Separation and Purification Technology 169 (2016) 17–24

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Triazole Diglycolamide Cavitand for lanthanide extraction

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ARTICLE INFO

Article history:
Received 9 February 2016
Received in revised form 27 May 2016
Accepted 1 June 2016
Available online 2 June 2016

Keywords:
DGA
Resorcinarene
Selective ionic separation
Lanthanide

ABSTRACT

Click chemistry, which relies on the efficiency of the copper (I)-catalyzed azide-alkyne cycloaddition, was used to link four diglycolamide (DGA) moieties to a resorcinarene platform leading to a specific tetra-DGA-resorcinarene ligand (c-methylcalix(4)methylresorcinarene-4-triazole-dioctyldiglycolamide denoted CR4-Tz-DODGA). The extraction ability of this ligand was studied in a mixture of toluene/iso-octanol (90/10, v/v) toward rare earth elements (REE) at different nitric acid concentrations, ranging from 1 to 5 M. The results show the efficient extractability of and selectivity towards heavy REEs. The stoichiometry of the extraction was established by the slope analysis method and an extraction mechanism was proposed based on estimates of the thermodynamic parameters. From the extraction behavior of the tetra-DGA-resorcinarene ligand, we present the possibility for the extraction and separation of dysprosium from used permanent magnets.

1. Introduction

Rare earth elements (REEs) comprise the family of lanthanides including scandium and yttrium. Due to their similar chemical properties, REEs are rarely separated from each other [1]. These elements have a wide range of technical applications, and the forecasted average annual demand growth of REEs is stated to increase to >8% every year by 2020 [2]. In contrast to increased REE demand, the supply of such materials is currently experiencing a shortage and as an alternative to increased mining operations, recycling can be used to reduce the stress on the rare earth supply [3]. In addition, REEs are significant byproducts of fission reactions as they represent approximately 40% of the fission product mass and include measurable amounts of all lanthanides. The separation of lanthanides from actinides can be a challenging obstacle in effective waste management [4].

Several methods have been investigated for the recovery of REEs by membrane filtration [5], solid–liquid separation using chelating organic resins [6], as well as organic-inorganic materials [7].

Solvent extraction has long been used for the recovery and the separation of REEs, which is usually accomplished by using phospho-compounds in organic solvents [8] and also in ionic liquid diluents [9,10]. Among many other extractants well-known in the field of metals extraction and nuclear fuel reprocessing, diglycolamides have gained importance within the field since first reported by Stephan and co-workers in 1991 [11,12].

Diglycolamides (DGAs) have favorable characteristics as they are tridentate O-donating ligands, which allows them to form stable complexes with lanthanides and actinides. DGAs consist of C, H, N, and O atoms and can be incinerated completely to form gaseous products after utilization [13–16]. Though several DGA compounds have been studied, the effect of DGA unit preorganization in a macrocyclic platform used in REE extraction has not been examined in detail. The positive effects on the extraction efficiency of ligand preorganization within a platform has been established [17].

Therefore the advantages preorganization of DGA sites in a calix[4]arene provide have been studied and proven to be far superior to TODGA, with comparable extractions at 100 times lower concentrations and increased efficiency with an increased number of DGA units [18,19]. The number of DGA units and the flexibility provided by spacer lengths is an important parameter in the extraction ability of the ligands. Among different macrocycles, cavitand analogues of C-methylcalix(4)methyl-resorcinarene provides an excellent preorganized platform for the coordination of host systems due to its conformational rigidity, which is assured by the methylene bridge between the hydroxyl groups of two neighboring phenyl rings. Its functionalization can be easily performed making the platform a focus of interest for a wide range of applications, such as being used as host molecules [20,21], components in liquid crystals [22], photoresistors [23], HPLC stationary phases [24], self-assembled capsules [25], surfactants, for potential

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http://dx.doi.org/10.1016/j.seppur.2016.06.003
1383-5866/

sensor applications [26], as an antibacterial agent [27], and with biomolecules [28].

Click chemistry, developed by Sharpless and co-workers [29], is widely utilized in various fields, including organic [30], medicinal [31], materials [32], and biological chemistry [33]. Its popularity stems from its simplicity, high conversion, the absence of side product formation, and mild reaction conditions. Therefore, copper-catalyzed azide–alkyne cycloaddition (CuAAC) is one of the most useful reactions for the covalent attachment of appropriate functional groups.

A cavitand containing azide groups was synthesized and engaged in a click reaction with the terminal alkyne of a DGA moiety. The success of the functionalization was monitored by FT-IR, NMR and MS analysis. The performance of the resulting Tetrakis(4-triazolomethyldioctyldiglycolamide)-tetramethyl cavitand (CR4-Tz-DODGA, Fig. 1) in solvent extraction experiments was evaluated for REEs under acidic feed conditions. The stoichiometry of the complexes and the extraction mechanism involved are discussed with regards to the extraction of the REEs. Finally, the ligand exhibited highly favorable separation behavior of REEs from a simulated solution of permanent magnets.

2. Methods and materials

2.1. Chemicals and analysis

Chemicals (analytically pure) were purchased from Sigma-Aldrich or Alfa Aesar and were used without further purification. Anhydrous solvents were purchased from Acros (AcroSeal®). Reactions were monitored by thin layer chromatography (Merck TLC Silica Gel 60 F254).

Flash chromatography was performed using a combiflash Agilent Intelliflash 971-FP. NMR analyses were performed on a Bruker 400 ultrashield VS spectrometer. Chemical shifts are reported in ppm using the solvent ($CDCl_3$: 7.26 ppm for ^1H; 77.16 ppm for ^{13}C) as an internal reference. Metal concentrations were determined using a spectro ARCOS ICPAES spectrometer. Fourier transform infrared (FTIR) measurements were performed on a Perkin Elmer Spectrum 100 instrument in ATR (Attenuated Total Reflection) mode. The measured range was from 400 cm^{-1} to 4000 cm^{-1} with a 4 cm^{-1} beam resolution. Background acquisition was conducted prior to measurement. ESI-MS was performed on a Flexar SQ 300 MS instrument.

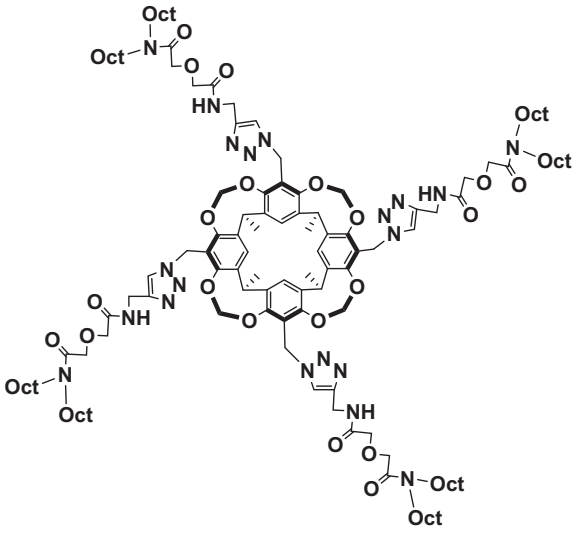

Fig. 1. Structure of CR4-Tz-DODGA.

2.2. Synthesis

2.2.1. Preparation of propargyl-DODGA **2**

1.62 g of 2-(2-(dioctylamino)-2-oxoethoxy) acetic acid **1** [34], (4.54 mmol) and 0.675 g of hydroxyl benzotriazole (4.99 mmol) were poured into 30 ml chloroform at 0 °C. The obtained suspension was stirred for 30 min at room temperature, then 0.25 g of propargyl amine (4.54 mmol) and 1.03 g of dicyclohexylcarbodiimide DCC (4.99 mmol) were added, and the resulting suspension was stirred for two days. After filtration and evaporation of the solvent, the crude product was purified using column chromatography (SiO_2, dichloromethane/methanol 5%), affording compound **2** as a brown dense oil with a yield = 72%. ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 0.89 (m, 6H, CH_2—CH_3), 1.29 (m, 20H, —NCH_2—CH_2—CH_3), 1.54 (m, H, J = 7.2 Hz, NH—CH_2—CH_2), 2.21 (t, 1H, J = 2.4 Hz, CH), 3.1 (t, 2H, 7.6 Hz, N-CH_2-heptyl), 3.23 (t, 2H, 7.6 Hz, N-CH_2-heptyl), 4.09 (d, 2H, J = 2.8 Hz, N-CH_2) 4.1 (s, 2H, CO—CH_2—CO), 4.25 (s, 2H, CO—CH_2—CO), 8.2 (s, 1H, NH—C=O). ^{13}C NMR (400 MHz, $CDCl_3$) δ [ppm]:14.1, 22.6, 26.9, 27.0, 27.6 (NH—CH_2), 28.5, 28.9, 29.2, 29.2, 29.3, 29.4, 31.7, 31.8, 46.2, 46.8 (—CH_2—), 71.2(≡CH), 69.6 & 71.8 (—CH_2O—), 79.5(—C≡), 168.1, 169.4 (C=O).

2.2.2. Preparation of cavitand **3**

Cavitand **3** was prepared as described by Cram et al., and identified by comparison of its ^1H NMR spectrum with literature values [35]. **3** was obtained as dark yellow powder (yield 88%). ^1H NMR (400 MHz, DMSO) δ [ppm]: 1.70 (d, 12 H, CH_3CH), 2.00 (s, 12 H, ArCH_3), 4.46 (q.4H, CH_3CH), 7.41 (s, 4 H, ArH), 8.70 (s, 8 H, ArOH). m/z: 543 [$(M-H)^+$].

2.2.3. Preparation of cavitand **4**

Cavitand **4** was prepared by adapting a procedure described in the literature by using dichloromethane instead of bromochloromethane [27]. **4** was obtained as a white powder (yield 84%) and the ^1H NMR spectrum was in agreement with the previously reported spectrum in the literature [35,36], ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 1.73 (d, 12 H, CH_3CH), 2.00 (s, 12 H, ArCH_3), 4.29 (d, 4 H, inner of OCH_2O), 5.20 (q, 4 H, CH_3CH), 5.92 (d, 4 H, outer of OCH_2O), 7.14 (s, 4 H, ArH).

2.2.4. Preparation of cavitand **5**

Cavitand **5** was prepared using a procedure described by Moran et al. **5** was obtained as a white powder (yield 90%). ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 1.75 (d, 12H, J = 7.4 Hz, CHCH_3), 4.42 (s, 8 H, CH_2Br), 4.57 (d, 4 H, J = 7.0 Hz, inner OCH_2O), 5.02 (q, 4 H, J = 7.4 Hz, CH), 6.04 (d, 4 H, J = 7.0 Hz, outer OCH_2O), 7.26 (s, 4 H, ArH).

2.2.5. Preparation of cavitand **6**

In a round bottomed flask, cavitand **5** (2 g, 2.4 mmol) was dissolved in 60 ml of acetone. Sodium azide (2 g, 30.76 mmol) was added to the solution. The mixture was stirred under reflux for 4 h. The mixture was filtered over Celite and washed with acetone. The collected solution was evaporated using a rotary evaporator and the residue was purified using column chromatography (SiO_2, ethyl acetate/cyclohexane, 65/35). Cavitand **6** was obtained as a white powder (yield 85%). ^1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 1.75 (d, 12H, J = 7.4 Hz, CHCH_3), 4.3 (s, 8 H, CH_2N_3), 4.42 (d, 4 H, J = 7.0 Hz, inner OCH_2O), 5.0 (q, 4 H, J = 7.4 Hz, CH_3CH), 6.0 (d, 4 H, J = 7.0 Hz, outer OCH_2O), 7.3 (s,4 H, ArH); ^{13}C NMR (CDCl3, 400 MHz), δ [ppm]: 153.3 (Ar—Cq), 139.1 (Ar—Cq), 122.2 (Ar—Cq), 120.3 (Ar—H), 99.7 (Ar—CH_2—Ar), 45.1 (Ar—CH_2—N3), 31.2 (Ar—CH—Ar), 16.1 (CH3). (m/z): 835 [$(M+Na)^+$]; FT-IR (ATR crystal): ν (cm^{-1}) 2090 (ν_{as} —N_3).