

# Theoretical Examination of the Thermodynamic Factors in the Selective Extraction of Am<sup>3+</sup> from Eu<sup>3+</sup> by Dithiophosphinic Acids

Jason M. Keith and Enrique R. Batista\*

Theoretical Division, Los Alamos National Laboratory, MS B268, Los Alamos, New Mexico 87545, United States

## Supporting Information

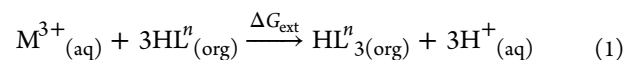
**ABSTRACT:** A detailed thermodynamic examination of the selective extraction of Am<sup>3+</sup> from Eu<sup>3+</sup> by two dithiophosphinic acids was performed using DFT. By examination of two extractants with two metal ions, the most uncertain terms of these calculations were eliminated, resulting in free energies ( $\Delta\Delta\Delta G_{\text{ext}}$ ) that are directly related to the selectivity data. The calculated relative selectivities agree well with experimental data, indicating that the extraction factor is primarily due to the binding free energy of the ligands to the metals and is not dependent on side reactions or complicated solvent effects.

Minor actinides found in spent nuclear fuel, such as Am and Cm, have isotopes with substantial radioactive half-lives that generate significant amounts of heat, which is detrimental to long-term waste storage. As a result, selective extraction of these actinides from spent reactor fuel is currently of great interest. In addition to reducing the radiotoxic lifetime and heat production of the remaining spent fuel, these minor actinides can be remediated by subsequently transmutating them in burner-type reactors once they have been separated.

In solution, minor actinides have ionic radii and properties similar to those of the trivalent lanthanides,<sup>1</sup> and these similarities make selective extraction from lanthanide fission products found in spent fuel difficult. Recently, Klaehn et al. developed a series of CF<sub>3</sub>-substituted diaryldithiophosphinic acids that can be used to extract Am<sup>3+</sup> in the presence of Eu<sup>3+</sup>, but the selectivity varies dramatically with slight modifications to the number and position of the CF<sub>3</sub> groups on the phenyl substituents.<sup>2</sup> For instance, bis[3,5-bis(trifluoromethyl)phenyl]-dithiophosphinic acid (HL<sup>1</sup>; Figure 1) shows only a modest

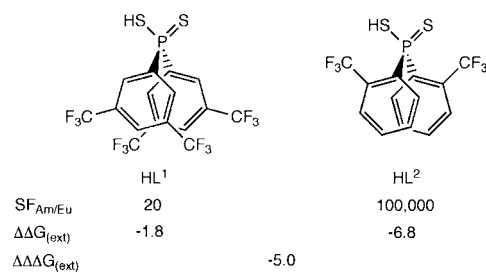
separation factor ( $SF_{\text{Am/Eu}}$ ) of  $\sim 20$ , while [bis(*o*-trifluoromethyl)phenyl]dithiophosphinic acid (HL<sup>2</sup>; Figure 1) shows a significant increase in the selectivity ( $SF_{\text{Am/Eu}} = \sim 10^5$ ).

Assuming that both the Am<sup>3+</sup> and Eu<sup>3+</sup> extractions employ the same stoichiometry and examining only the initial and final states, an equation for the extraction (eq 1). In this equation, the initial state supposes an aqueous ion, with the acid residing in the organic phase {trifluoromethylphenyl sulfone, [(CF<sub>3</sub>)-(Ph)SO<sub>2</sub>]}, while in the final state, the ion is complexed by three bidentate dithiophosphinates (L<sup>n</sup>) in the organic phase after the release of three protons. A similar procedure was employed recently by Dolg and co-workers to examine the selective extraction of Am and Cm from Eu using Cyanex301 [bis(2,4,4-trimethylpentyl)dithiophosphinic acid].<sup>3</sup> Employing this relationship, one can determine the free energy of extraction,  $\Delta G_{\text{ext}}$  which can then be used to compute  $\Delta\Delta G_{\text{ext}}$  corresponding to theselectivity for Am over Eu for each acid [ $SF = \sim \exp(-\Delta\Delta G_{\text{ext}}/RT)$ ] and  $\Delta\Delta\Delta G_{\text{ext}}$  corresponding to the selectivity difference between the two acids.<sup>4</sup> The experimental  $SF_{\text{Am/Eu}}$  values along with the corresponding values of  $\Delta\Delta G_{\text{ext}}$  for HL<sup>1</sup> and HL<sup>2</sup> and  $\Delta\Delta\Delta G_{\text{ext}}$  are listed in Figure 1.



To understand the different behavior of these two acids, Leavitt et al. examined their acidity and nucleophilicity.<sup>5</sup> The authors point out that when a CF<sub>3</sub> group is present in the ortho position, the phenyl rings twist because of steric S...F repulsions and that this distortion is possibly the key factor in determining the difference in the selectivity, perhaps because of some associated modification of the electronic structure. Bhattacharyya et al. have also pointed to electronic structural differences in their examination of the binding of dimethyldithiophosphinate to Am and Eu in an attempt to model the selective extraction reported for Cyanex301.<sup>6</sup> A detailed study and evidence of the said deformation is being submitted separately, along with *k*-edge core spectroscopy studies of these and other compounds. In this manuscript, we limit ourselves to validation of the computational model, showing that the difference in the separation factors stems directly from the difference in the coordination energy between the extractants and metals.

While the electronic structure may be the root cause, we feel that, before examining these complex effects, we should first



**Figure 1.** Dithiophosphinic acids HL<sub>1</sub> and HL<sub>2</sub> with separation factors and corresponding free-energy differences.<sup>2,4</sup> Energies in kcal/mol.

Received: September 21, 2011

Published: December 14, 2011

validate the model by determining if the expected differences in free energies due to these ligand modifications can be reproduced. We present here a detailed density functional theory (DFT) examination of the thermodynamics associated with this extraction in an effort to validate the model proposed in eq 1.

In order to examine eq 1, the thermodynamic cycle in Figure 2 was formulated.  $\Delta G_{\text{ext}}$  is unknown, while the other values

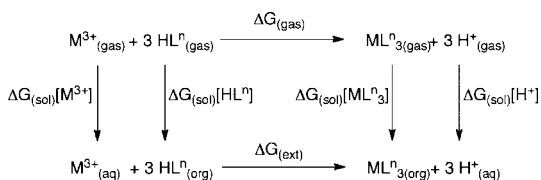


Figure 2. Thermodynamic cycle for  $M^{3+}$  extraction by  $HL^n$ .

were derived from both calculation and experiment. All calculations were performed with unrestricted DFT with the hybrid functional B3LYP,<sup>7,8</sup> as implemented in *Gaussian 09*.<sup>9</sup> Am and Eu were modeled with the small-core Stuttgart relativistic effective core potential with its associated basis set (with the most diffuse functions removed).<sup>10</sup> The singlet, triplet, quintet, and septet spin states were examined for all  $Am^{3+}$  and  $Eu^{3+}$  species, and a high-spin ground-state configuration was determined in agreement with experiment. All other atoms were modeled using a Pople-style double- $\zeta$  6-31G(d',p') basis set with polarization functions optimized for heavy atoms.<sup>11</sup>

From the analytical Hessian, zero-point energies as well as enthalpy and entropy corrections for 298.15 K were also calculated and added to the total energy to obtain a total free energy,  $\Delta G_{\text{gas}}$  (298.15 K). The gas-phase free energy of the proton,  $\Delta G_{\text{gas}}[H^+]$ , was set to  $-6.28$  kcal/mol.<sup>12</sup>

Solvent effects in the neutral species were added using the polarizable continuum model (PCM)<sup>13</sup> with radii and non-electrostatic terms from Truhlar and co-workers' SMD model.<sup>14</sup> The parameters  $\epsilon = 75.3553$  and  $40.245$  were used for  $H_2O$  and  $(CF_3)(Ph)SO_2$ , respectively. The solvent effects in the organic phase were calculated at geometries calculated in the gas phase, resulting in a free energy of solvation ( $\Delta G_{\text{sol}}[HL^n]$  and  $\Delta G_{\text{sol}}[ML^n_3]$ ). Solvation energies for ions in water are especially sensitive to the model and can offset the balance if they are not calculated carefully.<sup>16,17</sup> Four different methods were used to calculate  $\Delta G_{\text{sol}}[M^{3+}]$  with increasing complexity. Method A consists of placing the free cation in the PCM cavity. Method B uses the relationship  $M^{3+}_{\text{gas}} + 9H_2O(aq) \rightarrow [M(H_2O)_9]^{3+}(aq)$  in combination with the PCM. Methods C and D rely on a more accurate description of the solvent environment and cavitation effect and were developed by other authors. Method C relies upon the first-principles determination by Dolg and co-workers;<sup>3,15,16</sup> Method D takes advantage of semiempirical solvation energies provided by David et al.<sup>3,17,18</sup> The free energy of solvation for  $H^+$ ,  $\Delta G_{\text{sol}}[H^+]$ , was set to  $-264.0$  kcal/mol.<sup>13</sup>

The value  $\Delta G_{\text{gas}}$  was calculated for  $M = Am$  and  $Eu$  with both  $HL^1$  and  $HL^2$  (Table 1). These gas-phase values demonstrate that all four metal and acid combinations for this reaction are exergonic ( $\Delta G < 0$ ). The differences in these values ( $\Delta\Delta G_{Am-Eu}$ ) for each acid is  $>0$ , indicating that the binding energy of these ligands to  $Eu$  in the gas phase is stronger than to  $Am$ . This observation is inconsistent with the

Table 1.  $\Delta G_{\text{gas}}$  (298.15 K) in kcal/mol

M	ligand	$\Delta G_{\text{gas}}$	$\Delta\Delta G$	$\Delta\Delta\Delta G$
Eu	$HL^1$	-16.73	15.20	-1.96
Am	$HL^1$	-1.54		
Eu	$HL^2$	-18.58	13.24	
Am	$HL^2$	-5.34		

experimental results and is similar to the findings of Dolg and co-workers for the gas-phase binding energies of Cynex301, where they concluded that the aqueous-phase solvation energy of  $M^{3+}$  was the primary driving force in the selectivity.<sup>3</sup>

Free energies of solvation were determined for the complexes and acids in the organic phase (Table 2). As can be seen by

Table 2.  $\Delta G_{\text{sol}}$  (298.15 K) in kcal/mol

$EuL^1_3$	$AmL^1_3$	$EuL^2_3$	$AmL^2_3$	$HL^1$	$HL^2$
-10.9	-9.9	-14.34	-14.47	-5.04	-5.68

examination of  $\Delta G_{\text{sol}}[ML^n_3]$ , changing  $M$  does not result in an appreciable change in the free energy for either ligand complex. While the difference in the free energy of solvation for the acids is also small, the difference in the solvation energy for the complexes with different ligands is 4–5 kcal/mol.

While the organic-phase solvation energies had little variance, the aqueous-phase solvation of  $M^{3+}$  varies greatly between  $Am$  and  $Eu$  (Table 3). Because  $\Delta G_{\text{gas}}$  for complexation of  $Eu$  was

Table 3.  $\Delta G_{\text{sol}}[M^{3+}]$  (298.15 K) in kcal/mol ( $\Delta\Delta G_{\text{sol}}$ )

method A		method B	
Eu <sup>3+</sup>	Am <sup>3+</sup>	Eu <sup>3+</sup>	Am <sup>3+</sup>
-847.15	-880.30	-830.68	-827.28
	-33.14		3.40
method C		method D	
Eu <sup>3+</sup>	Am <sup>3+</sup>	Eu <sup>3+</sup>	Am <sup>3+</sup>
-753.35	-715.58	-777.29	-755.02
	37.77		22.27

more favorable than that for  $Am$  for both acids and the difference between  $\Delta G_{\text{sol}}[ML^n_3]$  values for  $Am$  and  $Eu$  for a given ligand was small, the experimental evidence would lead us to expect that  $\Delta G_{\text{sol}}[Eu^{3+}]$  must be less than (more negative than)  $\Delta G_{\text{sol}}[Am^{3+}]$ . This is true for all of the solvation methods except A, which simply puts the free ion in the PCM and is expected to be a very coarse and inaccurate method. The degree to which  $Eu$  is favored in water over  $Am$  with methods B–D varies significantly from 3.40 to 37.77 kcal/mol. On the basis of the features of each model, models C and D should be more accurate than model B. However, without experimental values to make a definite assessment, it is better to evaluate their effect in terms of  $\Delta G_{\text{ext}}$ .

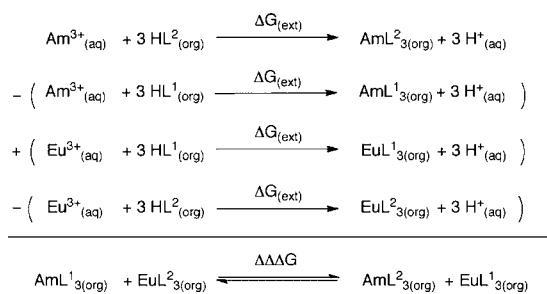
The value  $\Delta G_{\text{ext}}$  can be determined by combining the gas-phase free energies with the solvation free energies of all of the species involved. Table 4 lists the values for  $\Delta G_{\text{ext}}$  for all four of the ion and acid combinations with each solvation method. For methods A and B,  $\Delta G_{\text{ext}}$  is endergonic, which is inconsistent with the experimental results. For methods C and D, however,  $\Delta G_{\text{ext}}$  is exergonic. In order to better judge which method is best at reproducing the experimental extraction trends, an evaluation of  $\Delta\Delta G_{\text{ext}}$  is necessary. For methods C and D,  $\Delta\Delta G_{\text{ext}} < 0$ , meaning that  $\Delta G_{\text{ext}}[Am^{3+}]$  is less than

Table 4.  $\Delta G_{\text{ext}}$  (298.15 K) in kcal/mol

method	$M^{3+}(\text{sol})$	$\Delta G$	$\Delta\Delta G$	$\Delta\Delta\Delta G$
A	$\text{EuL}_3^1$	42.72	49.35	-3.09
	$\text{AmL}_3^1$	92.07		
	$\text{EuL}_3^2$	39.31	46.26	
	$\text{AmL}_3^2$	85.57		
B	$\text{EuL}_3^1$	26.25	12.81	-3.09
	$\text{AmL}_3^1$	39.06		
	$\text{EuL}_3^2$	22.84	9.72	
	$\text{AmL}_3^2$	32.56		
C	$\text{EuL}_3^1$	-51.08	-21.57	-3.09
	$\text{AmL}_3^1$	-72.65		
	$\text{EuL}_3^2$	-54.49	-24.65	
	$\text{AmL}_3^2$	-79.14		
D	$\text{EuL}_3^1$	-27.14	-6.07	-3.09
	$\text{AmL}_3^1$	-33.21		
	$\text{EuL}_3^2$	-30.55	-9.10	
	$\text{AmL}_3^2$	-39.70		

(more negative than)  $\Delta G_{\text{ext}}[\text{Eu}^{3+}]$ , which is consistent with selective Am extraction. The calculated numbers from method D are the most consistent with experiment.

To further evaluate the ability of the model to differentiate between the two different acids,  $\Delta\Delta\Delta G_{\text{ext}}$  for the two acids should be examined. This number should be consistent for every solvation method because the solvation energies of the ions and the acid cancel out (Figure 3) and the only remaining

Figure 3. Formulation of  $\Delta\Delta\Delta G_{\text{ext}}$ .

solvation energy is that of the complexes. In fact, as Figure 3 shows,  $\Delta\Delta\Delta G_{\text{ext}}$  corresponds to the free energy of the ligand exchange between  $\text{AmL}_3^1$  and  $\text{EuL}_3^2$ , a reaction devoid of complicated solvation issues, which our methods should therefore excel in. The value of  $\Delta\Delta\Delta G_{\text{ext}}$  was found to be  $-3.09$  kcal/mol in comparison with  $\sim -5$  kcal/mol from experiment.  $\Delta\Delta\Delta G_{\text{ext}} < 0$  correctly demonstrates that, according to the binding energies,  $\text{HL}^2$  should act as a better selective extractant for Am than  $\text{HL}^1$ .

In conclusion, we have performed a detailed DFT examination of the selective extraction of Am from Eu by two different dithiophosphinic acids. We found that, in order to obtain reasonable values of  $\Delta G_{\text{ext}}$  and  $\Delta\Delta G_{\text{ext}}$ , it is critical to accurately describe the solvation free energy of the free metal ion. From the four models that we used, method D yielded the most accurate results. However, for the purpose of comparing the relative separation abilities of two different extractants, a calculation of  $\Delta\Delta\Delta G_{\text{ext}}$  produced results in good agreement with experimental observations. This quantity does not depend on the solvation model and indicated to us that the extraction factor is primarily due to the binding free energy of the ligands to the metals and is not dependent on side reactions or

complicated solvent effects. Most notable is that this approach is able to distinguish between two ligands that differ only by the location and number of  $\text{CF}_3$  groups that are significantly removed from the metal center. These results suggest that the simplified model represented in eq 1 is sufficient to fully examine the bonding and electronic structures of these complexes, which is the focus of ongoing research.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

*E*, *H*, and *G* data and geometries for all species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [erb@lanl.gov](mailto:erb@lanl.gov).

## ■ ACKNOWLEDGMENTS

This project was funded by the U.S. Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program. J.M.K. acknowledges funding from a LANL Director's Postdoctoral Fellowship. The Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under Contract DE-AC5206NA25396. The authors thank Drs. Scott Daly, Stosh Kozimor, Andrew Gaunt, and Gordon Jarvinen for helpful discussion.

## ■ REFERENCES

- (1) Nash, K. L. *Solvent Extr. Ion Exch.* **1993**, *11*, 729.
- (2) Klaehn, J. R.; Peterman, D. R.; Harrup, M. K.; Tillotson, R. D.; Luther, T. A.; Law, J. D.; Daniels, L. M. *Inorg. Chim. Acta* **2008**, *361*, 2522.
- (3) Cao, X.; Heidelberg, D.; Clupka, J.; Dolg, M. *Inorg. Chem.* **2010**, *49*, 10307.
- (4)  $\text{DDG}_{\text{ext}} = \text{DG}_{\text{ext}}[\text{Am}] - \text{DG}_{\text{ext}}[\text{Eu}]$  and  $\text{DDD}_{\text{ext}} = \text{DDG}_{\text{ext}}[\text{HL}_2] - \text{DDG}_{\text{ext}}[\text{HL}_1]$ .
- (5) Leavitt, C. M.; Gresham, G. L.; Benson, M. T.; Gaumet, J.-J.; Peterman, D. R.; Klaehn, J. R.; Moser, M.; Aubriet, F.; Van Stipdonk, M. J.; Groenewold, G. S. *Inorg. Chem.* **2008**, *47*, 3056.
- (6) Bhattacharyya, A.; Ghanty, T. K.; Mohapatra, P. K.; Manchanda, V. K. *Inorg. Chem.* **2011**, *50*, 3913.
- (7) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (8) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (9) Frisch, M. J. et al. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.
- (10) (a) Fuentealba, P.; Preuss, H.; Stoll, H.; Von Szentpaly, L. A. *Chem. Phys. Lett.* **1982**, *89*, 418. (b) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245. (c) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535.
- (11) (a) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Matzaris, J. J. *Chem. Phys.* **1988**, *89*, 2193. (b) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081.
- (12) (a) Topol, I. A.; Tawa, G. J.; Burt, S. K.; Rashin, A. A. *J. Chem. Phys.* **1999**, *111*, 10998. (b) Tuttle, T. R. Jr.; Malaxos, S.; Coe, J. V. *J. Phys. Chem. A* **2002**, *106*, 925.
- (13) For a recent review, see: Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.
- (14) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.
- (15) Wiebke, J.; Moritz, A.; Cao, X.; Dolg, M. *Phys. Chem. Chem. Phys.* **2007**, *9*, 459.
- (16) Ciupka, J.; Cao-Dolg, X.; Wiebke, J.; Dolg, M. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13215.
- (17) David, F. H.; Vokhmin, V. *New J. Chem.* **2003**, *27*, 1627.
- (18) David, F. H.; Vokhmin, V.; Ionova, G. *J. Mol. Liq.* **2001**, *90*, 45.