Extraction of Nitric Acid, Americium(III), Curium(III) and Lanthanides(III) into DMDOHEMA Dissolved in Kerosene

Andreas Geist,[a] Laurence Berthon,[b] Marie-Christine Charbonnel,[b] Udo Müllich[a]

[a] Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE)
P. O. Box 3640, 76021 Karlsruhe, Germany

[b] CEA, DES, ISEC, DMRC, Univ. Montpellier, Marcoule, France

Abstract

Liquid-liquid distribution data were determined for the extraction of nitric acid, Am(III), Cm(III) and lanthanides(III) from 0.1–7 mol/L nitric acid into 0.5–1 mol/L *N,N'*-dimethyl-*N,N'*-dioctyl-2-[2-(hexyloxy)ethyl]-malonamide (DMDOHEMA) dissolved in kerosene. Nitric acid extraction was accurately modelled accounting for the adducts, $(HNO_3)L_2$, $(HNO_3)L$ and $(HNO_3)_2L$. To model Am(III) extraction the following complexes were taken into account, $Am(NO_3)_3L_4$, $Am(NO_3)_3(HNO_3)L_3$ and a third complex: $Am(NO_3)_3(HNO_3)_2\mathbf{L_3}$ (considering spectroscopic results) or $Am(NO_3)_3(HNO_3)_2\mathbf{L_2}$ (considering slope analysis results). Separation factors for Am(III) over Cm(III) and the lighter lanthanides(III) are practically independent of nitric acid concentration. Am(III)/Ln(III) separation factors decrease with increasing nitric acid concentration for the heavier lanthanides(III).

Keywords

DMDOHEMA, nitric acid, americium(III), curium(III), lanthanides(III), extraction, equilibrium model, DIAMEX, GANEX

Introduction

Alkylated malonamides[1-7] are used as extracting agents to co-extract tri-, tetra- and hexavalent actinides, An(III), An(IV), An(VI) and lanthanides, Ln(III), from highly acidic (3–5 mol/L HNO_3) PUREX raffinate solutions, separating them from other fission products and corrosion products. This application is relevant in the context of advanced nuclear fuel cycles, and typically coupled to a subsequent separation of actinides from lanthanides.[8-9] Recently, malonamides have been proposed as extracting agents for Pd(II).[10]

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Alkylated malonamides consist only of C, H, O and N atoms, making them combustible to gaseous products. This property is advantageous with respect to secondary waste management;[11] no solid waste is generated from degradation products of the malonamides.

N,N'-dimethyl-*N,N'*-dioctyl-2-[2-(hexyloxy)ethyl]-malonamide (DMDOHEMA, Figure 1)[12-13] was selected the reference extracting agent for several actinide extraction processes under development at the French commissariat à l'énergie atomique et aux énergies alternatives (CEA) and other European laboratories. Initially, DMDOHEMA was used in the development and demonstration of DIAMEX (DIAMide EXtraction) processes[14-18] to co-extract An(III) and Ln(III) from PUREX raffinate solutions. Later, DMDOHEMA was used in the development and demonstration of several processes combining An(III) and Ln(III) co-extraction with selective An(III)[19] or Am(III)[20] stripping from the loaded organic phase. Finally, DMDOHEMA was also implemented in various GANEX (grouped actinides extraction) flow-sheets to co-separate Np(VI), Pu(IV), Am(III) and Cm(III).[21-28]
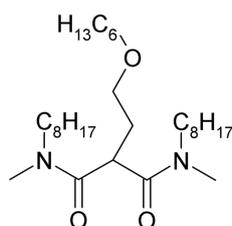
Figure 1. *N,N'*-dimethyl-*N,N'*-dioctyl-2-[2-(hexyloxy)ethyl]-malonamide (DMDOHEMA).

Several studies on the extraction of nitric acid and metal nitrates into alkylated malonamides (other than DMDOHEMA) and similar extracting agents have been published. The extraction of nitric acid is generally described by the formation of adducts such as HNO_3L_2 and $(HNO_3)_xL$ (with $x = 1–3$).[1, 29-32] Actinide(III) and lanthanide(III) nitrates are extracted from neutral nitrate solutions as $M(NO_3)_3L_x$ (with $x = 2–4$).[2, 33-36] Some authors suggest the formation of several additional complexes, $M(NO_3)_3(HNO_3)_xL_y$ (with $x = 1–2$ and $y = 2–4$) when extracting from nitric acid.[2, 32, 37-38]

Few studies report equilibrium distribution data for the extraction of nitric acid, actinides(III) and lanthanides(III) into DMDOHEMA dissolved in kerosene.[13, 34, 39] Conclusions regarding the composition of the extracted metal ion complexes are contradictory:

A simple slope analysis, plotting $\lg D_{M(III)}$ vs. $\lg [L]_{ini}$ and $\lg [HNO_3]_{eq}$, respectively, indicated the formation of $M(NO_3)_3L_2$ complexes upon extraction of Am(III), Eu(III) and Nd(III) from approximately 3 mol/L nitric acid.[39] The same study however concluded from a loading experiment using Ce(III) the formation of a $Ce(NO_3)_3L_3$ complex, for similar nitric

acid concentration. Then again, complexes prepared by extracting Am(III) and Ln(III) (Nd, Eu, Yb) from 3 mol/L nitric acid were identified by EXAFS as $[M(NO_3)_3L_2]$ or $[M(NO_3)_3(H_2O)L_2]$ species.[40] EXAFS and TRLFS analysis of DMDOHEMA organic phases loaded with Eu(III) showed speciation to depend on the acidity of the media: Extraction from acidic media resulted in the formation of $[Eu(\kappa^1\text{-}NO_3)_3(H_2O)_{1-2}L_2]$ while extraction from non-acidic media resulted in the formation of $[Eu(\kappa^2\text{-}NO_3)_2(H_2O)_{0-1}L_2]^+$, with additional outer-sphere DMDOHEMA molecules and an outer-sphere nitrate anion for charge compensation.[41] Increasing the metal cation concentration in the organic phase was shown to promote changes in the speciation.[42] The formation of $[CmL_4(H_2O)]^{3+}$ and $[CmL_3(NO_3)(H_2O)_2]^{2+}$ complexes was identified by TRLFS at low and elevated nitric acid concentrations, respectively.[43] The presence of one water molecule in the $[CmL_4(H_2O)]^{3+}$ complex is in agreement with findings from an analogous Eu(III) complex.[44]

It needs to be considered that in alkane diluents DMDOHEMA forms polydisperse aggregates consisting of four to ten molecules, depending on the experimental conditions.[41-42, 45-51] The extraction of solutes (lanthanide nitrates or nitric acid) in macro concentrations promotes aggregation. All these data (molecular characterization and structure of the aggregates) show that organic solutions of malonamides are complex. A full description of the speciation requires a multiscale approach, combining experimental tools to characterize the molecular and supramolecular speciation with theoretical tools (such as molecular dynamics simulation). The identification of all equilibria involved and the associated constants is difficult and not mandatory to represent the equilibrium state. In this paper, we have chosen to describe the macroscopic behaviour (i.e., distribution of metal nitrates and nitric acid) using a simplified model, accounting for the major solute-ligand complexes or adducts.

The present paper reports distribution data for the extraction of nitric acid, Am(III), Cm(III) and Ln(III) from nitric acid (0.1–7 mol/L) into DMDOHEMA (0.5–1 mol/L) in TPH ("hydrogenated tetrapropene", a kerosene diluent). New data were collected for a couple of reasons: nitric acid distribution data are not available; the few Am(III) distribution data reported in references[13, 34] and in reference[39] are not in good agreement; no Ln(III) distribution except a few values for Nd(III) and Eu(III) are available. An equilibrium model for calculating nitric acid and metal nitrates distributions is presented, based on slope analysis and results from spectroscopy.[43] The proposed model addresses flow-sheet calculations. It was kept rather simple, e. g. by neglecting non-ideality and aggregation[41-42, 45-51] in the organic phase. Nevertheless, it allows calculating distribution ratios with reasonable accuracy, over a wide range of nitric acid concentrations and for applied DMDOHEMA concentrations.

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Experimental

Organic phases were solutions of DMDOHEMA (Panchim, France; previously purified over Alumina B) in TPH (Prochrom, France) at 0.50, 0.65, 0.75, and 1.0 mol/L (241.0, 313.3, 361.5, and 482.0 g/L). They were pre-contacted with water. Aqueous phases were either nitric acid or ^{241}Am(III) (1 MBq/L, 3.3×10^{-8} mol/L) + ^{152}Eu(III) (1.6 MBq/L, 1.6×10^{-9} mol/L) in nitric acid of varied concentration (0.1–7 mol/L). Further experiments were carried out with aqueous phases additionally containing ^{244}Cm(III) (1 MBq/L, 1.4×10^{-9} mol/L) and stable lanthanide nitrates (Ln(III) = Y(III), La(III)–Lu(III) except Pm(III)) in concentrations of 7×10^{-5} mol/L each. Aqueous phases containing $Nd(NO_3)_3$ (≤ 0.3 mol/L) in HNO_3 (3–5 mol/L) were used to load the solvent.

Each 0.5 mL of organic and aqueous phases were contacted at (295±1) K on an orbital shaker (IKA KS 250) for 45 min and centrifuged. It had been verified by preliminary tests that this time by far was sufficient to attain equilibrium. Following centrifugation, phases were separated and taken for analysis.

^{241}Am and ^{152}Eu were determined on a gamma counter (Packard Cobra Auto-Gamma 5003) in both organic and aqueous samples. Lanthanides were determined by ICP-MS (Perkin-Elmer Elan 6100). ^{241}Am and ^{244}Cm were analysed by alpha spectrometry. For ICP-MS and alpha spectrometric analysis of organic samples, organic aliquots were stripped into dilute nitric acid with an appropriate *A/O* ratio.

Initial and equilibrium nitric acid concentrations in aqueous samples were determined by duplicate titration with 0.1 mol/L NaOH on a Metrohm Titroprocessor. Titration was repeated whenever values did not agree within 2%. To determine the nitric acid concentration in the organic samples, these were stripped into water with an appropriate phase ratio, *A/O* = 3–10, which was then titrated as described above. Samples containing low amounts of nitric acid were titrated with 0.02 mol/L NaOH. Preliminary experiments showed that TPH itself did not extract detectable concentrations of nitric acid.

Water concentration in organic phases was determined by Karl Fischer titration.

All experiments were performed in (at least) duplicate. Reported experimental data are mean values. Distribution data are reported in the Supplemental Information.

Treatment of aqueous phase non-ideality

Equilibrium models for the extraction of nitric acid and Am(III) were established using activities in the aqueous phase and concentrations in the organic phase.

Molal activities were used in aqueous phases. Molar nitric acid concentration c [mol/L] was converted to the molal concentration scale, m [mol/kg H_2O], according to[52]

$$m = 0.995\,c + 0.04\,c^2$$

Molal nitric acid concentration was then converted to molal activity using activity coefficients γ_i $(i = H^+$ and $NO_3^-)$ calculated with the Specific Interaction Theory (SIT).[53-54] To cover the range of nitric acid concentrations used in this work (≤ 7 mol/L), the SIT equation (see below) was extended using higher-order ion interaction coefficients $\varepsilon_n\,(H^+/NO_3^-)$: $\varepsilon_1 = 0.07$, $\varepsilon_2 = 1.0 \times 10^{-4}$, $\varepsilon_3 = -1.2 \times 10^{-4}$:

$$\lg \gamma_i = -z_i^2 \frac{A\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}} + \sum_{n=1}^{3} \varepsilon_n\,m^n$$

For nitric acid, the molal ionic strength I_m is equal to the molal concentration m. The mean activity coefficient $\gamma_\pm$ is equal to the ionic activity coefficients, $\gamma\,(H^+)$ and $\gamma\,(NO_3^-)$. The ionic charges z_i are 1 and -1, respectively. A and B are constants, a_i is an ion size parameter.

Nitric acid activity coefficients for 0.1–9 mol/L HNO_3 calculated accordingly agree within $\pm 3\%$ with literature data.[55-56]

Am^{3+} activity was calculated by SIT, see above. A SIT coefficient of $\varepsilon(Am^{3+}/NO_3^-) = 0.27$ was used, as estimated from the literature.[57-58]

No corrections for non-ideality were performed in the organic phase.

Results and discussion

Third phase formation

When contacting aqueous phases with initial nitric acid concentrations up to 6 mol/L with organic phases containing 0.5–1.0 mol/L DMDOHEMA in TPH, no third phase occurred. However, when the initial nitric acid concentration was 7 mol/L, the formation of a third phase was observed with 0.50 and 0.75 mol/L DMDOHEMA, but not with 1.0 mol/L DMDOHEMA. These observations agree with results reported earlier.[13, 34, 50]

Loading an organic phase (0.75 mol/L DMDOHEMA in TPH) by extracting Nd(III) from an aqueous solution containing $Nd(NO_3)_3$ in 5 mol/L HNO_3, third phase formation was observed for initial aqueous Nd(III) concentrations ≥ 0.1 mol/L. For 0.48 mol/L and 0.62 mol/L DMDOHEMA in TPH at 3 mol/L HNO_3, third phase was observed for initial aqueous Nd(III) concentrations of 0.15 mol/L and 0.2 mol/L, respectively. Organic phase Nd(III)

concentrations were 0.082 mol/L and 0.108 mol/L, respectively and aqueous phase Nd(III) concentrations were 0.074 mol/L and 0.089 mol/L, respectively.

Nitric acid extraction

Similar to other neutral extracting agents,[59-67] DMDOHEMA in TPH extracts significant amounts of nitric acid. Figure 2 shows the amount of nitric acid extracted as a function of initial aqueous nitric acid concentration (initial concentration is reported to represent nitric acid extraction for given experimental conditions, i. e. initial nitric acid and DMDOHEMA concentrations). E.g., for an initial aqueous nitric acid concentration of 5 mol/L, the organic equilibrium nitric acid concentration exceeds the total extracting agent concentration. Species such as $(HNO_3)_xL$ (with $x > 1$) must be present in the organic phase. This agrees with results from other studies with similar extracting agents. [1, 29-32] Details on the calculations (lines in Figure 2) are given in the section "Equilibrium model for nitric acid extraction" below.
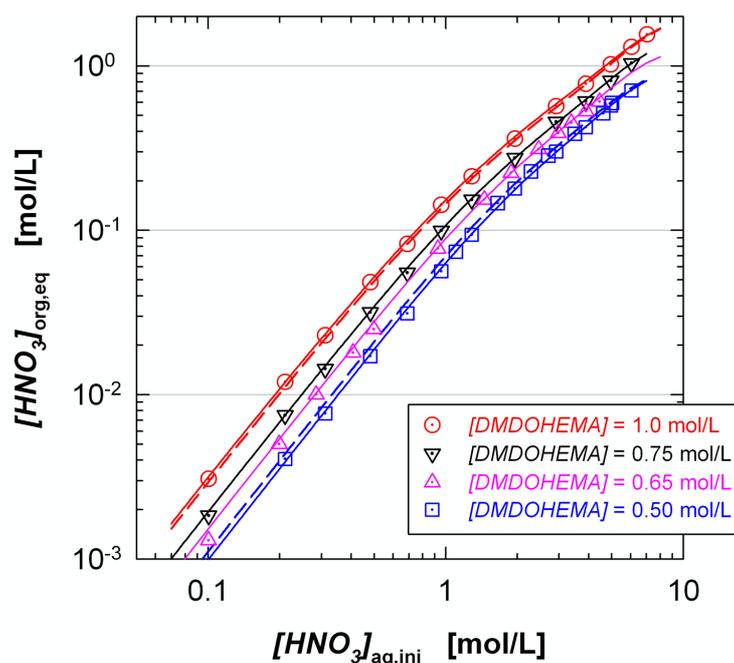
Figure 2. Extraction of nitric acid into DMDOHEMA in TPH. Equilibrium organic nitric acid concentration as a function of initial aqueous nitric acid concentration. Organic phase, DMDOHEMA in TPH. Aqueous phase, HNO_3 or [241]Am(III) (1000 Bq/mL) + [152]Eu(III) (1600 Bq/mL) in HNO_3. T = 295 K, A/O = 1. Lines, calculated using fixed (dashed lines) or conditional (solid lines) extraction constants (see "Equilibrium model for nitric acid extraction"). See Table SI 1 for numerical values.

Extraction of americium(III) and europium(III)

The distribution of Am(III) as a function of initial nitric acid concentration is shown in Figure 3. Am(III) is extracted (i.e., $D_{Am(III)} > 1$) from nitric acid with a concentration > 2 mol/L (for 0.5 mol/L DMDOHEMA) or > 1.5 mol/L (for 1.0 mol/L DMDOHEMA). Am(III) is back-extracted (i.e., $D_{Am(III)} < 1$) into dilute nitric acid.

Details on the calculations (lines in Figure 3) are given in the section "Am(III) equilibrium model" below.
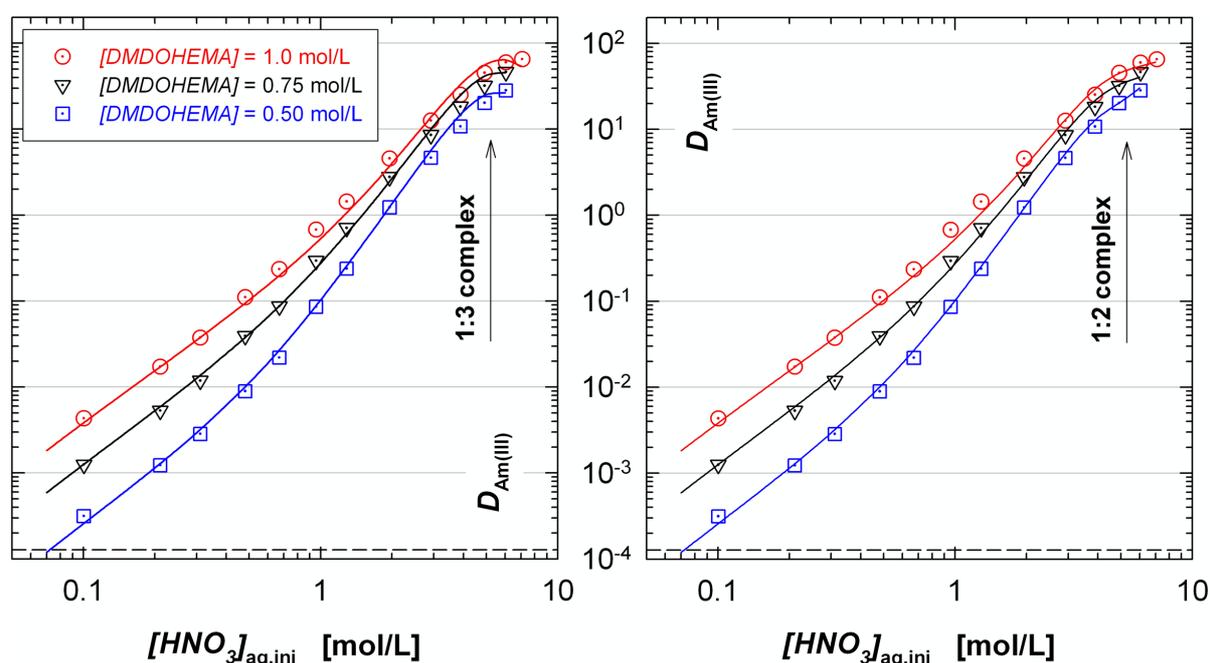
Figure 3. Extraction of Am(III) into DMDOHEMA in TPH. Distribution ratios as a function of initial aqueous nitric acid concentration. Organic phase, DMDOHEMA in TPH. Aqueous phase, [241]Am(III) (1000 Bq/mL) + [152]Eu(III) (1600 Bq/mL) in nitric acid. T = 295 K, A/O = 1. Dashed line, detection limit. Lines, calculated accounting for the Am(NO$_3$)$_3$(HNO$_3$)$_2$**L$_3$** complex (left) or the Am(NO$_3$)$_3$(HNO$_3$)$_2$**L$_2$** complex (right), see "Am(III) equilibrium model". See Table SI 1 for numerical values.

The experiments shown in Figure 2 and Figure 3 also contained [152]Eu(III). Figure 4 shows the respective Eu(III) distribution ratios (reported as Am(III)/Eu(III) separation factors, $SF_{Am(III)/Eu(III)} = D_{Am(III)} / D_{Eu(III)}$). Since the DMDOHEMA concentration did not show a significant or systematic effect on the separation factor, all values for a given nitric acid concentration were averaged.
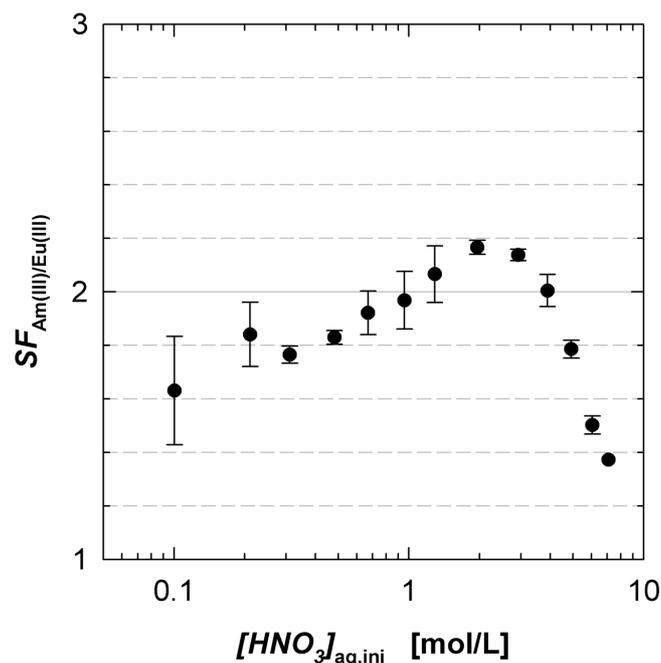
Figure 4. Am(III)/Eu(III) separation factor as a function of initial aqueous nitric acid concentration. Organic phase, (0.5–1.0 mol/L) DMDOHEMA in TPH. Aqueous phase, ^{241}Am(III) (1000 Bq/mL) + ^{152}Eu(III) (1600 Bq/mL) in nitric acid. $T = 295$ K, $A/O = 1$. See Table SI 1 for numerical values.

The $SF_{Am(III)/Eu(III)}$ values are in the range of 1.8 ± 0.4. The slight variation of $SF_{Am(III)/Eu(III)}$ values with nitric acid concentration appears to have a systematic trend which may originate from small differences in organic phase or aqueous phase speciation of Am(III) vs. Eu(III).

Extraction of curium(III) and lanthanides(III)

Further to the extraction of nitric acid, Am(III) and Eu(III), the extraction of Cm(III), lanthanides(III) (Ln(III) = La–Lu except Pm) and Y(III) was studied as these are the major species to be extracted in DIAMEX or similar processes.

Figure 5 shows distribution ratios for a DMDOHEMA concentration of 0.75 mol/L as a function of initial nitric acid concentration (0.11–3.0 mol/L). Results from a second experiment using a DMDOHEMA concentration of 1.0 mol/L and nitric acid concentrations of 2.6–6.1 mol/L are shown in Figure 6. The respective separation factors ($SF_{Am(III)/M(III)} = D_{Am(III)} / D_{M(III)}$) for Am(III) over M(III) (M = curium, yttrium and all lanthanides except promethium) are reported in Table 1.
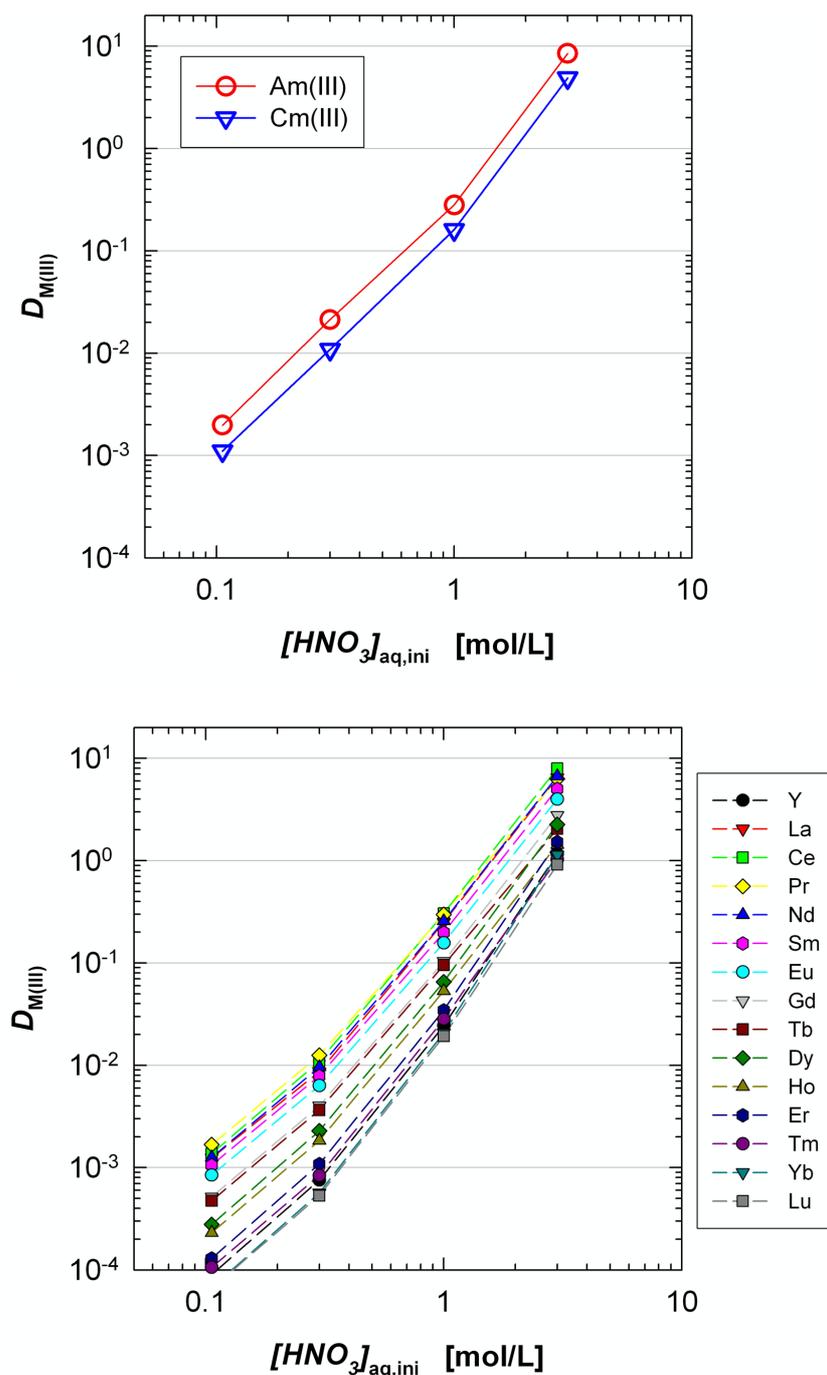
Figure 5. Extraction of Am(III), Cm(III), Y(III) and Ln(III) into DMDOHEMA in TPH. Distribution ratios as a function of initial aqueous nitric acid concentration. Top, Am(III) and Cm(III). Bottom, Ln(III) and Y(III). Organic phase, 0.75 mol/L DMDOHEMA in TPH. Aqueous phase, ^{241}Am(III) (1000 Bq/mL) + ^{244}Cm(III) (1000 Bq/mL) + ^{152}Eu(III) (1600 Bq/mL) + Ln(III) and Y(III) (7×10^{-5} mol/L each) in nitric acid. $T = 295$ K, $A/O = 1$.
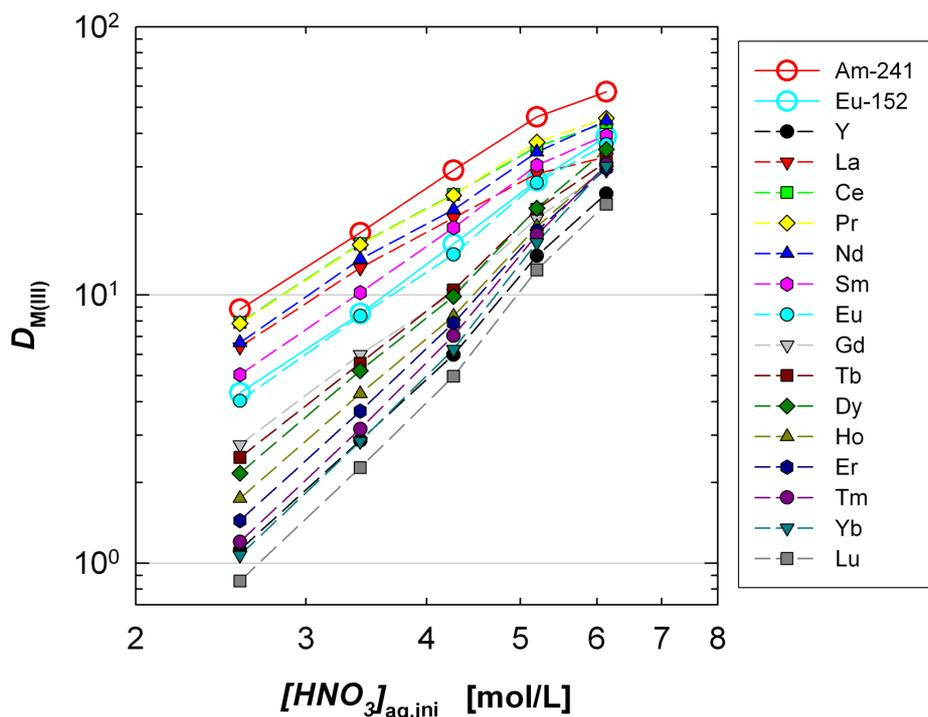
Figure 6. Extraction of Am(III), Ln(III) and Y(III) into DMDOHEMA in TPH. Distribution ratio as a function of initial aqueous nitric acid concentration. Organic phase, 1.0 mol/L DMDOHEMA in TPH. Aqueous phase, ^{241}Am(III) (1000 Bq/mL) + ^{152}Eu(III) (1600 Bq/mL) + Ln(III) and Y(III) (7×10^{-5} mol/L each) in nitric acid. $T = 295$ K, $A/O = 1$.

The Am(III)/Cm(III) selectivity $(SF_{Am(III)/Cm(III)} \approx 1.8)$ agrees reasonably well with data reported in the literature $(SF_{Am(III)/Cm(III)} \approx 1.6)$.[68] The extractability of the lanthanides(III) decreases with their atomic number, as observed earlier.[39] Cm(III) behaves similar to Sm(III), Y(III) behaves similar to Tm(III) and Yb(III). That is, affinity is primarily driven by the size of the respective trivalent metal ions, in agreement with results from other extracting agents such as HDEHP[69] or TODGA.[70]

Separation factors for Am(III) over Cm(III) and the lighter lanthanides(III) (up to Tb(III)) are practically independent of nitric acid concentration. However, the separation factors decrease with increasing nitric acid concentration for the heavier lanthanides(III), in particular for Er(III) and heavier Ln(III). This behaviour could be due to differences in aqueous or organic phase speciation. Generally, distribution data for An(III) and Ln(III) are in agreement with the scarce data reported in the literature.[13, 34, 71-72]

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Table 1. Extraction of Am(III), Cm(III), Y(III) and lanthanides(III) into DMDOHEMA in TPH. Am(III)/M(III) separation factors as a function of initial aqueous nitric acid concentration. Experimental conditions, see Figure 5 and Figure 6. $SF_{Am(III)/Cm(III)}$ from alpha spectroscopy data, $SF_{Am(III)/Eu(III)-152}$ from gamma spectroscopy data, all other values from Am(III) gamma spectroscopy and Ln(III) ICP-MS data.

$SF_{Am(III)/M(III)}$	$[HNO_3]_{aq,ini}$ [mol/L]								
	0.11	0.30	1.0	2.6	3.0	3.4	4.3	5.2	6.1
Cm	1.8	2.0	1.8	–	1.7	–	–	–	–
Y	18	16	13	7.9	7.4	5.9	4.9	3.3	2.4
La	1.4	1.4	1.3	1.4	1.3	1.4	1.5	1.6	1.7
Ce	1.2	1.1	1.1	1.1	1.1	1.1	1.2	1.3	1.3
Pr	1.0	1.0	1.1	1.1	1.4	1.1	1.2	1.2	1.3
Nd	1.3	1.3	1.3	1.3	1.3	1.3	1.4	1.4	1.3
Sm	1.6	1.6	1.6	1.8	1.7	1.7	1.6	1.5	1.5
Eu	2.0	1.9	2.1	2.2	2.2	2.0	2.1	1.8	1.6
Eu-152	1.9	1.8	2.1	2.1	2.1	2.0	1.9	1.7	1.5
Gd	3.2	3.1	3.1	3.2	3.0	2.8	2.9	2.4	2.0
Tb	3.6	3.4	3.4	3.6	4.2	3.1	2.8	2.2	1.8
Dy	6.0	5.4	5.0	4.1	3.8	3.3	3.0	2.2	1.6
Ho	7.3	6.7	6.1	5.1	6.0	4.0	3.5	2.6	1.9
Er	13	11	9.4	6.1	5.6	4.6	3.7	2.7	1.9
Tm	16	15	12	7.4	8.3	5.4	4.1	2.8	1.9
Yb	25	22	16	8.0	7.5	6.0	4.6	2.9	1.9
Lu	25	23	17	10	9.4	7.5	5.9	3.7	2.6

Equilibrium model for nitric acid extraction

Based on the experimental results (Figure 2) and concluding from earlier studies, [1, 29-32] nitric acid extraction by DMDOHEMA was calculated taking into account the formation of three adducts, $(HNO_3)L_2$, $(HNO_3)L$ and $(HNO_3)_2L$. Hydrated species were not considered since non-stoichiometric or weak interactions seem to prevail in the case of malonamides or similar systems, see references[1, 29-31] and Table SI 1. The following extraction constants were used, with activities in the aqueous phase and concentrations in the organic phase:

$$K_{H12} = \frac{[(HNO_3)L_2]}{(H^+) \cdot (NO_3^-) \cdot [L]^2}$$

$$K_{H11} = \frac{[(HNO_3)L]}{(H^+) \cdot (NO_3^-) \cdot [L]}$$

$$K_{H21} = \frac{[(HNO_3)_2L]}{(H^+)^2 \cdot (NO_3^-)^2 \cdot [L]}$$

This model allows describing the extraction of nitric acid without accounting for aggregation equilibria. With these equations, equilibrium aqueous activities and organic concentrations were calculated, the organic equilibrium nitric acid concentration $[HNO_3]_{org,eq}$ being

$$[HNO_3]_{org,eq} = [(HNO_3)L_2] + [(HNO_3)L] + 2\,[(HNO_3)_2L]$$

and the free DMDOHEMA concentration $[L]$,

$$[L] = [L]_{total} - (2\,[(HNO_3)L_2] + [(HNO_3)L] + [(HNO_3)_2L])$$

Initially, a set of three extraction constants independent of the total extracting agent concentration was used,

$$K_{H12} = 0.27 \text{ kg}^2 \text{ L mol}^{-3}$$

$$K_{H11} = 0.23 \text{ kg}^2 \text{ mol}^{-2}$$

$$K_{H21} = 0.003 \text{ kg}^4 \text{ mol}^{-4}$$

The results from the calculations are shown as dashed lines in Figure 2. The constants were fit to the experimental data at *[DMDOHEMA]* = 0.75 mol/L, resulting in excellent agreement. However, nitric acid extraction is overestimated ($\approx$ 10%) for 0.50 mol/L DMDOHEMA and underestimated ($\approx$ 5%) for 1.0 mol/L DMDOHEMA. Within this accuracy, these constants are valid for technically relevant DMDOHEMA concentrations (other than those reported,[45] where the extraction constants are valid for *[DMDOHEMA]* $\leq$ 0.1 mol/L).

Calculations using conditional extraction constants were performed to improve accuracy. Very good agreement with the experimental data is achieved using a fixed value for K_{H12} and conditional extraction constants K_{H11} and K_{H21},

$$K_{H12} = 0.27 \text{ kg}^2 \text{ L mol}^{-3}$$

$$K_{H11} = (0.23 + ([L] - 0.75) \times 0.16) \text{ kg}^2 \text{ mol}^{-2}$$

$$K_{H21} = (0.003 + ([L] - 0.75) \times 0.0032) \text{ kg}^4 \text{ mol}^{-4}$$

Organic phase nitric acid concentrations calculated with these values are shown as solid lines in Figure 2. The standard deviation between calculated and experimental values is 2% (which is in the range of the experimental uncertainty).

The calculated species distribution for a total DMDOHEMA concentration of 0.75 mol/L is shown in Figure 7. According to the calculations, nitric acid is mainly extracted as the 1:1 adduct, $(HNO_3)L$, and the 1:2 adduct, $(HNO_3)L_2$. The 2:1 adduct, $(HNO_3)_2L$, dominates

beyond an initial aqueous nitric acid concentration of 5 mol/L. The speciation is quite similar to that reported for DMDBTDMA,[31] except that the formation of the 3:1 adduct, $(HNO_3)_3L$, does not need to be considered in the case of DMDOHEMA. Despite the presence of water molecules in the organic phase (see Annex), the introduction of complexes including water was not necessary to represent nitric acid extraction.
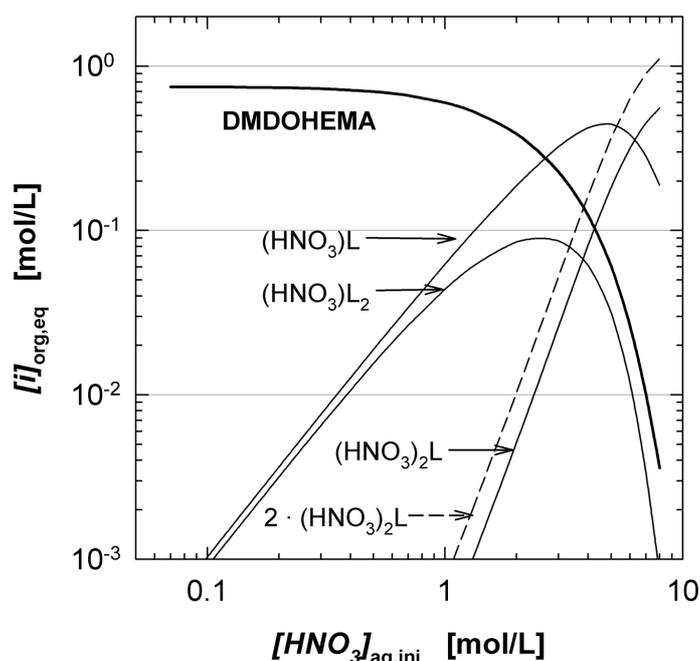
Figure 7. Extraction of nitric acid into 0.75 mol/L DMDOHEMA in TPH. Calculated organic phase speciation as a function of initial aqueous nitric acid concentration. Dashed line is twice the concentration of the $(HNO_3)_2L$ adduct, representing its contribution to the organic phase nitric acid concentration.

Equilibrium model for americium(III) extraction

Considering results from slope analysis (see below) based on the Am(III) distribution data presented in Figure 3 and on spectroscopy results,[43] an equilibrium model for the extraction of Am(III) was established.

Stoichiometry of Am(III)-DMDOHEMA complexes

The slopes of lg $D_{Am(III)}$ vs. lg $[HNO_3]_{aq,eq}$ (as derived from Figure 3) have values of 3.1, 2.8 and 2.6 (for 0.5, 0.75, and 1.0 mol/L DMDOHEMA). This must not be interpreted assuming the formation of a complex, $Am(NO_3)_3L_n$. In fact, such a simple slope analysis is not valid since the free DMDOHEMA concentration varies significantly with nitric acid concentration due to the pronounced nitric acid extraction.

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A more elaborate approach is required. To determine the number of DMDOHEMA molecules in the extracted complexes, Am(III) distribution ratios were plotted versus the free DMDOHEMA concentration at constant nitrate activity. Similarly, the number of nitrate anions was determined by plotting Am(III) distribution ratios versus equilibrium nitrate activity at a constant free DMDOHEMA concentration. In detail:

The number of DMDOHEMA molecules was determined by plotting $\lg D_{Am(III)}$ versus $\lg [DMDOHEMA]_{eq}$ at constant $[HNO_3]_{aq,eq}$ (and hence, constant $(NO_3^-)_{aq,eq}$). The free equilibrium DMDOHEMA concentration was calculated with the model reported above, using conditional K_{H11} and K_{H21} values. Am(III) distribution ratios at given aqueous equilibrium nitric acid concentrations were determined by plotting $\lg D_{Am(III)}$ versus $\lg [HNO_3]_{aq,eq}$ and reading out interpolated $D_{Am(III)}$ at constant $[HNO_3]_{aq,eq}$. Finally, these $\lg D_{Am(III)}$ values were plotted versus $\lg [DMDOHEMA]_{eq}$. The resulting slopes are reported in Table 2. The values of the slopes are close to four in the nitric acid concentration range of 0.1–1 mol/L, decreasing to values around three (2–3 mol/L HNO_3) and finally around two (≥ 5 mol/L HNO_3). These slopes insinuate a complex containing four DMDOHEMA molecules is dominant at lower nitric acid concentration, whereas complexes with three or two DMDOHEMA molecules become dominating with increasing acidity.

Table 2. Slopes for $\lg D_{Am(III)}$ versus $\lg [DMDOHEMA]_{eq}$ at a function of equilibrium nitric acid concentration.

$[HNO_3]_{aq,eq}$ [mol/L]	0.10	0.20	0.30	0.50	0.70	1.00	1.50	2.00	3.00	4.00	5.00
Slope	3.9	4.0	4.0	4.1	4.0	3.8	3.5	3.1	2.8	2.6	2.2

In a similar fashion, $\lg ([Am(III)]_{org}/(Am^{3+})_{aq})$ was plotted versus $\lg (NO_3^-)_{aq,eq}$ at constant $[DMDOHEMA]_{eq}$ (calculated as above). The slopes' values were found to increase with increasing $(NO_3^-)_{aq,eq}$ from approximately three to approximately five, see Figure 8. Slopes having values greater than three may be explained by the presence of complexes containing additional nitric acid molecules.
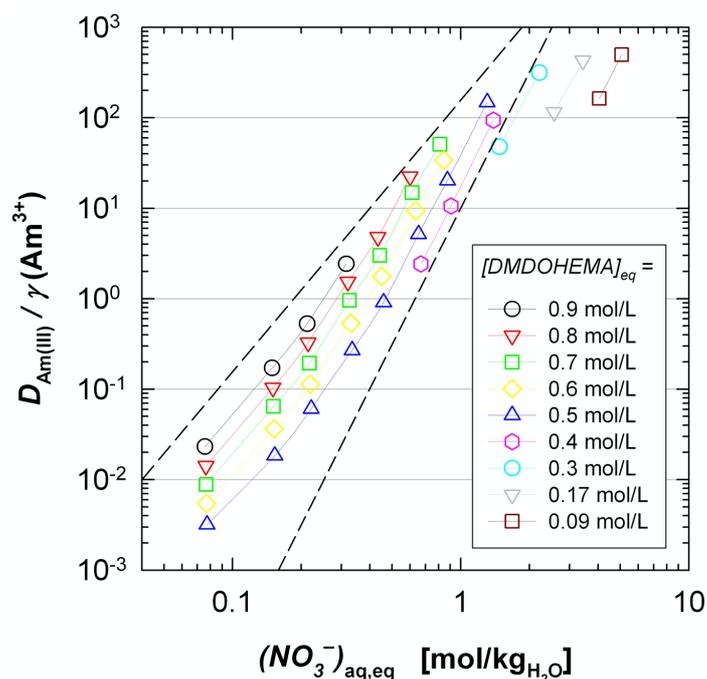
Figure 8. Am(III) distribution ratios corrected for Am^{3+} activity coefficients as a function of equilibrium nitrate activity at constant free DMDOHEMA concentration (as indicated in legend). Dashed lines, slopes 3 and 5.

The slopes from Table 2 and Figure 8, together with published results,[2,37] indicate the formation of three complexes, $Am(NO_3)_3L_4$, $Am(NO_3)_3(HNO_3)L_3$ and $Am(NO_3)_3(HNO_3)_2L_2$. Indeed, there is spectroscopic evidence for the presence of complexes containing four and three DMDOHEMA molecules at low and intermediate nitric acid concentrations, respectively.[43] However, this study did not identify a complex containing two DMDOHEMA molecules for nitric acid concentrations ≤ 6 mol/L HNO_3.

The change in stoichiometry with increasing nitric acid concentration is similar to changes observed in the Eu(III) complexes with increasing Eu(III) concentration.[42] It is also consistent with data indicating increasing aggregation with increasing acidity (i. e. decreasing critical aggregation concentration).[51] Extraction of nitric acid results in the formation of larger, more hydrated aggregates containing nitric acid molecules in the polar core. This could explain the change in the stoichiometry from $M(NO_3)_3L_4$ at low nitric acid concentration to $M(NO_3)_3(HNO_3)_2L_2$ at elevated nitric acid concentrations.

Am(III) equilibrium model

Based on slope analysis and/or spectroscopy results,[43] two equilibrium models for the extraction of Am(III) were developed and compared. Additionally to the nitric acid adducts

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(see above), the following complexes were taken into account, $Am(NO_3)_3L_4$, $Am(NO_3)_3(HNO_3)L_3$ and a third complex: $Am(NO_3)_3(HNO_3)_2\mathbf{L_3}$ (considering the spectroscopic results[43] that indicated the absence of a complex containing two DMDOHEMA molecules) or $Am(NO_3)_3(HNO_3)_2\mathbf{L_2}$ (considering slope analysis results, see Table 2) with the respective extraction constants,

- $K_{Am34} = \dfrac{[Am(NO_3)_3L_4]}{(Am^{3+})\cdot(NO_3^-)^3\cdot[L]^4} = 75$

- $K_{Am43} = \dfrac{[Am(NO_3)_3(HNO_3)L_3]}{(Am^{3+})\cdot(H^+)\cdot(NO_3^-)^4\cdot[L]^3} = 220$

- $K_{Am53} = \dfrac{[Am(NO_3)_3(HNO_3)_2L_3]}{(Am^{3+})\cdot(H^+)^2\cdot(NO_3^-)^5\cdot[L]^3} = 3$

    or

$$K_{Am52} = \frac{[Am(NO_3)_3(HNO_3)_2L_2]}{(Am^{3+})\cdot(H^+)^2\cdot(NO_3^-)^5\cdot[L]^2} = 0.06$$

Am(III) distribution ratios as a function of nitric acid and DMDOHEMA concentrations were calculated with either model. In any case, conditional constants for nitric acid extraction (Figure 2) were used. Using fixed constants for nitric acid extraction resulted in substantial deviations between calculated and experimental Am(III) distribution ratios for nitric acid concentrations greater than 3 mol/L.

Am(III) distribution ratios calculated accounting for the $Am(NO_3)_3(HNO_3)_2\mathbf{L_3}$ complex (Figure 3 left) or the $Am(NO_3)_3(HNO_3)_2\mathbf{L_2}$ complex (Figure 3 right), respectively, are compared to experimental distribution data.

For nitric acid concentrations less than 3 mol/L, the calculations agree with experimental values within approx. 10%, with the exception of the calculations for 1 mol/L DMDOHEMA and 0.5–2 mol/L HNO_3. For nitric acid concentrations greater than 3 mol/L, the model accounting for the $Am(NO_3)_3(HNO_3)_2\mathbf{L_2}$ complex (Figure 3 right) performs slightly better than the model accounting for the $Am(NO_3)_3(HNO_3)_2\mathbf{L_3}$ complex (Figure 3 left).

The contribution of the individual Am(III)-DMDOHEMA complexes to the extraction of Am(III) is shown in Figure 9. According to the calculations, $Am(NO_3)_3L_4$ is the predominant complex for initial nitric acid concentrations smaller than 0.7 mol/L. $Am(NO_3)_3(HNO_3)L_3$ is the dominating complex in the concentration range of 0.7–6 mol/L HNO_3. The third complex (either $Am(NO_3)_3(HNO_3)_2\mathbf{L_2}$ or $Am(NO_3)_3(HNO_3)_2\mathbf{L_3}$, depending on the model used) plays a role only for nitric acid concentrations beyond 6 mol/L. Since this concentration is close to the limit of third phase formation, no further distinction can be made by measuring Am(III) distribution ratios at nitric acid concentrations beyond 6 mol/L.
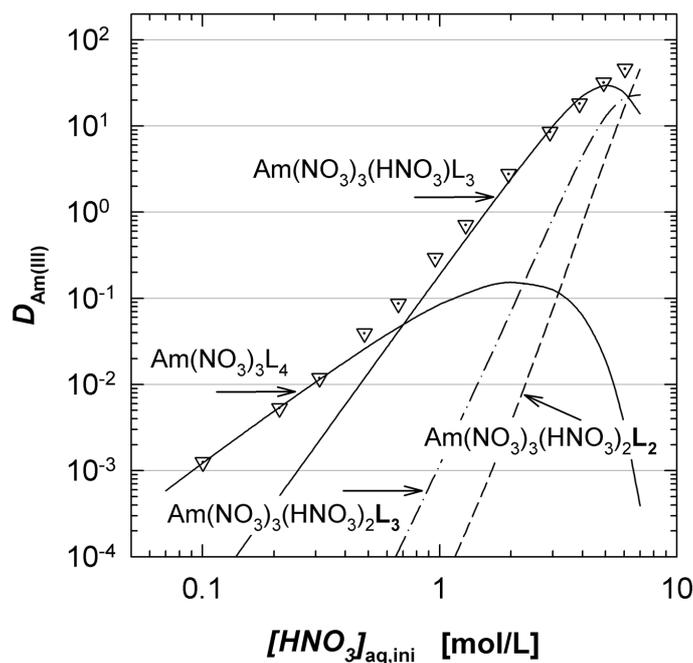
Figure 9. Am(III) extraction, contribution of the individual Am(III)-DMDOHEMA complexes. 0.75 mol/L DMDOHEMA.

Loading experiments

A Ce(III) loading experiment performed at approximately 3 mol/L nitric acid[39] supports the formation of a 1:3 complex, in agreement with results from spectroscopy[43] and slope analysis (Table 2). To help discriminating the formation of a 1:2 complex and a 1:3 complex at nitric acid concentrations ≥ 4 mol/L (see Figure 3), a Nd(III) loading experiment was performed at an initial nitric acid concentration of 5 mol/L. Unfortunately, third phase formation was observed for initial aqueous Nd(III) concentrations ≥ 0.1 mol/L. Calculated Nd(III) distribution ratios accounting for the 1:2 or the 1:3 complex differ by less than 20% for initial aqueous Nd(III) concentrations < 0.1 mol/L. Since such small differences fall within experimental uncertainties this loading experiment does not unambiguously support either the 1:2 or the 1:3 complex.

Conclusions

DMDOHEMA has been applied for the development and demonstration of DIAMEX and GANEX processes. Addressing a lack of published data, this paper reports distribution ratios for the extraction of nitric acid, Am(III), Cm(III) and lanthanides(III) from 0.1–7 mol/L nitric acid into 0.5–1 mol/L DMDOHEMA dissolved in kerosene.

Nitric acid extraction was modelled accounting for the adducts, $(HNO_3)L_2$, $(HNO_3)L$ and $(HNO_3)_2L$, as observed of other diamides. Using a set of extraction constants, experimental data are calculated within $\pm 10\%$. Better accuracy is achieved when using conditional extraction constants for the $(HNO_3)L$ and $(HNO_3)_2L$ adducts.

Am(III) extraction was modelled accounting for the complexes, $Am(NO_3)_3L_4$, $Am(NO_3)_3(HNO_3)L_3$ and a third complex: $Am(NO_3)_3(HNO_3)_2\mathbf{L_3}$ (considering spectroscopic results) or $Am(NO_3)_3(HNO_3)_2\mathbf{L_2}$ (considering slope analysis results). Small differences are observed between these models for initial nitric acid concentrations ≥ 4 mol/L, with the 1:2 complex yielding slightly better agreement between calculations and experiment. While this model does not account for aggregation it allows calculating distribution ratios for the extraction of nitric acid and of actinide(III) and lanthanide ions with reasonable accuracy.

Separation factors between Am(III) and Cm(III) or light lanthanides(III) essentially do not vary with nitric acid concentration. Hence, the proposed equilibrium model is applicable not only for the extraction of Am(III) but also Cm(III) and the "fission lanthanides".

While not intended to resolve the contradictions in organic phase speciation reported in the literature, the proposed equilibrium model may be useful as a basis for process flow-sheet calculations: it covers the full range of nitric acid concentrations expected across the extraction, scrubbing and stripping sections of a multi-stage counter-current process. Furthermore, the study covers a range of DMDOHEMA concentrations, 0.5–1 mol/L, relevant to process development.

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