Title
The Effects of Metal Ion Uptake on the Radiolysis of Solvent Extraction Ligands

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Author
Ngelale, Randy

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The Effects of Metal Ion Uptake on the Radiolysis of Solvent Extraction Ligands

Dissertation

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

In Chemical Engineering

by

Randy O. Ngelale

Dissertation Committee:
Professor Mikael Nilsson, Chair
Professor Martha Mechartney
Professor Stephen Mezyk (CSULB)

2019
DEDICATION

To

My parents for all of their love and support,
Mary and Agora for being the reason I strive to be more today than I was yesterday,
Charles for showing be the kind of man I should aspire to become,
and to all who bear the name “Ngelale”.

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ABSTRACT

Used nuclear fuel contains a mixture of highly radiotoxic elements and must be handled and stored with great care due to the potential for environmental damage. As such, special consideration must be given to how long and where the used fuel will be stored. However, used fuel is still quite rich in uranium and plutonium (~96-97% of the initial heavy metal) and therefore can be a viable feedstock for these metals. To minimize the waste volume as well as the storage time scale, various separation techniques to isolate useful material for possible reuse have been proposed [1]. Currently, the most widely practiced method is the Plutonium Uranium Redox Extraction (PUREX) process that was designed to address this issue by utilizing tributyl phosphate (TBP) to selectively extract plutonium and uranium from used fuel by liquid-liquid extraction. More recent efforts have been aimed at the separation of the minor actinides from used nuclear fuel. These minor actinides would still remain in the high-level waste after the PUREX step and would require further extraction steps to be removed. The Actinide-Lanthanide Separation (ALSEP) process, utilizing the solvating extractant N,N,N',N'-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) as well as the acidic 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) for the co-extraction of lanthanides and actinides from solutions of high nitric acid concentration is currently under development to tackle this problem [2], [3].

Due to the intense radiation of used fuel, solvent extraction processes designed to treat used nuclear fuel experience degradation of the extracting ligands. The products of the degradation can adversely affect the efficiency of the overall extraction process as well as form a third phase or lower the selectivity of the extraction. Prior studies of the radiolysis of
TBP without metal contact as a function of various types of radiation have been done [4],[5].

In this study, the degradation is caused by low linear energy transfer (LET) radiolysis and high LET radiolysis (using the $^{10}$B $(n, \alpha)^{7}$ Li reaction) of ALSEP solution with and without nitric acid uptake as well as metal loaded TBP. The results discussed will be of systems of 0.1M TBP/dodecane, 1M TBP/dodecane contacted with nitric acid and varying concentration of uranyl nitrate to observe the effect of increased metal loading. I also establish preliminary degradation constants for the ALSEP ligands HEH[EHP] and T2EHDGA as a function of low and high LET radiation as well as acid uptake.
INTRODUCTION

Nuclear Energy

Several factors such as global population increase, rapid technological growth in developing countries and the desire for higher standards of living contribute to the projected increase in energy demand currently facing the world. This in turn requires that methods of producing the energy required to meet these demands in a sustainable, environmentally benign and economically favorable fashion must be developed. Currently, nuclear power is a promising avenue for energy production. Current (2018) statistics indicate that there are 451 operable nuclear reactors globally with 56 reactors scheduled for construction, 148 reactors planned and 337 proposed [6]. Figure 2.1 shows the number of reactors planned by country.
Figure 2.1. Number of reactors planned by country [6].

Used Nuclear Fuel

Estimates of the global used fuel inventories, as well as projected values, were compiled by the International Atomic Energy Agency and show an upward trend in the waste volumes. Figure 2.2 indicates how much waste is generated and what amount of that waste goes on to be stored or reprocessed. Particularly noteworthy is the fact that from 1990 to 2020, the accumulation of used fuel increases faster than the rate of reprocessing, leading to more and more used fuel being stored in repositories. The compilation was done in 2008 and therefore
values beyond this are estimates [7]. Interestingly, in 2013, a study by the IAEA corroborated these predictions by confirming a total spent fuel inventory of 367,600 tonnes of heavy metal (tHM) of which 120,300 were reprocessed as of 2013[8]. Both of these values are in good agreement with the values forecasted in 2008.

![Cumulative Spent Fuel Arisings, Storage and Reprocessing, 1990-2020](image.png)

**Figure 2.2.** Spent fuel (SF) discharged from reactors, stored and reprocessed compiled in 2008. Values beyond 2008 are projections [7].

Initial composition of the fuel material, cooling time, as well as the burn up may vary from reactor to reactor, therefore the chemical speciation of the resulting used fuel matrix will also vary. However, after a typical burnup of 33MWD/kg Uranium, the resulting mixture is comprised of about 95% non-fissile $^{238}$U, 0.9% plutonium, 0.1% minor actinides (Np, Am, Cm from successive neutron capture by uranium [9]) 3% fission products and a remainder of 1% fissile $^{235}$U by mass [10].
Figure 2.3. Used fuel composition and average percentages adapted from IAEA-TECDOC-1587 [7] and Japan Nuclear Fuel Limited “Nuclear Fuel Cycle” [11].

Long Term Storage and Radiotoxicity

A major concern regarding long term storage of used nuclear fuel is the potential for future radiological hazards. Long term storage takes place in geological repositories in locations preferably without the likelihood of major seismic activity. The issue facing the disposal of used fuel in geological repositories are more to do with the length of time required for the radioactivity to return to acceptable levels. Figure 2.3 shows the initial activity being predominantly due to decay of short-lived fission products ($^{137}\text{Cs}$ and $^{90}\text{Sr}$), but there are also long-lived fission product radionuclides, such as $^{99}\text{Tc}$ (213,000 year half-life), $^{135}\text{Cs}$ (2.3 million year half-life) and $^{129}\text{I}$ (15.7 million year half-life) [12].
The long-term danger posed by these different radionuclides depends on their mobility under the geochemical conditions. Assuming the worst case scenario of a potential rupture of the cladding of the storage canisters as well as the fuel coming in direct contact with ground water, the actinides are typically immobile under reducing conditions [13]. However, radiolytic decomposition of water in direct contact with the surface of the fuel can create oxidizing species such as hydrogen peroxide (H$_2$O$_2$) and the hydroxide radical (OH$^-$), and oxidizing conditions increase the solubility of actinides in solution by promoting them to higher oxidation states (V/VI) [14]. They can then form strong complexes with carbonates readily found in solution in groundwater and be transported away from the repository [13].

With this in mind, dealing with the long-term presence of plutonium and the minor actinides is of utmost importance due to their long-term activity as well as the potential for contamination of ground water. As seen in Figure 2.4, it would take about 100,000 years for the ingestion radiotoxicity of the waste to reach the reference level of ingestion hazard from 7 equivalents of natural uranium (the amount required to make 1 equivalent of fuel) [15]. If plutonium were to be extracted and removed from the used fuel, the time required for the toxicity to reach the reference level decreases to 10,000 years, is predominantly due to the presence of the minor actinides. If the minor actinides are removed, the reference level is reached after approximately 500 years.

Separation of plutonium and the minor actinides is a topic of major concern going forward, and is critical to the success and public acceptance of nuclear energy in the foreseeable future. The work presented in this thesis focuses on the PUREX (Plutonium Uranium Redox
Extraction) process as well as the ALSEP (Actinide-Lanthanide Separation) process a means of separating plutonium, uranium and the minor actinides from used fuel.

![Graph showing ingestion radiotoxicity of various key components in used fuel as a function of time.](image)

**Figure 2.4.** Ingestion radiotoxicity of various key components in used fuel as a function of time. Data represents fuel with enrichment of 4.2%, 50 GWd/ton U burnup and 6 years of cooling. Effective dose coefficients from the International Commission for Radiological Protection [16]. Figure reproduced from data published by Magill et al. [12]
BACKGROUND

Solvent Extraction

Solvent extraction techniques have been developed to address the lingering concerns about the long-term radiotoxicity of the used fuel. Attempts to mitigate said radiotoxicity have manifested in the form of several extraction techniques aimed at the partitioning and recycling of various components of used fuel [1]. The overarching principle of these techniques is based on liquid-liquid extraction whereby the solute metal in question is dissolved in a liquid phase that is in contact with another immiscible liquid phase. The equilibrium law relating the composition of a solute distributing between two liquid phases is given by:

\[ K_{D,s} = \frac{a_s^{\text{org}}}{a_s^{\text{aq}}} \]  

Eq. 3.1

\( aq \) and \( org \) denote the aqueous and organic phases and \( a_s \) is the activity of the distributed solute. This relationship governs the transfer of a solute that exists as one species, however, in the case of used fuel the solute in question can be present as many different species (complexes). In this case, the more commonly used IUPAC definition states that the distribution ratio is [17]:

“The ratio of the total analytical concentration of a solute in the extract (regardless of its chemical form) to its total analytical concentration in the other phase.”

\[ D_s = \frac{[s]_{\text{total org}}}{[s]_{\text{total aq}}} \]  

Eq. 3.2

Most conventional solvent extraction techniques employ an organic phase consisting of:
1) An extractant – a component initially dissolved in the diluent, that selectively coordinates to the metal solute and facilitates its movement from one phase to another.

2) A diluent – forming the bulk of the organic phase, which houses the extractant.

The distribution ratio can vary greatly with temperature and is largely dictated by the extractant’s affinity for the metal and strength of the complex formed. This affinity is dictated by the size and oxidation state of the metal. Typically, higher values of \( D_s \) are favorable, but it must be taken into consideration that the metal-ligand complex must not be too strong to prevent back stripping of the metal.

Due to the similar ionic radii and charge of the lanthanides and minor actinides, a major challenge in solvent extraction comes in the form of selectivity. It is preferential for an extractant to be highly selective for one or a few elements over others, and so extraction systems must be designed with this in mind. The separation factor (\( SF_{a/b} \)) is defined by IUPAC as [17]:

"The ratio of the respective distribution ratios of two extractable solutes measured under the same conditions."

\[
SF_{a/b} = \frac{[D]_a}{[D]_b}
\]

Eq. 3.3

Additionally, because these organic systems will be in direct contact with the aqueous dissolved used fuel, they must show some degree of radiation resistance. If not, then they can undergo unwanted chemical changes which may affect the overall distribution ratio and by extension, the separation factor. These reactions occur due to radiolysis of either the
extractant and/or the diluent. These are some key criteria that solvent extraction techniques must meet in order to be considered viable. Additionally, in order to be implemented on a large industrial scale, the solvents must not be overly expensive.

**PUREX Process**

The PUREX process employs ~30 vol% tributyl phosphate (TBP) as the extractant in an inert aliphatic diluent (kerosene, n-dodecane etc.) to form the organic phase. The corresponding aqueous phase consists of used fuel dissolved in concentrated nitric acid, further adjusted to ~3M HNO₃. TBP is a good choice of extractant due to its selectivity for U(VI) as UO₂(NO₃)₂ and Pu(IV) as Pu(NO₃)₄ in the acidic solution. Generally speaking, TBP extracts tetravalent and hexavalent metal cations quite readily, so it is crucial to implement process steps to back extract or scrub out unwanted tetravalent as well as certain other contaminants (Zr, Ru, Re, Tc) [18]. As a side note, it is deemed unwise to perform the extraction process with TBP concentrations in excess of 30 vol%. TBP has a density of 0.97 g/ml which is similar enough to water to result in poor phase separation, and sometimes even phase inversion, in the liquid-liquid extraction process if the concentration of TBP is too high. Additionally because TBP forms strong complexes with U and Pu, more TBP in the extraction step would require enormous volumes of aqueous phase to perform back extractions to isolate both U and Pu in addition to changes to phase separation due to the increased density of the organic phase from increased U and Pu uptake[19].

The goals of the PUREX process as outlined by Irish and Reas et al. are as follows [20]:

- Extraction of U and Pu from aqueous medium into the organic TBP-diluent phase.
- Partitioning of the U and Pu from one another.
• Removal of residual contaminants and recovery of the uranium.
• Removal of residual contaminants and recovery of the plutonium.
• TBP and diluent recovery.
• Nitric acid recovery (including waste concentration).

The very delicate set of chemical conditions required to meet these goals as well as the necessary engineering and flowsheet design is truly remarkable, and is discussed in detail elsewhere [18]. It comes as no surprise then that sudden changes in chemical species in the organic phase caused by radiation can result in unwanted excursions from optimal extraction conditions in all of the aforementioned steps.

Radiation induced degradation of both the TBP and the organic diluent during contact with the radioactive metal laden aqueous feed is thus an issue of great concern. In addition to requiring addition to make up for lost TBP, some of the degradation products, dibutyl and monobutyl phosphoric acid (HDBP and H$_2$MBP respectively), have high affinities for uranium and plutonium. This combined with radiolysis products of the diluent can form interfacial cruds or additional phases that retain fission products and other metals [21]. Conventional separation process equipment such as centrifugal contactors are designed to only handle two distinct phases and therefore additional phases can cause a reduction in product stream purity. The study of the interactions of radiation and TBP form the basis for the work done in this thesis and will be the focus of subsequent sections.

**Actinide Separations and the ALSEP Process**

Separation of the minor actinides (primarily americium, neptunium and curium) has been an ongoing area of research. $^{237}$Np is the most abundant minor actinide and is produced from
successive neutron capture of $^{235}$U to $^{237}$U which then decays to $^{237}$Np [12]. However, its long half-life of 2.15 million years makes it the least active of the minor actinides. Conversely, americium comes primarily in three main isotopes in used fuel, $^{241}$Am, $^{242m}$Am and $^{243}$Am. $^{241}$Am has a half-life of 432 years. Its presence becomes significant after roughly a century as it is produced by the decay of $^{241}$Pu which has a half-life of 14 years[22]. In the short term (within the first century) the radioactivity of the minor actinides is dominated by $^{244}$Cm which has a relatively short half-life of 18 years [12].

The task of separating the trivalent actinides from their lanthanide counterparts presents a unique challenge due to their preference for the trivalent oxidation state as well as their similar ionic radii [23]. Current attempts have determined that the most viable approach for a single stage extraction would involve the use of an acidic extractant as well as a neutral extractant in an organic medium. These are intended to facilitate the coextraction of both trivalent lanthanides and actinides from aqueous media. This step is followed by a separation of the aqueous and organic phases and contacting the metal laden organic phase with a new aqueous phase polyamonicarboxylate ligand. These acids have been shown to bind more strongly to the trivalent actinides over lanthanides [24]. Some choices of extractant combinations have been compiled by Lumetta et.al. and are shown in Table 3.1 and Figure 3.1
Figure 3.1: Chemical structures of acidic and neutral extractants proposed for An(III)/Ln(III) separation.
Table 3.1: Extraction systems proposed for An(III)/Ln(III) separation.

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<tr>
<th>Neutral Extractant</th>
<th>Acidic Extractant</th>
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<tr>
<td>CMPO</td>
<td>HDEHP</td>
<td>[25][26][27]</td>
</tr>
<tr>
<td>CMPO</td>
<td>HEH[EHP]</td>
<td>[28]</td>
</tr>
<tr>
<td>TODGA</td>
<td>HDEHP</td>
<td>[29]</td>
</tr>
<tr>
<td>TODGA</td>
<td>HEH[EHP]</td>
<td>[30]</td>
</tr>
<tr>
<td>T2EHDGA</td>
<td>HDEHP</td>
<td>[31][32]</td>
</tr>
<tr>
<td>T2EHDGA</td>
<td>HEH[EHP]</td>
<td>[2]</td>
</tr>
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Utilization, Partitioning and Transmutation

Ideally a combined flowsheet that incorporates first the PUREX process to separate plutonium and uranium into a product stream to be repurposed, and the ALSEP process to clean up the PUREX raffinate to separate the trivalent lanthanides and actinides. Further processing steps can eventually separate the trivalent lanthanides from actinides.

These separation steps yield highly radioactive metals and must be further processed. The depleted but fertile uranium (\(^{238}\text{U}\)) and fissile plutonium (\(^{239}\text{Pu}\)) can be combined to form mixed oxide (MOX) fuel for Fast Breeder Reactors [33]. The minor actinides can further be exposed to high neutron fluxes, undergo neutron capture and then fission or decay into either stable isotopes or isotopes with shorter half-lives [34].

Due to the highly radioactive nature of used nuclear fuel, the extractants employed in such separation systems must be able to handle the deposition of large quantities of energy in the form of ionizing radiation without suffering structural damage that may lead to the separation system being compromised. The destruction by radiation of chemical bonds
within molecules is the basis of this work. Here I will examine the various interactions of ionizing radiation on used nuclear fuel separation process relevant ligands.

**Radiolysis**

Radiation (photons or charged particles) causes ionization in matter by deposition of sufficient energy to disrupt the electrons surrounding a nucleus or breaking chemical bonds. This mode of chemically altering the structure of a molecule or chemical bond by exposure to ionizing radiation is termed radiolysis. Radiolysis events scale with absorbed radiation dose (D), where the dose is defined as the amount of energy absorbed by a sample of matter per unit mass of the sample. The corresponding SI unit of dose is Gray (Gy), defined as J/kg. The extent to which radiation alters or destroys matter is quantified by a G-value, the G-value is given as the number of molecules or moles of the consumed species that were destroyed (negative value) or the number of molecules of the produced species that were formed (positive value), per unit energy input, i.e. dose.

**Linear Energy Transfer (LET)**

For a given type of radiation travelling through a material, linear energy transfer (LET) is a measure of how much energy is deposited into a material per unit distance travelled by the ionizing particle or photon. High LET deposits the entirety of its energy over a short distance, whereas low LET can travel longer distances before losing all of its energy. As can be seen by the cloud chamber diagrams in Figure 3.1, alpha particles form thicker, shorter and more linear paths while gamma rays are much more dispersed. This appearance of dispersion for beta and gamma ray tracks is due to secondary electrons that form due to incident radiation.
Radiolysis in the PUREX Process.

Under PUREX process conditions, the incoming aqueous phase of dissolved fuel contains a vast array of radioactive elements and isotopes. As a result, various modes of decay are at play in the dissolved solution. Upon dissolution of the fuel in nitric acid, the water that is present in the aqueous phase undergoes radiolysis to form several species according to Eq. 3.4[4]. The G-values corresponding to each species produced may vary depending on the nature of the incident radiation and therefore the equation is LET dependent. Due to the shorter, more condensed, volume of the tracks created by high LET, the likelihood of radical recombination within this smaller volume is expected to be greater. This results in the yield of radical species becoming lower while that of molecular species becoming higher [4].

$$\text{H}_2\text{O}^{\text{Radiation}} \rightarrow [G_{OH}] \cdot \text{OH} + [G_{e_{aq}^-}] e_{aq}^- + [G_H^+] H^+ + [G_{H_2O_2}] H_2O_2 + [G_{H_3O^+}] H_3O^+ + [G_{H_2}] H_2$$

Eq. 3.4
Upon phase contact and mixing, TBP and the organic diluent become irradiated by both high and low LET radiation. In addition to this, many of the species produced in Eq 3.4 are highly reactive and can chemically attack TBP causing degradation:

Zaitsev et.al [36][37]:\[
e^{-}_{aq} + (C_4H_9O)_3PO \rightarrow C_4H_9 + (C_4H_9O)_2OPO^- \quad \text{Eq. 3.5}
\]

Mincher et.al [38]:\[
H^+ + (C_4H_9O)_3PO \rightarrow (C_4H_9O)_2(C_4H_9O)PO + H_2 \quad \text{Eq. 3.6}
\]

\[
\cdot OH + (C_4H_9O)_3PO \rightarrow (C_4H_9O)_2(C_4H_9O)PO + H_2O \quad \text{Eq. 3.7}
\]

Where the products of Eq. 3.5 are a butyl radical and DBP (dibutyl phosphate), which can combine with dissolved hydrogen common in acidic solutions and become DBP (dibutyl phosphoric acid). DBP is commonly known to be the most prominent degradation product of TBP in terms of negative impact on PUREX separation [39]. Due to the prevalence of hydrogen atom abstraction by the radical oxygens in the phosphate ligands DBP rapidly accepts a hydrogen atom to form HDBP (dibutyl phosphoric acid). The product in equations 3.6 and 3.7 is a TBP radical and has yet to fully degrade to HDBP but can do so by direct radical decay or reacting with water:

Burr et.al. [40]:\[
(C_4H_9O)_2(C_4H_9O)PO \rightarrow \cdot C_4H_8 + (C_4H_9O)_2OPO^- \quad \text{Eq.3.8}
\]

Sonntag [41]:\[
(C_4H_9O)_2(C_4H_9O)PO + H_2O \rightarrow (C_4H_9O)_2OPO^- + C_4H_9OH + H^+ \quad \text{Eq.3.9}
\]

Equations 3.5-3.9 are important factors to consider when discussing TBP radiolysis, however they are causes of indirect radiolysis of TBP. Direct radiolysis occurs when TBP comes under direct attack by incident radiation. In this scenario HDBP remains the primary degradation product and is formed by direct scission of a C-O bond [42]:

\[
(C_4H_9O)_3PO \xrightarrow{\text{Radiation}} \cdot C_4H_9 + (C_4H_9O)_2OPO^- \quad \text{Eq.3.10}
\]
In light of the severity with which radiation consumes TBP, the necessary questions that must be addressed relative to the scope of this document are:

- At what rate does TBP respond to dose?
- What role, if any, do the metal-TBP complexes play in the degradation?
- What role, if any, does LET play in radiolysis of TBP?

**TBP Degradation and Product Formation**

Preferential radiolytic scission of the C-O bond of the butyl groups causes increased likelihood of formation of specific degradation products. As previously mentioned, DBP is formed when TBP loses a butyl group. However, as irradiation continues, DBP can also undergo C-O bond scission to form MBP (monobutyl phosphate) which also becomes H₂MBP (monobutyl phosphoric acid) due to hydrogen atom abstraction.

**Pure TBP**

The net yield of these products was shown by Williams and Wilkinson [43] to have a rate of 1.52 molecules HDBP formed/100eV and 0.12 molecules H₂MBP formed/100eV. This indicates that for their system of pure TBP irradiated by a 1.25 MeV electron beam there is a nine fold difference between the expected amounts of HDBP versus H₂MBP [43]. Table 3.1 below shows a comparison of literature values for the irradiation of pure TBP with various low LET radiation sources. More recently, reports for G values have been given in units of μmol/Joule therefore the values in Table 3.1 have been converted to reflect this change in units.
Table 3.2. G-Values for TBP radiolysis in μmol/joule. Table adapted from Tahraoui et.al [33].

<table>
<thead>
<tr>
<th>Radiation Source</th>
<th>GHDBP (μmol/joule)</th>
<th>GH2MBP (μmol/joule)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25 MeV electrons</td>
<td>0.16</td>
<td>0.01</td>
<td>[30]</td>
</tr>
<tr>
<td>60Co gamma rays</td>
<td>0.18-0.19</td>
<td>0.03</td>
<td>[31]</td>
</tr>
<tr>
<td>1 MeV electrons</td>
<td>0.23</td>
<td>0.04</td>
<td>[32]</td>
</tr>
<tr>
<td>1.66 MeV electrons</td>
<td>0.25</td>
<td>0.01</td>
<td>[27]</td>
</tr>
</tbody>
</table>

TBP/Alkane Diluent Systems

Because the studies shown above are of the irradiation of neat TBP solutions, they do not fully capture the effect of radiation on the organic phase during solvent extraction. In addition to TBP, the diluent also undergoes radiolysis to form reactive species that can recombine to form polymers or become substituted R groups on DBP or MBP in place of one or more of the butyl tails [44]. Therefore, it is quite conceivable that diluent choice plays a large role in degradation product formation. Burger and McClanahan [45] conducted low LET irradiations of pure TBP dissolved with various diluents, the results of which can be seen in Table 3.2.

Table 3.3. G-Values for DBP in μmol/joule. Table adapted from Burger and McClanahan [45].

<table>
<thead>
<tr>
<th>System</th>
<th>GDBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TBP</td>
<td>~0.18</td>
</tr>
<tr>
<td>30% in iso-octane</td>
<td>~0.25</td>
</tr>
<tr>
<td>30% in Soltrol-70</td>
<td>~0.23</td>
</tr>
<tr>
<td>30% in carbon tetrachloride</td>
<td>~1.87</td>
</tr>
</tbody>
</table>
These results are somewhat at odds those of Egorov et al. who reported a $G_{DBP}$ value of 0.15 for a system of 30% TBP/decane although direct comparison is difficult due to differences in solvent choice [46].

**TBP/Aqueous Systems**

To be an accurate depiction of radiolytic degradation during solvent extraction, the effect of the aqueous phase in contact with the organic must also be considered when analyzing the degradation of TBP. As mentioned earlier, the irradiation of water produces many active species and can therefore change the radical chemistry of the system. Adamov et al. [44] irradiated TBP with water and 3M HNO$_3$ and found that for the absence of an aqueous phase $G_{TBP}$ (consumption) was 0.26. In the presence of water, the value remained the same but upon addition of nitric acid, $G_{TBP}$ increased to 0.38 meaning increased loss of TBP. Mincher et al. postulate the increase in TBP consumption and consequently DBP production in the presence of nitric acid may be due to reaction with the NO$_3$ radical [4][38]. Stieglitz and Becker et al. [47] as well as Kulikov [42] also report increases in HDBP production with increasing aqueous phase nitric acid content. In Kulikov's scenario, a change from 0 to 0.7 mol/L nitric acid induced a change in $G_{HDBP}$ from 0.7 to 1.1 molecules/100 eV.

**TBP/Metal Systems**

The presence of metal species and the formation of TBP-metal complexes must also be given consideration. Kulikov et al. reported increased HDBP formation with increased plutonium and uranium loading for their system of 30% TBP in n-paraffin in contact with 3M HNO$_3$. Burger and McLanahan [45] on the other hand reported that both pre-equilibrating the organic phase (30% TBP/CCl$_4$) with aqueous UO$_2$(NO$_3$)$_2$ as well as contacting the organic
phase with aqueous UO$_2$(NO$_3$)$_2$ during irradiation, yielded a decrease in HDBP formation. Kuno and Hina dissolved TBP in a plutonium nitrate aqueous phase and measured TBP degradation as a function of mixed alpha and beta radiation from plutonium decay. They reported that a threefold increase in plutonium concentration yielded roughly a threefold decrease in the TBP consumption rate [48]. Stieglitz and Becker [47] reported a decrease in HDBP formation upon addition of uranium to 30% TBP/alkane/3M HNO$_3$. Mincher et al. attributes this decrease to a decrease in the rate constant associated with the reaction of TBP with free radical species once TBP becomes complexed [4]. Based on these conflicting data, further studies on the effect of metal ions on TBP radiolysis are required.

**Effect of LET on TBP Radiolysis**

Referring back to section 3.4, high LET particles and low LET photons differ greatly in their interactions with matter. As such, it stands to reason that the radiolysis experience by TBP differs when comparing high and low LET radiation sources. Thus far the authors cited above have primarily focused on the effect of low LET radiation, however because alpha emitters are present in used fuel ($^{238}$U, $^{239}$Pu etc.) their effect must also be considered. Pearson et al [49] gave a review and comparison of $G_{DBP}$ values from various sources which can be seen in Table 3.3. Current literature indicates that alpha particles affect TBP to a lesser extent than gamma rays. This could be due to the fact that the much more condensed tracks created by alpha particles can allow for more recombination of radical species that would otherwise chemically attack TBP.

Performing high LET irradiations can be more challenging than employing x or γ rays, primarily due to the short track length of high LET particles. Helium ion beams experience
difficulty passing through most solution containers and if the beam is fired directly into the solution then the solution must be well mixed during irradiation in order to assume uniform dispersion of radiation. Other methods include the dissolution of alpha emitters such as plutonium or curium in solution, but this requires the experiment to be designed around the inclusion of a metal species. Recently, boron compounds have provided an alternative method for high LET irradiations of liquid systems relying on the neutron capture and subsequent fission of boron to yield $^{4}\text{He}^+$ (alpha particle) and $^{7}\text{Li}^+$ particles in solution.

**Table 3.4. G values for DBP production by high LET radiation. Data adapted from Pearson [49].**

<table>
<thead>
<tr>
<th>Source</th>
<th>Author</th>
<th>Solution</th>
<th>Conditions</th>
<th>G&lt;sub&gt;DBP&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>He&lt;sup&gt;+&lt;/sup&gt; Ion</td>
<td>Ladrielle [50]</td>
<td>30% TBP/n-dodecane</td>
<td>Sealed in quartz</td>
<td>0.07</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>Hui-bo [51]</td>
<td>30% TBP/kerosene</td>
<td>Pre-equilibrated - 3M HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.08</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>Kawaguchi [52]</td>
<td>30% TBP/n-dodecane</td>
<td>Pre-equilibrated - 3M HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.09</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>Lloyd [39]</td>
<td>30% TBP/n-dodecane</td>
<td>Pre-equilibrated - 3M HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.1</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>Kulikov [53]</td>
<td>30% TBP/paraffin</td>
<td>In contact - 3M HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.1</td>
</tr>
<tr>
<td>$^{10}\text{B}$</td>
<td>Pearson[49]</td>
<td>30% TBP/n-dodecane</td>
<td>Degassed with Nitrogen</td>
<td>0.047</td>
</tr>
</tbody>
</table>

**Radiolysis of Actinide Separations Ligands**

**TODGA**

The radiolysis of TODGA has been studied extensively by Galán et. al. who has identified both TODGA radiolysis products as well as degradation constants under a variety of conditions [54],[55]. Galán et. al. employed the use of a $^{60}\text{Co}$ gamma ray source to irradiate TODGA in mixtures of TPH (hydrogenated tetra propylene, a branched aliphatic solvent) and octanol
as a diluent. Continuing a similar theme seen in the radiolysis of TBP discussed earlier, preferential scission of the TODGA C-O bond seems to yield the greatest quantity of radiolysis products, especially when in contact with nitric acid. This trend holds true when the samples were pre-equilibrated with water as well as 3M HNO₃.

The inclusion of nitric acid also seemed to have a protective effect on TODGA. This protective effect is reflected in kₜₒ₂₅₉₆₈ (the exponential constants derived from fitting the concentration vs absorbed dose to an exponential function, analogous to first order kinetics) for 0.05 M TODGA in n-dodecane reported as 4.1±0.3 x 10⁻³ kGy⁻¹. When pre-equilibrated with 2.5 M HNO₃ the degradation constant decreased slightly to 3.8±0.3 x 10⁻³ kGy⁻¹ [55]. These degradation constants were further corroborated by Zarzana et. al. who also utilized ⁶⁰Co to study the degradation of 0.5 M TODGA in n-dodecane in contact with an equal volume aqueous phase consisting of either 0.1 M or 2.5 M HNO₃ and found values identical to Galán et. al. as well as a value of 4.5±0.2 x 10⁻³ kGy⁻¹ when contacted with 0.1 M HNO₃ [56].

\[
\text{Figure 3.3. Key degradation products of TODGA according to Galán et.al. [54]. Species 1 and 3, when combined make up the original structure of TODGA while species 2 is most prevalent under acidic conditions.}
\]

**T2EHDGA**

T2EHDGA performs similarly to TODGA under radiolysis both in terms of radiolytic stability as well as the propensity to form certain degradation products. Zarzana et. al. irradiated
samples of 0.05 M T2EHDGA in n-dodecane as either the pure organic phase or contacted with equal volumes of 0.1 M HNO₃. The degradation of T2EHDGA also follows pseudo first order kinetics and degradation constants of 4.3±0.3 x 10⁻³ kGy⁻¹ and 3.7±0.2 x 10⁻³ kGy⁻¹ were observed for pure organic and contacted with 0.1M HNO₃ respectively [56]. Interestingly, Peterman et. al. found the T2EHDGA degradation constant to be 1.6±0.0 x 10⁻³ kGy⁻¹, though no reason for this discrepancy was provided.

This indicates that T2EHDGA and TODGA perform very similarly under radiolysis. Furthermore, Zarzana et. al. observed degradation products of T2EHDGA that indicate that the propensity for the formation of certain species follow the same pattern as TODGA.

HEHEHP and HDEHP

Comparatively less is known about the rates at which HDEHP and HEHEHP degrade. Current literature seems to indicate strong radiolytic stability by both HDEHP and HEHEHP [57][58][59].

Mincher et. al. noted that the key degradation product of HDEHP radiolysis is formed due to preferential scission of the C-O bond [59]. This observation was also corroborated by Shu et.al. who proposed structures seen in Figure 3.5 [60]. Peterman et. al. detected the phosphonic acid 2-ethylhexylphosphonic acid (H2EHP) formed during the irradiation of HEHEHP [57]. This agrees with the notion of preferential scission of the C-O bond as well as the similarity in degradation product formation of HDEHP and HEHEHP.

Once again, these degradation studies were carried out under the effects of gamma radiolysis. There are no major studies on the effects of alpha radiation on ALSEP type ligands or the resulting degradation constants or radiolysis products.
Figure 3.5a. HDEHP Degradation product formation mechanisms proposed by Shu et. al. [60].

Figure 3.5b. HEHEHP Degradation product formation mechanism proposed by Peterman et al. [57].
RESEARCH GOALS

The research presented here is aimed at establishing key radiation parameters that can aid in the understanding of how radiation affects ligands in fuel recycling. These parameters can:

1. Influence the choice which ligand to employ based on radiolytic stability.
2. Form a database for simulating radiolysis in existing processes, which can be used to model ligand concentration profiles under various conditions without the need for much chemical handling and can therefore improve safety.

My focus will be on radiolytic effects on the PUREX and ALSEP processes for the extraction of uranium and plutonium as well as the minor actinides.

Degradation Constants and G Values for TBP Radiolysis.
In light of the work discussed in prior sections pertaining to the determination of G values for radiolysis of TBP under PUREX conditions, the effect of formation of TBP-metal complexes, and the role they play in the radiolytic degradation of TBP, is not fully understood. This work seeks to determine G values and degradation constants for various species in the organic phase for the interaction of both low and high LET radiation on the uranium laden organic phase.

Degradation Constants and G Values for HDBP Formation.
In addition to the unwanted decrease of extractant concentration in the PUREX process, degradation product formation is also a key area of concern. As such investigations into the formation of degradation products with neat TBP, acid contacted TBP and uranium loaded
TBP, will be carried out and G values and degradation constants will be ascertained for each scenario.

**Degradation Constants for T2EHDGA and HEHEHP.**

This work seeks to determine degradation constants of these two ALSEP process relevant extractants. The conditions examined include:

1. Neat organic phase gamma irradiations
2. Neat organic phase gamma and heavy ion irradiations
3. 3M HNO3 contacted organic phase gamma irradiations
4. 3M HNO3 contacted organic phase gamma and heavy ion irradiations

The overall goal is to determine which form of radiation dominates the destruction of these ligands as well as whether the inclusion of acid enhances or inhibits the ligand degradation.

**Radiolytic Product formation in ALSEP Solvent.**

Here I also seek to determine the formation of degradation products of both HEHEHP and T2EHDGA under the conditions listed above and, furthermore, determine whether and to what extent the formation of certain species is favored over others under the various conditions.
PUREX PROCESS STUDIES

Sample Preparation

Separate organic solutions containing 0.1 or 1.0 M TBP (Fluka 99%), as well as 0.25 M HDBP (Sigma Aldrich 97%) in n-dodecane (Alfa Aesar 99+ %) were prepared. Aqueous phases of 3 M nitric acid (Macron) containing varying concentrations of uranium as follows: 0 M, 0.0125 M, 0.025 M, 0.05 M, and 0.1 M for low TBP conc.; 0 M, 0.025 M, 0.05 M, 0.1 M and 0.25 M for high TBP conc.; and 0 M, 0.0075 M, 0.015 M, 0.0225 M and 0.03 M for HDBP. The uranium was added by mass as uranyl nitrate hexahydrate and consisted of depleted uranium of ~0.2 mol% $^{235}$U (International Bio-Analytical Industries Inc., ACS grade).

Approximately 5 mL aliquots of the organic phase were contacted in borosilicate glass vials with equal volumes of the various aqueous phases. The vials were shaken by way of a vortex mixer (Fisher Scientific Model 02215365) at ~160 rpm for 15 minutes and then centrifuged at 3000 rpm for 5 minutes to allow the phases to separate. The organic phase was then removed from contact with the aqueous and visually inspected to ensure no presence of aqueous phase bubbles were detected. For the samples that would be exposed to high LET radiation, after separation of the phases, bis pinacolato diboron (Sigma Aldrich 99%) was added to all organic phases to a final concentration of 0.4 M boron. The boron used in this work was of natural abundance.

Low LET Dosimetry and Irradiation

Prior dosimetry was done using Fricke Dosimetry [61]. This method utilizes the conversion of Fe(II) to Fe(III) caused by radiation in solutions containing 1 mM Fe(II), 1 mM NaCl and 0.4 M H$_2$SO$_4$. This solution was then bubbled with air to ensure proper aeration for a
minimum of 1 hour. Samples were then sealed in Falcon™ 15mL Conical Centrifuge Tubes and irradiated in a gamma ray cell with a $^{137}\text{Cs}$ source (CS137 Irradiator Mark-I, Model 68, JL Shepherd & Associates) located at the UCI Reactor Facility. Fe(II) conversion to Fe(III) was determined by UV-VIS spectrometry using a Cary 14 Spectrophotometer with 1 cm quartz cuvettes by observing the peak at 304 nm associated with the formation of Fe(III). The dose rate was then determined by converting the Fe(III) concentration using the G$_{\text{Fe(III)}}$ value of 1.55 µmol/J corresponding to gamma irradiation of aerated Fricke solution [1].

The dose rate received by the sample at the position of interest within the gamma irradiator was found to be ~2.14 kGy/hr. The organic solutions were irradiated for intervals of 0 to 28 days to achieve doses of 0 to 1,440 kGy. Solutions of TBP in n-dodecane that had not been contacted with an aqueous phase was also placed in the Cs-source to benchmark this experiment to previous work. Identical samples to those irradiated were kept outside of the Cs-source to serve as standards. Volumes of each solution were irradiated and at the end of each interval a small sample of 150 µL of each organic solution was removed for analysis by gas chromatography (GC). After the sample was removed the container with the remainder of the solution was placed back in the gamma cell. During the irradiations, the solutions are sealed but opening the containers for sampling will introduce air back in the container. However, any oxygen is assumed to be consumed very rapidly once the solution is placed back in the irradiation field and we assume that the effect of oxygen to our irradiated solutions is negligible.

**High LET Dosimetry and Irradiation**

High LET dose rates were determined using the model proposed by Pearson et al [62]. This involves the use of the $^{10}\text{B} (n, \alpha)^{7}\text{Li}$ nuclear reaction, whereby $^{10}\text{B}$, upon neutron capture,
fissions to produce an alpha particle and a $^{7}$Li nucleus. For this we utilize the UCI TRIGA® mk. II reactor which outputs a thermal neutron flux of $8 \times 10^{11}$ neutrons per square centimeter per second at a steady state operation at 250 kW. The average energy of each boron fission event is on the order of 2.35 MeV, therefore if the number of neutrons captured by the sample is known then the total energy imparted into the solution is known. Because of the assumption that the boron dissolved in the system is uniformly distributed, it follows then that under irradiation, the high LET events are occurring equally uniformly within the solution. In the cylindrical coordinate system of our sample vials the diffusion of neutrons becomes.

$$\frac{1}{r} \frac{\partial}{\partial r} \left( D_r \frac{\partial \phi(r,z)}{\partial r} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial \phi(r,z)}{\partial z} \right) - N_B \sigma_B \phi(r,z) = 0 \quad \text{Eq. 5.1}$$

where $\phi(r,z)$ is the neutron flux, $r$ is the radius of the sample vial, and $z$ is the height of the solution in the vial (defined from $z = -H/2$ to $H/2$). The radial and axial dependence are illustrated in Eq 5.1 but the angular term is neglected due to the lack of angular dependency in the diffusion of neutrons. The boundary conditions are such that at the edges ($r=R$ and $z=H/2$ and $-H/2$) the flux is equal to $8 \times 10^{11}$n/cm$^2$s and at the center line the derivative of the flux with respect to position is zero. The final term on the left-hand side of Eq 5.1 corresponds to the absorption of neutrons by $^{10}$B. $N_B$ and $\sigma_B$ are the number of boron-10 atoms present and the neutron capture cross section of boron-10 (~3840 barns).

The MATLAB® PDEtoolbox™ was used to determine a solution for Eq 5.1 as $\phi(r,z)$. This in turn can then be integrated over the volume of the sample in a manner illustrated by Eq 5.2 to yield the total number of neutrons absorbed during the time of irradiation.
\[ \Delta N = \int_0^Z \int_0^{2\pi} \int_0^r \epsilon_{irr} N_B \sigma_B \phi(r, z) r dr d\theta dz \]  

Eq. 5.2

The corresponding dose rate for high LET is then:

\[
\text{High LET dose rate } \left( \frac{\text{Gy}}{s} \right) = \frac{\Delta N \cdot E}{t_{irr} \cdot m} 
\]

Eq. 5.3

where \( E \) is the aforementioned energy of 2.35 MeV per boron n,\( \alpha \) reaction, \( t_{irr} \) is the irradiation time and \( m \), the mass of the sample. Therefore, in order to vary the high LET dose rate, one must increase the initial boron concentration and perform the neutron irradiation in a higher thermal neutron flux. For a 0.4 M boron solution under irradiation for 1 hour, the dose was found to be \(~211 \text{ kGy}\) which agrees with Pearson’s prediction [49].

The Lazy Susan specimen rack is located in the reflector outside the core and thus the epithermal neutron flux is at least one order of magnitude lower than the thermal and is expected to make a negligible contribution to the dose under the conditions used here. The irradiation times were chosen in order to achieve total doses comparable to the gamma irradiation in the Cs-source. Organic samples without boron were irradiated simultaneously to correct for the low LET contribution from the core. At the end of each interval the samples were removed and 150 \( \mu \text{L} \) of each irradiated organic solution was removed for analysis by Gas Chromatography (GC).

Due to the ongoing decay of fission products in the core, the samples will also receive a background gamma dose of about 40.4 kilogray per hour during normal reactor operations at 250 kW[38].

Though industrial application of the PUREX process calls for 30 vol% TBP in kerosene (~1 M TBP), our high LET study was performed only with 0.1 M TBP and a maximum aqueous phase concentration of 0.1 M uranium. This allowed us to work with lower concentrations.
of uranium as the reactor irradiations would produce significant amount of activation products.

**Determination of TBP and HDBP Concentrations.**

Post irradiation, samples were diluted 1:150 in hexane (95% Sigma Aldrich) containing triphenyl phosphate as an inert internal standard to monitor gas chromatography performance and consistency. For additional calibration and standardization purposes, stock solutions of HDBP were prepared. This solution was derivatized by adding excess diazomethane, such that the normally clear diluted solution turned slightly yellow. This derivatization is done in order to add methyl groups to acidic radiolysis products that might react with, and be retained by, the silica within the GC columns. Diazomethane was prepared within a diazomethane generator kit (Sigma Aldrich) using diazald (Sigma Aldrich 99%), Carbitol (Sigma Aldrich 99%) and potassium hydroxide (Fischer Scientific). The diazomethane gas was captured in hexane. All samples were analyzed by Gas Chromatography using the flame ionization detector in a Hewlett Packard 5890 Gas Chromatograph with a 30 m DB-5ms column (Agilent Technologies) and an associated Hewlett Packard Controller 7673A integrator. The heating program began at 60°C and increased at a rate of 10°C/min until a final temperature of 350°C with a final hold time of 10 min.

**Determination of Uranium Concentrations.**

Neutron activation analysis (NAA) was used to measure uranium uptake by TBP. Known concentration standards for uranium ranging from 0.0125 M to 0.5 M UO$_2$ in 3 M HNO$_3$ were irradiated at 250 kW in the Lazy Susan position in the UC Irvine TRIGA reactor for 1 hour. Alongside of the standards, aqueous and organic samples of phases from extraction
experiments using varying total uranyl concentration that had been contacted for 15 mins with organic phases of 0.1 M or 1 M TBP in n-dodecane followed by separation, were irradiated. During the irradiation $^{238}\text{U}$ captures a neutron and forms $^{239}\text{U}$ which will decay with a half-life of 23.45 min to $^{239}\text{Np}$.

The irradiated samples were analyzed the day following the irradiation to ensure that all $^{239}\text{U}$ had decayed to $^{239}\text{Np}$. The activity of $^{239}\text{Np}$ was measured using a High Purity Germanium Detector (Canberra, 30% relative efficiency) with Genie 2000 software. Samples were counted for 15 mins each and corrected for decay. A calibration curve relating corrected count rates to known concentrations was made using the uranium standards. This curve was then used to determine uranium concentrations of both the aqueous and organic phases after extraction.

The samples of HDBP contacted with 3 M HNO$_3$ and varying concentrations of uranyl proved to not be stable during the irradiation and formed a gelatinous phase below the liquid organic phase rendering quantification of the HDBP-metal complex degradation constant futile.
PUREX PROCESS – RESULTS

TBP/n-Dodecane Irradiations

Low LET irradiations of 0.1 M TBP solutions in n-dodecane yielded results similar to those shown in previous studies discussed in Table 3.2 in Section 3.6.2. Worthy of noting is the fact that \( G_{\text{TBP}} \) is actually the sum of \( G_{\text{HDBP}} + G_{\text{H2MBP}} + G_{\text{H3PO4}} \) and all other radiolysis products, therefore \( G_{\text{TBP}} \) must be greater than \( G_{\text{HDBP}} \) (within reason). The value of \( G_{\text{TBP}} \) was determined by taking the slope of the plot of concentration (µmoles/kg) of TBP remaining in the solution vs. dose (Gy, i.e. J/kg). \( G_{\text{TBP}} \) was found to be 0.036 ± 0.001 µmol/J. For 1 M TBP, we found \( G_{\text{TBP}} \) to be 0.38 ± 0.012 µmol/J which agrees well with Pearson et al. who reported a value of 0.36 µmol/J[6] for a system of 1 M TBP/n-dodecane. Since \( G \)-values are concentration dependent the values from 0.1 M TBP or 1 M TBP found in our study differs by a factor of ten.

Figure 6.1. TBP concentration vs dose for the \(^{137}\text{Cs}\) low LET gamma radiolysis of TBP in n-dodecane. The degradation model is a linear fit of the data and \( G_{\text{TBP}} \) determined from the slope of the dashed line.
Figure 6.2 shows the result of low LET irradiation by background gamma rays and neutrons in the reactor born from fission and the decay of fission products. As shown by earlier dosimetry, the background dose rate of 40.4 kGy/hr yields result consistent with the low LET results from the $^{137}$Cs source. The value of $G_{\text{TBP}}$ caused by background radiation was found to be $0.038 \pm 0.001 \mu\text{mol}/\text{J}$ and only differs slightly from the value corresponding to the $^{137}$Cs source. Due to the difference in low LET dose rates between the $^{137}$Cs source and the reactor background, there could be a potential dose rate effect. However, given the overlapping values of the degradation this does not appear to be the case. Figure 6.2 also shows the linear degradation trend calculated using the $G$-value established by the $^{137}$Cs irradiations for comparison.

**Figure 6.2.** TBP concentration vs dose for the low LET irradiation of TBP in n-dodecane using the UC Irvine reactor and a comparison between reactor background (40.4 kGy/hr) degradation with degradation model derived from
the $^{137}$Cs source (2.14 kGy/hr) degradation data. The lines are linear fits of the data and the $G$ values represents the slope.

To estimate the degradation of TBP from high LET, the decrease in TBP concentration that was observed in the corresponding samples (samples that had been exposed to the same total neutron flux) without boron can be used to correct the concentration found in the samples that contained boron. The assumption that the high and low LET are additive was used in previous work [49] and was shown to yield results comparable to past literature. The decrease in TBP concentration due to predominantly high LET with background low LET included is plotted below in Figure 6.3. The value for $G\text{-TBP}$ by the combination of a total of 1,440 kGy high LET and 299 kGy background low LET was found to be $0.017 \pm 0.002$ µmol/J which, again, is about 1/10th of the value determined by Pearson using the same method (0.14 µmol/J). Again, it is worth noting here that the order of magnitude difference is due to initial concentration differences.

The results show a slightly more than twofold increase in the TBP consumption for low LET compared to high LET. This is attributed to the increased likelihood of recombination of radical species (that would otherwise attack TBP[36], [38]) in the more condensed tracks caused by high LET radiation.
Figure 6.3. TBP concentration vs dose for the mixture of high and low LET irradiation of TBP in n-dodecane using the UC Irvine reactor. The degradation model is a linear fit of the experimental data and the G values represents the slope of the dashed line.

TBP/Acid/n-Dodecane Irradiations

Literature values provided by Adamov et al. [44] indicated that the presence of 3 M HNO3 enhanced the degradation of TBP under gamma radiation. However, their study did not separate the aqueous and organic phases after contact but rather irradiated both phases together. Our results, Figure 6.4, show that the irradiation of TBP with nitric acid uptake has no significant difference in G-TBP compared to the system without acid. The degradation constants are shown in Table 6.1.
Figure 6.4a. (Top): Result of $^{137}$Cs low LET irradiation of TBP after acid uptake.

Figure 6.4b. (Bottom): Result mixture of high and low LET irradiation of TBP after acid uptake.

The degradation model is a linear fit of the data and the G values represents the slope of the dashed lines.

Despite G values being calculated by fitting a straight line to the concentration profile of TBP, G values can vary greatly as a function of where the linear fit is drawn. This may account for the discrepancies previously seen when comparing literature values. In addition to this, as discussed before, the G value depends on specific initial conditions and is not a universal
measure. For this reason some authors [49][5] have endeavored to express the radiolysis yield as degradation constants.

In this work, we encountered trouble expressing the effect of metal complexes in terms of G values, whereas degradation constants provide a better fit and allow for easier estimation of the individual contributions from low and high LET. The aforementioned G values are reported along with corresponding degradation constants in Table 6.1. The degradation constants are found by treating the decrease in TBP with dose as a function of the degradation constant multiplied with the TBP concentration, providing an expression for an exponential decrease in TBP concentration, see Equations 6.1 and 6.2 below for example. The experimental values of TBP concentration determined by chromatography were used to fit the corresponding equations and to find degradation constants for low and high LET following procedures outlined by Pearson et al. [49]

\[
\frac{dTbp}{d\text{Dose}} = -k_\gamma [Tbp]
\text{Eq 6.1}
\]

\[
[Tbp] = [Tbp]_0 e^{-(k_\gamma)\text{Dose}}
\text{Eq 6.2}
\]

The experimental values determined by chromatography were fit to equation 6.2 as a model and the value of \( k_\gamma \) was determined by using the chi-squared method. We seek minimize the difference between the experimental values and model values by finding a \( k_\gamma \) that satisfies the stipulation that the sum of all chi squared values, is at a minimum.
Table 6.1. G-values and degradation constants for TBP radiolysis. Results compared to those reported previously by Pearson et al.[49]

<table>
<thead>
<tr>
<th>System</th>
<th>G_{TBP} (µmol/J)</th>
<th>k\gamma or k\alpha (1/kGy)</th>
<th>Pearson k\gamma or k\alpha (1/kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M TBP (Low LET γ)</td>
<td>-0.036 ± 0.001</td>
<td>2.93 ± 0.08x10^{-4}</td>
<td>-</td>
</tr>
<tr>
<td>1.0 M TBP (Low LET γ)</td>
<td>-0.38 ± 0.012</td>
<td>3.13 ± 0.19x10^{-4}</td>
<td>2.92 ± 0.23x10^{-4}</td>
</tr>
<tr>
<td>0.1 M TBP/3M HNO₃ (Low LET γ)</td>
<td>-0.034 ± 0.002</td>
<td>2.69 ± 0.16x10^{-4}</td>
<td>-</td>
</tr>
<tr>
<td>1.0 M TBP/3M HNO₃ (Low LET γ)</td>
<td>-0.31 ± 0.017</td>
<td>3.05 ± 0.24x10^{-4}</td>
<td>-</td>
</tr>
<tr>
<td>0.1 M TBP (High LET α)</td>
<td>-0.017 ± 0.002</td>
<td>1.29 ± 0.15x10^{-4}</td>
<td>1.11 ± 0.08x10^{-4}</td>
</tr>
<tr>
<td>0.1 M TBP/3M HNO₃ (High LET α)</td>
<td>-0.016 ± 0.003</td>
<td>1.21 ± 0.22x10^{-4}</td>
<td>-</td>
</tr>
</tbody>
</table>

**TBP/Uranium/3M HNO₃ /n-Dodecane Irradiations**

Prior to any irradiation, all samples were analyzed for TBP content in order to establish a baseline. As can be seen in Figure 6.5, when the metal concentration in the aqueous phase increases there was a proportional decrease in the amount of TBP observed based on GC analysis. This indicates that as the TBP-Uranyl complexes form, the amount of TBP detected by the flame ionization detector decreases suggesting that gas chromatography on metal loaded TBP shows only the TBP that is not complexed to a metal ion. This unbound TBP will be referred to as “free TBP” for the purposes of this work. In order to validate this assumption, neutron activation analysis of the organic phases was conducted to determine the UO₂ concentration extracted in each organic phase. The results of the NAA is shown in Figures 6.6 for 0.1 M TBP and 1 M TBP, respectively.
Figure 6.5a. (Top) Organic phase TBP concentration as a function of aqueous phase condition for samples with 0.1 M TBP.

Figure 6.5b. (Bottom) Organic phase TBP concentration as a function of aqueous phase condition for samples with 1 M TBP.
If indeed the amount of TBP free in solution is governed by the amount of UO₂ present then the relationship should follow the known stoichiometry of two TBP molecules per UO₂ [63]. Figure 6.6 shows the relationship between organic metal concentration and TBP to be linear. If for every uranium extracted, two TBP molecules become bound then the relationship for free TBP at any given metal loading must be:

\[ [\text{TBP}] = [\text{TBP}]_0 - 2[UO_2] \]  

Eq. 6.3

Where \([\text{TBP}]\) is the free TBP concentration, \([\text{TBP}]_0\) is the initial concentration prior to extraction and \([UO_2]\) is the metal ion concentration in the organic phase determined by neutron activation analysis. The solid line in Figures 6.6 is calculated based on Equation 6.3 and show an almost identical slope as the experimental values from GC analysis but a discrepancy in the y-axis intercept. However, this calculation is based on an upper limit of TBP in the organic phase and as such does not account for any TBP that may have been lost to the aqueous phase during the extraction process, or uptake of water, nitric acid and uranium into the organic phase which may cause a change in the volume of the organic phase. Nevertheless, these results verify that varying the uranium uptake into the organic phase accounts for the discrepancy in the concentrations of TBP that can be analyzed by the GC.
Figure 6.6a. (Top) 0.1M TBP versus organic phase UO₂ concentration.

Figure 6.6b. (Bottom) 1M TBP versus organic phase UO₂ concentration.

The experimental data represents the raw data taken from GC analysis. Predicted represents the initial TBP concentration of 0.1 M or 1 M with a decrease calculated from equation 3 based on the uranium concentration.
obtained from neutron activation analysis. Deviations in initial values are attributable to extraction of water and nitric acid into the organic phase as well as losses of TBP to the aqueous phase.

The free TBP concentration as a function of gamma radiation of the organic solutions containing the highest concentration of uranium can be seen in Figure 6.7. As the metal ion concentration increases the trend of free TBP, based on the GC analysis, as a function of dose changes. At the highest metal loading of 17 mM and 200 mM uranyl (for 0.1 M TBP and 1 M TBP, respectively) there is a sharp increase in the amount of free TBP as compared with the lower metal loading, which looks more similar to the trend with pure TBP or from contact with HNO₃, i.e. a more typical exponential decay trend. It is worth noting that the trends for 0.1 M TBP and 1 M TBP are very similar. Figure 8 shows the corresponding trends for the 0.1 M TBP samples irradiated in the reactor and exposed to a mixed field of high and low LET radiation.
Figure 6.7a. (Top) Gamma irradiation of 17 mM uranyl in 0.1M TBP

Figure 6.7b. (Bottom) Gamma irradiation of 200 mM uranyl in 1M TBP

The Y axis represents the free TBP in solution. The dashed line corresponds to the model from Equation 8 with fitted degradation constants \( k_{1\gamma} = 6.9 \times 10^{-3} \pm 0.25 \times 10^{-3} \text{ kGy}^{-1} \) and \( k_{1\gamma} = 6.6 \times 10^{-3} \pm 0.90 \times 10^{-3} \text{ kGy}^{-1} \), for the 0.1 and 1 M TBP case, respectively.
Figure 6.8. Experimental data of the evolution of free TBP as a function of mixed high and low LET radiation dose. The lines correspond to theoretical calculations using the model in Equation 6.10.

Radiolysis of TBP-UO₂ Complexes by Low LET Radiation

The initial increase in TBP concentration with dose at higher metal loading, Figures 6.7 and 6.8, can be explained as radiation disrupting the metal-ligand complex and freeing up previously bound TBP. Hence, this reaction should have a corresponding degradation constant. As a starting point, it is assumed that the reaction whereby the complex breaks to free up TBP depends on dose and on the amount of complex at any given time, in analogy with Equation 1 for free TBP. Because the free TBP also undergoes radiolysis, this process
can be treated as a sequence of first order reactions. Written only with consideration for TBP (i.e. metal and nitrate ions are disregarded in the balance for the equation):

\[
(UO_2)(NO_3)_2(TBP)_2 \xrightarrow{k_1} 2TBP \xrightarrow{k_2} \text{Degradation products} \quad \text{Eq 6.4}
\]

Where \(k_1\) and \(k_2\) are the corresponding degradation constants for the complex and free TBP, respectively. \((UO_2)(NO_3)_2(TBP)_2\) will henceforth be referred to as “complex” in subsequent equations. The necessary equations would then be:

\[
\frac{d \text{[Complex]}}{dt_{irr}} = -\left( k_{1Y} \dot{D}_\gamma \right) \text{[Complex]} \quad \text{Eq 6.5}
\]

\[
\frac{d \text{[Tbp]}}{dt_{irr}} = 2\left( k_{1Y} \dot{D}_\gamma \right) \text{[Complex]} - \left( k_{2Y} \dot{D}_\gamma \right) \text{[Tbp]} \quad \text{Eq 6.6}
\]

In these equations, the dose rate, \(\dot{D}_\gamma\), is used instead of dose. The dose and dose rate are easily interchangeable using the irradiation time. The dose rate is constant during an irradiation and it allows one to use time as a variable rather than dose. This is especially useful for a source of mixed high and low LET radiation where the dose rates of each type are different. The degradation of free TBP by low LET radiation, \(k_{2Y}\), was determined before, and is listed as \(k_Y\) in Table 1. Integration of Equations 5 and 6 yields the concentration of both complex and TBP at any given time:

\[
\text{[Complex]} = [\text{Complex}]_0 \cdot e^{-(k_{1Y})\cdot\text{Dose}} \quad \text{Eq 6.7}
\]

\[
\text{[Tbp]} = 2[\text{Complex}]_0 \cdot \frac{(k_{1Y})}{(k_{2Y}) - (k_{1Y})} \left( e^{-(k_{1Y})\cdot\text{Dose}} - e^{-(k_{2Y})\cdot\text{Dose}} \right) + [\text{Tbp}]_0 e^{-(k_{2Y})\cdot\text{Dose}} \quad \text{Eq 6.8}
\]
Here, the unknowns are [Complex] and $k_{1\gamma}$. The model for TBP presented in Eq 6.8 was fit to experimental data at each metal concentration to determine $k_{1\gamma}$ for each concentration. Figure 6.7 above shows the examples at the highest metal loading of 17 mM and 200 mM uranyl uptake, where $k_{1\gamma}$ was found to be $6.9 \times 10^{-3}$ kGy$^{-1}$ and $6.6 \times 10^{-3}$ kGy$^{-1}$, respectively. It can be seen in Figure 6.7 that the model fit well with the experimental values and the fitted degradation constants for 0.1 M and 1 M TBP overlap within one standard deviation.

Although there are slight variations in the determined values of $k_{1\gamma}$ as the metal loading is varied, the constants are identical within error and an average gamma degradation constant for the complex was determined. The results for 1 M TBP contacted with a higher range of uranyl concentrations, also shown in Table 6.2, are in excellent agreement with the low LET degradation constant from 0.1 M indicating that the TBP concentration dependency can be overcome by using degradation constants rather than G-values. An overall degradation constant for the breakdown of the TBP-uranyl complex due to low LET radiation was calculated and is listed in Table 2.

**Break up of TBP-UO$_2$ Complexes by high LET Radiation**

Because the reactor contains a mixed field of gamma and beta radiation in addition to the high LET radiation within the sample, it is important to represent the contribution of low and high LET separately in order to see the true effect each has. Hence Equations 6.5 and 6.6 require the addition of two terms, $k_{1\alpha}$ and $k_{2\alpha}$ for the corresponding reactions caused by high LET. Because of the difference in dose rates between high and low LET, time is used as a
variable, as discussed above. The resulting equations for describing the TBP-metal complex and free TBP concentration become:

\[
[\text{Complex}] = [\text{Complex}]_0 \cdot e^{-(k_{1\alpha}D_\alpha + k_{1\gamma}D_\gamma) t_{irr}} \\
[\text{Tbp}] = 2[\text{Complex}]_0 \cdot \frac{(k_{1\alpha}D_\alpha + k_{1\gamma}D_\gamma)(e^{-(k_{1\alpha}D_\alpha + k_{1\gamma}D_\gamma) t_{irr}} - e^{-(k_{2\alpha}D_\alpha + k_{2\gamma}D_\gamma) t_{irr}})}{(k_{2\alpha}D_\alpha + k_{2\gamma}D_\gamma) - (k_{1\alpha}D_\alpha + k_{1\gamma}D_\gamma)} + [\text{Tbp}]_0 e^{-(k_{2\alpha}D_\alpha + k_{2\gamma}D_\gamma) t_{irr}}
\]

In these equations \(k_{1\gamma}\) is known from the previous fit at low LET only. Both \(D_\alpha\) and \(D_\gamma\), the alpha and gamma doserates, were determined by dosimetry. Again, we can then substitute the degradation constants shown in Table 1 for both low and high LET as \(k_{2\gamma}\) and \(k_{2\alpha}\) respectively. Hence, the only unknowns are \([\text{Complex}]\) and \(k_{1\alpha}\).

As before, the model from Equations 6.9 and 6.10 were fit to the experimental data. The data from this fit can be seen in Figure 8 above while the degradation constants at each metal loading can be seen in Table 2. As for the low LET degradation constants there are slight discrepancies between each metal loading but overall the constants are within error of each other and an average was calculated, as before. Overall the model provides a good fit to the experimental data for all conditions investigated.

Similar to the studies of LET effects on free TBP radiolysis, when examining the degradation constants for the complex, low LET appears to have twice the effect of high LET. The reason for this is likely the same as for free TBP. The high LET radiation causes the formed radicals
to recombine in a dense track and are therefore less likely to interact with the TBP or TBP-UO$_2$ complex. For low LET the radicals produced are more sparsely distributed and the probability of them interacting with TBP or the complex increases.

Few authors have published on the topic of the effect of metal uptake on TBP degradation. However, the few that do, agree that the presence of metal ions inhibits TBP degradation and HDBP formation, though differences in experimental systems makes direct comparison difficult [47], [48]. Our studies show a highly nonlinear response to the free TBP concentration with increasing radiation dose which was described as the TBP-UO$_2$ complex broken by incident radiation to free the previously bound TBP. Overall it seems that the susceptibility of radiation of the complex is about an order of magnitude greater than that of free TBP. One possible explanation is the relative differences in enthalpy. For example, the enthalpy associated with the C-O bond that, when broken, yields HDBP is on the order of 355 kJ/mole while Stas et al.[64] reported an enthalpy value for the extraction of UO$_2$ from 0.5 and 1 M HNO$_3$ by TBP in kerosene as ~16 and ~23 kJ/mole respectively and Orabi et al. report 55.72 kJ/mole [65] using 25 vol% TBP in Kerosene at a phase ratio 1:1. It is important to note that these values reflect the energy of transfer between the aqueous and organic phases in addition to the energy of complex formation, and are likely over-estimates for the electrostatic bond itself. What is certain, however, is that the TBP-metal complex is held together by relatively weak electrostatic forces and energy deposited in the solution can affect the stability of these complexes. This explanation does not necessarily consider a reaction pathway that includes indirect radiolysis where a radical or reactive species formed by the incoming radiation reacts with the free TBP or TBP-metal complex. Based on the
difference in low and high LET degradation constants it appears that the indirect radiolysis is more likely at the conditions studied here. Further work is needed to identify the degradation paths of the various species.

*Table 6.2.* Compilation of degradation constants for the break-up of TBP-UO2 complexes by both low and high LET for 0.1M TBP study.

<table>
<thead>
<tr>
<th>TBP conc. (M)</th>
<th>Org. Uranium Concentration (M)</th>
<th>$k_1\gamma$ (kGy$^{-1}$)</th>
<th>$k_1\alpha$ (kGy$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.002</td>
<td>6.6 ± 1.1 x10$^{-3}$</td>
<td>3.4 ± 0.24 x10$^{-3}$</td>
</tr>
<tr>
<td>0.1</td>
<td>0.008</td>
<td>7.7 ± 1.2 x10$^{-3}$</td>
<td>3.8 ± 0.10 x10$^{-3}$</td>
</tr>
<tr>
<td>0.1</td>
<td>0.012</td>
<td>7.1 ± 0.20 x10$^{-3}$</td>
<td>3.3 ± 0.16 x10$^{-3}$</td>
</tr>
<tr>
<td>0.1</td>
<td>0.017</td>
<td>6.9 ± 0.25 x10$^{-3}$</td>
<td>3.4 ± 0.10 x10$^{-3}$</td>
</tr>
<tr>
<td><strong>Average for 0.1 M TBP</strong></td>
<td></td>
<td>7.1 ± 0.85 x10$^{-3}$</td>
<td>3.5 ± 0.15 x10$^{-3}$</td>
</tr>
<tr>
<td>1.0</td>
<td>0.02</td>
<td>7.3 ± 0.7 x10$^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>0.04</td>
<td>6.2 ± 0.9 x10$^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>0.12</td>
<td>6.4 ± 1.2 x10$^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>0.20</td>
<td>6.6 ± 0.9 x10$^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td><strong>Average for 1 M TBP</strong></td>
<td></td>
<td>6.6 ± 0.63 x10$^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td><strong>Average (all combinations)</strong></td>
<td></td>
<td>6.9 ± 0.60 x10$^{-3}$</td>
<td>-</td>
</tr>
</tbody>
</table>

**Potential Role of HDBP**

Due to the relatively low starting concentration of TBP in the system, we could not accurately determine the concentration profile for HDBP in a reliable manner using GC. HDBP is the key
radiolysis product of TBP and it also has a high affinity for forming complexes with uranium.

We speculate that the increase in TBP observed with increasing dose, in addition to being caused by break-up of the TBP-UO$_2$ complex, there is a possibility that HDBP might displace some of the complexed TBP and potentially form mixed TBP-UO$_2$-HDBP complexes. To this end, extractions were performed in the same manner described in Section 5.1, however, after separating the organic phases, HDBP was added to the metal loaded organic phase to make solutions ranging from 0 to 0.1 M HDBP. Because the intention was to capture the effect of HDBP only, these samples were not subject to any irradiation, rather they were shaken for another 15 mins to ensure proper mixing with respect to HDBP concentration. Once again GC was used to determine the amount of free TBP in all samples. The results are shown below in Figure 6.9.

![Figure 6.9. Change in free TBP in a TBP-UO$_2$ system with the addition of HDBP.](image)

There is a definite upward trend in the amount of free TBP measured by GC. This seems to confirm our suspicion that the production of HDBP by TBP radiolysis seems to enhance the
break-up of the TBP-UO₂ complexes by displacing TBP. It then begs the question; to what extent does this affect the complexes under irradiation over the dose ranges applied in this experiment? Because we were unable to chromatographically determine the HDBP concentration, the best estimate lies in the rate equation for HDBP production:

\[
[HDBP] = [Complex]_0 \times \left(1 + \frac{k_{1Y}e^{-k_{2Y}Dose} - k_{2Y}e^{-k_{1Y}Dose}}{k_{2Y} - k_{1Y}} \right) + [TBP]_0 \left(1 - e^{-k_{2Y}Dose} \right)
\]

Eq. 6.11

The choice using the scenario of low LET radiation when estimating HDBP production is doubly beneficial in that low LET has a greater impact on TBP and therefore is suitable for providing an upper limit estimation for HDBP production, it is also much less complex than the high LET mixed radiation scenario. The upper limit scenario also does not take into account the degradation of HDBP to H₂MBP, but rather assumes that all HDBP molecules are ready and able to substitute with TBP. Additionally, the highest uranium concentration of 17 mM was selected as this would yield the largest number of complexes for HDBP to interact with.
In the dose range that these low LET irradiations were performed, the upper limit on HDBP concentration seems to be 0.03 M. Now in order to ascertain how great of an effect this concentration would have when considering the substitution of HDBP with TBP, we can now input this value into the trend line in Figure 6.9 to yield a potential increase in initial TBP from 0.058 M to 0.065 M, a net gain of about 13% of the initial value.

**HDBP Formation and Degradation**

In order to assess the formation and degradation rates of HDBP in these systems it was important to first establish that our methods were viable. To this end we analyzed samples of 1 M TBP without contact with an aqueous phase for HDBP production and compared our results to degradation constant values for HDBP given by Pearson et. al. [49]. The model used to fit the experimental data is represented by Equation 6.12 where $k_{(\text{+HDBP})}$ represents the formation of HDBP from TBP by gamma radiolysis and $k_{(\text{-HDBP})}$ represents the subsequent degradation constants for HDBP and $k_\gamma$ is the TBP degradation constant from equation 2. The
A comparison of a model using the values for $k_{(+\text{HDBPγ})}$ and $k_{(-\text{HDBPγ})}$, determined by Pearson et al., of $1.48 \times 10^{-4}$ kGy$^{-1}$ and $2.49 \times 10^{-4}$ kGy$^{-1}$ respectively, is shown in figure 6.11.

Figure 6.11. Experimental data for 1 M TBP showing the degradation of TBP as well as the formation of HDBP with no contact with an aqueous phase. The “TBP Model” was plotted using Equation 2 with $k_γ = 3.13 \times 10^{-4}$. The “HDBP Model” was plotted using Equation 6.12 with $k_{(+\text{HDBPγ})} = 1.48 \times 10^{-4}$ and $k_{(-\text{HDBPγ})} = 2.49 \times 10^{-4}$ as cited by Pearson et al.

\[
\text{[HDBP]} = \frac{(k_{+\text{HDBPγ}})}{(k_{-\text{HDBPγ}}) - (k_γ)} \left( e^{- (k_γ) \times \text{Dose}} - e^{- (k_{-\text{HDBPγ}}) \times \text{Dose}} \right) 
\]

Eq 6.12

In order to see what role the uptake of nitric acid from contact with an aqueous phase would play on HDBP formation and degradation, we performed irradiations on two solutions, 1 M TBP/n-dodecane as well as a solution of 0.25 M HDBP in n-dodecane, both contacted with an aqueous phase of 3M HNO₃. The degradation constant of HDBP in an organic solution
contacted with 3 M nitric acid, \( k_{(-\text{HDBP}\gamma H^+)} \), was determined to be \( 4.18 \times 10^{-4} \) kGy\(^{-1} \) using Equation 6.13. The fit of Equation 6.13 to the experimental data is shown in Figure 6.12. After fitting \( k_{(-\text{HDBP}\gamma H^+)} \), we analyzed the irradiated TBP after contact with nitric acid using Equation 6.14 to find the value of the formation constant of HDBP by TBP degradation, \( k_{(+\text{HDBP}\gamma H^+)} \). The constant was determined to be \( k_{(+\text{HDBP}\gamma H^+)} = 9.81 \pm 0.08 \times 10^{-5} \) for the formation of HDBP in irradiated 1 M TBP contacted with 3 M HNO\(_3\). Figure 6.13 shows the fit of Equation 6.14 to the experimental data for HDBP concentration found in the irradiated solutions.

\[
[HDBP] = [HDBP]_0 e^{-(k_{(-\text{HDBP}\gamma H^+))Dose}} \quad \text{Eq 6.13}
\]
\[
[HDBP] = \frac{k_{+\text{HDBP}\gamma H^+}}{k_{-\text{HDBP}\gamma H^+} - k_y} \left( e^{-(k_y)Dose} - e^{-(k_{-\text{HDBP}\gamma H^+})Dose} \right) \quad \text{Eq 6.14}
\]

**Figure 6.12.** Degradation plot of 0.25 M HDBP after contact with 3M HNO\(_3\). The degradation model reflects equation 6.13, \( k_{(-\text{HDBP}\gamma H^+)} = 4.18 \times 10^{-4} \).
Figure 6.13. Experimental data for 1M TBP showing the degradation of TBP as well as the formation of HDBP after contact with 3M HNO$_3$. The “TBP Model” was plotted using Equation 2 with $k_T = 3.13\times10^{-4}$ for acid contacted TBP radiolysis. The “HDBP Model” was plotted using Equation 11 with $k_{\text{HDBP}_{\text{uran}}}$ found to be $9.81\times10^{-5}$.

We were able to determine the concentrations of HDBP in the irradiated solutions of 1 M TBP with various concentrations of uranium. From these results we observe less HDBP present as the metal ion concentration in the organic phase increases. This may be due to complexation of HDBP to uranyl effectively reducing the ‘free’ HDBP that we would observe in the GC analysis. As discussed in a prior section, HDBP readily competes with TBP and coordinates with the uranyl. In addition to this, we would also need to determine the degradation constant for the HDBP-uranium complex, similar to what was done for TBP. However, as mentioned in the experimental section, upon irradiation the solutions of HDBP containing extracted uranyl showed significant third phase formation and the experiment was aborted. The presence of third phase was not unsurprising as it is well known that significant amounts of HDBP may promote third phase formation during the PUREX process.
[66]. Due to this complication no degradation constants of the metal-HDBP complex were determined.
Figure 6.14. Free TBP and HDBP plotted against absorbed low LET dose. Concentration of uranium in the organic phase was determined to be 0.02, 0.04, 0.12 and 0.2 M for plots in descending order. The TBP model reflects $k_1\gamma = 7.1 \pm 0.60 \times 10^{-3} \text{ kGy}^{-1}$.

Discussion

G-values for the destruction of TBP in TBP/n-dodecane systems by both low and high LET were determined by fitting a straight line to the concentration profile of TBP with absorbed energy. The values for $G_{TBP}$ with both gamma and alpha radiation were in good agreement with prior studies done by Pearson et al with low LET being roughly twice as potent as high LET. However, due to a factor of ten difference in initial concentration, $G_{TBP}$ varied by a factor of ten. This is the first indication that G values while being a simple approximation, might not necessarily be the most adequate descriptor of radiolysis yield.

Some Sources state that the inclusion of an aqueous phase has been known to increase the rate of TBP consumption, however, our studies (which were merely single-phase irradiations, after contact with and separation from, an aqueous phase and extraction of water and acid) indicate that the nitric acid uptake by TBP during extraction had little effect on TBP degradation. This result was consistent across both low and high LET studies.
Few authors have published on the topic of the effect of metal uptake on TBP degradation. However, the aforementioned authors in Section 3.6.4 all agree that the presence of metal ions inhibits TBP degradation and HDBP formation. Our studies show a highly nonlinear response by TBP concentration with increasing radiation dose, hence a G value cannot be calculated. Another shortcoming of G values as descriptors for radiation damage yield is that it is highly affected by where the linear fit is drawn and is therefore very open to interpretation.

In light of this, we make analogies to kinetic modelling for a more accurate representation. Degradation constants for radiolysis by low and high LET were $2.93\pm0.08\times10^{-4}$ and $1.29\pm0.15\times10^{-4}$, respectively which agree well with Pearson et al. Similar to the G value comparison the effect is roughly double for low LET vs high LET.

In order to explain the nonlinear behavior seen in Figure 6.8, the assumption was made that the TBP-UO$_2$ complex is broken by incident radiation to release the previously bound TBP. Analogous equations were derived to relate the concentration of metal-TBP complexes as a function of dose with the concentration of TBP. For both low and high LET, the models presented in Equations 6.8 and 6.10 respectively were fit to experimental data for the concentration profile of TBP using the determined degradation constants seen in tables 6.1 and 6.2.

Overall it seems that the rate at which the complex breaks up is about an order of magnitude greater than the rate with which TBP is affected by low LET ($7.1\times10^{-3}$ vs $2.93\times10^{-4}$ 1/kGy). One explanation is the relative differences in enthalpy. For example, the enthalpy associated with the C-O bond that, when broken, yields HDBP is on the order of 355 kJ/mole while Stas
et al. [64] reported an enthalpy value for the extraction of UO$_2$ from 0.5 and 1 M HNO$_3$ by TBP in kerosene as $\sim$16 and $\sim$23 kJ/mole respectively.

Similar to the studies of LET effects on TBP radiolysis, when examining the rate constants for complex break-up, low LET damage occurs at twice the rate of high LET damage. Degradation constants of 7.1±0.85x10$^{-3}$ and 3.5±0.15x10$^{-3}$ kGy$^{-1}$ were found for low and high LET respectively. The formation of HDBP appears to be inhibited by acid uptake at 3 M HNO$_3$, which seems to confirm the observations of Gao et. al.[67]. We observed a decrease from 1.48±0.04x10$^{-4}$ kGy$^{-1}$ to 9.81±0.08x10$^{-5}$ kGy$^{-1}$ for the formation constant of HDBP by gamma radiolysis of 1 M TBP when comparing ‘dry’ vs solutions contacted with 3 M HNO$_3$. 


ALSEP PROCESS – EXPERIMENTAL SETUP

Sample preparation:
Organic solutions of 0.5 M HEH[EHP] (Marshallton Labs 98+ %) and 0.05 M T2EHDGA (Marshallton Labs 98+ %) in n-dodecane (Alfa Aesar 99+ %) were prepared and half of these samples were contacted with an aqueous phase of 3 M nitric acid (Macron). Approximately 5 mL aliquots of the organic phase were contacted in borosilicate glass vials with equal volumes of the aqueous phase. The vials were shaken by way of a vortex mixer (Fisher Scientific Model 02215365) at ~160 rpm for 15 minutes and then centrifuged (Eppendorf) at 3000 rpm for 5 minutes to allow the phases to separate. The organic phase was then removed from contact with the aqueous and visually inspected to ensure no presence of aqueous phase bubbles were detected. For the samples that would be exposed to high LET radiation, after separation of the phases, bis pinacolato diboron (Sigma Aldrich 99%) was added to all organic phases for a final concentration of 0.4 M boron. The boron used in this work was of natural abundance.

Low LET irradiations:
For low LET irradiations a Cs-137 source (Shepard Instruments) for 661 keV gamma rays were used. The source was calibrated for dose to water by Fricke dosimetry [61] prior to the start of the irradiation. The dose rate at the position of our samples was 2.14 ± 0.06 kGy/hr. The organic solutions were irradiated for intervals of 0 to 15 days to achieve doses of 0 to ~700 kGy. At the end of each interval, 150 μL of each organic solution was removed for analysis by gas chromatography (GC). During the irradiations, the samples are sealed and opening the containers for sampling will introduce air back in the container. However, any
Oxygen is assumed to be consumed very rapidly once the sample is placed back in the irradiation field and we assume that the effect of oxygen to our irradiated samples is negligible.

**High LET irradiations:**

Organic solutions were exposed to a mix of high and low LET by introducing samples in the neutron flux of the UC Irvine TRIGA® reactor. Details of the method has been presented in previous work from our group [62][49]. The background low LET dose from the core has been verified to be approximately 40.4 kGy/h during normal reactor operations at 250 kW. The organic phases were irradiated for intervals of 0 (for standard samples) up to 3.5 hours at 250 kW of reactor power, in the rotating Lazy Susan specimen rack. In this position, the samples receive a thermal neutron flux of approximately $8 \times 10^{11}$ neutrons per square centimeter per second. The Lazy Susan specimen rack is in the reflector outside the core and thus the epithermal neutron flux is at least one order of magnitude lower than the thermal and is expected to make a negligible contribution to the dose under the conditions used here.

The irradiation times were chosen in order to achieve total doses comparable to the gamma irradiation in the Cs-source. Irradiations were performed such that after each increment of time, a reactor scram was initiated to stem the flux of further thermal neutrons, thereby inhibiting further boron fissions. After a brief waiting period to ensure that, the gaseous air activation products had died away, and the sample was safe for retrieval, samples were removed in accordance with their received dose. Following this, the reactor was then brought back up to full power and the irradiation continued. It should be noted that during both the waiting period before sample removal and during the rise back up to full power, the
samples were still exposed to some low LET gamma rays and fast neutrons from the reactor core.

Organic samples without boron were irradiated simultaneously to correct for the low LET contribution from the core. At the end of each interval the samples were removed and 150 μL of each irradiated organic solution was removed for analysis by GC.

**Determination of ligand Concentrations:**
Post irradiation, samples were diluted 1:12.5 in hexane (95% Sigma Aldrich) containing triphenyl phosphate (an inert internal standard) and diazomethane (derivatization agent). This derivatization is done in order to add methyl groups to acidic radiolysis products that might react with and be retained by the silica within the GC column. Diazomethane was prepared within a diazomethane generator kit (Sigma Aldrich) using diazald (Sigma Aldrich 99%), Carbitol (Sigma Aldrich 99%) and potassium hydroxide (Fischer Scientific). The diazomethane gas was captured in hexane. All samples were analyzed by a Hewlett Packard 5890 Gas Chromatograph using a flame ionization detector. The GC was equipped with a 30 m DB-5ms column (Agilent Technologies) and an associated Hewlett Packard Controller 7673A integrator. The heating program began at 60°C and increased at a rate of 10°C/min until a final temperature of 350°C and a final hold time of 20 min.

**Analysis of degradation products:**
Samples of gamma irradiated T[2EH]DGA and HEH[EHP] in n-dodecane were analyzed by liquid chromatography mass spectrometry (LC-MS) using a Waters Acuity UPLC H Class in positive and negative mode. This was used in conjunction with a single quadrupole detector as well as a photodiode detector. The stationary phase (column) was a Waters B8 C18
column, 50mm in length and 1.7 µm particle size. The mobile phase aqueous (A) solvent consisted of water with 0.1% formic acid and the organic solvent (B) consisted of 100% acetonitrile.
ALSEP PROCESS – RESULTS

Low LET Studies - 0.5 M HEH[EHP] / 0.05 M T2EHDGA / n-Dodecane.
Degradation constants were found by treating the decrease of each ligand (L) with dose as a function of the decay constant multiplied with ligand concentration, providing an expression for exponential decrease in concentration.

\[
\frac{d[L]}{d \text{Dose}} = -k_\gamma [L] \quad \text{Eq 8.1}
\]

\[
[L] = [L]_0 e^{-(k_\gamma)\text{Dose}} \quad \text{Eq 8.2}
\]

Equation 8.2 forms the basis of the degradation model used to characterize the degradation profile and yield corresponding degradation dose constants (k_\gamma). Figure 8.1 shows the fit between our experimentally determined concentration profiles after irradiation and the degradation model.

After gamma irradiation of 0.5 M HEH[EHP] / 0.05 M T2EHDGA / n-Dodecane ALSEP solutions, it is clear that T2EHDGA undergoes radiolysis at a much faster rate than HEH[EHP]. Degradation constants were determined to be and (3.23 \pm 0.28) \times 10^{-3} and (6.01 \pm 0.66) \times 10^{-4} for T2EHDGA and HEH[EHP] respectively.

The degradation dose constant for T2EHDGA appears to agree somewhat well with the value of (4.3 \pm 0.3) \times 10^{-3} reported by Zarzana et. al [56] for the system of 0.05M T2EGDA in n-dodecane, but is twice the value reported by Peterman et. al. of (1.6 \pm 0.04) \times 10^{-3} [58].
Figure 8.1a. (Top): HEH(EHP) concentration as a function of absorbed low LET dose.

Figure 8.1b (Bottom): T2EHDGA concentration as a function of absorbed low LET dose.

**Low LET Studies - 0.5M HEH[EHP] / 0.05M T2EHDGA / n-Dodecane/3 M HNO₃**

After acid uptake, degradation constants for both T2EHDGA as well as HEH[EHP] seem slightly lowered, which suggests an protective effect from the inclusion of acid. The corresponding constants were found to be $(2.45 \pm 0.33) \times 10^{-3}$ kGy$^{-1}$ for T2EHDGA and $(5.08 \pm 0.54) \times 10^{-4}$ kGy$^{-1}$ for HEH[EHP]. The reduction in the T2EHDGA degradation constant with
the uptake of nitric acid was also observed by Zarzana et. al. as they reported a change from $(4.3 \pm 0.3) \times 10^{-3}$ to $(3.7 \pm 0.2) \times 10^{-3}$ when T2EHDGA was contacted with $0.1 \text{ M HNO}_3$ [56].

Figure 8.2a. (Top): HEH(EHP) concentration as a function of low LET dose after acid uptake.

Figure 8.2b. (Bottom): T2EHDGA concentration as a function of low LET dose after acid uptake.

**High and low LET Studies - 0.5 M HEH[EHP] / 0.05 M T2EHDGA / n-Dodecane.**

A similar method was used to determine the high LET degradation dose constants as seen in the low LET scenario. However, due to the reactor core being a mixed radiation field,
Equation 8.2 needs to be modified to account for both the high and low LET contributions to the degradation of the ligand. Equation 8.3 relates the concentration of ligand (L) to the high and low LET dose rates, $\dot{D}_\alpha$ and $\dot{D}_\gamma$, respectively. Similarly, $t_\alpha$ and $t_\gamma$ represent the irradiation times for high and low LET while $k_\alpha$ and $k_\gamma$ are their respective dose constants.

$$[L] = [L]_0 * e^{-(k_\alpha \dot{D}_\alpha t_\alpha + k_\gamma \dot{D}_\gamma t_\gamma)}$$ \hspace{1cm} \text{Eq 8.3}

Because the initial and final concentrations of ligand are known, the irradiation times are recorded, and the dose rates have previously been determined, the only unknowns in Equation 8.3 are the dose constants. However, if we utilize the previously determined low LET dose constants, then Equation 8.3 becomes solvable. For the sake of ensuring consistency, samples containing no boron were irradiated with the assumption that degradation profile for both HEH[EHP] and T2EHDGA by the background gamma rays and neutrons matches the low LET profile determined from the $^{137}$Cs source irradiations. Figure 3 below shows the comparison.

\hspace{1cm} \text{Figure 8.3 : T2EHDGA degradation by reactor low LET dose and Cs source low LET dose.}
HEH[EHP] still demonstrates a fairly linear response to absorbed dose to a considerable value of 1000 kGy, showing good radiolytic stability. The inclusion of nitric acid seems not to have a pronounced effect on the overall degradation of HEH[EHP].
Mixed high and low LET irradiations of 0.5 M HEH[EHP] / 0.05 M T2EHDA / n-Dodecane/3 M HNO₃

Figure 8.5a. (Top): T2EHDA concentration as a function of mixed high and low LET dose.

Figure 8.5b. (Bottom): T2EHDA concentration as a function of mixed high and low LET dose with HNO₃ uptake.

With regards to the role of high LET radiaition, a comparison of the degradation constants for both low and high LET seems to suggest that low LET dominates the destruction of both HEH[EHP] and T2EHDA. The difference seems greater for T2EHDA than HEH(EHP),
though T2EHDGA demonstrates less radiolytic stability overall, as seen by the consistently higher degradation constants compared to HEH[EHP]. Once again, nitric acid uptake seems to slightly inhibit degradation of the ligand, but not to a large degree. Comparisons for dose constants can be seen in Table 8.1.

**Table 8.1: High vs low LET dose constant comparison.**

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Ligand</th>
<th>Dose Constants, (1/kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>High LET, $k_\alpha$</td>
</tr>
<tr>
<td>0.5 M HEH[EHP] / 0.05 M T2EHDGA</td>
<td>HEH[EHP]</td>
<td>(4.67 ± 0.21) x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>T2EHDGA</td>
<td>(1.03 ± 0.13) x 10^{-3}</td>
</tr>
<tr>
<td>0.5 M HEH[EHP] / 0.05 M T2EHDGA / 3 M HNO₃</td>
<td>HEH[EHP]</td>
<td>(4.37 ± 1.1) x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>T2EHDGA</td>
<td>(9.45 ± 0.39) x 10^{-4}</td>
</tr>
</tbody>
</table>

**Degradation Products of T2EHDGA**

The chromatogram for irradiated solutions of the ALSEP solvent are overlaid in Figure 8.6 below (Day 0 bottom, Day 11 top). In the Day 0 (not irradiated) chromatogram, there are significant peaks at an elution time of 2.7 and 4.4 minutes. The peak at $t= 2.7$ minutes reveals a m/z of 307.2 which corresponds to protonated HEH[EHP] (M+H) and the peak at $t= 4.4$ minutes reveals a m/z of 581 which corresponds to protonated T2EHDGA (M+H). Unfortunately, there are also significant peaks at 1.89 and 2.01 minutes in the Day 0 samples (m/z of 242 and 223) which are yet to be determined but due to their decrease with increasing irradiation time could be a result of T2EHDGA fragmentation in the LC-MS itself as there is successively less T2EHDGA as irradiation continues.
As total absorbed dose increases, the peak at elution time of 4.4 minutes corresponding to T2EHDGA decreases in intensity significantly. Also, features appear at the range of 2.2-2.4 minutes, and this is where radiolytic degradation products are most likely eluting.

Further analysis of the band of degradation products that appear and proliferate form the range of 2.2-2.4 minutes in Figure 6.8 was performed. The mass spectra in Figure 8.7 correspond to m/z which elute in the time frame of 2.2 - 2.4 minutes of the Day 11 samples (corresponding to an absorbed dose of ~ 564.96 kGy).
**Figure 8.6.** Overlaid chromatograms of irradiation times of 0 days to 11 days at 2.14 kGy/hr.
The most abundant degradation products appear to have m/z values of 209, 298, 343, 411, 523 and 539. The corresponding structures have yet to be identified, however we believe that the degradation product corresponding to m/z 298 corresponds to the \( N,N \)-dioctyl-glycolamide structure proposed by Zarzana et al [56].
For reference we will be referring back to figure 3.4 to compare our results.


Here, we propose a few new potential degradation product species in accordance with our mass spectrometry data.
Figure 8.8: Proposed structures for degradation products of T2EHDGA where R is the ethyl-hexyl group. M/z for structures are 342, 412, 242, 242 and 524 for structures I, II, III, IV and V respectively.

Structure I in Figure 8.8 corresponds to a similar structure observed by Zarzana et al., where an amide group has been modified such that the C-N bond has been removed and capped and protonated. This results in a mass of 341 which we speculate, could be the peak at 343.25 in Figure 8.7. Structure II is derived from the cleavage of the central C-O bond in T2EHDGA and capped by an ethyl-hexyl R group. This R group may likely originate from being removed from one of the amide groups resulting in compound 1 in Figure 3.4. The mass of this compound when protonated results in the m/z of 412 observed in Figure 8.7. Structure III can be viewed as the corresponding T2EHDGA degradation product of compound II with the exception that the ethyl-hexyl R group has undergone cleavage at the ethyl branch yielding a mass of 242 when protonated. Structure IV could potentially be responsible for the peak at 242 and is derived from a likely cleavage of the C-N bond. Lastly, structure V is a rupture within an R group resulting in the removal of a butyl tail from the main hexyl chain. Further

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analysis is needed to characterize and identify other key degradation products of T2EHDGA and assess their impacts. The identification of HEHEHP degradation products will be the focus of future studies.
SUMMARY

To meet the growing demand for energy, caused by an ever-expanding global population as well as rapid technological advancement in developing nations, nuclear energy is a strong candidate for electrical power generation in the near future. However, in addition to relatively pessimistic popular opinion, the lingering concerns of environmental stewardship when dealing with the creation of long-term radiotoxic waste materials that could pose serious health and environmental hazards for hundreds of thousands of years, are serious drawbacks that must be addressed.

Partitioning and transmutation of used nuclear fuel in an attempt to bring the radiotoxicity timescale into a more manageable regime has led to the creation of several metal extraction techniques. Foremost among these is the PUREX process which selectively extracts hexavalent uranium and tetravalent plutonium from nitric acid solutions using tributyl phosphate in aliphatic diluents. The ALSEP process is currently being evaluated for use in tandem with the PUREX process to facilitate the extraction of the highly radiotoxic minor actinides (Am and Cm) from PUREX raffinate streams. Intense radiation in these systems causes the ligands in the working fluid to degrade, leading to poor extraction efficiency, increased costs and potential hazards associated with improper accumulation of metals in third phase formation.

Understanding and characterizing TBP degradation has been an ongoing topic of research. The work done here has presented degradation constants for the radiolysis of tributyl phosphate as a function of various PUREX process variables such as the inclusion of nitric acid as well as metal uptake induced in addition to alpha and gamma radiation exposure.
Results indicate that gamma radiolysis occurs at roughly twice the rate of alpha, and that acid uptake by TBP has little effect on the overall degradation rate for both alpha and gamma irradiations. The inclusion of metal uptake inhibits the consumption of TBP by both alpha and gamma radiation, by forming protective complexes that absorb a portion of the energy deposited by radiation. These TBP-metal complexes are then destroyed during irradiation. Degradation constants for the complex destruction were determined for both alpha and gamma radiation. Similar to TBP, gamma radiation affects complexes at twice the rate of alpha radiation.

For the dual extractants, HEHEHP and T2EHDGA utilized in the ALSEP process, HEHEHP is far less susceptible to radiation damage than T2EHDGA. Here again low LET is the dominant mode and causes the most degradation. Further understanding of the species formed in the degradation of ALSEP process ligands as well as their role in the overall efficiency of the process is required.
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