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Radiolytic evaluation of acetohydroxamic acid (AHA) under biphasic (*n*-dodecane and TBP/DEHBA/DEH*i*BA) used nuclear fuel reprocessing conditions

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ABSTRACT

Acetohydroxamic acid (AHA) has been proposed as a substitute for uranium(IV) and hydrazine as a plutonium complexant and neptunium reductant for simplified, single-cycle used nuclear fuel reprocessing flowsheets. However, the chemical behavior of AHA in an intense multi-component radiation field is poorly understood, especially under representative biphasic reprocessing solvent system conditions. In response to this critical knowledge gap, this study has investigated the gamma radiolytic integrity of AHA in aqueous nitric solutions in contact with an organic phase, comprising current and future reprocessing ligands (TBP, DEHBA, and DEH*i*BA) dissolved in *n*-dodecane diluent. Our data show negligible effect of the organic phase on the radiolytic behavior of AHA compared to complementary single-phase experiments.

I. INTRODUCTION

Uranium (U) and plutonium (Pu) can be recovered from used nuclear fuel (UNF) by reprocessing technology for the fabrication of new fuel. The *Plutonium Uranium Reduction EXtraction* (PUREX) process is the industrial standard for reprocessing UNF. The PUREX solvent system employs tributyl phosphate (TBP, **Figure 1 B**) as the current ligand for the extraction of tetravalent (Pu(IV)) and hexavalent U (U(VI)) from UNF. However, *N*,*N*-di-(2-ethylhexyl)butyramide (DEHBA, **Figure 1 C**) and di-2-ethylhexylisobutyramide (DEH*i*BA, **Figure 1 D**) are under consideration for replacing TBP due to advantages they offer, such as improved radiolytic stability and selectivity for U, as well as more benign radiolytic degradation products.[1] DEHBA and DEH*i*BA are also made entirely of carbon, hydrogen, oxygen, and nitrogen (CHON), which facilitates more facile waste management via incineration.

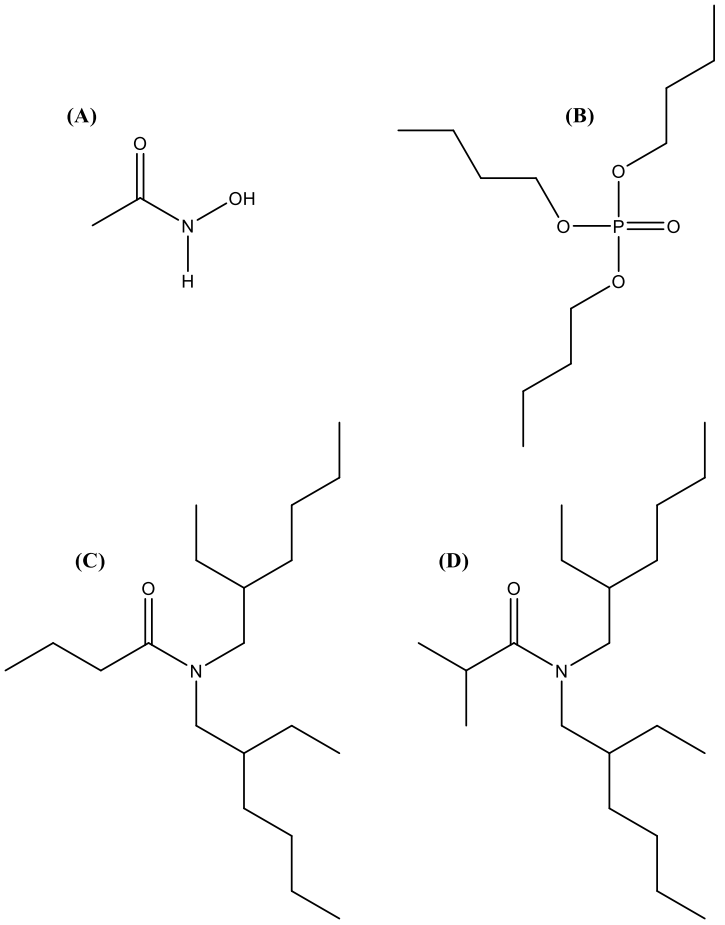


Figure 1. Molecular structures for acetohydroxamic acid (AHA, **A**), tri-butyl phosphate (TBP, **B**), *N*,*N*-di-(2-ethylhexyl)butyramide (DEHBA, **C**), and di-2-ethylhexylisobutyramide (DEH*i*BA, **D**).

A single-cycle flowsheet for a simplified PUREX process is in development to reduce costs, waste, and environmental impacts. This advanced PUREX process would utilize acetohydroxamic acid (AHA, **Figure 1 A**) instead of ferrous sulfamate, hydrazine-stabilized ferrous nitrate, or hydrazine-stabilized uranous nitrate reductants for separating

Pu(IV) and neptunium (Np) from U(VI).[2,3,17] Ferrous sulfamate introduces sulfate ions into the system, which cause problems. Sulfate complexes with Pu, resulting in a loss of Pu product. Additionally, sulfate is corrosive to process equipment and increases the volume of waste and difficulty of managing it. Ferrous nitrate and uranous nitrate do not present these issues, however, they require stabilization by hydrazine (N_2H_4). Nitric acid (HNO_3) is easily reduced to nitrous acid (HNO_2), which presents problems for maintaining Pu in its non-extractable trivalent state, Pu(III). To remedy this, these reductants are used in tandem with N_2H_4, which reacts with HNO_2 to stabilize Pu(III). However, the reaction of N_2H_4 with HNO_2 in a TBP-HNO_3 systems can form hydrazoic acid (HN_3), which is unstable, hazardous, and explosive. Additionally, hydrazine itself is corrosive and harmful to the human body.[3,17]

To avoid adding additional metals to a UNF reprocessing waste stream and generating HN_3 from N_2H_4, alternative reductants are under investigation. Simple hydroxamic acids, such as AHA and formohydroxamic acid (FHA), have been studied for substitution into reprocessing flowsheets. AHA is a most promising candidate, as it has been shown to be less susceptible to hydrolysis than FHA.[4] Further, AHA complexes tetravalent Np (Np(IV)) and Pu(IV), in addition to reducing extractable hexavalent Np (Np(VI)) to inextricable pentavalent Np (Np(V)) for separation from U.[2] However, under envisioned process conditions, a reprocessing solvent system is subjected to substantial amounts of ionizing radiation. This radiation affects the performance of the solvent system through the destruction of active compounds (e.g., AHA and extraction ligands) and formation of degradation products. The aqueous (H_2O and HNO_3) and organic (RH) solvents undergo direct radiolysis (⇝) to yield a variety of reactive radiolysis products, as shown in **Equations 1-3**:[6,20,21]

$$H_2O \rightsquigarrow e_{aq}^-,\ H^\bullet,\ {}^\bullet OH,\ H_2O_2,\ H_2,\ H_{aq}^+, \quad (1)$$

$$HNO_3 \rightsquigarrow e_{aq}^-,\ {}^\bullet NO_3,\ HNO_2,\ O^\bullet,\ H_{aq}^+, \quad (2)$$

$$RH \rightsquigarrow e^-,\ RH^{\bullet+},\ R^\bullet,\ {}^\bullet CH_3,\ H^\bullet,\ H_2. \quad (3)$$

Many of these radiolysis products are capable of propagating radiolysis in a solvent system's active compounds. For example, the *n*-dodecane radical cation ($RH^{\bullet+}$) from organic diluent radiolysis has been linked to initiating extractant ligand degradation, as demonstrated by **Equation 4**:[18]

$$TBP/DEHBA/DEH\textit{i}BA + RH^{\bullet+} \rightarrow [TBP/DEHBA/DEH\textit{i}BA]^{\bullet+} + RH, \quad (4)$$

with all three ligands exhibiting essentially diffusion limited rates of reaction (k) with $RH^{\bullet+}$: $(1.56 \pm 0.08) \times 10^{10}$, $(1.04 \pm 0.02) \times 10^{10}$, and $(1.52 \pm 0.11) \times 10^{10}$ M^{-1} s^{-1}, respectively.[8,9,10] Radiolytic degradation of the aforementioned extraction ligands leads to the formation of a variety of degradation products, for example, HDBP and H_2MBP from TBP,[11] b2EHA and MEHBA from DEHBA,[9] and b2EHA and MEH*i*BA from DEH*i*BA.[10] Many of these degradation products are detrimental to process performance as they alter the physical and chemical properties of the system.

With regards to the radiation-induced behavior of AHA, very little is known, especially under biphasic conditions.[13,22,23] What is known is that AHA is subject to indirect radiolysis through reaction with the primary products of water and HNO_3 radiolysis (**Equations 1 and 2**), for example, **Equation 6:**

$$AHA + {}^{\bullet}OH/{}^{\bullet}NO_3 \rightarrow AHA^{\bullet} + H_2O/HNO_3 \quad (6)$$

Further, the main degradation products under single phase conditions are hydroxylamine (HA) and acetic acid. In terms of AHA's behavior under reprocessing conditions, all that exists is a single study by Sánchez-Garcia *et at.,* whom conducted single phase irradiations of AHA in nitric acid with constant concentrations of AHA and HNO_3 up to 50 kGy.[19] In this study, AHA was investigated both alone and in conjunction with sulphonated bis-triazinylpyridine (SO_3-Ph-BTP), a ligand used for stripping trivalent actinides in the *i*-SANEX process. However, these results are constrained to the aqueous phase. To replicate reprocessing conditions, a biphasic system with current (TBP) and future (DEHBA, DEH*i*BA) extraction ligands needs to be studied.

In response to this critical knowledge gap, this study has investigated the gamma radiolytic integrity of AHA in aqueous nitric solutions in contact with an organic phase, comprising current and future reprocessing ligands (TBP, DEHBA, and DEH*i*BA) dissolved in *n*-dodecane diluent.

II. EXPERIMENTAL

A. Materials

DEHBA (99%) and DEHiBA (99%) were supplied by Technocomm Ltd. (Wellbrae, Scotland, UK). 8-quinolinol (≥99%), acetic acid (≥99%), acetohydroxamic acid (AHA, 98%), ethanol (>95%), hydrochloric acid (HCl, 37%), iron(III) chloride (FeCl3, 97%), iron(II) sulfate heptahydrate (FeSO4, ≥99%), hydroxylamine hydrochloride (≥99.999% trace metals basis). n-dodecane (≥99% anhydrous), N-(1-naphthyl)ethylenediamine dihydrochloride (≥98%), nitric acid (HNO3, ≥99.999% trace metals basis), potassium carbonate (K2CO3, ≥99% anhydrous),sodium chloride (NaCl, ≥99.5%), sodium hydroxide (NaOH, 50% in H2O), sodium nitrite (≥99.999% trace metals basis), sulfanilamide (≥99%), sulfuric acid (H2SO4, 95.0-98.0%), formic acid (98%-100%), and TBP (≥99%) were sourced from MilliporeSigma (Burlington, MA, USA). Sodium nitrate (NaNO3, ≥99.0%) was from GFS Chemicals (Columbus, OH, USA).

All chemicals were used without further purification. Ultrapure water (18.2 MΩ) was used for the preparation of all aqueous solutions.

B. Sample Preparation

Each ligand (TBP, DEHBA, and DEH*i*BA) was prepared as a separate 0.05 M solution in *n*-dodecane and preequilibrated with 0.2 M HNO_3 solution, contacted in a 1:1 ratio. These organic phases were contacted with HNO_3 in centrifuge tubes, which were then agitated using a VWR (Radnor, PA, USA) standard vortex mixer for 2 minutes, with 15 seconds of manual shaking before and after the first minute. Agitated samples were subsequently put into a Labnet (Edison, NJ, USA) Hermle Z206A centrifuge for 3 minutes at 3150 rpm. The organic phases were then separated, and this process repeated two more times using the separated organic phase and fresh HNO_3. The organic phases for each ligand from each centrifuge tube were then consolidated, and the samples for each ligand for irradiation were then prepared from these consolidated solutions.

Samples for irradiation were composed of either 5 ml of single (aqueous) phase or 10 ml of biphasic (1:1 aqueous-to-organic). The aqueous phase consisted of 0.5 M AHA

dissolved in 0.2 M HNO_3. The organic phase comprised of the preequilibrated 0.05 M ligand/*n*-dodecane solution. To minimize AHA hydrolysis, the HNO_3 was added to the AHA immediately before irradiating.

C. Irradiations

The Idaho National Laboratory (INL) Center for Radiation Chemistry Research (CR2) Foss Therapy Service Model 812 cobalt-60 gamma irradiator was used for all irradiation procedures. All samples were irradiated in triplicate up to 110 kGy under deaerated conditions. The vials were stationary and sealed, causing oxygen to be consumed at low gamma doses. Fricke dosimetry[5] was performed to determine the dose rate for each irradiator position used for both 5 and 10 ml of Fricke solution in 20 ml screw-cap scintillation vials. The Fricke dosimetry absorbances were corrected for baseline shift, and absorbed doses (D_D) were calculated using the following equation:[6]

$$D_D = \frac{Abs}{\Delta\varepsilon l \rho G(Fe^{3+})}, \quad (5)$$

where $\Delta\varepsilon$ is the molar extinction coefficient (2197 cm^{-1} M^{-1}), l is the path length (1 cm), ρ is the density (1.024 kg/L), and $G(Fe^{3+})$ is the G value of Fe(III) (1.61E-6 mol/J). The dose rates ranged between 84.64 and 111.62 Gy min^{-1}, with the 10 ml Fricke samples absorbing, on average, 2.38% higher than that of the corresponding 5 ml samples. The dose rate for each position in the sample rack was corrected daily for the decay of cobalt-60.

D. Analysis

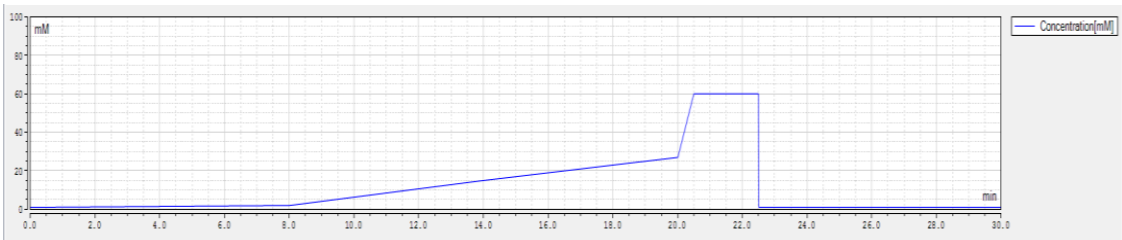
1. UV-vis spectroscopy. An Agilent Technologies (Santa Clara, CA, USA) Cary 6000i UV-Vis-NIR Spectrophotometer was used to determine the concentrations of AHA, HA, and nitrite (NO_2^-)/HNO_2.

- AHA concentrations were measured using the method reported by Andrieux, Boxall, and Taylor.[12] The specific method employed by this work was developed by our group with some influence from Wang[13] *et al.*: 4.88 ml of ultrapure water and 10 µL of 2 M NaOH were preprepared; 10 µL of irradiated sample was added, and hydrolysis was stopped upon addition due to neutralization with the base; the Fe(III) complex was formed with the addition of 100 µL of 0.25 M $FeCl_3$ in 0.25 M HNO_3; and the solution was run through the UV-vis immediately. The concentration was determined using λ_{max}= 496 nm and a molar extinction coefficient of 1048 cm^{-1} M^{-1}.
- The spectrophotometric method used for HA was adapted from Frear and Burrell.[14] Instead of the plant material, 1.99 ml of ultrapure water was preprepared, and 10 µL of diluted, irradiated sample (100 µL of sample in 500 µL of ultrapure water, vortex mixed) was added. Then, our procedure followed theirs exactly, starting with the addition of the 8-quinolinol solution. However, Frear and Burrell used 1.0 g of 8-quinolinol and 1.0 M sodium carbonate while we used 0.797 g of 8-quinolinol and 1.0 M potassium carbonate. These differences did not affect the results. The concentration was determined using λ_{max}= 708 nm and a molar extinction coefficient of 14213 cm^{-1} M^{-1}.
- A modified version of the Shinn method was used to determine NO_2^-/HNO_2 concentrations, as outlined by Bendschneider and Robinson.[15] 3.59 ml of

ultrapure water and 80 µL of 58 mM sulfanilamide in 1.2 M HCl were preprepared. 250 µL of irradiated sample was added, and after 2-6 minutes, 80 µL of 1.92 mM *N*-(1-naphthyl)ethylenediamine dihydrochloride was added. After 10 minutes, the solution was run through the UV-vis. The concentration was determined using λ_{max}= 542 nm and a molar extinction coefficient of 49500 cm^{-1} M^{-1}.

To maximize efficiency, the modified Shinn method was performed first. Next, the HA method was performed, and while those samples cooled, the AHA method was performed. The HA samples were run through the UV-vis after completion of the AHA samples.

2. Ion Chromatography (IC). A Thermo Scientific (Waltham, MA, USA) Dionex AS-AP Autosampler and Thermo Scientific Dionex ICS-5000$^+$ DP equipped with an anion column (IonPac AS11-HC analytical column with a AG-11-HC guard column), was used to measure acetic acid (CH_3COOH), NO_2^-, nitrate (NO_3^-), and formic acid (HCOOH) concentrations following irradiation. IC calibration standards consisted of 1.5, 1.0, 0.5, 0.25, and 0.125 mM solutions of acetic acid, NO_2^-, NO_3^-, and formic acid, with formic acid 5 times more dilute than the other three components. A quality control standard of 0.75 mM (formic acid was also 5 times more dilute) was used to check the accuracy of the instrument throughout the run. The IC vials for the irradiated samples consisted of 1.48 ml ultrapure water and 10 µL of 2.0 M NaOH preprepared, with 10 µL of irradiated sample added. Calibration standards and sample vials were vortex mixed before insertion into the instrument. The IC method employed was a modified version of that outlined in Chen, De Borba, and Rohrer.[16] For the runs, the eluent was potassium hydroxide the pump flow rate was 0.4 ml min^{-1}, the sample chamber temperature was 4 °C, and the compartment and column temperatures were 25 °C. The IC eluent concentration profile is shown in more detail in **Figure 2**.



No	Time	Concentration [mM]	Curve
1	Initial Tim	Instrument Setup	
2	Initial Tim	1.00	
3	0.000	Run	
4	0.000	1.00	5
5	8.000	2.00	5
6	8.010	2.00	5
7	14.000	15.00	5
8	14.010	15.00	5
9	20.000	27.00	5
10	20.010	27.00	5
11	20.500	60.00	5
12	22.500	60.00	5
13	22.510	1.00	5
14	25.000	1.00	5
15	New Row		
16	30.000	Stop Run	

Figure 2. Detailed method for IC eluent (KOH) concentration *vs.* run time for each injection.

III. RESULTS AND DISCUSSION

The concentration of AHA as a function of absorbed gamma dose is shown in **Figure 3** for single and biphasic systems.

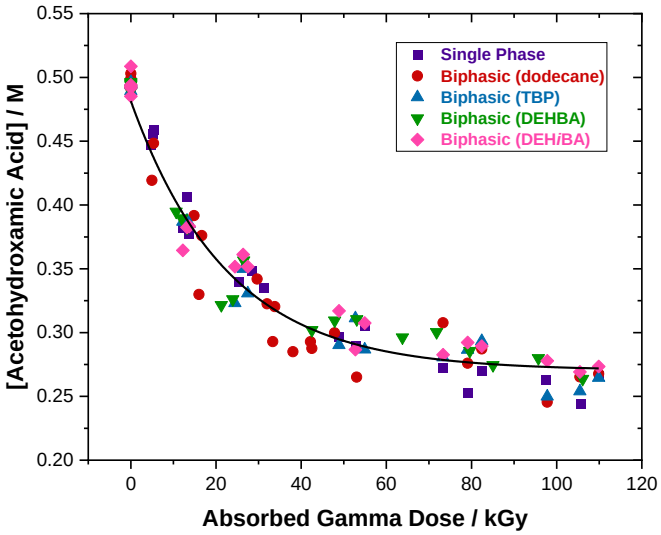


Figure 3. Concentration of AHA in 0.2 M HNO_3 as a function of absorbed gamma dose for: single phase (**purple square**); biphasic – *n*-dodecane (**red circle**); biphasic – 50 mM TBP/*n*-dodecane (**blue upward triangle**); biphasic – 50 mM DEHBA/*n*-dodecane (**green downward triangle**); and biphasic – 50 mM DEH*i*BA/*n*-dodecane (**pink diamond**). Fitted curve is an average exponential fit to data to guide the eye.

For all investigated solvent systems, AHA degrades exponentially with absorbed dose, allowing for the calculation of dose constants (*d*),[7] shown in **Table 1**.These dose constants represent the effects of both AHA hydrolysis and radiolysis, as the respective contribution of these two interconnected phenomena cannot be easily separated. Nevertheless, the presented dose constants are still a good measure for relative comparison of the effect of the organic phase on the rate of radiation-induced AHA degradation. The values shown in **Table 1** demonstrate that the organic phase has negligible effect upon the rate of AHA radiolysis, within our confidence limits, affording an average dose constant of (-58.66 ± 6.10) × 10^{-4} kGy^{-1}.

Table 1. Dose constants (*d*) for each type of AHA solvent system investigated.

Solvent System	**Dose constant** (10^{-4} kGy^{-1})
AHA/HNO_3	-64.86 ± 4.84
AHA/HNO_3:*n*-dodecane	-59.47 ± 7.26
AHA/HNO_3:TBP/*n*-dodecane	-58.14 ± 6.02
AHA/HNO_3:DEBHA/*n*-dodecane	-57.11 ± 6.64
AHA/HNO_3:DEH*i*BA/*n*-dodecane	-53.72 ± 5.73

These findings suggest that organic phase radiolytic transients (**Equation 3**) and steady-state degradation products (e.g., HDBP, H_2MBP, b2EHA, MEHBA, and MEH*i*BA) have limited capacity for migrating across the aqueous-organic interface and undergoing subsequent chemistry with AHA within the investigated dose range (≤ 110 kGy).

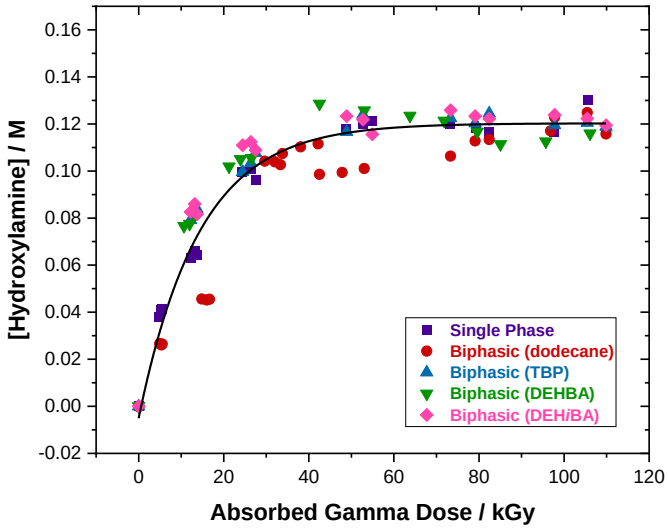


Figure 4. Concentration of HA as a function of absorbed gamma dose from the irradiation of 0.5 M AHA in 0.2 M HNO_3 for: single phase (**purple square**); biphasic – *n*-dodecane (**red circle**); biphasic – 50 mM TBP/*n*-dodecane (**blue upward triangle**); biphasic – 50 mM DEHBA/*n*-dodecane (**green downward triangle**); and biphasic – 50 mM DEH*i*BA/*n*-dodecane (**pink diamond**). Fitted curve is an average exponential fit to data to guide the eye.

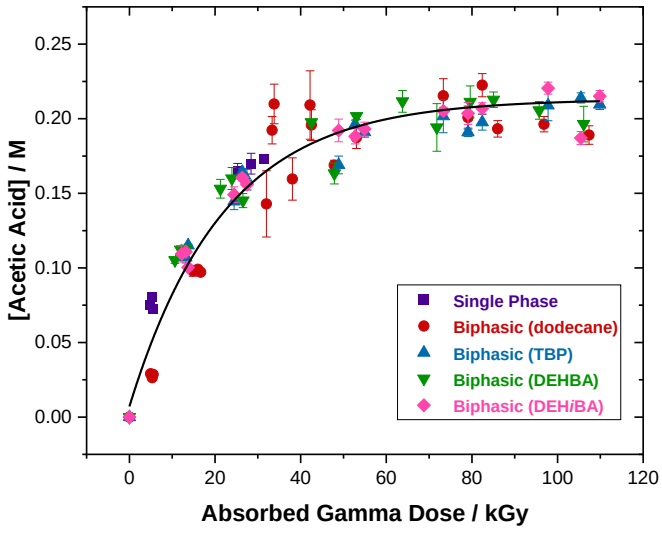


Figure 5. Concentration of acetic acid as a function of absorbed gamma dose from the irradiation of 0.5 M AHA in 0.2 M HNO_3 for: single phase (**purple square**); biphasic – *n*-dodecane (**red circle**); biphasic – 50 mM TBP/*n*-dodecane (**blue upward triangle**); biphasic – 50 mM DEHBA/*n*-dodecane (**green downward triangle**) and biphasic – 50 mM DEH*i*BA/*n*-dodecane (**pink diamond**). Fitted curve is an average exponential fit to data to guide the eye.

Degradation products from the combined hydrolysis and radiolysis of AHA are shown as a function of absorbed gamma dose in **Figure 4**, **5**, and **6** for HA, acetic acid, and NO_3^-, respectively. Both NO_2^- and formic acid were not detected. All detectable degradation products also showed negligible dependence on the presence and composition of organic phase. Overall, gamma irradiation of AHA in 0.2 M HNO_3 promotes its decomposition into HA and acetic acid, as shown in **Figure 4** and **5**. These AHA degradation products are also subject to radiolysis, as indicated by their exponential growth behavior and eventual attainment of a steady-state concentration.

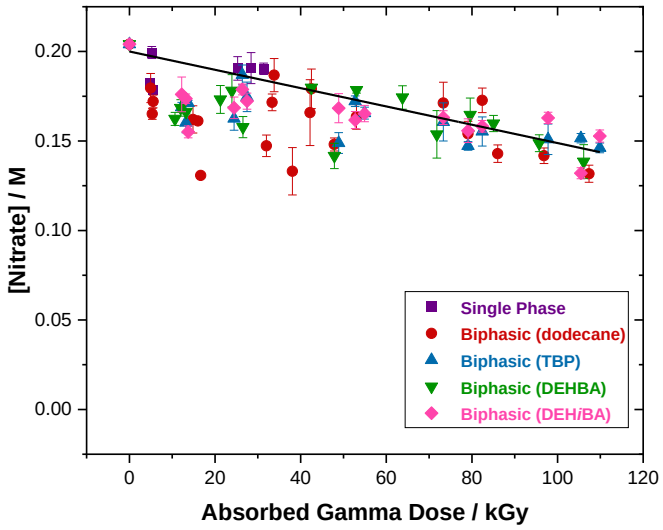


Figure 6. Concentration of nitrate as a function of absorbed gamma dose from the irradiation of 0.5 M AHA in 0.2 M HNO_3 for: single phase (**purple square**); biphasic – *n*-dodecane (**red circle**); biphasic – 50 mM TBP/*n*-dodecane (**blue upward triangle**); biphasic – 50 mM DEHBA/*n*-dodecane (**green downward triangle**); and biphasic – 50 mM DEH*i*BA/*n*-dodecane (**pink diamond**). Fitted line is an average linear fit to data to guide the eye.

The decrease in NO_3^- concentration with absorbed gamma dose in **Figure 6**, indicates that HNO_3 radiolysis is occurring, and therefore, AHA is experiencing indirect radiolysis through reaction with $^{\bullet}NO_3$ and possibly nitrous acid (HNO_2).

IV. CONCLUSIONS

Irradiation of biphasic AHA solvent systems revealed little change in the rate of AHA radiolysis, indicating that the presence of an organic phase and extraction ligand identity had negligible effect on aqueous phase radiation chemistry. These findings support the substitution of AHA for current reprocessing Pu(IV)/Np(VI) reductants and holdback reagents.

V. ACKNOWLEDGEMENTS

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