Methods for Enhancing the Rates of Dissociation of the *f*-Element / Aminopolycarboxylate Complex for Efficient Differentiation of Trivalent Actinides from Trivalent Lanthanides in the ALSEP Process

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Potentiometric and spectroscopic techniques were used to evaluate the coordination behavior and thermodynamic features of trivalent *f*-element complexation by modified aminopolycarboxylate reagents, HEDTTA and DTTA-BuA. Time dependency trends for the forward extraction of trivalent europium present in aqueous environments of HEDTTA or DTTA-BuA are compared with conventional aminopolycarboxylates. The Eu^{3+} distribution patterns show that significant enhancements to the rates of metal extraction may result either from reduction of reagent's polydenticity (HEDTTA) or manipulation of reagent's acid/base chemistry to capitalize on proton–catalyzed dissociation of *f*-element complexes (DTTA-BuA). When translated onto ALSEP chemistry platform, where trivalent americium is back-extracted from organic solvent containing solvating diglycolate extractant TEHDGA and phosphonic acid extractant HEH[EHP], the latter strategy of using a reagent of enhanced total acidity proves promising.

1. Introduction

Actinide Lanthanide Separation (ALSEP) extraction process was developed to isolate trivalent americium from aqueous effluents remaining after the initial recovery of uranium and/or plutonium from dissolved used nuclear fuel [1]. The initial step of the process co-extracts trivalent actinides (An^{3+}) and trivalent lanthanides (Ln^{3+}) from a diverse mixture of fission, activation and corrosion products using a combination of diglycolamide extractant, *N,N,N′,N′*-tetra(2-ethylhexyl)digylcolamide (TEHDGA), and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]), dissolved in an aliphatic diluent. This ALSEP solvent, when "loaded" with the trivalent *f*-elements, is later equilibrated with an aqueous mixture containing the aminopolycarboxylate complexant to afford a complete differentiation of trivalent An^{3+} from trivalent Ln according to a well-known reversed TALSPEAK concept [2]. Such strategy for An^{3+} back-extraction affords best results when using diethylenetriamine-*N,N,N′,N′′,N′′*-pentaacetic acid (DTPA), capable of octadentate coordination of trivalent *f*-elements [3].

While the octadentate coordination of *f*-elements by DTPA yields efficient An^{3+}/Ln^{3+} separation it is also responsible for slow rate of liquid-liquid mass transfer. The binding pocket contains seven
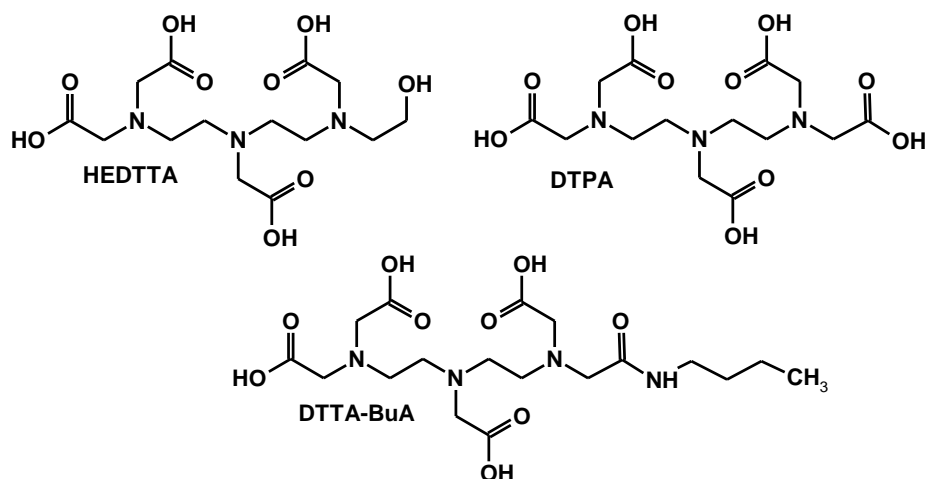
Figure 1. Structures of *N*-hydroxyethyl-*N,N′,N″,N″*- diethylenetriaminetetraacetic acid, HEDTTA, *N*-butylacetaamide-*N,N′,N″,N″*-diethylenetriaminetetraacetic acid, DTTA-BuA and diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid, DTPA.

stable five-membered chelate rings, with three nitrogens and five oxygens coordinating the metal ion. Accordingly, the metal is well shielded from the interactions with the water molecules, resulting in kinetic inertness. Accordingly, numerous investigations have been focused on structure-function relationships for aminopolycarboxylate aqueous holdback reagents, with an ultimate goal of improving the observed kinetic impediment [4-6].

The interfacial mass transfer of trivalent metal ions in liquid-liquid systems of TALSPEAK-type chemistry is fully controlled by the rate of interfacial chemical reactions, as argued by Danesi and Cianetti [7]. Here, all aqueous species (Eu^{3+}, Eu-hydroxy-carboxylic acid, Eu-aminopolycarboxylate, and complexes with secondary ligand) interact with surface-active liquid cation exchanger at the interface. Accordingly, direct structural modification of molecular species partaking in the interfacial reactions offers one opportunity to enhance the mass transfer.

For the aminopolycarboxylate aqueous holdback complexants, the structural alteration of one or more acetate pendant arms of DTPA molecule may reduce its denticity and/or modify its acid/base chemistry. Such changes to the coordination chemistry offer options for the enhancement of phase transfer kinetics in liquid-liquid systems containing aminopolycarboxylates. Two strategies for structural modification of DTPA to enhance the phase transfer kinetics in liquid-liquid distribution systems designed for efficient An^{3+}/Ln^{3+} differentiation are discussed. First, a replacement of single acetate functionality of DTPA with *N*-hydroxyethyl group (*N*-hydroxyethyl-*N,N′,N″,N″*-diethylenetriaminetetraacetic acid, HEDTTA) reduces the coordination sphere of a metal ion. Second, substitution of acetate arm by strongly electron-withdrawing *N*-amide group (*N*-butylacetamide-*N,N′,N″,N″*-diethylenetriaminetetraacetic acid, DTTA-BuA), while maintaining an octadentate environment, impacts the protonation equilibria of this reagent. Figure 1 compares the structures of HEDTTA, DTTA-BuA with that of DTPA. Metal ion coordination behavior and the kinetic studies for the distribution of trivalent *f*-elements in liquid-liquid systems containing HEDTTA and DTTA-BuA are presented.

2. Experimental

2.1 Reagents

All chemicals were reagent grade or higher and used without further purification except where noted. Aqueous solutions were prepared using de-ionized water (MilliQ, 18 MΩ). Sodium perchlorate and sodium nitrate (GFS Chemicals) were purified by recrystallization from hot water. The $NaClO_4$ and $NaNO_3$ stock solutions were prepared by dissolving solid salts in HPLC-grade water. The concentrated solutions of $NaClO_4$ and $NaNO_3$ were filtered through a glass fine frit filter to remove undissolved particulates and recrystallized. Resulting crystals were dissolved in 18MΩ H_2O and standardized by ion exchange (Dowex 50X8, H^+ form). The column eluent was titrated with standardized NaOH (triplicate analysis). $Eu(NO_3)_3$ (Molycorp, 99.99%) was used to prepare solutions for Eu^{3+} complexation studies by potentiometry. Aqueous holdback reagents H_5DTPA and H_4EDTA were recrystallized from hot water. Novel aqueous holdback reagents *N*-hydroxyethyl-*N,N′,N″,N″*-diethylenetriaminetetraacetic acid and *N*-butylacetaamide-*N,N′,N″,N″*-diethylenetriaminetetraacetic acid were prepared at ORNL as hydrochlorate salts with >97 % purity. Concentrated perchloric (Aldrich, 99.999% trace metal basis) was used to prepare the acid solutions used in potentiometric work. Concentrated reagent grade nitric acid (Aldrich, 70% w/w, ACS reagent grade) and 50% w/w aqueous NaOH (Aldrich) were used for pH adjustment of aqueous mixtures for solvent extraction studies. The extractant 2-(ethylhexyl)phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) was purchased from Marshallton Laboratories, and *N,N,N′,N′*-tetra(2-ethylhexyl)diglycolamide (TEHDGA) was purchased from Eichrom Technologies. Both reagents were used as received. Radiotracers [241]Am, [139]Ce and [154]Eu were introduced using a working stock mixtures prepared by blending aliquots of stocks purchased from Eckert&Ziegler.

2.2 Potentiometry

Potentiometric titrations were carried out using a Mettler Toledo T-70 Graphix auto-titrator equipped with a Ross Orion semi-micro glass electrode (5 mol·L^{-1} NaCl filling solution). The p[H^+] operational scale for the glass electrode was developed by Gran analysis [4] of a strong acid-strong base titration. All titrations were performed at 25.0 ± 0.1 °C (maintained with a circulating water bath attached to a jacketed beaker). Sodium perchlorate was used to control ionic strength at $I = 2.0$ mol·L^{-1}. Hydrated nitrogen gas was blanketed over titration solutions to prevent CO_2 absorption. Potentiometric titrations of initially standardized HEDTTA and DTTA-BuA solutions with NaOH were performed in triplicate and analyzed using Hyperquad 2013 software [4] to resolve the acid dissociation constants (K_a) and Eu^{3+} binding stability constants (β_{MHL}).

2.3 Phase transfer kinetic studies

The distribution experiments were measured using equal volumes (0.5 mL) of each phase. Samples were equilibrated using a Glass-Col multi-tube vortexer. Temperature was maintained at 20 ± 0.3°C using sample chamber connected to water circulator. At each time interval the retrieved samples were centrifuged for 30 seconds, and each phase sampled (0.3 mL) for radiometric measurements. Distribution ratios were defined as the quotient of concentration of the metal ion in the non-aqueous phase and the concentration of metal ion in the aqueous phase at equilibrium ($D = [M]_{org}/[M]_{aq}$), as

indicated by the detected radioisotope activity of both phases (cps_{Light}/cps_{Heavy}). Aqueous phases contained holdback complexant in 1 M $NaNO_3$, and were adjusted to $p[H^+] = 3.0$ (HEDTTA, DTPA, EDTA) and $p[H^+] = 2.0$ (DTTA-BuA) using NaOH. Buffers were omitted from the forward extraction experiments in order to slow down the phase transfer equilibrium. This strategy sought to magnify differences for the studied complexants when studied on a kinetic scale. To reduce uncertainty in liquid-liquid distribution the radiotracer [154]Eu was introduced into the aqueous mixture before the contact with the organic phase. The concentration of cation exchanger in the non-aqueous phase was chosen to ensure that bulk (>80%) of metal ion was extracted at liquid-liquid distribution equilibrium. Samples were vortexed (motor speed setting: 50), centrifuged, and sampled phases counted on the Packard D5003 Cobra Gamma counter. The 15-300 keV energy window was chosen for radiometric counting of [154]Eu.

The non-aqueous solvent used for the back-extraction kinetic studies was 0.05 M TEHDGA, 0.5 M HEH[EHP] in *n*-dodecane. The solvent was pre-equilibrated with 3 M HNO_3 prior to metal loading. After triplicate washing with 0.2 M citrate the three *f*-element radiotracers ([241]Am, [139]Ce, [154]Eu) were quantitatively co-extracted from 3 M HNO_3 into the solvent. The back-extraction of [241]Am was facilitated using three strip mixtures: a) 0.125 M HEDTTA, pH = 3.0, b) 0.015 M DTTA-BuA, pH = 2.0, c) 0.015 M DTPA, pH = 2.0, all buffered using 0.2 M ammonium citrate. For back-extraction experiments the pH was defined using NIST buffers 4 and 7. The centrifuged, separated phases were counted on an ORTEC GEM50P4 coaxial HPGe detector equipped with DSPEC gamma spectrometer (59.54 keV peak for Am-241, 123.07 keV peak for Eu-154, and 165.86 keV peak for Ce-139).

3. Results and Discussion
3.1 Acid dissociation constants and Eu^{3+} complexation

The influence of *N*-hydroxyethyl- and *N*-butylacetamide- functionalization on the hydrogen ion dissociation equilibria for HEDTTA and DTTA-BuA, respectively, was investigated using potentiometry. Table 1 summarizes the acid dissociation constants for all protonated species quantified using the glass electrode according to equation 1

$$H_{8-n}L^{4-n} \Leftrightarrow H_{7-n}L^{3-n} + H^+ \tag{1}$$

as compared with acid dissociation constants of DTPA generalized by equation 2.

$$H_{9-m}L^{4-m} \Leftrightarrow H_{8-m}L^{3-m} + H^+ \tag{2}$$

The reported acid dissociation constants for HEDTTA match closely with those reported for DTPA in 2.0 M $NaClO_4$ suggesting *N*-hydroxyethane- pendant arm substitution makes minimal inductive impact on the diethylenetriamine backbone. In contrast a clear indication of strong electronic influence of the amide functionality is present for DTTA-BuA, reflected in the enhanced acidity of its amine sites, relative to DTPA.

Table 1. Acid dissociation constants quantified using glass electrode for
HEDTTA, DTTA-BuA and DTPA at 25.0 ± 0.1 °C. I = 2.00 M
$(H^+,Na^+)ClO_4$. Uncertainties reported at ±3σ.

HEDTTA	n	$-\log_{10}K_a^{\,n}$	DTTA-BuA	n	$-\log_{10}K_a^{\,n}$	DTPA	m	$-\log_{10}K_a^{\,m}$
HL^{3-}	7	9.49 ± 0.02	HL^{3-}	7	9.34 ± 0.01	HL^{4-}	8	9.50
H_2L^{2-}	6	8.19 ± 0.01	H_2L^{2-}	6	6.65 ± 0.01	H_2L^{3-}	7	8.31
H_3L^-	5	4.31 ± 0.02	H_3L^-	5	4.09 ± 0.01	H_3L^{2-}	6	4.38
$H_4L_{(aq)}$	4	2.56 ± 0.02	$H_4L_{(aq)}$	4	2.42 ± 0.02	H_4L^-	5	2.53
H_5L^+	3	2.15 ± 0.02	H_5L^+	3	2.01 ± 0.03	$H_5L_{(aq)}$	4	2.41
H_6L^{2+}	2	-	H_6L^{2+}	2	-	H_6L^+	3	-
H_7L^{3+}	1	-	H_7L^{3+}	1	-	H_7L^{2+}	2	-
					-	H_8L^{3+}	1	-

While the *N*-hydroxyethyl group of HEDTTA does not partake in the metal ion coordination the amidic oxygen of DTTA-BuA chelates the metal ion, completing an octadentate coordination sphere similar to DTPA. Table 2 lists the stability constants for the complexation of Eu^{3+} by the reagents investigated here. The reduction of stability constant for the complexation of trivalent europium by

Table 2. Eu^{3+} complexation constants by HEDTTA, DTTA-BuA and DTPA at 25.0
± 0.1 °C. I = 2.00 M $(H^+,Na^+)ClO_4$. Uncertainties reported at ±3σ.

$\text{Log}\beta_{mhl}$	m=1, h=0, l=1	m=1, h=1, l=1
HEDTTA	17.92 ± 0.01	20.34 ± 0.02
DTTA-BuA	18.49 ± 0.02	20.40 ± 0.02
DTPA	21.03	22.53

HEDTTA matches the expected weakening due to the elimination of one 5-membered chelate ring from a coordination sphere of the metal ion [6]. The observed decreased value of the β_{101} for Eu^{3+}/DTTA-BuA stems from a significantly lower coordination strength of carbonyl-type oxygen, relative to carboxylic-type. Figure 2 shows the distribution of tracer (10^{-5} M) Eu^{3+} species calculated for a 1 < p[H^+] < 5 range using the assembled thermodynamic data for HEDTTA and DTTA-BuA. The speciation plot for 0.02 M HEDTTA, when compared to that calculated for DTPA, shows that *N*-hydroxyethyl functionality shifts the reagent's operational complexing scale to higher p[H^+]. In contrast, the electron-withdrawing influence of the *N*-butylacetamide group renders the DTTA-BuA more acidic, relative to DTPA, thus enabling the metal ion complexation in regions of higher acidity. The Eu^{3+} speciation plots lay out the foundations to explore two distinct mechanisms for enhancing the rates of metal extraction. First, for HEDTTA, the enhancement may result from the reduction of reagent's polydenticity and weakening of complexant's hold on the metal ion. Second, for
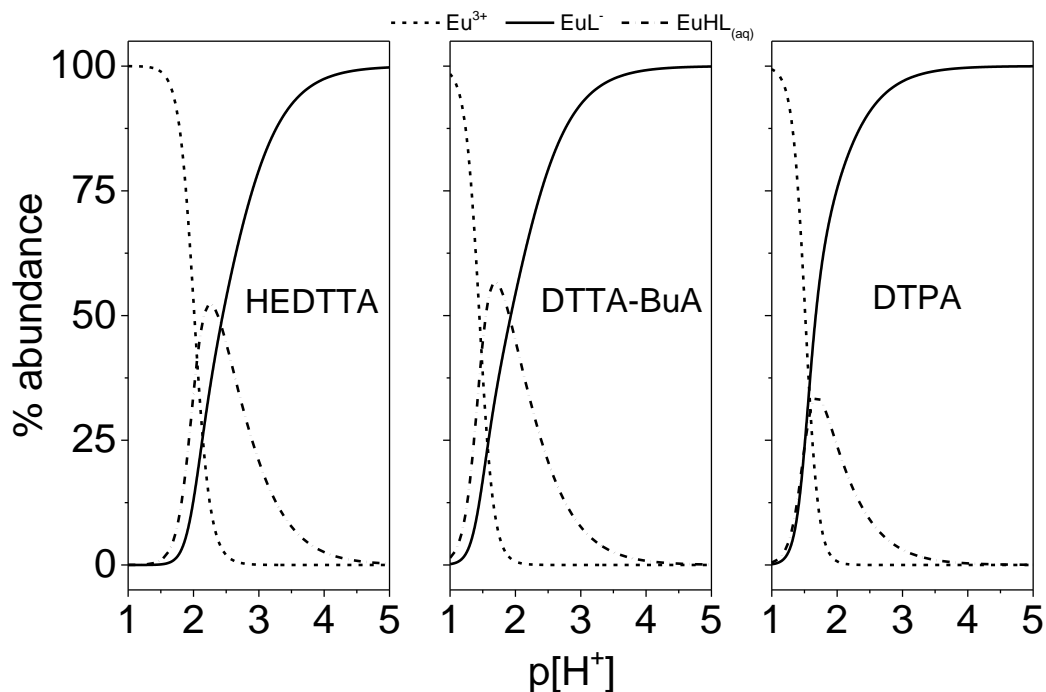
Figure 2. Distribution of species for mixtures of 0.02 M HEDTTA or DTTA-BuA and 10^{-5} M Eu^{3+} plotted as a function of $p[H^+]$.

DTTA-BuA, may capitalize on increased rate of dissociation of *f*-element complexes in regions of higher acidity due to initial complex protonation step [2].

3.2 Forward Eu^{3+} extraction kinetics

Figure 3 compares the Eu^{3+} phase transfer kinetic trends observed for the liquid-liquid systems containing two aqueous holdback complexants considered in this study (HEDTTA and DTTA-BuA) with typical kinetic trends collected when either a hexadentate (EDTA) or octadentate (DTPA) reagent is utilized at $p[H^+]$. The forward extraction tests did not include buffer in aqueous mixtures to slow down the distribution equilibrium and magnify the time dependencies for various complexants. The distribution of Eu^{3+} for liquid-liquid system containing 20 mM HEDTTA at $p[H^+] = 3.0$ shows a rapid rate transfer enhancement, relative to
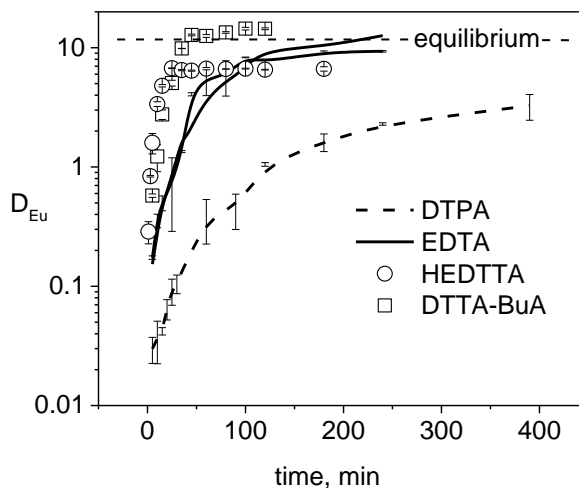

Figure 3. Time-dependent liquid-liquid distribution of [154]Eu between aqueous aminopolycarboxylate mixtures and organic solutions of HEH[EHP] in *n*-dodecane. Experimental: (○) 20 mM HEDTTA, $p[H^+]$ 3.0 / 0.065 M HEH[EHP]. (□) 15 mM DTTA-BuA, $p[H^+]$ 2.0 / 0.95 M HEH[EHP]. (--) 5 mM DTPA, $p[H^+]$ 3.0 / 0.3 M HEH[EHP]. (—) 20 mM EDTA, $p[H^+]$ 3.0 / 0.2 M HEH[EHP].

DTPA and EDTA-based chemistries. With a heptadentate coordination environment around the metal a trend intermediate to those observed for hexadentate (EDTA) and octadentate (DTPA) would be expected for mixtures of equivalent acidity. The faster kinetic trend may be attributed to lower concentration of phase transfer reagent required to yield a $D_{Eu} \sim 10$ at equilibrium. Launiere and Gelis showed that interfacial mass transfer rate for the back-extraction of americium from loaded organic phase containing HEH[EHP] nearly triples when the concentration of the strong cation exchanger is halved [8]. Accordingly, the weakening of the metal ion coordination offers one opportunity to elevate the mass transfer rates in such liquid-liquid distribution systems.

The distribution of Eu^{3+} for liquid-liquid system containing 15 mM DTTA-BuA was studied at $p[H^+]$ of 2.0 to emphasize this reagent's ability to efficiently coordinate Eu^{3+} and delay the competition from the ligand protonation equilibria. From Figure 3, roughly a 10-fold enhancement in the rate of Eu^{3+} extraction observed for DTTA-BuA chemistry, relative to DTPA's trend at $p[H^+]$ of 3.0, follows the expected linear relation between the rate of complex decomposition and concentration of hydrogen ions in solution. Thus, lowering the operational pH scale for complexing the trivalent *f*-elements by aminopolycarboxylate complexants incorporating strongly electron-withdrawing functionalities offers the second avenue for enhancing the phase transfer kinetics, capitalizing on proton-catalyzed mechanism of complex dissociation.

3.3 Am^{3+} back-extraction kinetics

Figure 4 compares the collected time dependent stripping trends for [241]Am, which distributes from the initially loaded and washed ALSEP solvent (0.05 M TEHDGA, 0.5 M HEH[EHP]) to aqueous mixtures of HEDTTA or DTTA-BuA or DTPA. This partitioning scenario proceeds much faster, relative to the forward extraction studies designed to slow the mass transfer rates, mainly due to the presence of citrate buffer in the aqueous environment. A weaker coordination of trivalent *f*-elements by HEDTTA explains the elevated distribution of americium ion. Using 0.125 M HEDTTA at pH 3.0 yielded a relatively inefficient stripping of americium ($D_{Am} \sim 0.7$). The liquid-liquid system containing HEDTTA also showed slowest liquid-liquid partitioning results. In the back-extraction experimental setting the mass transfer rate is not enhanced through modification of the non-aqueous environment.
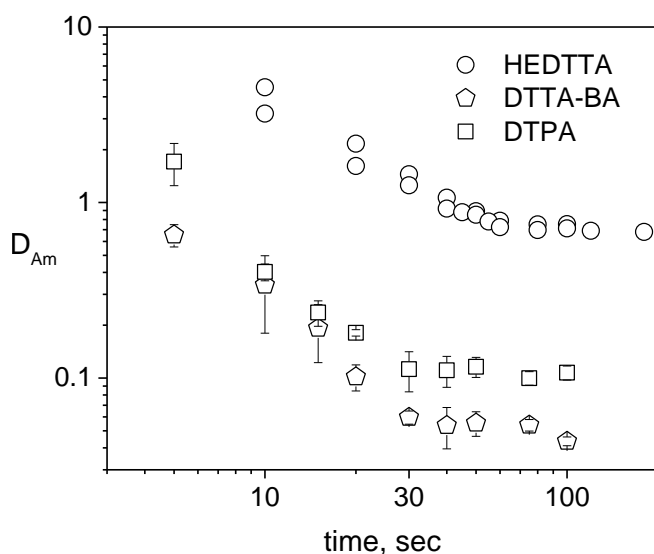

Figure 4. Time-dependent back-extraction of [241]Am from 0.05 M TEHDGA / 0.5 M HEH[EHP] in *n*-dodecane using (circle) 0.125 M HEDTTA, pH 3.0, (square) 15 mM DTTA-BuA, pH 2.0, (diamond) 15 mM DTPA, pH 2.0. Buffer: 0.2 M citrate.

The benefit of utilizing a stronger metal complexant, capable of efficient An^{3+}/Ln^{3+} separation in the

aqueous conditions of increased acidity, shows for the back-extraction time-dependent partitioning of Am^{3+} as facilitated by both DTTA-BuA and DTPA at pH of 2.0. Both stripping chemistries reach equilibrium within 30 seconds of phase contact. The partitioning equilibrium for americium is lower for DTTA-BuA ($D_{Am} \sim 0.05$) as compared to DTPA ($D_{Am} \sim 0.11$).

4. Conclusion

Potentiometric techniques were used to describe the thermodynamic features of trivalent *f*-element complexation by modified aminopolycarboxylate reagents. One modification replaced a single acetate pendant arm of DTPA reagent with *N*-hydroxyethane functionality, yielding *N*-hydroxyethyl-*N*,*N*′,*N*″,*N*″-diethylenetriaminetetraacetic acid, HEDTTA. Another structural change substituted the acetate group with *N*-butylacetamide to afford *N*-butylamide-*N*,*N*′,*N*″,*N*″-diethylenetriaminetetraacetic acid, DTTA-BuA. Time dependency trends for the forward extraction of europium by HEH[EHP] in *n*-dodecane from aqueous environments of HEDTTA or DTTA-BuA are compared with typical trends produced by hexadentate EDTA-type complexants and octadentate DTPA-type complexants. The kinetic studies for the partitioning of Am^{3+} between ALSEP solvent and aqueous mixtures containing HEDTTA and DTTA-BuA are compared with that yielded by DTPA. The Eu^{3+} distribution patterns show that significant enhancements to the rates of metal extraction may result either from reduction of reagent's polydenticity (HEDTTA) or manipulation of reagent's acid/base chemistry to capitalize on proton–catalyzed dissociation of *f*-element complexes (DTTA-BuA). The results of Am^{3+} back-extraction show that HEDTTA is too weak to efficiently balance the thermodynamics imposed by the ALSEP environment, but DTTA-BuA may be regarded as an attractive alternative to DTPA chemistry.

Acknowledgement

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