Coprecipitation of ^{133}Ba, ^{226}Ra, and ^{152}Eu with calcium oxalate for the chemical study of nobelium

R. Nakanishi,[*1,*2] E. Watanabe,[*1,*2] S. Otaka,[*1,*2] R. Masuda,[*1,*2] R. Wang,[*1,*2] Y. Itakura,[*2,*3] T. Yokokita,[*2,*4] Y. Shigekawa,[*2] A. Nambu,[*2] X. Yin,[*2] H. Haba,[*2] A. Shinohara,[*5] and Y. Kasamatsu[*1,*2]

Superheavy elements (SHEs) with $Z \geq 101$ are synthesized by heavy-ion-induced nuclear reactions. The production rates of these elements are very low, and their half-lives are usually short.[1] Therefore, it is difficult to investigate their chemical properties. Element 102, nobelium (No), is one of the actinide elements. No has unique property that the element exists stably as No^{2+} ion in aqueous solutions,[2] whereas all lanthanide and actinide elements have the most stable valency of +3 or higher. Previous chemical studies on No have reported that No exhibits similar chemical behavior to those of the group 2 elements in the periodic table.[3] In this study, we focused on oxalic acid, which precipitates the group 2 elements by bonding with metal ions, and malonic acid, which has a slightly longer carbon chain length than oxalic acid. We expect that the complexation behavior of these dicarboxylic acids with No can be investigated by the coprecipitation method. Studies for complexation with organic ligands are scarce in SHE chemistry, and through the present study, the dependence of the No behavior on the ligand size and shape is expected to be discussed. In this report, we present the results of the precipitation and coprecipitation experiments of Ca, Sr, Ba, Ra, and Eu with oxalic acid. We determined the suitable experimental conditions for investigating the properties of No-oxalic complexes.

Oxalic acid precipitation experiments for Ca, Sr, and Ba were performed to determine the carrier metal elements that rapidly and fully precipitate by bonding with oxalic acid. The precipitation experiments were performed at pH = 2, 3, 4, and 5 with reaction times of 3 min. 5 mL of 2 mM Ca^{2+}, Sr^{2+}, or Ba^{2+} hydrochloric acid (pH = 2, 3, 4, or 5) was mixed with 5 mL of 4, 20, and 200 mM oxalic acid (pH = 2, 3, 4, or 5). The amounts of Ca and Sr in the precipitate and filtrate samples were analyzed by EDTA titration and that of Ba was determined by γ-ray measurement for ^{133}Ba tracer with a Ge semiconductor detector. The precipitation yields were estimated from the amounts.

Based on the precipitation results, coprecipitation experiments of ^{133}Ba, ^{226}Ra, and ^{152}Eu with calcium oxalate were performed using Ca as the carrier at pH = 3. 20 μL of hydrochloric acid (pH = 3) containing ^{133}Ba, ^{226}Ra, and ^{152}Eu was added to 230 μL of 2.17 mM Ca^{2+} hydrochloric acid (pH = 3), which was followed by addition of 250 μL of 20 and 200 mM oxalic acid (pH = 3). The mixture was shaken for 5 min. The coprecipitation yield of each element was determined by γ-ray measurement for ^{133}Ba and ^{152}Eu with the Ge semiconductor detector, and by α-particle measurement with a Si detector for ^{226}Ra.

The results of the oxalic acid precipitation experiments of Ca, Sr, and Ba showed that the precipitation yield of Ca rapidly reached about 100%, and a clear difference in the precipitation yields of Ca (92.6 ± 4.9%), Sr (5.8%), and Ba (0.6 ± 0.3%) was observed under the condition of 10 mM oxalic acid at pH = 3. Consequently, we determined suitable experimental conditions, as Ca carrier will be used in coprecipitation at pH = 3, to observe the similarity of No behavior to which group 2 element.

Figure 1 shows the coprecipitation yields of ^{133}Ba, ^{226}Ra, and ^{152}Eu with calcium oxalate. The yields for ^{133}Ba and ^{226}Ra were low and increased with increasing oxalic acid concentration, in the range 10–40% for ^{133}Ba and 5–20% for ^{226}Ra. The coprecipitation yields for ^{152}Eu were over ∼90% at all oxalic acid concentrations studied. The coprecipitation yields were in the order of Ca ≈ ^{152}Eu > ^{133}Ba > ^{226}Ra, which is inverse order of the ionic radius[4]: Ca^{2+} (1.12 Å) ≈ Eu^{3+} (1.066 Å) < Ba^{2+} (1.42 Å) < Ra^{2+} (1.48 Å). This suggests that smaller metal ions tend to match the size of oxalic acid and stably form complexes. We plan to investigate the coprecipitation behavior of No with oxalic acid to discuss the ionic radius of No.

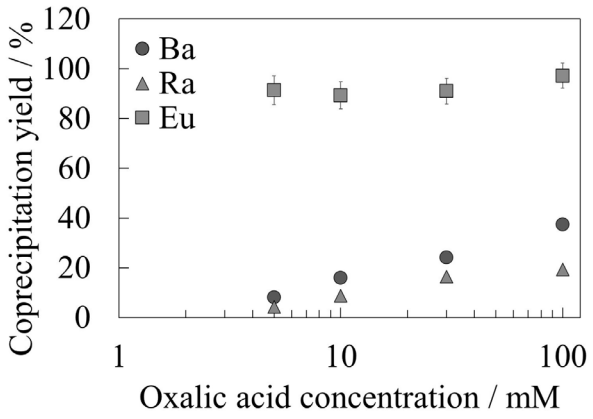

Fig. 1. Coprecipitation yield of ^{133}Ba, ^{226}Ra, and ^{152}Eu.

*1 Graduate School of Science, Osaka University
*2 RIKEN Nishina Center
*3 Department of Chemistry, Osaka University
*4 Salesian Polytechnic
*5 Osaka Aoyama University

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