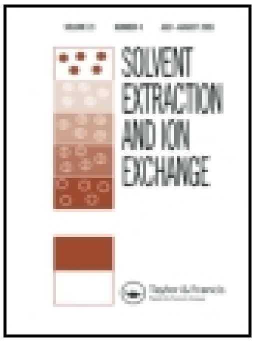

Solvent Extraction and Ion Exchange

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Extraction Selectivity of a Quaternary Alkylammonium Salt for Trivalent Actinides over Trivalent Lanthanides: Does Extractant Aggregation Play a Role?

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ABSTRACT

The extraction behavior of a quaternary alkylammonium salt extractant was investigated for its selectivity for trivalent actinides over trivalent lanthanides in nitrate and thiocyanate media. The selectivity was evaluated by solvent extraction experiments through radiochemical analysis of ^{241}Am and $^{152/154}$Eu. Solvent extraction distribution and slope-analysis experiments were performed with americium(III) and europium(III) with respect to the ligand (nitrate and thiocyanate), extractant, and metal (europium only) concentrations. Further evaluation of the equilibrium expression that governs the extraction process indicated the appropriate use of the saturation method for estimation of the aggregation state of quaternary ammonium extractants in the organic phase. From the saturation method, we observed an average aggregation number of 5.4 ± 0.8 and 8.5 ± 0.9 monomers/aggregate for nitrate and thiocyanate, respectively. Through a side-by-side comparison of the nitrate and thiocyanate forms, we discuss the potential role of the aggregation in the increased selectivity for trivalent actinides over trivalent lanthanides in thiocyanate media.

KEYWORDS

Aliquat-336; americium; europium; separations; solvent extraction; thiocyanate

Introduction

The separation of trivalent actinides (An(III)) from trivalent lanthanides (Ln(III)) is a challenge with implications ranging from the nuclear energy industry applications to the modeling of contaminant fate and transport.[1–4] With renewed interest globally in advanced nuclear energy technologies, in which the actinides are recycled, the lanthanides must be excluded because they strongly absorb neutrons and their presence will inhibit the ability to reuse the material.[5–7] While the separation of actinides from lanthanides can greatly improve the front and the back end of the nuclear fuel cycle, the separation efficacy is challenging due to their near analogous chemistry.[6,8] The predominant contribution of electrostatic forces to their bonding, combined with their similar ionic radii, renders difficult the specific separation of trivalent *f*-ions. Despite these similarities, the extraction of the actinides relative to the lanthanides has been shown to be greatly enhanced in the presence of thiocyanate (SCN^-).[9,10] The enhanced selectivity for extracting actinides into organic phases containing a variety of extractants provides an opportunity to improve our understanding of the fundamental factors impacting efficient separation processes.

This selectivity in thiocyanate media has been observed with many different organic phase extractants (e.g., quaternary ammonium salts and organophosphorus reagents). From a practical standpoint, ammonium-based extractants are preferable, since their degradation products, unlike organophosphorus extractants, are innocuous and do not interfere with metal separation.[10–15]

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The thiocyanate ion is characterized as ambidentate in nature as it can bind with either the S-terminus to form the thiocyanato complex or the N-terminus to form the isothiocyanato complex with a metal (however, for general complex formation, thiocyanate will be used exclusively in this manuscript). Its ambidentate nature, with coordination occurring through the N- or S-terminus, has been the focus of considerable interest, especially in investigations of heavy metals. There is a general agreement that the thiocyanate ion binds through the N terminus with hard cations (such as Ln(III) and An(III)) and through the S-terminus with soft cations.[16]

In spite of the reported ability of thiocyanate to enhance actinide–lanthanide separations, the underlying mechanistic factors contributing to its efficacy remain unidentified. From a fundamental perspective, the foremost interest is in the use of this separation as a probe of the subtle differences in bonding preferences between the 4f and 5f valence orbitals.[17] While many have speculated on the driving factors for the selectivity of An(III) over Ln(III), many of these hypotheses lack direct experimental evidence and are challenged by often subtle evidence.[8] One hypothesis argues that the interaction of An(III) with soft-donor ligands such as SCN^- is stronger.[9,18] Early workers postulated that the differences in ion hardness between 4f and 5f elements promotes an enhanced tendency of an actinide over a lanthanide to form inner-sphere complexes with thiocyanate—which, therefore, would promote extraction into an organic phase. This hypothesis is inconsistent with studies that show that complexant energetics can be the same for both inner- and outer-sphere correlations.[19] Another possible explanation for the observed selectivity is the differences in Lewis acid/base character: Am^{3+} is a softer Lewis acid than Eu^{3+} and therefore more readily forms complexes with a soft Lewis base in SCN^-, bound by the S-terminus.[9] This hypothesis is not supported by solid-state structural data obtained on f-ion systems.[17,18,20–22] Another contributing factor may be found in the thermodynamics of the extraction process, where it was shown that the heat of extraction with tri-*n*-octylphosphine oxide (TOPO) from SCN^- for Am(III) and Eu(III) is roughly the same. This result suggests that the nearly 10-fold increase in the observed distribution ratio of Am(III) results from a more favorable net entropy change.[15] Other studies investigated the enthalpy differences in the extraction of Am and Eu by bis(2-ethylhexyl) phosphoric acid and by Cyanex-301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid) from thiocyanate medium.[23,24] The results indicated an enhanced covalence between Am and the sulfur donor atoms, as indicated with a $\Delta(\Delta H)$ of –25.5 kJ/mol for Am over Eu.[24] The separation may thus be explained by a more favorable bonding enthalpy of the actinide complex with the thiophosphinic acid extractant of Cyanex-201.[23] Overall, the stability constants of f-ion thiocyanate complexes, which include both enthalpic and entropic components, have not been well studied.[25] Taken together with a detailed structural description of the relevant species, these data provide the basis for predictive modeling of solute behavior.[19,26] This consideration applied to the An(III)-thiocyanate complexes reveals that The Martell and Smith Database only reports the stability constants for the first Am-NCS complex;[27] however, it is very likely that higher complexes are formed as found in the past by various investigators.[10,28–30]

While there are many studies aiming to understand the selectivity of extraction systems in thiocyanate media from a metal-centric approach, we report herein a study to evaluate this systems from a solvent-centric perspective.[31] Using this approach, the organic structure and ordering is evaluated to observe how aggregation and micellization influence metal extraction. Recent studies have linked extractant aggregation and reverse-micelle type ordering in the organic phase as a critical component of solvent extraction.[2,31–34] Extraction systems containing quaternary ammonium salt extractants have been found to be highly aggregated.[35] However, recent investigation of the role of their aggregation and its influence on the extraction of actinide and lanthanide elements is sparse.[36] The scope of this work was twofold: 1) to measure the extraction Am(III) and Eu(III) by a commercially available high-molecular-weight quaternary alkylammonium salt extractant (Aliquat-336) from two different media; and 2) to evaluate the selectivity of Am(III) over Eu(III) relating the observed selectivity to the state of aggregation of the quaternary ammonium salt in the organic phase.

Experimental section

Safety

The use of radioactive isotopes poses a potential health hazard, and appropriate ALARA principles should be considered prior to conducting experiments. Radionuclides used in these experiments ^{241}Am (alpha and gamma emitter) and $^{152/154}$Eu (beta and gamma emitter) should only be used only with appropriate training and only with engineered controls available in facilities designed to safely handle these hazardous materials.

General

Acids and salts used in extraction experiments were 99% trace metal or higher (Sigma-Aldrich, St. Louis, MO), including nitric acid (HNO_3), hydrochloric acid (HCl), sodium nitrate ($NaNO_3$), sodium thiocyanate (NaSCN), ammonium thiocyanate (NH_4SCN), europium chloride hexahydrate ($EuCl_3•6H_2O$), and europium nitrate pentahydrate ($Eu(NO_3)_3•5H_2O$). All radioactive standards (^{241}Am and $^{152/154}$Eu) were prepared from purified radioisotope stocks at Argonne National Laboratory stored in 2.5 × 10^{-3} M HNO_3 and radiometrically assayed by an automatic gamma counter (Packard Cobra II, Midland, ON, Canada).[37] All organic solvents and extractants (*o*-xylene and Aliquat-336 in chloride form) were used as purchased from Sigma Aldrich (St. Louis, MO). Half-life information and radioactive decay (alpha particle, beta particle, and gamma ray) energies were obtained from the Evaluated Nuclear Structure Data File (ENSDF) and from the United States National Nuclear Data Center (NNDC, Brookhaven National Laboratory, U.S. Department of Energy).

Solutions of Aliquat-336, made by using the conventional average molecular weight of 442 g/mol, were converted from the chloride form to the extraction form used in this study (nitrate and thiocyanate). Working solutions of Aliquat-336•Cl were prepared by diluting the quaternary ammonium salt gravimetrically in *o*-xylene to a concentration of 0.5 M. To prepare the thiocyanate form, 50 mL of 0.5 M Aliquat-336•Cl was added to a separatory funnel along with 50 mL 1 M NaSCN. The contents were shaken and the phases were allow to fully separate. The aqueous phase was discarded, and an additional 50 mL 1 M NaSCN was added to the funnel. This process was repeated three times, and the final organic phase consisting of 0.5 M Aliquat-336•SCN was collected and stored in the dark. To prepare the nitrate form of Aliquat-336, the same process was performed as described for the thiocyanate form, except for 50 mL of 2 M $NaNO_3$ was used for the conversion to Aliquat-336•NO_3. In the case of the nitrate form, the quantitative conversion was achieved by repeating the contact with 2 M $NaNO_3$ up to the disappearance of Cl^- ions by utilizing argentometry.[38]

Solvent extraction and distribution data

Three general series of solvent-extraction experiments were performed to assess the behavior of Am and Eu using both nitrate and thiocyanate forms of Aliqat-336 as extractants with *o*-xylene as the diluent: anion dependence, extractant dependence, and metal dependence (for Eu only). Experiments to assess the extraction behavior of Am and Eu with respect to the anion were performed with constant acidity (NO_3^-: 0.01 M HNO_3; SCN^-: 0.01 M HCl) and constant organic phase concentration (NO_3^-: 0.5 M Aliquat-336•NO_3; SCN^-: 0.5 M Aliquat-336•SCN). The anion concentrations ranged from low to high through the aqueous-phase concentrations of salt (NO_3^-: 0.1–4 M $NaNO_3$; SCN^-: 0.01–2 M NH_4SCN). Experiments to assess the uptake of Am and Eu with respect to the extractant were performed with constant acidity (NO_3^-: 0.01 M HNO_3; SCN^-: 0.01 M HCl) and constant salt concentration (NO_3^-: 4 M $NaNO_3$; SCN^-: 1 M NH_4SCN). The extractant concentrations ranged from low to high concentration in the organic phase (NO_3^-: 0.0–0.5 M Aliquat-336•NO_3; SCN^-: 0.05–0.5 M Aliquat-336•SCN). Experiments to assess the uptake of Eu with respect to the Eu ion concentration were performed with constant acidity (NO_3^-:0.01 M

HNO_3; SCN^-: 0.01 M HCl;) and constant salt concentration (NO_3^-:4 M $NaNO_3$; SCN^-: 1 M NH_4SCN), and constant extractant concentration (NO_3^-: 0.5 M Aliquat-336•NO_3; SCN^-: 0.5 M Aliquat-336•SCN), where the Eu concentration ranged from trace (<1 mM) to 1 M by the additional of $EuCl_3$•$6H_2O$.

For all solvent extraction experiments, the distribution ratio (D) of the metal (Am or Eu) was analyzed radiometrically following mixing, equilibration, and phase separation. The distribution ratio was determined as the ratio of the total metal concentration $[M_T]$ in each of the two phases:

$$D = \frac{[M_T]_{organic}}{[M_T]_{aqueous}} \tag{1}$$

Extraction systems were prepared in glass centrifuge tubes: 0.9 mL of an organic phase and an aqueous phase were carefully spiked with 2 µL of radiometal (^{241}Am or $^{152/154}$Eu). The phases were mixed via vortexer, and then the emulsions were maintained for 10 min via a shaker table. Following the mixing stage, the samples were centrifuged to assure complete phase separation. The organic phase was then carefully removed and stored in a separate glass vial, and the interface was removed to ensure the aqueous phase was free of organic content. Next, 0.2 mL of each phase were transferred to a counting tube to be measured by sodium iodide gamma spectroscopy to determine the count rate in each phase by standard laboratory counting protocols created to specifically measure the gamma emission of the analyte metal. Analytical uncertainties are within ±5% (and ±10% for the lowest measured D values), as determined from repeated analyses and counting statistics.

Results

Extraction equilibrium constant and calculated distribution ratios

Estimations of the extraction equilibrium constants (*K*ex) were made by calculating distribution ratios and upon an understanding of the chemical equilibrium of the extraction process. The chemical equilibrium describing the extraction of a metal ion, M^{3+} (Am^{3+} or Eu^{3+}), in solution of anionic ligand, L^- (NO_3^- or SCN^-), by a highly aggregated extractant, E (Aliquat-336•L), can be written as:

$$M^{3+} + 3L^- + \bar{E} \rightleftharpoons \overline{EML_3} \tag{2}$$

where for simplicity $\bar{E}$ represents the aggregated species $\overline{(RL)}_q$ and R in turn indicates the $R_1R2R3CH3N^+$ tetraalkylammonium cation. In Eq. (2), species with a bar above them denote organic phase species. Equation (2) is defined with a corresponding chemical equilibrium constant *K*ex.

The chemical equilibrium constant can be written as:

$$K_{ex} = \frac{[\overline{EML_3}]}{[M^{3+}]*[L^-]^3 y_{L^-}^3 * [\bar{E}]} \tag{3}$$

where y_{L^-} is the aqueous molar activity coefficient of the ligand from Table 1 for both $NaNO_3$[39] and NaSCN[40] (as proxy for NH_4SCN) electrolyte solutions, and $[M^{3+}]$ is the aqueous-phase equilibrium concentration of the metal cation. The activity coefficient of the cation was omitted because its concentrations in solution were at the tracer level, where the cation is assumed to behave ideally. The activity coefficient of the organic extractant was omitted as well because any observed deviations from ideality in the organic phase were assumed to be attributed to aggregation.

The total equilibrium metal concentration in the aqueous phase can be written as[41]

$$[M^{3+}]_{tot} = [M^{3+}] * (1 + \beta_1[L^-]y_{L^-} + \beta_2[L^-]^2 y_{L^-}^2) \tag{4}$$

where β_1 and β_2 are the formation constants for the first and second aqueous-phase metal nitrate[10] and thiocyanate complexes.[42] The formation-constant values were extrapolated from literature values to zero

Table 1. Molar activity coefficients used to calculate the activities of thiocyanate and nitrate solutions.

$[SCN^-]$	y±	a_{SCN^-}
0.1	0.965	0.097
0.2	0.727	0.145
0.5	0.739	0.369
0.7	0.690	0.483
0.8	0.694	0.555
0.9	0.695	0.626
1.0	0.702	0.702
1.5	0.750	1.126
1.79	0.789	1.415
$[NO_3^-]$	y±	a_{NO3^-}
0.1	0.762	0.076
0.2	0.717	0.143
0.4	0.652	0.261
0.7	0.591	0.414
1.0	0.561	0.561
2.0	0.503	1.006
3.0	0.473	1.419
3.5	0.464	1.624
4.0	0.455	1.820

ionic strength using the Debye–Hückel equation.[43] The formation constants used in these calculations are provided in Table 2. By substituting the equilibrium metal concentration in the aqueous phase (from Eq. (4)) and the distribution ratio (Eq. (1)) into the expression for the equilibrium constant (Eq. (3)), we obtain (Eq. (5)):

$$K_{ex} = \frac{D\left(1 + \beta_1 [L^-]\gamma_{L^-} + \beta_2 [L^-]^2 \gamma_{L^-}^2\right)}{[L^-]^3 \gamma_{L^-}^3 * [\bar{E}]} \tag{5}$$

which can be rearranged with respect to the distribution ratio:

$$D = \frac{K_{ex}[L^-]^3 \gamma_{L^-}^3 * [\bar{E}]}{\left(1 + \beta_1 [L^-]\gamma_{L^-} + \beta_2 [L^-]^2 \gamma_{L^-}^2\right)} \tag{6}$$

Equation (6) was used to obtain calculated D values at various concentrations of ligand or extractant at tracer metal concentrations to compare with experimental D values.

In fitting the experimental distribution data, through data processing with Excel Solver, only the Kex was adjusted to minimize the error function of the fit. The formation constants and activity coefficients were constrained to literature values. Calculated distribution ratios as a function of the ligand ($[NO_3^-]$ or $[SCN^-]$) and the extractant ([Aliquat-336•NO_3] or [Aliquat-336•SCN]) are plotted with experimental data. The calculated Kex values were used to evaluate the extraction systems.

Table 2. Formation constants for the first and second metal-ligand complex for Am and Eu with thiocyanate and nitrate, and experimentally determined equilibrium constants, as log *K*ex, for the extraction, as described in the text.

Species	log β_1*	log β_2*	log *K*ex (anion dependence, Fig. 1)	log *K*ex (extractant dependence, Fig. 2)
Am-SCN^-	0.42	0.82	3.31 ± 0.05	3.21 ± 0.05
Am-NO_3^-	0.51	0.38	1.26 ± 0.03	1.26 ± 0.04
Eu-SCN^-	0.39	0.54	1.84 ± 0.05	1.71 ± 0.05
Eu-NO_3^-	0.56	0.30	0.81 ± 0.03	0.83 ± 0.03

*β_1 and β_2 literature values for nitrate[10] and thiocyanate[42] complexes.

Evaluation of the distribution ratios

Anion dependence

Solvent extraction experiments were performed to measure the *D*Am and *D*Eu as a function of the concentrations of nitrate and thiocyanate by the addition of $NaNO_3$ and NH_4SCN, respectively. The results from these experiments are summarized in Figs. 1 The logarithmic plot of *D* vs. nitrate concentration is linear, with a slope of approximately 2 when the $[NO_3^-] < 1$ M and for $[SCN^-]$ over the entire concentration range. The calculated *D* values agree well with experimental *D* values when the slope is near 2, when $[NO_3^-] < 1$ M, using the literature values for β_1 and β_2 extrapolated to zero ionic strength (Table 2). The resulting equilibrium constants (log *K*ex) were determined to be 1.26 and 0.81 for Am and Eu, respectively. However, when the $[NO_3^-] > 1$ M, the slope approaches 3 for both the Am^{3+} and Eu^{3+} data, and the equilibrium expression and calculated *D* values no longer sufficiently represent the extraction process. This observation is attributed to the added salting out effect at increased $NaNO_3$ concentrations.[12,14,44] As our chemical equilibrium, and extraction calculation, do not include a term to represent the salting out effect, the calculated *D* values poorly represent the extraction system when salting out is a significant factor in the system behavior.

In the case of the extraction of Am and Eu with the thiocyanate form of Aliquat-336, the slope of the logarithmic plot of *D* versus $[SCN^-]$ (Fig. 1B) is approximately 2 for both *D*Am and *D*Eu. The experimental *D* values were fit with a calculated *D* function using the equilibrium constants (log *K*ex) 3.31 and 1.84 for Am and Eu, respectively (Table 2). The calculated *D* values agree well with the experimental results, with only slight deviations at low $[SCN^-]$. No salting out is observed in the concentration range of the experiments in thiocyanate media, as expected from the chaotropic nature of the thiocyanate anion.

Extractant dependence

The extractant dependence of Am and Eu extraction by Aliquat-336•NO_3 was evaluated by measuring the distribution ratio with respect to changes in the extractant concentration from 0.05 to 0.5 M.

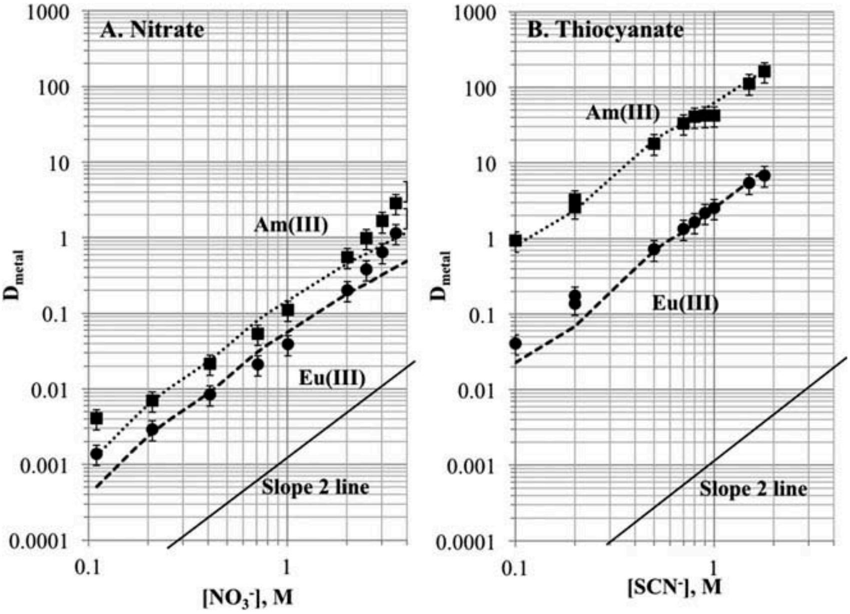

Figure 1. Anion-dependency plots for *D*Am or *D*Eu versus the anion concentration. The data points were experimentally determined, and the solid lines represent calculated *D* values from Eq. (6) and Table 2. $[^{241}Am]_{initial} \approx 54.5$ pM and $[^{152}Eu]_{initial} \approx 1.8$ pM. **(A)** Nitrate dependency: 0.5 M Aliquat-336•NO_3 in *o*-xylene contacted with 0.01 M HNO_3 with 0.1–4 M $[NaNO_3]$. **(B)** Thiocyanate dependency: 0.5 M Aliquat-336•SCN in *o*-xylene contacted with 0.01 M HCl with 0.1–2 M $[NH_4SCN]$.

The results plotted as log *D* versus log[Aliquat-336•NO_3] in Fig. 2 reveal a slope >1 when the [Aliquat-336•NO_3] was less than 0.1 M. When the [Aliquat-336•NO_3] was increased above 0.1 M, the slope was 1. The calculated *D* values were determined to minimize the error function of the experimental data points when [Aliquat-336•NO_3] > 0.1 M, using β_1 and β_2 from Table 2 and log *K*ex values of 1.26 and 0.83 for Am and Eu, respectively. The extractant dependence of Am and Eu extraction by Aliquat-336•SCN was also evaluated by measuring *D* values in the extractant concentration range from 0.05–0.5 M. The data exhibit a slope of about 1 throughout the range investigated. The calculated *D* values were determined to minimize the error function of the experimental data points when the [Aliquat-336•NO_3] > 0.1 M.

To an approximation, the extractant dependencies for the extraction Am and Eu by Aliquat-336 in NO_3^- (0.2–0.5 M) and SCN^- (0.1–0.5 M) forms resulted in fits with slopes of ~1. Within the context of fitting extraction dependences of distribution ratios, the determination of a slope of 1 represents the special case in which the extractants exist in a highly aggregated state while the aggregation number does not change upon extraction.[45] For example, this behavior has been observed with mono-(2-ethylhexyl)-phosphoric acid (H_2MEHP) in aromatic diluents,[46] dinonylnaphthalene sulfonic acid,[47] and other quaternary ammonium salts.[14] The rationale for this case can be seen when the mass balance equation of the extractant is written as:

$$C_e = \left[\overline{RL}\right] + q\left[\left(\overline{RL}\right)_q\right] \tag{7}$$

where C_e is the analytical total extractant concentration. In a highly-aggregated system, the monomer concentration, $\overline{RL}$ is negligible and the equation becomes:

$$C_e = q\left[\left(\overline{RL}\right)_q\right] \tag{8}$$

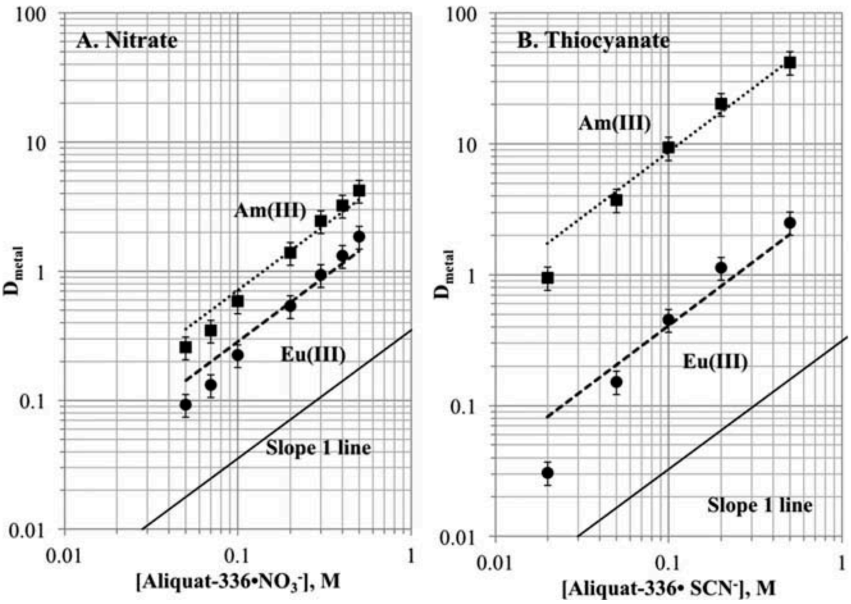

Figure 2. Extractant-dependency plots for *D*Am or *D*Eu versus the extractant concentration. The data points were experimentally determined, and the solid lines represent calculated *D* values from Eq. (6) and Table 2. $[^{241}Am]_{initial} \approx 54.5$ pM and $[^{152}Eu]_{initial} \approx 1.8$ pM. **(A)** 0.05–0.5 M Aliquat-336•NO_3 in *o*-xylene contacted with 0.01 M HNO_3 + 4 M $NaNO_3$. **(B)** 0.05–0.5 M Aliquat-336-SCN in *o*-xylene contacted with 0.01 M HCl + 1 M NH_4SCN.

Substituting Eq. (8) into Eq. (6), we obtain:

$$D = \frac{K_{ex}[L^-]^3 \gamma_{L^-}^3 * C_e}{(1 + \beta_1[L^-]\gamma_{L^-} + \beta_2[L^-]^2 \gamma_{L^-}^2)} \tag{9}$$

By keeping constant the aqueous-phase conditions, a log-log plot of D versus the analytical concentration of the extractant, which is also equal to $[\bar{E}]$ at trace metal concentrations, will have a slope of 1.

Metal dependence

Metal-dependence experiments were performed to assess how the concentration of Eu in the initial aqueous solution impacts the *D*Eu values. Aqueous nitrate solutions were prepared with fixed $[NaNO_3]$ = 4 M and $[HNO_3]$ = 0.01 M and $[Eu(NO_3)_3]$ ranging from trace (<1 mM) to 0.75 M. These aqueous solutions were contacted with organic phases of *o*-xylene containing 0.5 M Aliquat-336•NO_3. The resulting plot (Fig. 3A) shows that *D*Eu remains relatively constant (around $\bar{D}$ 1.5) at $[Eu(NO_3)_3]$ > 0.04 M, before decreasing with higher $[Eu(NO_3)_3]$ with a slope of approximately –1. The organic phase is becoming saturated with Eu and asymptotically approaches the maximum [Eu] in the organic phase of 0.1 M (Fig. 4).

The *D* value dependence on Eu concentration was also evaluated with the thiocyanate form of Aliquat-336. Experimentally, the aqueous phase consisted of a range of $EuCl_3$ from trace (<1 mM) to 1 M in 2 M NH_4SCN/0.01 M HCl contacted with 0.5 M Aliquat-336•SCN. The results show that *D*Eu remains constant at about 6.5 for concentrations up to $[EuCl_3]$ = 0.01 M, after which, for concentrations exceeding 0.1 M, *D*Eu decreases with a slope of approximately –1. This occurs as the organic phase is becoming saturated with Eu (Fig. 3). The organic phase becomes saturated at around 0.09 M as shown by the plot of the equilibrium concentration of Eu in each of the phases (Fig. 4), and the $[Eu]_{org}$ asymptotically approaches the saturation concentration. Using established methods, these $[Eu]_{org}$ values can be used to determine the average aggregation number.

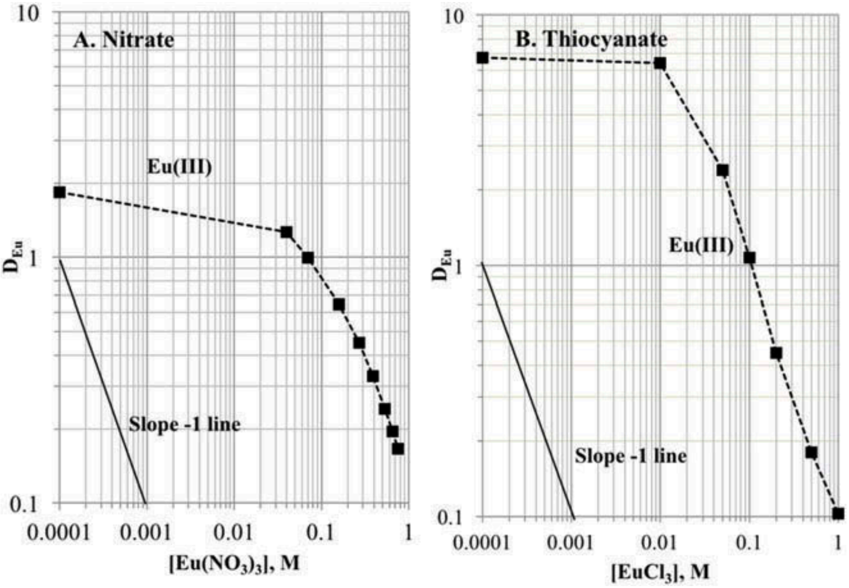

Figure 3. Metal-dependency plots for *D*Eu versus the metal concentration. (**A**) 0.5 M Aliquat-336•NO_3 in *o*-xylene contacted with 0.1 mM to 0.75 M $Eu(NO_3)_3$ in 0.01 M HNO_3 + 4 M $NaNO_3$. (**B**) 0.5 M Aliquat-336•SCN in *o*-xylene contacted with 0.1 mM to 1 M $EuCl_3$ in 0.01 M HCl + 2 M NH_4SCN.

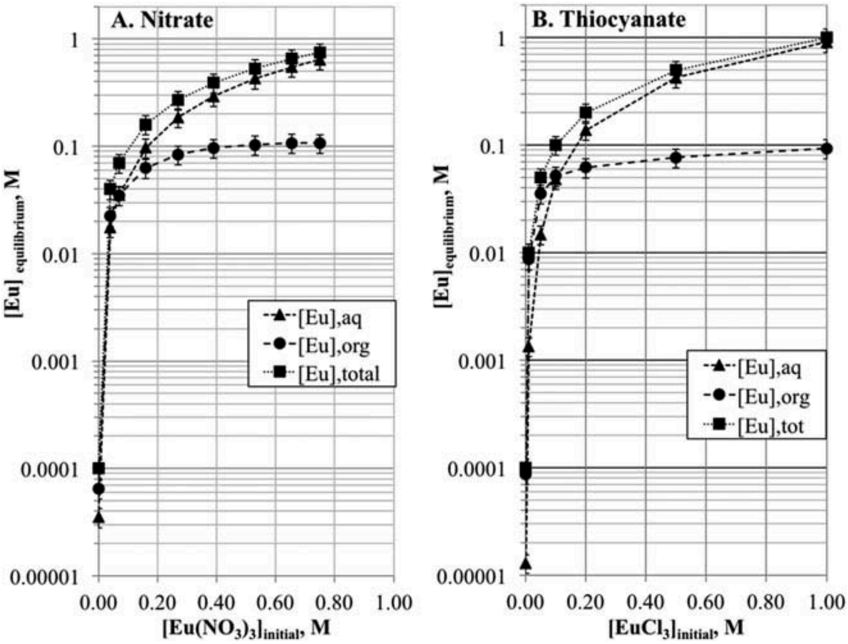

Figure 4. Equilibrium [Eu] versus the initial aqueous [Eu]. The plot shows the equilibrium concentrations in the aqueous, organic, and total [Eu]. **(A)** 0.5 M Aliquat-336•NO_3 in *o*-xylene contacted with 0.1 mM to 0.75 M $Eu(NO_3)_3$ in 0.01 M HNO_3 + 4 M $NaNO_3$. **(B)** 0.5 M Aliquat-336•SCN in *o*-xylene contacted with 0.1 mM to 1 M $EuCl_3$ in 0.01 M HCl + 2 M NH_4SCN.

Saturation method and average aggregation number

Assuming that the organic phases are highly aggregated, from the extractant dependence slope of 1,[44,45] the average aggregation number, that is the number of extractant molecules per aggregate, can be determined from the metal-dependency data using the saturation method.[48–50] Using the chemical equilibrium (Eq. (2)) and equilibrium constant (Eq. (3)) expressions, we derive an equation that allows the estimation of the average number of monomers per aggregate.[48] By recalling that $\bar{E}$ in Eqs. (2) and (3) represents the aggregated species $\overline{(RL)q}$, we write the mass balance for the extractant taking into account the initial, equilibrium, and extracted species as:

$$\left[\overline{(RL)_q}\right]_{initial} = \left[\overline{(RL)_q}\right]_{equilibrium} + \left[\overline{ML_3(RL)_q}\right] \tag{10}$$

or

$$\left[\overline{(RL)_q}\right]_{equilibrium} = \left[\overline{(RL)_q}\right]_{initial} - \left[\overline{ML_3(RL)_q}\right] \tag{11}$$

From Eq. (6), at constant $[L^-]$, it holds for the distribution ratio:

$$D = K'\left[\overline{(RL)_q}\right]_{equilibrium} \tag{12}$$

By substituting Eqs. (11) into (12), we obtain:

$$D = K'\left[\overline{(RL)_q}\right]_{initial} - K'\left[\overline{ML_3(RL)_q}\right] \tag{13}$$

A plot of D vs. the concentration of the metal in the organic phase (equal to $\left[\overline{ML_3(RL)_q}\right]$) should give a straight line with slope = K', intercept = $K'\left[\overline{(RL)_q}\right]_{initial}$, and the ratio of intercept to slope = $\left[\overline{(RL)_q}\right]_{initial}$.

By recalling that the mass balance for highly aggregated extractants is given by Eq. (8), it follows:

$$q = [Ce] / \left[\overline{(RL)_q}\right]_{initial} \tag{14}$$

where $[C_e]$ represents the analytical total concentration of the extractant.

This result can be generalized by stating that from plots of *D* vs. the organic metal concentration, the aggregation number can be simply obtained through the relation:

$$n_{agg} = [Ce] * \frac{slope}{intercept} \tag{15}$$

From data plotted following this methodology, provided in Fig. 5, the aggregation numbers were determined from the slopes and intercepts of the best-fit lines, when *D*Eu is plotted versus $[\mathrm{Eu}]_{\mathrm{organic}}$. The aggregation numbers $n_{agg} = 5.4 \pm 0.8$ in nitrate form and $n_{agg} = 8.5 \pm 0.9$ in the thiocyanate form were obtained when the $[\mathrm{Eu}]_{\mathrm{organic}} \leq 10\%$ of the [Aliquat-336].

Discussion

Overall, broadly similar results are found from experiments assessing the distribution equilibria of Am^{3+} and Eu^{3+} between immiscible solutions, water and *o*-xylene, the latter of which contains dissolved Aliquat-336 in either the nitrate or thiocyanate form. In both the Am^{3+} and Eu^{3+} cases, the plots of the $\mathrm{NO_3}^-$ and SCN^- dependencies (Fig. 1) have a slope of ~2, indicating that, upon extraction, two anions are added to the metal which is already bound to one anion in the aqueous phase. Previous studies have also demonstrated, through slope-analysis investigations, an average stoichiometric relationship between anion and extracted metal.[49]

Although the anion dependencies are similar, the magnitude of the individual *D* values is significantly different. The equilibrium constants determined from both the anion-dependence and the extractant-dependence experiments provide similar results. The *K*ex values for both Am^{3+} and

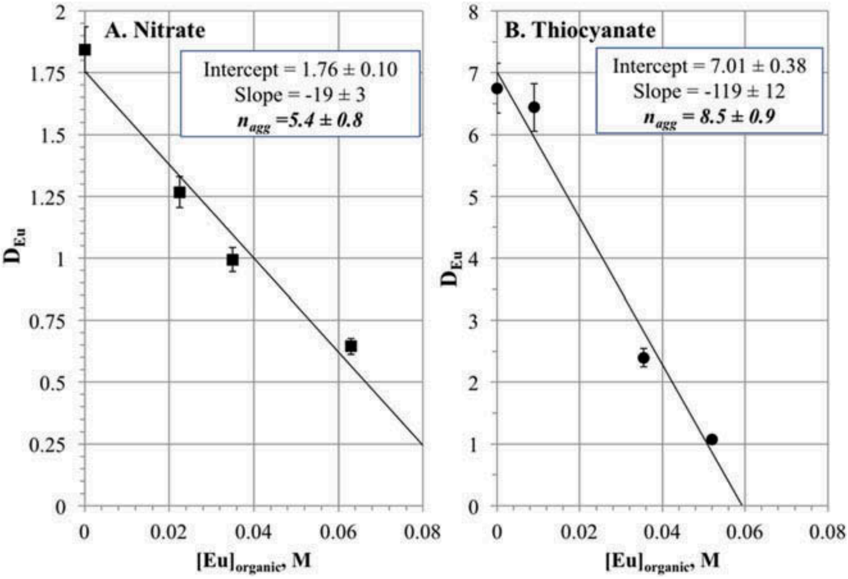

Figure 5. Europium distribution ratio (*D*Eu) versus the equilibrium $[\mathrm{Eu}]_{\mathrm{organic}}$ from the metal-dependency experiments. The plot is fit to a linear regression line for $[\mathrm{Eu}]_{\mathrm{organic}} \leq 10\%$ of the [Aliquat-336]. **(A)** 0.5 M Aliquat-336•$\mathrm{NO_3}$ in *o*-xylene contacted with 0.1 mM to 0.75 M $\mathrm{Eu(NO_3)_3}$ in 0.01 M $\mathrm{HNO_3}$ + 4 M $\mathrm{NaNO_3}$. **(B)** 0.5 M Aliquat-336•SCN in *o*-xylene contacted with 0.1 mM to 1 M $\mathrm{EuCl_3}$ in 0.01 M HCl + 2 M $\mathrm{NH_4SCN}$.

Eu^{3+} are larger in the thiocyanate relative to the nitrate case, although the extraction of Am^{3+} is considerably more enhanced. The log *K*ex for Am^{3+} extraction increases from 1.26 to 3.31, whereas log *K*ex for Eu^{3+} increases from 0.81 to 1.84. In other words, the Am^{3+} extraction increases by a factor 100 when the ligand is changed from nitrate to thiocyanate, whereas the Eu^{3+} increase is limited to a factor 10 under the same conditions. The difference in the *K*ex as a result of changing the ligand from nitrate to thiocyanate increases the separation factor, given by the ratio of *K*ex values from ~10 to ~100. These results suggest that the main effect influencing the enhanced extraction may not be based on the ligand stoichiometry in the extraction reaction, because the observed anion and extractant dependency plots share the same slope for Am^{3+} and Eu^{3+} in both NO_3^- and SCN^- media.

The slope of the extractant-dependency plot can provide insight into the aggregation behavior. In the thiocyanate system, the slopes are approximately 1 for both Am and Eu, when [Aliquat-336•SCN] = 0.1–0.5 M, indicating that the aggregation number is increasing as the [Aliquat-336•SCN] is increased. As expressed in Eq. (9), the observed slopes of ≈ 1 for the extractant dependences plotted in Fig. 2 constitute the special case where the extractants are highly aggregated. However, in the case of the nitrate system, the slope of the Am plot is approximately 1, while the slope of the Eu plot appears to be slightly larger than 1, when [Aliquat-336•NO_3] = 0.2–0.5 M. This may suggest that the product species consists of monomer units at lower concentrations, which becomes aggregated as the [Aliquat-336•NO_3] is increased. The observation of extractant aggregation in the organic phase of a solvent extraction system is not without precedent, either in general or in the specific case of Aliquat-336. In a previously published study investigating the extraction of Am^{3+} and Eu^{3+} from formic acid solutions by a series of quaternary alkylammonium salts, unusual extraction behavior was observed with *p*-trifluoromethylbenzyldimethyldodecylammonium chloride and attributed to differences in the aggregation among the quaternary ammonium salts, which were assumed to be identical.[14] Furthermore, a recent study investigating the impact of the lanthanide contraction on the extraction of lanthanides with *N,N*'-dimethyl-*N,N*'-dibutyl-tetradecyl-malonamide reported a striking correlation between the intercluster interaction energy and the separation factor of Ce^{3+} over Yb^{3+}.[51] A similar result has been reported from previous studies evaluating the extraction of indium by Aliquat-336 in toluene from 1 M HCl.[52] This suggests that in both nitrate and thiocyanate systems, Aliquat-336 forms a highly aggregated system when concentrations exceed 0.1 M.[14] Each aggregated system extracts a single metal whether it is Am^{3+} or Eu^{3+}, as a component of the aggregated unit.

There is an observed enhancement in the separation factor of Am^{3+} over Eu^{3+} by Aliquat-336 in thiocyanate form relative to the nitrate form as reflected by log *K*ex values. From extraction distribution studies, these systems are very similar; the β_1 values for Am^{3+} and Eu^{3+} complexes in nitrate and thiocyanate are approximately the same, whereas the β_2 values are significantly higher for Am^{3+} and Eu^{3+} complexes in thiocyanate. This factor alone would not explain the enhanced extraction of Am^{3+}over Eu^{3+} in thiocyanate.

Following up on the slope analyses, which indicate the presence in the organic phase of aggregates for both the nitrate and thiocyanate forms of Aliquat-336, the saturation method[48] was used to estimate the average number of monomers per aggregate. The average aggregation numbers for the polymeric Aliquat-336 species were 5.4 ± 0.8 and 8.5 ± 0.9 in nitrate and thiocyanate forms, respectively. The thiocyanate salt of Aliquat-336 forms aggregates containing almost twice as many monomers as does the nitrate form for the extraction of either Am^{3+} or Eu^{3+}. It is well known that quaternary alkylammonium salts readily form aggregated species in solution. As reported in previous studies, in solvents with low dielectric constants (i.e., *o*-xylene, $\varepsilon = 2.57$), at low concentrations (<0.02 M) Aliquat-336 exists as a monomer; however, it rapidly undergoes dimerization and continues to form higher species as the concentration is increased above 0.05 M.[52] Likewise, it was observed that aggregated species of Aliquat-336 primarily exist when acid concentrations are low (<1 M). For example, as the organic phase acidity (from extraction of HCl) increases, a decrease in aggregation was observed as a result of increased H-bonding that acts to stabilize the Aliquat-336•HCl ion-pair.[53] For the systems investigated in the present studies, the solution acidity was maintained at 0.01 M by HCl or HNO_3, in the range where Aliquat-336 is expected to exist as highly polymeric species.

These studies clearly demonstrate that Aliquat-336 in the thiocyanate form favors the formation of larger aggregates than the nitrate form as exhibited by Fig. 5. These results help support our hypothesis that organic phase ordering is a critical component in solvent extraction systems. Although these aggregate sizes do not change with metal-ion constituents, the larger aggregates in the thiocyanate case are associated with an order-of-magnitude increase in the separation factor of Am^{3+} over Eu^{3+}. The reason for this enhancement is not clear from the experiments presented herein. It can be hypothesized that the larger aggregate provides a coordination and solvation environment more suitable for the larger, softer actinide ion than for the smaller lanthanide one to minimize their free energy of solution in the micellar medium. This may reflect subtle differences in the ligation environments of the two metal-ions in the aqueous phase. Although various structural scenarios have been suggested for these subtle differences, including differences in inner- versus outer-sphere complexation,[8] there has been little direct support for these assertions. Other considerations, including changes in hydrogen bonding, or the role of inter-aggregate interactions, have yet to be tested. Additional spectroscopic studies are required to pinpoint a physical description as to the role of aggregation on the selectivity of Aliquat-336•SCN to extract Am^{3+} over Eu^{3+}.

Conclusions

We have investigated the extraction of Am^{3+} and Eu^{3+} by Aliquat-336 in thiocyanate and nitrate forms from a solvent-centric approach. This study suggests that differences in the aggregation of Aliquat-336 in nitrate versus thiocyanate forms have a significant impact on the separation factor of Am^{3+} and Eu^{3+}. Distribution studies are combined with slope analyses and a saturation methodology to determine the presence of extractant aggregates in both forms. These studies reveal that the thiocyanate salt of Aliquat-336 forms bigger aggregates, which we hypothesize is linked to its increased separation factor. This approach does not disprove the previous hypothesis regarding the impact of the aqueous-phase chemistry on this system. However, it provides alternative, and possibly supplemental, information that will greatly improve our understanding of this separation process. Building upon this approach, future investigations into the role of aggregation on the selectivity of extraction systems have the potential to increase selectivity in current solvent extraction systems for metal ions with similar chemistries.

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