Stability of Novel Cyclic Monoamide Extractants for U(VI) against γ-Ray Irradiation in HNO₃

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INTRODUCTION: Uranium is the predominantly major component of spent fuels, and extractants with high selectivity and capacity to U(VI) and radiation stability in nitric acid media are desired in the world. Monoamide extractants have been studied for the purpose due to very little generation of the secondary waste resulting from the spent extractants. Above all, "branched monoamodes" have been studied almost exclusively so far, probably because of relatively easy synthesis[1]. On the other hand, extensive studies on pyrrolidone and its related derivatives, which are categorized into "ring monoam-ides", convinced us that some ring monoamides with high symmetry would exceed branched monoamodes on the above-mentioned properties[2,3]. Based on the back-ground, we focused on 1,3-dialkyl-2-pyrrolidone (DRP) (Fig. 1). In this study, fundamental stability of two DRPs, 1,3-dibuthyl-2-pyrrolidone (DBP) and 1,3- dihex-yl-2-pyrrolidone (DHP), against γ-ray irradiation was investigated.
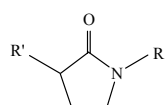
(R, R': hydrocarbon group)

Fig. 1. Chemical structure of DRP.

EXPERIMENTS: DBP and DHP were synthesized by modifying the method shown in the reference[4]. For the sample for γ-ray irradiation to DBP and DHP, solutions consisting of 30 vol% DBP or DHP in *n*-dodecane as the organic phase and 3 or 6 mol/dm³ (= M) HNO₃ as the aqueous phase were prepared in a Pyrex tube. Irradiation was carried out by the ^{60}Co source up to 1.14 MGy at room temperature under ambient atmosphere, similarly to the earlier study[5]. Irradiated samples were analyzed by ^{1}H NMR. CDCl₃ containing a known weight of TMS which is a standard material was used as the NMR solvent for the organic phase. The residual ratio of MEC was calculated by the area ratio of each signal with that of TMS.

RESULTS: No distinguished appearance changes were observed for the irradiated samples. In a ^{1}H NMR spectrum, neat DRP shows several signals. The calculated residual ratios for DHP irradiated in 3 and 6 M HNO₃ are shown in Fig. 2, respectively, together with the relationship between the position of hydrogen in the structure of DHP and that of the signal. For the sample irradiated in

3 M HNO₃ (Fig. 2(a)), the residual ratios calculated through (A) to (C) in DHP show an identical trend, where nearly no decomposition occurred after irradiation at ca. 0.8 MGy. This suggests that the stability of DHP in 3 M HNO₃ is better than that of water-soluble *N*-butyl- pyrrolidone (NBP) with the residual ratio of ca. 85 % at 0.8 MGy, although the solution conditions of both compounds during irradiation are different in a precise sense with each other[3]. On the other hand, for the sample irradiated in 6 M HNO₃ (Fig. 2(b)), the calculated residual ratios were found to differ depending on the position of hydrogen atom in DHP. While the residual ratio calculated from hydrogen of the side chain (A) remains nearly 100 % after irradiation at ca. 0.75 MGy, those calculated from hydrogen in the ring ((B) and (C)) decrease down to 40 through 60 %. The residual ratios of ca. 50 % were in accordance with the results for NBP. These facts indicate that DHP possesses satisfying radiation stability at around 3 M HNO₃. Further detailed investigations are ongoing.
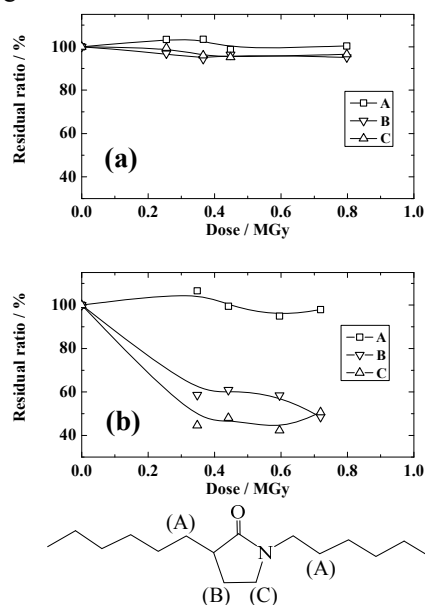

Fig.2. Dependence of residual ratio of DHP on dose; (a) 3 M HNO₃, (b) 6 M HNO₃.

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CO9-2 Search for the Ultraviolet Photons Emitted from ^{229m}Th in its Deexcitation Process

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INTRODUCTION: Thorium-229m lies in the first excited state of the ^{229}Th nucleus and this excitation energy is extremely low to be 7.8 ± 0.5 eV [1] corresponding to vacuum ultraviolet (VUV) photon of which the wavelength is about 160 nm. Thorium-229m is expected to decay by the gamma transition and/or the internal conversion (IC) process. Because its excitation energy value is in the same energy scale with that of the chemical bond, ^{229m}Th would decay by IC process in some chemical forms and in the other forms, the IC may be hindered. Consequently, the decay process of ^{229m}Th is able to vary depending on its chemical form. This phenomenon is unique to ^{229m}Th and makes ^{229m}Th nucleus very fascinating. Recently, photon emissions from the ^{229m}Th sample implanted into MgF$_2$ glass were reported and its half-life was evaluated to be about 6 h [2]. However, it is controversial [3]. In our study, the results of the photon detection for the hydroxide and fluoride precipitates of ^{229m}Th grown for 2 h or 13 h were previously reported [4]: decaying photons were observed for 13-h growth samples. Here, the results of the photon detection for the ^{229m}Th precipitates after purified and the ^{229m}Th samples implanted into the MgF$_2$ glass are reported.

EXPERIMENTS: Thorium-229m precipitated samples were prepared by the method reported previously [4]. In this study the additional procedure to purify the ^{229m}Th was performed before ^{229m}Th was coprecipitated with Sm, assuming that the half-life of ^{229m}Th would be long: about several hours. After ^{229m}Th was separated from ^{233}U, the ^{229m}Th eluent was heated to dryness. Then, 8 M HNO$_3$ solution was added and ^{229m}Th was adsorbed on the anion-exchange resin (Muromac 1×8 200-400 mesh, 1 mL). The daughter nuclides of ^{229}Th were removed by pouring 8 M HNO$_3$ solution. After that, 2 M HCl solution was passed through the ^{229m}Th column and ^{229m}Th was eluted.

In the case of the ^{229m}Th samples implanted into MgF$_2$ glass, ^{229m}Th was collected as the recoil product from the electrodeposited sample of ^{233}U in vacuum.

RESULTS: On the results of the photon detection for the ^{229m}Th samples after purified, there was no decaying photon emission. In addition, on the result of the long-time measurement, the count rate of photons increased as time passed. This result is shown in Fig. 1. These growing photons agreed with the growth of the daughter nucleus ^{212}Bi. Taking into account the result in ref. 4, we concluded that no significant photons from ^{229m}Th were observed although we used about 200 mg of ^{233}U: this amount was about 400 times larger than that in the study in ref. 2.

Because in the experiment on the ^{229m}Th precipitates,

VUV photons deriving only from the daughter nuclides were observed, we measured the photons emitted from the same ^{229m}Th samples as those in ref. 2 to search the photons derived from ^{229m}Th in MgF$_2$. On the result of the MgF$_2$ glass samples, decaying photons probably originating from multiple components including the daughter nuclides were observed. This result is shown in Fig. 2. We are precisely analyzing these data to elucidate these origins.
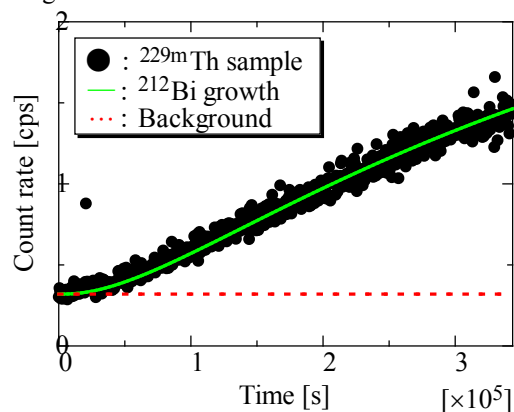

Fig. 1. The photon count for the ^{229m}Th precipitate (hydroxide form) grown for about 13 h. Black dots denote the photon count rate of the ^{229m}Th sample, solid curve describes the growth of ^{212}Bi and dotted line describes the count rate of background.
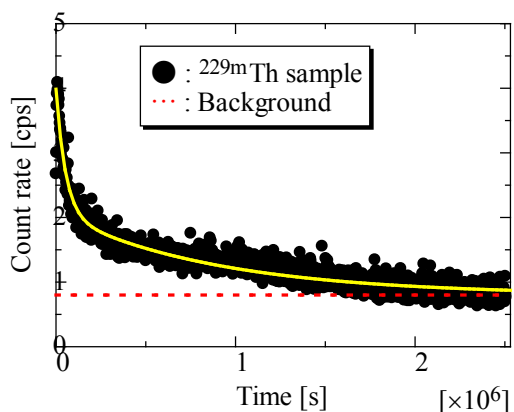

Fig. 2. The photon count for the ^{229m}Th implanted into the MgF$_2$ glass for about 26 h. Black dots denote the photon count rate of the ^{229m}Th sample and the solid curve describes the fitted decay curve consisted of two decaying components: these half-lives are about 10 h and 7 d.

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