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# The Radiolytic and Thermal Stability of Diamides of Dipicolinic Acid

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The thermal and radiolytical stabilities of three isomers of *N,N'*-diethyl-*N,N'*-ditolyl-dipicolinamide (EtTDPA) were investigated. Radiolysis was performed at doses up to 125 kGy and thermogravimetric analysis was performed at temperatures of up to 450°C. Infrared data showed increasing amounts of aromatic nitration by nitric acid correlating to larger doses. However, gamma ray doses of up to 125 kGy did not cause any significant effects in separation performance with the studied extraction mixtures containing americium or europium within the studied range. The highest separation factor between americium and europium was seen using the meta isomer with an average value of 4.1 across all doses applied in this work.

**Keywords** diamides; dipicolinic acid; extraction; radiolysis; UNEX

## INTRODUCTION

In the nuclear waste management industry it is of great importance to understand the effects of radiation on the effectiveness of separation processes. Several widely used extractants such as TBP are known to have degradation products that are undesired (1). Thus the radiolytic stability of any material to be used in conditions imposed by such an industry requires study before any large-scale usage can be utilized.

Within the past two decades, there has been interest in developing soft-donor complexing agents. These are promising extractants for the separation of lanthanides and trivalent actinides and have received significant attention. The separation of these elements is a complex task because their chemistries are nearly identical, and differ only in a slightly stronger interaction of trivalent actinides with certain ligand donor atoms (2). A soft donor atom such as nitrogen can covalently coordinate the 5f-elements, showing higher selectivity than the harder oxygen atom towards actinide (5f) over lanthanide (4f) elements; therefore, amides

are a subject of extensive research as potential extractants of minor actinides from PUREX raffinate.

Present research has led to the development of new N-containing reagents and methods with significant potential for accomplishing the separation of trivalent metals from wastes such as substituted malonic diamides (DIAMEX) (2,3) and tetra-alkyl-diglycolamides (TODGA) (4,5). Substituted diamides of dipicolinic acid are of interest due to their pyridine nitrogen in proximity to the carbonyl allowing it to possibly participate in coordination. Previously it was reported that among other dipicolinamides, *N,N'*-diethyl-*N,N'*-ditolyl-dipicolinamide (EtTDPA, Fig. 1) shows the best extractability toward americium with a slight extraction preference over europium (6). A significant synergistic effect was observed in the extraction of trivalent metals by different dipicolinamides (DPA) in the presence of CCD (7), leading to some diamides of dipicolinic acid being proposed instead of CMPO as components of a modified UNEX solvent with the ultimate goal of increasing the separation of the trivalent actinides and lanthanides (8). Recently, results on the investigation of extraction of Am and lanthanides (Ln) with different diethyl-ditolyl-diamides of dipicolinic acid as a function of their structure and nitric acid concentration (9) and their synergistic effect with chlorinated cobalt dicarbollide (CCD) on the extraction of Am and Ln with diamides (10) were reported. The aim of the present work was to investigate the effect of previous acidic hydrolysis and radiolysis on the extraction performance of isomers of the diethyl-ditolyl-diamides of dipicolinic acid and to identify the effect of the methyl group position in the tolyl ring on the stability, extractability, and selectivity of the studied EtTDPA toward the separation of Am from the lanthanides.

## EXPERIMENTAL

### Synthesis of Organic Ligands

*N,N'*-diethyl-*N,N'*-ditolyl-dipicolinamides were synthesized by the reaction of thionyl chloride with 2,6-pyridinedicarboxylic acid (dipicolinic acid). The acyl chloride was then reacted with the desired isomer of N-ethyltoluidine

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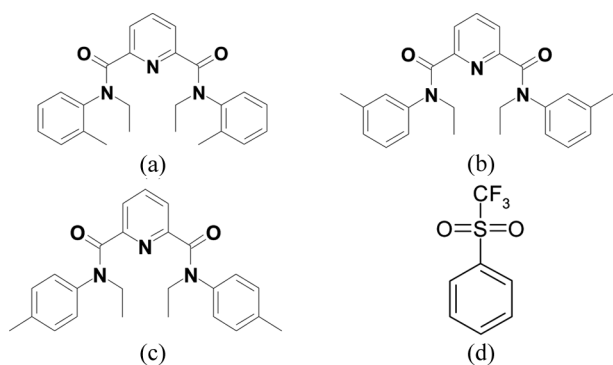


FIG. 1. Structures of metal extractant and solvent (a) Et(o)TDPA, (b) Et(m)TDPA, (c) Et(p)TDPA, (d) FS-13.

to produce the desired EtTDPA molecule (11). Chemicals used in the synthesis of EtTDPA were purchased from TCI Co. LTD and of analytical grade and were used without further purification. The purities of the synthesized ligands were checked by using elemental analysis and NMR.

### Thermogravimetric Analysis

Thermogravimetric analyses of samples were performed using a Mettler-Toledo TGA 850. Experiments were run under air from 25–450°C with aluminum pans at a temperature rate of 5°C/min. Testing of the ligand:metal complex stability was done by dissolving dry samples of ortho and para isomers of EtTDPA in chloroform and contacted with an equal volume with a solution containing a stoichiometric excess of aqueous cerium(III) nitrate in nitric acid. The aqueous phase was then removed and the solvent allowed to evaporate to dryness.

### Extraction Procedure

The three different organic ligands were studied using 0.2M concentrations of the desired isomers diluted into the polar solvent FS-13 (trifluoromethylphenyl sulfone). FS-13 was obtained from Marshallton Research Laboratories Inc. (King, NC, USA) and used as received. Prior to extraction with 0.2M EtTDPA, the organic phase was pre-equilibrated with an aqueous phase that was identical in composition to the extraction without the studied metal. The 0.2M solution of the organic phase was shaken with nitric acid for 5 min and centrifuged to split phases. A pre-equilibrated organic phase was then contacted with a fresh portion of the aqueous phase, spiked with the radio-tracer (Eu-152/154 or Am-241), and agitated for 5 minutes. The organic:aqueous phase volume ratio during all extraction experiments was 1:1. After extraction, 0.2 mL samples of the aqueous and organic phases were taken for radio-metric analysis. The concentrations of both metals were measured by gamma ray spectroscopy with a 3" NaI(Tl) well detector. The reported experimental values of the

distribution ratios are an average from at least two extraction experiments. The distribution ratios and separation factors of the studied metals were determined as the ratio of the appropriate specific gamma ray activities in the organic and aqueous phases:

$$D = \frac{A_{org}}{A_{Aq}}; \quad SF = \frac{D_{Am}}{D_{Eu}} \quad (1)$$

### Radiolysis

For the radiolytic degradation experiment, the samples of organic solvent, pre-saturated with 3M nitric acid, were irradiated in sealed glass vials to varying absorbed gamma-ray doses, using the Oregon State University Co-60 irradiator (Gammacell) providing a center-line dose of 0.45 kGy/hr as calibrated by the manufacturer. The duration of irradiation was varied to achieve the desired absorbed dose (0–125 kGy). A portion of the irradiated organic solutions was then agitated with a fresh portion of 3M nitric acid solution of equal volume. These samples were then spiked with a small amount of Am or Eu tracer and then centrifuged in the same manner as above. The phases were then split and aliquots of both portions were taken for the metal concentration analysis.

### FTIR Spectroscopy

Infrared analysis of the organic phase was performed with a Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer equipped with a 0.015 mm spacer and AgCl liquid cells. Samples of the organic phase were injected into the cell using a syringe. Data for each sample were obtained in the 400–4000 cm<sup>-1</sup> region by collecting 32 scans each, with a resolution of 2 cm<sup>-1</sup> and using the spectrum of the solvent FS-13 as a blank.

## RESULTS AND DISCUSSION

### Thermal Stability

Crystallized samples of EtTDPA were evaluated for their thermal stability by thermogravimetric analysis. Et(m)TDPA showed weight loss beginning slightly after 180°C, Et(o)TDPA at 200°C, and finally Et(p)TDPA after 220°C. During heating no plateaus were seen corresponding to the formation of a stable intermediate during decomposition. Complete evaporation of all isomers occurred by 360°C with the meta isomer completing first, followed by ortho, then para. This result is consistent with the results previously obtained for analyses of other amidic extractants (12). After ending the temperature at 450°C only a slight layer of black char residue remained in the pan.

Macroscopic amounts of non-active europium were unavailable during experimentation. Previous experiments have shown that the extraction of Ce(III) is very similar

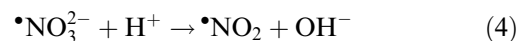
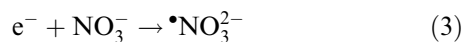
to that of Eu(III) and therefore Ce(III) was used as an analogue for Eu(III) (9). Unlike other lanthanide nitrates, cerium nitrate is known to decompose directly to cerium oxide at much lower temperatures (13). However, this process does not occur until approximately 330°C (14) and therefore should not interfere greatly with ligand decomposition measurements.

After the evaporation step outlined in the experimental section, only Et(o)TDPA formed a crystal-like structure. Et(m)TDPA and Et(p)TDPA instead formed an extremely viscous sap-like material which proved problematic for analysis as the material would quickly harden when attempting to transfer the material to the aluminum pan requiring dissolution in order to remove it from the spatula. Thus this data was only obtained for the ortho isomer. No changes in mass were observed until 175–225°C, when there was a 3.5% increase in mass. Although the reason for this is unclear it did not occur during heating of the pure ligand and thus is likely related to a change in cerium or nitrate. A second increase in mass occurred after 335°C and is consistent with the oxidation of Ce(III) to Ce(IV) as stated in reference (14). Evaporation of the ligand began at approximately 10–15°C later than with the pure Et(o)TDPA, and decreased at the same rate as also observed with Et(o)TDPA alone. This process completed at 10°C higher than Et(o)TDPA alone, indicating that some stability is gained during complexation, requiring extra thermal energy to disrupt complexation before evaporation can take place.

### Radiolytic Stability

Mowafy (15,16) recently reported that symmetrical diamides are the most stable over unsymmetrical and branched amides. Furthermore, shorter branching substituents on the amide nitrogen led to higher stability as well. EtTDPA has both of these characteristics indicating that some stability against radiation is expected. In our previous work the infrared spectroscopic data of EtTDPA isomers in FS-13 was reported (17). Et(o)TDPA, Et(m)TDPA, and Et(p)TDPA show strong carbonyl absorptions at 1650, 1651, and 1654 cm<sup>-1</sup> respectively with concentrations of 0.2 M ligand concentration. These functional groups play a strong role in the mechanism of neutral ligand extractions and thus it is important that they remain mostly intact in order to be of use in waste raffinate. Analysis of irradiated EtTDPA shows a decrease in absorption of the amidic nitrogen absorption bands as well as the amide carbonyl stretches in all isomers, though there was not a significant change in the intensities of these peaks.

It is well known that under radiolysis nitric acid produces radical nitro groups by the mechanisms:



which are capable of nitrating aromatic rings (18). In addition, one of the radiolysis products of FS-13 is believed to be sulfuric acid (19) which acts as a catalyst for the electrophilic nitration of aromatic groups (20). Thus it is highly likely that EtTDPA will undergo some form of aromatic nitration during irradiation. The carbonyl spectrum of Et(p)TDPA can be seen in Fig. 2. The various doses have been offset on the y-axis for clarity, and the spikes at 1590 and 1480 cm<sup>-1</sup> are merely artifacts of the solvent spectrum subtraction. At 125 kGy the carbonyl peak for Et(p)TDPA is slightly broadened at energies greater than 1654 cm<sup>-1</sup> by less than 2 cm<sup>-1</sup> compared to that at 25 kGy. An electron withdrawing group such as nitro could remove the electron density from the C=O stretch causing it to shift to higher energies. Thus even though it is only a small broadening effect the direction is consistent with that expected from the nitration of the aromatics.

With an increasing absorbed dose two new peaks begin to grow in at 1537 and 1738 cm<sup>-1</sup>. Nitrated aromatics typically have strong absorptions in the region of 1490–1560 cm<sup>-1</sup>, with nitrobenzene having a peak at 1527 cm<sup>-1</sup> (21). Though electrophilic nitration most likely did occur, all of the samples were subjected to the same concentrations of nitric acid and were of the same age when analyzed. The extra production of sulfuric acid in longer irradiated samples should not have a large effect on this reaction as it merely acts as a catalyst and should not increase the yield by any significant amount. Thus the primary nitration mechanism should occur by radiolytical radical production.

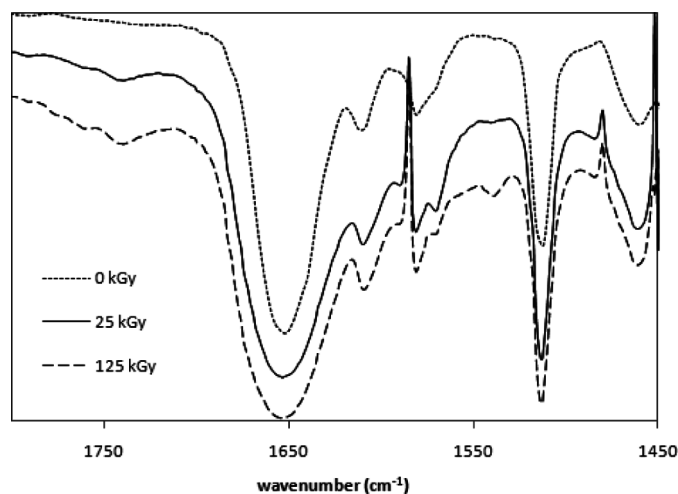


FIG. 2. Infrared spectrum of the carbonyl absorption region of Et(p)TDPA.

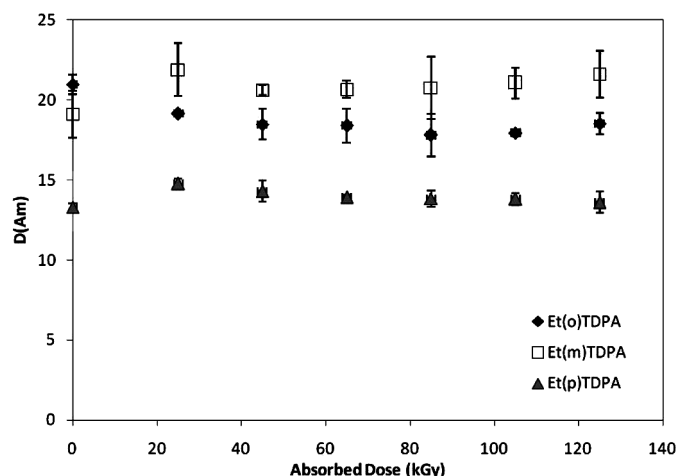


FIG. 3. Extraction of americium from 3 M  $\text{HNO}_3$  with 0.2 M EtTDPA.

### Effects on Extraction

Previous experiments have shown (22) that a significant extraction of Am and Eu with EtTDPA begins at 3 M nitric acid; therefore, all extraction experiments were performed from this nitric acid for each isomer of EtTDPA. The dependence of the post-irradiation distribution ratios for Am with 0.2 M EtTDPA on the absorbed dose is shown in Fig. 3. There was no effect based on increasing absorbed doses observed for extraction of Am with the irradiated phase of EtTDPA in FS-13. In previous extraction studies americium was shown to be most extracted by Et(m)TDPA followed closely by Et(o)TDPA in 3 M nitric acid with Et(p)TDPA last (9) and this trend is continued from 0–125 kGy. With the exception of the initial Et(m)TDPA data point, each isomer remains relatively constant within the measurement errors. The extraction of europium

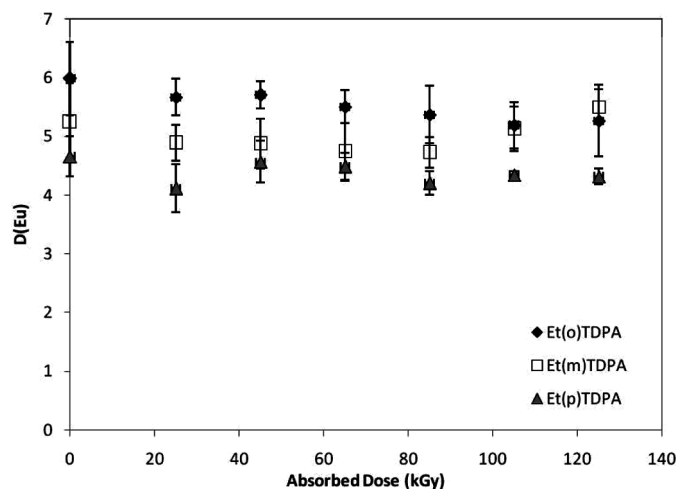


FIG. 4. Distribution ratios of europium after extraction from 3 M  $\text{HNO}_3$  with 0.2 M EtTDPA.

TABLE 1

Separation factors of Am and Eu for EtTDPA mixtures after radiolysis

Dose (kGy)	Et(o)TDPA	Et(m)TDPA	Et(p)TDPA
0	3.3	3.6	3.0
25	3.3	4.5	3.4
45	3.4	4.2	3.4
65	3.3	4.1	3.3
85	3.2	4.4	3.3
105	3.5	4.1	3.1
125	3.5	3.9	3.2

(Fig. 4) also behaved in a similar manner to americium, though with significantly lower distribution values. Et(o)TDPA and Et(m)TDPA are reversed in extractability of Eu compared to Am and Et(p)TDPA remains the lowest for extractability.

The lack of changes in the distribution ratio is consistent with the infrared spectra showing little disruption of the carbonyl region which is where neutral complexation occurs (23). These similar distribution ratios were also previously seen with trivalent metals. Fe(III) with irradiated tetra-octyl-DPA as reported by Mowafy (15) shows fluctuating distribution ratios with an increased absorbed dose (above 40 kGy), and is similar to the extraction of Am and Eu with irradiated EtTDPA as reported in the present paper (15,16).

### Separation Factors

A summary of the Am/Eu separation factors after radiolysis is listed in Table 1. At 0 hours a good separation factor is obtained for all extraction mixtures and is relatively maintained throughout the studied dose ranges. None of the separation factors deviated by more than 10% of the average for each isomer, with Et(m)TDPA giving the best separation factors at all observed doses. This result was identical to the separation factor order for americium and europium obtained for these three isomers from nitric acid in our previous work without radiolysis (9). Therefore regardless of the methyl position the extractions remain nearly unaffected under the studied dose ranges.

### CONCLUSIONS

The three isomers of EtTDPA were found to be thermally stable with no intermediate products produced at higher temperatures after extended periods of time during thermogravimetric analysis. Evaporation of the ligand began the earliest for Et(m)TDPA at 180°C with Et(p)TDPA starting last at 220°C. EtTDPA was shown to be largely stable to radiolysis as only small but noticeable

changes were seen using infrared spectroscopy for irradiated samples up to doses of 125 kGy. The most notable change in the spectra was the nitration of the aromatic rings by radicals produced by the radiolysis of nitric acid in solution. No large effect was seen on the distribution ratios of either americium or europium from nitric acid. As such the separation factors of americium and europium were not greatly affected, with Et(m)TDPA providing the best separation at all doses.

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