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Radiolytic stability of pillar[5]arene-based diglycolamides

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Abstract: Radiolytic stability of pillar[5]arene-based diglycolamides (P5DGAs) against gamma irradiation up to 1000 kGy adsorbed dose was studied. The results reveal the increase of radiation damage degree on P5DGAs with dose. The radiolysis products of P5DGAs including the gaseous and solid products were fully characterized by ^1H NMR, HR-ESI-MS, GC, and HPLC techniques. It was found that the main radiolytic gas products of P5DGAs under argon are H_2 , N_2 , CO and gaseous hydrocarbons. The solid degradation products contain phenolic hydroxyl groups and secondary amine groups. In addition, solvent extraction toward Eu(III) was performed with P5DGAs, in which about 50% decrease on extraction efficiency was observed for irradiated P5DGAs with dose of 1000 kGy in comparison with the non-irradiated one. A radiolytic degradation pathway was also proposed based on the above results. This is the first time to investigate the radiolytic stability of neat P5DGAs and P5DGAs in molecular diluent in detail and provides useful information for further application of P5DGAs in practical applications for spent fuel reprocessing.

Keywords: diglycolamides; gamma irradiation; pillar[5]arene; radiolytic degradation; solvent extraction.

1 Introduction

Pillararenes, a new intriguing class of macrocycles discovered in 2008 by Ogoshi et al., have been the focus of considerable researches because of their facile synthesis, unique structural architectures, efficiency in metal ion

separation and host-guest chemistry [1–5]. Pillar[5]arenes are made up of dialkoxybenzene units linked by methylene bridges at the 2,5-positions, which resemble calixarenes in structural unit but have symmetric pillar conformation. Benefiting from their relatively rigid structure and diverse functionalization on each portal, pillararenes have been recognized as ideal molecular platform to pre-organize metal chelating groups, making them as promising candidates for metal ion separation [6, 7]. In recent years, it has been reported that pillar[5]arenes functionalized with phosphine oxides (PO) [8], carbamoylmethylphosphine oxides (CMPO) [9] and *N,N*-dimethyldithiocarbamoyl modified pillar[5]arenes [10] present excellent performance as extractants for lanthanide/actinide separation or Mercury removal.

Diglycolamides (DGAs) as multidentate extractants are considered to be one of the most efficient extractants for the separation of trivalent lanthanides and actinides from PUREX high active raffinates or dissolved spent nuclear fuel [11–15]. A series of diglycolamide-functionalized extractants such as DGA-functionalized task specific ionic liquids [16, 17], tripodal DGA (T-DGA) [18–20] and DGA-functionalized calix[4]arenes [21–23] have been extensively studied for Ln(III)/An(III) separation from acidic feeds. Inspired by the finding that pillar[5]arenes serve as an excellent preorganization platform for metal complexation [8, 9] and the outstanding performance of DGAs in Ln(III)/An(III) separation [24, 25], our group synthesized pillar[5]arene-based diglycolamides, where 10 DGAs moieties were introduced onto the pillar[5]arene framework in 2014. Notably, P5DGAs exhibit highly efficient extraction and separation ability for Eu(III) and Am(III) partitioning in 1-octanol from aqueous acidic solution. The distribution coefficients (D_{Eu}) of three P5DGAs ligands ($[L] = 10^{-3}$ M) with different spacer lengths in 1 M HNO_3 reach 25.7–127. Greater extraction efficiency of these ligands was observed in ionic liquid ($\text{C}_8\text{minNTf}_2$) system. At 1 M HNO_3 , the D_{Eu} values of the three P5DGAs ($[L] = 5 \times 10^{-4}$ M) in $\text{C}_8\text{minNTf}_2$ are 865–7803, which are 36–61 times higher than those in 1-octanol system [26, 27]. These results demonstrate the great potential of P5DGAs as promising candidates for nuclear waste remediation.

In the actual post-treatment for nuclear waste based solvent extraction, the extractant ligand is dissolved in organic diluents and contacted with spent nuclear fuel dissolved in an

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aqueous acidic solution to extract desirable elements. The extractants will inevitably be exposed to radiation field generated by radionuclides decay [28]. Radiation on organic phase may result in radiolytic degradation of extractants, giving lower metals mass-transfer coefficients, reduced distribution ratios and separation factor due to the generation of unwanted complexing products, as well as deterioration of solvent performance. In view of this, study on the radiolytic stability of P5DGAs is important to assess their application feasibility in nuclear fuel recycle [13, 29–32].

Recently, we found that the skeleton of the alkylated pillar[5]arenes and phosphine oxide functionalized pillar[5]arenes was stable to a great extent when the dose of electron beam was lower than 100 kGy, indicating that the excellent radiation stability of pillar[5]arene [32, 33]. Although the radiolytic stability of P5DGAs in ionic liquids was reported by Arijit et al., they only investigated the effect of gamma irradiation on the Pu^{4+} extraction ability of P5DGAs/ $\text{C}_8\text{mimNTf}_2$ systems. It was found that the P5DGAs/ $\text{C}_8\text{mimNTf}_2$ systems are radiolytically stable for the extraction of Pu^{4+} and the extraction efficiency decreased by 51% at most after irradiation at a dose of 1000 kGy. To the best of our knowledge, no systematic study on radiolytic stability of neat P5DGAs or solutions of P5DGAs in molecular diluent 1-octanol has been reported, and the corresponding radiolysis mechanism still remains unknown [30]. Thus, it is necessary to explore radiolytic behavior of P5DGAs and the possible changes in the extraction behavior upon gamma irradiation.

In this work, we report on the results of radiation stability of three P5DGAs **1a–c** (Figure 1) irradiated by ^{60}Co source to a dose ranging from 0 to 1000 kGy. Since the P5DGAs contain five repeating units, the acyclic analog of P5DGAs (**2a**), serving as a control compound, was also assessed for its radiation stability under the same condition. The radiolytic degradation rate of P5DGAs under different dose was investigated by HPLC and ^1H NMR spectroscopy, and the main resulting radiolytic products were identified by high-resolution ESI-MS and GC. Extraction experiments were also carried out to evaluate the extraction properties of irradiated **1a–c**. This study represents the first attempt to study the radiolytic degradation of neat P5DGAs and P5DGAs in a molecular diluent.

2 Experimental

2.1 Materials

Compounds **1a**, **1b** and **1c** were prepared as previously reported [26]. Compound **2a** was synthesized as a control compound. The molecular

Figure 1: Chemical structures of pillar[5]arene-based diglycolamides (P5DGAs) **1a–c** and control compound **2a**.

structures of these compounds were confirmed by ^1H NMR and ESI-MS spectroscopy. **1a** was chosen as the representative compound for radiolytic degradation study. Deuterated solvents including CDCl_3 and CD_3OD were purchased from Cambridge Isotope Laboratories (CIL). The organic reagents used in the synthesis and analysis were purchased from Energy Chemical, China. Solvents used in the optical spectroscopic studies were HPLC grade. Ultrapure nitric acid and ultrapure water were used for preparing nitric acid solutions. All other solvents were analytical-grade reagent and used without further purification.

2.2 Irradiation

The samples were irradiated (298 ± 4 K) using a ^{60}Co source with an average dose rate of *ca.* 50 Gy/min (Irradiation Preservation Technology Key Laboratory of Sichuan Province, Sichuan Institute of Atomic Energy, Chengdu 610101, China). The dose rate was calibrated by potassium (silver) dichromate dosimeter. Radiolytic degradation experiments involved the irradiation of samples, composed of (1) neat **1a** in an air or argon atmosphere (2) neat control compound **2a** in an air or argon atmosphere (3) a 0.1 M solution of **1a**/1-octanol, **1b**/1-octanol and **1c**/1-octanol in an air atmosphere. The dose of irradiated samples was accumulated to 50, 100, 200, 500, 800, and 1000 kGy, respectively.

2.3 Characterization

The ^1H NMR spectra were measured with a Bruker AVANCE AV II-400 MHz spectrometer at a constant temperature of 298 K. High resolution electrospray ionization-mass spectrometry (HRESI-MS) data

were obtained by WATERS Q-TOF Premier. Mass analysis was performed in positive ionization mode (70 eV). Weighed quantities of **1a** and **2a** were subjected to thermogravimetric analysis (TGA) using a DTG-60(H) instrument, and the samples were heated from room temperature to 800 °C with 10 degrees per minute under in an air atmosphere. The samples were analyzed on high-performance liquid chromatography system (HPLC, SPD-20A, Japan) with a with a positive phase silica gel column (Hypersil GOLD Slica Dim, 5 µm, 250 × 4.6 mm). A mixture of dichloromethane and methanol at a ratio of 92:8 for one was used as mobile phase with a flow rate of 1.0 mL/min. Detection was performed with a UV-Vis diode array detector at the wavelength of 285 nm. Samples were diluted by dichloromethane and the injection volume was 10 µL. The data from three injections were averaged. The radiolytic gas products of irradiated samples were analyzed on GC2002 gas chromatography. A thermal conductivity detector (TCD) and a TDX-13 × 5A column were used to measure H₂ and N₂ concentrations. A flame ionization detector (FID), TDX-01 column and Al₂O₃ capillary column were used to measure CO, CO₂, CH₄, C₂H₄ and C₂H₆, respectively. The carrier gas was high purity argon with the flow rate of 500 mL/min. Inductively coupled plasma optical emission spectroscopy (ICP/OES, PerkinElmer ICP optima 8000) was used to determine the europium ion concentrations of the aqueous phase.

2.4 Extraction studies

Solvent extraction procedure follows the reported work [34]. The organic phase contains ligand **1a–1c** (5×10^{-6} M) in 1-octanol. All organic phases were pre-equilibrated by mixing with an equal volume of nitric acid solution (1.0 M) with continuously shaking for 2.5 h before extraction. The aqueous phase contains Eu³⁺ (5×10^{-5} M) at 1.0 M nitric acid. A 1 mL aliquot of each phase was thoroughly mixed by mechanically shaking in a stoppered glass tube at (25 ± 1) °C for 4 h, which has been proven to be long enough to reach the extraction equilibrium [26]. After equilibration, the tubes were centrifuged at 2000 rpm for 5 min. 0.5 mL aliquot of aqueous phase was removed into a volumetric flask using micro syringe and was then diluted to 5 mL for ICP-OES test (with a detection limit below 0.01 ppm). The distribution ratio (*D*) values could be calculated from the concentration of the aqueous phase before and after:

$$D = \frac{C_i - C_f}{C_f}$$

where, C_i and C_f are the initial and final concentration in the aqueous phases. All the experiments were carried out in triplicate.

3 Results and discussion

3.1 Thermogravimetric analysis

Thermal stability of irradiated extractants could be used to reflect the degradation under irradiation condition [33]. Thus, the thermal stability of irradiated **1a** was probed by

TGA, and the result was compared with that of unirradiated **1a**.

As shown in Figure 2, the degradation processes of all samples mainly present two stages. The first distinct thermal weight loss of unirradiated **1a** and irradiated **1a** in the TG curves is observed at 200–420 and 150–420 °C, respectively. In this stage, the weight loss reaches 64.13% for original **1a**, 64.17% for irradiated **1a** in argon, and 65.43% for irradiated **1a** in air, which is close to the theoretical value 65.23% calculated by the formula weight of 10 diglycolamide groups. Thus, the first distinct thermal weight loss could be a result of the degradation of diglycolamide groups on P5DGAs. The second weight loss occurs between 420 and 580 °C due to the breakage of the P5DGAs skeleton, which is similar to our previous observation on irradiated phosphine oxide functionalized pillar [5]arenes [33]. The thermal degradation rate of the three samples follows the order of unirradiated **1a** > irradiated **1a** in argon > irradiated **1a** in air, indicating that gamma irradiation lowers the thermal stability of P5DGAs.

3.2 Analysis of radiolytic degradation products

The structures of different organic species present in the radiolysis products of pillar[5]arene-based diglycolamides were subject to several characterization techniques including ¹H NMR, ESI-MS, GC and HPLC.

Figure 2: TG curves of unirradiated neat **1a** and irradiated ones under different atmosphere.

3.2.1 Proton NMR analysis

The NMR experiments of irradiated **1a** at different dose were performed. The ^1H NMR spectra are presented in Figure 3a. Almost no chemical shift is witnessed at the dose below 200 kGy. As the dose is over 200 kGy, several new small signals show up at 9.41, 8.20, 8.12, and 4.77 ppm, respectively, and the intensity increases along with the increase of dose. The results above indicate a remarkable structure change of ligand **1a** after irradiation. The signal at 9.41 ppm is assigned as phenolic hydroxyl groups [35–37]. The other two new signals at 8.20 and 8.12 ppm are ascribed to $-\text{NH}$ groups [21], which are generated by **1a** losing isopropyl groups. Because the degradation products containing $-\text{NH}$ groups, which are produced by removing one isopropyl group from each side chain, account for a small portion in the total radiolytic degradation products of **1a**, only the signals of very low intensity at 8.20 and 8.12 ppm are observed. The strong signal at 7.96 ppm before irradiation corresponds to the $-\text{NH}$ of the amide groups close to the portal of the pillar[5]arene. After irradiation, a small part of **1a** degrades to the species containing $-\text{NH}(\text{CH}(\text{CH}_3)_2)$ group which resonates at a lower field (8.20 and 8.12 ppm), thereby leading to the different chemical shifts of $-\text{NH}$ groups in **1a** before and after irradiation. Furthermore, the assignment of phenolic hydroxyl and secondary amine signals was confirmed by methanol- d_4 (CD_3OD) exchange experiments. All the three new signals disappear with the addition of CD_3OD (Figure 3b). In contrast, the signal at 4.77 ppm remains unchanged with the addition of CD_3OD , indicating that the hydrogen at 4.77 ppm is not an active hydrogen and is assigned as alkoxy groups according to its chemical shift. The addition of deuterated methanol gives rise to the enhancement of solvent polarity and the formation of hydrogen bond between deuterated methanol and $-\text{NH}$ group [38], which leads to a considerable downfield shift of $-\text{NH}$ signal (7.96–8.13 ppm, see Figure 3b). Based on the NMR spectroscopy analysis, the radiolytic products containing phenolic hydroxyl and secondary amine groups are formed during irradiation, which implies the breakage of pillar[5]arenes-based diglycolamides skeleton to some extent under high-dose irradiation.

3.2.2 GC analysis

Due to the less radiolysis degradation of **1a** and **2a** at low irradiation dose, it is difficult to qualitative and quantitative analyses of the trace gaseous radiolytic products. Therefore, the gaseous radiolytic products of **1a** and **2a** irradiated at 1000 kGy dose were analyzed by using gas chromatography. As shown in Figure 4, the main gaseous

radiolytic products of **1a** under air are CO , CH_4 , C_2H_4 and C_2H_6 except for the undetected hydrogen and nitrogen, while those under argon are H_2 , N_2 , CO , CH_4 , C_2H_4 , C_2H_6 without CO_2 . Heller and Gordon [39, 40] reported that isopropyl radical rearrangement can form gaseous hydrocarbons such as C_2H_6 and C_3H_6 . Thus, the formation of gaseous hydrocarbons of ligand **1a** and **2a** is mainly due to the rearrangement of isopropyl radicals. In addition, the type of radiolytic gas products of **1a** is identical to that of **2a**, suggesting that the similarity of the degradation pathway of these two ligands.

Table 1 lists the amount of gas radiolytic products produced by irradiated samples at 1000 kGy in this study. The amounts of CH_4 , C_2H_4 and C_2H_6 produced by irradiated **1a** in argon are 10.2, 11.6 and 2.5 times those of the gas radiolytic products in air, respectively. The amounts of gaseous hydrocarbons produced by irradiated **1a** in argon are much more than those of in air. The similar phenomenon is also observed in irradiated **2a**. During the irradiation process,

Figure 3: (a) ^1H NMR spectra of the irradiated **1a** (400 MHz, CDCl_3) at different doses; (b) Methanol- d_4 exchange experiment of **1a** (400 MHz, CDCl_3).

Figure 4: GC analysis of gas radiolytic products from neat **1a** and **2a** irradiated at 1000 kGy. (a) Gas chromatography of CO and CO₂; (b) Gas chromatography of H₂, N₂, CH₄, C₂H₄ and C₂H₆.

oxygen could easily produce oxidizing free radicals and ozone [41, 42], which will affect the radiolysis pathway of extractants. The oxygen in the air will impede the radiolysis pathway of P5DGAs, leading to the less generation of gaseous hydrocarbons. It is concluded that irradiation atmosphere plays a vital role in the radiolysis of **1a**.

3.2.3 Quantitative analysis by HPLC

Three irradiated ligands **1a–c** are employed for high performance liquid chromatography analysis of the extent of degradation to which radiolytic decomposition proceeds. The HPLC chromatograms of irradiated solution of **1b**/1-octanol with a dose range from 0 to 1000 kGy are shown in Figure 5. The first peak with the shortest retention time (ca. 3.8 min) represents the P5DGAs (**1b**) molecule. Compared with the chromatogram of unirradiated **1b**, a new peak (ca. 6.4 min) appears in the chromatogram of irradiated **1b**/1-octanol at 50 kGy. The peak area of the new peak gradually increases with dose. It implies that the degradation degree of P5DGAs increases with dose. It is consistent with result from ¹H NMR experiment.

In order to assess the degradation rate quantitatively, the ratio of ligands **1a–c** concentration before and after irradiation as a function of dose was measured by HPLC using external standard method. Figure 6 shows the degradation trend of ligands **1a–c** against the radiation dose. At the dose range of 0–1000 kGy, the residual of

ligands **1a–c** decreases with dose and the degradation rate gradually slows down. Degradation rates of **1a–c** exhibit a few different at the low dose. However, the radiation resistance of each irradiated samples is obviously different at the dose exceeds 200 kGy. In the case of a 27% gap appears between solution of **1a**/1-octanol and **1c**/1-octanol at 1000 kGy. The longer chain is inclined to result in easy breakage of pillararene framework with dose. This phenomenon is in agreement with the irradiated alkylated pillar[5]arene and phosphine oxide functionalized pillar[5]arenes [32, 33]. An 18% gap is also observed between neat **1a** and solution of **1a**/1-octanol at 1000 kGy, indicating that the presence of 1-octanol affects negatively the stability of **1a**. This could be ascribed to the sensitization

Figure 5: HPLC chromatograms of irradiated ligand solution of **1b**/1-octanol in air at different doses.

Table 1: Amount of gas radiolytic products of neat **1a** and **2a** after gamma irradiation at a dose of 1000 kGy in different atmospheres.

Samples	Atmosphere	mmol/L						
		H ₂	N ₂	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆
1a	Air	Not determined	Not determined	1.656	3.155	2.080	0.592	0.115
	Argon	1.409	10.985	1.206	0	21.115	7.020	0.292
2a	Air	Not determined	Not determined	1.299	2.872	1.199	0.375	0
	Argon	1.533	10.329	1.263	0	29.525	8.078	0.347

Figure 6: C/C_0 of **1a–c** at different doses.

effect of 1-octanol on the radiolysis of **1a** [43–45]. It should be noted that these ligands still remain more than 30% even 57% when the dose is up to 500 kGy, *viz.*, pillar[5]arene-based diglycolamides exhibit good radiation stability at dose less than 500 kGy.

3.2.4 Qualitative analysis by ESI-MS

Electrospray ionization mass spectrometry (ESI-MS) was chosen as the measurement technique to identify

degradation products of irradiated samples. To avoid the complexity of pillar[5]arenes in mass spectra, compound **2a**, which is similar to **1a** in constitutional structures, was tested to elucidate a possible pathway of the degradation.

As shown in Figure 7, three intense signals ($m/z = 633.33$, $m/z = 617.35$ and $m/z = 595.37$) of irradiated **2a** are assigned to $[2a + K]^+$ (theoretical $m/z = 633.33$), $[2a + Na]^+$ (theoretical $m/z = 617.35$) and $[2a + H]^+$ (theoretical $m/z = 595.37$), respectively. For most of these radiolytic degradation products, reasonable structures are inferred based on simple homolytic cleavage of the parent structure, followed by capping of the resultant radical [46]. The rupture of the chemical bond between amide and alkyl on **2a** gives rise to products **A**, **B**, **B'**, **D** and **E**. Species **A** ($m/z = 553.33$) is generated by the cleavage of one $C_{isopropyl}-N$ bond of **2a**. It should be noted that the different species **B** ($m/z = 511.28$) and **B'** ($m/z = 511.28$) with the identical mass-to-charge ratio could be obtained by the losing of two isopropyl groups from same side chain and different side chain in **2a**, respectively. The peak at $m/z = 396.25$ is assigned to the species **D** formed from the $C_{carbonyl}-N$ breakage of the initial molecule. Species **E** ($m/z = 354.20$) is produced by the above two bond cleavage modes. Besides, the cleavage of $C_{carbonyl}-CH_2$ bond should generate the species **C** ($m/z = 424.21$). With the information retrieved from m/z values of the major fragments, the degradation product pathway of **2a** was given in Figure 8.

As illustrated in Figure 9a, three intense signals of irradiated **1a** correspond to multi-charged ions, all of which are

Figure 7: HRESI-MS spectrum of irradiated **2a** at 1000 kGy.

Figure 8: Proposed pathway for the radiolytic products of **2a**. (a) Generation of species **A**, **B**, **C**, **D** and **E**; (b) Generation of species **B'**.

attributable to an adduct of the molecule with protons and alkali cations. Peaks at $m/z = 1536.40$, $m/z = 1528.41$ and $m/z = 1517.42$ are assigned to $[1a + H + K]^{2+}$ (theoretical $m/z = 1536.40$), $[1a + H + Na]^{2+}$ (theoretical $m/z = 1528.41$) and $[1a + 2H]^{2+}$ (theoretical $m/z = 1517.42$), respectively. Previous reports reveal that the main ruptures of diglycolamide-based compounds (such as *N,N,N',N'*-tetraoctyl diglycolamide, TODGA) take place in $O_{ether}-CH_2$ and $C_{carbonyl}-N$ bonds under irradiation [44, 45, 47]. Indeed, Species **1** ($m/z = 1465.84$) and **2** ($m/z = 1457.83$) are formed by the cleavage of $O_{ether}-CH_2$ bond. Peaks at $m/z = 1417.84$ and $m/z = 1347.29$ are assigned to species **4** and **7**. These two species are formed from the cleavage of $C_{carbonyl}-N$ bond. Species **5** ($m/z = 1396.34$) is produced by the breakage of one of the 10 appending arms attached to the pillararene framework. Synchronous cleavage $C_{carbonyl}-N$ and $C_{isopropyl}-N$, $C_{carbonyl}-N$ and $O_{ether}-CH_2$, from either one of two rims of pillar[5]arene framework results in the original molecule to yield a fragment ions of $m/z = 1446.86$ (species **3**) and $m/z = 1366.29$ (species **6**), respectively. In addition, species **8** ($m/z = 1317.79$) is generated by the loss of one of 10 arms accompanied by the cleavage of $O_{ether}-CH_2$. The result of species **5** and **8** containing phenolic hydroxyl groups is consistent with the result of 1H NMR experiments. The signal of degradation products produced by the rupture of two $C_{isopropyl}-N$ bonds was not found in the mass spectrum of irradiated **1a** (Figure 9), indicating that this degradation product was scarcely formed in the radiolysis of **1a**. With the information retrieved from m/z values of several major fragments, the schematic representation of

the radiolytic degradation of **1a** was proposed accordingly (Figure 10). Similar to the cleavage sites in irradiated TODGA [47], the major sites for radiolytic attack are also $O_{ether}-CH_2$, $C_{isopropyl}-N$ and $C_{carbonyl}-N$ bonds in P5DGAs molecules. Generally, radiolytic degradation of the P5DGAs leads to the formation of fragments such as the pillar[5]arene skeleton, de-alkylation, de-amination, and ether linkage cleaved products.

3.3 Solvent extraction studies

To evaluate the effect of gamma irradiation on the extraction ability of extractants, the D_{Eu} values under different dose were investigated by solvent extraction experiment. As shown in Figure 11, the distribution ratios of Eu(III) decrease with the increase of dose, indicating that the radiolytic degradation of **1a–1c** increases with dose. The D_{Eu} values of unirradiated ligands **1a–1c** are 8.31, 16.12 and 20.51, which are similar to the result that we reported before [26]. When the dose up to 500 kGy, the D_{Eu} values of **1a**/1-octanol, **1b**/1-octanol and **1c**/1-octanol decrease to 1.40, 1.47 and 0.99, respectively. Compared with the D_{Eu} values of irradiated samples **1a**/1-octanol and **1b**/1-octanol, the D_{Eu} values of irradiated **1c**/1-octanol are higher at dose ranging from 0 to 500 kGy, which may be attributed to the radiolytic products of **1c** having better affinity towards Eu(III). The extraction ability of solutions **1a–1c**/1-octanol is almost lost with the dose up to 1000 kGy. In contrast, only 20–50% decrease in the

Figure 9: Expanded HRESI-MS spectra of irradiated neat **1a** at 1000 kGy. (a) Magnification of the $m/z = 1400\text{--}1560$ region; (b) Magnification of the $m/z = 1310\text{--}1405$ region (the peak intensity in the top figure is magnified four times).

extraction efficiency towards Pu^{4+} is observed for solution **1a–1c**/ $C_8mimNTf_2$ at 1000 kGy [30]. This indicates that the radiolytic stability of solvent system P5DGAs/ $C_8mimNTf_2$ is better than that of P5DGAs/1-octanol. It is noteworthy that when the dose is up to 500 kGy, the pillar[5]arene-based diglycolamides still show about 50% efficiency towards Eu^{3+} . The maximum radiation dose during

actinide partitioning from actual high-level nuclear waste depends on the design of the contactor and the flow rates of the aqueous and organic streams and may not exceed a few hundred kGy in each cycle [15]. It suggested that the extractants pillar[5]arene-based diglycolamides hold potential practical application for spent fuel reprocessing in a few cycles of continuous use.

Figure 10: Proposed pathway for the radiolytic degradation of 1a. (a) Generation of species 1, 2 and 8; (b) Generation of species 3, 6 and 7; (c) Generation of species 4 and 5.

Figure 11: Distribution ratio of Eu^{3+} by irradiated **1a–c** under different irradiation conditions. Aqueous phase: $5.0 \times 10^{-5} \text{ Eu}^{3+}$ in 1.0 M HNO_3 , organic phase: $5.0 \times 10^{-4} \text{ M 1a–c}$ in 1-octanol.

4 Conclusion

In conclusion, the radiolytic stability and thermal stability of three pillar[5]arene-based diglycolamides (neat **1a** and **1a–1c** in molecular diluent) were investigated by various techniques including ^1H NMR, TG, GC, HPLC and ESI-MS. Owing to the sensitization effect of 1-octanol on P5DGAs radiolysis, the P5DGAs dissolved in 1-octanol present a worse radiolytic stability in comparison with the neat P5DGAs. Based on the analysis by both high-resolution ESI-MS and ^1H NMR, dealkylation of the isopropyl chain and breakage of amide or ether linkage on P5DGAs lead to the formation of radiolytic products containing secondary amine and phenolic hydroxyl groups. Additionally, the gas radiolytic products of P5DGAs were confirmed to be H_2 , N_2 , CO and gaseous hydrocarbons. The amount of gaseous hydrocarbons for P5DGAs in an argon atmosphere is much higher than that in an air atmosphere. Based on the analysis of the radiolytic products of P5DGAs and control compound **2a**, the possible pathway of their radiolytic and chemical degradations was proposed, from which the degradation is speculated to occur at the most vulnerable bonds associated with ether and amide moieties of the diglycolamide functional groups, including $\text{O}_{\text{ether}}\text{--CH}_2$, $\text{C}_{\text{carbonyl}}\text{--N}$, and $\text{C}_{\text{isopropyl}}\text{--N}$ bonds. Results from the solvent extraction experiments reveal that P5DGAs still show about 50% efficiency towards Eu^{3+} at 500 kGy. The present study provides useful information for understanding the mechanism of irradiation-induced degradation of P5DGAs, which is helpful for designing new extractant with excellent radiation stability for spent fuel reprocessing.

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