



## Room temperature ionic liquid diluent for the mutual separation of europium(III) from americium(III)

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### ARTICLE INFO

#### Article history:

Received 3 December 2010

Received in revised form 18 April 2011

Accepted 19 April 2011

Available online 14 May 2011

#### Keywords:

Lanthanide-Actinide separation

Solvent extraction

Room temperature ionic liquid

Distribution ratio

Separation factor

### ABSTRACT

The extraction behavior of  $^{152+154}\text{Eu(III)}$  and  $^{241}\text{Am(III)}$  in a solution of bis(2-ethylhexyl)phosphoric acid (D2EHPA) or bis(2-ethylhexyl)diglycolamic acid (HDEHDGA) in the ionic liquid, 1-octyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide (omimNTf<sub>2</sub>), was studied at 298 K. The extractant HDEHDGA was synthesized and characterized by IR, <sup>1</sup>H NMR and mass spectroscopy. The effect of various parameters such as the concentrations of nitric acid, D2EHPA, HDEHDGA and diethylenetriaminepentacetic acid (DTPA) on the extraction behavior of  $^{241}\text{Am(III)}$  and  $^{152+154}\text{Eu(III)}$  was studied and the results are reported in this paper. Superior extraction of the target metals and excellent separation factors achieved with the use of the ionic liquid diluent indicates the feasibility of separating lanthanides from actinides present in high-level liquid waste (HLLW).

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### 1. Introduction

By definition, room temperature ionic liquids (RTILs) are organic salts molten at temperatures lower than 373 K [1]. RTILs are receiving an upsurge for possible applications in the area of nuclear fuel cycle [2–6]. The properties such as insignificant vapor pressure, amazing ability to dissolve organic and inorganic compounds, and tunability to get task-specific form make RTILs popular for reprocessing applications. Initially, RTILs were explored as diluents in solvent extraction procedures. Dai et al. [2] and Visser et al. [4] studied the extraction of group I and II metals ions by crown ether present in ionic liquid. Chun et al. [7] studied the influence of structural variation in RTILs on the selectivity and efficiency of competitive alkali metal ion extraction in crown ether. The results obtained from those studies indicated that the extractants in conjunction with RTIL diluents have provided unusual extraction of target metals from aqueous solution under the condition that gave negligible or meager extraction with customary diluents. This was attributed to the extraordinary solvating ability of RTILs in the extracted phase. Dietz and co-workers [8,9] studied the extraction behavior of several metal ions of nuclear interest by appropriate neutral extractants present in RTIL medium. The mechanism of extraction in RTIL phase was reported to differ significantly in many cases depending upon the experimental conditions. Ion exchange between the target metal ion and RTIL was reported as one of the prevalent mode of metal transfer in RTIL phase. Rout

et al. [10,11] studied the extraction of americium(III) and europium(III) from nitric acid medium using a solution of *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) and tri-*n*-butylphosphate (TBP) in the ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide (bmimNTf<sub>2</sub>) medium. Shimojo et al. [12] and Yoon et al. [13] studied respectively the extraction of lanthanides from nitric acid medium by a solution of diglycol amide (TODGA) and bis(2-ethylhexyl)phosphoric acid (D2EHPA) in ionic liquid medium.

The most challenging task at the back end of the nuclear fuel cycle is the lanthanide (Ln)–actinide (An) separation. This is due to the similarity in the physical and chemical properties of lanthanides and actinides present in high-level liquid waste (HLLW) [14–17]. However there are some marginal differences with respect to the chemical reactivity of lanthanides and actinides towards certain reagents, and such differences have been exploited for the Ln/An separation. In this context, several authors have reported the separation of lanthanides from actinides or vice versa using liquid–liquid extraction procedures [18–25], and in the recent past TALSPEAK (Trivalent Actinides and Lanthanides Separation by Phosphorous based Extractants from Aqueous Complexes) process is emerging as the promising technique [22–24] for such applications. This process essentially exploits the differential complexing abilities of lanthanides and actinides towards the extractant, bis(2-ethylhexyl) phosphoric acid (D2EHPA), and the aqueous complexing agent diethylenetriamine-*N,N,N',N''*-pentacetic acid (DTPA) for efficient separation [23,24]. Recently, Suneesh et al. [25] studied the separation of Ln(III) from An(III) present in DTPA–citric acid(CA)–HNO<sub>3</sub> mixture using a solution

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of bis(2-ethylhexyl) phosphoric acid in octanol-*n*-dodecane (*n*-DD). However, to the best of our knowledge, there is no data reported so far in the literature for the separation of lanthanide-actinide using room temperature ionic liquid as the medium.

The aim of the present investigation is to study the extraction behavior of a representative lanthanide,  $(^{152+154}\text{Eu(III)})$ , and the trivalent actinide,  $^{241}\text{Am(III)}$  from the nitric acid medium by a solution of D2EHPA (or bis(2-ethylhexyl)diglycolamic acid (HDEHDGA)) present in 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl) imide (omimNTf<sub>2</sub>). The effect of concentration of HNO<sub>3</sub>, DTPA on the extraction behavior of  $(^{152+154}\text{Eu(III)})$  and  $^{241}\text{Am(III)}$  was studied and the separation factor of Eu(III) over Am(III) achieved with the use of ionic liquid diluent is reported in this paper. The choice of HDEHDGA is due to the fact that alkyldiglycolamides (DGA) are emerging as superior candidates for the separation of trivalents from high-level liquid waste [26–30]. Introduction of an etheric oxygen between the two amide groups, as in DGA's, increases the extraction of minor actinides due to the enhanced tridentate complex formation with trivalents. Since, the extractant, HDEHDGA being a derivative of glycolamic acid, it is also expected to be a superior candidate for the separation of lanthanides and actinides from aqueous medium. The structure of HDEHDGA, D2EHPA, omimNTf<sub>2</sub> and DTPA are shown in Fig. 1. Shimojo et al. [31–33] studied the extraction behavior of lanthanides using N,N-dioctyldiglycolamic acid (DODGAA) and reported the mutual separation of lighter, middle and heavier lanthanides using DODGAA and tetrakis(2-pyridylmethyl)ethylenediamine (TPEN). However, Ln–An separation was not studied and there is no data reported so far in the literature for lanthanide-actinide separation using bis(2-ethylhexyl)diglycolamic acid (HDEHDGA) and omimNTf<sub>2</sub> as solvent medium.

## 2. Experimental

### 2.1. Materials/reagents

All the chemicals and reagents used in the study were of analytical grade. The chemicals, D2EHPA, diglycolic anhydride and N,N-(2-ethyl)hexylamine (Aldrich), DTPA (E.Merck) and bis(trifluoromethanesulfonyl)imide lithium salt (Li (NSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>; NTf<sub>2</sub> = (NSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>) (Fluka) and 1-chlorooctane (Lancaster) were used as received. 1-methylimidazole (Lancaster) was distilled before use.  $(^{152+154}\text{Eu(III)})$  nitrate was procured from Board of Radiation and Isotope Technology, Mumbai, India, and  $^{241}\text{Am(III)}$  was obtained from Bhabha Atomic Research Centre, India.

### 2.2. Preparation of omimNTf<sub>2</sub> and HDEHDGA

The procedure adopted for preparing the ionic liquid is described elsewhere [3]. Briefly it involved refluxing a mixture of 1-methylimidazole with 1-chlorooctane in the mole ratio of 1:1.2. The resulting product was washed few times with ethyl acetate followed by hexane and evaporated under vacuum. Near quantitative yield was obtained. The ionic liquid (omimNTf<sub>2</sub>) was prepared by adding a pre-cooled aqueous solution of LiNTf<sub>2</sub> (1.3 mol) to the aqueous solution of 1-octyl-3-methylimidazolium chloride (1 mol) at 298 K. The entire mixture was stirred overnight and the bottom ionic liquid layer was separated, washed several times with water. The ionic liquid was evaporated to remove moisture at 343 K using rotary evaporator. Yield ~ 85%. The synthesis and characterization of di-2-ethylhexyldiglycolamic acid (HDEHDGA) is described elsewhere [26]. Diglycolic anhydride (0.03 mol) was mixed with 30 ml of dichloromethane and stirred in a round bottom flask equipped with a CaCl<sub>2</sub> guard tube for about 10 min. Di-(2-ethyl)hexylamine (0.033 mol) was added drop-wise to the solution of diglycolicanhydride and the reaction mixture was then stirred at room temperature for about 6 h. The crude reaction mixture was dried in a rotary evaporator at 353 K to remove the solvent, and then dissolved in hexane followed by washing with 1 M hydrochloric acid (20 mL × 5). The organic phase was separated out and washed with distilled water (20 mL × 5). The separated organic phase was dried in a rotary evaporator at 353 K. A pale yellow colored oil was obtained with >90% yield. The NMR spectra (<sup>1</sup>H and <sup>13</sup>C) of the samples were characterized using Bruker Avance III 500 MHz (AV500) and FTIR spectra were obtained using Bomem FTIR spectrometer model-103. The results for HDEHDGA are given below. FTIR:  $\nu/\text{cm}^{-1}$ : 3454 (COOH), 1739 (–CO in COOH), 1622 (–CO in –CON), 1226. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta/\text{ppm}$  relative to TMS): 10.67 (s, 1H, COOH), 4.32 (s, 2H, –OCH<sub>2</sub>–), 4.11 (s, 2H, –CH<sub>2</sub>O–), 3.17–3.31 (m, 4H, 2 × CH<sub>2</sub>–N), 2.96–2.98 (m, 2H, 2 × CH), 1.15–1.24 (m, 16H, 8 × CH<sub>2</sub> of alkyl chain), 0.77–0.84 (m, 12H, 4 × CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta/\text{ppm}$  relative to TMS): 172.22 (CO), 172.14 (CO), 77.21 (–OCH<sub>2</sub>–), 71.1 (–CH<sub>2</sub>O–), 49.34 (2 × –CH<sub>2</sub>–N), 37.16 (2 × CH), 30.35 (2 × –CH<sub>2</sub>–), 28.47 (2 × CH<sub>2</sub>), 23.58 (2 × CH<sub>2</sub>), 22.86 (2 × CH<sub>2</sub>), 13.93 (2 × CH<sub>3</sub>), 10.47 (2 × CH<sub>3</sub>). A home built reflectron time of flight mass spectrometer was used for mass analysis. The EI mass spectrum shows the peak corresponding to M<sup>+</sup> at 356.5. All the above results confirm the purity and structure of HDEHDGA shown in Fig. 1.

### 2.3. Equilibration procedure

All the extraction studies were carried out at 298 K. The organic phase (1 mL) was equilibrated with aqueous phase (1 mL) for 1 h. The desired concentrations of HDEHDGA (or D2EHPA) varied from 0.02 M to 0.2 M in omimNTf<sub>2</sub> were prepared. The organic phase was pre-equilibrated with desired concentration of nitric acid to fix the equilibrium acidity. Extraction of americium(III) and europium(III) as a function of nitric was studied by equilibrating the organic phase with aqueous phase containing desired concentrations of DTPA and nitric acid spiked with  $^{241}\text{Am(III)}$  (or  $(^{152+154}\text{Eu(III)})$  tracer (20 mg/L in all experiments). The pH of the aqueous solution was varied from pH 1 to 3.5. After 1 h of equilibration, the radioactivity of  $^{241}\text{Am(III)}$  and  $(^{152+154}\text{Eu(III)})$  distributed between organic and aqueous phases were measured using a well-type NaI(Tl) scintillation detector. The pH of the aqueous phase at equilibrium was measured. The distribution ratio ( $D_M$ ) of metal ion was determined using Eq. (1). The separation factors were computed using Eq. (2). The effect of concentrations of citric acid (CA), ethylenediamine tetraacetic acid (EDTA), acetohydroxamic acid (AHA), and DTPA in aqueous phase on the distribution ratio ( $D_M$ ) was studied by varying their concentrations from 10<sup>–5</sup> M to 0.05 M. Similarly the

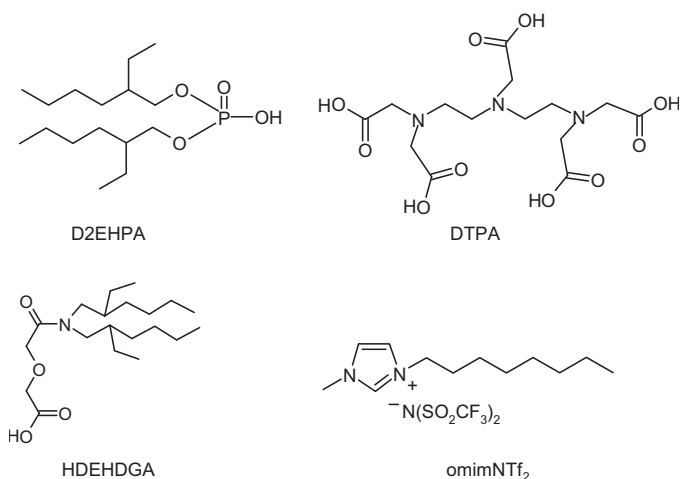


Fig. 1. Structure of D2EHPA, HDEHDGA, omimNTf<sub>2</sub> and DTPA.

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