



Liquid–Liquid extraction of americium(III) using a completely incinerable ionic liquid system



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ABSTRACT

Americium(III) was extracted by a new CHNO based ionic liquid based extraction system. The extractant used was a diglycolamide, *N,N,N',N'*-tetra(ethylhexyl)diglycolamide (T2EHDGA) and the diluent used was an incinerable ionic liquid, trioctylmethylammonium nitrate ($[N_{1888}][NO_3]$). The extraction of americium (III) using such type of ionic liquid as diluent is highlighted for the first time in this paper. The extraction behavior of americium(III) was investigated as a function of various parameters, such as aqueous phase acidity, extractant concentration, isomeric forms of the extractant and temperature. The extraction trend in T2EHDGA was compared with the other neutral extractant such as octylphenyl(*N,N*-diisobutylcarbamoylmethyl)-phosphinoxide (CMPO) and *N,N*-dimethyl-*N,N*-di-octyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA) in the ionic liquid, $[N_{1888}][NO_3]$ and T2EHDGA was found to be superior as compared to the former two extractants. Changing the extractant type in to the isomeric form of T2EHDGA (*N,N,N',N'*-tetraoctyl diglycolamide (TODDGA) and *N,N*-di(2-ethylhexyl)-*N',N'*-dioctyldiglycolamide (DEHDODGA)) doesn't exhibit any appreciable change in the extraction efficiency. Metal extraction was found to adopt neutral solvation pathway. Effect of thermodynamic parameters on the americium extraction was investigated in detail. The extracted americium(III) was stripped back from the ionic liquid phase using dilute nitric acid.

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1. Introduction

Ionic liquids are composed entirely of ions. They have a negligible vapor pressure and they are non-volatile [1,2]. Ionic liquids (ILs) are considered as suitable alternative to conventional molecular diluents in solvent extraction processes [3–8]. Most of studies reported in literature on the extraction of metal ions use molecular extractants dissolved in ionic liquid diluents containing imidazolium cations and fluorinated anions, such as the 1-alkyl-3-methylimidazolium hexafluorophosphates or bis(trifluoromethyl sulfonyl)imides [9–25]. However, from an environmental and economical point of view, such ionic liquids are not ideal for extraction as the main mechanistic pathway follows cation exchange mechanism wherein the cation of ionic liquid is lost to the aqueous phase leading to aqueous contamination and issue of recyclability of organic phase. Furthermore, ionic liquids with fluorinated anions are more expensive than their nonfluorinated counterparts as a result of which the use of these ionic liquids hampers the general application of ionic liquids in solvent extraction processes. Although the loss of ionic liquid can be minimized by structural

variation of the ionic liquid, for example, by increasing the alkyl chain length of the cation or fluorination of the alkyl chain of the anion, these modifications often have a negative effect on the distribution ratios and extraction efficiency [26,27]. However, there are some ionic liquids such as trioctylmethylammonium chloride (Aliquat 336), trioctylmethylammonium nitrate $[N_{1888}][NO_3]$, and trihexyl(tetradecyl)phosphonium chloride (Cyphos 101) that are nonfluorinated and exhibit no cation exchange with the aqueous phase during extraction [28–33]. Use of these types of ionic liquids could solve several issues associated with the fluorinated ionic liquids.

Diglycolamide based extractants have received particular attention of separation groups engaged in the area of actinide partitioning [34–41]. These extractants display high affinity for trivalent metal ions as compared to hexavalent metal ions. The complexation constant is high for diglycolamides as compared to other neutral extractants due to the presence of an extra etheric linkage. They have several merits over other nuclear extractants given the fact that they have high loading capacity, strong coordination ability, completely incinerable and enable aqueous soluble degraded products while dealing with radioactive metal separation [40]. *N,N,N',N'*-tetra(ethylhexyl)diglycolamides (T2EHDGA) is a class of diglycolamide extractant used for minor actinide

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partitioning in conjunction with molecular diluent, *n*-dodecane (*n*-DD) [35–37]. There are no reports yet on the T2EHDGA – ionic liquid based extraction.

In this paper, we report the result on the efficient extraction of americium(III) using *N,N,N',N'*-tetra(ethylhexyl)diglycolamides (T2EHDGA) dissolved in the CHNO based ionic liquid diluent, trioctylmethylammonium nitrate, [N₁₈₈₈][NO₃]. The extraction behavior of T2EHDGA/[N₁₈₈₈][NO₃] system was investigated as a function of different extraction parameters such as aqueous acidity, temperature and extractant concentration. Extraction trend was compared with that in other class of extractants. Mechanistic aspects have been detailed. The stripping of Am(III) from the ionic liquid phase and re-use of the ionic liquid in a next extraction step was also investigated in detail.

2. Experimental

2.1. Materials and reagents

All the chemicals and reagents used in this study were of analytical grade and they were used as received without further purification. Nitric acid, acetone, Aliquat 336 (98%), diglycolic anhydride (99%), bis(2-ethylhexyl)amine (99%) and sodium nitrate (99%) were purchased from Sigma–Aldrich. Sodium hydroxide was obtained from Alfa Aesar. ²⁴¹Am(III) was obtained from Oak Ridge National Laboratory (ORNL), USA as AmO₂. Europium(III) nitrate hexahydrate (>99%) was purchased from ACROS Organics. The synthesis and characterization of *N,N,N',N'*-tetra(ethylhexyl)diglycolamide (T2EHDGA) is described elsewhere [34]. Trioctylmethylammonium nitrate ([N₁₈₈₈][NO₃]) was synthesized according to the literature procedure [42].

2.2. Equilibration procedure

The extraction experiments with solutions of T2EHDGA in [N₁₈₈₈][NO₃] were performed at 298 K. The ionic liquid phase was pre-equilibrated with the desired concentration of nitric acid to fix the equilibrium acidity. Extractions were performed by intensive shaking of the mixture, typically for 1 h. After the extraction, two phases were separated by centrifugation and taken for metal assay using well-type NaI(Tl) scintillation detector. The *distribution ratio (D)* is the ratio of the concentration of the metal ion (americium in this paper) in the organic phase (ionic liquid phase) to the concentration of the metal ion in aqueous phase, at equilibrium.

$$D = \frac{[\text{Am}]_{\text{IL}}}{[\text{Am}]_{\text{aq}}} \quad (1)$$

Stripping efficiency is evaluated by

$$\%S = \frac{[\text{Am}]_{\text{aq}}}{[\text{Am}]_{\text{IL}}} \times 100 \quad (2)$$

2.3. Instrumentation and analysis

The concentrations of americium(III) in the aqueous as well as in the ionic liquid phase were determined using a gamma counter with a well-type NaI(Tl) scintillation detector. The extraction experiments were performed in a 10 ml capacity test tube immersed in a constant temperature water bath. The tubes were rotated in upside down manner. After 1 h of equilibration, the aqueous phase was sampled for metal assay. All the experiments were carried out in duplicate (some are with triplicate) and all the results were obtained with an accuracy of ±5%. After extraction, the samples were centrifuged using a Rana centrifuge (Model No: I.

A.117; SR No: 1087) in order to have clear phase separation. All the acid concentrations used for aqueous phase were standardized by acid–base titration using desired concentration of sodium hydroxide. FTIR spectra was recorded using ABB Bomem MB 3000 FTIR spectrophotometer. Luminescence spectra were recorded on an Edinburgh Instruments FS-920P spectrofluorimeter.

3. Results and discussions

3.1. Influence of nitric acid phase

The variation in the distribution ratio of Am(III) in 0.1 M T2EHDGA/[N₁₈₈₈][NO₃] as a function of nitric acid concentration is shown in Fig. 1. The concentration of nitric acid was varied from 0.1 M to 8.0 M. It can be seen that the distribution ratio of Am(III) in T2EHDGA/[N₁₈₈₈][NO₃] increases gradually with increase in the concentration of nitric acid, reaches a maximum value at 5 M followed by a plateau with further increase in nitric acid concentration. The reason for increasing trend up to 5 M nitric acid could be attributed to the neutral solvation mechanism wherein the metal salt rather than only metal ion gets extracted in to the ionic liquid phase. Above 5 M, the nitric acid extraction in T2EHDGA seems to occur predominantly over Am(III) extraction and decreases the distribution ratio of Am(III). A similar extraction trend was reported for the extraction of Am(III) in a molecular diluent phase composed of 0.1 M T2EHDGA + 0.5 M DHOA in *n*-DD [34–41]. In view of this, [N₁₈₈₈][NO₃] type of ionic liquids receive merit over the conventional imidazolium ionic liquids that loses the cation to the aqueous phase during extraction.

In *n*-dodecane (*n*-DD) medium, the extraction of Am(III) could not be studied in the absence of DHOA in the given acid range due to third phase formation. DHOA was usually added as phase modifier in T2EHDGA to overcome the undesirable third phase formation. The present study clearly indicates that the use of ionic liquid, [N₁₈₈₈][NO₃], in place of *n*-DD avoids third phase formation during the extraction of Am(III) by T2EHDGA, whereas in molecular diluent system the phase modifier such as DHOA was necessary.

It is necessary to compare the extraction trend observed in the present study using [N₁₈₈₈][NO₃] with other conventional imidazolium based ionic liquids. The extraction behavior of Am(III) in a solution of *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) present in 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imi-

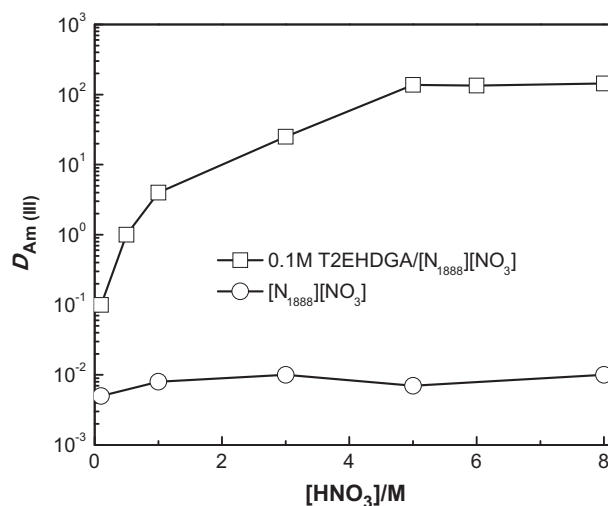


Fig. 1. Variation of the distribution ratio of Am(III) as a function of the nitric acid concentration in the aqueous phase. Organic phase: 0.1 M T2EHDGA/[N₁₈₈₈][NO₃] or [N₁₈₈₈][NO₃] alone; aqueous phase: [HNO₃] = 0.1–8.0 M and [Am(III)] = 10⁻⁴ M; temperature = 298 K; equilibration time = 1 h; phase volume ratio = 1.

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