

Assembled diglycolamide for f-element ions sequestration at high acidity



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ABSTRACT

Diglycolamides (DGA) form reverse-micellar type of supramolecular aggregates upon equilibration with a nitric acid solution that enhances DGA affinity extraordinary towards f-elements. To mimic DGA aggregates, DGA molecules have been preorganized on chemical platforms to form assemblies having a good affinity towards f-elements. However, the synthetic procedures used are quite laborious that limits their large scale applications. To address this problem, a new DGA-bearing monomer *N,N*-dioctyl,*N'*-propyl-2-methylacrylamide diglycolamide has been synthesized. This DGA-methacrylate monomer can be polymerized easily, and shows an interesting affinity towards f-element ions both in monomeric and polymeric forms at high nitric acid concentrations. This makes it very promising for the development of fixed-site membranes, resins, and magnetic assemblies for a variety of applications. DGA-methacrylate monomer has been found to assemble on magnetic nanoparticles Fe₃O₄. DGA-methacrylate coated Fe₃O₄ particles capture representative trivalent actinide ²⁴¹Am with a very high efficiency. However, it has been observed that HNO₃ induced preorganization of DGA-methacrylate plays an important role in sorption of f-element ions in the polymeric form and self-assembled molecules on the magnetic nanoparticles.

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1. Introduction

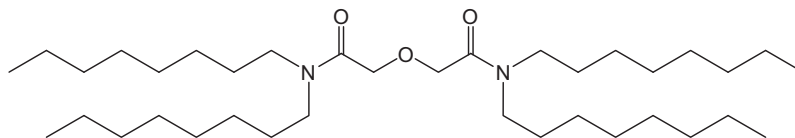
Nuclear waste treatment is at present one of the most important ecological problems faced by nuclear energy industries. The solution to this problem not only involves development of an efficient method for high level waste partitioning and disposal but also isolation and determination of radionuclides from a variety of complex aqueous matrices [1]. The ligands have been anchored on silica support for selective sequestration of actinides and fission products from aqueous media [2–5]. Actinide selective ligands have also been anchored on superparamagnetic Fe₃O₄ particles to develop magnetic-sorbents [6–11]. The magnetically assisted chemical separation has become one of the promising methods for removal of the toxic metal ions from aqueous solution. The magnetic-sorbents have larger surface area, can be quickly recovered from the medium using an external magnetic field, and liquid waste is not generated. However, sorption selectivity

and efficiency of these materials towards targeted radionuclides have still scope for improvement.

The affinity of diamides towards f-element ions is highly dependent on the molecular structure of the bridge between the two amide groups. The bridges that make a diamide to chelate with f-elements ions have been found to be methylene groups (malonamides or succinamides), an oxygen (diglycolamides) or a sulphur atom (thiadiglycolamides) [12,13]. The ether linkage makes a diglycolamide (DGA) as tridentate ligand having a high extractability for trivalent actinides [14,15]. Since nitric acid promotes the complexation of diglycolamides with f-element ions, this class of extractants, especially *N,N,N',N'*-tetraoctyl diglycolamide (TODGA), shown in Scheme 1, has been explored extensively for partitioning of minor actinides from the radioactive high-level liquid wastes at high nitric acid concentrations [14,15]. Small angle neutron scattering (SANS), small angle X-ray scattering (SAXS), and vapor pressure osmometry (VPO) studies have indicated that diglycolamides in *n*-dodecane form reverse-micellar type of supramolecular aggregates containing four ligand molecules upon equilibration with nitric acid solutions [16–18]. The supramolecular DGA aggregates have an extraordinary affinity towards Ln(III)/An(III,IV) ions in solutions having high nitric acid concentrations as normally encountered in the nuclear reprocessing plants [15]. DGA

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Scheme 1. Chemical structure of *N,N,N',N'*-tetraoctyl diglycolamide (TODGA).

molecules have been anchored on different chemical platforms to form DGA assemblies. Zhu et al. observed that the ionic radii of the cations affect the efficiency of their extraction by TODGA. It has been observed that all monovalent metal ions, divalent ions with ionic radii smaller than 80 pm, trivalent ions with ionic radii smaller than 70 pm, tetravalent ions with ionic radii smaller than 60 pm and pentavalent ions are weakly extracted by TODGA from nitric acid [19]. The strongly extracted ions ionic radii are 100 pm for divalent ions, 87–116 pm for trivalent ions and 83–105 pm for tetravalent ions [19]. The ionic radii of Ln(III), An(III), and An(IV) ions are in this range, and DGA can thus coordinate strongly with trivalent and tetravalent Ln and An ions.

DGA groups have been preorganized on trialkylphenyl and calix[4]arene platforms and also as bisdiglycolamide [20–22]. These studies clearly demonstrated that preorganization of DGA units on a molecular platform enhances the extraction of Am(III) and Eu(III). Therefore, it would be very interesting to study how DGA groups behave in the polymer chains and self-assembly on superparamagnetic particles. The DGA-containing polymers and superparamagnetic DGA-functionalized nanoparticles are not only of interest for designing new strategies for actinide partitioning [23], but also for developing chemical sensors [24] and preorganized multidentate sequestering agents for actinides in biological systems [25].

In the present work, *N,N*-dioctyl, *N'*-propyl-2-methylacrylamide diglycolamide (methacryloyl-DGA) monomer was synthesized to study the actinide extractability of DGA in the polymeric form and as self-assembly on Fe₃O₄ nanoparticles. The methacryloyl-DGA was polymerized along with cross-linker by UV-initiator induced bulk polymerization. The f-element ions extraction studies were carried out using a conventional solvent extraction method for monomer methacryloyl-DGA and TODGA dissolved in a *n*-dodecane and 1-decanol mix solvent. For poly(methacryloyl-DGA) and methacryloyl-DGA coated Fe₃O₄, solid phase extraction studies were carried out using appropriate radiotracers of f-element ions.

2. Experimental

2.1. Synthesis and characterization of methacryloyl-DGA

2.1.1. General

All moisture-sensitive reactions were carried out under an argon atmosphere. The solvents (LPS solvents, Zoetermeer, The Netherlands) and all reagents (Sigma Aldrich) were obtained from commercial sources and used without further purification. All known compounds viz. *N,N'*-dioctyldiglycolamic acid (**1**) [26] and *N,N'*-dibenzyl-3-aminopropane (**2**) [27] were prepared according to literature procedures. Solvents were dried according to standard procedures and stored over molecular sieves. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Unity INOVA (300 MHz) spectrometer in CDCl₃. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) chemical shift values are reported as δ using the residual solvent signal as an internal standard. Electrospray Ionization (positive mode) high resolution mass spectra were recorded on a WATERS LCT mass spectrometer. Analytical TLC was performed using Merck prepared plates (silica gel 60 F-254 on aluminium). Column

chromatography was carried out with Merck silica gel 60 (230–400 mesh).

2.1.2. Dibenzylaminopropyl-DGA (**3**)

A mixture of *N,N'*-dioctyldiglycolamic acid (**1**) (5.00 g, 13.9 mmol), and *N,N'*-dibenzyl-3-aminopropane (**2**) (3.55 g, 13.9 mmol), triethylamine (1.50 g, 15.0 mmol), *N,N*-dicyclohexylcarbodiimide (DCC) (3.00 g, 14.5 mmol), and 1-hydroxybenzotriazole (HOBT) (1.96 g, 14.5 mmol) in chloroform (150 mL) was stirred for 2 days at room temperature. The solvent was evaporated and the resulting solid dissolved in *n*-hexane (100 mL). After filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO₂, ethyl acetate) to obtain compound **3** (5.73 g, 69%) as an oil. The chemical structure and purity were confirmed by characteristic chemical shifts in the ¹H NMR spectrum (δ 0.82–0.96 (6H, m, CH₃), 1.16–1.36 (20H, m, CH₃(CH₂)₅), 1.44–1.58 (4H, m, NCH₂CH₂), 1.87 (2H, pentet, *J* = 6.4 Hz, OCH₂CH₂), 2.67, 3.07 (2H, t, *J* = 7.5 Hz, NCH₂), 3.29 (4H, t, *J* = 7.5 Hz, NCH₂), 3.76 (4H, s, ArCH₂), 4.11 (2H, t, *J* = 6.4 Hz, OCH₂), 4.02, 4.16 (2H, s, OCH₂), 7.21–7.39 (10H, m, ArH), 7.91 (1H, broad singlet, NH)) and ¹³C NMR spectrum (δ 14.1, 22.6, 26.9, 27.6, 28.9, 29.2, 31.8, 37.2, 46.2, 46.8, 50.8, 58.3, 69.4, 71.7, 126.9, 128.2, 128.9, 168.1, 169.4). The experimental *m/z* 594.4703 [M + H]⁺ obtained from HRMS was in good agreement with the calculated *m/z* 594.4635 for C₃₇H₆₀N₃O₃.

2.1.3. Aminopropyl-DGA (**4**)

A solution of dibenzylaminopropyl-DGA (**3**) (5.00 g, 8.4 mmol) in ethanol (150 mL) in the presence of 10% Pd/C (0.5 g) was kept under an atmosphere of H₂ for 24 h. After removal of the catalyst by filtration, the solvent was evaporated under reduced pressure to obtain compound **4** as an oil in quantitative yield. Compound **4** was characterized by ¹H NMR (δ 0.81–0.94 (6H, m, CH₃), 1.17–1.40 (20H, m, CH₃(CH₂)₅), 1.42–1.61 (4H, m, NCH₂CH₂), 1.67 (2H, pentet, *J* = 6.4 Hz, OCH₂CH₂), 2.75 (2H, t, *J* = 7.5 Hz, NCH₂), 3.08 (2H, t, *J* = 7.5 Hz, NCH₂), 3.30 (4H, t, *J* = 7.5 Hz, NCH₂), 3.39 (2H, t, *J* = 7.5 Hz, NCH₂), 4.06, 4.22 (2H, s, OCH₂), 7.91–8.01 (1H, m, NH)), ¹³C NMR (δ 13.99, 22.5, 26.7, 27.5, 29.1, 31.7, 32.5, 36.2, 39.1, 46.1, 46.7, 69.5, 71.7, 168.1, 169.7), and HRMS (*m/z* 414.3651 [M + H]⁺; calculated: 414.3696 for C₂₃H₄₈N₃O₃).

2.1.4. Methacryloyl-DGA (**5**)

To a solution of an aminopropyl-DGA (**4**) (7.45 g, 18.0 mmol) and triethylamine (2.00 g, 19.8 mmol) in dichloromethane (120 mL) was added a solution of methacryloyl chloride (2.61 g, 25.0 mmol) in dichloromethane (20 mL) at 0 °C. The reaction mixture was brought to room temperature and stirred overnight. The solvent was evaporated under reduced pressure and the residue was dissolved in ethyl acetate (100 mL). The resulting solution was washed successively with 10% NaHCO₃ solution (8 × 100 mL) and water (2 × 100 mL). The organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure to obtain pure **5** (7.2 g, 83%) as an oil. Compound **5** was characterized by ¹H NMR (δ 0.75–0.93 (6H, m, CH₃), 1.11–1.36 (20H, m, CH₃(CH₂)₅), 1.39–1.59 (4H, m, NCH₂CH₂), 1.71 (2H, pentet, *J* = 6.0 Hz, NHCH₂CH₂), 1.98 (3H, s, CH₃-methacryl), 3.08 (2H, t, *J* = 7.5 Hz, NCH₂),

3.23–3.34 (4H, m, NCH₂-octyl, NHCH₂), 3.35–3.41 (2H, m, NHCH₂), 4.08, 4.25 (2H, s, OCH₂), 5.31, 5.79 (1H, s, =CH₂), 7.05–7.17, 8.15–8.26 (1H, m, NH)), ¹³C NMR (δ 14.1, 18.6, 22.6, 26.8, 27.6, 28.9, 29.1, 31.7, 35.7, 46.3, 46.8, 53.4, 69.7, 71.9, 119.5, 139.9, 168.3, 170.6) and HRMS (*m/z* 482.4011 [M + H]⁺; calculated: 482.3958 for C₂₇H₅₂N₃O₄).

2.2. Preparation of poly(methacryloyl-DGA)

Methacryloyl-DGA was polymerized to form a crosslinked polymer. The required amounts of methacryloyl-DGA, ethylene glycol dimethacrylate (EGDM) (10 mol% of monomer) and α-α'-dimethoxy-α'-phenyl acetophenone (2 wt% of monomer) were dissolved in a minimum volume of DMF. EDGM and α-α'-dimethoxy-α'-phenyl acetophenone were obtained from Sigma–Aldrich and used as obtained. The polymerizing solution was homogenized by ultrasonication for two min. This homogenized polymerizing solution was irradiated in a multi-lamp photoreactor with 365 nm light for 15 min. The UV multi-lamp photoreactor used was procured from Heber Scientific, Chennai, India (model No. HML-SW-MW-LW-888) fitted with eight 8 W mercury UV lamps (Sankyo Denki, Japan); the sample was placed at the centre. After polymerization, the solid fraction was separated and soaked in boiled water for 1 h. The cross-linked polymer was washed repeatedly with 1-decanol solution to dissolve the un-polymerized monomer, and subsequently dried in a vacuum oven. The yield was determined gravimetrically and the chemical structure of the polymer was confirmed by ¹H NMR.

2.3. Self-assembly of methacryloyl-DGA on Fe₃O₄ nanoparticles

Methacryloyl-DGA was coated on Fe₃O₄ particles having 20–30 nm size (obtained from J.K. Impex, Mumbai, India) in a mixture of 10:1 *n*-dodecane and 1-decanol. For this, 0.1 g of Fe₃O₄ was dispersed in 1.5 mL of 0.1 mol L⁻¹ methacryloyl-DGA. The coating was also carried out after equilibrating a methacryloyl-DGA solution with 3 mol L⁻¹ HNO₃ for a known period of time. These solutions containing Fe₃O₄ were constantly agitated for 30 min at room temperature (or 40 °C) using a constant temperature shaking bath, and then for 16 h at room temperature under static conditions. Subsequently, the solutions were centrifuged and the supernatant was discarded. Finally, the coated Fe₃O₄ particles were washed 4–5 times with methanol, and dried under vacuum at room temperature.

2.4. Extraction experiments

For solvent extraction experiments, 0.5 mL of organic phase containing the required concentration of extractant (TODGA/methacryloyl-DGA) was pre-equilibrated with 0.5 mL of the aqueous phase, containing the same HNO₃ concentration as in the aqueous phase to be studied for Ln/An extraction, for 30 min at room temperature with constant shaking in a temperature bath. After pre-equilibration, the aqueous phase was discarded after centrifugation. This pre-equilibrated organic phase was equilibrated with the same volume of aqueous phase having the same HNO₃ concentration with the appropriate activity of desired Ln/An ions. After equilibration, the aqueous and organic phases were separated by centrifugation, and 0.3 mL samples of both organic and aqueous phases were taken for radioactivity counting. The isotopes used in the experiments were ²⁴¹Am(III), ²³³U(VI), ²³⁹Pu(IV), and ¹⁵⁴Eu(III). The oxidation state of the Pu isotopes was adjusted to Pu(IV) using NaNO₂. The radioactivity of ²⁴¹Am and ¹⁵⁴Eu was counted by γ-spectrometry using a NaI(Tl) detector coupled to a multichannel analyzer. Upon addition of the samples to cocktail-O, the radioactivity of ²³³U(VI) and ²³⁹Pu(IV) was counted by liquid

scintillation counting. The composition of cocktail-O was: 2,5-diphenyloxazole (10 g), 1,4-bis-2-(5-phenyloxazolyl)benzene (0.25 g), and naphthalene (100 g) in 1000 mL of toluene, and 5 v/v% bis(2-ethylhexyl) phosphoric acid (HDEHP). The liquid scintillation counting was carried out in a home built liquid scintillation counter. The extraction studies for poly(methacryloyl-DGA) and methacryloyl-DGA coated on Fe₃O₄ were carried out in a similar fashion, except that a weighted amount (0.03 g) of solid phase was taken, and the radioactivity of the aqueous phase before and after equilibration was used to determine the distribution coefficient (*D*) value. The pre-equilibration and equilibration of the solid phase with the aqueous phase (1.5 mL) was carried out for 2 h.

The *D* values for liquid–liquid extraction systems were obtained as the mean ratios (average of 4 experiments) of the radioactivity or concentration of f-element ions in organic to aqueous phases. The *D* value involving a liquid–solid phase system was obtained using the following equation:

$$D = \frac{(C_0 - C_e)}{W} \times \frac{V}{C_e} \quad (1)$$

where *C*₀ and *C*_e represent the radioactivity of an f-element initially and after equilibration in the aqueous phase, *W* and *V* were the weight of the solid phase (poly(methacryloyl-DGA) or methacryloyl-DGA coated Fe₃O₄) and the volume of the equilibrating aqueous phase, respectively.

2.5. De-sorption experiments

For the de-loading experiments, the determined ²⁴¹Am radioactivity was loaded in a known volume/weight of methacryloyl-DGA (0.05 mol L⁻¹ in a 10:1 mixture of *n*-dodecane and 1-decanol), methacryloyl-DGA coated Fe₃O₄, and poly(methacryloyl-DGA). The radioactivity loaded in samples was obtained from the difference of the total radioactivity before and after equilibration in the aqueous phase. The de-loading experiments were carried out using a 0.02 mol L⁻¹ disodium salt of EDTA solution in water (0.5 mL) with constant shaking for 5 h at room temperature (27 °C) or at elevated temperature (45 °C). The de-loading efficiency was obtained using the following equation:

$$\text{Desorption}(\%) = \frac{C_d}{C_l} \times 100 \quad (2)$$

where *C*_d and *C*_l are the radioactivity of ²⁴¹Am recovered in 0.02 mol L⁻¹ disodium salt of EDTA solution and the radioactivity of ²⁴¹Am loaded in the sample from 3 mol L⁻¹ HNO₃, respectively.

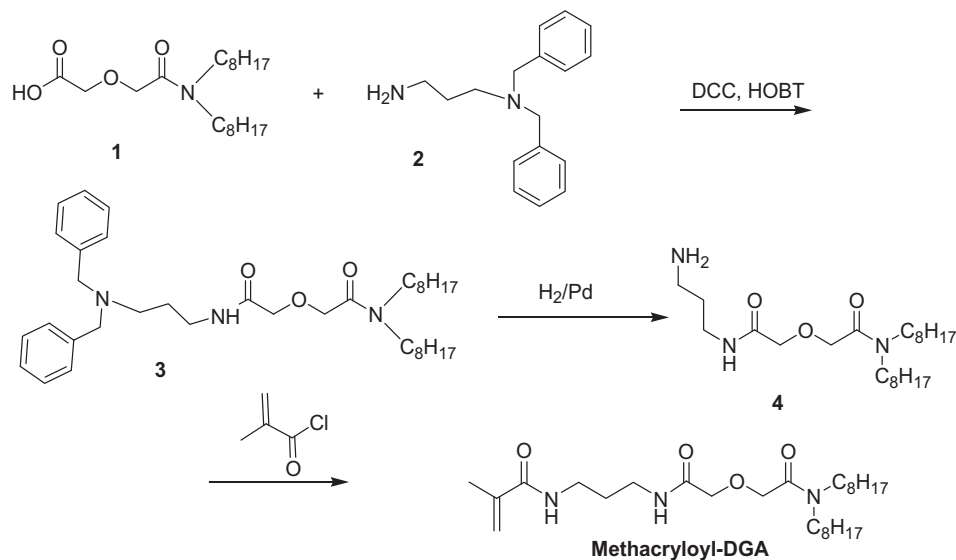
2.6. Mössbauer characterization

Mössbauer spectra (MS) at room temperature were recorded using a Mössbauer spectrometer (Nucleonix Systems Pvt., Ltd., Hyderabad, India) operated in constant acceleration mode (triangular wave) in transmission geometry. The source employed was Co-57 in a Rh matrix of 50 mCi strength. The calibration of the velocity scale was done by using an enriched α-⁵⁷Fe metal foil. The inner line width of the calibration spectrum is 0.23 mm/s. The isomer shift values are relative to (0.0 mm/s) α-⁵⁷Fe metal foil.

3. Results and discussion

3.1. Synthesis of methacryloyl-DGA and poly(methacryloyl-DGA)

N,N-dioctyl,*N'*-propyl-2-methylacrylamide diglycolamide (methacryloyl-DGA) monomer was synthesized as shown in Scheme 2. Reaction of *N,N*-dioctyldiglycolamic acid [26] (1) with *N,N*-dibenzyl-3-aminopropane [27] (2) in the presence of



Scheme 2. Synthesis of methacryloyl-DGA.

1-hydroxybenzotriazole (HOBT), *N,N*-dicyclohexylcarbodiimide (DCC), and triethylamine gave dibenzylaminopropyl-DGA **3** in 69% yield. Upon hydrogenolytic debenylation of **3** using 10% Pd/C as a catalyst, the resulting aminopropyl-DGA **4** was reacted with methacryloyl chloride to give methacryloyl-DGA in 83% yield.

Methacryloyl-DGA was converted into crosslinked poly(methacryloyl-DGA) in 70–80 wt.% yield by UV-initiator (α,α' -dimethoxy- α' -phenylacetophenone) induced free radical polymerization. Ethylene glycol dimethacrylate was used as a cross-linker. The cross-linking was kept as 10 mol.% of monomer for imparting mechanical integrity and avoiding swelling induced changes in geometrical arrangements of poly(methacryloyl-DGA).

3.2. Extraction studies

To compare the extraction behaviour of methacryloyl-DGA with that of TODGA, slope analyses were carried out in the plots of the log of the distribution coefficient of Am(III) (D_{Am}) as a function of the log of concentration of TODGA/methacryloyl-DGA in 10:1 mixture (for solubility reasons) of *n*-dodecane and 1-decanol as shown in Fig. 1. The concentration of HNO_3 in the equilibrating aqueous phase was kept as 3 mol L^{-1} . As can be seen from Fig. 1, the slopes

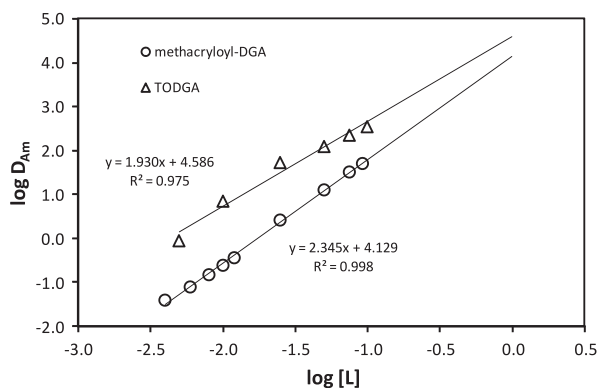


Fig. 1. Log of the distribution coefficient of Am(III) (D_{Am}) as a function of the log of concentrations of TODGA and methacryloyl-DGA (L , mol L^{-1}) in a 10:1 mixture of *n*-dodecane and 1-decanol equilibrated with an aqueous phase containing 3 mol L^{-1} HNO_3 .

are almost identical for both methacryloyl-DGA and TODGA indicating extraction of 1:2 Am(III):methacryloyl-DGA/TODGA species. This is similar to that reported for TODGA in a polar solvent [28]. However, TODGA was more efficient than methacryloyl-DGA for the extraction of Am(III). The extraction efficiency of methacryloyl-DGA comes closer to that of TODGA upon increasing its concentration. This is very promising for the application of assembled methacryloyl-DGA in both polymers and self-assembled forms.

Poly(methacryloyl-DGA) was subjected to ^{241}Am extraction at different HNO_3 concentrations in the equilibrating aqueous phase. Fig. 2 clearly shows that the extraction trend of ^{241}Am in poly(methacryloyl-DGA) is similar to that of its monomeric form,

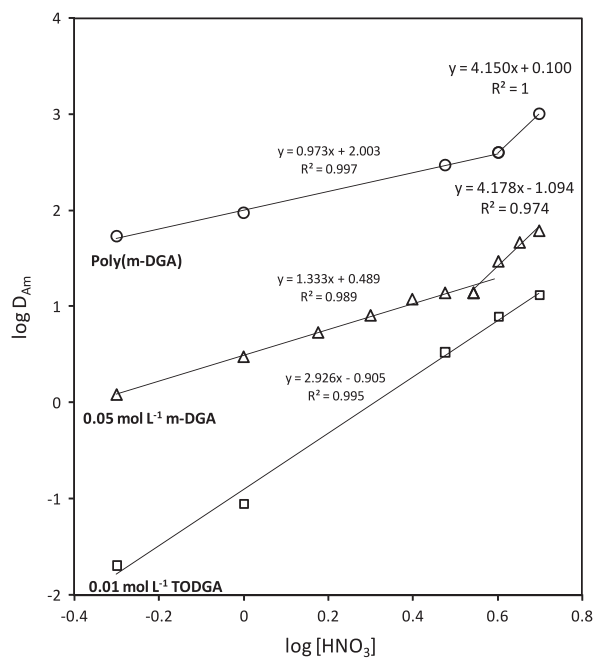


Fig. 2. Plots of log D_{Am} versus log $[HNO_3]$ (mol L^{-1}) in aqueous phases equilibrated with an organic phase containing TODGA (0.01 mol L^{-1}), organic phase containing methacryloyl-DGA (0.05 mol L^{-1}), and poly(methacryloyl-DGA) solid phase. (In the latter case the unit of D_{Am} is $mL g^{-1}$).

Table 1
 D values of TODGA, methacryloyl-DGA, and poly(methacryloyl-DGA) towards representative f-element ions at 3 mol L⁻¹ HNO₃. D_I values are the average of 4 experiments having $\pm 5\%$ variation.

Ions (I)	TODGA (0.01 mol L ⁻¹)		Methacryloyl-DGA (0.05 mol L ⁻¹)		Poly (methacryloyl-DGA)	
	D_I	(D_I/D_{Am})	D_I	(D_I/D_{Am})	D_I (mL g ⁻¹)	D_I/D_{Am}
Am(III)	3.3	1	14	1	293	1
Eu(III)	14.9	4.5	72	5	1044	3.6
Pu(IV)	6.1	1.8	18	1.3	292	1
U(VI)	0.04	0.01	0.3	0.02	18	0.02

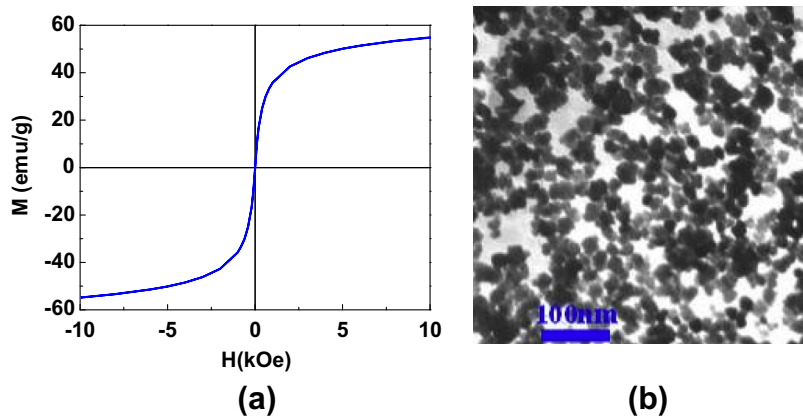


Fig. 3. Hysteresis plot (a) and TEM image (b) of 'DGA-coated' Fe₃O₄ nanoparticles.

but quite different from that of TODGA. However, a direct comparison of the D_{Am} values is not possible as poly(methacryloyl-DGA) involves solid phase extraction having a mass-weighted D_{Am} , see Eq. (1). In case of TODGA, a slope of 3 is observed as expected for neutral Am(NO₃)₃ extraction. For both methacryloyl-DGA and poly(methacryloyl-DGA) the slopes change significantly around 3–4 mol L⁻¹ HNO₃ i.e. at lower acidities the slopes are around 1, while at higher acidities the slopes are 4. A slope of 4 seems to suggest the extraction of Am(NO₃)₃·HNO₃. DGA is a neutral ligand and, therefore, it binds with neutral chemical species. Slopes other than three suggest that a different extraction mechanism is involved. HNO₃ binds with DGA through hydrogen bonding that may change the shape of the DGA aggregates and may give rise to a more favourable geometry for f-element ion binding. The extraction efficiencies of TODGA, methacryloyl-DGA, and poly(methacryloyl-DGA) towards different representative f-element ions are compared in Table 1. The concentration of HNO₃ in the aqueous phase was kept at 3 mol L⁻¹, encountered commonly in the nuclear fuel reprocessing streams [15]. As can be seen from Table 1, U(VI) is not extracted significantly, while Eu(III), Am(III), and Pu(IV) are extracted with a high efficiency (>90%). The relative extraction efficiencies showed in all cases a similar pattern being Eu(III) the most preferred and U(VI) the least preferred ion. Diglycolamide based extractants aggregate in an organic phase equilibrated with an aqueous solution having high a concentration of HNO₃. It has been reported in literature [15,19] that the cavity of diglycolamide aggregates favours extraction of Ln(III)/An(III,IV), and that it is least favourable for actinides having higher oxidation states like U(VI). This argument can also be used to explain the extraction behaviour of monomer methacryloyl-DGA. However, it is not clear why poly(methacryloyl-DGA) has the same behaviour as DGA in the organic phase.

3.3. Coated magnetic nanoparticles

Methacryloyl-DGA molecules self-assembled on Fe₃O₄ nanoparticles having a size of 20–30 nm. The most common strategy

adopted for coating on Fe₃O₄ nanoparticles utilizes the hydroxyl groups generated on the surface of Fe₃O₄. In the present case, methacryloyl-DGA molecules self-assembled on the Fe₃O₄ nanoparticles in organic solution. Both the hysteresis plots, confirming the superparamagnetic properties, and the Transmission Electron Microscopy (TEM) images of the uncoated and the 'DGA-coated' Fe₃O₄ nanoparticles did not show any detectable changes (Fig. 3). The simulated room temperature Mössbauer spectra given in Fig. 4 show similar shapes for DGA-coated and pristine Fe₃O₄ samples. For DGA coated Fe₃O₄, the hyperfine field values were increased slightly as compared to that of pristine Fe₃O₄ indicating aggregation of some particles during DGA coating. The VSM magnetization curves for pristine and methacryloyl-DGA coated Fe₃O₄ were almost the same indicating very thin coating. It is expected that methacryloyl-DGA molecules would not have any chemical interactions with Fe₃O₄. Thus, the slight increase in the

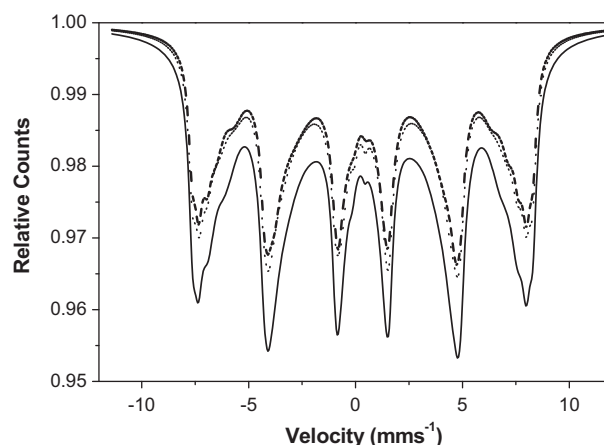


Fig. 4. Comparison of room temperature Mössbauer spectra of Fe₃O₄ (solid line), DGA-coated Fe₃O₄ (dashed line) and HNO₃-treated-DGA coated Fe₃O₄ (dotted line).

hyperfine field values for methacryloyl-DGA coated Fe_3O_4 with respect to pristine Fe_3O_4 could be attributed to aggregation of methacryloyl-DGA coated Fe_3O_4 .

The Fe_3O_4 nanoparticles were coated with DGA dissolved in solvent, as such and after equilibration with $3 \text{ mol L}^{-1} \text{ HNO}_3$. With uncoated Fe_3O_4 nanoparticles, Am(III) uptake could not be detected. The extraction with the 'DGA-coated' Fe_3O_4 nanoparticles was quite reproducible, since the spread in the D_{Am} values was only $\pm 10\%$ using 'DGA-coated' Fe_3O_4 nanoparticles from different batches. Also, there was no significant ($\leq 1\%$) loss of iron content from DGA-coated Fe_3O_4 during equilibration with $3 \text{ mol L}^{-1} \text{ HNO}_3$ for overnight. The 'DGA-coated' Fe_3O_4 nanoparticles as such and after equilibration with $3 \text{ mol L}^{-1} \text{ HNO}_3$ gave D_{Am} values of 39 ± 3 ($n = 8$) and 85 ± 9 ($n = 8$), respectively. The two times higher D_{Am} value of 'DGA-coated' Fe_3O_4 nanoparticles prepared by using HNO_3 equilibrated methacryloyl-DGA may be attributed to acid-induced organization of DGA molecules. The D_{Am} value of the self-assembled methacryloyl-DGA on Fe_3O_4 ($85 \pm 9 \text{ mL g}^{-1}$) is considerably lower than the D_{Am} value of poly(methacryloyl-DGA) ($293 \pm 10 \text{ mL g}^{-1}$). However, it has a better extraction ability for Am(III) than the malonamide-grafted resin (50 mL g^{-1}) [29]. Considering that it is only a coating of methacryloyl-DGA on Fe_3O_4 , its Am extraction efficiency is remarkable.

The methacryloyl-DGA coating on Fe_3O_4 could be completely removed in an organic phase like dioxane and propanol, and removed partially in *n*-dodecane. The reusability of methacryloyl-DGA coated Fe_3O_4 particles was tested in two cycles of loading and elution of Am(III). It was observed that Am(III)-sorption efficiency of the methacryloyl-DGA coated Fe_3O_4 was not affected during two cycles. However, methacryloyl-DGA coated Fe_3O_4 would not have long term stability as the coating is not held by chemical bonding. One way to make the coating highly stable is polymerization of methacryloyl-DGA to give an encapsulation of Fe_3O_4 .

3.4. De-sorption of f-element ions

De-loading of Am(III) from methacryloyl-DGA in solution (10:1 mixture of *n*-dodecane and 1-decanol), methacryloyl-DGA coated on Fe_3O_4 , and poly(methacryloyl-DGA) was studied using 0.02 mol L^{-1} disodium EDTA in water. It was observed that 96% Am(III) was de-loaded from methacryloyl-DGA and methacryloyl-DGA coated on Fe_3O_4 at room temperature. In case of poly(methacryloyl-DGA), the Am(III) de-loading was very low (10–15%) at room temperature. However, it could be improved till 55% by increasing the temperature to 45°C in a single equilibration. It was observed that 80% of Am could be desorbed by repeated equilibration under similar conditions with a fresh EDTA solution. This indicates that Am(III) is very strongly bound in poly(methacryloyl-DGA) probably due to the favourable geometrical arrangement of the DGA units in the polymer chain. On increasing temperature, the expansion of polymer chains would have destroyed the favourable coordination geometry leading to release of Am(III) ions.

4. Conclusions

DGA-bearing monomer methacryloyl-DGA developed in the present work was found to have good affinity towards f-element ions in the monomeric and polymeric forms. The interpretation of the variation of D_{Am} as a function of the HNO_3 concentration

shows that HNO_3 induced preorganization plays an important role in the affinity of different DGA assemblies towards f-element ions. The most preferred and least preferred Ln/An ions in poly(methacryloyl-DGA) from $3 \text{ mol L}^{-1} \text{ HNO}_3$ were found to be Eu(III) and U(VI) ions, respectively. It was observed that 96% Am(III) could be de-loaded from methacryloyl-DGA in the organic phase and methacryloyl-DGA coated on Fe_3O_4 at room temperature. However, Am(III) de-loading from poly(methacryloyl-DGA) was possible at 45°C . Methacryloyl-DGA molecule coating on Fe_3O_4 nanoparticles provides a possibility of growing polymer-DGA chains on Fe_3O_4 . Since methacryloyl-DGA is easily polymerizable and has a reasonable good affinity towards f-element ions, this would find potential application in developing resins, magnetic beads, fixed-site membranes and other polymeric materials for sequestration of lanthanides and actinides from aqueous streams having a high concentration of HNO_3 .

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