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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 Fe_3O_4. DGA-methacrylate coated Fe_3O_4 particles capture representative trivalent actinide ^{241}Am with a very high efficiency. However, it has been observed that HNO_3 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.

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 Fe_3O_4 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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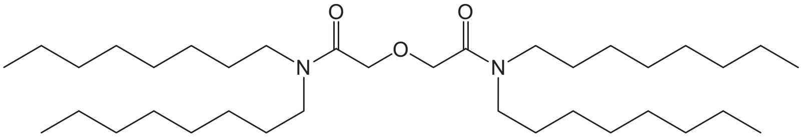

Scheme 1. Chemical structure of *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA).

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 Fe_3O_4 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 Fe_3O_4, 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 ^{13}C NMR spectra were recorded on a Varian Unity INOVA (300 MHz) spectrometer in $CDCl_3$. ^1H NMR (300 MHz) and ^{13}C 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 (SiO_2, 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, CH_3), 1.16–1.36 (20H, m, $CH_3(CH_2)_5$), 1.44–1.58 (4H, m, NCH_2CH_2), 1.87 (2H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 2.67, 3.07 (2H, t, $J = 7.5$ Hz, NCH_2), 3.29 (4H, t, $J = 7.5$ Hz, NCH_2), 3.76 (4H, s, $ArCH_2$), 4.11 (2H, t, $J = 6.4$ Hz, OCH_2), 4.02, 4.16 (2H, s, OCH_2), 7.21–7.39 (10H, m, ArH), 7.91 (1H, broad singlet, NH)) and ^{13}C 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 $C_{37}H_{60}N_3O_3$.

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 H_2 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, CH_3), 1.17–1.40 (20H, m, $CH_3(CH_2)_5$), 1.42–1.61 (4H, m, NCH_2CH_2), 1.67 (2H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 2.75 (2H, t, $J = 7.5$ Hz, NCH_2), 3.08 (2H, t, $J = 7.5$ Hz, NCH_2), 3.30 (4H, t, $J = 7.5$ Hz, NCH_2), 3.39 (2H, t, $J = 7.5$ Hz, NCH_2), 4.06, 4.22 (2H, s, OCH_2), 7.91–8.01 (1H, m, NH)), ^{13}C 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 $C_{23}H_{48}N_3O_3$).

2.1.4. Methacryloyl-DGA (5)

To a solution of a 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% $NaHCO_3$ solution (8 × 100 mL) and water (2 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$ 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, CH_3), 1.11–1.36 (20H, m, $CH_3(CH_2)_5$), 1.39–1.59 (4H, m, NCH_2CH_2), 1.71 (2H, pentet, $J = 6.0$ Hz, $NHCH_2CH_2$), 1.98 (3H, s, CH_3-methacryl), 3.08 (2H, t, $J = 7.5$ Hz, NCH_2),