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Effect of room temperature ionic liquid on the extraction behavior of Plutonium (IV) using a novel reagent, bis-(2-ethylhexyl) carbamoyl methoxy phenoxy-bis-(2-ethylhexyl) acetamide [Benzodioxodiamide, BenzoDODA]

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ABSTRACT

A novel Plutonium (Pu) (IV) selective ligand, bis-(2-ethylhexyl) carbamoyl methoxy phenoxy-bis-(2-ethylhexyl) acetamide (BenzoDODA) was studied for its Pu(IV) extraction behavior in presence of 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imide {[$C_n$mim][Tf_2N]}ionic liquids. BenzoDODA was observed to behave differently in RTIL compared to n-dodecane toward Pu(IV) extraction. The presence of C_4mimTf_2N tends to bring about significant enhancement in the extraction of Pu in both the acidic media (HCl and HNO_3) as compared to that of using n-dodecane as diluent. The investigation of the extraction mechanism revealed that while using in RTIL (as diluent), the cation-exchange prevails up to 3 M acidity, in contrast to anion exchange mechanism ruling above 3 M acidic strength. However, in n-dodecane (as diluent) the metal extraction takes place via formation of anion-assisted neutral complex formation only at all acidities. Studies on the nature of species formed by Pu(IV) and BenzoDODA in both HNO_3 and HCl medium showed formation of a di-solvate species for RTIL in contrast to mono-solvate formed in n-dodecane. Selectivity of BenzoDODA-RTIL system appears to be lost at lower acidities due to significant extent of extraction of other matrix elements along with target metal ion. However at higher nitric acid concentration (7 M) BenzoDODA was found to be selectively extracting Pu(IV).

1. Introduction

Selective extraction of Plutonium from acidic medium is a challenge to the synthetic as well as radio-chemists. Various research groups worldwide have been working on the development of Pu selective ligands and there have been reports about various ligands for this purpose. The ligands include tertiary and quaternary amines [1], sulphoxide [2], alkylated monoamides [3], carbamoyl methylene phosphine oxides [4], catecholamides [5], terepthalimides [5], pyrolidones [6] etc. The draw-back of the ligands includes co-extraction of other actinides and fission products in appreciable fractions. Recently a novel ligand, BenzoDODA [7,8] has been reported by our group with high extractability and excellent selectivity of Pu over other elements expected to be present in various nuclear waste solutions. Detailed solvent extraction experiment has shown promise for the application of BenzoDODA for selective separation of Pu(IV) from nitric acid medium [8]. The diluent used for BenzoDODA in these works was n-dodecane, molecular diluent used world-wide for hydrometallurgical applications.

There have been an increasing number of studies in the last decade on the application of room temperature ionic liquids (RTIL) for metal ion extraction from various mediums [9–15]. RTILs are known to have non-measurable vapor pressure, non-inflammability, high thermal stability and as a consequence are known to be 'green' alternatives to the presently used organic solvents though there has been report against the 'greenness' of RTILs with respect to their interest in industrial applications [16,17]. They are also 'tunable' with respect to the properties like polarity, viscosity, water-immiscibility by varying the cations and anions. High conductivity, prevention of third phase formation and wide electrochemical window of the RTILs can be beneficial toward extraction and electro-deposition of metal ions. The applicability of RTILs for the separation of actinides and fission products from nuclear waste solutions has been the subject of research of various groups world-wide [18–20]. Recently two reviews on the

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application of RTILs for the separation of actinides and fission products relevant to advanced nuclear fuel cycle [21,22] describe the potentiality and challenges in this field. The most widely used extractant in nuclear waste management is tri butyl phosphate (TBP) and its extraction behavior for UO_2^{2+} in C_4mimPF_6 or C_4mimTf_2N has been reported by Giridhar et al. [23]. They described the extraction mechanism to be solvation below 4 M HNO_3 and ion-exchange at higher acidity. Dietz et al. [24] investigated the mechanistic aspect of UO_2^{2+} extraction by TBP in ionic liquid where they showed that the mode of UO_2^{2+} partitioning in ionic liquid phase changed from ion-exchange to traditional solvation mechanism with increasing hydrophobicity of ionic liquid. Extraction behavior of Pu(IV) using TBP in C_4mimTf_2N as extractant has been reported by us [25] where we found the existence of dual mechanism depending on the acidity of the aqueous phase. Pu(IV) extraction behavior of octyl(phenyl)-N,N-diisobutylcarbamoylmet hylphosphine oxide (CMPO) or crown ether in ionic liquid has also been reported by Lohithakshan et al. [26,27]. Ouadi et al. [28,29], reported task specific ionic liquids containing 2-hydroxybenzylamine and TBP moiety for the extraction of Am(III) and U(VI),respectively. Rout et al. [30] described the extraction behavior of U(VI) and Pu(IV) using N,N-dimethyl-N,N-dioctyl-2-(2-hexy loxyethyl)malonamide (DMDOHEMA) in C_4mimTf_2N where they reported the mechanism to be anion-exchange above 4 M HNO_3 and below 4 M HNO_3 the most plausible mechanism of metal ion transfer was cation-exchange. Recently the solvent extraction properties of trivalent lanthanides have been reported by Shimojo et al. [31] using N,N,N′,N′-tetraoctyl diglycolamide (TODGA) as extractant in C_nmimTf_2N as diluent. They reported that extraction of the lanthanides enhances greatly in presence of RTILs compared to n-dodecane. Extraction of Am^{3+} has been reported by Sengupta et al. [32] using TODGA and a diglycolamide functionalized calixarene in C_nmimPF_6 ionic liquids. Solvent extraction behavior of An^{n+} ions using TODGA in C_nmimTf_2N as diluent have been reported by Panja et al. [33] and favored extraction of the actinides in RTIL compared to n-dodecane as diluent was observed.

In the present investigation we describe the comparative extraction behavior of Pu(IV) using BenzoDODA as extractant in C_nmimTf_2N – a greener solvent and n-dodecane – a molecular diluent. Various parameters like kinetics of extraction, effect of feed acid concentration, effect of nature of acid, mechanism of extraction, stripping of loaded organic and extraction of other metal ions have been investigated to understand the greenness of the RTIL.

2. Experimental

2.1. Materials

Bis-(2-ethylhexyl) carbamoyl methoxy phenoxy-bis-(2-ethylhexyl) acetamide [BenzoDODA] was synthesized as per reported procedure [7] and characterized by elemental analysis and ^1H NMR. Ionic Liquids ($C_nmim^+ \cdot NTf_2^-$ and $C_nmim^+ \cdot Cl^-$ where $n = 4, 6, 8$) were procured from Io-Li-Tec, Germany and were used as received. ^{239}Pu solution was used as stock after converting it to Pu(IV) using $NaNO_2$ followed by TTA extraction and stripping at higher acidity. Diluted HLW solution generated during operation of PUREX process (Diluted in 3.0 M HNO_3/HCl) was used to study the transport properties of different fission products. The composition of the HLW solution used for the study had the following composition: U – 5.54 g/L, Pu – 4.12 mg/L, ^{137}Cs – 7.82 Ci/L, ^{106}Ru – 8.21 Ci/L, ^{144}Ce – 23.67 Ci/L, ^{90}Sr – 4.16 Ci/L, ^{95}Zr – 0.3 Ci/L. To carry out the experiment inside a fume hood, the activity of the solution was needed to be brought down to a permissible level and for which the HLW was diluted by a factor of 10^3. The concentrations of U and Pu in the diluted solution were kept similar to actual HLW by spiking of U and Pu. Due to very low level of activity of Eu in the diluted solution, tracer solution of $^{152+154}Eu$ was spiked in the solution. $^{85+89}Sr$ (a gamma emitter) was spiked in the solution due to pure beta activity of the ^{90}Sr present in the HLW. All other reagents were of AR grade and were used without further purification.

2.2. Method

Liquid–liquid extraction studies were carried out by equilibrating equal volume of the organic and aqueous phases for 60 min at room temperature (ca. 298 K) followed by centrifugation for phase separation. 100–500 μL of each phase was taken for radiometric assay of various radionuclides using High Purity Germanium (HPGe) detector based gamma spectrometry system [8]. Plutonium was assayed by alpha counting in a ZnS(Ag) based alpha counter. A high purity germanium detector coupled to a 4096 channel analyzer was used to assay the activity of the radio nuclides during HLW experiment. Energies used for the various radio nuclides were as follows: ^{106}Ru – 621 keV, ^{137}Cs – 662 keV, ^{144}Ce – 133 keV, ^{241}Am – 59 keV, ^{152}Eu – 121.8 keV and $^{85+89}Sr$ – 514 keV. Spectrophotometry using Br-PADAP as chromogenic reagent was used to analyze uranium while TTA extraction followed by radiometry was used to analyze plutonium in presence of other elements.

For radiation degradation experiments 0.01 M BenzoDODA in C_4mimTf_2N solutions were taken in a glass vial in contact with 1 M HNO_3 and irradiated with γ-rays from ^{60}Co source at a dose rate of 22 Gy/min in air at room temperature. After a particular absorbed dose the samples were removed from the chamber and distribution ratio of Pu(IV) was determined.

For reusability experiments, the extractant (0.01 M BenzoDODA in C_4mimTf_2N) after extraction and complete stripping cycle was given a wash with 0.1 M C_4mimCl solution to compensate for the loss of C_4mim^+ cation during extraction study. In another set of experiment, the extractant (0.01 M BenzoDODA in C_4mimTf_2N) was reused without equilibration with 0.1 M C_4mimCl.

The results were reported as distribution ratio and are calculated as radioactivity of the corresponding radionuclide in the organic phase divided by that in the aqueous phase. Each experiment was done in duplicate and results agree within ±5%.

3. Results and discussion

3.1. Kinetics of extraction

The kinetics of extraction of metal ions using using RTILs as diluents are in general slower compared to molecular diluents like n-dodecane. This has been ascribed in various literature reports due to higher viscosity associated with RTILs [31,33]. In the present study, Pu(IV) extraction kinetics using BenzoDODA as extractant were compared for C_4mimTf_2N and n-dodecane as diluent. While comparing the kinetics behavior, the nature of aqueous phase acid was also varied (HNO_3 and HCl). The acidity of the aqueous phase in all the experiments was maintained as 6 M. The results from the kinetics experiment are shown in Fig. 1. It is very much evident from Fig. 1 that the kinetics of extraction of Pu(IV) is much faster for BenzoDODA using n-dodecane as diluent for both HNO_3 and HCl medium compared to C_4mimTf_2N as diluent. The equilibrium was attained within ~5 min of equilibration time for n-dodecane whereas it took around ~45 min to reach the equilibrium for C_4mimTf_2N. As mentioned earlier, the higher viscosity of C_4mimTf_2N compared to n-dodecane is the probable reason behind the slower kinetics of extraction. Hence the time of equilibration in further studies was kept at ~60 min for RTIL as diluent. From the