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Project # 81936

Combined Extraction of Cesium, Strontium, and Actinides for Alkaline Media: An Extension of the Caustic-Side Solvent Extraction (CSSX) Process Technology

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Description of the Project

CSSX process selected as preferred technology by USDOE for separation of radioactive cesium from Savannah River Site salt wastes

Prior to the cesium extraction step, removal of strontium and actinides using MST

Development of selective molecules that extract strontium and actinides along with cesium by ***solvent extraction***. Combination of extractants or extractant with multi coordination sites

Relevance to EM Mission

Need to explore more efficient processes for the combined separation of cesium, strontium, and transuranic elements

Combined separation of the radionuclides from the wastes

Disposal of the treated waste as low level waste

Significant reduction of the volume of high level waste

Potential alternative to ***cesium*** extraction from ***Hanford wastes*** and ***actinide/strontium*** extraction from ***SRS*** wastes.

Relevance to EM Mission

Benefits: reduction in
- the number of operations
- the amount of secondary wastes
- the footprint of the process.

Combined extraction of cesium, strontium, and actinides is more appealing

- Removal of cesium and strontium from the high-level waste
  - uranium and transuranium elements are present in large enough quantities that the raffinate would still be transuranic waste (TRU).

- Actinides removed along with cesium and strontium
  - only one stream of HLW would then be generated
  - raffinate could be disposed as LLW

Goals

Obtaining fundamental information for the development of more efficient processes for the combined separation of cesium, strontium, and actinides

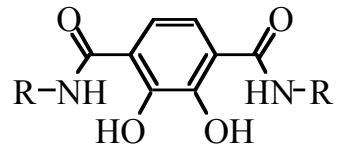
- Determine the best extractant(s) for strontium
- Determine the best extractant(s) for uranium, neptunium, and plutonium
- Determine the potential antagonistic effects of these ligands with BOBCalixC6
- Determine the feasibility of a "combined" process in 1 step or subsequent stages

Actinide Extraction

Experimental Section

- Extractants in 1-octanol at 10 mM
- Use of cetyl pyridinium bromide salt
- Aqueous phase: SRS simulant spiked with
  - $5x10^{-5}$ M ^{233}U
  - $5x10^{-6}$ M ^{237}Np
  - $5x10^{-6}$ M ^{239}Pu

Extractants



Terephthalamide (TAM)

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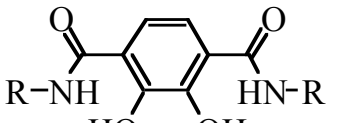
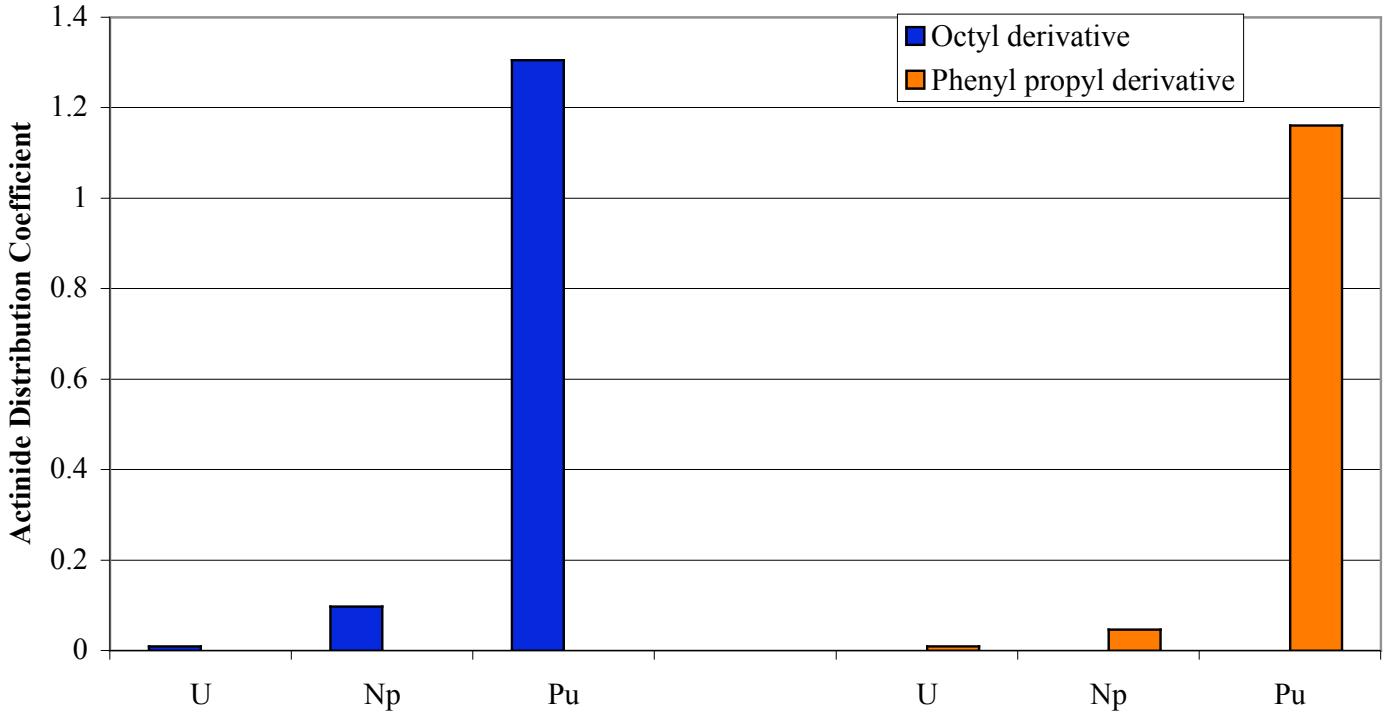
Actinide Extraction Results



Terephthalamide (TAM)

R = octyl or phenyl propyl



- **Promising extraction of plutonium**
- **Unexpected differences of behavior among the actinides**

Strontium Extraction

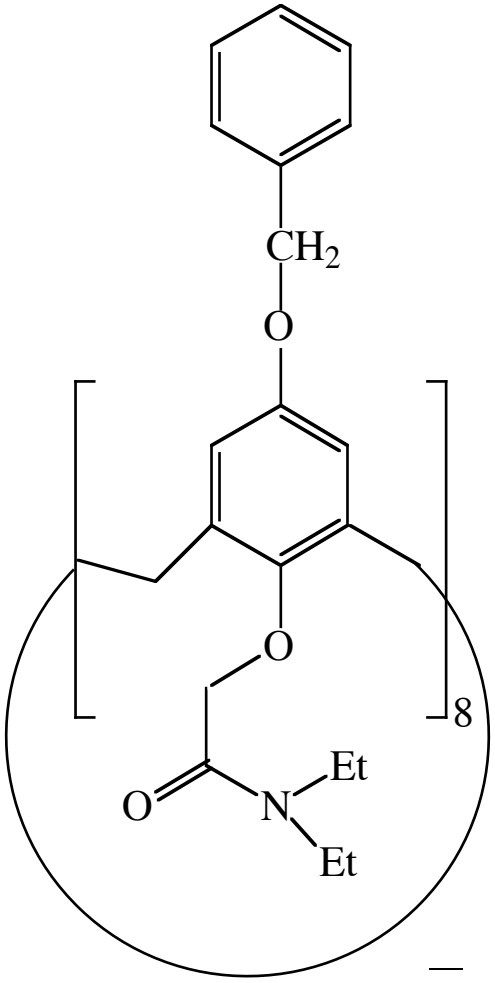
Strontium present in small quantities in the caustic wastes

Typically 10^{-6} - 10^{-5} M

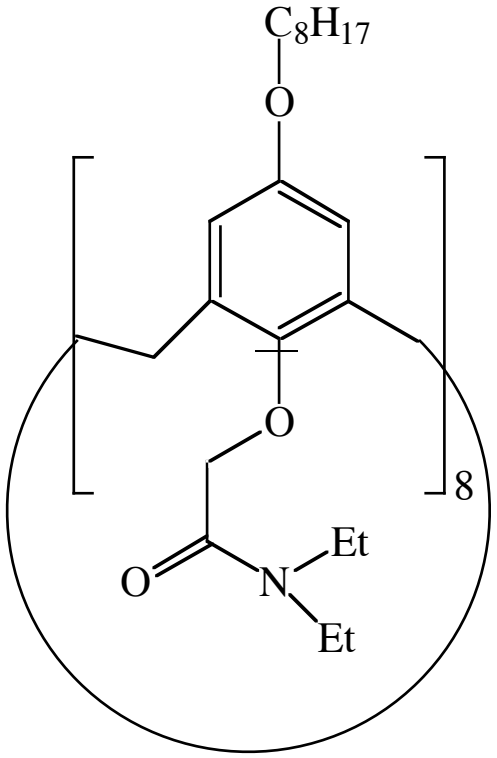
- Use of Monosodium titanate at SRS to remove Sr and An
- Solvent extraction: the reference is dicyclohexano 18-crown-6
- Used with TBP in the SREX process (extraction of Sr from acidic wastes)

- Studies developed in Europe on calixarenes showed promising strontium extraction results with calix[8]arenes. Acid/neutral side only.

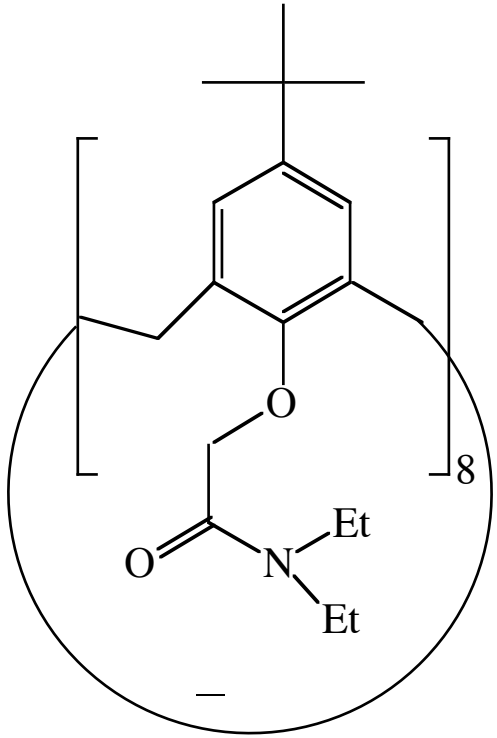
Presentation of Calix[8]arenes



C20

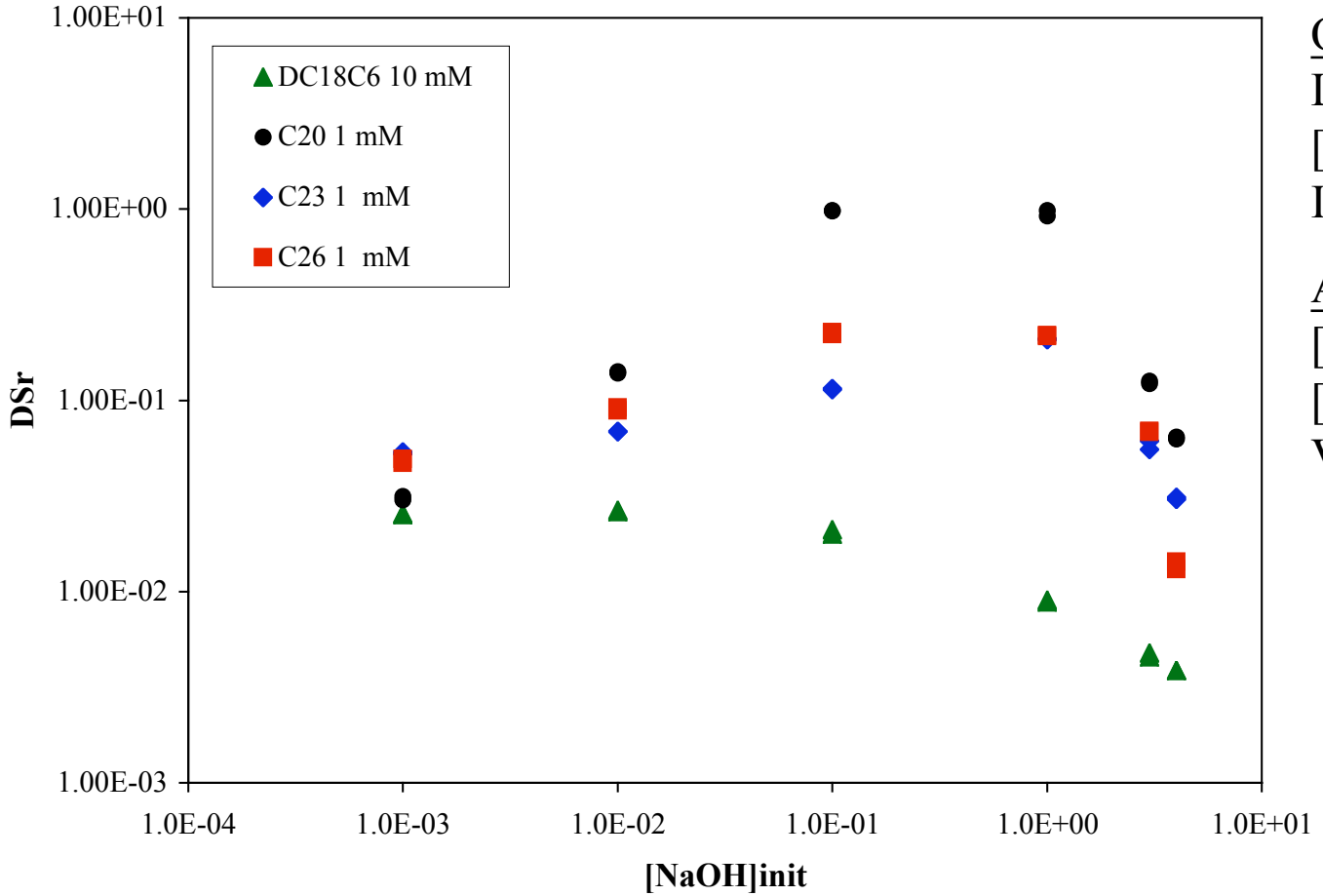


C23



C26

Survey Conditions and Results



Organic Phase:
Ligand
[Cs7-SB] = 0.75 M
In Isopar® L

Aqueous Phase:
$[NaNO_3]$ = 0.1 M
$[Sr(NO_3)_2]$ = 0.1 mM
Variable [NaOH]

Calix[8]arenes octaamides exhibit extraction powers 100-1000 times greater than DC18-crown-6 under the same alkaline conditions

Simulant Tests

Simulant of SRS wastes containing:
2 M $NaNO_3$, 3 M NaOH, $5x10^{-4}$ M $CsNO_3$, and 10^{-4} M $Sr(NO_3)_2$

Organic phase: CSSX solvent + C20 5 mM

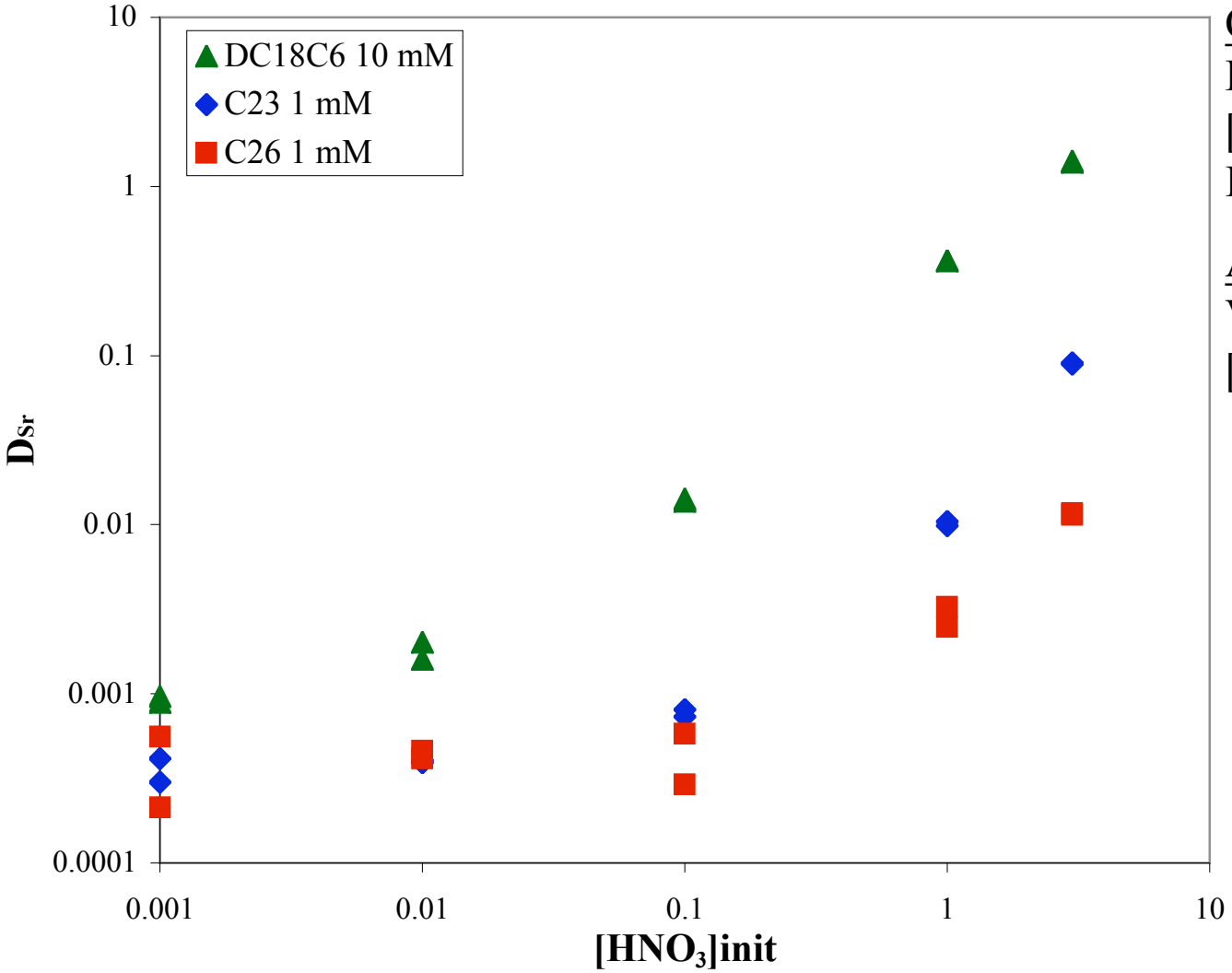
Third-phase formation, D_{Sr} = 0.1

Too soon !

Need more fundamental investigation

Upside: no activity in the third-phase
complete stripping
no extraction of Cs by calix[8]arene octaamide, no Sr extraction by BOBCalixC6

Strontium Extraction from HNO_3

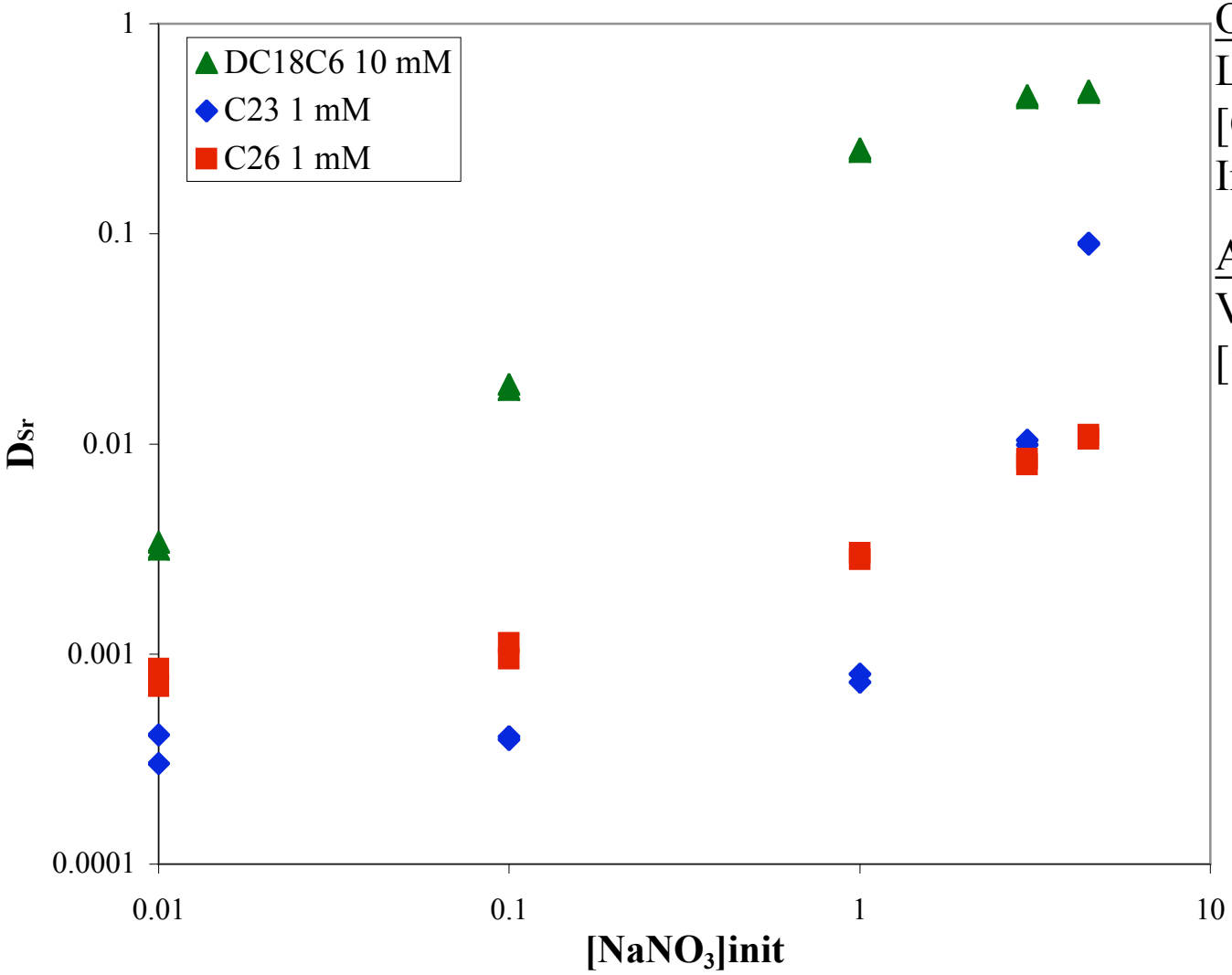


Organic Phase:
Ligand
[Cs7-SB] = 0.75 M
In Isopar® L

Aqueous Phase:
Variable $[HNO_3]$
$[Sr(NO_3)_2]$ = 0.1 mM

DC18C6 and calixes have a similar behavior. Upside: possibility to ***strip strontium***

Strontium Extraction from $NaNO_3$



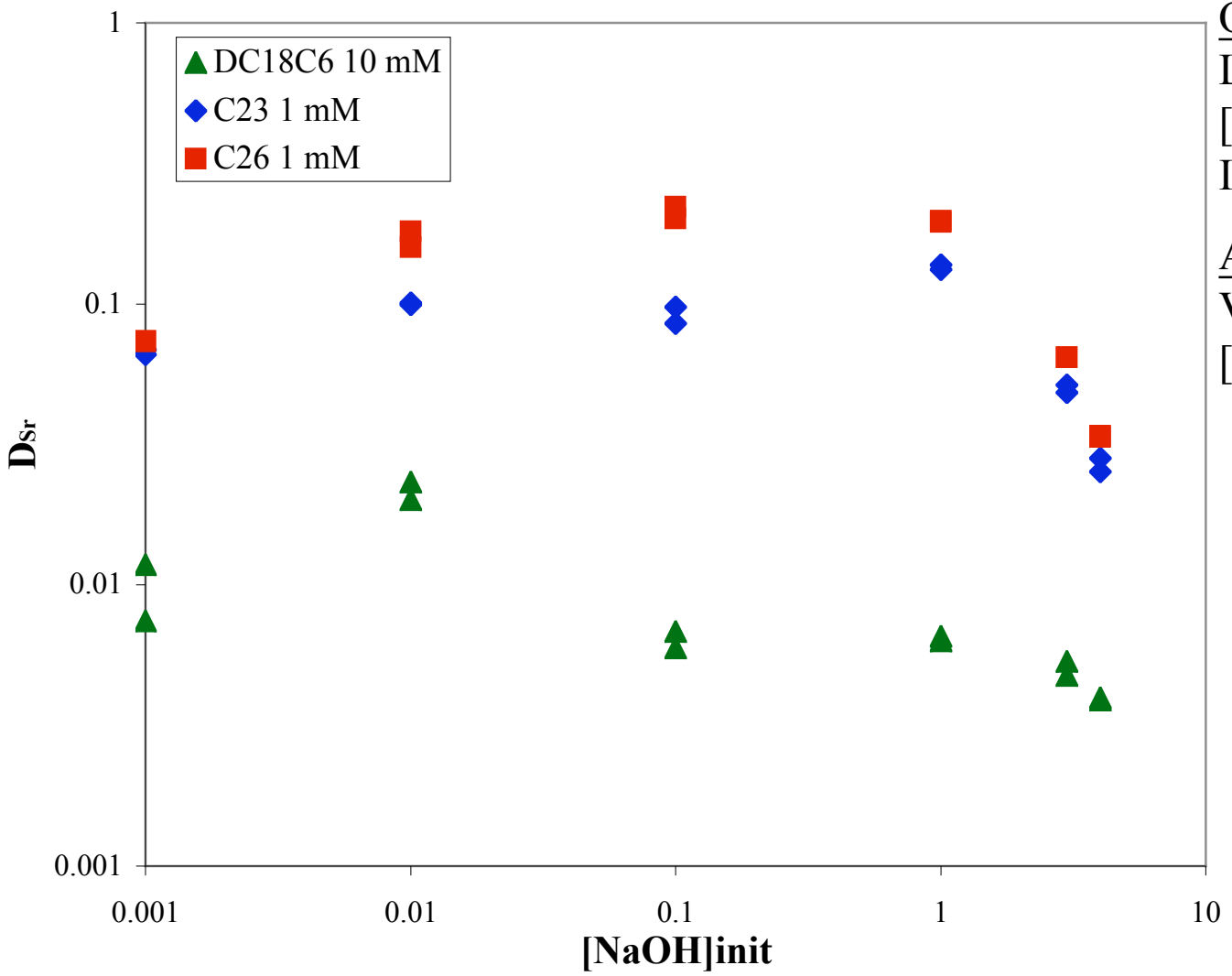
Organic Phase:
Ligand
[Cs7-SB] = 0.75 M
In Isopar® L

Aqueous Phase:
Variable $[NaNO_3]$
$[Sr(NO_3)_2]$ = 0.1 mM

Unexpected behavior based on the survey results.

DC18C6 appears to be a better than the calixes.

Strontium Extraction from NaOH

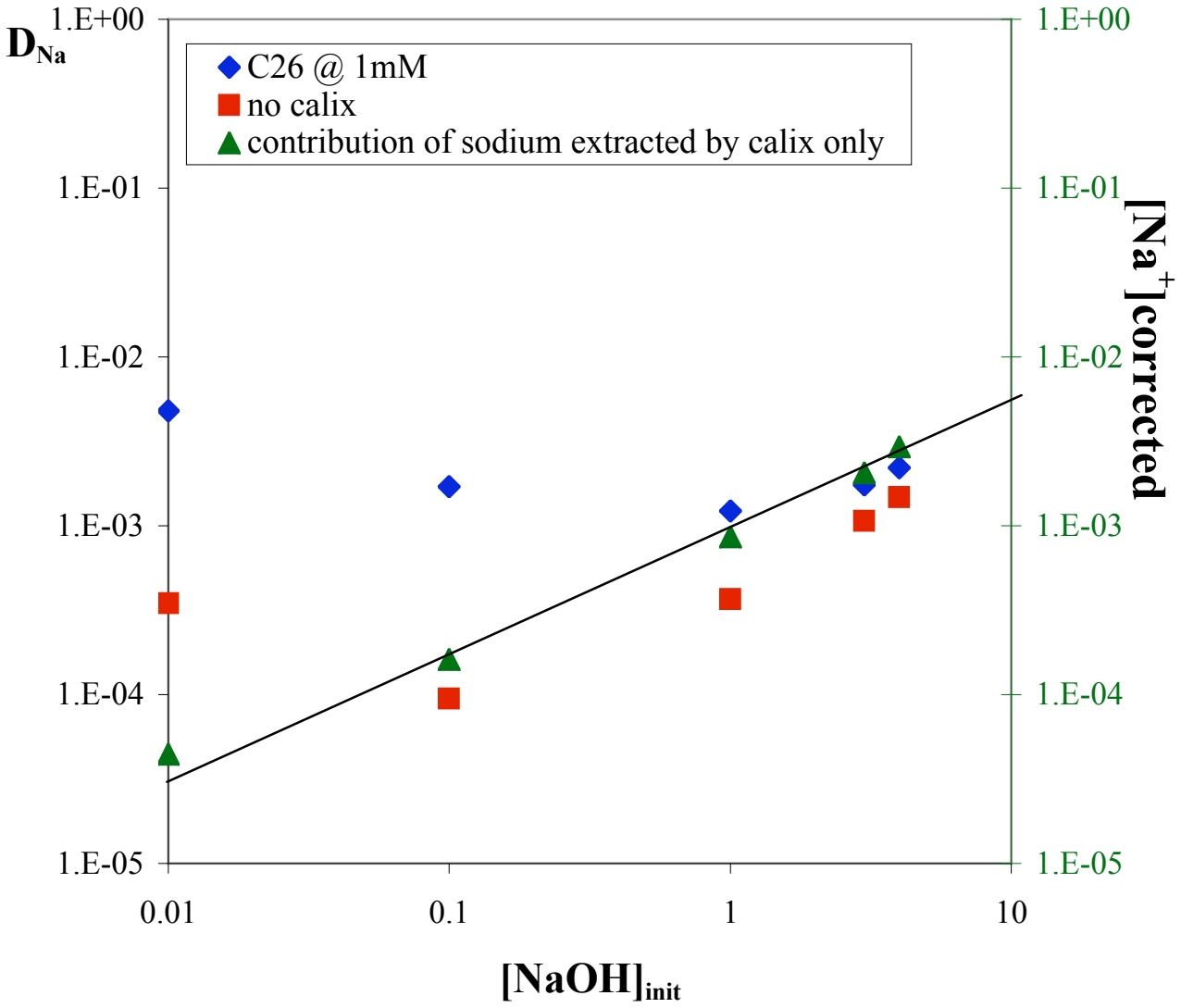


Organic Phase:
Ligand
[Cs7-SB] = 0.75 M
In Isopar® L

Aqueous Phase:
Variable [NaOH]
$[Sr(NO_3)_2]$ = 0.1 mM

Calixarenes are MUCH more effective than DC18C6 in caustic media

Steep Decrease of D_{Sr} at high [Na^+]



Organic Phase:
Ligand C26
[Cs7-SB] = 0.75 M
In Isopar® L

Aqueous Phase:
Variable [NaOH]
No strontium

Definite extraction of sodium by the system

2 Na^+ cations seem to be extracted by the calix C26 alone

No sign of saturation for sodium

Summary

Strontium extraction looks very promising.

- Establishment of an informal collaboration with Pr. Alessandro Casnati and Pr. Rocco Ungaro from the University of Parma
- Best calixarene (benzyloxycalix[8]octaamide) should be received mid-May (1g)
- Further interactions are expected: improvement of the structure of the calixarene
- Anticipated testing of small quantities of new calixarenes

Species Determination

Need to have an idea of the kinds of species that can be encountered in the waste, at least in simple waste simulants

Calculations: Thermodynamical Data Base, OECD, Ed. North Holland

Species: Uranium, neptunium, and plutonium

Hydroxide: $UO_2(OH)_4^{2-}$, $NpO_2(OH)_2^-$, only neutral species reported for Pu (in disagreement with Rao's latest results)

Carbonate: $UO_2(CO_3)_2^{3-}$, $NpO_2(CO_3)_2(OH)^{4-}$, $NpO_2(CO_3)_3^{4-}$, $PuO_2(CO_3)^-$, $PuO_2(CO_3)_3^{4-}$

Nitrate: No significant complexes when the anion is in competition with hydroxide and carbonate.

Conclusions

Strontium Extraction

- Calix[8]arenes octaamides appear to be selective Sr extractants particularly well suited for caustic solvent extraction systems.
- The functional group para of the phenolic unit seems to influence the extraction strength of the ligand.
- More needs to be done to determine the best solvent composition to test with waste simulants.

Actinide Extraction

- Terephthalamides ligands appear to perform fairly well to extract actinides from caustic waste simulant.
- Interesting and surprising fact: there is a difference in the extraction of U, Np, and Pu. This suggests an oxidation state recognition.
- Encouraging results suggesting an effective extraction upon increasing the ligand concentration in the organic phase.

Future Experiments

Strontium Extraction

- Determine the behavior of C20 under different sets of conditions (diluent, conc…)
- Test other derivatives
- Determine the interaction with BOBCalixC6
- Demonstrate the strontium extraction performance
- Demonstrate the possibility to combine Cs and Sr extraction from waste simulants
- Provide SRS with the best solvent composition for real waste tests

Actinide Extraction

- Obtain distribution ratios from $NaOH/NaNO_3/Na_2CO_3$ systems
- Determine the influence of the initial Pu oxidation state on its extraction
- Test new compounds designed to be more resistant to oxidation
- Study the extraction performance from waste simulants
- Test new compounds combining Sr and An extraction (TAM + CE)

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Acknowledgments

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