showing 252.3 and $435.5\mu\text{s}$ fluorescence lifetimes correspond to europium dicarbonate and europium tricarbonate complex, respectively, as shown in Fig. 1., Fig. 2. and Fig. 3.. The hydration number of dicarbonate and tricarbonate europium are 3.6 and 1.8 according to Horrocks' equation. In the steric point of view, a carbonate anion is larger than a water molecule. Therefore it may be predicted that two or more water molecules are replaced by one carbonate anion. These results agree well with previous results [2,3].

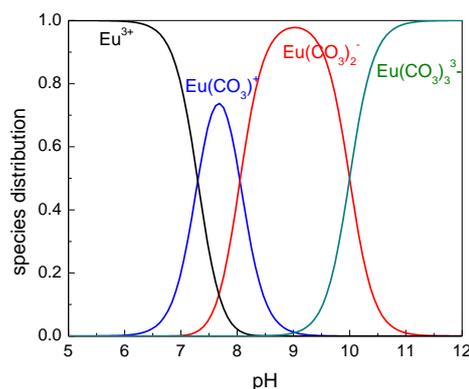


Fig. 1. Speciation diagram of Eu(III) in water ($p\text{CO}_2=10^{-3.5}$)

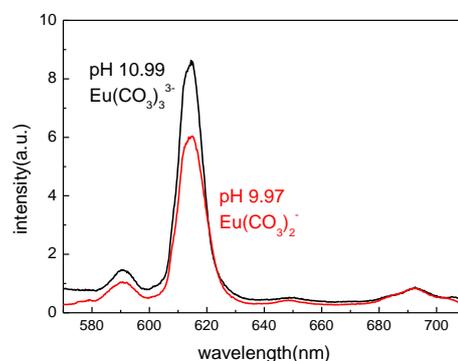


Fig. 2. Europium fluorescence at pH 9.98 and pH 10.99

The results of fluorescence measurement in the present study are represented in Table 1. But fluorescence intensity measured from pH 7.92 to pH 9.78 without

magnetic stirrer was decreased as time goes by. It reflect the fact that the concentration of Eu is exceeded its solubility limit.

Table I: Spectroscopic characteristic of the Eu(III) complexes at $[Eu(III)]_t = 10^{-4}M$ and $pCO_2 = 10^{-3.5}$

pH	Lifetime (μs)	I_2/I_1
3.39	108	0.5
7.92	84	6.5
8.30	110	5.3
8.50	153	4.9
8.77	204	4.9
8.92	172	5.0
9.03	168	5.0
9.51	242	9.1
9.78	254	7.6
9.98	252	11.7
10.99	435	13.9

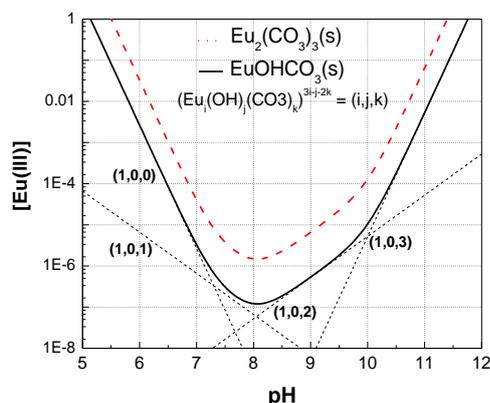


Fig.3. Solubility of europium in water, $pCO_2=10^{-3.5}$ ($\log K_{sp}(EuOHCO_3(s)) = -20.18$; $\log K_{sp}(Eu_2(CO_3)_3(s)) = -31.78$)

The best known carbonate minerals are lanthanite ($Eu_2(CO_3)_3 \cdot nH_2O$) and bastnaesite ($EuOHCO_3$). These are formed with varying CO_2 partial pressure. It is reported that Eu^{3+} ions in atmospheric CO_2 partial pressure (pH 5~7) precipitate as $Eu_2(CO_3)_3(s)$ initially and undergoes phase transition into $EuOHCO_3(s)$ within 20 days by the ageing effect [4]. Therefore it is possible to assume that $EuOHCO_3(s)$ is one of the solubility limiting solid phase in our experiment. It seems possible that $Eu_2(CO_3)_3(s)$ is formed at higher pH region (pH 9.51 and 9.78) since it is well known that $Eu_2(CO_3)_3(s)$ is formed in carbonate-rich environments [4].

In addition, from the solubility of $EuOHCO_3(s)$ and $Eu_2(CO_3)_3(s)$ (Fig. 3.), only $Eu_2(CO_3)_3(s)$ precipitate can explain formation of $Eu(CO_3)_2^-$ at pH 9.98. Fig. 4. shows two distinct peak shapes in the saturation region. The samples at pH 7.92~9.03 show fundamentally the same spectral shape compared that at pH 8.3. The spectral shape for the sample at pH 9.78 is almost identical to that at pH 9.51. Lifetime of Eu in the

neutral becomes more shorter than that in the alkaline region (Table I).

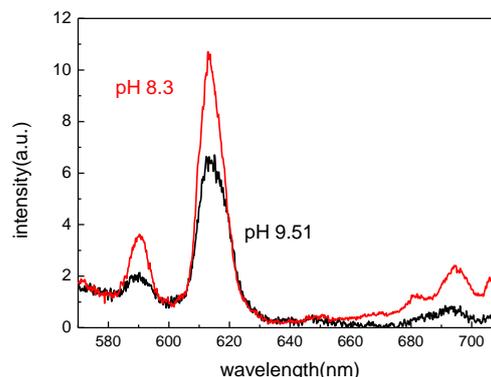


Fig. 4. Europium fluorescence at pH 8.3 and pH 9.51

This may indicate that the OH quencher of europium complex in the neutral region is substituted by carbonates anions in the alkaline range. From this results, we conclude that $EuOHCO_3(s)$ and $Eu_2(CO_3)_3(s)$ are formed at pH 7.92 ~ 9.03 and at pH 9.51 ~ 9.78 respectively.

3. Conclusions

The present work demonstrates that lifetime and peak profile of $Eu(CO_3)_2^-$ and $Eu(CO_3)_3^{3-}$ are well in accord with previous results. In the saturation region, two distinct spectral shapes appeared and the lifetime tends to be longer with increasing pH. With a help of the previous solubility data and precipitation experiments, it is proposed that $EuOHCO_3(s)$ and $Eu_2(CO_3)_3(s)$ are formed in pH 7.92 ~ 9.03 and pH 9.51 ~ 9.78, respectively. However it is still not clear that what kinds of species are really formed in the saturation region. The structural analysis of precipitates should be under investigation.

REFERENCES

- [1] W.D. Horrocks, Jr., and D.R. Sudnick, Lanthanide Ion Probes of Structure in Biology, Journal of the American Chemical Society, Vol. 101:2, p. 334-340, 1979
- [2] J.I. Kim, R. Klenze, H.Wimmer, W. Runde and W. Hauser, A study of the carbonate complexation of Cm(III) and Eu(III) by time resolved laser fluorescence spectroscopy, Journal of Alloys and Compounds, Vol. 213/214, p. 333-340, 1994
- [3] G. Plancque, V. Moulin, P. Toulhoat, C. Moulin, Europium speciation by time-resolved laser-induced fluorescence, Analytica Chimica Acta, Vol. 478, p. 11-22, 2003
- [4] W.Runde, G.Meinrth, J.I.Kim, A study of solid-liquid phase equilibria of trivalent lanthanide and actinide ions in carbonate systems, Radiochimica Acta, Vol. 58/59, p. 93-100, 1992