Assessing the Binding of Lanthanides and Actinides with Sulfur Donating Ligands

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1. Introduction

In the nuclear fuel cycle, used fuel contains heavy actinides in addition to fission products and unused uranium and/or plutonium. If a partially or fully closed fuel cycle were to be used, it would be necessary to separate the heavy actinides from the used fuel. Since the lanthanides and the heavy actinides have similar radii and the same charge they are difficult to separate. A promising method for this separation is utilizing the actinides' greater covalency than the lanthanides as the basis for a liquid-liquid extraction[1]. Current methods for separating lanthanides and trivalent actinides include TALSQuEAK and TALSPEAK which are methods of solvent extraction that use phosphoric acid based extractants in the organic phase combined with aminopolycarboxylates in the aqueous phase to retain the actinides while the lanthanides are preferentially extracted into the organic phase[2,3]. Replacing nitrogen donating aminopolycarboxylates with softer, sulfur donating ligands such as 2,5-thiophenedicarboxylic acid (TPA) and 2,5-thiophenediboronic acid (TBA) may provide a better separation by more fully exploiting the actinides covalency.
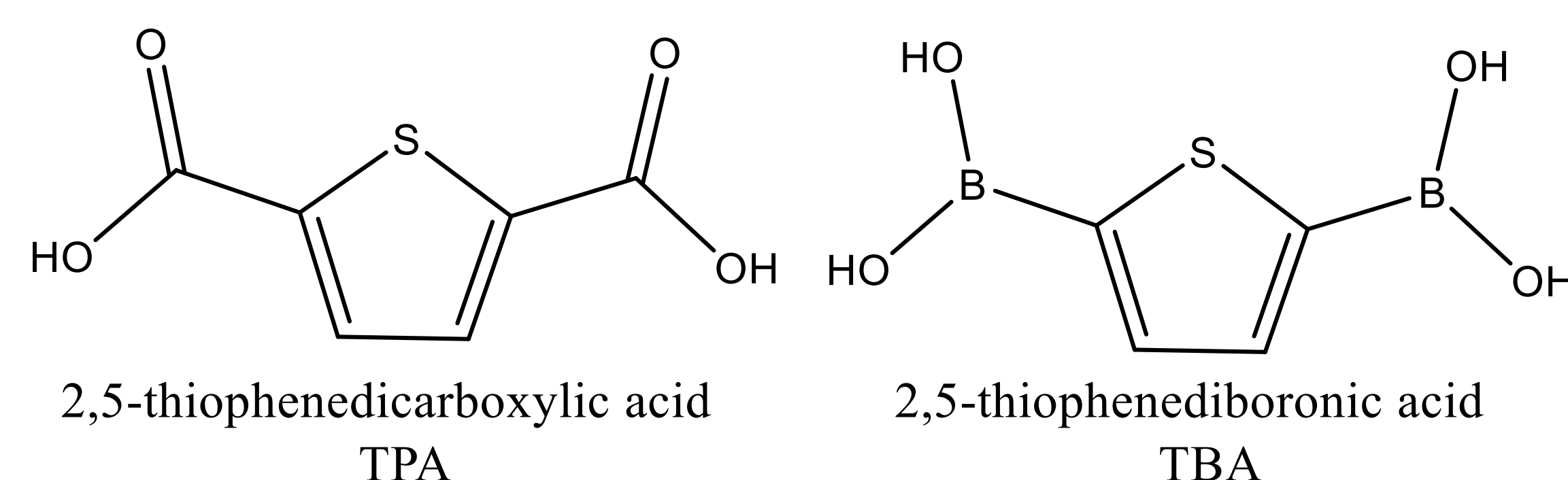

2,5-thiophenedicarboxylic acid
TPA

2,5-thiophenediboronic acid
TBA

Figure 1: Structures of TPA and TBA

2. Method

To determine if TPA and TBA are viable for the separation of lanthanides and heavy actinides the formation constants of the ligands with the lanthanides and actinides must be determined. This has been done by competitive extraction and UV-vis titrations. Amsterdam Density Functional (ADF) has been used to model the complexes that have been created experimentally.

$$M^{3+} + n\,L^{2-} \rightleftharpoons ML_n^{(3-2n)+}$$

$$\beta_n = \frac{[ML_n^{(3-2n)}]}{[M^{3+}][L^{2-}]^n}$$

Competitive Extraction

Solvent extraction with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEHEHP) was performed to determine formation constants for Eu^{3+} and Bk^{3+} by comparing the change in the distribution ratio that occurred when increasing the concentration of TPA. Equation 1 shows how the formation constants were fit to the data.

$$\frac{D_0}{D} - 1 = \beta_{101}[L^{2-}] + \beta_{102}[L^{2-}]^2 + \beta_{103}[L^{2-}]^3 + \cdots \qquad \text{Equation 1}$$

UV-vis Titration

Spectrophotometric titrations were performed on several of the lanthanides with hypersensitive transitions (Nd, Ho) to determine the formation constants with TPA and TBA. HypSpec2014 was used to fit the data.

ADF

ADF was used to determine the geometry of the 1:1 complexes and to compare TPA and TBA with the similar ligands 2,2'-(thiophene-2,5-diyl)diacetic acid, dibenzo[b,d]thiophene-4,6-dicarboxylic acid, 2,5-furandicarboxylic acid, and pyridine-2,6-dicarboxylic acid.

3. Results and Discussion

The formation constants for Nd^{3+}, Eu^{3+}, Ho^{3+}, and Bk^{3+} with TPA are shown in Table 1. The formation constants for Nd^{3+} and Ho^{3+} were measured by spectrophotometric titration and the values for Eu^{3+} and Bk^{3+} were determined from a competitive extraction. The formation constants for Nd^{3+} and Eu^{3+} have been found for multiple temperatures enabling the enthalpy and entropy of complexation to be calculated using a van't Hoff plot.

Element	$\log \beta_{1,\,25^oC}$	ΔH (kJ/mol)	ΔS (J/mol)
Nd^{3+}	7.95 ± 0.08	-73 ± 11	-91 ± 39
Eu^{3+}	5.38 ± 0.05	-23.7	23.4
Ho^{3+}	5.58 ± 0.06	-	-
Bk^{3+}	4.77 ± 0.03	-	-

Table 1: Formation constants, enthalpy, and entropy of complexation for Nd, Eu, Ho, and Bk
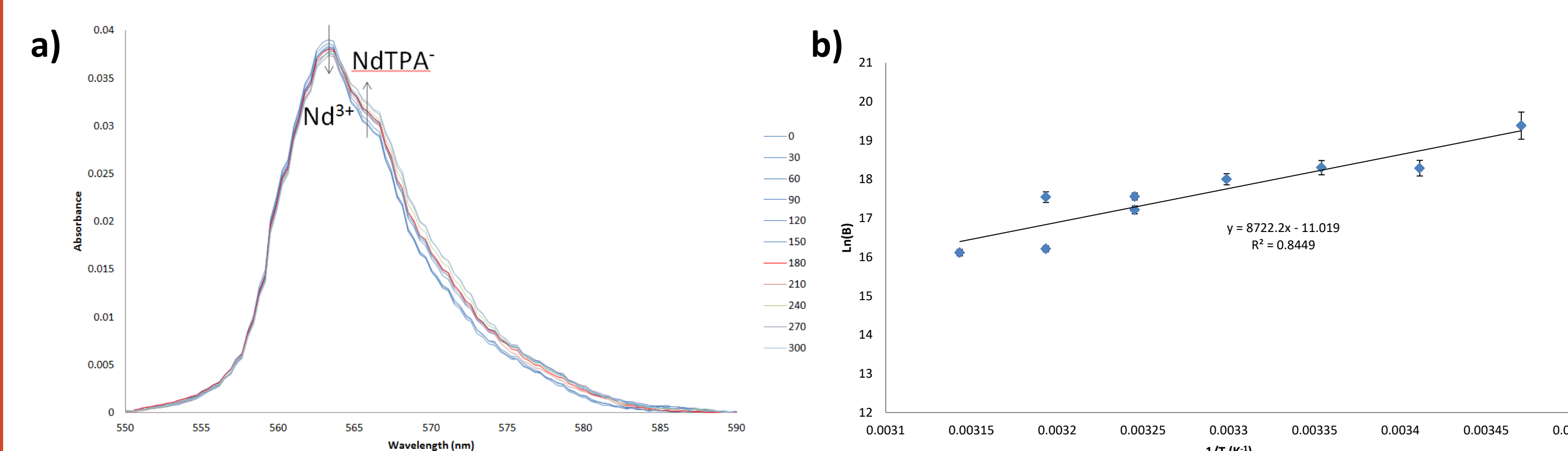

Figure 2: a) Spectra measured during a titration of neodymium with TPA in which dilution has been accounted for and b) the van't Hoff plot for the reaction of neodymium with TPA.

Figure 2 shows an example of a UV-vis titration of neodymium with TPA and the van't Hoff plot for the same reaction. As the titration proceeds, the peak for unbound Nd^{3+} decreases while a peak for $NdTPA^+$ increases

The trend of formation constants is opposite of the expected trend where the soft, sulfur donating TPA would bond more strongly with the actinides than the lanthanides . This trend would suggest that the sulfur has little to no interaction with the metal and that the ligand is bonding using only the carboxylic acid groups.

The enthalpy of the reaction of the lanthanides, particularly neodymium, with TPA as calculated with a van't Hoff plot is surprisingly exothermic. It is far more exothermic than the reaction with similar ligands. To determine if the reaction is truly this exothermic, isothermal titration calorimetry will be performed.

ADF was used to optimize the geometry of the 1:1 complexes as shown in Figure 3. With TPA, 2,2'-(thiophene-2,5-diyl)diacetic acid, and dibenzo[b,d]thiophene-4,6-dicarboxylic acid minimal interaction was observed between the sulfur and the metal. Additionally, the metal was not kept in the same plane as the ligand. When sulfur was replaced with oxygen in 2,5-furandicarboxylic acid or nitrogen in pyridine-2,6-dicarboxylic acid, interaction was seen between the metal and the oxygen or nitrogen and the complex was planar.
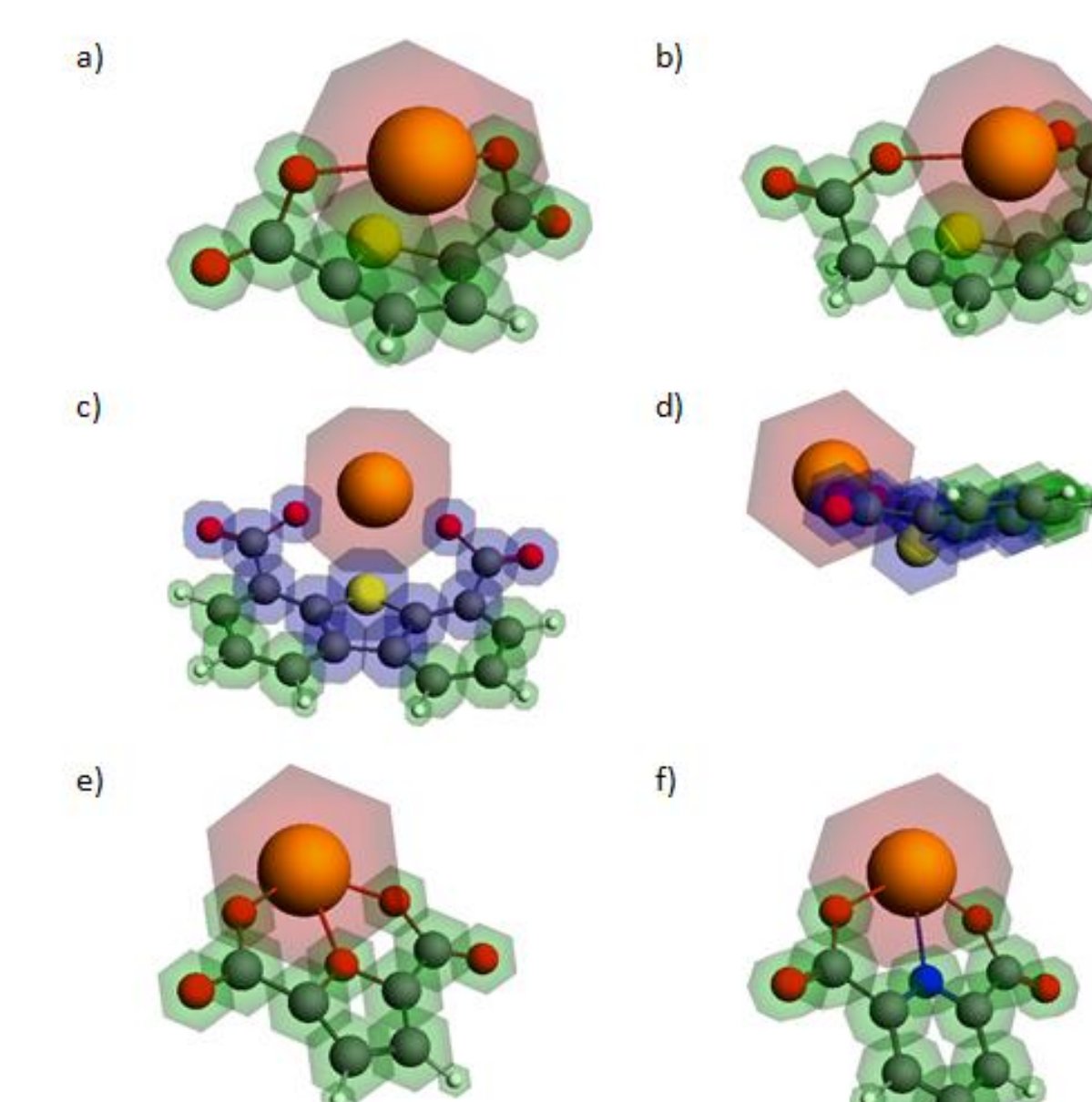

Figure 3: Geometry optimized structures of lanthanum with a) TPA, b) 2,2'-(thiophene-2,5-diyl)diacetic acid, c) and d) dibenzo[b,d]thiophene-4,6-dicarboxylic acid, e) 2,5-furandicarboxylic acid and f) pyridine-2,6-dicarboxylic acid

4. Conclusions

The formation constants for TPA with several lanthanides and berkelium were measured by UV-vis titrations and competitive extraction. The formation constants were found to be higher for the lanthanides than for the actinides which is contrary to the expected trend. To gain insight into why this was occurring, geometry optimizations using ADF showed that the sulfur had minimal interactions with the metal and therefore it does not contribute significantly to the strength of the interaction between TPA and the metal.

5. Future Work

Although the formation constants of TPA with the lanthanides were greater than for berkelium, that difference could still be exploited for the separation of lanthanides and actinides and further research is warranted.

To further characterize the interactions of TPA with the actinides, competitive extraction will be done with Am, Cm, Cf, and Es. Additionally, UV-vis titrations will be done with macroscopic quantities of Am so that the stoichiometry of the complexes of TPA with the actinides can be determined more robustly than if determined by competitive extraction alone.

The formation constants for the most of the lanthanides will be determined by isothermal titration calorimetry as this technique will work for the lanthanides that do not have hypersensitive transitions or are difficult to use as radiotracers.

To determine the structure of the TPA complexes with Nd, Gd, Sm, and Er experimentally, single crystal x-ray diffraction will be used.

6. Acknowledgements

7. References

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(3) Braley, J. C.; Grimes, T. S.; Nash, K. L. *Ind. Eng. Chem. Res.* **2012**, *51*, 629–638