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Synergistic extraction of uranium(VI) with TODGA and hydrophobic ionic liquid mixtures into molecular diluent

A.N. Turanov [a], V.K. Karandashev [b,c], M. Boltoeva [d,e,*], C. Gaillard [f], V. Mazan [d,e]

[a] Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia
[b] Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences, 142432 Chernogolovka, Russia
[c] National University of Science and Technology MISiS, Moscow, Russia
[d] Université de Strasbourg, IPHC, 23 rue du Lœss, 67037 Strasbourg, France
[e] CNRS, UMR 7178, 67037 Strasbourg, France
[f] Institut de Physique Nucléaire de Lyon, Université de Lyon, CNRS-IN2P3, 69622 Villeurbanne cedex, France

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ABSTRACT

The extraction of uranium(VI) from aqueous nitric acid solutions with a neutral extractant, *N,N,N′,N′*-tetra(*n*-octyl)diglycolamide (TODGA), and with the mixtures of TODGA and a hydrophobic ionic liquid, 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ($[C_4mim][Tf_2N]$), into a molecular diluent, 1,2-dichloroethane, has been systematically investigated. The extraction efficiency of U(VI) ions was greatly enhanced by addition of a small amount of ionic liquid to an organic phase containing TODGA. The synergistic effect comes from the higher hydrophobicity of U(VI) extracted species formed by TODGA and weakly coordinating Tf_2N^- anions as compared to those formed by TODGA and NO_3^- anions as counterions in the conventional extraction system. Based on our experimental results, we concluded that the partition of Tf_2N^- anions between the two liquid phases is the dominant factor governing the extractability of uranium(VI) with the mixture of TODGA and ionic liquid as extractant. We showed that the extraction of U(VI) from aqueous nitric acid solutions both by TODGA alone and its mixtures with $[C_4mim][Tf_2N]$ into 1,2-dichloroethane can be quantitatively described on the basis of the solvation extraction mechanism. However, in the extraction system with added hydrophobic ionic liquid, the partition of Tf_2N^- anions between the two immiscible phases and the interaction between *bis*(trifluoromethylsulfonyl)imide acid, HTf_2N, and TODGA molecules in the organic phase should be taken into account.

1. Introduction

Ionic liquids (ILs) are a class of compounds composed solely of ions and having a melting point below 373 K [1]. Recently, their use as new separation media in liquid–liquid extraction processes has been actively investigated [2–25]. Due to a unique combination of physicochemical properties of ILs, such as negligible vapor pressures, nonflammability and excellent solvation properties, they are regarded as possible alternatives to conventional molecular organic solvents [26,27]. Moreover, it has been recognized that the simple replacement of organic diluent by hydrophobic ionic liquid often greatly enhances the extraction efficiencies of many well-known extracting agents. For instance, the pioneering work of Dai et al. [3] reported remarkably high metal distribution ratios in the extraction of strontium(II) from water by dicyclohexano-18-crown-6 ligand into several *N,N′*-dialkylimidazolium-based ILs as compared to those obtained with any conventional organic diluents. Visser and Rogers [4] showed that the extraction of plutonium(IV), thorium(IV) and uranium(VI) into 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) with a mixture of two complexing organic ligands, octyl(phenyl)-*N,N′*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and tri-*n*-butyl phosphate (TBP), is at least an order of magnitude higher than the one obtained for the same extractant concentration in dodecane. Nakashima et al. [5] found that CMPO dissolved in $[C_4mim][PF_6]$ ionic liquid greatly enhances the extractability and selectivity of lanthanide cations compared to their solutions in conventional organic diluents. The higher extraction efficiency was attributed to some synergistic factors: (*i*) ion-recognition capabilities of complexing ligands; (*ii*) unique ionic solvation environments provided by ILs for ionic species; (*iii*) ion-exchange capabilities of ILs [8].

It should be noted that the great enhancement of the extraction efficiency of neutral donor extractants towards metal ions is

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[*] Corresponding author at: IPHC, 23 rue du Lœss, 67037 Strasbourg, France.
E-mail address: maria.boltoeva@iphc.cnrs.fr (M. Boltoeva).

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observed only with ionic diluents with relatively short alkyl chain radicals attached to the cationic part of ILs [28–31]. The noticeable aqueous solubility of this kind of ILs leads to the contamination of the aqueous phase with IL component ions [13,32]. This drawback as well as the high cost and viscosity of ILs limit their industrial application as diluents.

In our previous works [33–38], we found that ILs used as additives to the traditional extraction systems is a way to improve liquid–liquid extraction systems of metal ions. A considerable synergistic effect was observed in the presence of even small amounts of ILs in the organic phase containing diglycolamide ligand [33,36], carbamoylmethylphosphine oxides [34,37,38] and tetraphenylmethylenediphosphine dioxides [35], when lanthanide and alkaline earth cations were extracted from nitric acid solutions. Pribylova et al. [39,40] reported the increase of americium (III) extraction from nitric acid solutions by more than two orders of magnitude when a small amount of IL was added to a diphenyl (dibutyl)carbamoylmethylphosphine oxide in dichloroethane.

It seems that this kind of synergistic extraction system is very promising for the preconcentration and separation of metal ions at least on a laboratory scale. The addition of a small amount of IL to molecular solvents does not lead to modification of the organic phase viscosity [41]. Moreover, the large number of possible "extracting agent-hydrophobic IL-molecular diluent" mixtures offers the possibility to design an extraction system for each particular application. This approach allows maintaining the high efficiency and selectivity of the extraction processes with the IL without any significant rise in price.

Several recent studies have shown that alkyl-substituted diglycolamide ligands demonstrate a high extraction ability towards actinides and lanthanides ions in nitric acid media [42–46]. Diglycolamides (DGA) contain three oxygen atoms, so they act as tridentate ligands. As compared to bidentate neutral organophosphorus compounds, DGA have advantages such as an easy synthesis, milder stripping requirements and a chemical composition of fully incinerable elements. The hydrophobicity of DGA extractants is controlled by the length of the alkyl radicals linked to the amidic N atoms. In the case of *N,N,N′,N′*-tetra(*n*-octyl)diglycolamide (TODGA), the octyl chains give sufficient lipophilicity of the TODGA molecule to dissolve in various organic diluents [47].

To date, several studies have investigated the extraction behavior of actinides and lanthanides in DGA-IL systems [16]. Solutions of DGA extractants in 1-alkyl-3-methylimidazolium hexafluorophosphate ([$C_n$mim][PF_6], $n = 4$, 6, and 8) [48,49] and 1-alkyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ([$C_n$mim][Tf_2N], $n = 4$, 6, and 8) [50] provide an efficient extraction of U(VI) ions from aqueous solutions under low acidity conditions, whereas they show a negligible extraction in traditional organic solvents such as chloroform. Higher distribution ratios were obtained for short alkyl chain ILs which was attributed to their higher ion-exchange capabilities as compared to the hydrophobic long alkyl chain imidazolium ILs [50].

In this work, we report our experimental results on the investigation of the hydrophobic ionic liquid [C_4mim][Tf_2N] as synergist in the extraction of U(VI) with TODGA dissolved in organic diluent 1,2-dichloroethane. In order to elucidate the extraction mechanism in this extraction system, we aim: (*i*) to investigate the distribution of nitric acid and water between aqueous acidic phase and 1,2-dichloroethane solutions of TODGA; (*ii*) to measure the distribution of hydrophobic ionic liquid anions Tf_2N^- in the liquid–liquid system containing TODGA and [C_4mim][Tf_2N] in the organic phase and HNO_3 in the aqueous phase; (*iii*) to determine the effect of various parameters on the extraction of uranium(VI) with TODGA alone and its mixtures with [C_4mim][Tf_2N]; (*iv*) to compare the extraction mechanism in the synergistic extraction system containing TODGA and [C_4mim][Tf_2N] in the organic phase to that in the conventional extraction system. The results obtained are discussed on the basis of the solvation extraction mechanism. The findings of this study are of interest for the understanding of the complicated chemistry and mechanisms involved in metal ions extraction in the presence of ILs and for the development of organic extractant mixtures for preconcentration and separation of metal ions from aqueous solutions.

2. Experimental

2.1. Chemical reagents

N,N,N′,N′-tetra(*n*-octyl)diglycolamide (abbreviated as TODGA) was prepared, purified and characterized according to the published method [51]. 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid (designated as [C_4mim][Tf_2N]) was synthetized and purified as reported previously [52]. The salts, namely uranyl nitrate hexahydrate $UO_2(NO_3)_2 \cdot 6H_2O$, lithium *bis*(trifluoromethylsulfonyl)imide $LiTf_2N$, ammonium nitrate NH_4NO_3, nitrates of Fe(III), Cr(III), Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) Pb(II), Sr(II), and nitric and hydrochloric acids were of chemical and analytical grade and used as supplied. Molecular diluent 1,2-dichloroethane (DCE) of chemical grade was used without any further purification. All aqueous acidic solutions were prepared from distilled water and concentrated acid.

2.2. Extraction procedure

In this study, the batch experiments were carried out at room temperature.

A stock uranium solution was made by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ salt in water and diluting down to $1 \cdot 10^{-5}$ M U(VI) with aqueous HNO_3 solution. An organic phase was prepared by dissolving weighed quantities of TODGA and [C_4mim][Tf_2N] in 1,2-dichloroethane.

The preconditioning of the organic phase, *i.e.*, its pre-equilibration with aqueous acidic solution, before measurements of the distribution ratio was not carried out. All extraction samples were prepared using precisely weighed aliquots of each phase in centrifuge tubes equipped with sealing plugs. A 1:1 volume ratio of organic and aqueous phases was employed. The biphasic mixtures obtained by putting together aqueous and organic phases were shaken vigorously using a rotor mixer at the rate of 60 rpm for 1 h. It was checked in the preliminary trials that this time of phase contact is sufficient to achieve the equilibrium. To promote phase separation, the extraction tubes were centrifuged and then the aliquots of each phase were sampled for further analysis.

The values of the distribution ratio D_U were calculated as $[U]_{org}/[U]$. The subscript "org" denotes the uranium species in the organic phases, while it is omitted for the species in the aqueous phase.

Duplicate experiments showed that the reproducibility of the D_U measurements was within 10%.

2.3. Analysis

The concentration of U(VI) in the aqueous phase was determined using inductively coupled plasma mass spectrometry (ICP-MS) on a mass spectrometer X-7 (Thermo Electron, USA) according to the previously described procedure [53].

Aqueous Tf_2N^- concentrations were determined by sulfur content measurement using inductively coupled plasma atomic emission spectrometry (ICP–AES) on an ICAP-61 spectrometer (Thermo Jarrel Ash).

The concentration of HNO_3 in the aqueous phase was determined by potentiometric titration of the protons H^+ with NaOH