INL/EXT-14-33295

Perform Thermodynamics Measurements on Fuel Cycle Case Study Systems

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September 2014

The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

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Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Perform Thermodynamics Measurements on Fuel Cycle Case Study Systems

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Materials Recovery and Waste Form Development Campaign
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28th September, 2014
FCRD-SWF-2014-000232

SUMMARY

This document was prepared to meet FCR&D level 3 milestone M3FT-14IN0304022, "Perform Thermodynamics Measurements on Fuel Cycle Case Study Systems." This work was carried out under the auspices of the Thermodynamics and Kinetics FCR&D work package. This document reports preliminary work in support of determining the thermodynamic parameters for the ALSEP process. The ALSEP process is a mixed extractant system comprised of a cation exchanger 2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) and a neutral solvating extractant N,N,N',N'-tetraoctyldiglycolamide (TODGA). The extractant combination produces complex organic phase chemistry that is challenging for traditional measurement techniques. To neutralize the complexity, temperature dependent solvent extraction experiments were conducted with neat TODGA and scaled down concentrations of the ALSEP formulation to determine the enthalpies of extraction for the two conditions. A full set of thermodynamic data for Eu, Am, and Cm extraction by TODGA from 3.0 M HNO_3 is reported. These data are compared to previous extraction results from a 1.0 M HNO_3 aqueous medium, and a short discussion of the mixed HEH[EHP]/TODGA system results is offered.

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Acronyms

ALSEP	Actinide Lanthanide SEParation process
CMPO	Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide
FCR&D	Fuel Cycle Research and Development
HEH[EHP]	2-ethylhexyl-phosphonic acid mono-2-ethylhexy ester
HDEHP	Di-(2-ethylhexyl)phosphoric acid
INL	Idaho National Laboratory
TALSPEAK	Trivalent Actinide Lanthanide Separations by Phosphoric reagent Extraction from Aqueous Komplexes
TRUEX	TRansUranic Extraction
TODGA	N,N,N’,N’-tetraoctyldiglycolamide
US DOE	United States Department of Energy
UREX	Uranium EXtraction

MATERIALS RECOVERY AND WASTE FORM DEVELOPMENT CAMPAIGN

1. INTRODUCTION

Removal of the minor actinides (MAs) continues to be an important step in closing the used nuclear fuel cycle. Separating the Am and Cm isotopes from dissolved used nuclear fuel matrixes would reduce the heat load on future repositories by a factor of 100. Currently, one process, developed by the Sigma Team for Minor Actinide Separations, for this type of separation is the Actinide Lanthanide SEParation process (ALSEP).[1,2] The ALSEP process simplifies the UREX suite of solvent extraction systems by combining both the TRansUranic Extraction (TRUEX) and Trivalent Actinide Lanthanide Separations by Phosphoric reagent Extraction from Aqueous Komplexes (TALSPEAK) process. The ALSEP formulation co-extracts actinides and lanthanides away from the fission product matrix (approx. 3.0 M HNO_3). The actinides are then selectively stripped from the loaded organic phase by contact with a citric acid buffered aqueous phase containing a polyaminopolycarboxylate complexant at a pH between 3 and 4.5.

The ALSEP process achieves the co-extraction from the acidic aqueous medium by combining a cation exchanging extractant 2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) and a neutral solvating extractant N,N,N',N'-tetraoctyldiglycolamide (TODGA) in an aliphatic organic diluent dodecane (Figure 1).

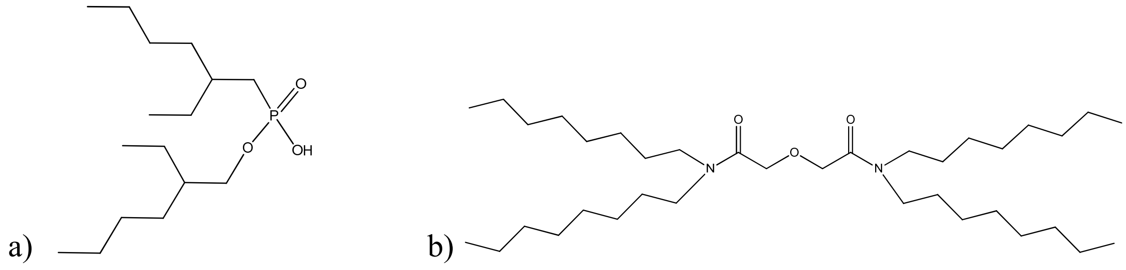

Figure 1. Structures of (a) 2-ethylhexyl-phosphonic acid mono-2-ethylhexy ester HEH[EHP] and (b) N,N,N',N'-tetraocty ldiglycolamide, TODGA.

The extraction system is effective at f-element group extraction; however, the presence of two extractants in the system creates complicated organic phase chemistry. Although the use of TODGA/ HEH[EHP] has reduced the organic phase extractant interactions (compared to earlier variations with CMPO and HDEHP),[1] the two extractants may still form complexes with each other via hydrogen bonding. As a result, the exact mechanism of extraction for this system is still unknown. Modeling of this system will require sophisticated organic phase mass balance equations, biphasic equilibrium expressions, and extraction constants combined with carefully determined thermodynamic parameters. Equations 1-3 (shown below) are the biphasic equilibrium expressions for each of the extractants in the combined system. The system of equations ignores any complex formation between the extractants and aqueous metal/nitrate complexation (HA stands for HEH[EHP]).

$$M^{3+} + 3(HA)_{2(org)} \rightleftarrows M[H(AHA)_2]_{3(org)} + 3H^+ \tag{1}$$

$$M^{3+} + 3NO_3^- + n\mathrm{TODGA}_{(org)} \rightleftarrows M(NO_3)_3 \cdot n\mathrm{TODGA}_{(org)} \tag{2}$$

$$HNO_3 + n\mathrm{TODGA}_{(org)} \rightleftarrows HNO_3 \cdot n\mathrm{TODGA}_{(org)} \tag{3}$$

The overarching goal of the work presented here is to thermodynamically identify the important processes of this complicated mixed extractant system and determine the organic phase extractant interactions, extraction mechanism, and eventually attempt to model the complex system using mass balance equations and biphasic equilibrium expressions that represent the chemistry of the f-element co-extraction. A first step in accomplishing this is to determine the fundamental thermodynamic parameters for the individual extractants used in the ALSEP process.

2. EXPERIMENTAL

2.1 Reagents

Nitric acid (≥69.0% TraceSELECT®) was purchased from Sigma-Aldrich. The 2-ethylhexyl phosphonic acid-2-ethylhexyl ester (Yick-Vic Chemicals & Pharmaceuticals, >95%) was purified by a literature procedure. The TODGA was purchased from Eichrom and n-dodecane was purchased from Sigma-Aldrich (≥99%), both were used as received.

2.2 Temperature Dependent Solvent Extraction

Temperature dependent extraction studies were conducted to determine the enthalpy of extraction by van‘t Hoff analysis. Aqueous phases (3.0 M HNO_3) were pre-equilibrated for 10 min. by vigorous shaking with neat n-dodecane. Organic phases (0.0035 M TODGA) were pre-equilibrated 3 times, 10 min. each at room temperature with a fresh aqueous phase containing 3.0 M HNO_3 followed by 5 min. of centrifugation. All samples (0.5 mL of each phase) were then spiked with radiotracer ^{154}Eu, ^{243}Am or ^{248}Cm and shaken at 10 °C, 20 °C, 25 °C, 30 °C, 40 °C ± 1.0 °C followed by overnight gravity settling in a temperature controlled sample holder connected to a constant temperature water bath. Organic and aqueous phase samples (300 µL) were analyzed using an ORTEC GEM50P4 coaxial HPGe monitoring the γ-radiation from the ^{154}Eu and ^{243}Am. For the ^{248}Cm experiments, the aqueous and organic phase were sampled as previously described mixed with 10 mL of scintillation cocktail (Ultima Gold) and analyzed by liquid scintillation counting using a Perkin Elmer Tri-Carb.

2.3 RESULTS

The cation exchanging extractant HEH[EHP] has a pKa of 3.4,[3] as such, optimal metal ion extraction occurs in systems with aqueous acidity adjusted to pH 3.0 and higher. The ALSEP process utilizes an aqueous phase of 3.0 M HNO_3, at this acidity it is assumed the HEH[EHP] extractant alone should not extract the trivalent metal ions to the organic phase. This makes it difficult to study an extraction system with two extractants that perform at such differing acidities. To overcome this challenge, we initially focused on the extraction behavior of the TODGA extractant alone. Eventually, HEH[EHP] was added to observe the impact on the mixed extractant system. A comprehensive literature search for trivalent f-element extraction with TODGA produced one report by Ansari et al.[5] describing the thermodynamics of TODGA extraction in 1.0 M HNO_3 aqueous medium.

The temperature dependence for Eu, Am, and Cm is shown in Figure 2. The D_{ratios} for Eu show it is most strongly extracted followed by Cm and Am. These data show a Eu/Am separation factor of about 10 and Eu/Cm separation factor of about 7. These results are consistent with extraction data found in the literature, and can be attributed to the electrostatic attraction of the hard-sphere cations with the oxygen donor atoms of the TODGA extractant.[4]

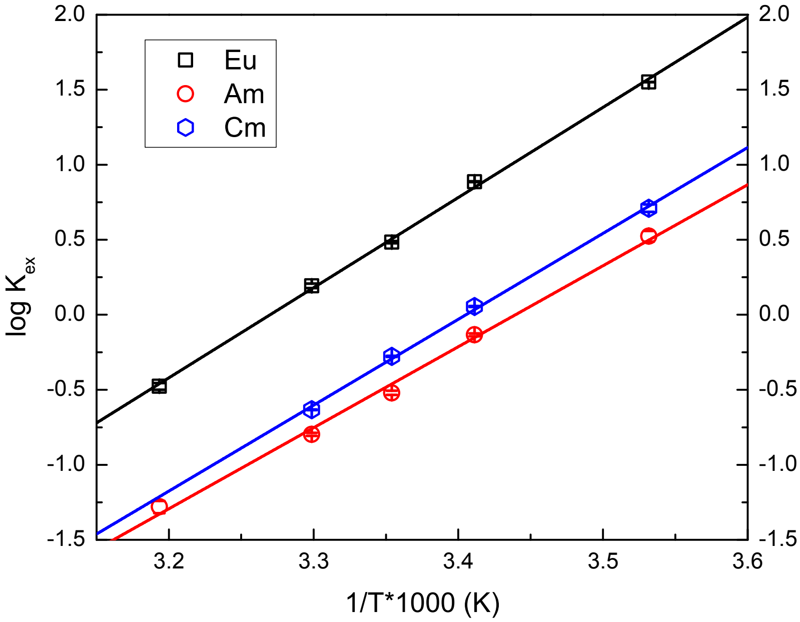

Figure 2. Temperature dependence for the extraction of Eu, Cm, Am by TODGA. Organic phase: 0.0035 M TODGA in dodecane. Aqueous phase: 3.0 M HNO_3.

Recent studies by Grimes et al.[6] have reported stability constant data for NO_3^- complexation with Eu, Am and Cm at 4.0 M ionic strength. These data were used to correct the D_{ratios} for the metal ions at 25 °C and calculate extraction constants, (K_{ex}) for the target metal ions with TODGA. The K_{ex} enables the calculation of the ΔG, combined with the ΔH (from the temperature dependence), ΔS was calculated. The complete set of thermodynamic parameters is presented in Table 1.

Table 1. Complete set of thermodynamic parameters for Eu, Cm, Am extraction with TODGA from 3.0 M HNO_3. The thermodynamic data reported in Ref. 4 for Am extraction with TODGA from 1.0 M HNO_3 is shown for comparison.

	log K_{ex}	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)	
Eu	9.60 ± 0.01	-54.8 ± 0.1	-115.1 ± 2.4	-202.2 ± 4.3	p.w.
Cm	8.70 ± 0.01	-49.7 ± 0.1	-110.0 ± 2.9	-201.2 ± 5.4	p.w.
Am	8.47 ± 0.01	-48.4 ± 0.1	-103.4 ± 4.0	-186.6 ± 7.1	p.w.
Am	9.4	-27.9	-47.6	-66.1	Ref. 5

The results shown in Table 1 are the first ever reported thermodynamic parameters for Eu, Cm, Am extraction by TODGA at 3.0 M ionic strength. The free energy terms for Am extraction differ by ~20 kJ/mol with the 3.0 M system showing more favorable free energy. The favorable free energy shift observed for the higher ionic strength medium can be directly attributed to the increased metal ion solvation by the NO_3^- ion. The greater degree of metal ion solvation lowers the energy requirements for the transport of the neutral metal ions to the organic phase; as a result, the free energy term is shifted to reflect a more favorable extraction system.

Am extraction data show a two fold increase in the enthalpy term and 3 fold increase in the entropy term for the 3.0 M system. The observed increase in extraction enthalpy can be attributed to the formation of the $M(NO_3)^{2+}$ and the $M(NO_3)_2^+$ driven by the increased concentration of the nitrate ion. The increased metal ion solvation reduces the energy required for dehydration in the aqueous phase, thus lowering the energy cost for biphasic metal ion transport. In turn, the enthalpy of extraction is increased to maintain the energy balance metal ion transfer is increased as the aqueous phase salt concentrations are increased. This phenomenon is described as "salting out" the metal ions from the aqueous phase to the organic phase by increasing the aqueous phase salt concentration.

The increased entropy term for Am extraction observed in the 3.0 M HNO_3 system can be attributed to the formation of $M(NO_3)^{2+}$ and $M(NO_3)_2^+$ species (since the $M(NO_3)_2^+$ complex is not present in the 1.0 M system), this complex formation reduces the number of H_2O molecules released during extraction so the net ordering of the system is increased when compared to the 1.0 M system that requires more H_2O dehydration or released during extraction.

Upon completion of the temperature dependent studies with neat TODGA phases, HEH[EHP] was combined with TODGA to observe the effect on extraction heats. The ALSEP process utilizes an extractant mixture of 0.050 M TODGA/0.75 M HEH[EHP]. These concentrations are impractical for these studies since distribution ratios collected between 0.1-10 are desired. For these studies, TODGA was reduced to 0.0035 M, a factor of 0.07 compared to the optimal ALSEP conditions. The combined extractant temperature dependencies were carried out using 0.0035 M TODGA/0.0053 M HEH[EHP] where both extractants were scaled down by a factor of 0.07 and 0.0035M TODGA/0.75M HEH[EHP]. Since the mechanism of extraction is unknown for the ALSEP process, the distribution ratios were used in the analysis and the enthalpy of extraction reported for the mixed systems represent the overall heats of extraction for the system. At this point it is impossible to assign heats to any single component of the extraction system. The temperature dependence for the 0.0035 M TODGA/0.0053 M HEH[EHP] system is shown in Figure 3.

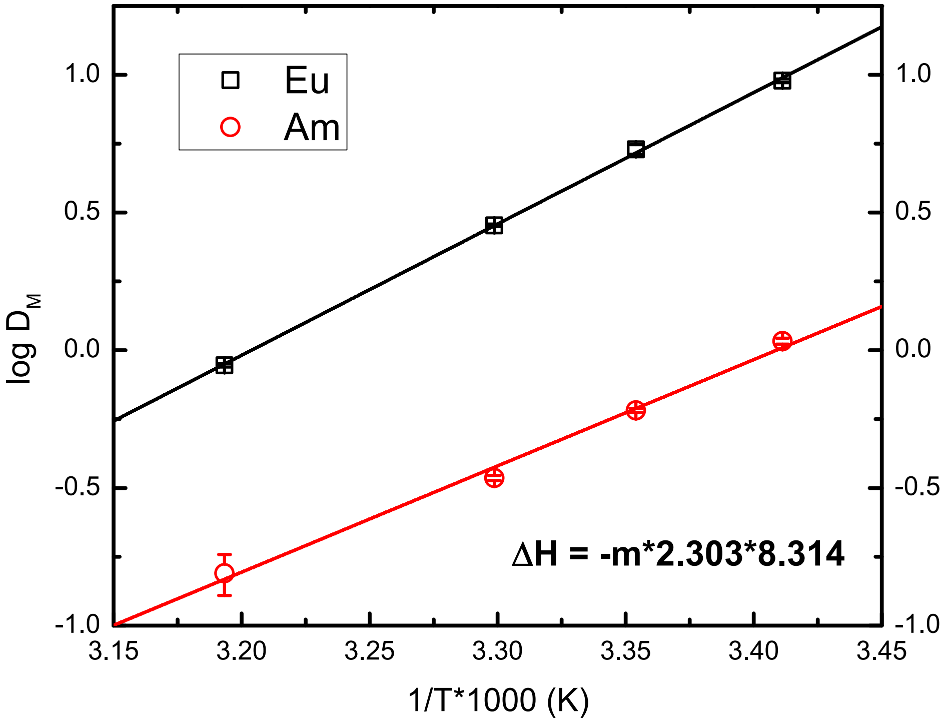

Figure 3. Temperature dependence of the ALSEP formulation organic phase scaled down by a factor of 0.07. Organic phase: 0.0035 M TODGA/0.0053 M HEH[EHP]. Aqueous phase: 3.0 M HNO_3.

The enthalpy heats calculated from the data in Figure 3 are listed below in Table 2.

Table 2. Heats of extraction for Eu and Am extraction by 0.0035 M TODGA/0.0053 M HEH[EHP. The extractant ratios were scaled down to reflect the original ALSEP formulation.

	ΔH (kJ/mole)
Eu	-91.34 ± 1.5
Am	-73.88 ± 4.3

The distribution ratios from the mixed system were consistently higher than the neat TOGDA system across the temperature range with the exception of the 10 °C data points where the extractions matched the 20 °C data points. It is currently unknown if this is a result of the low temperature or experimental error, more tests are needed to clarify this result. The linearity of the temperature dependence suggests the temperature affects the mixed system uniformly across the temperature range. The reduced heats of extraction may reflect the change in the extraction mechanism due to the addition of the HEH[EHP] extractant. It is possible the organic phase extractant interactions may be strong enough to form new extractant species that compete with the TODGA extraction. If this is occurring it could account for the reduced heats. Without some further understanding of the fundamental chemistry of the organic phase interactions or the mechanism of extraction for the mixed system, it is hard to draw any real conclusions from these types of studies. However, these experiments are a good first step in peeling back the layers of the complex chemistry offered in these mixed extractant sytems.

3. CONCLUSION

Thermodynamic parameters for the extraction of Eu, Am, and Cm by TODGA from 3.0 M HNO_3 are reported for the first time. The comparison to 1.0 M ionic strength data showed the TODGA extraction at 3.0 M behaved similarly. Temperature dependent extractions for a mixed TODGA/HEH[EHP] system showed increased distribution ratios for Eu and Am compared to the neat TODGA system. This suggests that the HEH[EHP] is enhancing the extraction from the 3.0 M system through some extractant interaction with the TODGA to create a new extractant molecule complex. However, the heats of extraction for this system were lower than the neat TODGA system. We feel a good first step has been taken toward peeling back the layers of this complex extractant system.

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