Radiolytic Stability of TODGA: Characterization of Degraded Samples under Different Experimental Conditions

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Abstract

The radiolytic stability of TODGA (N,N',N''-tetraoctyldiglycolamide), which is considered one of the extractants with higher possibilities to be applied for nuclear hydrometallurgical partitioning processes, has been studied in this paper against gamma radiation. Several irradiation experiments have been carried out both, at different experimental conditions and solvent formulations, to know their influence on the ligand stability. After qualitative analysis by HPLC-MS, the identified degradation products were synthesised to verify the assigned structures, to test their extraction properties, and to quantify them in all degraded TODGA samples.

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1. Introduction

The new reactor concepts under development will be able to re-use most of the U, Pu, and the minor actinides (MA: Am, Np, Cm) and to get them it is necessary to develop suitable partitioning processes [1]. So far, TODGA (N,N,N',N''-tetraoctyldiglycolamide) is considered one of the extractants with higher possibilities to be applied to...
industrial scale, since it has demonstrated most of the required needs for processes development. Some partitioning processes for advanced fuel cycles are based on TODGA, and most of them have been developed in the framework of the ACSEPT Project, such as: DIAMEX based on TODGA [2], 1cycle-SANEX [3], and GANEX (Group ActiNide EXtraction) [4].

To evaluate the applicability of solvents for process development, it is necessary to demonstrate not only their good extraction properties, but also their degradation resistance, since the organic phase is in contact with highly radioactive solutions and high nitric acid concentrations. The solvent degradation leads to undesirable effects such as decrease of selectivity, third phase formation, etc. Therefore, it minimizes the regeneration of the used solvent, increasing the volume of the secondary wastes and the process cost. Most often, the new species generated have extracting properties that markedly differ from those of the original ligands.

In the literature it can be found studies about TODGA stability [5-7]. Nevertheless, in most of them solvent degradation was directly related to the variation of distribution ratios and the remaining amount of ligand, but it is not explored from a structural point of view. Detailed information about TODGA structural degradation, in different diluents considered for industrial processes is missing. Only, in a Sugo’s et al. and Mincher et al. works [5-6] it can be found information about structural degradation of TODGA.

Herein it is described a complete characterisation of TODGA degraded solvents, irradiated by external $^{60}$Co sources under different experimental conditions, to explore how and why the experimental conditions affect on the ligand stability and the amounts and proportions of subproducts formed during irradiation. Analytical methods based on LC-MS have been used to identify and quantify the degradation products. Specifically, Atmospheric Pressure Ionization (API) has been used, which is a general weak ionisation mode that allows identifying the molecular weight of subproducts. The identified degradation products were synthesised to verify the assigned chemical structures, to test their trivalent lanthanides (Ln(III)) and actinides (An(III)) extraction properties, and to quantify them in the different degraded TODGA samples. A better understanding of structural stability rules it is possible with the results obtained.

2. Experimental

2.1. Synthesis

All compounds were synthesised at UAM or ICIQ laboratories. TODGA was synthesised in multi-gram scale, modifying an existing literature procedure [8-9]. Compounds I-VI were prepared according to the procedure described in a previous work [10] and compounds VII-IX as is described following. All reagents were used from commercially available sources without further purification.

$N,N,N'$-trioctyldiglicolamide (VII): A mixture of N-octylamine (0.19 g, 1.48 mmol) and compound II [10] (0.550 g, 1.48 mmol) was prepared in a 35 mL MW container. The vessel was sealed and introduced into the MW oven. The reaction was programmed at 155°C for 25 min by using a 5 min temperature ramp. Then, the mixture was extracted with CH$_2$Cl$_2$ (2x10 mL). The organic phase was washed with HCl 1 mol/L (1x10 mL), brine (1x10 mL), and dried (MgSO$_4$). The solvent was eliminated under reduced pressure, and the residue was purified by column chromatography (silica gel; (98:2)%vol CH$_2$Cl$_2$/MeOH) to give VII as yellow oil (0.35 g, 50%). $^1$H-NMR (CDCl$_3$, 400 MHz, 25ºC). δ (ppm) = 7.73-7.64 (sa, 1H, NHCO), 4.22 (s, 2H, CH$_2$O), 4.06 (s, 2H, CH$_2$O), 3.33-3.25 (m, 4H, CH$_2$N), 3.09 (t, $^3$J(H,H) = 7.8 Hz, 2H, CH$_2$NH), 1.53-1.52 (m, 6H, CH$_2$CH$_2$N), 1.35-1.17 (sa, 30H, CH$_2$), 0.90-0.86 (m, 9H, CH$_3$). $^{13}$C-RMN (75 MHz). δ (ppm) =: 169.4, 168.2 (C O), 72.1, 69.7 (O C H$_2$), 46.9, 46.3 (NCH$_2$), 39.1 (NHCH$_2$), 31.9 29.6, 29.4, 29.3, 27.1(CH$_2$), 14.1 (CH$_3$).

2-Hydroxy-N-octylacetamide (VIII): Prepared following the same procedure as for compound VII, from N-octylamine (0.51 g, 3.93 mmol) and methylglicolate (0.35 g, 3.93 mmol). The reaction was programmed at 155°C for 30 min by using a 5 min temperature ramp. The residue was purified by column chromatography (silica gel; (97:3)%vol CH$_2$Cl$_2$/MeOH) to give VIII as an oil (0.65 g, 88%). $^1$H-RMN (CDCl$_3$, 300 MHz, 25°C).
δ(ppm) = 8.00 (s, 1H, NHCO), 4.42 (s, 2H, CH₂OH-CO), 3.34-3.14 (m, 2H, CH₂), 1.58-1.40 (m, 12H, CH₂), 1.38-1.13 (m, 12H, CH₂CH₂N), 0.85 (t, J(H,H) = 6.4 Hz, 3H, CH₃). 13C-RMN (CDCl₃, 75 MHz, 25°C). δ(ppm) = 171.0 (CO), 62.1 (C₆H₁₂O), 39.2 (C₆H₁₂N), 31.9, 29.32, 29.26, 27.0, 22.7 (CH₂), 14.1 (CH₃).

N-octylacetamide (IX): Prepared following the same procedure as for compound VII, from N-octylamine (0.26 g, 2.00 mmol) and acetic acid (0.14 g, 2.40 mmol). The reaction was programmed at 160°C for 15 min by using a 5 min temperature ramp. The residue was purified by column chromatography (silica gel; (97:3) %vol CH₂Cl₂/Methanol) to give IX as yellow oil (0.21 g, 60%). ¹H-RMN (CDCl₃, 300 MHz, 25°C). δ(ppm) = 5.60 (sa, 1H, NHCO), 3.29-3.12 (m, 2H, CH₂N), 1.96 (s, 3H, CH₃), 1.56-1.39 (m, 2H, CH₂CH₂N), 1.33-0.97 (m, 10H, CH₂). 0.86 (t, J(H,H) = 6.4 Hz, 3H, CH₃). ¹³C-RMN (75 MHz, CDCl₃, 25°C). δ(ppm) = 171.0 (CO), 59.7 (C₆H₁₂O), 46.1, 45.8, (C₆H₁₂N), 31.8, 29.6, 29.28, 29.21, 27.0, 22.7 (CH₂), 23.3, 14.1 (CH₃).

2.2. Stability studies: sample preparation and irradiation procedures

Mixtures of TPH (hydrogenated tetrapropylene), an industrial diluent, and octanol were used as diluents (100)%vol TPH, (95:5)%vol TPH/octanol or (50:50) %vol TPH/octanol). Ultrapure water (18 MΩ/cm) was used for aqueous solutions. Three different types of samples were prepared for irradiation and aging control: 1/ without any diluent (raw); 2/ using dry diluents; and 3/ using diluents pre-equilibrated. TODGA was dissolved in the corresponding diluent up to 0.1 mol/L. Dry diluents were prepared removing residual water by the addition of activated 4 Å molecular sieves (5 days). The diluents pre-equilibration was performed twice (5 min, at room temperature) by mixing 600 μL of both solutions, organic and aqueous (3 mol/L HNO₃ or pure H₂O). Both phases were separated by centrifugation at 5000 rpm. Organic phases (500 μL) were conditioned in glass vials with Teflon screw caps. Samples for aging control were kept in the laboratory during the irradiation process. Irradiation was performed at CIEMAT Náyade irradiation facility, which is a pool 1.2 m² by 4.5 m deep. It consists of 60 sources of 60Co, distributed in six lots with total activity of 1.1x10¹⁴ Bq. The irradiation container used provides homogeneous irradiation flux. TODGA samples were irradiated up to 100 kGy and 1000 kGy at 2.5 kGy/h dose rate.

2.2.1. Distribution ratios determination

The behaviour of An(III) and Ln(III) was simulated by ²⁴¹Am (1000 Bq/mL) and ¹⁵²Eu (1000 Bq/mL), respectively, supplied as MCl₃, in HCl 1 mol/L, by Isotope Products Laboratories, California (USA). The extraction experiments were performed immediately after the irradiation, by mixing for 15 min, 500 μL of both, aqueous and organic solutions. Both phases were separated by centrifugation at 5000 rpm and 400 μL of each phase were spiked and conditioned into a 5 mL glass vials for high energy gamma spectrometry measurements, using the γ-lines at 59.5 keV and 121.8 keV for ²⁴¹Am and ¹⁵²Eu determination, respectively. The distribution ratios (D₃₅) were calculated as [M(III)]org/[M(III)]aq relation.

2.2.2. HPLC-APCI⁺ measurements procedure

Samples were characterised by HPLC-MS methods, using APCI⁺ (Atmospheric-pressure chemical ionization) which is a specific type of API, at UAM laboratories. Measurements were performed with a C-8 Zorbax column and CH₃CN/H₂O/HCO₂H(0.1%vol) as mobile phase. Samples were analysed without pre-evaporation and diluted up to 0.2 mmol/L in a (90:10)%vol MeOH/octanol mixture. Calibration curves (0.05-0.5 mmol/L) were performed with TODGA and each degradation product. All measurements were repeated twice.

3. Results and Discussion

TODGA samples were irradiated with external ⁶⁰Co sources under different solvent conditions: raw and in different TPH/octanol mixtures (100)%vol, (95:5)%vol and (50:50)%vol. Due to different behaviours observed
previously for diglicolamides (DGAs) \cite{5,10}, and to understand the influence of water and nitric acid presence during the irradiation, solvent formulations were used as following: dry, pre-equilibrated with water or with 3 mol/L nitric acid.

After irradiation, the Am(III) and Eu(III) extraction with all degraded TODGA samples was assessed. The $D_M$ values, obtained with all aging control samples, are similar than those obtained with fresh TODGA samples.

Otherwise, no significant differences were observed between aging control samples and those which were irradiated at 100 kGy. Therefore only results obtained with samples irradiated at 1000 kGy irradiation are discussed in this paper.

After irradiation at 1000 kGy, Am(III) and Eu(III) $D_M$ values decrease in all irradiated samples (Fig.1.). As expected the minimum effect was observed in samples irradiated raw (without diluent). The $D_M$ values obtained with samples irradiated in solution show that the highest extraction occurs in samples dissolved in 100\% TPH, suggesting that the presence of octanol affects negatively the stability of TODGA, which is in agreement with previous papers \cite{5,7}. Comparing the data obtained with the different pre-treatments used, for 100\% TPH there are only small differences between them, whether the solvent is dry or pre-equilibrated with water or nitric acid. However, when TPH/octanol mixtures are used, $D_M$ values change depending on the pre-treatment. For both formulations containing octanol, the highest $D_M$ values are obtained when solvents are pre-equilibrated with nitric acid. On the other hand, when solvents are dry or pre-equilibrated with water, $D_M$ values decrease dramatically. These results suggest that the presence of nitric acid during the irradiation has a protective effect on the TODGA molecule.

![Fig. 1. Am(III) and Eu(III) $D_M$ values by freshly and irradiated TODGA samples in different solvents. Organics: 0.1 mol/L of TODGA in 100\%vol TPH, (95:5)\%vol TPH/octanol or (50:50)\%vol TPH/octanol. Aqueous: $^{241}$Am and $^{152}$Eu in 3 mol/L HNO$_3$.](image)

In the qualitative HPLC-MS analysis of all irradiated TODGA samples the same nine degradation compounds have been identified, although they are formed in different proportions depending on the experimental conditions (Fig. 2.). Four of them (I, II, IV and V) are in agreement with those previously described by Sugo et al. \cite{5}. The main degradation products found in the irradiated samples are compounds IV and V. Fig. 2. a) shows that in the absence of nitric acid the chromatographic peak of TODGA is slightly detected, but when nitric acid is present, this chromatographic peak is clearly defined and intense. Similar results were obtained for all diluents studied and suggest again the protective role previously assigned to the presence of the nitric acid during the irradiation (Fig.1.). Moreover, chromatograms show that the relative amounts of main degradation products IV and V depend on the pre-treatment, particularly on the presence or not of nitric acid.
In the analysis of the TODGA samples for aging control, small chromatographic signals corresponding to compounds I, II and III were identified, mainly in samples pre-equilibrated with nitric acid since these compounds are formed by hydrolytic degradation, which is favoured in acid medium. All these qualitative results are in good agreement with previous reports describing TODGA stability against hydrolysis [5-7].

The identified degradation compounds were synthesised and their structures were verified by HPLC-APCI+. Am(III) and Eu(III) extraction by each synthesised degradation compound was assessed using the reference conditions (0.1 mol/L ligand, (95:5)% vol TPH/octanol pre-equilibrated with 3 mol/L nitric acid). The $D_M$ values obtained are much lower than those obtained with fresh TODGA samples, only $D_M$ values for I, IV and VII are higher than 0.1 (Fig. 2. b). These results explain why the irradiated TODGA samples lose their Am(III) and Eu(III) extraction properties, on the contrary that bis-DGA compounds, and particularly UAM-069, 2-[[($',N'$-dioclyl carbamoyl)methoxy]-N-{3-[[2-($''$,N''-dioctylcarbamoyl) methoxyacylamino]methyl]benzyl]acetamide [10], which maintains its extraction properties after irradiation, since some of UAM-069 degradation products extract Am(III) and Eu(III) effectively.

Calibration curves were performed by HPLC-MS for TODGA and each synthesised degradation product and the concentration of all of them was calculated in each samples.

The concentration of TODGA, for all aging control samples, is higher than 0.08 mol/L, indicating that the hydrolytic degradation itself is not significant, which are in agreement with previous qualitative experiments and reported studies [5-7].
In the case of irradiated samples (Fig. 3.), there is an important decrease of TODGA concentration after 1000 kGy integrated dose and the main degradation products are IV and V. Concentration of compounds I, II, VI, VII and VIII is under the detection limit (<0.001 mol/L). The highest TODGA concentration is observed for samples irradiated without any diluent (raw samples). When diluents are pre-equilibrated with nitric acid, a higher concentration of TODGA is found for samples diluted in (50:50)%vol TPH/octanol, which is the mixture with higher nitric acid concentration. If we compare data from samples irradiated under the same pre-treatment, in presence of nitric acid, the main degradation compound is always IV, however, when there is no nitric acid the main degradation compound is fragment V, and TODGA is dramatically degraded.

![Graph showing concentration of TODGA and compounds III, IV, V, IX in the different TODGA irradiated samples (up to 1000 kGy) and the corresponding DM values.](image)

Fig. 3. Concentration of TODGA and compounds III, IV, V and IX in the different TODGA irradiated samples (up to 1000 kGy) and the corresponding DM values. Samples 1: 100%vol TPH. Samples 2: (95:5)%vol TPH/octanol. Samples 3: (50:50)%vol TPH/octanol.

All these studies indicated a protective role of nitric acid on DGA stability. Therefore, samples of TODGA in (95:5)%vol TPH/octanol are being irradiated pre-equilibrated with 0.5 to 5 mol/L HNO₃ to explore the effect of the different nitric acid concentration in the organic phase during the irradiation.

Moreover, all these results would indicate that compound IV, which has a 2-hydroxacetamide group, is stabilized by nitric acid since it does not degrade into fragment V. Therefore, to understand the reasons of this behaviour, similar irradiation experiments have been carried out for compounds IV and V separately. In that case, it is observed that fragment IV is quite stable and degraded into acetamide V mainly in absence of nitric acid. Compound V is practically unaffected by gamma radiation, so acetamide groups look quite stable.

Otherwise, to know if the protection is due to the presence of protons or nitrates ions, TODGA degradation is being studied in presence of different ions, using HNO₃, NaNO₃, HClO₄ and NaClO₄.

4. Conclusions

The HPLC-MS analysis of the irradiated TODGA samples showed that, after 1000 kGy, there is an important decrease of TODGA concentration, especially in absence of nitric acid, and it is broken into nine degradation compounds (I-IX). Distribution ratios obtained with compounds I-IX were very low, which explains that TODGA degraded samples do not maintain its extraction properties.
The final concentration of TODGA and the relative proportion of the main degradation compounds (IV and V) depend on the pre-treatment used. In the presence of nitric acid, the main degradation compound is 2-hydroxiacetamide IV and the TODGA concentration is halved, however, when there is no nitric acid the main degradation compound is acetamide V, and TODGA is dramatically degraded. These results confirm the protective role assigned to the presence of the nitric acid during the irradiation.

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