

Complex formation of Fr with crown ethers

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Francium (Fr) is the heaviest known alkali metal with atomic number 87. It is one of the least-studied elements among the naturally occurring elements because all its isotopes are short-lived. The half-life of its longest-lived isotope, ^{223}Fr , is only $T_{1/2} = 21.8$ min. Owing to experimental difficulties, the chemical properties of Fr have not been studied in detail so far. We aim to clarify the chemical bonding nature of Fr, which is influenced by relativistic effects, through complex formation studies of Fr. Recently, Haverlock *et al.* examined the complex formation of Fr^+ with calix[4]arene-bis(benzocrown-6) (BC6B).¹⁾ They reported that Fr^+ is more effectively extracted with BC6B than Cs^+ . However, the reason for the selectivity is still unclear. In this work, we studied the complex formation of Fr using seven types of crown ethers: 18-crown 6-ether (18C6), dicyclohexano-18-crown 6-ether (DC18C6), dibenzo-18-crown 6-ether (DB18C6), 24-crown 8-ether (24C8), dibenzo-24-crown 8-ether (DB24C8), 21-crown 7-ether (21C7), and dibenzo-21-crown 7-ether (DB21C7). Complex formation stability and selectivity of alkali metals with the crown ethers depend on the ring cavity size and substituent groups of the crown ethers. Therefore, in this work, we will investigate the effects of the cavity size and substituent groups of the crown ethers on the stability and selectivity of the complex formation of Fr.

We produced the second longest-lived isotope of Fr, ^{212}Fr ($T_{1/2} = 20$ min), in the $^{206}\text{Pb}(^{11}\text{B}, 5n)^{212}\text{Fr}$ reaction. Four sets of an $864\text{-}\mu\text{g}/\text{cm}^2$ ^{206}Pb target on a $10\text{ }\mu\text{m}$ Be foil were placed in a 12 mm spacing in 129-kPa He. They were irradiated with a ^{11}B beam at an energy of 86 MeV. The beam energies on the four ^{206}Pb targets are calculated to be in the range of 70–79 MeV, which covers the peak region of the excitation function of the $^{206}\text{Pb}(^{11}\text{B}, 5n)^{212}\text{Fr}$ reaction.²⁾ The ^{212}Fr atoms that recoiled out of the ^{206}Pb target were thermalized in He gas, attached to KCl aerosol particles, and transported through a Teflon capillary to a chemistry laboratory. In the chemistry laboratory, the aerosols were collected on a piece of Naflon sheet for 20 s. The aerosols were dissolved with $100\text{ }\mu\text{L}$ of 1 M nitric acid and transferred into a polypropylene (PP) tube. Another $600\text{ }\mu\text{L}$ of 1 M HNO_3 and $700\text{ }\mu\text{L}$ of nitrobenzene containing each of the crown ethers were then added into the PP tube. The PP tube was shaken for a certain time for extraction. After centrifuging the PP tube for 2 min, $500\text{ }\mu\text{L}$ of each phase was subjected to γ -ray spectrometry to determine the distribution ratios (D) of Fr. The D values were measured as functions of the shaking time and the concentration of each crown ether. These results were compared with those of RIs of lighter alkali metals such as ^{24}Na , ^{43}K , and ^{137}Cs .

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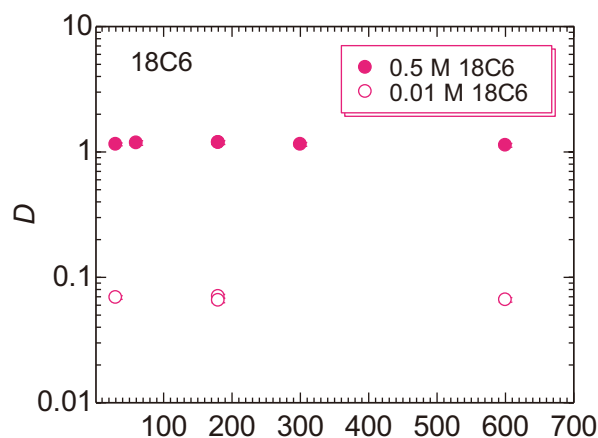


Fig. 1. Variations of D values of Fr^+ as a function of shaking time in solvent extraction with 0.01 and 0.5 M 18C6.

Figure 1 shows the variation of the D values of Fr^+ as a function of the shaking time in the solvent extraction with 0.01 and 0.5 M 18C6. We found that the extraction equilibrium time of Fr^+ is as fast as within 30 s. Therefore, we fixed the shaking time to be 3 min. The 18-membered rings, with a cavity diameter of 2.6–3.2 Å,³⁾ show the highest affinity for K^+ because their cavity sizes fit the size of K^+ ion (ionic diameter: 2.66 Å⁴⁾). The cavity diameter of the 24-membered crowns is in the range of 4.5–5.0 Å,⁵⁾ which is larger than all alkali metal ions. Thus, they show affinity for larger alkali metal ions such as Cs^+ (3.34 Å⁴⁾ and Fr^+ (3.46 Å⁶⁾). The cavity diameter of 21-membered crowns is in the range of 3.4–4.3 Å.³⁾ When using DB21C7, the D values of Cs^+ are slightly larger than those of Fr^+ , while the D values of Cs^+ and Fr^+ are almost the same when using 21C7. Two benzene rings of DB21C7 may affect the selectivity between Cs^+ and Fr^+ .

In this work, the D values of Fr^+ with several types of crown ethers are almost the same as those of Cs^+ , which can be qualitatively understood by the relation between the size of the alkali metal ions and the ring cavity diameter of the crown ethers. However, in the previous study using calixarene, the D values of Fr^+ are almost one order of magnitude higher than those of Cs^+ .¹⁾ To interpret these results and elucidate the reason of complex formation selectivity between Fr^+ and Cs^+ , we will perform further investigations, for example, XAFS studies of the Cs^+ -crown ether and Cs^+ -calixarene complexes, and quantum chemistry calculations for Fr^+ as well as Cs^+ .

References

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