

Solvent extraction of Fr and Cs with calix[4]arene-bis(benzocrown-6)

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Francium (Fr) is the heaviest alkali metal, with the 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. For that purpose, we performed solvent extraction experiments on ^{221}Fr ($T_{1/2} = 20$ min) with several crown ethers and compared the results with those on ^{137}Cs ($T_{1/2} = 30.1$ y).¹⁾ We found that the distribution ratios (D) of Fr and Cs are almost the same, although the D values of Cs are slightly higher than those of Fr in the extraction with dibenzo-21 crown-7 (DB21C7). Haverlock *et al.* examined the complex formation of Fr^+ with calix[4]arene-bis(benzocrown-6) (BC6B) in 2003.²⁾ The D values of Fr are almost one order of magnitude higher than those of Cs. Such a large difference is surprising because the ionic radius of Fr (173 pm^3) is close to that of Cs (167 pm^4). However, the mechanism for the large difference has not been clarified yet. The higher affinity of BC6B for Fr than for Cs is interesting and important to understand the chemical properties and chemical bonding of Fr. In this work, we reinvestigated the solvent extraction behavior of Fr and Cs with BC6B to confirm the large difference between Fr and Cs.²⁾

We used ^{221}Fr ($T_{1/2} = 4.8$ min) produced as the α -decay daughter of ^{225}Ac ($T_{1/2} = 9.9$ d). First, we prepared an $^{225}\text{Ac}/^{221}\text{Fr}$ generator. 4 MBq of ^{225}Ac was dissolved in 1 mL of 0.01 M HNO_3 . It was loaded onto an LN resin column (100–150 μm ; $\varphi 5 \text{ mm} \times \text{H}10 \text{ mm}$). ^{225}Ac was adsorbed on the LN resin, and its daughter nuclide ^{221}Fr was generated inside the column. ^{221}Fr was repetitively eluted with 0.5 mL of 0.01 M HNO_3 after its growth. The yield of ^{221}Fr was $\geq 98\%$ with one-time elution. 500 Bq of ^{137}Cs dissolved in 5 μL of H_2O was added into the ^{221}Fr solution. The solution was dried up, following which ^{221}Fr and ^{137}Cs were dissolved in 1.4 mL of 10^{-4} –3 M NaNO_3 aqueous solutions to achieve ^{221}Fr and ^{137}Cs concentrations of $\sim 10^{-13}$ – 10^{-12} M and $\sim 10^{-10}$ M, respectively. 700 μL of this aqueous solution was shaken for 5 min together with an equal volume of an organic phase, 1.5×10^{-3} M BC6B in 1,2-dichloroethane. After centrifugation, 500 μL of each phase was subjected to γ -ray spectrometry with Ge detectors to determine the D values as $D = [\text{M}^+]_{\text{organic}}/[\text{M}^+]_{\text{aqueous}}$, where M denotes ^{221}Fr or ^{137}Cs . We also investigated the D values of Cs under almost the same experimental condition as Haverlock *et al.*²⁾ by dissolving ^{221}Fr and ^{137}Cs with 10^{-4} –3 M $\text{NaNO}_3/10^{-4}$ M CsNO_3 aqueous solutions.

The time required for Fr and Cs to reach extraction equilibrium was confirmed to be less than 1 min, which agrees with the results of Haverlock *et al.*²⁾ Fig-

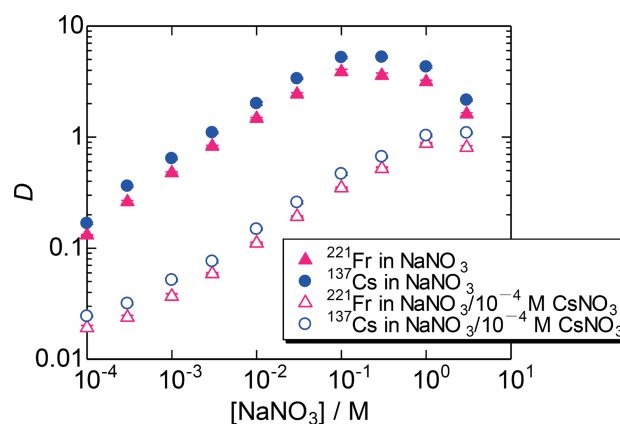


Fig. 1. Variation of D values of Fr and Cs as a function of NaNO_3 concentration $[\text{NaNO}_3]$ in their extraction from 10^{-4} –3 M NaNO_3 and 10^{-4} –3 M $\text{NaNO}_3/10^{-4}$ M CsNO_3 aqueous solutions into 1.5×10^{-3} M BC6B in 1,2-dichloroethane.

ure 1 shows the D values of Fr and Cs as a function of NaNO_3 concentration. Closed symbols indicate the D values from the 10^{-4} –3 M NaNO_3 aqueous solutions, and open ones indicate those from 10^{-4} –3 M $\text{NaNO}_3/10^{-4}$ M CsNO_3 aqueous solutions. The D values of Fr and Cs are comparable in both the solutions, although the D values of Cs are slightly higher than those of Fr. These results are reasonable when considering the similar ionic radii of Fr and Cs and our previous results obtained using crown ethers.¹⁾ In the 10^{-4} –3 M $\text{NaNO}_3/10^{-4}$ M CsNO_3 aqueous solutions, however, the D values of both Fr and Cs are smaller by factors of 2 to 14 than those in the 10^{-4} –3 M NaNO_3 aqueous solutions. This might be because macro amounts of Cs (10^{-4} M) inhibit the extraction of Fr and Cs, although an excess amount of BC6B exists in the extraction system (the concentration ratio of $[\text{Cs}]:[\text{BC6B}] = 1:15$). Note that our D values of Fr from 10^{-4} –3 M NaNO_3 aqueous solutions and those of Cs from 10^{-4} –3 M $\text{NaNO}_3/10^{-4}$ M CsNO_3 aqueous solutions are consistent with those reported by Haverlock *et al.*²⁾ Because Haverlock *et al.*²⁾ independently obtained the D values of Fr and Cs using the ^{221}Fr tracer and 10^{-4} M CsNO_3 , respectively, the large difference between the D values of Fr and Cs was observed.

The slightly higher D values of Cs than those of Fr using BC6B are similar to those using DB21C7.¹⁾ The reason of the order of the D values of $\text{Cs} > \text{Fr}$ in the extraction with BC6B and DB21C7 is unclear at this moment. Quantum chemistry calculations for Fr as well as Cs are needed to interpret the experimental results and to discuss the electronic state and chemical bonding nature of Fr.

References

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