

Interpretation of solubility based on solid-state of trivalent lanthanide hydroxides and oxides

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INTRODUCTION: Safety assessment of radioactive waste disposal requires a quantitative prediction of the migration behavior of radionuclides under the waste disposal conditions. Radionuclides in trivalent states such as Am(III) and Cm(III) undergo strong hydrolysis reactions, and poorly soluble hydroxide precipitates ($M(OH)_3(s)$) in the neutral to alkaline pH range in the absence of any complexing ligands. In order to predict the migration behavior of these nuclides, it is necessary to understand the solubility of $M(OH)_3(s)$ and their thermodynamic data, such as hydrolysis constants and solubility products [1]. For the solubility of tetravalent metal hydroxides ($M(OH)_4(s)$), their solubility products have been found to increase in inverse proportion to their particle size [2]. Therefore, it is interesting to explore the particle size effect for $M(OH)_3(s)$. In this study, the solubility samples for La(III) hydroxide solid phase ($La(OH)_3(s)$) were prepared and investigated together with the solid phase analysis such as crystal structure and particle size. An interpretation of solubility was discussed based on the solid phase structure.

EXPERIMENTS: Sample solutions containing La(III) solid phase were prepared using the oversaturation and unsaturation methods. In the oversaturation method, a 0.01 mol/L La(III) nitrate was prepared as a mother solution, and the pH was adjusted to pH 7 to 12 by the addition of NaOH to precipitate $La(OH)_3(s)$. In the unsaturated method, $La_2O_3(cr)$ was added as a solid phase to a sample solution whose pH was adjusted in advance to 7 to 12. Sample solutions were kept at 25°C or 90°C for one month. After the aging, the supernatant was ultrafiltered through a 3 kDa membrane filter. The La concentration contained in the filtrate was determined by ICP-MS. The solid phase contained in each sample solution was collected in a suspended state and filled into a Kapton membrane cell with a thickness of 1 mm. These samples were measured at the small-angle X-ray scattering (SAXS) beamline (BL8S3) at the Aichi Synchrotron Center. The X-ray wavelength used in the measurements was 0.92 Å, and the X-rays scattered by the sample were detected at three camera lengths (0.21 m, 1.23 m, and 3.97 m) using a large-area pixel detector (PILATUS 2M detector).

RESULTS: Regarding the SAXS intensity ($I(q)$) of the solid phase prepared by the oversaturation method, in the range of scattering vector q ($q = 4\pi\sin\theta/\lambda$, θ is the scattering angle) > 10 (nm^{-1}), a diffraction peak appeared, identified as $La(OH)_3(cr)$ based on the peak position. Since it has been found that $La_2O_3(cr)$ changed to $La(OH)_3(cr)$ in the unsaturated method [3], and the oversaturation and undersaturation methods obtained the same crystal structure. In the region of $0.06 < q < 4$ (nm^{-1}), an inflection point was observed around $q = 0.8$ and 0.25 (nm^{-1}) for the sample solutions kept at 25°C and 90°C, respectively. This suggests that both solid phases have the same crystal structure, but the respective primary particle sizes are different. The solubility of $La(OH)_3(cr)$ kept at 90°C was about two orders of magnitude lower than those kept at 25°C, indicating the particle size effect for the solubility $La(OH)_3(cr)$.

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Redox potential of U in NaCl-CaCl₂ melt at 799 - 848 K

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INTRODUCTION: A NaCl-CaCl₂ mixture melt is proposed as a candidate of a base salt for molten chloride salt fast reactor. There are very limited reports on electrochemical properties such as redox potential of actinides in the melt, which are basic data to construct a reprocessing process of the spent molten chloride fuel salt. In this study, electrochemical measurements were carried out to obtain the redox potential of U in eutectic NaCl-CaCl₂ melt at a temperature range between 799 and 848 K.

EXPERIMENTS: All electrochemical measurements were performed in eutectic NaCl-CaCl₂ salt (50:50 mol%) containing UCl₃ which was melted in the electric furnace placed in the glove box filled with a purified Ar gas. W wire (1 mm ϕ) and glassy carbon rod (3 mm ϕ) were used as the working and counter electrodes, respectively. The Ag/AgCl reference electrode was used, of which potential was calibrated to be -1.257 V, -1.267 V and -1.273 V (vs. Cl₂/Cl⁻) at 799 K, 837 K and 848 K, respectively.

RESULTS: Fig. 1 shows a cyclic voltammogram using W wire electrode in the melt at 799 K. A couple of cathodic and anodic currents was observed at around -2.5 V (vs. Cl₂/Cl⁻), which was ascribed to U metal deposition (reaction 1) and its dissolution (reverse reaction of reaction 1), respectively,



Based on the results of the cyclic voltammetry, galvanostatic electrolysis at -18 mA cm⁻² was performed for 5 seconds to deposit U metal on the W wire electrode. Then, the redox potential of the U metal deposited on the W (E_U) was measured in the melt by changing the applied current to 0 mA. The same procedure was carried out to obtain E_U at different temperatures, 837 K and 848 K. The obtained values were plotted against temperature as seen in Fig. 2, showing a linear relationship between E_U and temperature. The similar tendency was reported for the formal standard redox potential of U in LiCl-KCl melt at 673-823 K [1].

The concentration of UCl₃ in the melt (C_{UCl_3}) will be measured in near future to convert the obtained E_U to the formal standard redox potential of U ($E_U^{0'}$) according to the following Nernst equation,

$$E_U = E_U^{0'} + \frac{RT}{3F} \ln C_{\text{UCl}_3} \quad (2)$$

where R is gas constant, T is temperature in Kelvin, F is faraday constant.

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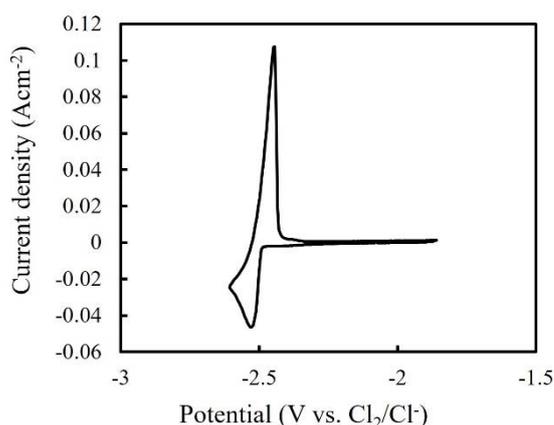


Fig. 1. Cyclic voltammogram using W wire electrode in NaCl-CaCl₂-UCl₃ melt at 799 K. Scan rate was 50 mV s⁻¹.

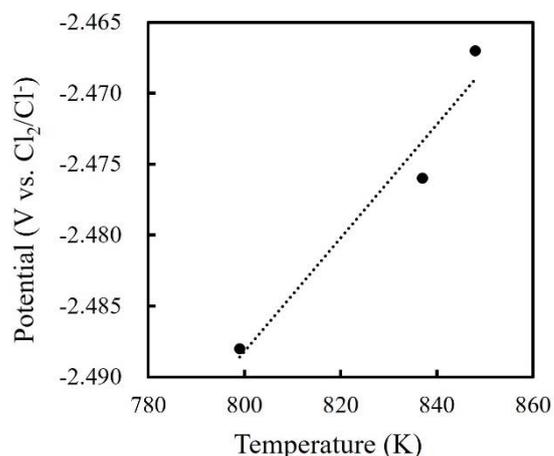


Fig. 2. Measured redox potentials of U in NaCl-CaCl₂-UCl₃ melt at 799 K, 837 K and 848 K.

Effect of Cyclic Structures of Water-soluble Cyclic Monoamide Compounds on Stability against γ -Ray Irradiation

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INTRODUCTION: It is of great importance to develop compounds with selectivity for uranium(VI) species in nitric acid media. Under such a background, we have investigated stability against γ -ray irradiation for a lot of monoamide compounds as candidates for resins[1-3]. This year, 2-piperidone (PP) and 2-pyrrolidone (PR) which are both water-soluble and compose the functional group of monoamide resins, VBPP[2] and VBPR[3], respectively, were taken. As seen in Fig. 1, both compounds are categorized into “cyclic monoamides”. The former and the latter have a 6- and 5-membered ring, respectively, and the other parts are identical from the viewpoint of chemical structure. Previously, the difference in the stability between 6- and 5-membered rings of cyclic monoamides was investigated by using compounds where hydrocarbon atoms are bound with the nitrogen atom in cyclic monoamides, but clear tendency was not observed. In this study, γ -ray irradiation to both compounds was performed in nitric acid and hydrochloric acid solutions.

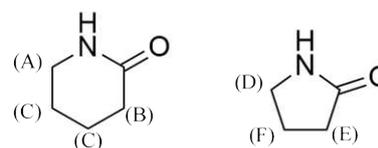


Fig. 1. Chemical structures of PP (left) and PR (right)

EXPERIMENTS: 6 mol/dm³ (= M) HNO₃ solutions containing 0.5 M PP and PR, respectively, were prepared in Pyrex tubes for the samples for γ -ray irradiation. 6 M HCl solutions containing 0.5 M PP and PR, respectively, were also similarly prepared[1]. Irradiation was carried out by the ⁶⁰Co source up to 0.34 and 0.43 MGy for PP and PR, respectively, at room temperature under ambient atmosphere. Irradiated samples were analyzed by ¹H NMR. D₂O containing a known weight of formic acid which is a standard material was used as the NMR solvent. The residual ratios of PP and PR were calculated by the area ratio of each signal with that of formic acid.

RESULTS: In ¹H NMR spectra, neat PP and PR show several signals attributed to the position of hydrogen in the structure of both compounds. Those for PP and PR are shown as (A) through (C), and (D) through (F), respectively, in Fig. 1. The results on the stability are shown in Fig. 2. For both compounds, the residual ratios are found higher for HCl than for HNO₃. In addition, PP would be more stable than PR. The tendency is clearer in HCl media. One of the reasons for higher stability in the 6-membered ring might be larger number of possible steric structures leading to dispersion of given energy.

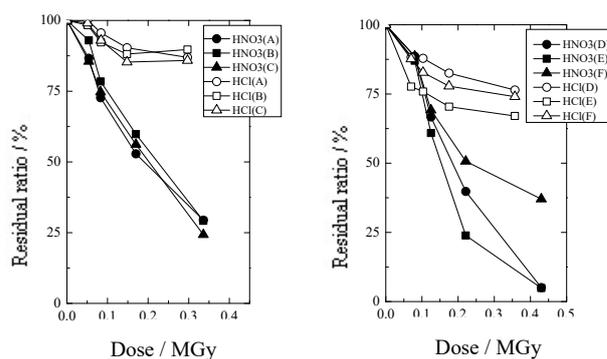


Fig. 2. Dependence of dose on residual ratio for PP (left) and PR (right).

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Solid-liquid extraction experiments of ^{47}Ca for the chemical study of nobelium

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INTRODUCTION: Element 102, nobelium (No), is the second element from the back of the actinide series. Unlike all other lanthanides and actinides, No was reported to exist as a divalent ion rather than trivalent in aqueous solutions and to have similar chemical properties to those of alkaline earth metals [1]. We focus on solid-liquid extraction using crown ether supporting resin (Sr resin), and have indeed performed extraction experiments with it. Sr resin is commercially available crown-ether supported resin and the crown ether has extraction selectivity for alkaline earth ions. This selectivity is sensitive to ligand ions in the aqueous solutions such as Cl^- and NO_3^- [2,3].

Our previous solid-liquid extraction experiment of ^{255}No in Sr resin/ HNO_3 system has suggested that No exhibits similar behaviors to that of Pb, which is softer than alkaline earth metals [4]. For the systematic understanding of the chemical property of No, further investigation is needed.

This study performed extraction experiments using radioactive tracers of alkaline earth metals (^{47}Ca , ^{85}Sr , and ^{133}Ba) by Sr resin (tBuCH18O6 impregnated resin) in dithiophosphate which is softer than the nitrate ion to investigate the properties of No as a soft metal. In addition, the complex structure should be clear for calculation of the electron state of the complexes. We predicted complex structures of No and alkaline earth metals using the relativistic DFT calculation method to investigate the chemical properties of No.

EXPERIMENTS: ^{47}Ca was produced by thermal neutron irradiation to 280 mg of $^{\text{nat}}\text{CaO}$ for 1 h (5 MW) at Kyoto University research Reactor (KURNS). After irradiation, CaO was dissolved in conc. HCl solution and purified through an anion-exchange resin in conc. HCl system. In solid-liquid extraction, 0.5-1.0 mL of 60-320 mM sodium dithiophosphate solutions containing metal tracers (^{47}Ca , ^{85}Sr , and ^{133}Ba) was contacted with 50 mg of Sr resins for 1-30 min. After that, the resin and solution was separated through a filter unit.

After the extraction experiments, the samples were subjected to γ -ray measurement with a Ge semiconductor detector to measure the amount of ^{47}Ca , ^{85}Sr , and ^{133}Ba . The distribution coefficients, K_d , were calculated by the equation

$$K_d = (A_{\text{STD}} - A_s)V / A_s w,$$

where A_s and A_{STD} are radioactivities of the aqueous phase and the control (standard) sample which was obtained in the extraction without the resin. V is the volume of the aqueous phase (mL), and w is the mass of the dry resin (g).

RESULTS: The K_d values of all elements were almost constant for shaking time from 1 to 30 min. This result indicates that the chemical reactions involved in the present complexation and extraction are sufficiently fast for investigating the extraction behavior of ^{255}No whose half-life is about 3 min.

As depicted in Figure 1, the K_d values of Ca, Sr, and Ba depend on the concentration of dithiophosphate. In this system, the K_d values of Ca are extremely lower than those of Sr and Ba. It is presumed that the ionic size of calcium does not align with the size selectivity of the 18C6 ring. Being different from the values in the previous studies, the K_d values of Sr are lower than those of Ba, even though DFT calculations results show that the radius of Ba does not match the size of the crown ether ring. This phenomenon is considered to be attributed to strong bonding between soft acid and soft base: Ba and dithiophosphate. Owing to superior ion size selectivity, the No could exhibit higher K_d values compared to Ba, assuming that No possesses chemical properties of a soft acid.

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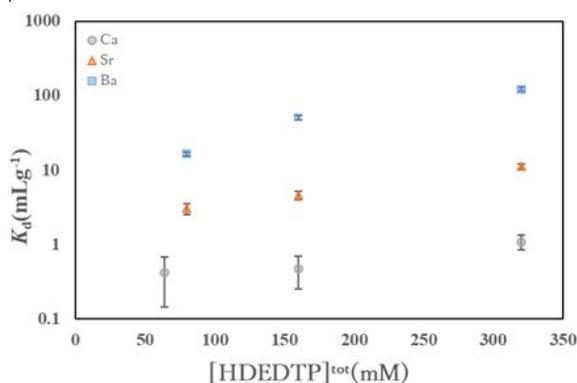


Figure 1 K_d dependence of Ca, Sr, and Ba on dithiophosphate concentration at pH 3.5