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**Idaho National Laboratory
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

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Gregory P. Horne^{a*}, Stephen P. Mezyk^{b*}, Bruce J. Mincher^a, Christopher A. Zarzana^a, Cathy Rae^a, Richard D. Tillotson^a, Nicholas C. Schmitt^a, Richard D. Ball^a, Joakim Ceder^{a,c}, Marie-Christine Charbonnel^d, Philippe Guilbaud^d, George Saint-Louis^d, and Laurence Berthon^d

^a*Idaho National Laboratory, Center for Radiation Chemistry Research, Idaho Falls, ID, P.O. Box 1625, 83415, USA.*

^b*California State University Long Beach, Department of Chemistry and Biochemistry, 1250 Bellflower Boulevard, Long Beach California, 90840-9507, USA.*

^c*KTH Royal Institute of Technology, Department of Chemical Engineering, Teknikringen 42, S-100 44, Stockholm, Sweden.*

^d*CEA, DEN, DMRC, Univ. Montpellier, Marcoule, France*

* Corresponding authors. e-mails: Gregory.Horne@inl.gov and Stephen.Mezyk@csulb.edu

ORCID

Gregory P. Horne	0000-0003-0596-0660
Stephen P. Mezyk	0000-0001-7838-1999
Bruce J. Mincher:	0000-0003-3108-2590
Christopher A. Zarzana	0000-0001-9617-7123
Cathy Rae	0000-0002-4520-1645
Richard D. Tillotson	_____ - _____ - _____
Nicholas C. Schmitt	0000-0002-5946-2694
Richard D. Ball	0000-0002-4798-6044
Joakim Ceder	0000-0003-3509-6754
Marie-Christine Charbonnel	0000-0002-0552-7405
Philippe Guilbaud	0000-0001-9777-8326
George Saint-Louis	_____ - _____ - _____
Laurence Berthon	0000-0003-3474-8474

ABSTRACT

Di-2-ethylhexylbutyramide (DEHBA) has been proposed as part of a hydro-reprocessing solvent extraction system for the co-extraction of uranium and plutonium from spent nuclear fuel. However, there remains a lack of quantitative understanding of the impact of chemical environment on the radiation chemistry of DEHBA, especially under conditions expected in real-world solvent extraction processes. Therefore, we have undertaken a systematic investigation into the radiolytic degradation of DEHBA in *n*-dodecane under fully aerated and biphasic conditions. DEHBA integrity and degradation product formation were measured for both extraction (in contact with 4.0 M HNO_{3(aq)}) and stripping (in contact with 0.1 M HNO_{3(aq)}) formulations. At the lower acidity the rate of DEHBA/*n*-dodecane degradation was slow ($G = 0.26 \pm 0.02 \mu\text{M J}^{-1}$) whereas at the higher acidity this degradation was about 35% faster ($G = 0.35 \pm 0.02 \mu\text{M J}^{-1}$). Both values were much less than analogous measurements under deaerated conditions. Under continuously aerated conditions, FTIR and ESI-MS measurements identified the two major degradation products, *bis*-2-ethylhexylamine (b2EHA) and *N*-(2-ethylhexyl)butyramide (MEHBA), as well as the presence of additional oxidized product species. Solvent system performance was also investigated using uranium extraction and strip distribution ratio measurements. These studies showed that there was only minimal change in uranium extraction and stripping performance with absorbed gamma dose.

INTRODUCTION

Efficient partitioning of long-lived α -emitters from spent nuclear fuel (SNF) is necessary to minimize the ultimate volume of high-level radioactive waste destined for long-term disposal in a repository, and to maximize the efficiency of uranium and plutonium usage. While hundreds of solvent-extraction based reprocessing formulations have been developed world-wide, representing over 60 years of research and development [1], the Plutonium Uranium Redox Extraction (PUREX) process remains the dominant standard. The PUREX process typically utilizes ~30 vol. % tributyl phosphate (TBP) dissolved in a hydrocarbon diluent contacted with a concentrated nitric acid (HNO_3) aqueous phase that contains the dissolved SNF, whereupon TBP complexes of uranium and plutonium are readily extracted into the organic phase, and thus separated from the fission products and other actinides [2]. The recovery of uranium and plutonium accounts for over 90% of the elemental mass of SNF, affording a significant reduction in α -emitting radiotoxicity.

In addition to their selective complexation ability, SNF solvent extraction ligands must maintain their extraction and subsequent stripping efficiencies in the presence of an intense, multi-component radiation field. The impacts of radiation on various separation systems has been reviewed previously [3-6]. These reviews highlighted the need for quantitative kinetics and mechanisms involving the reactions of these ligands and diluents with transient and steady-state radiolytically-produced species, in order to allow quantitative prediction of radiation-induced impacts. These data are particularly essential for aqueous partitioning processes that involve new extractants or complexing ligands and alternative diluents. [X] Unfortunately TBP has been shown to degrade to form undesirable, interfering degradation products when subject to such radiation fields under process conditions [3,7] 34. Moreover, TBP does not satisfy the CHON

(carbon, hydrogen, oxygen, nitrogen-containing) principle [5], thus preventing complete incineration of the used extraction solvent, adding to the waste disposal problem. Consequently, extensive effort has been made to identify and optimize alternative ligands to improve upon the radiolytic performance of TBP.

A particular class of chemicals, the *N,N*-dialkylmonoamides, has demonstrated excellent potential in this regard, with their easy structural modifications allowing selective tunability for different actinide ions. One

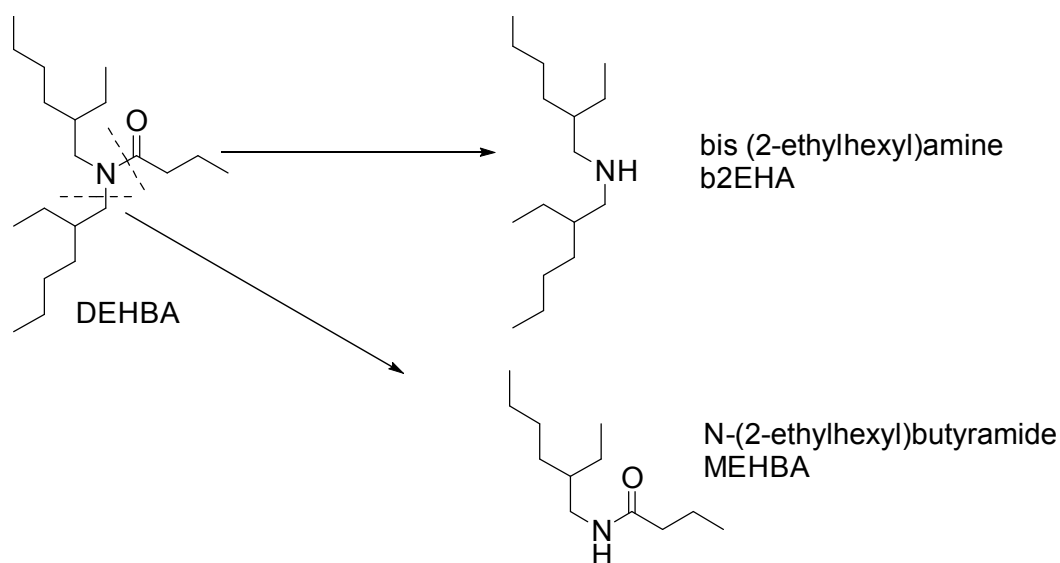


Figure 1. Structures of *N,N*-di-(2-ethylhexyl)butyramide (DEHBA) and its major degradation products: bis-(2-ethylhexyl)amine (b2EHA) and *N*-(2-ethylhexyl)butyramide, (MEHBA).

extremely promising TBP alternative is the monoamide *N,N*-di-(2-ethylhexyl)butyramide (DEHBA), shown in Figure 1. This amide contains branched alkyl chains and an *n*-alkane acyl group. The *n*-alkane acyl group facilitates co-extraction of hexavalent uranium and tetravalent plutonium. Monoamides are also characterized by greater selectivity for uranium over fission products, and reputed higher radiolytic stability, relative to TBP [6-8]. Further, it has been shown

that combinations of DEHBA with other extractants (e.g., BTBP, bis-triazine bipyridines) allows actinide ion extraction in most valence states, avoiding complications from redox control chemistry [Y].

The radiolysis of several *N,N*-dialkyl monoamides has shown considerable promise, as they appear to decompose to form relatively benign degradation products [9]. In particular, the radiolysis of DEHBA was recently investigated in-depth [10]. Two major degradation pathways were identified: (i) cleavage of the acyl C–N bond leading to *bis*-2-ethylhexylamine (b2EHA), and (ii) cleavage of the alkyl C–N bond to yield *N*-(2-ethylhexyl)butyramide (MEHBA), both shown in Figure 1. Of these two major degradation products, only b2EHA was found to negatively impact plutonium extraction and stripping performance [10]. Furthermore, Drader *et al.* identified the main degradation products formed from the radiolysis of three different monoamides with linear or branched chains as a function of radiation quality (alpha irradiation from the self-radiolysis of plutonium and gamma rays from an external source) [11,12]. They found that radiation quality did not significantly affect the distribution of ligand degradation products.

Several studies on the extraction behavior of gamma irradiated *N,N*-dialkylamides have now shown relatively consistent behavior for solvent-extraction of uranium and plutonium as a function of absorbed dose and the structure of the monoamide [6-8,13,14]. Hexavalent uranium extraction and stripping was found to be practically unchanged with increasing absorbed gamma dose [10,11]. In contrast, plutonium extraction and retention exhibit complex dependencies on the chemical environment during irradiation [10,15]. When DEHBA was irradiated in pure *n*-dodecane that had not been contacted with aqueous nitric acid solutions, enhanced plutonium

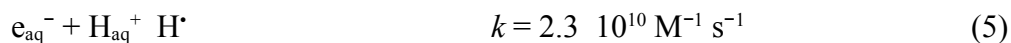
extraction and retention attributed to the presence of the degradation product b2EHA occurred, while acid contacts inhibited this effect and promoted significant plutonium retention for the highest acidity [10].

However, it is important to note that all these previous high-dose gamma irradiation studies were performed using samples that were irradiated in sealed vials [10,11]. Consequently, these solutions are considered ‘deaerated’ during irradiation, owing to the radiolytic consumption of dissolved oxygen (O₂) upon exposure to relatively low absorbed gamma doses. Therefore, observations pertaining to these deaerated solutions are far from envisioned aerated process conditions. The presence of O₂ in either phase of a solvent extraction system has significant influence over the distribution of degradation products and thus the potential extent of DEHBA degradation. For example, irradiation of an organic phase yields carbon-centered radicals (R[•]) which may undergo any number of typical radical processes (e.g., addition, abstraction, and recombination). However, in aerated systems O₂ can add to these radicals potentially altering DEHBA degradation rates and degradation product distribution, for example through the formation and decay of the corresponding tetroxides (R–O–O–O–O–R) [16]:



Further, under 0.1 M HNO_{3(aq)} contact strip conditions, O₂ can compete for the hydrogen atom (H[•]), which is the predominant radiation-induced reducing species from water radiolysis in acidic environments [17]:





Conversion of the H^\bullet to the hydroperoxyl radical (HO_2^\bullet) ultimately shifts the chemistry of the irradiated system to more oxidizing conditions, previously shown to enhance DEHBA degradation rates [10].

As DEHBA is one of the major monoamides proposed for co-extraction of uranium and plutonium from SNF, its radiation chemistry needs to be fully quantified under envisioned process conditions, where solutions would remain aerated. Therefore, in this study we have investigated the effects of gamma irradiation on DEHBA integrity and solvent system performance for biphasic solutions that were continuously air-sparged. DEHBA degradation rates, irradiation effects on uranium extraction and stripping, and degradation product identification are reported for solvent system formulations representative of envisioned large-scale process conditions.

EXPERIMENTAL

Chemicals. Nitrate salt solutions of natural uranium were prepared using on-hand stocks at the Idaho National Laboratory's (INL) Radiochemistry Laboratory (RCL). DEHBA (99%) was obtained from Technocomm Ltd. (Wellbrae, Scotland, UK), nitric acid (HNO_3 , $\geq 99.999\%$ trace metals basis) and *n*-dodecane ($\geq 99\%$ anhydrous) were from Sigma Aldrich, 2-propanol (*Optima LC/MS grade*) from Fisher, and Triton X100 (*laboratory grade*) from Sigma Life Sciences. All chemicals were used as received without further purification. Ultra-pure water ($> 18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used to prepare all aqueous solutions.

Steady-State Irradiation. Gamma irradiations were performed using the INL Center for Radiation Chemistry Research Nordion Gammacell 220 Cobalt-60 Irradiator Unit. Samples comprised biphasic solvent systems of 1.0 M DEHBA in *n*-dodecane contacted with an equivalent volume of either aqueous 0.1 M (stripping acidity) or 4.0 M (extraction acidity) HNO₃ in 20 mL screw cap scintillation vials pierced with Teflon needles. During irradiation, samples were continuously sparged with air at a rate of 1 mL min⁻¹, delivered from a compressed air cylinder regulated by a mass flow controller. This ensured that the dissolved oxygen concentration remained constant in these solutions throughout irradiation. Dosimetry was performed using Fricke solution [18], with corrections for the radioactive decay of cobalt-60 and sample solution density (*n*-dodecane (ρ) = 0.75 g mL⁻¹), giving an effective sample dose rate of 0.82 Gy s⁻¹. The irradiation sample chamber temperature was 23 ± 2 °C. Irradiated samples were split for subsequent analysis by the collaborating laboratories at CEA-Marcoule and INL.

Quantification of DEHBA. Samples were analyzed using an Agilent (Santa Clara, CA, USA) 7890 Gas Chromatograph equipped with an Agilent 7693 autosampler and a flame ionization detector (FID). The GC used a Restek Rtx-5 (30 m × 0.32 mm ID × 0.25 µm df) column with an injector temperature of 300 °C; oven temperature of 100 °C for 1 minute, ramped to 275 °C at 15 °C min⁻¹ and held at 275 °C for 1 minute. The split ratio was 20:1 with 1.9 mL min⁻¹ flow through column. The FID temperature was 300 °C. The retention time of DEHBA was 10 minutes. Seven calibration points including a blank were used, spanning from 0 mM (blank) up to ~12 mM DEHBA, prepared from neat DEHBA in 2-propanol. Each standard was injected four times and analyzed in order of increasing concentration. Quality control (QC) standards made at three different concentrations (low, mid, and high) were also analyzed at the mid-point of the analysis and at the end to ensure validity of the calibration curve through-out

the entire measurement period. End-run QC standards were placed in separate vials from the mid-run QC standards to reduce the effects of diluent evaporation.

The organic phase of each sample was diluted by a factor of 100 in 2-propanol four separate times, and each dilution replicate was injected four times. The dilution process was repeated 3 times to capture uncertainty due to sample dilution. The dilution replicate injection order was randomized to help differentiate systematic instrument drift from real trends in the samples, but the quadruple injections per dilution replicate were conducted sequentially, to reduce perturbations due to diluent evaporation. The aqueous phase of each sample was analyzed undiluted, and was injected 4 times, also in randomized order.

Organic phase solution analysis. Analyses of degradation product analysis was performed by a combination of infrared and mass spectrometry techniques. Infrared spectra were acquired on a Bruker Vertex 70 spectrometer equipped with an attenuated total reflectance cell. All IR spectra were collected between 400–4000 cm^{-1} , at a resolution of 4 cm^{-1} . Mass spectrometry analyses were performed using a micrOTOF-Q II (Bruker Daltonik GmbH, Bremen, Germany) electro spray ionization (ESI) quadrupole time-of-flight (TOF) mass spectrometer. Samples were delivered at a rate of 90 $\mu\text{L h}^{-1}$ to the electrospray source using a syringe infusion pump, KDS 100 Legacy (kdScientific, Holliston, MA, USA). The QTOF was mass calibrated daily using an Agilent (G1969-85000) ESI-L Low Concentration Tuning Mix solution. The capillary voltage was set to -4500 V with an end-plate offset voltage of -500 V. Nitrogen was employed as the nebulizing and drying gas. The drying gas flow rate was 4.0 L min^{-1} , the nebulizing gas pressure was 0.4 bar, and the source temperature was 180 $^{\circ}\text{C}$. Samples were diluted by a factor of 10,000 in 1:1 acetonitrile/water mixture prior to injection into the ESI-

MS. To favor compound ionization and minimize the formation of sodiated adducts, samples irradiated in contact with 0.1 M HNO₃ were further acidified by the addition of 1 drop of 1.0 M HNO₃ before analysis. Two different acquisition methods were used, one tuned to masses around 100-600 m/z and another for masses between 400-2000 m/z. Species were identified by comparison with an isotopic pattern calculated using the software *DataAnalysis 4.2*. Collision-Induced Dissociation (CID) experiments were used to help identify the structures of various species through fragmentation studies.

Uranium Solvent Extraction. Following gamma irradiation, solvent extraction studies were performed using duplicate, equal phase volume contacts of the irradiated organic solutions with nominally 120 ppb uranium in 4.0 M HNO₃ (extraction acidity). Stripping of the loaded organic phases was achieved using an equal volume contact of 0.1 M HNO₃ (strip acidity) at 21 ± 1 °C.

Distribution Ratios Determination. Post-contact concentrations of uranium were determined by inductively-coupled-plasma mass spectrometry (ICP-MS) using a Thermo X Series 2 ICP-MS equipped with an ESI (Elemental Scientific, Inc., Omaha Nebraska) Teflon sample introduction system consisting of an ESI μFlow PFA nebulizer and PC³ Peltier spray chamber chiller. Standards were made from single- or mixed element stock solutions supplied by VHG Labs (Manchester, NH, USA) or Spex Certiprep (Metuchen, NJ, USA). A continuing control verification (CCV) standard was prepared from stocks from the other vendor; e.g. if VHG was used for calibration, Spex was used for CCV and spikes. A minimum of 5 calibration standards were prepared in the range of 0 – 100 ng mL⁻¹ to provide a usable calibration range and span the detector cross calibration point. The CCV standard was made in the 5 – 10 ng mL⁻¹

range. A blank and CCV was analyzed at a minimum of every 10 samples. One or more duplicates, and one or more spikes (depending on the size of the experiment), were prepared and analyzed with each experimental run.

During the analysis of organic solutions, 0.2 L min^{-1} of 20% oxygen in argon was added to the spray chamber to aid the combustion of organic material. 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 1:50. The organic phase samples were agitated for 30 s prior to analysis. Distribution ratios (D_U) were calculated according to the equation:

(7)

Only data whose mass balance analysis fell within the range 90 – 110% were used. The mean of the duplicate distribution ratios is reported, with an average uncertainty of $\pm 10\%$ over all samples.

RESULTS AND DISCUSSION

DEHBA Degradation Rates. Under continuously air-sparged conditions, the degradative loss of DEHBA contacted with 0.1 and 4.0 M $\text{HNO}_{3(\text{aq})}$ was found to follow a linear decay, as shown in Figure 2.

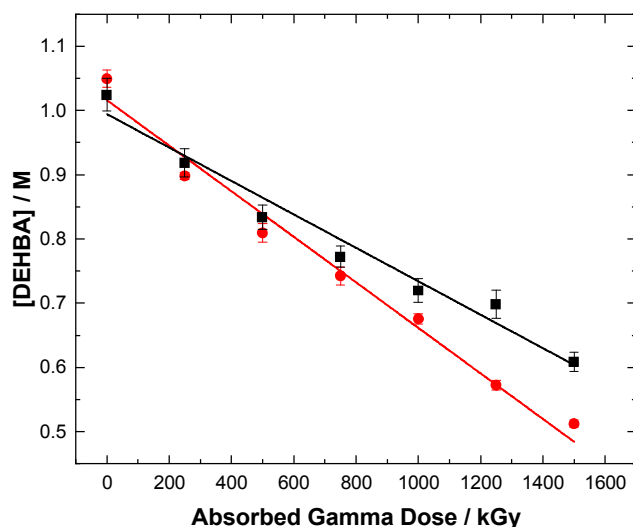


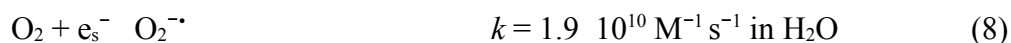
Figure 2. Concentration of DEHBA as a function of absorbed gamma dose (0.82 Gy s^{-1}) for air-sparged, nominally 1.0 M DEHBA in *n*-dodecane solutions contacted with 0.1 (■) and 4.0 (●) M $\text{HNO}_{3(\text{aq})}$.

Comparison of the biphasic DEHBA G -values in Table 1 shows that the presence of dissolved O_2 decreases the rate of DEHBA degradation by 50 - 28% in going from 0.1 ($G = -0.26 \pm 0.02 \mu\text{mol J}^{-1}$) to 4.0 M $\text{HNO}_{3(\text{aq})}$ ($G = -0.35 \pm 0.02 \mu\text{mol J}^{-1}$) contacts. These DEHBA loss values under anticipated real-world reprocessing conditions also compare well to previously published values for TBP ($G = -0.37 \mu\text{mol J}^{-1}$, [11]). It is clear that a degradation mitigation effect occurs when O_2 is continuously present.

Table 1: Radiolytic yields ($\mu\text{mol J}^{-1}$) for DEHBA obtained from linear fits to curves for the gamma radiolysis of 1.0 M DEHBA in *n*-dodecane solutions under various biphasic conditions.

Sample	Degradation G -Value ($\mu\text{mol J}^{-1}$)	Reference
0.1 M $\text{HNO}_{3(\text{aq})}$ contacted deaerated	-0.53 ± 0.02	10
0.1 M $\text{HNO}_{3(\text{aq})}$ contacted air sparged	-0.26 ± 0.02	<i>this work</i>
3.0 M $\text{HNO}_{3(\text{aq})}$ contacted deaerated	-0.49 ± 0.02	10
4.0 M $\text{HNO}_{3(\text{aq})}$ contacted air sparged	-0.35 ± 0.02	<i>this work</i>

The continuous presence of a relatively high dissolved O₂ concentration (4.9 mM at 1 atm air at room temperature [19]) in the organic phase would have several effects on the overall DEHBA degradation mechanism. Firstly, O₂ is an effective scavenger of solvated electrons (e_s⁻) [15] and excited states (R*) [20,21,22]:



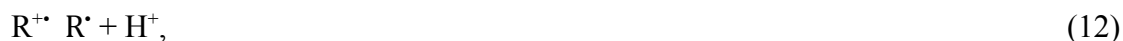
which would inhibit degradative pathways for DEHBA in the irradiated organic phase:



However, having O₂ present would also enhance the available radiolytic yield of the corresponding *n*-dodecane radical cation (R^{•+}) [23]. This cation would be expected to react with DEHBA either directly by electron transfer:



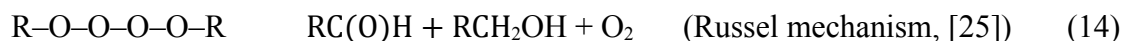
or, by proxy, through pre-formation of a carbon-centered radical:



and subsequent reaction of this radical with DEHBA by hydrogen-atom abstraction:



However, as previously discussed, O_2 can react with R^{\cdot} to yield the corresponding peroxy radicals (RO_2^{\cdot}), reaction (1), thus minimizing the overall degradation of DEHBA. Further, peroxy radicals are relatively non-reactive, and predominately decay through formation of a tetroxide [14], reaction (2). Although no specific products have been determined for the decay of the tetroxide in the organic phase, by analogy with tetroxide decay chemistry in water [24], it would be expected that a mixture of alcohols, aldehydes and ketones, as well as other oxygenated species would be formed:





For biphasic DEHBA irradiations, the presence of extracted HNO_3 and water in the organic phase was shown to enhance degradation [10]. This was attributed to the radiolytic formation of the highly reactive nitrate ($\bullet\text{NO}_3$) and hydroxyl ($\bullet\text{OH}$) radicals. As shown in Table 1, the rate of DEHBA degradation does increase for acid contacted solutions, relative to deaerated organic-only ($G = -0.31 \pm 0.02 \mu\text{mol J}^{-1}$ [10]), but the presence of air sparging somewhat mitigates this effect. While these two strongly oxidizing radicals do not react with oxygen directly, it is possible that the oxidized tetroxide decay products could compete with DEHBA for these radicals in the organic phase, affording a competitive reaction pathway that would reduce the overall degradation of DEHBA. Such secondary degradation product mediated inhibition has been reported for other ligands [27,28]. The lesser protection seen for DEHBA in contact with 4.0 M $\text{HNO}_{3(\text{aq})}$ is probably due to the higher acidity in the organic phase. This would lead toward protonated radiolysis products that would move to the aqueous phase, thus minimizing their protective effect in the organic phase.

Irradiated Solvent FTIR Analyses. FTIR analyses were performed for these continuously air-sparged, irradiated DEHBA solutions in an attempt to identify the products formed under these conditions. The FTIR spectra obtained for DEHBA in *n*-dodecane solutions contacted with 4.0 M HNO_{3(aq)} irradiated to contact doses up to 1250 kGy under continuously air sparged conditions are shown in Figure 3.

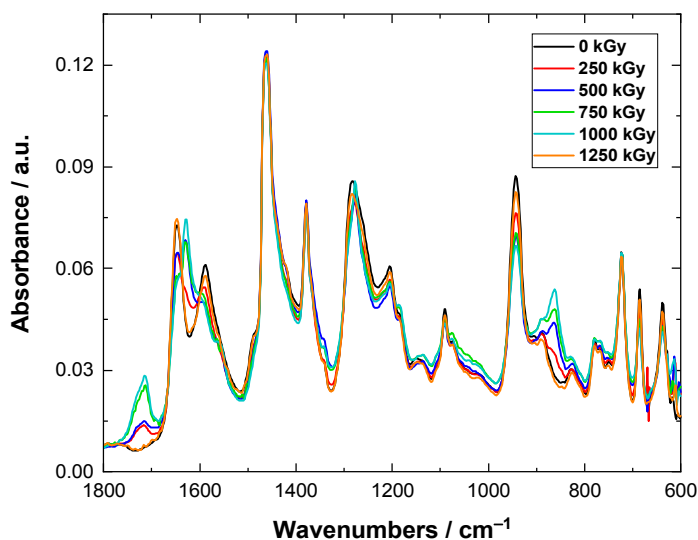


Figure 3. FTIR spectra of continuously air-sparged gamma-irradiated, organic phases of nominally 1.0 M DEHBA in *n*-dodecane solutions contacted with 4.0 M HNO_{3(aq)}.

When compared with complimentary deaerated spectra [10], we observe new peaks appear at 1715 (carboxylic acid), 1630 (amidic species), and 862 cm⁻¹ (C-N or C=C bonds) after irradiation, consistent with the oxidized product species anticipated from peroxy radical formation and decay. Further, there is only a minimal decrease in the absorbance of other prominent bands under continuously air-sparged conditions, supporting the hypothesis that these products would compete with DEHBA for these radicals in the organic phase to minimize DEHBA degradation.

Irradiated Solvent ESI-MS Analyses. Additional insight into the radiation-induced degradation mechanism for DEHBA under continuously air-sparged extraction conditions (4.0 M $\text{HNO}_{3(\text{aq})}$ contact) was obtained using ESI-MS, shown in Figure 4. In addition to the expected protonated and sodiated DEHBA monomer and dimer compounds at $m/z = 312.2$, 334.2 and $m/z = 623.0$, 645.5, products at $m/z = 200.1$, 242.2, and 310.2 were observed. These correspond to the radiation-induced DEHBA degradation products MEHBA and b2EHA, respectively [10].

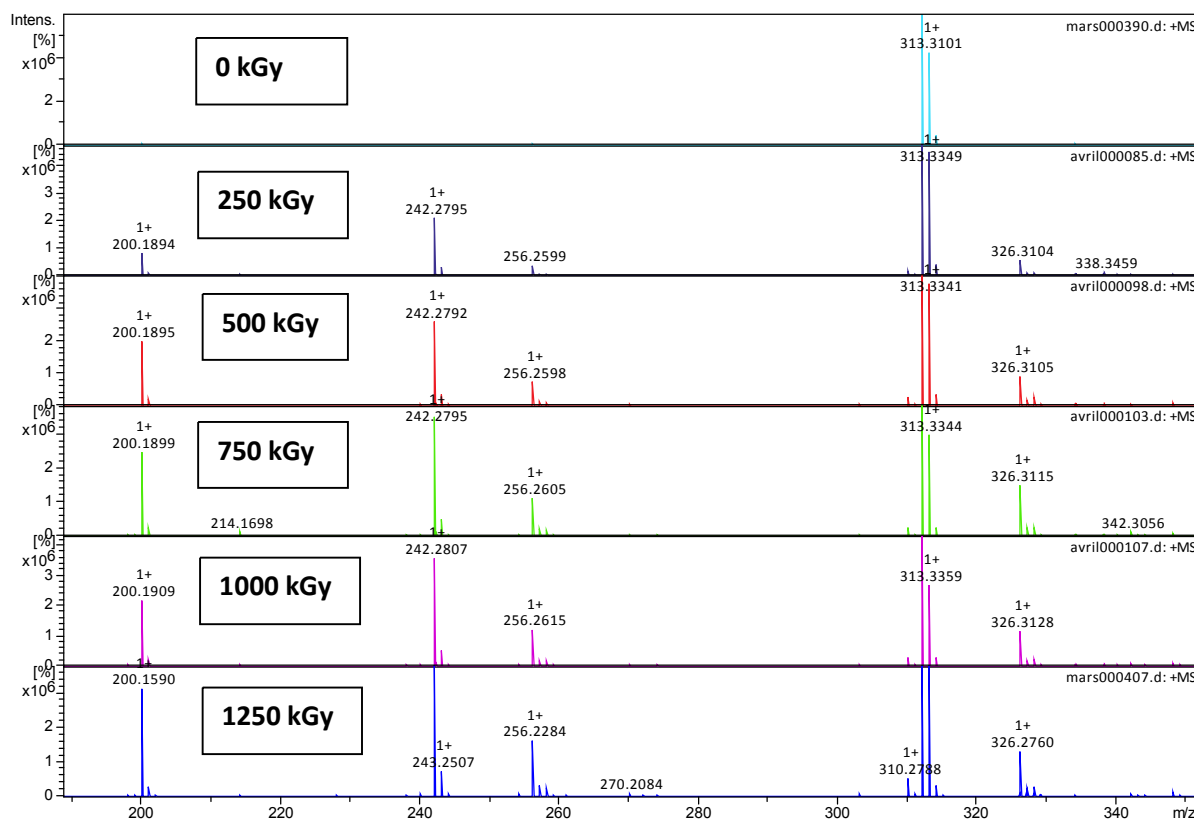


Figure 4. ESI-MS spectra for continuously air-sparged organic phases of nominally 1.0 M DEHBA in *n*-dodecane solutions contacted with 4.0 M $\text{HNO}_{3(\text{aq})}$ irradiated to 1250 kGy.

Compared with deaerated systems [10], new species were observed for continuously air-sparged irradiated samples at $m/z = 158.1$, 256.2, 348.2, 326.2, 373.2, 511.5, 553.6, and 567.5. For $m/z = 256.2$ and 326.2, these ions correspond to $[\text{C}_{16}\text{H}_{33}\text{NO}]^+$ and $[\text{C}_{20}\text{H}_{39}\text{NOO}]^+$, indicating oxidation of a methylene group into a carbonyl group in the alkyl chain of the amine

(b2EHA) or the monoamide (MEHBA), respectively. The peaks at $m/z = 553.6$ and 567.5 correspond to the species $[(C_{20}H_{41}NO)(C_{16}H_{35}N)]H^+$ and $[(C_{20}H_{41}NO)(C_{16}H_{33}NO)]H^+$, respectively. These two peaks are attributed to adducts formed between DEHBA and b2EHA ($m/z = 553.6$) and DEHBA and an amine with a carbonyl group in the alkyl chain ($m/z = 567.5$), this confirm the large quantity of these two compounds in the solution (b2EHA and its oxidized form). The other peaks at $m/z = 158.1, 348.2, 373.2,$ and 511.5 could not be definitively assigned; however, by simulating these ion molar masses using mass spectroscopy library data with appropriate boundary conditions (species containing C, H, O, N, Na, and K, and with degrees of unsaturation less than 3), all four peaks had multiple molecular formulae containing at least one oxygen atom. These ESI-MS data, along with the FTIR spectra, demonstrate that the presence of acid and O_2 during irradiation of DEHBA afford various additional oxygen-containing product species, a summary of which is given in the SI.

Effects on Uranium Partitioning and Stripping. The impact of gamma irradiation on DEHBA solvent extraction performance was determined by performing batch contacts for extraction (4.0 M $HNO_{3(aq)}$ contact) and strip conditions (0.1 M $HNO_{3(aq)}$ contact). The extraction stage was simulated by separating previously irradiated, continuously air-sparged organic phases contacted with 4.0 M $HNO_{3(aq)}$ and re-contacting them with fresh 4.0 M $HNO_{3(aq)}$ solutions spiked with uranium. Following extraction, the actinide loaded organic phases were then separated and again re-contacted with fresh 0.1 M $HNO_{3(aq)}$ to achieve stripping. The measured irradiated DEHBA distribution ratios for uranium under extraction and strip conditions are given in Figure 5.

For uranium extraction, D_U decreased linearly with absorbed gamma dose. In previous

work under deaerated conditions, uranium extraction was effectively constant within experimental error [10]. Our current data are similar to the findings of Ruikar *et al.* for several dihexyl [6], and methylbutyl substituted hexan-, octan-, and decan-amides [8], irradiated in *n*-dodecane that had been pre-equilibrated with 3.5 M $\text{HNO}_{3(\text{aq})}$.

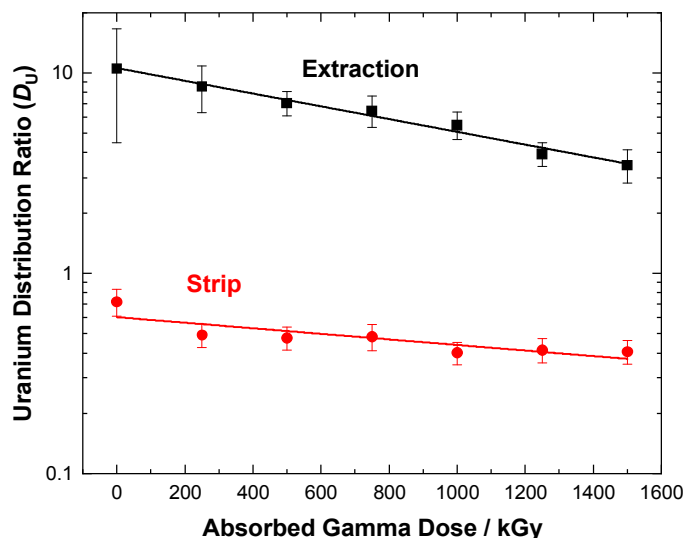


Figure 5. Uranium distribution ratios (D_U) as a function of absorbed gamma dose for extraction (■) and strip (●) contacts using continuously air sparged nominally 1.0 M DEHBA in *n*-dodecane solutions irradiated in contact with 4.0 M $\text{HNO}_{3(\text{aq})}$.

This loss of extraction D_U for DEHBA is not particularly concerning, as the D_U only decreased from about 10 to ~5 in going from 0 to 1500 kGy, which corresponds to an 8% drop in uranium extracted. Further, the absorbed gamma doses used in these experiments are very high compared to the envisioned lifetime exposure of a given solvent system.

For the corresponding uranium strip data, Figure 5, D_U remains almost constant (the slight slope seen is significantly influenced by the first, non-irradiated, point), in agreement with previous deaerated results [10]. These observations suggest progressively easier recovery of uranium for samples irradiated in the presence of acid, which is advantageous for solvent

extraction performance.

CONCLUSIONS

The rate of DEHBA degradation by gamma radiolysis under continuously aerated conditions was found to be $G = -0.26 \pm 0.02 \mu\text{mol J}^{-1}$ (0.1 M $\text{HNO}_{3(\text{aq})}$ contact) and $G = -0.35 \pm 0.02 \mu\text{mol J}^{-1}$ (4.0 M $\text{HNO}_{3(\text{aq})}$ contact), considerably slower than previously determined for analogous deaerated conditions ($G = -0.53 \pm 0.02$ and $-0.49 \pm 0.02 \mu\text{mol J}^{-1}$, respectively) and TBP ($G = -0.37 \mu\text{mol J}^{-1}$). FTIR and ESI-MS investigations provided evidence for multiple additional oxidized degradation products, as expected from the decay of the peroxy radicals formed by the initial DEHBA reactions with radiation-induced radical and ionic species.

Solvent system performance was also investigated using natural uranium extraction and strip distribution ratio measurements. Extraction D_U decreased linearly with absorbed dose while the corresponding strip values were effectively constant with applied gamma dose.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

SUPPLEMENTAL MATERIAL

The Supplemental Material is available free of charge on the *'journal'* website at DOI:

AUTHOR INFORMATION

Corresponding Author:

E-mail: gregory.horne@inl.gov¹

 stephen.mezyk@csulb.edu²

Address: 1. Idaho National Laboratory, PO Box 1625, Idaho Falls, ID, 83415

 2. Department of Chemistry and Biochemistry, California State University at
 Long Beach, California, 90840, USA

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Supplemental Material: DEHBA (di-2-ethylhexylbutyramide) radiolysis under solvent extraction process conditions

Gregory P. Horne^{a*}, Stephen P. Mezyk^{b*}, Bruce J. Mincher^a, Christopher A. Zarzana^a, Cathy Rae^a, Richard D. Tillotson^a, Nicholas C. Schmitt^a, Richard D. Ball^a, Joakim Ceder^{a,c}, Marie-Christine Charbonnel^d, Philippe Guilbaud^d, George Saint-Louis^d, and Laurence Berthon^d

^aIdaho National Laboratory, Center for Radiation Chemistry Research, Idaho Falls, ID, P.O. Box 1625, 83415, USA.

^bDepartment of Chemistry and Biochemistry, California State University Long Beach, 1250 Bellflower Boulevard, Long Beach California, 90840-9507, USA.

^cKTH Royal Institute of Technology, Department of Chemical Engineering, Teknikringen 42, S-100 44, Stockholm, Sweden.

^dCEA Marcoule, DEN/DRCP/SMCS/LILA, Bât. 181, BP 17171, 30207 Bagnols-sur-Cèze, France.

* Corresponding authors. e-mails: Gregory.Horne@inl.gov and Stephen.Mezyk@csulb.edu

Table S1. Comparison of compounds observed in the organic phase as a function of experimental conditions. L stands for DEHBA.

m/z	Formula	Non-irradiated [10]	0.1 M HNO _{3(aq)} Deaerated [10]	4.0 M HNO _{3(aq)} Deaerated [10]	4.0 M HNO _{3(aq)} Air-Sparged [This Work]
130.1	[C ₈ H ₁₇ NH ₂] H ⁺			*	
158.1					*
171.1		*			
200.2	[C₁₂H₂₄NO]H⁺	*	*	*	*
242.2	[C₁₆H₃₅N] H⁺		*	*	*
256.2	[C₁₆H₃₃NO]H⁺	*	*		*
270.2	[C ₁₆ H ₃₁ NO ₂]H ⁺		*		
310.2	[C₂₀H₃₉NO]H⁺		*	*	*
312.2	LH⁺	*	*	*	*
326.0	[C₂₀H₃₉NOO]H⁺			*	*
328.0	[C ₂₀ H ₄₀ NOOH]H ⁺			*	*

334.2	LNa ⁺			*	
348.2					*
350.0	LK ⁺			*	
357.3				*	
373.2					*
379.2				*	
382.3			*		
410.5	[C ₂₈ H ₅₉ N]H ⁺		*		
422.4			*		
447.3		*			
480.5	[C ₃₂ H ₆₅ NO]H ⁺		*		
511.5					*
533.5			*		
551.7	[C ₃₆ H ₇₄ N ₂ O]H ⁺		*		
553.6	[(C ₂₀ H ₄₁ NO)(C ₁₆ H ₃₅ N)]H ⁺				*
567.5	[(C ₂₀ H ₄₁ NO)(C ₁₆ H ₃₃ NO)]H ⁺				*
621.6	[C ₄₀ H ₈₀ N ₂ O ₂]H ⁺		*		
623.6	L ₂ H ⁺	*	*	*	*
645.5	L ₂ Na ⁺	*	*	*	*
661.1	L ₂ K ⁺			*	

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