

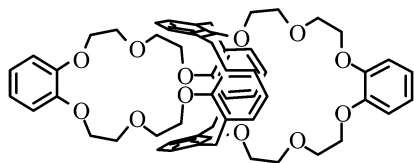
Selectivity of Calix[4]arene-bis(benzocrown-6) in the Complexation and Transport of Francium Ion

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Toward elucidating selectivity in alkali metal binding and transport, we report herein for the first time the binding and extraction of Fr^+ by a representative member of the “cesium-selective” calix[4]arene-crown-6 family. Although the short half-lives of all of its isotopes ($t_{1/2} \leq 22$ min) have made francium one of the least studied among the naturally occurring elements, interest in it has recently intensified. From the theoretical point of view, francium is a gateway to understanding heavy elements, a gateway recently thrust open by advances in computational methods, isotope-production techniques, and spectroscopy via atomic laser trapping.¹ Better theory has encouraged attempts to forecast both electronic^{1a,2a} and chemical² properties of superheavy elements such as eka-francium, element 119. In this regard, relativistic effects come into play, even for francium.^{1a,b,e} Indeed, properties such as electron affinities^{1a} and van der Waals coefficients^{1b,e} do not extrapolate from the smaller alkali metals to francium, raising questions concerning the reliability of classical empirical estimates of thermodynamic properties extended to the heavy elements. In that little thermodynamic data in fact exist for francium,³ investigations of its chemical behavior may thus be timely. Accordingly, the question has arisen^{3b} as to how the complexation behavior of alkali metal cations might extend to Fr^+ . Binding of alkali metal cations tends to be weak, but calix[4]arene mono- and biscrown-6 compounds, well known for their highly selective and relatively strong binding of Cs^+ ,⁴ afford an excellent opportunity to explore this question. Rewards for doing so may ultimately be found in potential applications in separations of Fr^+ for synthesis of radiopharmaceuticals,⁵ removal of Cs^+ from nuclear waste,⁶ and models for environmental and biological behavior of metals at extreme dilution.^{2a,7} With regard to the radiopharmaceuticals, potential routes to highly pure ^{213}Bi entail the selective extraction of ^{221}Fr from ^{225}Ac (a decay product of ^{233}U) and subsequent decay of ^{221}Fr to ^{213}Bi . A potent α emitter, the latter is a potential anti-cancer agent when bound to appropriate antibodies.⁵



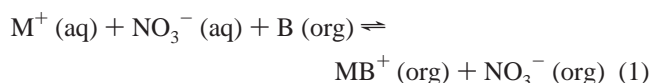
BC6B

As a first step in addressing the above question, initial experiments were conducted to compare the extraction of Fr^+ and Cs^+ by calix[4]arene-bis(benzocrown-6) (BC6B) in 1,2-DCE. In particular, it is of interest whether the peak selectivity for binding of alkali metal ions by “cesium-selective” calix[4]arene-crown-6 hosts

actually lies with Cs^+ or with a heavier element in the group. The diluent 1,2-DCE has proven particularly useful in producing simple behavior in the extraction of alkali metal salts by crown ethers and calixcrowns,⁸ including the alkylated analogue of BC6B, calix[4]arene-bis(*tert*-octylbenzocrown-6).^{8b} All experiments employed 1.5 mM BC6B in distilled 1,2-DCE to extract trace Fr^+ or Cs^+ individually from an equal volume of a pH-neutral aqueous phase containing from 5×10^{-4} to 5.0 M NaNO_3 . Metal ion concentrations were measured radiometrically, and distribution ratios ($D_M = [\text{M}^+]_{\text{organic}}/[\text{M}^+]_{\text{aqueous}}$) were calculated as the ratio of the volumetric count rates of the radioisotope in each phase.⁹ Under the conditions used, Na^+ was expected to be extracted feebly,¹⁰ which was confirmed using ^{22}Na radiotracer ($D_{\text{Na}} < 2 \times 10^{-4}$). Because of its short half-life ($t_{1/2} = 4.8$ min), ^{221}Fr was generated in situ ($[\text{Fr}^+]_{\text{aq,initial}} \approx 1 \times 10^{-13}$ M) from the decay of its parent, ^{225}Ac ($t_{1/2} = 10$ days).¹¹ Extraction contacting was carried out quickly by vortexing 1 mL volumes of organic and aqueous phases together under ambient (22 ± 1 °C) conditions with subsequent centrifugation.¹¹ Cesium extractions were carried out by similar techniques at 25 ± 0.5 °C with aqueous NaNO_3 solutions containing 1×10^{-4} M CsNO_3 .¹²

As can be seen from Figure 1, francium is effectively extracted by the calixcrown. Given that the parent ^{225}Ac and matrix Na^+ ions are scarcely extracted, the experiment demonstrates a clean separation of francium. As alkali metal salts are readily stripped in such systems,¹⁰ an aqueous solution of purified francium may thus be obtained by extract-strip cycles or by configuring the system as a liquid membrane.

Toward understanding the complexation of Fr^+ by the calix-crown, one may compare its extraction curve with that of Cs^+ . Both extraction curves shown in Figure 1 exhibit an ascending linear region with a slope of approximately 0.5 followed by a maximum. On the basis of the previous mass-action analysis^{8b} of CsNO_3 extraction by the alkylated derivative calix[4]arene-bis(*tert*-octylbenzocrown-6) with the least-squares equilibrium modeling program SXLSQI,¹³ the following simple 1:1 equilibrium may be expected to account for the observed behavior at the minor loading of the calixarene:



where B is the calixarene, and M^+ is a univalent metal ion. The cesium extraction data could be fit by SXLSQI modeling based on eq 1 (where M^+ is Cs^+) only and the same system parameters reported earlier.^{8b} The best fit, as shown in Figure 1, was obtained with $\log K_{\text{ex}\pm} = -0.99 \pm 0.03$. This value is comparable to that reported for calix[4]arene-bis(*tert*-octylbenzocrown-6) ($\log K_{\text{ex}\pm} = -0.92 \pm 0.03$), in accordance with the small effect of alkylation of the benzo group observed in survey experiments.¹⁰ Examination

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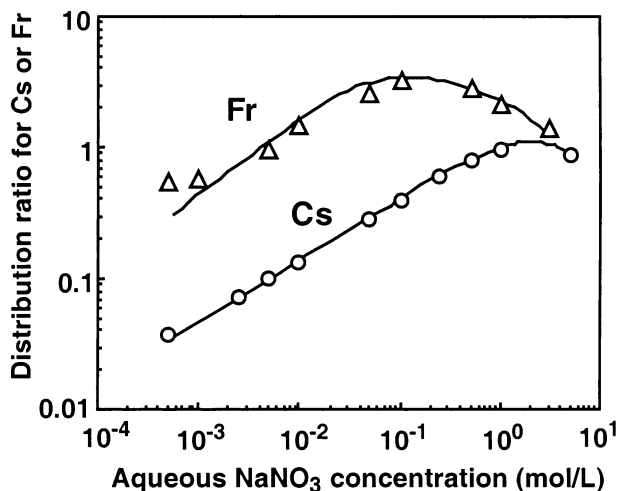


Figure 1. Distribution of Fr^+ and Cs^+ between aqueous NaNO_3 solution and 1,2-DCE containing 1.5 mM BC6B. The solid lines represent the fits calculated by the modeling program SXLSQI.

of the aqueous ionic activity coefficients calculated from SXLSQI using the Pitzer treatment¹⁴ showed that the maximum in the curve owes its origin to the rapidly decreasing mean activity coefficient for CsNO_3 above 1 M NaNO_3 . As Na^+ extraction is weak, its competing effect is negligible and does not have to be included in the model for a good fit in the case of cesium.

Modeling results indicate that the extraction of Fr^+ from the NaNO_3 matrix as shown in Figure 1 probably occurs by eq 1 also (where M^+ is Fr^+) but is complicated by additional factors. Because Pitzer parameters are not available for FrNO_3 , a minor extrapolation of those reported¹⁴ for the lower alkali metal nitrates versus the reciprocal cationic radii was used ($\beta_0 = -0.08$ and $\beta_1 = -0.14$). From these estimates, activity effects for FrNO_3 were found unlikely to produce the maximum seen in the francium curve. Rather, the observed behavior was readily reproduced mathematically (solid curve in Figure 1) by assuming that a weak competing equilibrium of the form of eq 1 occurs, with M^+ being Na^+ or another metal ion. According to such a model, the maximum observed is primarily due to the coupling of the two equilibria via the common organic phase nitrate ion. As the nitrate concentration in the organic phase increases with increasing aqueous NaNO_3 concentration, the Fr^+ extraction is thus suppressed by mass action. Even weak extraction of the competing cation can cause this effect, because of the exceedingly low concentration of Fr^+ . Although Na^+ would appear to be the obvious cation in the competing equilibrium, actual involvement of Na^+ could not be verified, because of the high correlation coefficient (0.91) between the two fitted $\log K_{\text{ex}\pm}$ values, as well as because of the fact that the extraction of NaNO_3 itself was too feeble to measure independently. Further work is in progress to arrive at a definitive result that will not only resolve the matter of the equilibrium mechanism but will also resolve the peak selectivity on the basis of the $\log K_{\text{ex}\pm}$ values for Fr^+ and Cs^+ . The present results provide an initial understanding of the Fr^+ extraction behavior and open up the possibility to selectively separate this ion for such applications as the synthesis of ^{213}Bi radiopharmaceuticals.

Acknowledgment. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, and the

Division of Nuclear Energy, Isotope Production, and Distribution Program, U. S. Department of Energy, under contract number DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

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- (9) The ^{137}Cs ($^{137\text{m}}\text{Ba}$ daughter) and ^{22}Na radioactivities were measured with a through-hole type $\text{NaI}(\text{Tl})$ γ -ray detector. A calibrated Ge γ -ray detector coupled to a multichannel analyzer was used for ^{221}Fr (218 keV) activity measurements. Taking into account all sources of error, we estimated the precision of distribution ratios D_M to be $\pm 5\%$ for ^{137}Cs and $\pm 10\%$ for ^{221}Fr . Caution: These radioisotopes represent a radiological hazard and must be handled accordingly.
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- (11) The ^{225}Ac was initially separated from ^{225}Ra by ion exchange and extraction chromatography as described in ref 5b. Stock solutions of purified ^{225}Ac were prepared in 1×10^{-4} M HNO_3 and stored in polypropylene vials. ^{225}Ac activity was quantified by measurement of ^{221}Fr daughter activity at secular equilibrium with the parent. In the ^{221}Fr extraction experiments, $<1\%$ of the ^{225}Ac was found to be coextracted. For a typical extraction, 1 mL of aqueous solution containing 10–20 μL of ^{225}Ac ($\sim 15 \mu\text{Ci}$) was contacted with 1 mL of organic phase for 1 min employing a laboratory Vortex mixer. Kinetics studies with ^{137}Cs showed this to be sufficient time for equilibrium to be reached. The activity of ^{221}Fr at the end of mixing (A^0) was then determined by first-order extrapolation from successive 1 min counts. The secular-equilibrium value of ^{221}Fr activity (A^*) was obtained by measuring the ^{221}Fr radioactivity in the aqueous phase 1 h later.
- (12) The difference in temperature was considered acceptable and not injurious to the conclusions of this work.
- (13) The program SXLSQI is available at the web site <http://www.ornl.gov/csg>. Its use is described in: Baes, C. F., Jr. "SXLSQI, A Program for Modelling Solvent Extraction Systems," Report ORNL/TM-13604, Oak Ridge National Laboratory, Oak Ridge, TN, Dec. 7, 1998. The physical chemistry used in the program is described in: Baes, C. F., Jr. *Solvent Extr. Ion Exch.* **2001**, *19*, 193–213. Examples of its use are given in ref 8.
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JA0255251