Radiation Chemistry of Diethylhexylbutyramide (DEHBA)

Fuel Cycle Research & Development

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SUMMARY

The rate of gamma radiolytic degradation of diethylhexylbutyramide (DEHBA) with and without contact with various aqueous nitric acid phases was measured, and the major degradation products were identified. The radiolytic degradation rate of DEHBA ($\sim 3.70 \times 10^{-4}$ kGy^{-1}) and associated products are analogous to those previously identified for diethylhexylisobutyramide (DEHiBA) under similar conditions. The amine and amide degradation products resulting from the two possible DEHBA C-N bond ruptures do not account for a complete mass balance; however, other minor degradation products that are possible based on analogy with results for DEHiBA were not amenable to the detection techniques used in the current work. The effects of gamma radiolysis on solvent extraction performance were greater for DEHBA, with D_{U} and D_{Pu} declining by up to 50 % by 1200 kGy. Uranium stripping was not affected; however, Pu stripping was adversely impacted. Furthermore, plutonium stripping was more dramatically impacted when DEHBA was irradiated in the presence of 4 M HNO_3. Color development was observed when DEHBA/dodecane was used in solvent extraction, but only for samples irradiated in the presence of 0.1 M HNO_3. These are indications that different degradation products, or a different abundance distribution occur for irradiation under different aqueous phase conditions. This work was performed in collaboration with CEA Marcoule, and is written in completion of milestone M3FT-17IN030104031.

CONTENTS

ACRONYMS

b2EHA	*bis*(2-ethylhexyl)amine
CEA	Commissariat á l'Énergie Atomique
DEHBA	diethylhexylbutyramide
DEHiBA	diethylhexylisobutyramide
DGA	diglycolamide
ESI	Electrospray Ionization
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
GC-FID	Gas Chromatography Flame Ionization Detector
GC-MS	Gas Chromatography Mass Spectrometry
TBP	tributylphosphate
UPLC	Ultra Performance Liquid Chromatography
UK	United Kingdom

RADIATION CHEMISTRY OF DEHBA

1. INTRODUCTION

The monoamide diethylhexylbutyramide (DEHBA) has good extraction efficiency for hexavalent uranium and tetravalent plutonium, and the metals are readily stripped from a loaded organic phase using dilute nitric acid acid (HNO_3). Although the monoamides are reputed to have exceptional radiation stability, it was recently shown that radiolytic yields, *G*-values, for degradation of the related compound diethylhexyl isobutyramide (DEHiBA) are actually similar to those for tributylphosphate (TBP). [1] However, since TBP has been used successfully for decades this is obviously adequate to enable a process, and DEHiBA *G*-values are superior to those measured for many other compounds. Still, some level of degradation is unavoidable and the nature of the decomposition products may be more important than the rate of parent ligand degradation. Here too, monoamides may have an advantage over TBP, in that the reported products are amines and lower molecular weight amides. Several reports, including our own recent work for DEHiBA have concluded that the degradation products are not adverse to uranium solvent extraction and stripping. [1-5]

In the work reported here, degradation rates under gamma-irradiation, degradation product identification, and effects on U and Pu extraction and stripping for 1 M DEHBA/dodecane solutions irradiated in pure organic solution, in contact with 4 M HNO_3, and 0.1 M HNO_3 are reported. This work was performed in collaboration with CEA Marcoule, and is written in completion of milestone M3FT-17IN030104031.

2. EXPERIMENTAL

2.1 Radiolysis

Solutions of 1 M DEHBA (Technocomm, UK)/dodecane were irradiated using a ^{60}Co Nordion Gammacell 220, at a dose rate of 3.5 kGy h^{-1}. The solutions were irradiated either as dry organic solutions, or in contact with either 0.1 M HNO_3 (stripping acidity), or 4 M HNO_3 (extraction acidity). Some samples, as indicated in the text, were irradiated in static, sealed containers, which are considered deaerated upon exposure to even low absorbed doses. Some samples were irradiated with air sparging at a rate of 1 mL min^{-1}, as delivered from a compressed air bottle through a mass flow controller. This was done to ensure that the samples so treated remained saturated with dissolved oxygen for comparison to deaerated samples. Following irradiation, the samples were split for analysis by the collaborating laboratories at CEA-Marcoule and INL. The samples were irradiated to 0, 250, 500, 750, 1000, and 1250 kGy.

2.2 DEHBA Quantification by GC-FID

All samples were analyzed by GC-FID, except for a replicate set also analyzed by GC-MS. For GC-FID, the DEHBA samples were diluted 1:100 (nominally 10mM unirradiated) in Fisher (Hampton, NH, USA) Optima methanol and analyzed on an Agilent (Santa Clara, CA, USA) 7890 Gas Chromatograph equipped with an Agilent 7693 autosampler and a flame ionization detector (FID). Each sample was diluted three different times and each of those diluted samples was run in triplicate, using the following conditions:

Gas Chromatography Conditions: Column: Restek Rtx-5 (30m x 0.32mm ID x 0.25μm df); Injector temp: 300 °C; Oven: 100 °C for 1 minute, ramp to 275 °C at 15 °C/min and then held at 275 °C for 1 minute; Split ratio: 20:1 with 1.9mL/min flow through column.

Flame-Ionization Detector Conditions: FID temperature: 300 °C.

Under these conditions, the retention time of DEHBA is 10.0 minutes. The DEHBA in each sample was quantified using a 6 point calibration curve generated from neat DEHBA dissolved in Fisher Optima methanol. The radiolysis product *bis*(2-ethylhexyl)amine was quantified in each sample using a 6 point calibration curve generated from neat *bis*(2-ethylhexyl)amine dissolved in Fisher Optima methanol. Each calibration standard was injected three times.

2.3 Degradation Product Analysis

The presence of *bis*(2-ethylhexyl)amine as a degradation product was confirmed by matching retention time and mass spectra using GC-MS with electron impact and chemical ionization with a known standard. Other radiolysis product structures are proposed based on interpretation of electron impact and chemical ionization mass spectra. For both methods the ion source temperature was 260 ^{o}C, and the interface temperature was 280 ^{o}C. Chromatographic conditions for all analyses were as described in Section 2.2.

2.4 Solvent Extraction

Solvent extraction was performed using equal phase volume contacts of the irradiated organic solution with 4 M HNO_3 containing nominally 3.0 ppm U and 0.1 ppm Pu. Stripping was conducted on the loaded organic phases from the extraction contact using an equal volume of 0.1 M HNO_3. All extractions were performed at a temperature of 23 ± 1^{o}C. The post-contact concentrations of the metals were determined by ICP-MS. Aliquots of 0.150 mL of each sample were diluted using Triton TX100 surfactant and 0.26 M HNO_3 for a dilution factor of 1:40. The organic phase samples were agitated for 30 sec just prior to analysis. Distribution ratios were calculated as the analytical concentration of each metal in the organic phase divided by its concentration in the aqueous phase.

3. RESULTS AND DISCUSSION

3.1 Degradation Rates

In preliminary FY17 experiments, the change in concentration for triplicate irradiations of initially 1 M DEHBA/dodecane in the absence of an aqueous phase and with no air sparging was analyzed using both GC-FID and GC-MS. The mean dose constants, *d*-value, obtained were $(2.2 \pm 0.2) \times 10^{-4}$ kGy^{-1}, for analysis by GC-FID, and $(3.4 \pm 0.6) \times 10^{-4}$ kGy^{-1}, for analysis by GC-MS. The mean value for both methods is $(2.7 \pm 0.3) \times 10^{-4}$ kGy^{-1}. This value may be compared with that previously obtained for DEHiBA under similar conditions of $(3.5 \pm 1.4) \times 10^{-4}$ kGy^{-1}.[1] Given the fairly large uncertainties for these values, the dose constants for both compounds must be considered the same. These uncertainties are attributed to the difficulty in measuring this low *d*-value, indicating favorable radiation stability for both monoamides.

In continued FY17 work, the concentration of initially 1 M DEHBA/dodecane as a function of absorbed dose irradiated in contact with a 0.1 M HNO_3 aqueous phase, a 4.0 M HNO_3 aqueous phase, and in contact with 4.0 M HNO_3 aqueous phase with air sparging were determined by GC-FID only. The results are shown in Figure 1. The degradation rate was again slow, with approximately 70% of the initial ligand remaining after 1250 kGy of absorbed dose. All dose constants measured in this work are shown in Table 1, along with the dose constants previously measured for DEHiBA [1] for comparison. From these data, it is concluded that the aqueous phase composition does not affect the radiolytic degradation rate of DEHBA, in agreement with results for DEHiBA [1], and several diglycolamides (DGAs) that were previously investigated under this program. [6, 7, 8] However, the result for 4.0 M HNO_3-contacted, aerated DEHBA may have an increased the degradation rate. Given that a similar effect has not been found for DEHiBA, or the DGAs, it seems more likely that the high result for this sample is better attributed to analytical uncertainty. For example, if it is assumed that the DEHBA results are the same values, a mean of $(3.70 \pm 1.04) \times 10^{-4}$ kGy^{-1} is obtained. If the results for the organic-only irradiations are included, the result becomes $(3.5 \pm 0.99) \times 10^{-4}$ kGy^{-1}. This may be favorably compared with the mean value of $(3.0 \pm 0.9) \times 10^{-4}$ kGy^{-1} for the irradiation of DEHiBA under various solution conditions. [1] These dose constants indicate that both monoamides are approximately a factor of 10 more stable under irradiation than are the DGAs. [6, 7, 8]

Table 1: Dose constants (kGy^{-1}) for DEHBA gamma-radiolysis under various conditions. Uncertainties are 99% confidence intervals calculated from the standard error of regression based on three injections of three dilutions of each sample. Previously measured DEH*i*BA [1] dose constants are included for comparison.

Sample	**DEHBA Dose Constant** (10^{-4} kGy^{-1})	**DEH*i*BA Dose Constants [1]** (10^{-4} kGy^{-1})
No aqueous phase	2.7 ± 0.3	3.5 ± 1.4
0.1 M HNO_3 contacted	3.0 ± 0.2	2.6 ± 0.6
4.0 M HNO_3 contacted	3.5 ± 0.2	2.0 ± 1.0
4.0 M HNO_3 contacted – air sparged	4.8 ± 0.2	2.0 ± 0.9

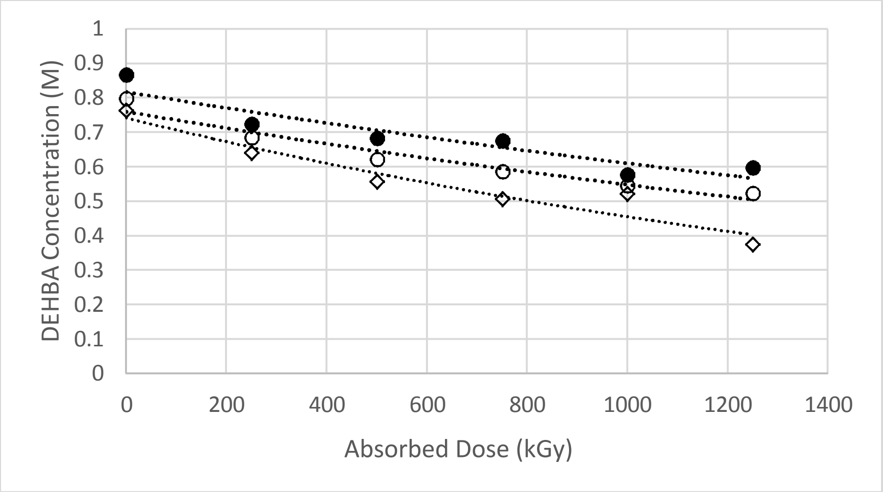

Figure 1. The change in DEHBA concentration versus absorbed dose for initially nominal1 M DEHBA/dodecane irradiated in contact with 0.1 M HNO_3 (closed circles), in contact with 4 M HNO_3 (open circles), or 4 M HNO_3 with air sparging (open diamonds).

3.2 Radiolysis Products

While the empirical rate of radiolysis of DEHBA is low, degradation products are still produced. The two predominant degradation products detected are *bis*(2-ethylhexyl)amine (b2EHA) which was confirmed using electron impact ionization mass spectrometry and retention time matching with a standard, and *N*-(2-ethylhexyl)butyramide, identified through electron impact and chemical ionization mass spectrometry. These products are analogous to those produced during the irradiation of DEH*i*BA. [1] However, irradiation of DEH*i*BA also created minor degradation products resulting from loss of H_2, addition of OH, and oxidation of added OH functional groups; [1] none of these species were observed for irradiated DEHBA when analyzed with GC-FID. The DEH*i*BA radiolysis products were determined using Ultra

Performance Liquid Chromatography with Electrospray-Ionization Mass Spectrometry (UPLC-ESI-MS), which is significantly more sensitive than GC-FID, so it is possible the analogous products are present in these samples below GC-FID detection levels. Experiments to analyze the DEHBA samples using UPLC-ESI-MS are currently underway.

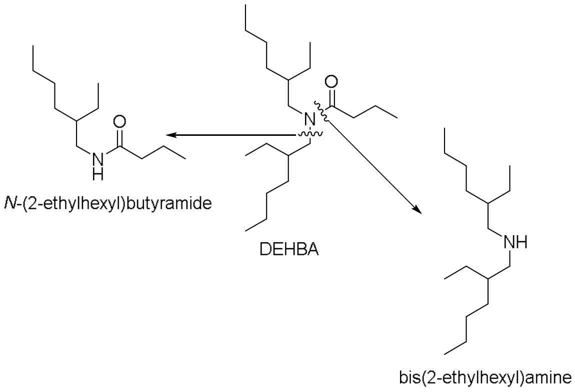

Figure 1: Proposed structures of the DEHBA degradation products.

The concentration of b2EHA and the normalized signal for *N*-(2-ethylhexyl)butyramide in DEHBA samples irradiated in contact with 0.1 M HNO_3 as measured with GC-FID are shown in Figs. 3 and 4 respectively. The concentration and normalized signals both increase with dose, complementary to the decrease in DEHBA concentration. The absolute concentration of *N*-(2-ethylhexyl)butyramide cannot be determined without the pure material being available for standards preparation. However, the sensitivity of GC-FID is roughly proportional to molecular weight. The absolute detected signal levels for the two degradation products are similar, so because their molecular weights are similar, their concentrations should be similar. By the maximum absorbed dose of 1250 kGy, the DEHBA concentration has decreased by hundreds of mM, while the sum of the produced b2EHA and *N*-(2-ethylhexyl)butyramide is likely only in the low tens of mM. Experiments contacting a known concentration of b2EHA in dodecane with pure water, 0.1 M HNO_3, and 4.0 M HNO_3 aqueous phases suggest that no significant partitioning of b2EHA into any of the aqueous phases occurred. However, the presence of acid in the aqueous phase degraded b2EHA in the organic phase. Thus, this large discrepancy is likely due to hydrolysis of b2EHA and possibly *N*-(2-ethylhexyl)butyramide. This does not preclude the formation of other degradation products that are not well detected by GC-FID. Measurement of the two degradation products in the 4.0 M HNO_3 contacted samples is ongoing.

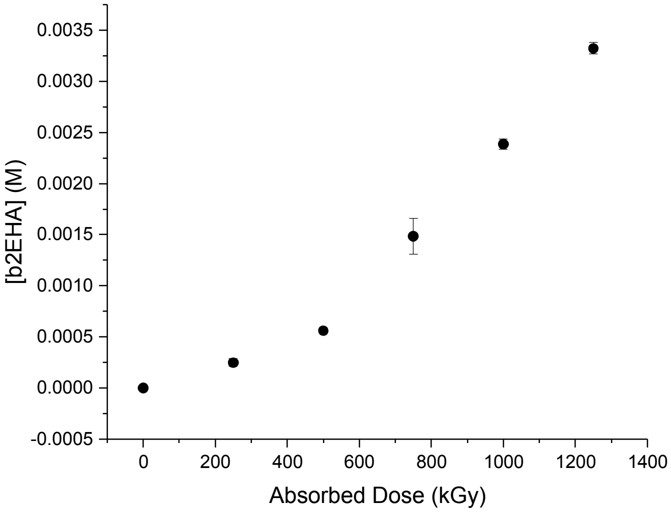

Figure 3: Concentration of *bis*(2-ethylhexyl)amine (b2EHA) in DEHBA samples irradiated in contact with 0.1 M HNO_3 measured with GC-FID. The data points are the mean of three injections, and error bars represent 99% confidence intervals.

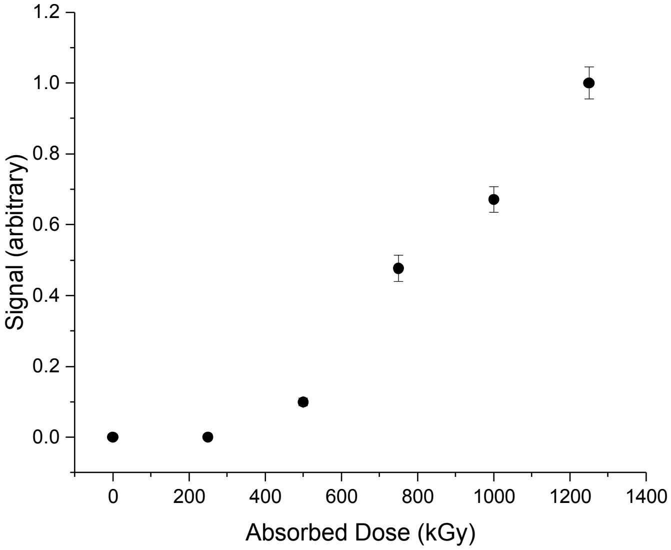

Figure 4: Normalized signal for *N*-(2-ethylhexyl)butyramide in DEHBA samples irradiated in contact with 0.1 M HNO_3 measured with GC-FID. The data points are the mean of three injections, and error bars represent 99% confidence intervals.

3.3 Solvent Extraction

Aliquots of the initially 1 M DEHBA/dodecane solution irradiated in contact with 4 M HNO_3 without air sparging were used to perform U and Pu solvent extraction experiments from 4 M

HNO_3, and the loaded organic phases were subsequently stripped with 0.1 M HNO_3. The extraction distribution ratios are shown in Fig. 5 as a function of absorbed dose. It can be seen that the D_U and D_{Pu} decreased with absorbed dose, resulting in values at approximately half of the initial values. This is in contrast to the results previously reported for DEHiBA, where no change in distribution ratios for uranium extraction were found, to a maximum absorbed dose of 1000 kGy. [1]

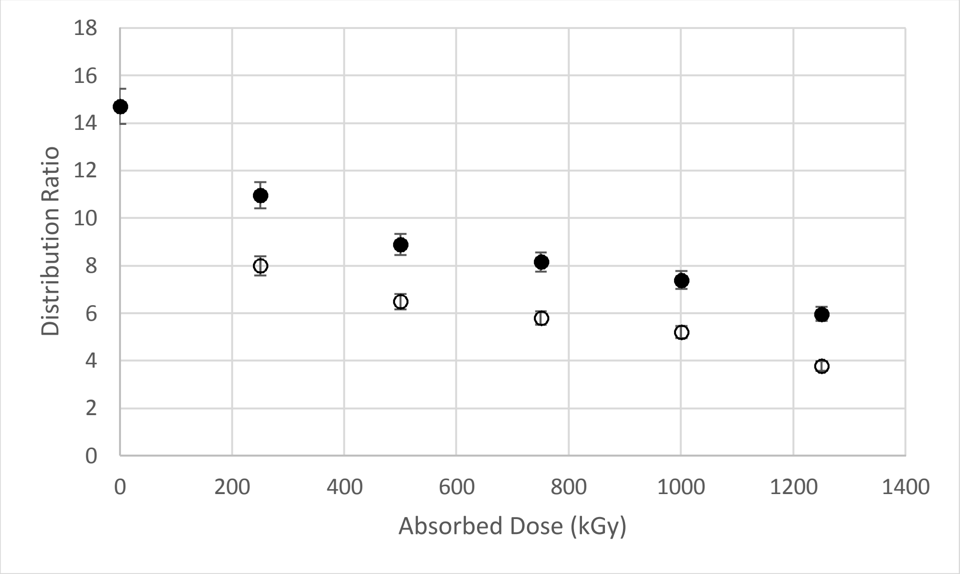

Figure 5. The distribution ratios for extraction from 4 M HNO_3, for uranium (D_U, solid symbols), and plutonium (D_{Pu}, open symbols) as a function of absorbed gamma-ray dose. The initially 1 M DEHBA/dodecane was irradiated in contact with 4.0 M HNO_3, with no air sparging. Error bars shown are ± 5% of the *D*-value.

The corresponding strip distribution ratios for both metals are shown in Fig. 6. The values for D_U decrease very slightly with absorbed dose, as was also previously shown for uranium stripping from irradiated DEHiBA. [1] In contrast, D_{Pu} increased with absorbed dose, and were greater than 1 by approximately only 100 kGy. The mean mass balance for the metal recovered in the stripping phases as compared to the original loaded organic phase was 74 % for U and 82 % for Pu. The increase in D_{Pu} with absorbed dose strongly suggests that one of the radiolysis products of DEHBA is an efficient complexing agent for Pu and has significant organic-phase solubility.

It should also be noted that when DEHBA/dodecane samples are used as the organic phase in solvent extraction, a red color develops upon contact with U/Pu-containing aqueous phase during solvent extraction. The color is more intense with irradiation to higher absorbed doses. This occurs only for samples irradiated in contact with 0.1 M HNO_3. An example is shown in Fig. 7. This may be due to formation of a radiolysis product/metal complex.

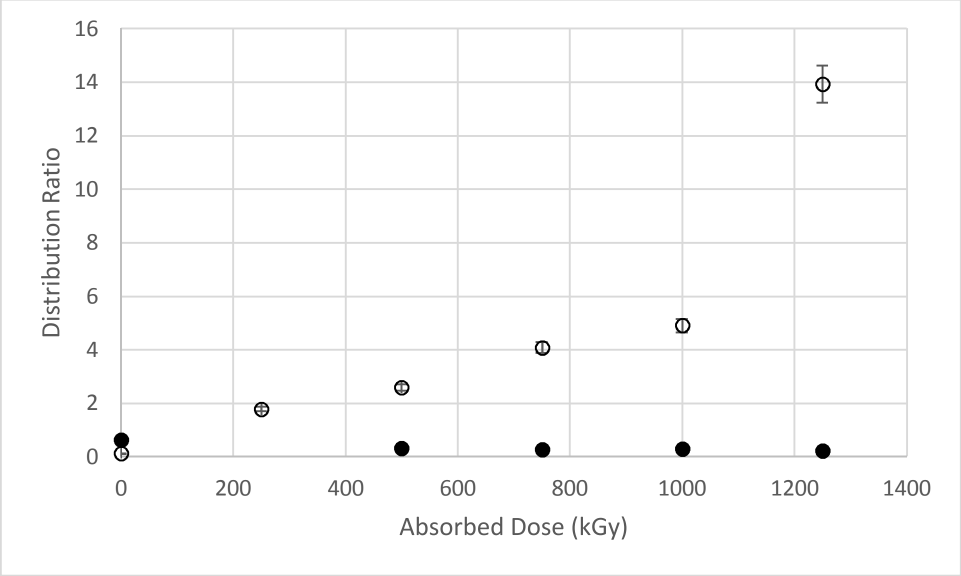

Figure 6. The stripping distribution ratios for uranium (D_U, solid symbols), and plutonium (D_{Pu}, open symbols) as a function of absorbed gamma-ray dose for metal-loaded, irradiated, nominally 1.0 M DEHBA/dodecane in contact with 4.0 M HNO_3. Error bars shown are ± 5% of the *D*-value.

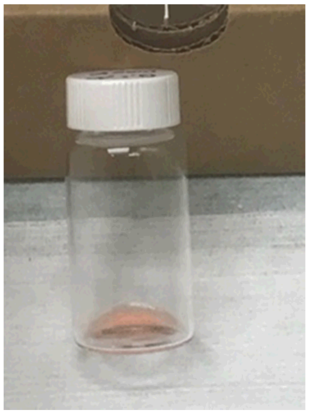

Figure 7. Color development in DEHBA/dodecane that was irradiated in contact with 0.1 M HNO_3, after contact with an 4 M HNO_3 aqueous phase containing U and Pu.

When 1 M DEHBA/dodecane was irradiated in contact with 0.1 M HNO_3, the results were less dramatic. Solvent extraction distribution ratios were essentially unchanged with absorbed dose, as was found for all irradiation conditions for DEHiBA. [1] This is shown in Fig. 8. Stripping distribution ratios, shown in Fig. 9, decreased slightly for U, but again increased with absorbed dose for Pu, although to a much lesser extent. The mean mass balance for the metal recovered in the stripping phases as compared to the original loaded organic phase was 86 % for U and 91 % for Pu. The increase in D_{Pu} with absorbed dose again suggests that one of the radiolysis products of DEHBA is an efficient complexing agent for Pu and has significant organic-phase solubility, but that it is produced in lower abundance in the absence of strong acid.

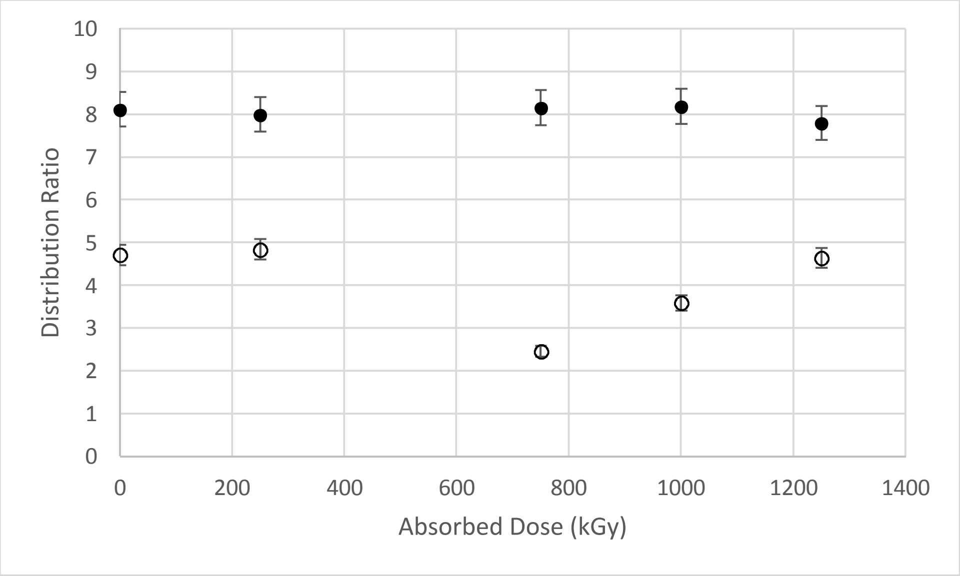

Figure 8. The distribution ratios for extraction from 4 M HNO_3, for uranium (D_U, solid symbols), and plutonium (D_{Pu}, open symbols) as a function of absorbed gamma-ray dose. The initially 1 M DEHBA/dodecane was irradiated in contact with 0.1 M HNO_3, with no air sparging. Error bars shown are ± 5% of the D-value.

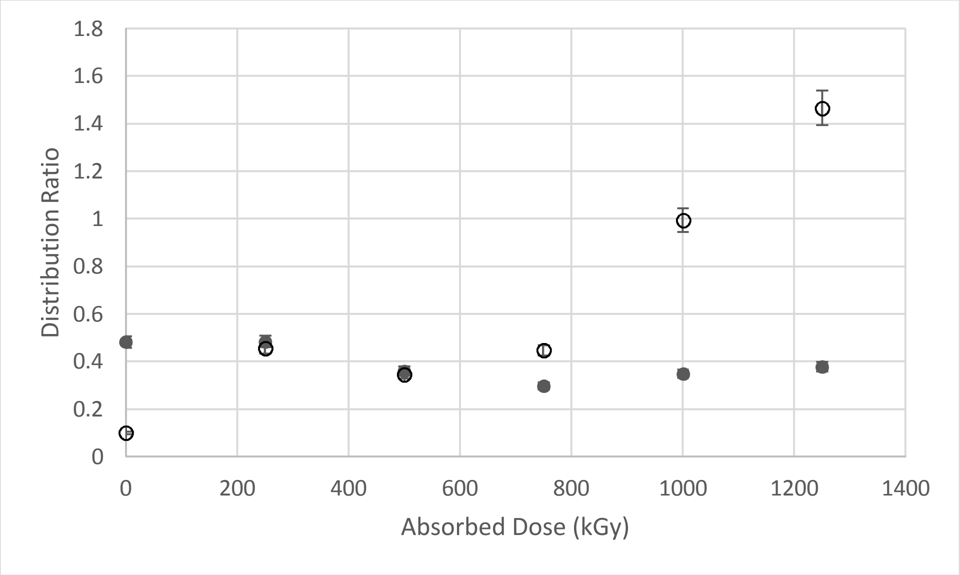

Figure 9. The stripping distribution ratios for uranium (D_U, solid symbols), and plutonium (D_{Pu}, open symbols) as a function of absorbed gamma-ray dose for metal-loaded, irradiated, nominally 1.0 M DEHBA/dodecane in contact with 0.1 M HNO_3. Error bars shown are ± 5% of the *D*-value.

4. CONCLUSION AND FUTURE WORK

The rate of radiolytic degradation of DEHBA is the same as that for DEHiBA, and unaffected by aqueous solution conditions or aeration, within analytical uncertainty. The major degradation products are the amine and the amide resulting from the two possible DEHBA C-N bond ruptures. Other minor products are possible based on analogy with results for DEHiBA but were not amenable to the detection techniques used in the current work. Although the rate of loss in DEHBA is similar to DEHiBA, the effects on solvent extraction were greater for DEHBA, with D_U and D_{Pu} declining by about 50 % by 1200 kGy under all conditions. However, it should be noted that this is a higher absorbed dose than is likely to be encountered under process conditions. Uranium stripping was not affected; however, Pu stripping was adversely impacted. Plutonium stripping was more dramatically impacted when DEHBA was irradiated in the presence of 4 M HNO_3. Color development was observed when DEHBA/dodecane was used in solvent extraction, but only for samples irradiated in the presence of 0.1 M HNO_3. These are indications that different products, or a different distribution in abundance of products occur for irradiation under different aqueous phase conditions. It is unclear what product or products are responsible for Pu complexation and/or color, however, work is on-going. Future work will concentrate on identifying the full suite of products sufficient to close the mass balance, and in identifying which products are responsible for Pu complexation.

5. REFERENCES

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