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## EVALUATION OF FACTORS AFFECTING CESIUM EXTRACTION PERFORMANCE BY CALIX[4]ARENE DERIVATIVES

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### ABSTRACT

Novel aza-crown derivatives of dioctyloxy-calix[4]arene crown-6 were examined for their cesium extraction performance at different pH levels. These studies are of interest in addressing high-level waste tank remediation and the removal of  $^{137}\text{Cs}$ , a major contributor to heat and radiation generation. Preliminary studies were done to assess the performance of these calixarene compounds under varying conditions. Results showed an increase of cesium extraction with pH as well as expected trends in diluent effects and anion selectivity. Poor extraction performance of some aza-crown derivatives raised questions regarding the possibility of intramolecular hydrogen-bonding. A novel methylated derivative was used to address these questions. Additional experiments were conducted to determine the extraction effect on pH. Results indicate an increase in cesium extraction with pH, as shown in preliminary studies. Mono-aza derivatives were shown to exhibit better cesium extraction performance than their di-aza counterparts. The methylated derivative showed poorer extraction performance than the non-methylated derivative, indicating that completely removing the possibility of intramolecular hydrogen-bonding has negative effects on extraction performance. This suggests that the hydrogen-bonding facilitates anion co-extraction, which would lead to better overall extraction. Mono-aza derivatives were shown to cause unexpected changes in pH. This could possibly be attributed to protonation of the calix crown.

### INTRODUCTION

Seven aza-crown derivatives of dioctyloxy-calix[4]arene were evaluated for their cesium extraction performance in the interest of addressing high-level tank waste belonging to the Department of Energy. Since  $^{137}\text{Cs}$  is a major contributor to heat and radiation generation in these waste tanks, methods for extracting it are of significant interest [1-2]. In the most basic sense, this means developing a compound, often referred to as an extractant, that will bind  $^{137}\text{Cs}$  and pull it out of the mixture in the waste tanks using solvent extraction. The idea is that the extractant, once dissolved in an organic solvent, can be contacted with the aqueous tank waste, at which time the extractant binds the cesium and pulls the ion pair (an anion is co-extracted to ensure the electroneutrality of the organic phase) into the organic phase. By removing  $^{137}\text{Cs}$  from the high-level waste tanks, the heat and radiation output of the tanks is reduced, and the radiation source is in a more easily controlled environment.

Additionally, the remaining tank waste could be re-classified and the cost of processing it would be reduced. An ideal extractant would need to be highly selective over competing cations like sodium and potassium, which are present in these tanks in much greater proportions than cesium [3].

Dioctyloxy-calix[4]arene crown-6 has been shown to effectively extract cesium from solution and is known to be selective over sodium, the major competing cation in the matrices in question [4-7]. Aza-crown derivatives of dioctyloxy-calix[4]arene crown-6 were then developed in order to further investigate anion recognition issues. Preliminary studies assessed the extraction performance of two unsubstituted di-aza compounds as well as two di-aza compounds with functional arms attached to the nitrogen atom in the crown.

These four compounds were incorporated into the continued study as a means of comparison, and three new aza-crown derivatives were also studied. These new derivatives, shown in Figure 1, consist of substituted and unsubstituted mono-

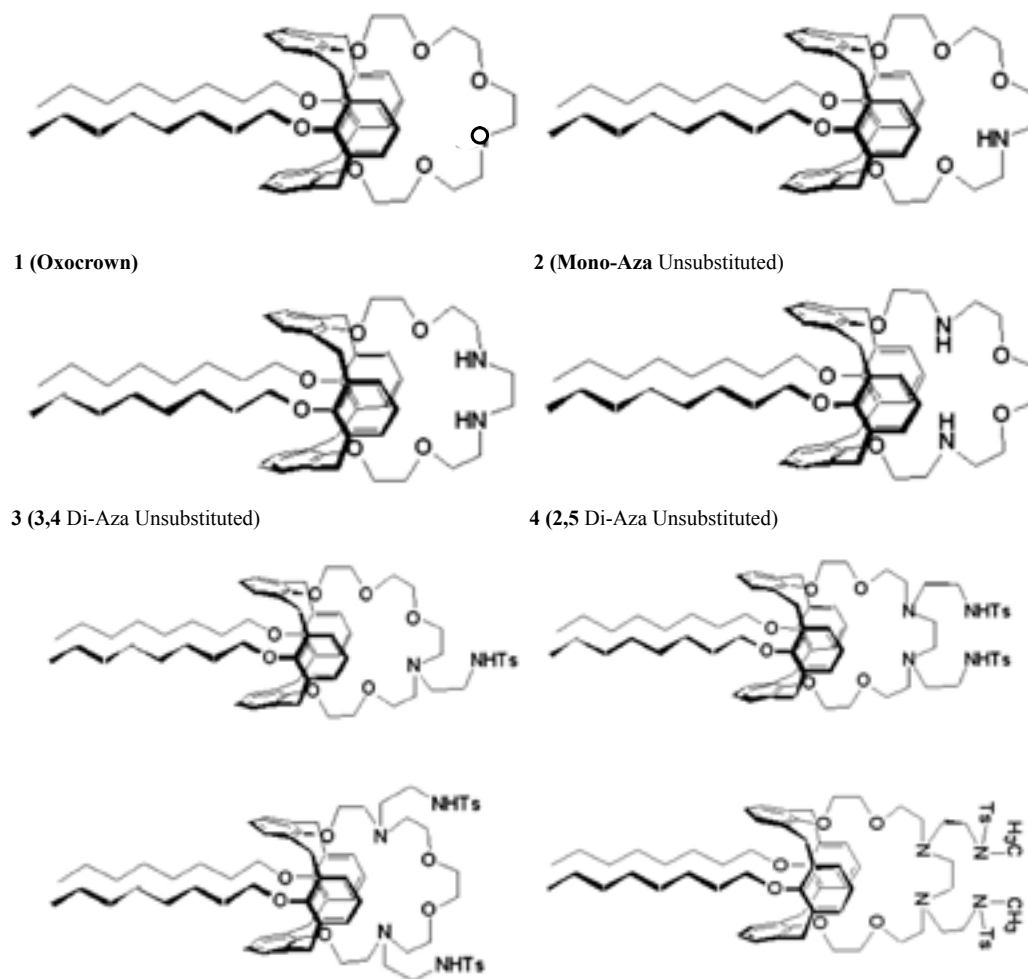


Figure 1. Calix[4]arene compounds studied.

aza compounds (5 and 2 respectively) and a di-aza derivative substituted with functional arms designed to prevent intra-molecular hydrogen-bonding (8).

All compounds were assessed for their extraction performance as related to pH. A select group was used in a study of pH changes brought about by extraction.

## EXPERIMENTAL

### Materials

Sodium nitrate (99.0% purity) was obtained from EM Science. Cesium nitrate (99.0% purity) and sodium perchlorate (99.0% purity) were both obtained from Aldrich Chemical Company, Inc. All salts were used as purchased without further modification. All aqueous solutions were prepared using distilled deionized water obtained from a Barnstead Nanopure filtering system (resistivity: 18 MΩ · cm). Diocetyloxy-calix[4]arene crown-6 and all aza-crown derivatives were synthesized in-house. 1,2-dichloroethane, obtained from EM Science as an Omnisolv® solvent (99.98%), was used to

prepare all organic solutions. <sup>137</sup>Cs was used as the radio-tracer in all extraction experiments and was obtained from Isotope Products, Burbank, California.

### Extraction

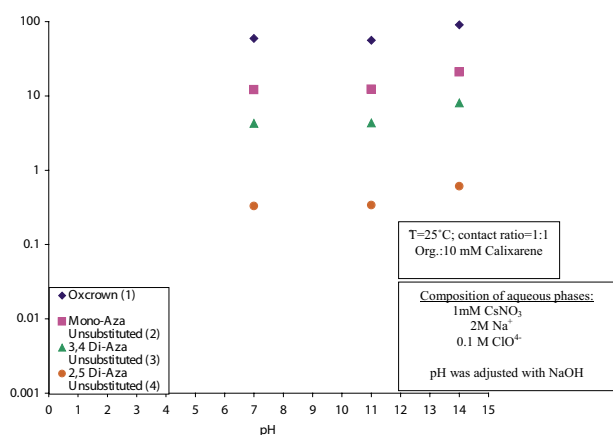
All extraction experiments were carried out in 2 mL polypropylene vials. All samples were prepared in a 1:1 (0.75 mL: 0.75 mL or 0.5 mL:0.5 mL) aqueous: organic ratio. In order to obtain a reliable concentration of calixarene in the organic phase, 1,2-dichloroethane was used as the partitioning solvent. Due to its volatility, it would not be a suitable solvent for large-scale extraction from nuclear waste. Cesium concentration in the initial aqueous phase was controlled with <sup>133</sup>Cs, and <sup>137</sup>Cs was used as a radiotracer. The radioisotope was introduced by adding 4 μL spikes of <sup>137</sup>CsCl to the prepared samples. All samples were prepared in duplicate except for 6 and some samples of 4 and 7.

Sample vials were sealed, and phase interaction was induced by vertical rotation for one hour at 25°C on a Glascol® laboratory rotator and then centrifuged for 5 minutes at 3000 RPM using a Beckman Coulter Allegra™ 6R Centrifuge.

<sup>137</sup>Cs was used as the radiotracer, and extraction data was obtained using a Packard® Colora Quantum Model 5003 gamma counter with 3-inch NaI crystal detector. The distribution ratio for cesium,  $D = [Cs]_{org} / [Cs]_{aq}$ , was used to measure extraction efficiency.

### pH Measurements

All pH measurements were made using an Orion pH meter Model 230A, an Orion 8103 Ross combination pH electrode, a ThermoOrion Micro-Combination pH/sodium electrode Model 9802, and a ThermoOrion Micro-Combination pH/sodium electrode Model 9810. A two-point calibration was performed, using buffers at pH 4.01 and pH 10.01. A pH 7.00 buffer was used to check the accuracy of the calibration. Slope following calibration ranged from 93.0 to 95.7. Electrodes were checked for drift between each measurement.



**Figure 2.** Cesium extraction performance of unsubstituted aza-crowns (1,2,3, and 4) as a function of pH.

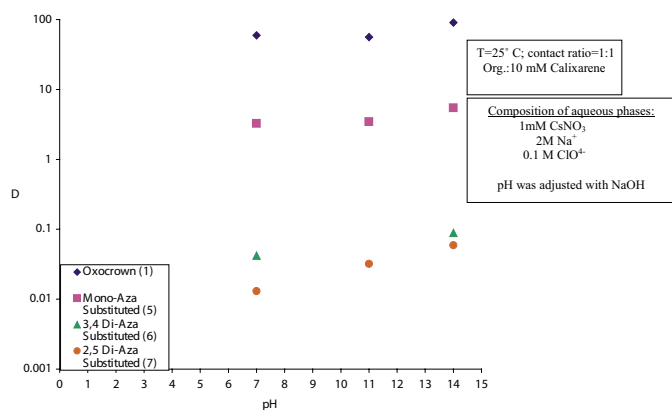
## RESULTS

### Cesium Extraction Survey

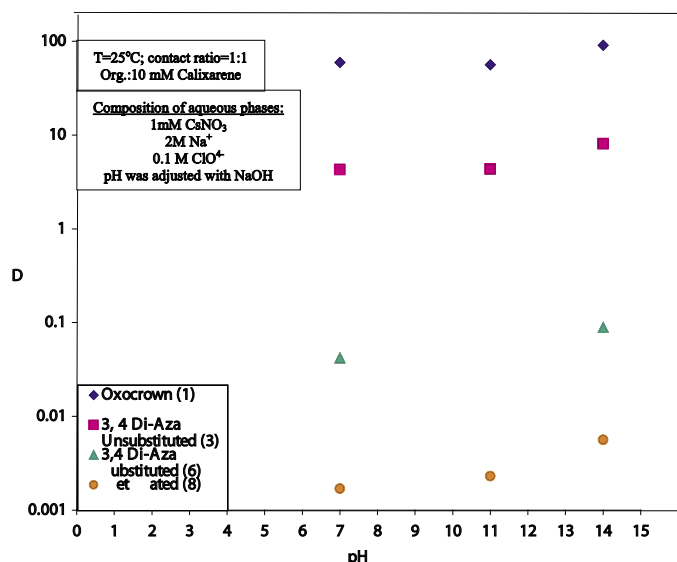
A survey was designed to obtain information about the extraction performance of the oxocrown (1) and the seven aza-crown derivatives at neutral pH as well as mild and highly basic pH. The survey was also expected to provide a basis for comparison to preliminary studies and to identify compounds for future study.

Several trends emerged as a result of the survey, as can be seen in Figure 2, 3, and 4. The mono-aza derivatives (2 and 5) have higher distribution ratios than comparable di-aza derivatives (3 and 6). Di-Aza derivatives with nitrogen substituted for oxygen at the 3 and 4 positions in the crown were shown to be better extractants than the 2,5 di-aza derivatives at every pH level as shown in Figures 2 and 3. The free base derivatives (2,3, and 4) perform better than the substituted alternatives (5,6, and 7 respectively), as can be seen in Figure 2 and Figure 3.

Compound 8 was designed to gain insight into the possible effects of intramolecular hydrogen bonding in the substituted derivatives (5,6, and 7). Its performance is best put into per-



**Figure 3.** Cesium extraction performance of substituted aza-crowns (1,5, 6, and 7) as a function of pH.



**Figure 4.** Effects of substitution and hydrogen-bonding capability (1,3, 6, and 8) on cesium extraction performance as a function of pH.

spective when compared to the performance of 6, as both are substituted 3,4 di-aza compounds. The methylated derivative (8) has an extraction efficiency 16-25 times lower than that of 6.

### pH Experiment

The goal of this experiment was to learn more about pH changes caused by 2 and 8 upon extraction. Compound 1 is used as a control. Information about pH changes could then provide useful information about which form of the free-base derivative (2) participates in extraction. Results are shown in Figure 5.

All samples were prepared in duplicate in a 2:1 (aqueous: organic) ratio. In order to obtain a sample volume large enough to yield reliable data, the second equivalent of the aqueous phase was needed. The pH of the aqueous phase was measured before and after contact.

At pH 1.70, the unsubstituted mono-aza derivative (2) shows a slight but significant increase in pH. It exhibits larger increases in pH when contacted with solutions that are initially slightly acidic, neutral, or slightly basic. It shows a slight decrease when the initial pH is approximately 8.50.

The oxocrown (1) showed no appreciable change in pH at levels of high acidity. It showed slight decreases in the slightly acidic to neutral range. Even smaller decreases were shown at low basicity.

The methylated derivative (8) shows little to no change in pH except for small decreases in the slightly acidic to neutral range.

### Extraction as Affected by pH

The unsubstituted mono-aza derivative (2) and the unsubstituted 3,4 di-aza derivative (3) were used in this study of

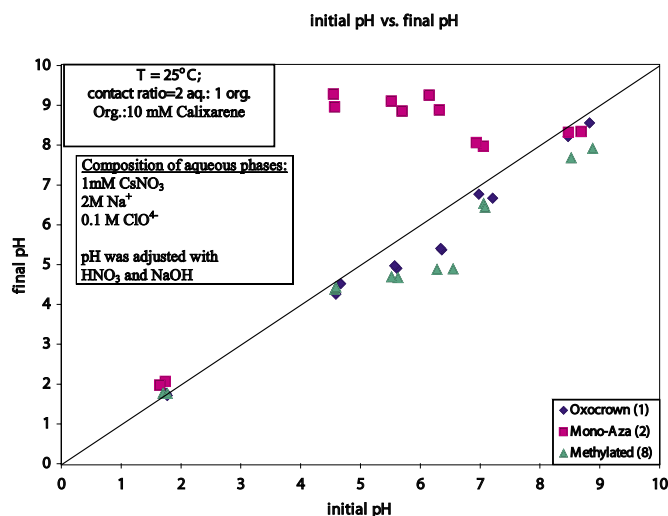


Figure 5. Changes in pH due to extraction with 1, 2, and 8

extraction performance over a broader pH range than in the pH survey.

As shown in Figure 6, both derivatives exhibit poor extraction performance at high acidity. A white solid was observed at the interface in the unsubstituted 3,4 di-aza (3) samples.

All D values were fairly constant from mild acidity through mild basicity.

Both compounds show slight increases in extraction performance at levels of high basicity.

## DISCUSSION

### Cesium Extraction Survey

The driving force behind the aza-crown research is the idea that placing nitrogen in the crown allows for the attachment of functional arms, an addition that cannot be made to the oxocrown (1). However, the trends previously described indicate that extraction performance decreases every time oxy-

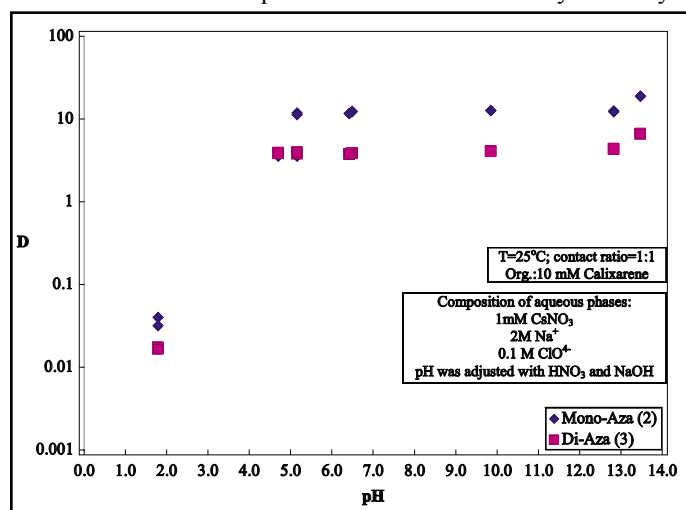


Figure 6. Extraction performance of mono-aza and 3,4-di-aza derivatives (2 and 3) over a broad pH range.

gen in the crown is replaced by nitrogen. One might consider replacing the oxygen atom in the crown with sulfur, but this substitution would make the addition of functional arms less favorable. Additionally, sulfur would bind the cesium less tightly than oxygen, which would suggest that a thiocrown derivative would have a poorer extraction efficiency than the oxocrown.

The functional arms attached to the crown, as seen in Compounds 5, 6, and 7, were introduced to facilitate anion binding. The idea was that these groups could be functionalized to hold onto anions via hydrogen bonding and balance out the charge distribution; this would then theoretically result in better extraction performance. However, extraction performance in these compounds is noticeably lower than in the unsubstituted derivatives. One explanation for this is intramolecular hydrogen bonding of the functional arm, making the lone pair on the nitrogen present in the crown unavailable for cesium binding.

To test this theory 8, which has no hydrogen-bonding capability, was synthesized and studied alongside its non-methylated predecessor (6). The extremely poor extraction performance of 8 suggests that the hydrogen-bonding capabilities of the functional arms is more important than preventing the formation of the 5-membered ring structure. This suggests that while some of the functional arms are hydrogen-bonded to the anion, others form intramolecular hydrogen bonds. This would explain why the substituted derivatives exhibit poorer extraction performance than the unsubstituted derivatives; there is some intramolecular hydrogen bonding. It would also explain why completely removing the possibility of hydrogen bonding so seriously reduces extraction performance; it is impossible for the anion to bind.

### pH experiment

The purpose of this experiment was to use knowledge of pH changes to monitor proton extraction and derive information about the form of the calix[4]arene that participates in extraction.

After taking the contact ratio into account, the changes in pH were used to calculate the total change in  $[H^+]$  in the aqueous phase. This change in concentration can then be divided by the known concentration of extractant in the organic phase. This ratio then shows approximately how many protons are moving into the organic phase per molecule of extractant present. As a control, plain 1,2-dichloroethane was contacted with solutions of pH 1.77 and pH 4.50. There was no appreciable change in pH, which indicates that any pH change in other samples is due to the extractant and not the diluent.

Slight increases in pH observed after 2 was contacted with a solution of pH 1.77 corresponds to the extraction of two protons per calixarene molecule. While this number may be overestimated, the observation supports the notion that protons are being extracted into the organic phase by the calix[4]arene. Larger increases at levels of low acidity also agree with the idea that the free-base derivatives will extract protons. When  $[H^+]$  is very low, the equilibrium pH is more sensitive to proton

extraction. It is important to note that there is no indication of calixarene deprotonation in this system. The slight shift noticed at pH greater than 7 can be due to carbon dioxide effects.

At levels of high acidity, the oxocrown and the methylated derivative show no changes in pH. Each compound shows slight decreases in pH when contacted with slightly acidic or neutral solutions. These changes are possibly due to traces of acid or base remaining after the synthetic workup of the calixarene.

#### *Extraction as Affected by pH*

The white solid observed in highly acidic samples of **3** suggest that at high [H<sup>+</sup>] the extractant becomes protonated and precipitates. While no precipitate was observed in **2** at this pH, the compound's poor extraction performance also supports the theory that the calixarene is protonated at low pH. When protonated, there would be an overall positive charge on the extractant. Under these conditions, electrostatic forces would then make the extraction of positively charged cesium unfavorable. This explains the poor extraction performance observed at low pH, as can be seen in Figure 6.

The relatively constant distribution ratios exhibited by **2** and **3** from pH 5 to pH 10 suggest that both **2** and **3** are in their neutral states.

The slight increases in extraction performance at high pH are not large enough to suggest deprotonation at high pH, and the changes are likely the result of activity effects.

#### CONCLUSION

While the extraction performance of dioctyloxy-calix[4]arene crown-6 is not matched by any of the aza-crown derivatives, considerable progress has been made toward the understanding of how various features of these derivatives affect cesium extraction performance.

Replacing even one oxygen in an oxocrown with nitrogen reduces the extraction performance, and replacing a second oxygen reduces the efficiency even more.

Questions regarding the hydrogen-bonding behavior of the functional arms in the substituted compounds have been resolved. The decrease in extraction performance following the addition of functional arms suggests that some intramolecular hydrogen bonds are forming. The further reduced efficiency of the methylated derivative (**8**) with no hydrogen-bonding capabilities, in turn, supports the idea that some of the functional arms bind anions as well.

It has also been established that the free-base derivatives are protonated at pH < 4 and neutral above that point.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- [1] Gerow, I.H., Davis, Jr., M.W. (1979). *Sep. Sci. Technol.*, 14, 395.
- [2] Shuler, R.G., Bowers, Jr., C.B., Smith, Jr., J.R., Van Brunt, V., Davis, Jr., M.W. (1985) *Solv. Extract. Ion Exch.*, 3, 567.
- [3] Moyer, B.A., Alexandratos, S.D., Bonnesen, P.V., Brown, G.M., Caton, Jr., J.R., Delmau, L. H., Duchemin, C.R., Haverlock, T.J., Levitskaia, T.G., Maskarinec, M.P., Sloop, Jr., F.V., Stine, C.L. (February 2002) "Caustic-Side Solvent Extraction Chemical and Physical Properties: Progress in FY 2000 and FY 2001," Report ORNL/TM-2001/285, Oak Ridge National Laboratory, Oak Ridge, TN.
- [4] Dozol, J.F.; Rouquette, H.; Ungaro, R.; Casnati, A. (1993) Calix[4]arènes-couronnes, leur procédé de préparation et leur utilisation pour l'extraction sélective du césium et des actinides. *Brevet français* n°93 04566 B11599.3/MDT.
- [5] Dozol, J.F.; Asafari, Z.; Hill, C.; Vincens, J. (1992) Calix[4]arènes-bis-couronnes, leur procédé de préparation et leur utilisation pour l'extraction sélective du césium et des actinides. *Brevet français* n°92 14245 B11385.3/MDT.
- [6] Dozol, J.F.; Böhmer, V.; McKervey, A.; Lopez Calahorra, F.; Reinhoudt, D.; Schwing, M.J.; Ungaro, R.; Wipff, G. (1995) New macrocyclic extractants for radioactive waste treatment : ionizable crown ethers and functionalized calixarenes. *Nucl. Sci. Tech.* Report EUR 17615.
- [7] Ungaro, R.; Casnati, A.; Ugozzoli, F.; Pochini, A.; Dozol, J-F.; Hill, C.; Rouquette, H. (1994) 1,3-Dialkoxy-calix[4]arene crowns-6 in 1,3-Alternate conformation: cesium-selective ligands that exploit cation-arene interactions. *Angew. Chem. Int. Ed. Engl.*, 33, 1506-1509.