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First Calorimetric Determination of Heat of Extraction of ^{248}Cm in a Bi-Phasic System

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SUMMARY

This report presents a summary of the work performed to meet FCR&D level 2 milestone M21SW050201, "Complete the first calorimetric determination of heat of extraction of ^{248}Cm in a bi-phasic system". This work was carried out under the auspices of the Thermodynamics and Kinetics FCR&D work package. To complement previous work undertaken under this work package we have extended out heat of extraction studies by di-2-ethylhexyl-phosphoric acid to curium. This report also details the heat of extraction of samarium in the same system. This work was performed to not only test the methodology but also to check for consistency with the heats of extraction obtained with those in the prior literature. The heat of extraction for samarium that was obtained in this study was -9.6 kJ mol^{-1}, which is in reasonable agreement with the previously obtained value of -10.9 kJ mol^{-1}. The curium heat of extraction was performed under two sets of conditions and the obtained heats of extraction were in reasonable agreement with each other at -16.0 ± 1.1 and -16.8 ± 1.5 kJ mol^{-1}.

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ACRONYMS

D	Distribution coefficient
DIAMEX	DIAMide EXtraction
DTPA	Di 2-ethylenetriamine-N,N,N',N”,N”-pentaacetic acid
FCR&D	Fuel Cycle Research and Development
HDEHP	Di ethyl hexyl phosphoric acid
ICPMS	Inductively Coupled Plasma Mass Spectrometry
INL	Idaho National Laboratory
MOX	Mixed Oxide Fuel
ORNL	Oak Ridge National Laboratory
PUREX	Plutonium Uranium EXtraction
SANEX	Selective ActiNide EXtraction
TALSPEAK	Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes
US DOE	United States Department of Energy
UV-vis	Ultra Violet-visible
WSU	Washington State University

1. INTRODUCTION

The distribution of a solute between two immiscible solvents is one of the most important technologies for the separations industry. Liquid-liquid distributions have long been used for purification of chemicals in a wide variety of industrial applications from pharmaceuticals to industrial waste treatment.[1] Currently, solvent extraction is the main industrially deployed process for the treatment of used nuclear fuel. Such is the robustness of the PUREX (Plutonium Uranium EXtraction)[2] process; it has been operated for over half a century to recover uranium and plutonium for recycle into Mixed Oxide (MOX) fuel with only minor modifications from its original formulation. As such, it is envisioned that, in the near term at least, any future "fully closed" fuel cycles will operate solvent extraction for the recovery and separation of the desired metal ions. The greatest challenge posed to this particular separations community currently is that of the separation of the trivalent actinides from the trivalent lanthanides (or vice versa dependent on the chosen process).

If the US is to develop a sustainable closed nuclear fuel cycle, significant developments in the area of fuel utilization and reducing the radiotoxicity in the final waste-forms will have to be made. There are two options that are being considered for closing the nuclear fuel cycle; "Full Recycle" where all of the actinides are separated from the used fuel or "Modified Open" where some level of processing is performed to recover a reduced level of the actinides for re-use or burning in a reactor. There are currently two main philosophies for the recycle of the minor actinides using solvent extraction. The first is the use of ligands that contain soft donor atoms (such as N or S) for the group separation of the trivalent actinides and lanthanides, these processes lend themselves more to a "full recycle" scenario. Examples of this group separation strategy exist in the DIAMEX-SANEX[3-5] process under development in Europe and TRUEX-TALSPEAK[6-8] in the US. However, it should be noted that both of these options have limitations that would need to be overcome before industrial deployment could be considered. The second approach is utilizing the higher oxidation states of americium for its selective separation from curium and the lanthanides. If americium can be oxidized to the +6 oxidation state this would allow for the group separation of Np, Pu and Am as all of the hexavalent actinides can be extracted in a process similar to PUREX using neutral organophosphorus donors. The JASPER concept (Joint Actinide Separation by Phosphorus Extractant Reagent) has been successfully demonstrated at bench scale at the INL.[9] This separation methodology perhaps could be considered to be a "Modified Open" strategy as it lets any residual curium in the raffinate go to the final waste product.

Although very different types of chemistry are used in the group separation vs americium oxidation approach, there are still basic thermodynamic forces that drive the extraction/separation of these metal ions. In all solvent extraction systems the solute under study is influenced by many factors including its interactions with the aqueous phase electrolyte and organic reagents required to complete the separation.[10] As such, a thorough comprehension of the physicochemical properties of any separations system under study is essential to determine not only the final product but the mechanism via which the extraction takes place.[11] Studying the thermodynamic properties of a solvent extraction system ($\Delta G°$, $\Delta H°$ and $\Delta S°$) will provide an insight into the driving forces for the separation process, and possibly the end product. In some cases though, especially in the case of americium and curium separations, due to high radioactivity and limited supply of longer lived isotopes the physical and chemical measurements simply have not been performed. While tracer studies give a reasonable approximation of how the metal ion will behave in a separations system, they do not give absolute values. Those types of experiments require a direct measurement of the reaction under study.

Curium is one of the key actinides that is targeted for separation in the TALSPEAK process, but the chemical interactions of this element with the ligands that facilitate this process (lactic acid, di 2-ethylenetriamine-N,N,N',N”,N”-pentaacetic acid , DTPA, and di-2- ethyl hexyl phosphoric acid HDEHP) are, for reasons detailed above, simply not well defined because they have not been extensively studied. To that end, the study on the direct measurement of the heat of extraction of curium by HDEHP was highlighted as an area that could begin to expand this field of research. By studying the thermochemistry of curium extraction from nitrate media by HDEHP using a calorimetric approach, we will further expand our thermodynamic understanding of this liquid-liquid extraction system. Further it should be re-iterated at this point that examples of these types of biphasic heats of extraction experiments are limited in the literature, but more importantly this has never before been performed with curium.

2. APPROACH

In this report we will detail the direct calorimetric measurement of the liquid-liquid partitioning of curium. This is only the second such measurement with a transuranic element reported to date. To measure the biphasic heat of extraction of curium we have used a recently developed two-phase calorimetric methodology to study the thermochemical features of HDEHP-facilitated phase transfer of metal ions across a liquid-liquid boundary. This technique was successfully demonstrated with radioactive isotopes in FY-10 by measuring the heat of extraction of americium. Isothermal titration calorimetry can accurately measure microjoule heat events inside of a 1mL reaction vessel (Figure 1). The experiment followed the transfer of the Cm(III) ion from an aqueous nitrate solution into an organic phase containing bis(2-ethylhexyl)phosphoric acid (HDEHP) – a hard electron donor dissolved in *n*-dodecane. The extraction of metal ions by HDEHP is a well characterized liquid-liquid partitioning system, utilizing a cation exchanging organophosphate phase transfer reagent.

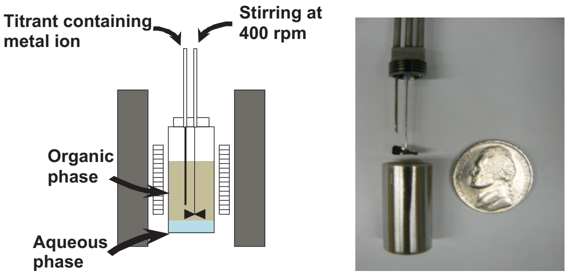

Figure 1. Schematic illustration of the calorimetric titration vessel, and calorimetric cup to scale.

When aqueous mildly acidic (pH ~ 3) solutions containing metal ions of the oxidation states II, III, and IV are contacted with the organic mixtures of HDEHP the hydration sphere of the metal is replaced by a number of coordinating donor groups of HDEHP. This reaction occurs at the aqueous/organic interface, where the metal is coordinated by three HDEHP dimers, the metal ion then crosses the phase boundary and enters the organic environment according to Equation 1 where HL is HDEHP and the horizontal bar represents species in the non-aqueous phase:[12]

$$Cm^{3+} + \overline{3(HL)_2} \leftrightarrow \overline{Cm(LHL)_3} + 3H^+ \qquad \text{Equation 1.}$$

The net enthalpy of reaction for the liquid-liquid partitioning of a metal ion across a phase boundary is the product of all of the enthalpy terms involved in the process including, but not limited to, metal ion dehydration, electrostatic bonding interactions and solvation of the newly formed extracted species in the organic phase. The overall change of energy in the system can be detected calorimetrically. The change in the enthalpy of transfer across the liquid-liquid boundary – ΔH_{tr} – describes the process quantitatively according to $\Delta H_{tr} = q/\Delta m$, where q is the calorimetrically detected heat associated with the reaction and Δm is the molar amount of solute that crosses the liquid-liquid interface.

Direct calorimetric measurement of ΔH_{tr} was afforded by careful design of experimental conditions to facilitate liquid-liquid partitioning process. The calorimetric vessel contained both aqueous (120 μL) and non-aqueous (800 μL) solutions and the reference cell was also filled with 120 μL nitrate solution and 800μL of organic phase. The aqueous phase consisted of 1.0 M sodium nitrate adjusted to a pH of 3.0. The organic phase was a 0.2 M solution of HDEHP in *n*-dodecane. The stirrer was rotating at 400 rpm to achieve good mixing of the two phases. Sequential additions of 10 or 20 uL of the appropriate titrant solution introduced the metal ion under study into the calorimetric reaction vessel. Initially, the experiments were performed with samarium, a lanthanide element with ionic radii similar to that of curium.[13] Two samarium conditions were tested prior to conducting the curium experiments, in the first experiment the samarium concentration in the titrant solution was 50 mM. As the curium concentration would be significantly lower than this a further test experiment was conducted using 5 mM Sm in the titrant to observe if the heat responses would be adequate at these metal ion concentrations. The initial curium experiment, 20 uL of 6.6 mM Cm in 1.0 M sodium nitrate was injected into the calorimetric cup. The second experiment was performed using the same titrant but only injecting 10 uL into the reaction vessel.

3. SUMMARY OF RESULTS

Figure 2 shows the calorimetric heat response for the extraction of Sm(III) by HDEHP from sodium nitrate solution at pH 3.0 ([Sm] = 5 mM, injection volume = 20μL). Each peak corresponds to the increasing heat transfer rate (μW/sec) as the calorimeter responds to the exothermic transfer of samarium ions across the liquid-liquid interface. Initial method development for calorimetric investigations of the heat of extraction of metal ions identified that other processes that accompany metal partitioning in a two-phase system yield insignificant heat signatures. As such the observed heat responses are solely responsible for the transfer of the metal ion across the phase boundary.[14]

The area under the peak can be integrated to give a net change of energy in the system (*q*), which is directly related to the concentration of metal ion titrated into the calorimetric reaction vessel via Equation 2.

$$\Delta H = \frac{q}{\Delta m} \qquad \text{Equation 2}$$

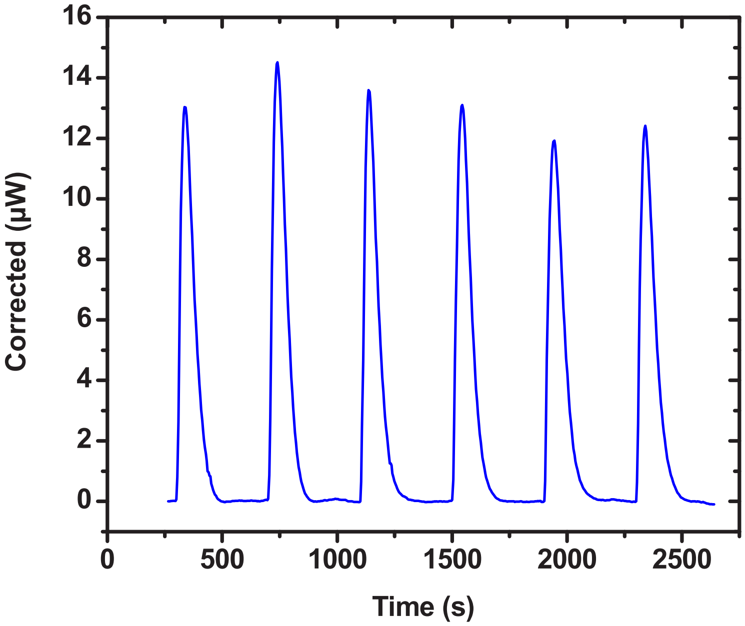

Figure 2. Calorimetric power compensation trace collected for the *liquid-liquid* distribution of Sm(III). Aqueous phase: pH 3.0, [NaNO$_3$] = 1.0 M, [Sm(III)] = 5 mM . Organic phase: 0.2 M HDEHP in *n*-dodecane, titrant injection size = 20 μL.

For the two samarium experimental conditions studied (titrant metal concentration of 50 mM and 5 mM) the average heat of extraction obtained was –10.7 ± 1.0 kJ mol-1. This value is in reasonable agreement with the previously obtained value -10.9 kJ mol^{-1}, obtained by Zalupski using the same methodology at Washington State University (WSU). With the setup and methodology at INL reproducing viable results, the curium experiments were conducted. Figure 3 shows the power compensation trace for the extraction of 6.6 mM curium into 0.2 M HDEHP in dodecane. To obtain reasonable heat compensation traces in the initial investigation 20 μL injections of titrant were made as with the samarium experiment. On inspection of Figure 3 it can be seen that the heat responses were significantly higher than those obtained in the samarium experiments. As such, the subsequent experiment performed used a 10 μ L sample injection size (Figure 4). One qualitative point of note is that in the curium experiments there is some tailing on these peaks. This feature notably extends the time to complete the experimental heat of extraction determination. It is worthy of mention here that this was not observed in the americium experiments that were conducted in FY-10 and possibly could be due to kinetic differences in the extraction of curium over the other elements that have been studied using this technique. Further solvent extraction experiments would be required to verify that this is the case. The results for all of the heats of extraction experiments are shown in Table 1.

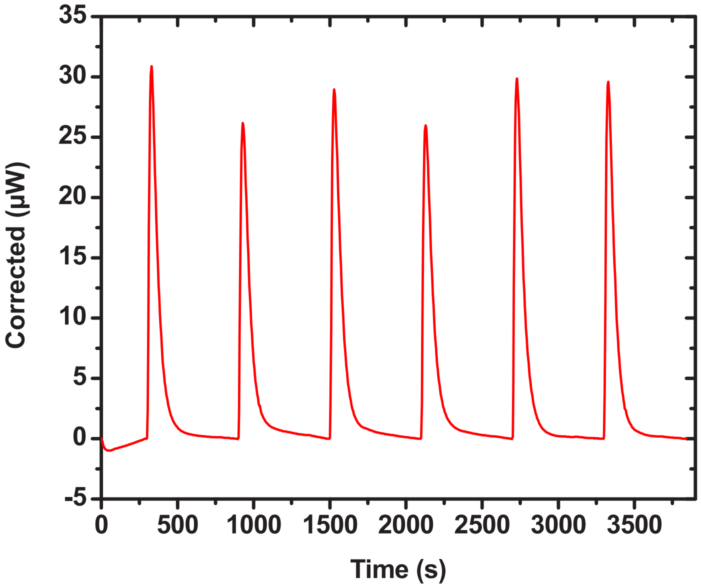

Figure 3. Calorimetric power compensation trace collected for the *liquid-liquid* distribution of Cm(III). Aqueous phase: pH 3.0, $[NaNO_3] = 1.0$ M, $[Cm(III)] = 6.6$ mM . Organic phase: 0.2 M HDEHP in *n*-dodecane, titrant injection size = 20 μL.

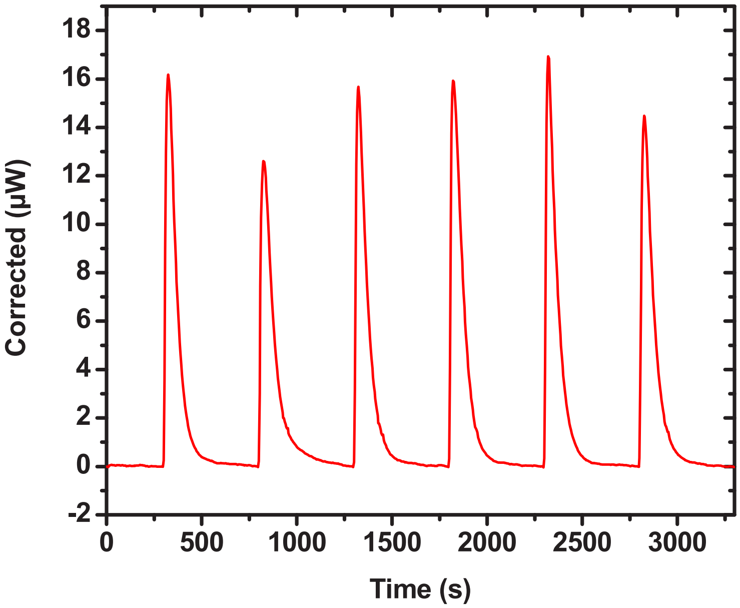

Figure 4. Calorimetric power compensation trace collected for the *liquid-liquid* distribution of Cm(III). Aqueous phase: pH 3.0, $[NaNO_3] = 1.0$ M, $[Cm(III)] = 6.6$ mM . Organic phase: 0.2 M HDEHP in *n*-dodecane, titrant injection size = 10 μL.

Table 1. Heats of extraction and errors determined for samarium and curium in the biphasic calorimetry experiments.

Experiment	Average peak area/ μJ	Standard deviation	% RSD	ΔH extraction/ kJ mol^{-1}
[Sm] = 50 mM, 10 μL injection	-5838.08	228.96	-3.9	-11.7 ± 0.9
[Sm] = 5 mM, 20 μL injection	-957.40	36.37	-3.8	-9.6 ± 0.7
[Cm] = 6.6 mM, 20 μL injection	-2107.23	70.12	-3.3	-16.0 ± 1.1
[Cm] = 6.6 mM, 10 μL injection	-1110.09	50.52	-4.6	-16.8 ± 1.5

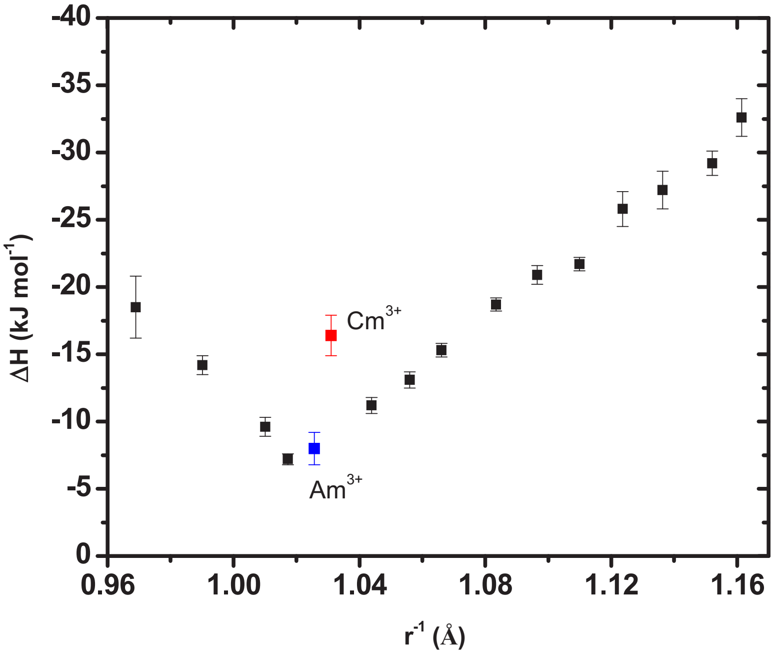

Figure 5. The comparison of the heat of extraction for the HDEHP-facilitated liquid-liquid partitioning of Cm and Am with those reported for the lanthanide series as a function of ionic radii for 6 coordinate metal ion.

Although the experimentally determined heats of extraction for curium are internally consistent they are surprisingly high (Figure 5). In the americium experiments that were conducted in FY-10 the average peak area for these extractions was calculated as -402 ± 30 μJ (±1σ), this is equivalent to a ΔH extraction of -8.0 ± 1.2 kJ/mol (±2σ). This is somewhat unusual as there is literature precedence that heats of extraction for americium and curium being similar when the same extractant system is being studied.[15] Unfortunately, due to the rarity of curium research, there are no reported heats of extraction for curium extraction by HDEHP in the open literature for direct comparison. Further, unlike the americium work reported on in FY-10, we cannot calculate the entropy term for this reaction until solvent extraction experiments have been performed to develop K_{ex} for this reaction and, correspondingly, the Gibbs free energy of extraction.

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