

Talspeak Curve: An Illustration of a See-Saw Effect in Separations

11th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation

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November 2010

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



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TALSPEAK CURVE: AN ILLUSTRATION OF A SEE-SAW EFFECT IN SEPARATIONS

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Abstract

A superbly balanced thermodynamic struggle for metal ion coordination by aqueous aminopolycarboxylate reagent, DTPA, and non-aqueous organophosphorous phase transfer reagent, HDEHP, affords the separation of trivalent actinides from trivalent lanthanides under the umbrella of the Talspeak liquid-liquid distribution process. This thermodynamic relationship has been linked to an analogous “see-saw” behavior, where the balance is distorted when either of the key complexing players is subject to adverse conditions that interfere with their optimal operation. The thermodynamic balance is tipped in favour of HDEHP whenever increased acidity of the aqueous solution out-competes the metal ion complexation by aqueous complexing agent. Also enhanced steric crowding may switch-off efficient coordination of the metal ion. When HDEHP is depolymerised due to the presence of aliphatic alcohol in the organic phase its phase transferring power is diminished. Such complication paves way for DTPA to establish its dominance on the distribution of trivalent metal ions in the 2-phase system. The illustrated sensitivity of the thermodynamic balance between DTPA and HDEHP in Talspeak-type systems may serve as informative tool when studying less-predictable realms of Talspeak chemistry.

Introduction

In solvent extraction the modification of the aqueous phase conditions to produce a holding-back influence that opposes the phase transfer process allows to design some of the most challenging of separations. An example of such system positions an aqueous soft donor aminopolycarboxylate complexing agent, diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid, DTPA, against a powerful cation exchanger, di(2-ethylhexyl)phosphoric acid, HDEHP. Such is the backbone of the TALSPEAK process ((Trivalent Actinide – Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes), a liquid-liquid distribution system designed to accomplish the An/Ln inter-group separation [1]. Scheme 1 shows the structures of the main components of the Talspeak process. An aqueous complexant preferentially holds the actinides in aqueous lactate buffer solution, while lanthanides are extracted into an organic phase by HDEHP. Although never quantified, weak covalent interactions between the soft Lewis base ligands such as DTPA and the actinides have been suggested as the source of the observed complexing preference over lanthanides [2]. Otherwise, *f*-element contraction renders the aqueous chemistries of Am(III) and Cm(III) equivalent to Nd(III), Pm(III) and Sm(III) when electrostatic interactions dominate the complexation by oxygen-donating ligands [3]. However, the actinide/lanthanide separation in this system is not accomplished solely due to the enhanced thermodynamic stability of DTPA/ An^{3+} complexes. Rather, it is the influence that the resultant product of the “DTPA vs. HDEHP battle” has on the lanthanide group extraction. The opposing complexing forces of DTPA and HDEHP illustrate a striking thermodynamic relationship, which, depending on the experimental conditions, favors either side and determines the final shape of the characteristic Talspeak lanthanide extraction curve. This relationship affects the U-shape of the curve similarly to a “see-saw” balancing act. Here we present several fundamental liquid-liquid distribution exercises that clearly illustrate this remarkable effect.

Scheme 1. Structures of key components of Talspeak-type actinide/lanthanide separation, i.e. diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid and di(2-ethylhexyl)phosphoric acid.

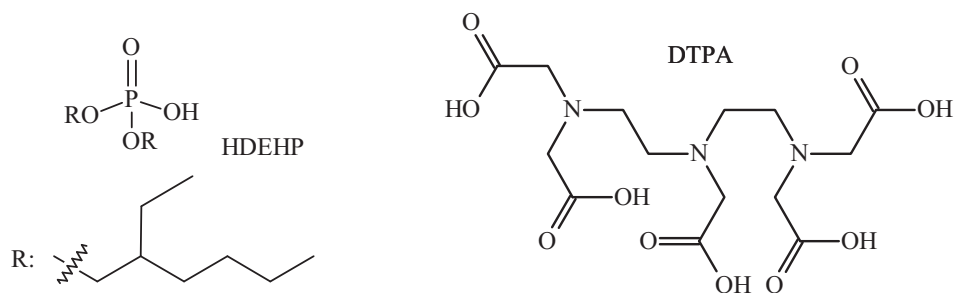
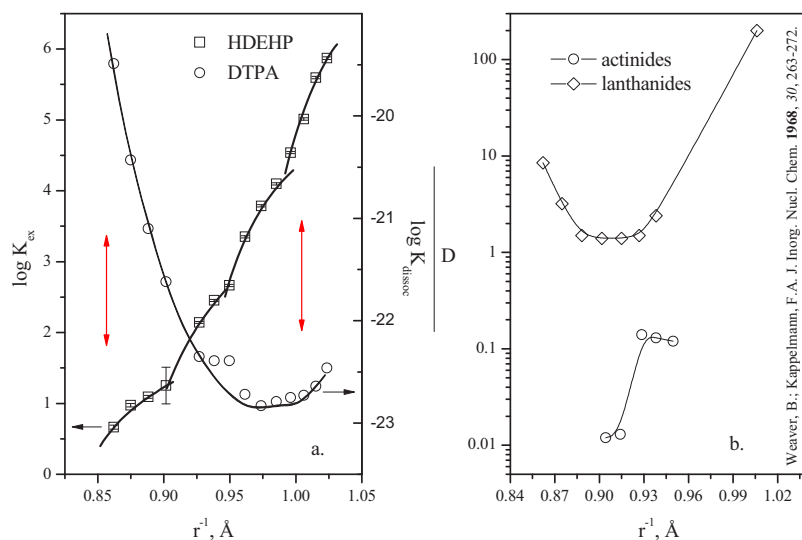


Figure 1 details the origins of the thermodynamic balance established between DTPA and HDEHP. Without mutual intrusion the strength of complex formation for both reagents is governed predominantly by the increasing charge density of a trivalent lanthanide metal ion. The remarkable range of electrostatic interaction, spanning over 5 orders of magnitude across the lanthanide series, has been a signature of the phase transfer characteristics of HDEHP [4]. Examining the thermodynamic trend for the lanthanide de-complexation constants [5] conveys the influence of DTPA on the liquid-liquid distribution of lanthanides more clearly as such complexes must dissociate prior to phase transfer. The trend illustrates large differences in the bonding strength for the light members of the lanthanide series, while, largely due to the steric clashes, the complexation of heavier lanthanides by DTPA deviates from the predicted trend based on electrostatics. The thermodynamic trends presented this way illustrate the balancing relationship that guides the extraction of lanthanides in Talspeak-type separations. When a two-phase system lines up DTPA and HDEHP against each other the

thermodynamic power struggle positions the reagents at the ends of the Talspeak lanthanide curve, where their complexing influence is most prominent. The relative ease of dissociation of light lanthanide DTPA complexes enhances their partitioning into the organic phase, twisting up the linear K_{ex} trend of HDEHP. This exact feature of DTPA-containing mixtures allows to accomplish the separation of actinides from lanthanides and renders Talspeak successful. At the other end of this thermodynamic “see-saw” rests HDEHP, whose electrostatic interactions with the heavier lanthanides favour the extraction.

The clash between the holdback reagent and the phase transfer reagent presents an intriguing test ground for further examination of the described thermodynamic relationship. The Talspeak-type distribution system may be manipulated to study the shifting balance of lanthanide extraction curve as the experimental conditions interfere with an optimal performance of either reagent. Such strategic experimental complications illustrate a see-saw effect in solvent extraction. This study presents several liquid-liquid distribution exercises where the lanthanide complexation of DTPA was progressively switched-off as the pH of the aqueous phase is decreased. This interfering pH effect on the DTPA speciation was counterbalanced by employing polyaminophosphonates as more acidic holdback reagents to determine if the relationship persists. To disrupt the HDEHP-controlled end of the Talspeak lanthanide curve the metal distribution was studied when conventional aliphatic diluent was replaced by a depolymerising aliphatic alcohol as an organic medium.

Figure 1. (a) Opposing thermodynamic forces in the Talspeak separation as quantified for lanthanide elements by extraction constants (HDEHP) and complex dissociation constants (DTPA), plotted as a function of reverse ionic radius. For extraction constants, org: HDEHP in *n*-dodecane, aq: 1.0 M (H^+, Na^+) ClO_4 . Dissociation constants were taken from NIST database. (b) Final liquid-liquid distribution of actinides and lanthanides – a result of the thermodynamic struggle for balance between DTPA and HDEHP.



Experimental

The ^{241}Am , ^{139}Ce and ^{154}Eu radioisotopes were obtained from Idaho National Laboratory (INL) stocks. Pentasodium salt of DTPA (Alfa Aesar) and heptasodium salt of DTPP (Aldrich) were

standardized using complexometric titration using stock solution of europium nitrate (standardized using ICPMS) and xylenol orange as an indicator. EDTP was purchased in acid form from Aldrich and sampled gravimetrically. Trisodium citrate, dimethyl glycine and ammonium sulfamate were purchased from Aldrich and used as received. Reagent grade *n*-dodecane (99%), bis(2-ethylhexyl)phosphoric acid (97%) and lactic acid (85% w/w) were purchased from Aldrich and used as received. Exxal 12 Dodecyl alcohol (98%) was purchased from Exxon Mobile Chemical as used as received. Aqueous metal ion solutions were prepared using water from a Barnsted E-pure system and 70% (w/w) HNO₃ (Aldrich, Trace Metal Grade). All aqueous solutions contained 0.05 M Na₅DTPA. Depending on the aqueous conditions a specific buffer was used, chosen for the proximity of a dissociation constant to pH under investigation. All solutions contained 1.0 M buffer concentrations, and the pH was adjusted to 3.5 (lactate), 3 (citrate), 2 (dimethyl glycine) and 1 (sulfamate) using nitric acid.

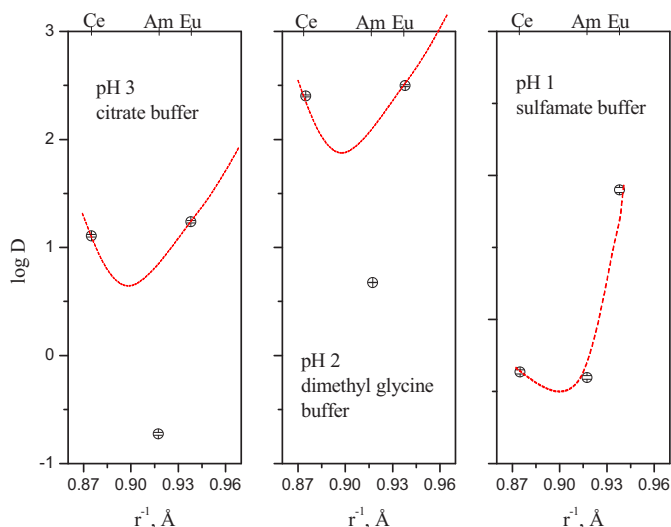
Metal extraction was quantified by the distribution ratio, *D*, calculated as the ratio of the equilibrium concentration of the radiotracer in the organic phase to that in aqueous phase. The organic solutions of the extractant were pre-equilibrated with equal volumes of aqueous perchlorate solution immediately prior to use. An aliquot of the pre-equilibrated organic phase was then contacted with an equal volume of the identical aqueous phase spiked with radiotracers. The two phases were vigorously shaken for 15 minutes at room temperature. The samples were centrifuged to facilitate phase separation and aliquot of each phase was taken for radiometric measurements using a HPGe gamma spectrometry.

Results and Discussion

Figure 2 illustrates the liquid-liquid distribution of Am(III), Ce(III) and Eu(III) for the investigated Talspeak-type systems, where the pH of aqueous phase was adjusted to 3, 2 and 1, respectively. Acidity in the aqueous solutions was controlled by different buffering reagents, chosen for the proximity of their dissociation constants to the targeted pH condition, to illustrate the inertness of the aqueous buffering media toward the overall outcome of the Talspeak separation. At pH 3 the extraction behavior of the investigated metal ions parallels the expected outcome for Talspeak actinide/lanthanide separation [1]. Based on the distribution ratios for Ce(III) and Eu(III) an expected distribution curve for the entire lanthanide series may be re-constructed based on its usual proportions. Inspecting the trend a separation factor between neodymium and americium was estimated at 21, and the separation factor between cerium and americium was 68. The accomplished separations, at the specified conditions, are indicative of well-balanced system of opposing forces in Talspeak. At pH of 3 an acid/base speciation of DTPA permits metal complexation, while HDEHP exerts a strong ion-exchanging influence. Consequently, all features of Talspeak separation are on display here, as the extraction of light lanthanides is enhanced and the americium is retained in the aqueous phase.

When the pH of the aqueous phase was decreased to 2 the separation failed. The thermodynamic balance between the DTPA and HDEHP is still maintained, judging from the consistent shape of the Talspeak lanthanide curve. However, aqueous complexation is now limited by the acid/base equilibria of DTPA (at pH of 2 50% exists as fully protonated acid) [5]. While the holdback influence of DTPA is compromised, it's preference for actinide coordination remains, yielding a separation factor of 19 between neodymium and americium. The dominance of HDEHP is exemplified by the significant enhancement of all metal distribution ratios, as the complexing power of DTPA is weakened by the increasing acidity.

Figure 2. Distribution of Am(III), Ce(III) and Eu(III) for DTPA-containing Talspeak-type liquid-liquid systems. Org: 0.1 M HDEHP in *n*-dodecane. Aq: 0.05 M DTPA, 1.0 M appropriate buffer adjusted to pH under investigation.

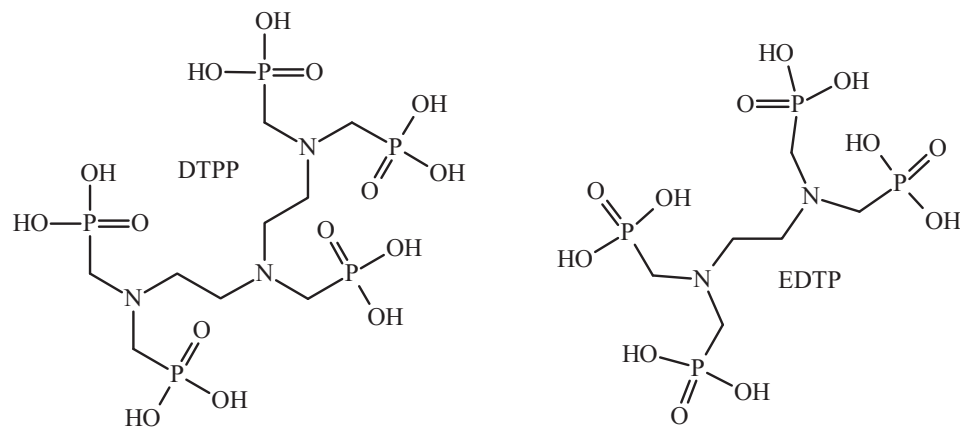


The final and most adverse condition ($\text{pH} = 1$) demonstrates a complete failure of the Talspeak-type separation, where beneficial complexing properties of DTPA are nearly completely switched off. The characteristic Talspeak lanthanide curve is distorted by the remaining coordinating force, tipping the balance of the thermodynamic “see-saw” in favour of HDEHP. As such the distribution ratios for the investigated metals shift in accordance with the expected linear trend for the extraction of the lanthanide series by HDEHP. The distribution of cerium decreases, relative to europium, and vice versa. As DTPA no longer interacts with americium its distribution is guided by electrostatic interaction with oxygen-donating HDEHP. As the charge density of trivalent americium is similar to that of Pm(III) [6] no actinide/lanthanide separation is observed and the distribution ratio of americium is pulled up toward lanthanide trend. The overall decrease in the extraction efficiency for all metals may be attributed to a steep correlation between the HDEHP-facilitated ion-exchanging mechanism of phase transfer and the acidity of the aqueous phase.

To further investigate the effect of acidity polyaminophosphonates holdback reagents were introduced into the system. Phosphonic acid functionality dissociates two protons and, due to the strong electron-inducing influence of the initially dissociated proton, the second deprotonation step is much delayed, relative to the carboxylic acid. Accordingly, polyaminophosphonates are stronger acids, and, as such, their complexing behavior, i.e. holdback influence, should be extended into aqueous conditions of higher acidity. Scheme 2 shows the structures of the diethylenetriamine- $\text{N,N,N',N'',N'''}\text{-pentaphosphonic acid}$, DTPP, and the ethylenediaminetetraphosphonic acid, EDTP, employed in the study.

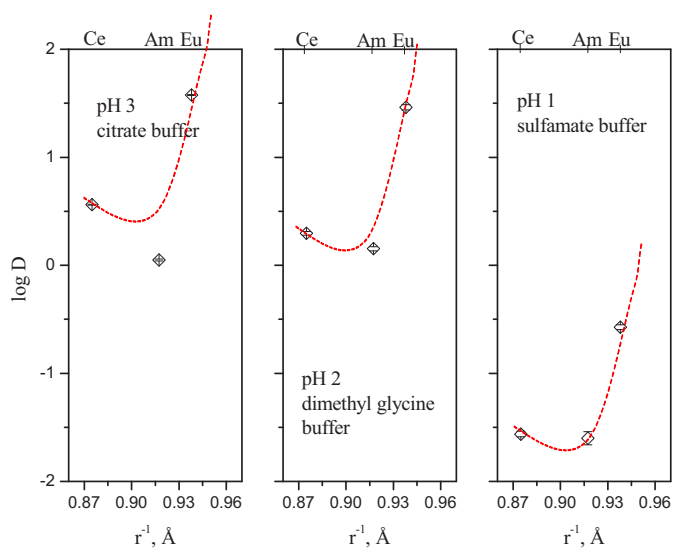
Figure 3 shows the distribution of Am(III), Ce(III) and Eu(III) between aqueous solutions of varying acidity, when DTPP was present as an aqueous complexant, and organic solution of HDEHP in *n*-dodecane.

Scheme 2. Structures of the aqueous phosphonic acid complexing agents investigated within Talspeak-type actinide/lanthanide separation framework, i.e. diethylenetriamine-N,N,N',N'',N'''-pentaphosphonic acid, DTPP, and the ethylenediaminetetraphosphonic acid, EDTP.



Inspecting the initial set of conditions (pH 3) it is apparent that the phosphonate analog of DTPA fails to differentiate between actinides and lanthanides. As such the presence of the phosphonic acid functionalities renders the complexing agent either too hard or too sterically hindered to allow for any weak covalent interactions with actinides. The steric factors may also explain why the Talspeak lanthanide extraction curve is skewed in favour of HDEHP-controlled extraction already at the pH of 3. Although the thermodynamic parameters for the complexation of lanthanides by

Figure 3. Distribution of Am(III), Ce(III) and Eu(III) for DTPP-containing Talspeak-type liquid-liquid systems. Org: 0.1 M HDEHP in *n*-dodecane. Aq: 0.05 M DTPA, 1.0 M appropriate buffer adjusted to pH under investigation.



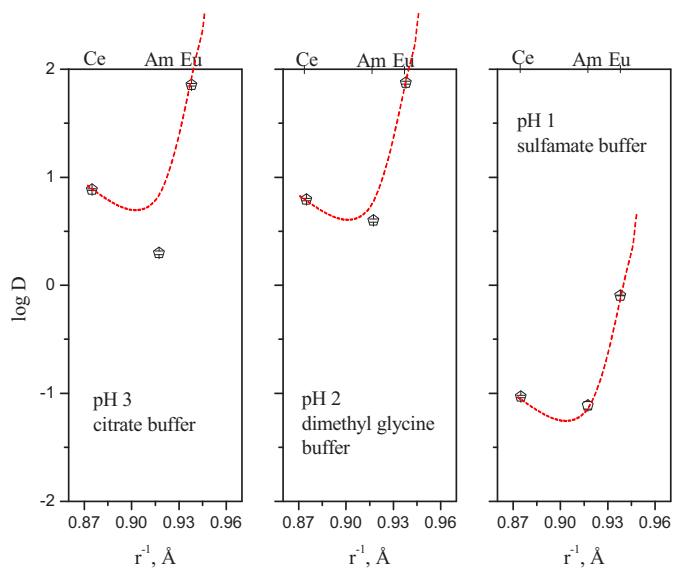
aminopolyphosphonates are not available it is reasonable to conclude that a characteristic increase in the stability of lanthanide:DTPA complexes for the light members of the series is diminished for the

phosphonate class of reagents [5]. Here, the steric clashes observed for the heavy lanthanides in the DTPA system are likely to affect the complex formation throughout the entire lanthanide series. Accordingly, a weaker influence of DTPP on the extraction of light lanthanides results in the off-balanced thermodynamic relationship between the coordinating reagents.

As hypothesized the holdback power of the aqueous complexing aminopolyphosphonate reagent is enhanced in the aqueous solutions of higher acidity. The metal distribution ratios are 1-2 orders of magnitude lower for the extraction of lanthanides from pH 2 solutions, relative to those collected with DTPA in solution. At pH of 1 the combination of strong aqueous complexation and high hydrogen ion concentration significantly suppress the distribution ratios.

Very little difference in the liquid-liquid distribution of Am(III), Ce(III) and Eu(III) was observed when a smaller aminopolyphosphonate reagent – a phosphonic acid derivative of EDTA – was used as aqueous complexant. Figure 4 illustrates similarly-affected extraction trends, suggesting that the steric crowding does not diminish as the number of phosphonic acid functionalities is decreased. The comparable behavior of DTPP and EDTP could possibly single out the general flexing inadequacy of bulky aminopolyphosphonate reagents when coordinating trivalent metal ions. The holdback efficiency is preserved, however, due to the purely electrostatic interactions. The aqueous complexation by EDTP is also reflected in the observed metal distribution ratios, which is a slightly weaker suppressant, relatively to DTPP.

Figure 4. Distribution of Am(III), Ce(III) and Eu(III) for EDTP-containing Talspeak-type liquid-liquid systems. Org: 0.1 M HDEHP in *n*-dodecane. Aq: 0.05 M DTPA, 1.0 M appropriate buffer adjusted to pH under investigation.

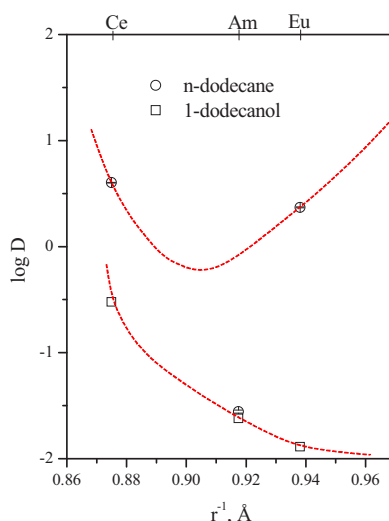


To shift the attention to the opposite end of the thermodynamic balancing act it is required to study the effects that complicate the extraction behavior of HDEHP. This organophosphate phase transfer reagent is a cation exchanger, which, in non-aqueous environment, forms dimers and possibly higher aggregates at high HDEHP concentrations [7]. A well-characterized HDEHP-mediated mechanism of trivalent metal ion phase transfer involves a coordination of the metal by three extractant dimers and the release of three protons into the aqueous phase [8]. It has been shown previously that this mechanism of metal extraction is compromised in presence of a depolymerizing

alcoholic diluent, such as dodecanol [9]. As such, a substitution of *n*-dodecane for an aliphatic alcohol, when studying Talspeak-type separation systems, presents an opportunity to interfere with the normal phase transfer behavior of HDEHP.

Figure 5 compares the distribution of Am(III), Ce(III) and Eu(III) for Talspeak-type separation systems, where aqueous phase is kept constant (0.05 M DTPA, 1.0 M H^+/Na^+ , Lac^- , pH 3.5, $[Lac^-] + [Cl^-] = 1$ M), and HDEHP is dissolved in aliphatic and alcoholic media. At pH 3.5 the influence of DTPA's complexation chemistry grows as shown by the hypothesized Talspeak curve for lanthanide extraction. The trend in the distribution ratios for Ce(III) and Eu(III) is reversed, relative to the system studied at pH 3, with cerium being extracted stronger than europium. Separation factors are also reversed ($SF_{Am}^{Ce} = 144$, $SF_{Am}^{Eu} = 84$ at pH = 3.5, $SF_{Am}^{Ce} = 68$, $SF_{Am}^{Eu} = 92$ at pH = 3.0) as DTPA strengthens its grip when balancing the extraction of light lanthanides.

Figure 5. The comparison of distribution ratios for Am(III), Ce(III) and Eu(III) collected at normal aqueous Talspeak conditions (0.05 M DTPA, 1.0 M H^+/Na^+ , Lac^- , pH 3.5), where an organic diluent varies between aliphatic hydrocarbon, *n*-dodecane, and aliphatic alcohol, 1-dodecanol.



A powerful phase transferring capacity of HDEHP is practically eliminated in a depolymerising alcoholic media. Dodecyl alcohol – a hydrogen bond donor – effectively coordinates with HDEHP, breaking up the extractant dimers. In this case the thermodynamic drive to the phase transfer of the metal ion into the organic environment is significantly diminished as the formation of the polar solvation packet is more difficult. Figure 5 illustrates the significant loss of extraction efficiency by HDEHP. To collect measurable distribution ratios the concentration of HDEHP was increased from 0.1 M to 0.3 M in the alcoholic media, further underlining the effect. Interestingly, the distribution of americium appears unaffected; reiterating that liquid-liquid distribution of trivalent actinides in Talspeak systems is dominated by the aqueous complexation chemistry of aminopolycarboxylate reagent. Similar distribution ratios for americium suggest that its partitioning is not influenced by the presence of powerful phase transfer reagent. In contrast, the extraction of lanthanides is significantly affected, with the efficiency of europium extraction suffering most.

With the elimination of strong thermodynamic drive to phase transfer exerted by HDEHP the thermodynamic balance is tipped in favour of the complexation by DTPA. The extraction of europium by HDEHP, based on the increasing effective charge density across the Ln series, is significantly

stronger to that of cerium. As a result the distribution ratio for europium in the alcohol-modified Talspeak system drops the most. Furthermore, owing to the relative ease of $\text{DTPA}:\text{Ce}^{3+}$ complex dissociation the extraction of cerium is promoted, relative to that of europium. In consequence, the trend for the extraction of trivalent metal ions in Talspeak-type system, where a depolymerising presence of alcohol turns off the usual mechanism of metal ion extraction by dimeric HDEHP, reverts to resembling a thermodynamic trend of lanthanide/DTPA complex dissociation. It is worth noting that a stronger complexation of Am(III) by DTPA, relative to similar trivalent lanthanides, does not contribute any meaningful enhancement in terms of An/Ln separation unless HDEHP is correctly functioning in the 2-phase system. It is the remarkable see-sawing balance between two powerful complexing agents that results in the accomplishment of one of the most challenging of separations.

Conclusions

A superbly balanced thermodynamic struggle for metal ion coordination by aqueous aminopolycarboxylate reagent, DTPA, and non-aqueous organophosphorous phase transfer reagent, HDEHP, affords the separation of trivalent actinides from trivalent lanthanides under the umbrella of the Talspeak liquid-liquid distribution process. This thermodynamic relationship has been linked to an analogous “see-saw” behavior, where the balance is distorted when either of the key complexing players are subject to designed adverse conditions that interfere with their optimal operation. The thermodynamic balance is tipped in favour of HDEHP whenever increased acidity of the aqueous solution outcompetes the metal ion complexation by aqueous complexing agent. Also enhanced steric crowding may switch-off efficient coordination of the metal ion. When HDEHP is depolymerised due to the presence of aliphatic alcohol in the organic phase its phase transferring power is diminished. Such complication paves way for DTPA to establish its dominance on the distribution of trivalent metal ions in the 2-phase system. The illustrated sensitivity of the thermodynamic balance between DTPA and HDEHP in Talspeak-type systems may serve as informative tool when studying less-predictable realms of Talspeak chemistry.

Acknowledgement

Support for this work was from the Fuel Cycle Research and Development program (FCR&D), U.S. Department of Energy, Office of Nuclear Energy, under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

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