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Extraction of Lanthanides with Diamides of Dipicolinic Acid from Nitric Acid Solutions. I.

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Abstract: Three ortho-, meta-, and para-derivates of ethyl(tolyl)diamides of dipicolinic acid were synthesized and tested on their extraction performance from nitric acids solutions. Extraction of americium and lanthanides (Ln) by these compounds as a function of nitric acid concentration was studied. Distribution ratios of studied metals were determined using ICP-OES method and radiotracer ^{241}Am. Am/Ln separation differs among studied diamides, and the best separation was found for N,N′-diethyl-N,N′-di(ortho)tolyl-diamide.

Keywords: Americium; Dipicolinic, diamides; Extraction; Lanthanides

INTRODUCTION

During the past two decades, the interest to develop soft-donor complexing agents that are promising extractants for the separation of lanthanides and trivalent actinides has received significant attention. As the chemistries of these elements are nearly identical, and differ only in a slightly stronger interaction of trivalent actinides with certain ligand donor atoms, their separation is a complex task (1). A soft donor atom such as nitrogen can covalently coordinate 5f-elements, showing a higher selectivity than the harder oxygen atom toward actinide (5f) over lanthanide (4f) elements; therefore, amides are a subject of extensive research as potential extractants of minor actinides from PUREX raffinate.

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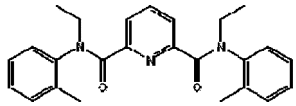
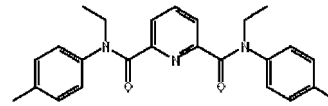
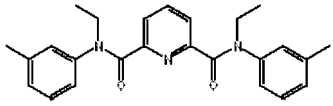
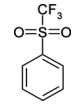
Current research has led to development of new N-containing reagents and processes with considerable potential for accomplishing the desired separation. After substituted malonic diamides (2–8), the interest shifted to tetraalkyl-diglycolamides that were extensively studied with emphasis on properties of tetraoctyl-diglycolamide (TODGA) (9–11), which was proposed, diluted with a hydrocarbon, as an extractant for Pu(IV), Np(IV), Am(III), and Cm(III) (12–14). The extractability of TODGA toward many other metals (15), and its high extractive capacity was shown to allow its application as a solid extractant (16,17). TODGA has been extensively evaluated for the separation of actinides(III) and lanthanides(III) from a high active PUREX raffinates in a batch and centrifugal extractor experiments (18,19).

A rather new class of diamidic extractants are the diamides of dipicolinic acid (DPA). (Note that the acronym PDA has previously been used for the diamides of dipicolinic acid (23,26). However, we prefer the acroymn DPA, consistent with our recent works (25,27)). Diamides of dipicolinic acid show very unusual extraction properties to americium. A very low extraction ability of tetraalkyl-diamides for americium and europium was shown in earlier works (20–21). It was later confirmed in another study (21) wherein the extraction of uranium and thorium by tetraalkyl-diamides of dipicolinic acid was investigated. However, we have found that some of dialkyldiaryldiamides in chloroform (22,23) or particularly in polar diluents (24–27) show a very good extractability not only toward uranium, but also toward minor actinides. Specifically, dialkyldiaryldiamides can extract americium over europium with a separation factor Am/Eu as large as 6. Additionally, unusual behavior was also observed for extraction of lanthanides by dimethyl-diphenyl-diamide of dipicolinic acid in chloroform – the heavy lanthanides are extracted better than the lighter ones. This trend is opposite to extraction with carbamoylphosphineoxide and diphosphinedioxide (28).

Recently we have reported (26) that among other substituted diamides of dipicolinic acid, the N,N′-diethyl-N,N′-di(para)tolyl-diamide shows the best extractability toward americium. Therefore, it was of great interest to study the extraction of lanthanides and americium by different diethyl-ditolyl-diamides of dipicolinic acid as a function of the extractant structure and nitric acid concentration, and evaluate their effect on separation of Am from lanthanides. The aim of the present work is to investigate the effect of the methyl group position in tolyl ring on the extraction performance of the ortho-, meta-, and para isomers of the studied diethyl-ditolyl-diamides of dipicolinic acid and indentify the isomer and concentration conditions with the best extraction ability and selectivity.

Table 1. Structures of diamides of dipicolinic acid studied in this work

	
N,N′-diethyl-N,N′di(ortho)tolyl-diamide of dipicolinic acid **Et(o)TDPA**	N,N′-diethyl-N,N′di(para)tolyl-diamide of dipicolinic acid **Et(p)TDPA**
	
N,N′-diethyl-N,N′di(meta)tolyl-diamide of dipicolinic acid **Et(m)TDPA**	Phenyltrifluoromethylsulfone, **FS-13**

EXPERIMENTAL

Materials and Methods

The synthetic procedure was previously described, a solution of dichloro-anhydride of dipicolinic acid in methylene chloride was added under stirring to solution of corresponding N-ethyl aniline and triethylamine in methylene chloride at 10–15°C (26). After addition, the mixture was stirred for one hour at room temperature and one hour at 30°C. The solution was washed by 1 M HCl (twice), water, 5% NaOH and water, dried and evaporated. The solid obtained was re-crystallized from an appropriate solvent. The structures of the DPA's studied in this work along with the diluent (FS-13) are presented in Table 1.

Solvent Extraction

It is known that DPA have good extraction properties in polar solvents (24); therefore, phenyltrifluoromethylsulfone (FS-13, see Table 1) was used as a diluent for 0.2 M DPA employed as organic extraction phase.

Aqueous solutions for extraction of lanthanides were prepared from multielement standard solution of lanthanides (VWR International, ARISTAR Multiple Elements Set 82025-926) initially containing Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and also U and Th,

Table 2. Extraction of Am from 3 M HNO_3. Solvent: 0.1 M EtTDPA in F-3; [Eu] = 1×10^{-5} M

Contact time [min]	D_{Am}
1	3.0
3	3.2
5	3.0
30	3.3
60	3.1

100 ppm of each in 5% nitric acid. This standard was diluted with required amounts of nitric acid and deionized water such that the concentration of metals in in desired nitric acid concentration of the aqueous extraction phase was maintained at 40 ppm ($\sim$40 mg/L, or $\sim$0.3 mM/L) of each lanthanide.

Lanthanides extraction experiments were carried out using 7 ml plastic vials. 2 ml of organic phase (pre-equilibrated with the desired nitric acid concentration) and 2 ml of aqueous phase were placed in vials. Samples were vigorously agitated for 3 minutes at room temperature ($21 \pm 1^{\circ}$C). The kinetic experiment confirmed that extraction equilibrium was established already after 1 minute of agitation (Table 2). Agitation time increased up to 60 min did not bring increased yields of Am or Eu.

Phases were separated after a short centrifugation for 5–10 min, and aliqutes were taken for analysis. Concentrations of lanthanide metals were determined by ICP-OES method. Raffinate solutions were diluted with 1% nitric acid to obtain the concentration of the analyte in the range of 10 ppm to 10 ppb of each lanthanide. Concentration of metals in organic phase was calculated as a decrease of metal concentration in the aqueous phase.

For americium extraction, the aqueous phase was prepared from 4×10^{-5} M solution of Eu in desired concentration of nitric acid and spiked with Am-241. Experiments were carried out in 2 ml plastic vials at room temperature ($21 \pm 1^{\circ}$C). Equal volumes (0.5 mL) of organic phase and aqueous phase were agitated for 3 minutes, split by centrifugation, and 0.4 mL aliquots of each phase were counted on concentration of americium using 3″ well-NaI(Tl) detector (Cobra Packard auto-gamma). The deviation between two parallel measurements was less than 10%.

RESULTS AND DISCUSSION

Lanthanide Extraction

Previously it was found (23) that the extraction of lanthanides (Ln) with 0.5 M solution of dimethyl-diphenyl-diamide of dipicolinic acid in

chloroform was effective only for nitric acid solutions with a concentration greater than 4 M HNO_3.

In the present work, we studied the extraction of Ln and Am by three structural isomers of diethyl-ditolyl-diamides of dipicolinic acid in a polar fluorinated diluent phenyltrifluoromethylsulfone (FS-13) (refer to Table 1). Experimental data on extraction of lanthanides by these structural isomers are presented in Figs. 1–3 as a function of the nitric acid concentration (0.5 M–5 M HNO_3). The plot of values of distribution ratios, D, for the different lanthanide elements (in the order of increasing atomic number) creates typical two-shoulder dependence with the gadolinium break point. The slope character of these shoulders depends strongly on the nitric acid concentration.

For 0.5 M and 1 M HNO_3, the metal distribution ratios decrease with decreasing of ionic radius of lanthanides. The extraction ability of diamides toward lanthanides goes down from La to Gd and is almost constant from Gd to Lu. This effect is especially notable for Et(**m**)TDPA and also in lesser extent for Et(**p**)TDPA. In the case of Et(**o**)TDPA, the metals of the cerium sub-group (Ce-Eu) are extracted a little better than all other lanthanides, so the distribution ratios rise from lanthanum to cerium, with maximum on Nd and Sm, then decrease from Sm to Gd and are almost constant for heavy lanthanides (Gd–Lu). A similar dependence was also obtained for N,N′-dimethyl-N,N′-diphenyl-diamide of dipicolinic acid by Shimada et al. (23).

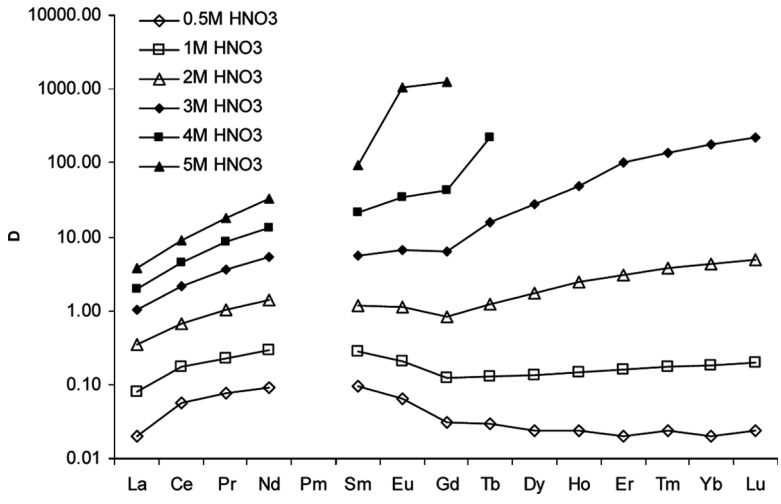


Figure 1. Extraction of Ln from the nitric acid. Solvent: 0.2 M Et(**o**)TDPA in FS-13.

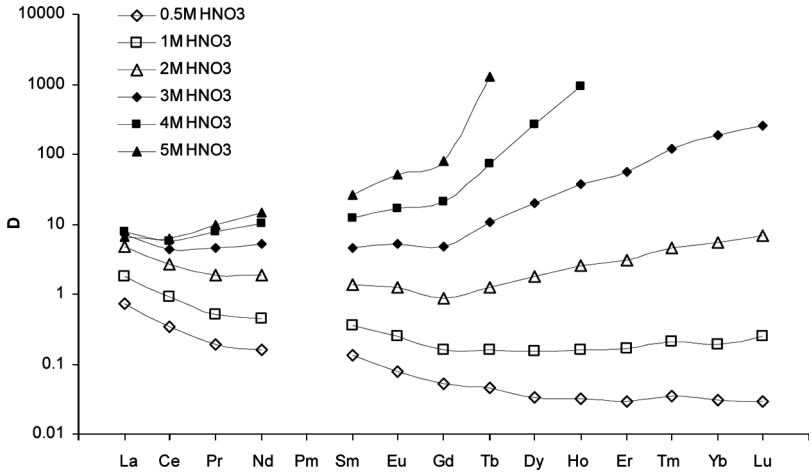


Figure 2. Extraction of Ln from the nitric acid. Solvent: 0.2 M Et(**m**)TDPA in FS-13.

Americium Extraction

The dependencies for extraction of Am from 0.5–5 M nitric acid solutions by the three studied structural isomers of diethyl-ditolyl diamide of dipicolinic acid are presented in Figs. 4 and 5. Americium is extracted only from nitric acid with a concentration above 1 M HNO_3, and the

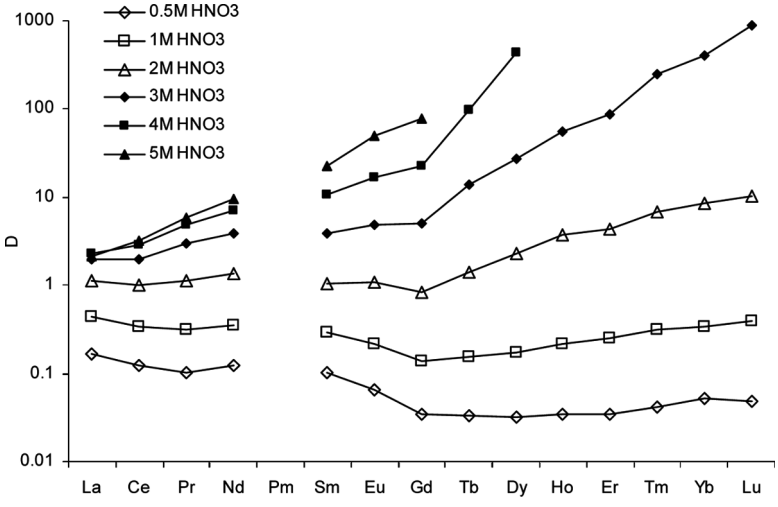


Figure 3. Extraction of Ln from the nitric acid. Solvent: 0.2 M Et(**p**)TDPA in FS-13.

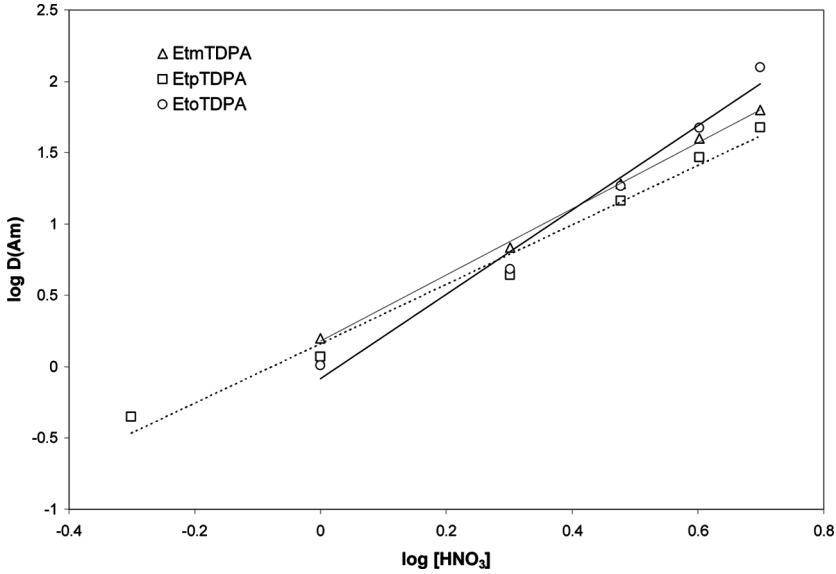


Figure 4. Dependence of americium extraction on nitric acid concentration. Solvent: 0.2 M DPA in FS-13.

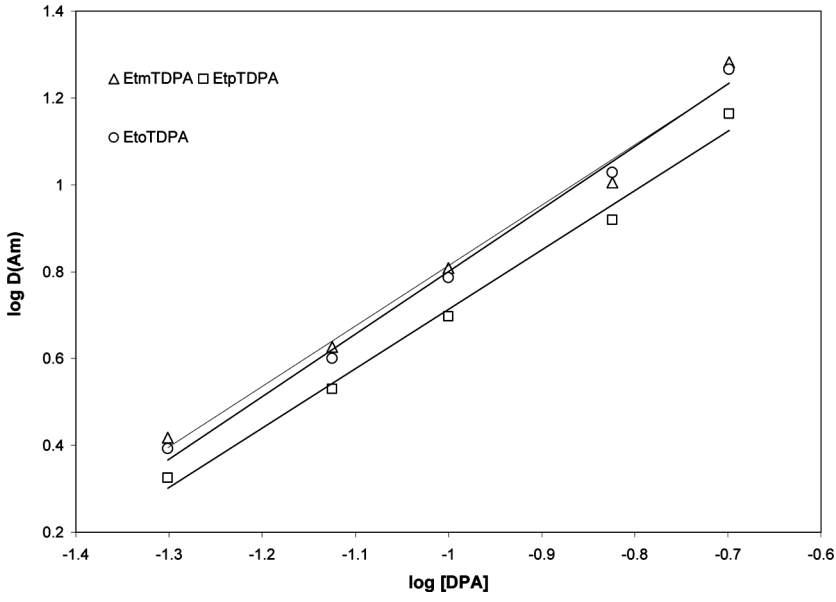


Figure 5. Extraction of americium from **3 M HNO_3**.

extraction dependencies for all three isomers are very similar. The extractability of Am with diamides increases with the increased HNO_3 concentration; however, the distribution ratios measured for Et(**o**)TDPA increase a little bit faster than for the other diamides.

Comparison of the Am extraction data for the three ethyl-tolyl diamides as a function of their concentration in the organic phase is shown in Fig. 5. Solvate numbers of americium obtained by slope analysis $lg[D_{Am}]$ vs. lg[DPA] are very similar to each other and come to 1.4 that suggests that americium is extracted into organic phase as a mixture of mono- and di-solvates.

Separation Factors

From the point of view of separation efficiency, it is important to compare distribution ratios of heavy and light lanthanides. Comparison of the extractability of lanthanides by three isomeric ethyl-tolyl diamides from 1, 2, and 3 M HNO_3 is shown in Figs. 6–8. The extraction ability of all three diamides toward almost all lanthanides (Pr–Lu) is very similar, but differs very much toward La and Ce, especially toward lanthanum that fits the studied diamide with methyl group of tolyl ring in meta-position the best, and gives about ten times larger distribution ratio than with ortho-isomer.

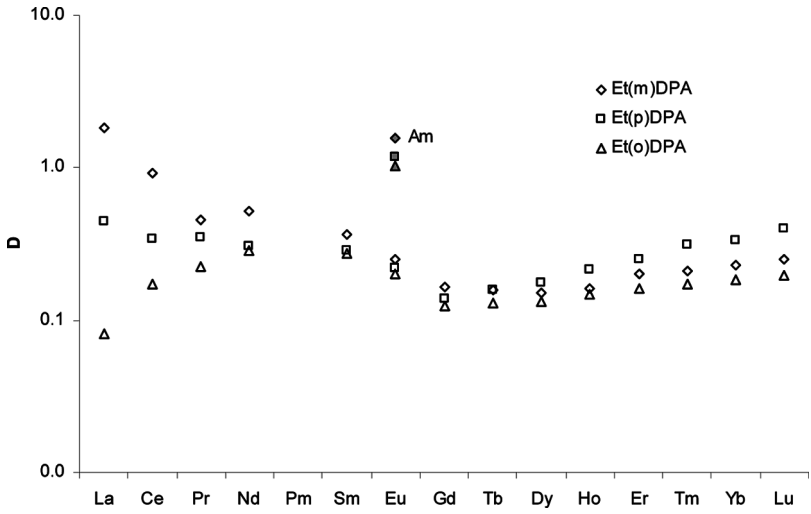


Figure 6. Extraction of REE and Am from **1 M HNO_3**. Solvent: 0.2 M DPA in FS-13.

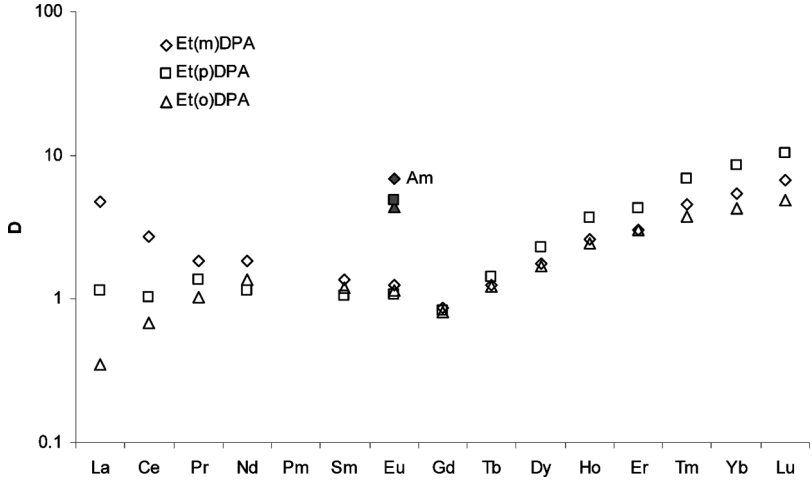


Figure 7. Extraction of REE and Am from **2 M HNO_3**. Solvent: 0.2 M DPA in FS-13.

At the nitric acid concentration above 2 M, all three diamides begin to extract the heavy lanthanides better than the light ones, and the slope of the Gd–Lu shoulder increases sharply (Figs. 6–8). The distribution ratios of the heavy lanthanides for extraction from 4 M and 5 M HNO_3 are very high (more than 1000) and are not indicated on the graphs since

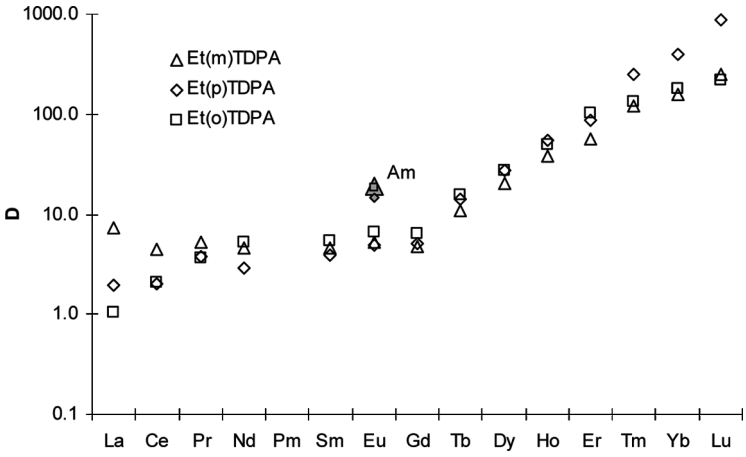


Figure 8. Extraction of REE and Am from **3 M HNO_3**. Solvent: 0.2 M DPA in FS-13.

Table 3. Separation factors Am/Ln for different diamides. Solvent: 0.2 M DPA in FS-13

Conditions	Am/La	Am/Ce	Am/Pr	Am/Nd	Am/Sm	Am/Eu	Am/Gd
				2M HNO_3			
Et(**o**)TDPA	16	6.8	4.8	3.4	4	4.4	6
Et(**m**)TDPA	1.4	2.5	3.8	3.6	4.9	5.7	8.5
Et(**p**)TDPA	4.0	4.4	3.5	4	4	4	5.8
				1M HNO_3			
Et(**o**)TDPA	12.5	5.8	4.3	3.5	3.6	5	8.3
Et(**m**)TDPA	0.9	1.8	3.5	3.1	4.4	6.3	9.8
Et(**p**)TDPA	2.7	3.5	3.4	3.9	4.3	5.7*	8.5

*Am/Eu separation factor from pure 1 M nitric acid was 6.

there is a great deal of uncertainty in the measurements. The observed trend is opposite to extraction with carbamoylphosphine oxide and diphosphine dioxide (28), which has been explained by a decrease of the coordination number of the ligand with the decrease in the space around an ion (17). However, the decrease in coordination number is not an invariable rule; examples are known where coordination number remains constant across the series, as in $Ln(bipy)_2(NO_3)_2$ and $Ln(phen)_2(NO_3)_2$ (Ln=La–Lu) where all are 10-coordinate in the solid state. When bidentate ligands are involved, loss of one of them may produce a too dramatic change in coordination number (29). Structures and coordination numbers of extracted complexes will be one of focuses of subsequent studies.

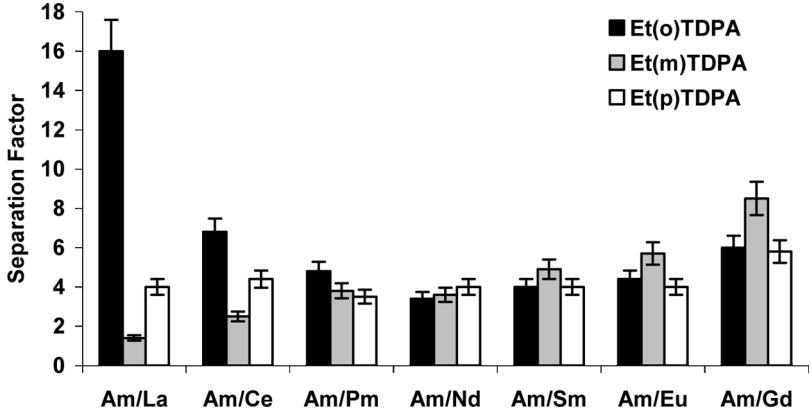


Figure 9. Am/Ln separation factors for extraction from 2 M nitric acid. Solvent: 0.2 M DPA in FS-13.

Presented data show that also Am is extracted better than light lanthanides for all three diamides. Separation factors Am/Ln for different extractants in 1 and 2 M nitric acid are presented in Table 3 and in Fig. 9. Separation factors depend on HNO_3 concentration and structure of extractant structure. Because of a strong effect of ortho-, meta-, and para-positions of the methyl group on the tolyl ring in the diamides, the separation factors for the pair Am/La varies from 16 to 1.4 for Et(**o**)TDPA and Et(**m**)TDPA, correspondingly.

CONCLUSION

The extraction properties of three ortho-, meta-, and para-derivates of ethyl(tolyl)diamides of dipicolinic acid toward lanthanides and americium were studied. Data about the extraction ability of different diamides of dipicolinic acid show that ortho-isomer of diethyl-ditolyl-diamides of dipicolinic acid has the most promising properties because it best balances the selectivity between the heavy and light lanthanides. Current studies involve other actinides (U, Th, Pu) and fission products (Zr, Mo). Future investigations will be focused on hydrolytic and radiolytical stability of extractants and extracted complexes, structure of metal-DPA complexes and speciation of metals in the organic polar phase.

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