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ARTICLE

Does Addition of 1-Octanol as a Phase Modifier Provide Radical Scavenging Radioprotection for *N,N,N',N'*-tetraoctyldiglycolamide (TODGA)?Received 13th August 2020,
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To mitigate third phase formation in next generation used nuclear fuel reprocessing technologies, the addition of 1-octanol has been trialed. However, contradictory reports on the radiolytic effect of 1-octanol incorporation on separation ligand degradation need to be resolved. Here, 50 mM *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) dissolved in *n*-dodecane was gamma irradiated in the presence and absence of 1-octanol (2.5-10 vol. %) and a 3.0 M HNO₃ aqueous phase. Radiation-induced TODGA degradation exhibited pseudo-first-order decay kinetics as a function of absorbed gamma dose for all investigated solution and solvent system formulations. The addition of 1-octanol afforded diametrically different effects on the rate of TODGA degradation depending on solvent system formulation. For organic-only irradiations, 1-octanol promoted TODGA degradation ($d = 0.0057 \text{ kGy}^{-1}$ for zero 1-octanol present vs. $\sim 0.0073 \text{ kGy}^{-1}$ for 7.5-10 vol. %) attributed to a favourable hydrogen atom abstraction reaction free energy (-0.31 eV) and the ability of 1-octanol to access a higher yield of *n*-dodecane radical cation (RH^{•+}) at sub-nanosecond timescales. This was rationalized by determination of the rate coefficient (k) for the reaction of 1-octanol with RH^{•+}, $k = (1.23 \pm 0.07) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. In contrast, irradiation in the presence of 1-octanol and a 3.0 M HNO₃ aqueous phase afforded significant radioprotection ($d = 0.0054 \text{ kGy}^{-1}$ for zero 1-octanol present vs. $\leq 0.0044 \text{ kGy}^{-1}$ for > 2.5 vol. %) that increases with 1-octanol concentration, relative to the single phase, organic-only solutions. This effect was attributed to the extraction of sufficiently high concentrations of HNO₃ and H₂O into the organic phase by TODGA and 1-octanol as adducts which interfere with the hydrogen atom abstraction process between the 1-octanol radical and TODGA. Our findings suggest that the addition of 1-octanol as a phase modifier will enhance the radiation robustness of TODGA-based separation technologies under envisioned solvent system conditions in the presence of aqueous HNO₃.

Introduction

The diglycolamide (DGA) *N,N,N',N'*-tetraoctyldiglycolamide (TODGA, Fig. 1 A) and its derivatives have found utility as group actinide/lanthanide complexing agents in several proposed scenarios for reprocessing used nuclear fuel (UNF).¹ Owing to the intense radiation field associated with UNF, the effects of radiation on this family of ligands have been the subject of multiple studies to evaluate the corresponding effects on their

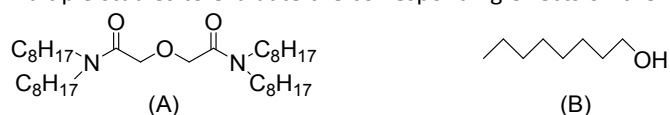


Fig. 1. Molecular structures for *N,N,N',N'*-tetraoctyldiglycolamide (TODGA, A) and 1-octanol (B).

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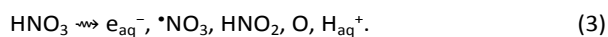
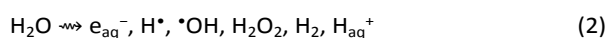
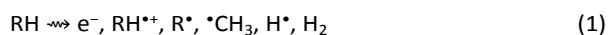
solvent extraction performance.²⁻¹⁴ A great deal of this work has naturally focused on the irradiation of process solvent mixtures that contain DGAs, followed by the measurement of changes in actinide/lanthanide extraction efficiency. For example, Modolo *et al.* reported little or no radiation-induced decrease in either Am or Eu distribution ratios for 0.2 M TODGA in TPH (hydrogenated tetrapropylene; an alkane diluent mixture), when irradiated to a maximum absorbed gamma dose of 600 kGy, in neat organic phase or in contact with a 3.0 M HNO₃ aqueous phase.³ Similarly, for a solvent system containing 0.2 M TODGA and 5 vol. % 1-octanol (Fig. 1 B) in *n*-dodecane diluent, as used in the *i*SANEX (innovative Selective ActiNide EXtraction) process,⁹ gamma irradiation in both batch samples and in a process-scale test loop showed consistently high distribution ratios for Am, Ce, Eu, and Nd to nearly 900 kGy.¹¹ However, in these studies the very high distribution ratios achieved for this TODGA concentration incurred large measurement uncertainty, and thus subtle changes in extraction efficiency may not have been observed.

The ALSEP (Actinide Lanthanide SEparation Process) solvent contains tetra-2-ethylhexyldiglycolamide (TEHDGA), a branched chained TODGA-analogue.¹⁵ When this solvent was irradiated at a lower DGA concentration (0.05 M TEHDGA/0.75 M

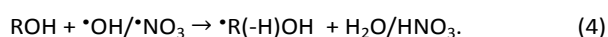
HEH[EHP]/*n*-dodecane) in a process test loop as a biphasic mixture in contact with a 4.0 M HNO₃ aqueous phase, a steady decrease in Am, Ce, and Eu distribution ratios was observed out to the maximum absorbed gamma dose of 850 kGy.¹² However, when this solvent was modified by the addition of 5 vol. % 1-octanol, a much lower change in Am extraction efficiency occurred with absorbed radiation dose, suggesting a DGA radioprotective effect induced by this alcohol.

Extraction efficiency measurements based on distribution ratios, such as those reported above, provide important information about process effects; however, they provide little mechanistic information about the degradation processes occurring. Distribution ratios are a poor proxy for changes in ligand concentration since ligand radiolysis products may also complex and extract metal ions. Among the main radiolysis products in common to all DGAs are compounds resulting from the rupture of the central ether linkage to generate the corresponding acetamides and glycolamides, rupture of the amide N-C bond to generate an acid and the corresponding amine, and rupture of the amine N-C bond leading to dealkylation.^{2,4-6,8,10,13,14} These products have been reported under all investigated conditions, including for the irradiation of long-chain diglycolamides in alkane diluents, short-chain diglycolamides in aqueous solution, and for irradiation of the mixed aqueous/organic phases typical of solvent extraction. Rupture of the amide N-C bond is enhanced by the presence of the aqueous HNO₃ phase, and the resulting organic acids are likely to be metal complexing agents. The lower molecular weight DGAs produced by dealkylation are also potential metal complexing agents. Thus, measurements of the change in DGA concentration with irradiation are important to understanding radiolysis effects, including possible radioprotection.

The addition of 1-octanol to TODGA-based solvent systems was originally adopted to suppress third-phase formation.¹⁶ The presence of the alcohol could also be expected to promote radioprotection by scavenging the deleterious species that originate from direct radiolysis of the organic diluent (*n*-dodecane or TPH, designated RH in the following equations) and aqueous phase water and HNO₃:

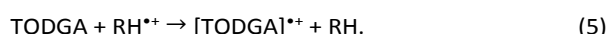


The radiation chemistry of alcohols has been well studied¹⁷ and is characterized by the scavenging of oxidizing radiolysis species such as hydroxyl ($\cdot\text{OH}$) and nitrate ($\cdot\text{NO}_3$) radicals produced in Equations 2 and 3. This mainly occurs through hydrogen-atom (H-atom) abstraction to yield the corresponding carbon-centred alcohol radical ($\cdot\text{R}(\text{-H})\text{OH}$):

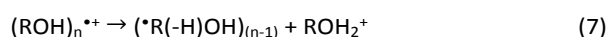
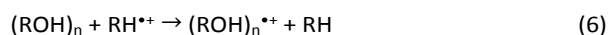


The rates for these scavenging reactions generally increase with increasing alcohol carbon-chain length.¹⁷ Regarding 1-octanol, bimolecular rate coefficients (*k*) have been determined for its reaction with both key aqueous phase oxidizing species: $k(\cdot\text{OH}) = 7.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$,¹⁸ and $k(\cdot\text{NO}_3) = (4\text{--}9) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.^{19,20} However, no such information exists for the reaction of 1-

octanol with the *n*-dodecane radical cation ($\text{RH}^{*\cdot}$), which is considered to be one of the key oxidizing radiolytic transients responsible for ligand degradation in *n*-dodecane diluent based solvent systems.^{8,14,21,22,23,24} The corresponding rate coefficient for $\text{RH}^{*\cdot}$ with TODGA is $k = (9.72 \pm 1.10) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁸



Consequently, 1-octanol must possess a $\text{RH}^{*\cdot}$ rate coefficient of similar magnitude to be able to scavenge a fraction of the available $\text{RH}^{*\cdot}$ yield from direct radiolysis and thus offer some level of TODGA radioprotection. It has been reported that 1-octanol can exist as a combination of alcohol monomers, dimers, and tetramers in non-polar alkane solvents depending on its concentration.²⁵⁻²⁷ The reaction of the $\text{RH}^{*\cdot}$ with any of these species would initially result in a 1-octanol radical cation species ($(\text{ROH})_n^{*\cdot}$) that rapidly deprotonates to yield the corresponding 1-octanol radical ($\cdot\text{R}(\text{-H})\text{OH}_{(n-1)}$).²⁵ This latter species is expected to be reactive, and may also propagate radiolytic degradation through either subsequent reaction with TODGA or via the chemistry of its secondary fragmentation products. Writing the generated 1-octanol species generically as $(\text{ROH})_n$, (*n* = 1, 2, or 4) we have:



This could potentially result in no radioprotection or even enhanced radiolytic TODGA degradation.

Sugo *et al.* performed steady-state gamma radiolysis experiments and quantified TODGA concentration by gas chromatography-mass spectrometry (GC-MS).⁴ The authors determined dose constants²⁸ for TODGA degradation and reported that the rate was increased by the presence of 1-octanol over that for in *n*-dodecane alone. Complimentary pulse radiolysis studies were also performed, and they spectroscopically observed the $\text{RH}^{*\cdot}$ electron transfer reaction with TODGA. This electron transfer process was proposed to be due to the lower ionization potential of TODGA relative to *n*-dodecane, though specific ionization potentials were not given nor measured. The negative effect of 1-octanol on the rate of TODGA degradation was explained by electron transfer reactions with the $\cdot\text{R}(\text{-H})\text{OH}_{(n-1)}$ species. Galán *et al.* also reported increased TODGA degradation in the presence of 1-octanol in TPH.⁵ For organic-only and water pre-equilibrated organic solutions, the presence of 5 and 50 vol. % 1-octanol increased the extent of TODGA degradation and decreased the distribution ratios for Am and Eu extraction. Interestingly, less degradation of TODGA and only slightly lower distribution ratios were measured for the corresponding samples when irradiated after 3.0 M HNO₃ pre-equilibration. This observation suggests that HNO₃ and/or its radiolytic degradation products may interfere with the deleterious effects of 1-octanol, which would be fortuitous as the majority of UNF reprocessing technologies employ HNO₃ in the aqueous phase. However, this latter finding was constrained to a single observation/data point, and thus needs to be more thoroughly evaluated.

Because 1-octanol is expected to be used in the development of new fuel cycle solvents as a phase modifier, it is necessary to specifically address the effect of its presence on TODGA degradation in irradiated solvent systems. Here we present a systematic investigation into the effects of 1-octanol on the radiolytic degradation of TODGA/*n*-dodecane solutions in the presence and absence of 1-octanol and/or a 3.0 M HNO₃ aqueous phase. A combination of time-resolved pulsed electron and steady-state gamma irradiations were employed to measure the reactivity of 1-octanol with RH^{•+} and evaluate the rate of 1-octanol mediated TODGA radiolysis, respectively.

Methodology

Chemicals. *N,N,N',N'*-tetraoctyldiglycolamide (TODGA, 99%) was supplied by Technocomm Ltd (Wellbrae, Scotland, UK). Nitric acid (HNO₃, ≥ 99.999% trace metals basis), *n*-dodecane (≥ 99% anhydrous), 1-octanol (≥ 99% anhydrous), potassium thiocyanate (KSCN, ≥ 99.0% ACS Reagent Grade), and dichloromethane (DCM, ≥ 99.8%) were sourced from Sigma Aldrich. Unless otherwise specified, all solvents for analyses were Fisher (Hampton, NH, USA) Optima LC/MS grade. All chemicals were used as received without further purification. Ultra-pure water (18.2 MΩ cm) was used to prepare all aqueous solutions.

Time-Resolved Pulsed Electron Irradiations. The reaction kinetics for 1-octanol in *n*-dodecane solutions were measured using the Brookhaven National Laboratory (BNL) Laser Electron Accelerator Facility (LEAF).²⁹ Samples were irradiated under aerated conditions in static 1.00 cm Suprasil cuvettes sealed with Teflon stoppers. The doses per pulse ranged from 20–40 Gy as determined by aqueous KSCN dosimetry.³⁰ The time-resolved absorption changes were measured by a FND-100 silicon diode detector and digitized using a LeCroy WaveRunner 640Zi oscilloscope (4 GHz, 8 bit). Interference filters (ca. 10 nm bandpass) were used for wavelength selection of the analysing light. The reaction kinetics of 1-octanol with RH^{•+} was determined by irradiating aerated 0.5 M DCM/*n*-dodecane solutions in the presence or absence of 1-octanol (0, 2.5, 5, 7.5, 10, and 12.5 mM). By following the rate of decay of RH^{•+} at 800 nm and plotting as a function of 1-octanol concentration the associated second-order rate coefficient was calculated.

Steady-State Gamma Irradiations. Static irradiation of 50 mM TODGA/*n*-dodecane solutions and solvent systems in the presence of a range of 1-octanol concentrations (0, 2.5, 5, 7.5, and 10 vol. %) was achieved using the Idaho National Laboratory (INL) Center for Radiation Chemistry Research (CR2) Nordion Gammacell 220E Cobalt-60 Irradiator and a Shepherd 109-68R Cobalt-60 Irradiator at the Notre Dame Radiation Research Laboratory (NDRL). Samples comprised of either an organic phase (*n*-dodecane only) or biphasic systems with a 3.0 M HNO₃ aqueous phase sealed in 5–20 mL screw-cap vials and irradiated under 'deaerated' conditions. Sealed vials were considered deaerated upon exposure to relatively low absorbed gamma doses due to radiolytic-induced consumption of oxygen (O₂). In the absence of agitation, the rate of headspace gas transfer into the liquid phase is slow compared to the radiolytic

loss of O₂ in the liquid, as demonstrated by experiments and calculations for the radiolysis of aqueous formate/formic acid.³¹ Gamma irradiations were performed in triplicate at laboratory room temperature maintained at 20 ± 1 °C. Absorbed gamma doses of up to 500 kGy were attained with dose rates between 3.5 (INL CR2) and 6.2 (NDRL) kGy h⁻¹, as determined by Fricke dosimetry.³² Dose rates were corrected for sample position and volume, radioactive decay (⁶⁰Co, τ_{1/2} = 5.27 years, E_{γ1} = 1.17 MeV and E_{γ2} = 1.33 MeV), and for the lower electron density of *n*-dodecane (0.78 times that of water).³³ The rates of TODGA degradation are expressed as dose constants (*d*); the exponential constant of the equation describing the pseudo-first order concentration change expressed with respect to absorbed dose rather than time, with units of kGy⁻¹.²⁸

TODGA Degradation Quantification. The concentration of TODGA was quantified using gas chromatography with flame ionization detection (GC-FID). The analysis was done using a pair of Agilent (Santa Clara, Ca, USA) 7890 Series II GCs. Separation was achieved using Restek (Bellefonte, PA, USA) Rtx-1 capillary columns (GC1: 30 m × 0.32 mm ID × 0.25 μm df; GC2: 30 m × 0.25 mm ID × 0.25 μm df). For both instruments, a 1:10 split ratio was used with the injector temperature held constant at 300 °C. The initial oven temperature was 100 °C, held for 1 min, then ramped at 15 °C min⁻¹ to 300 °C and then held for another 8 min. The FID was held at 300 °C. Since the two columns differed in their internal diameter, compound retention times were shifted by a small amount; nevertheless, TODGA eluted at ~22 min on both systems.

TODGA samples were analysed in batches corresponding to the absorbed gamma dose received. Each sample was diluted 1:50 in 2-propanol in triplicate prior to analysis. The dilution replicates were analysed in random (computer generated) order, and each was injected in triplicate. The triplicate injections were performed sequentially to minimize drift from sample evaporation after the vial septum was punctured. Thus, for each sample a total of nine injections was performed (three injections for each of three dilution replicates). TODGA was quantified using a seven-point calibration curve (including a blank), spanning 0.0–1.2 mM, equivalent to 0–60 mM prior to sample dilution. All TODGA calibration and quality control (QC) standards were initially prepared gravimetrically. Dilutions were conducted using Drummond Scientific (Broomall, PA, USA) positive-displacement microdispensers, which have lower uncertainty with non-aqueous solvents than air-displacement pipettes. Quality control standards at 0.6, 0.8, and 1.1 mM were injected in the middle and at the end of each batch to ensure there was no instrument drift during the analysis. Separate vials were used for the middle and end QCs to minimize signal changes due to solvent evaporation.

Water Extraction Quantification. The water content of water-saturated solvents of 50 mM TODGA dissolved in *n*-dodecane with 0, 2.5, 5.0, 7.5, and 10 vol. % 1-octanol was determined using Karl-Fischer titration.³⁴ The solvents were contacted with equal amounts of water and shaken for 15 min. The phases were then separated for analysis.

Computations. Electronic structure computations used the Gaussian16 and Gaussview6 programs.^{35,36} All geometries were determined using density functional theory (DFT) with the B3LYP functional and 6-31+G(d) basis set. Solvation was included in all calculations using the polarizable continuum model for *n*-dodecane. Reaction free energies were determined using corrections for standard states.^{37,38}

Results and discussion

Reaction of 1-octanol with the *n*-dodecane radical cation. Kinetics for the reaction of (ROH)_n with RH^{•+} (Equation 6) are shown in Fig. 2, for which a rate coefficient of $(1.23 \pm 0.07) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ was determined. These 1-octanol concentrations were chosen as only the monomer alcohol species is present.²⁷ This reaction is believed to proceed via electron transfer and not proton transfer, based on our computed reaction free energies (ΔG) of -0.12 vs. 0.33 eV, respectively. This rate coefficient is approximately 20% faster than the corresponding value for the reaction of RH^{•+} with TODGA ($k = (9.72 \pm 1.10) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).⁸ This indicates that 1-octanol could readily compete with ligands such as TODGA to scavenge a considerable fraction of the available yield of RH^{•+} and potentially other key radiolysis species, suggesting that addition of 1-octanol would offer some level of radioprotection.

Effect of 1-octanol on TODGA degradation rate. The radiolytic degradation of TODGA under organic-only and biphasic 3.0 M HNO₃ contact conditions as a function of absorbed gamma dose and 1-octanol composition are given in Fig. 3 (A) and (B), respectively. For these much higher 1-octanol

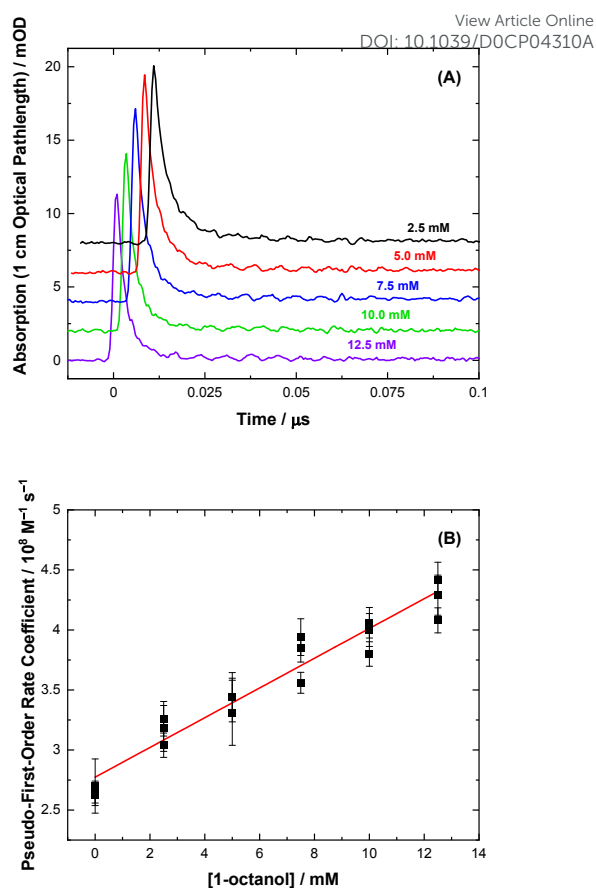


Fig. 2. (A) Measured kinetic traces at 800 nm for pulsed electron irradiated aerated 0.5 M DCM/*n*-dodecane at 24.0 °C. Kinetic traces are offset to aid visibility. Kinetic data were analysed using a double-exponential decay function. (B) Second-order determination of the rate coefficient for the reaction of 1-octanol with RH^{•+}. Individual data points are the faster pseudo-first-order component of the double-exponential fit to the data in (A). The weighted linear fit corresponds to a reaction rate coefficient of $k(\text{ROH} + \text{RH}^{•+}) = (1.23 \pm 0.07) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $R^2 = 0.94$.

concentrations it would be expected that some dimer/tetramer octanol species would also be present.²⁵⁻²⁷

Under both irradiation conditions, TODGA exhibits a pseudo-first-order decay with absorbed gamma dose, in agreement with previous work.²⁻¹² As the concentration of TODGA used here corresponds to a negligible electron fraction of 3.6% in the solvent, most of the radiation energy (96.4%) is directly deposited into the organic diluent promoting radiolysis as described by Equation 1.³⁹ Consequently, TODGA degradation is predominantly driven by indirect radiation effects, and thus its pseudo-first-order decay kinetics are dominated by reaction with an organic radiolysis product, for example the RH^{•+}, Equation 5.⁸ The corresponding dose constants are shown in Fig. 4. It is important to note that prior work did not correct the absorbed doses for the difference in electron density between *n*-dodecane (the irradiation diluent) and water (the dosimetry diluent).³³ The dose constants presented here in Fig. 4. utilized corrected absorbed doses, and thus are a more accurate measurement of TODGA radiolytic integrity. Further, dose constants for the 1-octanol-free

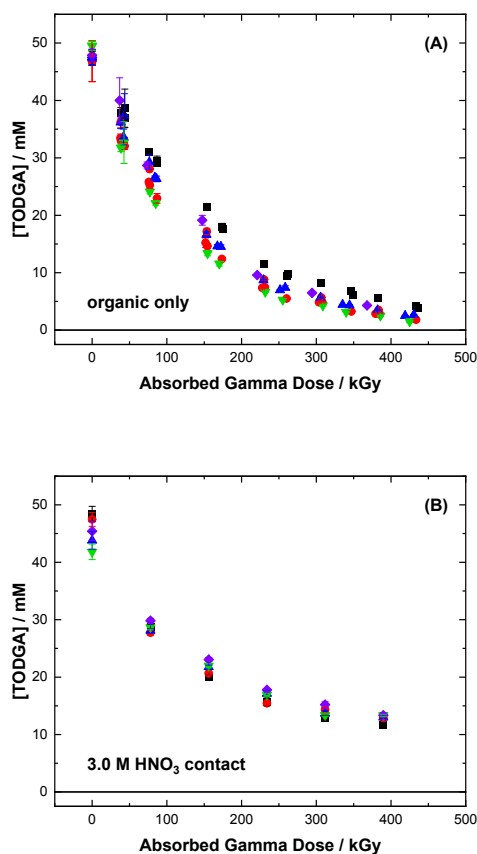


Fig. 3. Gamma radiolysis of formally 50 mM TODGA/*n*-dodecane under organic-only (A) and 3.0 M HNO₃ contact (B) conditions as a function of absorbed gamma dose and 1-octanol composition: 0 (■), 2.5 (●), 5.0 (▲), 7.5 (▼), and 10 (◆) vol. % 1-octanol. Error bars represent 99% confidence intervals.

samples calculated with uncorrected absorbed doses are consistent with prior DGA results.⁸

For the organic-only solutions in Fig. 3 (A) and Fig. 4, the rate of TODGA degradation increased with addition of 1-octanol by 30%. Our results contrast with Sugo *et al.* who reported no change in TODGA dose constants amongst permutations of *n*-dodecane and 1-octanol.⁴ Notwithstanding this difference, our results qualitatively agree that there is no radioprotection in the presence of 1-octanol.^{4,5} The observed effect of 1-octanol inclusion is attributed to the favourable reaction free-energy for hydrogen atom abstraction (Equation 8) vs. radical addition by (*R(-H)OH)_(n-1), calculated here using DFT as -0.31 and 1.78 eV, respectively. While other reactions between TODGA and (*R(-H)OH)_(n-1) may be possible, DFT results support the idea that radiation damage imparted to 1-octanol is transferred to TODGA. However, this rationale does not account for the observed increase in TODGA degradation rates. An explanation for this observation may be found by comparing the scavenging capacities ($k_{SC} = k \times [\text{solute}]$) of 1-octanol and TODGA for RH⁺⁺, given in Table 1.

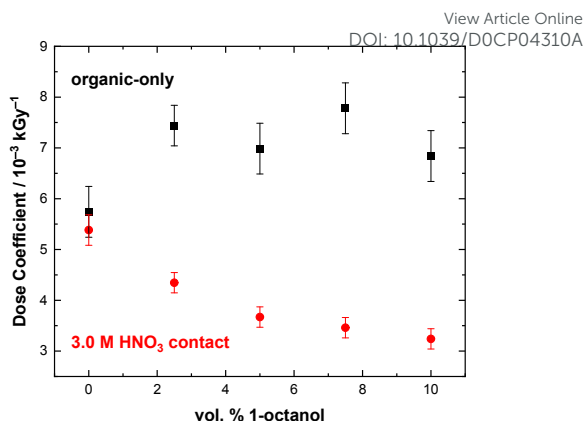


Fig. 4. Comparison of 50 mM TODGA dose constants under organic-only (■) and 3.0 M HNO₃ contact (●) conditions as a function of 1-octanol composition in *n*-dodecane. Error bars represent 99% confidence intervals.

Table 1. Scavenging capacity ($k_{SC} = k \times [\text{solute}]$) of TODGA and monomer 1-octanol in the investigated solution permutations, calculated using their rate coefficients for reaction with RH⁺⁺: $(9.72 \pm 1.10) \times 10^9$ and $(1.23 \pm 0.07) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, respectively.

Concentration of species	RH ⁺⁺ scavenging capacity (s ⁻¹)
50 mM TODGA	$(4.86 \pm 0.55) \times 10^8$
2.5 vol. % 1-octanol (159 mM)	$(1.95 \pm 0.11) \times 10^9$
5.0 vol. % 1-octanol (318 mM)	$(3.91 \pm 0.22) \times 10^9$
7.5 vol. % 1-octanol (476 mM)	$(5.86 \pm 0.33) \times 10^9$
10.0 vol. % 1-octanol (635 mM)	$(7.81 \pm 0.45) \times 10^9$

The lifetime of RH⁺⁺ has been reported as 3-4 ns,⁴⁰ owing to a combination of rapid ion-recombination (RH⁺⁺ + e⁻) and fragmentation processes.⁴¹ In the absence of 1-octanol, the initial yield of RH⁺⁺ is partitioned between decay processes and reaction with TODGA. At 50 mM TODGA, the scavenging capacity of TODGA for RH⁺⁺ is $(4.86 \pm 0.55) \times 10^8 \text{ s}^{-1}$, Table 1, which corresponds to scavenging the available yield of RH⁺⁺ at nanosecond timescales. However, in the presence of ≥ 2.5 vol. % 1-octanol, the sub-nanosecond yield of RH⁺⁺ is now accessible, owing to the higher scavenging capacity ($\sim 2\text{-}8 \times 10^9 \text{ s}^{-1}$) of 1-octanol compared to TODGA, Table 1. In this 1-octanol concentration range varying fractions of monomer, dimer, and tetramer species would be present.²⁵⁻²⁷ While no RH⁺⁺ reaction rate coefficients have been determined for the higher 1-octanol oligomers, their increased size would suggest faster rate coefficient values, but the overall lower species concentrations would give lower overall scavenging capacities. While we cannot quantitatively evaluate these two opposing trends at this time, we believe that the additional RH⁺⁺ scavenged by 1-octanol translates directly to additional TODGA degradation via Equations 8. Thus, as the concentration of 1-octanol is increased, more RH⁺⁺ is converted to (*R(-H)OH)_(n-1), which ultimately increases the rate of TODGA degradation. Unfortunately, no reaction rate coefficient has been reported for Equation 8. Interestingly, the rate of TODGA degradation

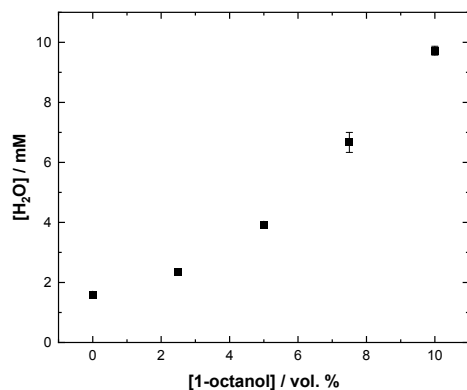


Fig. 5. Concentration of H₂O extracted into 50 mM TODGA in *n*-dodecane after pre-equilibration with DI water (1:1 O:A ratio) as a function of 1-octanol composition.

does not continue to increase with 1-octanol concentration after 2.5 vol. %, suggesting that a maximum RH^{•+} yield was scavenged for the concentrations of 1-octanol used in this work.

TODGA degradation rates were also measured for biphasic solutions of TODGA in *n*-dodecane contacted with a 3.0 M HNO₃ aqueous phase, and, as shown in Fig. 3 (B) and Fig. 4, are similar to those for the organic-only conditions when no 1-octanol is present. This observation is consistent with previous findings^{2,7,8} which reported no obvious effect of HNO₃ on radiation-induced TODGA degradation. Interestingly, the extent of TODGA degradation in biphasic systems is significantly less when irradiated in the presence of 1-octanol. The diametrically different effect of 1-octanol under biphasic HNO₃ conditions compared to organic-only, is attributed to the scavenging of (*R(-H)OH)_(n-1) in the organic phase by extracted HNO₃ and H₂O in the form of TODGA and/or 1-octanol adducts, thereby inhibiting Equation 8. TODGA and 1-octanol are known to extract HNO₃ through the formation of a variety of [(HNO₃)_n•TODGA/1-octanol] adducts.^{42,43} Previous measurements for 50 mM TODGA in Exxsol D80 diluent (a hydrocarbon mixture) found 48 mM HNO₃ was extracted into the organic phase from a 2.9 M HNO₃ aqueous phase.⁴³ Further, we found that 50 mM TODGA in *n*-dodecane also extracts 1.59 mM H₂O from pure H₂O into the organic phase, as shown in Fig. 5, presumably forming similar [(H₂O)_n•TODGA] adducts. In the absence of 1-octanol, the amount of [(HNO₃/H₂O)_n•TODGA] adducts is insufficient to interfere with RH^{•+} related processes, Equation 5. However, like TODGA, 1-octanol also contributes to the extraction of HNO₃ and H₂O as adducts,^{43,44} the extent of which increases with 1-octanol concentration. For example, for 50 mM TODGA and 5 vol. % 1-octanol in TPH or Exxsol D80 contacted with a 3.0 M HNO₃ aqueous phase, 70 mM HNO₃ was measured in the organic phase.⁴³ We also found that 3.93 mM H₂O was extracted for 50 mM TODGA and 5 vol. % 1-octanol in *n*-dodecane contacted with H₂O, Fig. 5. The additional [(HNO₃/H₂O)_n•1-octanol] adducts in the presence of 1-octanol are sufficiently high enough in concentration to scavenge (*R(-H)OH)_(n-1) and preserve a fraction of the TODGA relative to organic-only conditions. This may occur via a sacrificial mechanism similar to that reported for CMPO,⁴⁵⁻⁴⁷ ultimately

converting (*R(-H)OH)_(n-1) into relatively less reactive *NO and *OH.^{17,48} Therefore, the TODGA radioprotection trend shown in Fig. 3 (B) and Fig. 4, is a consequence of progressively more HNO₃ and H₂O being extracted into the organic phase as TODGA/1-octanol adducts with increasing 1-octanol concentration, in turn facilitating more extensive scavenging of (*R(-H)OH)_(n-1), thereby preserving a greater fraction of TODGA.

In summary, these findings suggest that the addition of 1-octanol as a phase modifier will also enhance the radiation robustness of TODGA-based separation technologies under envisioned solvent system formulation conditions using an aqueous HNO₃ phase.

Conclusions

The presence of 1-octanol in irradiated organic-only solution has been shown to enhance the degradation rate of TODGA in *n*-dodecane. This is attributed to the energetically favourable (-0.31 eV) reaction between TODGA and the 1-octanol radical, which may be produced by both direct alcohol radiolysis, or by reaction with the *n*-dodecane radical cation ($k = (1.23 \pm 0.07) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). Further, scavenging capacity calculations showed that the yield of 1-octanol radicals produced by reaction with the *n*-dodecane radical cation was much higher than the yield of radical cation reaction with TODGA directly. Thus, the higher yield of 1-octanol radicals produced by this reaction pathway increased the rate of TODGA degradation. However, in the presence of 1-octanol and an aqueous HNO₃ phase the rate of TODGA degradation was lower than for the pure organic solution. This is attributed to HNO₃ and H₂O in the organic phase extracted as TODGA/1-octanol adducts which interfere with the hydrogen atom abstraction process between the 1-octanol radical and TODGA. This result is fortuitous for the use of TODGA in UNF reprocessing, which is conducted in highly radioactive mixed phase solutions.

Conflicts of interest

There are no conflicts to declare.

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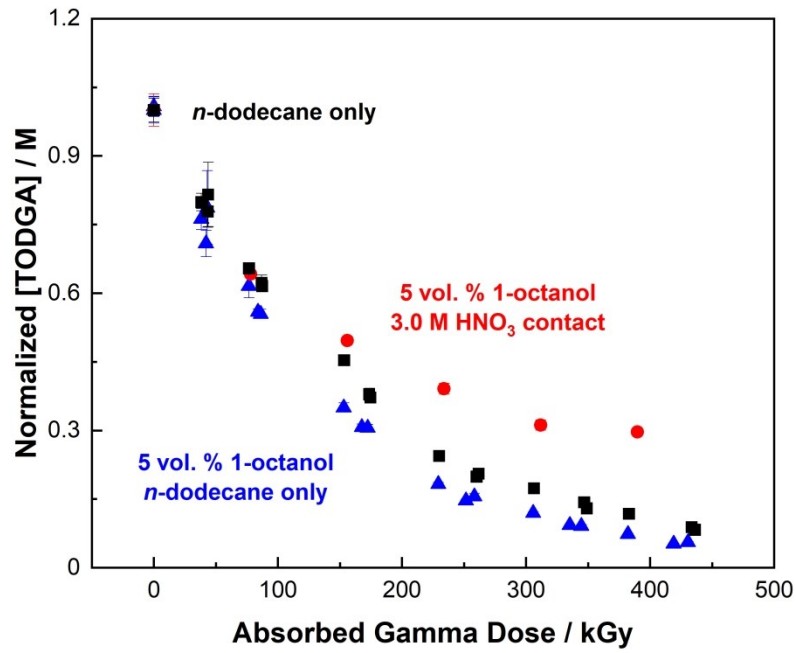
Pulsed electron irradiations reported herein were performed using the BNL LEAF of the BNL Accelerator Center for Energy Research, supported by the US-DOE Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under contract DE-SC0012704.

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