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A diglycolamide-functionalized task specific ionic liquid (TSIL) for actinide extraction: Solvent extraction, thermodynamics and radiolytic stability studies

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ABSTRACT

A diglycolamide (DGA)-functionalized task specific ionic liquid (TSIL) was used for the extraction of actinide ions such as Am^{3+}, Pu^{4+}, Np^{4+}, UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}. Trivalent actinide ion extraction was about one order of magnitude higher than that of the tetravalent ions, which in turn was one order of magnitude higher than that of the hexavalent actinide ions. Typically, using 3.6×10^{-2} M solution of the DGA-TSIL in $C_4mim{\cdot}NTf_2$, the *D* values at 3 M HNO_3 for Am^{3+}, Pu^{4+}, Np^{4+}, UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} were 34, 5.9, 3.5, 0.44, 0.38, and 0.32, respectively. The extraction of the actinide ions decreased with increasing aqueous phase acidity, which supports an ion-exchange mechanism that often operates for this type of extraction systems. The number of DGA-TSIL molecules present in the extracted species was about one for all actinide ions studied, suggesting species of the type $M(TSIL)_{IL}^{n+}$. Both the extraction constants ($\log K_{ex}$) and the thermodynamic parameters were calculated. The ΔG values were negative in case of all actinide ions suggesting spontaneity of the extraction, which was reflected in very high *D* values for the tri- and tetravalent actinide ions. Stripping and radiolytic degradation studies were also carried out and EPR spectroscopic measurements were performed to understand the nature of the degraded free radical species.

1. Introduction

Room temperature ionic liquids (RTIL) are proposed to be an alternative to the conventional molecular diluents due to their unique properties such as, negligible vapour pressure, high boiling point, wide liquid range, thermal stability, and noninflammability [1–5]. Out of the various areas in which RTILs may find applications, separation science has been widely investigated which is reflected in a flurry of research activities in this area [6–10]. One of the main observations in ionic liquid based separations is that the distribution ratio values have been found to increase manifold as compared to that in molecular diluents under identical experimental conditions [11,12]. This has been attributed to an ion-exchange extraction mechanism which helps in the favourable partitioning of the metal ion [13,14]. This, however, leads to a significant aqueous solubility of the ionic liquid, which is one of the major drawbacks of this type of solvents. This can be alleviated by the use of a special kind of ionic liquid to which the extractant is appended, which is often referred to as Task Specific Ionic Liquid (TSIL) or Functionalized Ionic Liquid (FIL). One of the first uses of the TSIL has been reported by Visser et al. [15] who have used a series of functional groups such as thiourea, thioether and urea for the effective extraction of Cd^{2+} and Hg^{2+} from weakly acidic and neutral pH aqueous media. Subsequently, other TSILs have been reported containing phosphoryl [16], mercaptobenzothiazole [17], crown-ether [18], ethylaminediacetic acid [19], 2-hydroxybenzylamine complexing units [20], etc., which have been used successfully for the recovery of metal ions. These TSILs showed a better efficiency for the recovery of metal ions than solvents containing specific extractants in either molecular diluents or RTILs.

Out of the metal ions whose extraction behaviour with ionic liquids has been investigated, actinides represent a special class for a variety of reasons out of which their recovery from various radioactive waste streams is considered the most important. Ionic liquid-based solvent systems have been used for the recovery of actinides using extractants such as TBP (tri-*n*-butyl phosphate) [21,22], CMPO (carbamoylmethylphosphine oxide) [23], malonamides [24,25], and diglycolamides [26,27]. It is worth mentioning that, while TBP is the preferred extractant for the recovery of actinides such as U and Pu, ligands such as CMPO, malonamides, and diglycolamides are relevant for the recovery of trivalent minor actinides such as Am(III) and Cm(III), which are non-extractible by TBP. TSILs containing phosphoryl groups analogous to TBP have been used for the extraction

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of actinide ions [16] such as UO_2^{2+} and distribution ratio values of more than 2 orders of magnitude higher have been reported as compared to those obtained with TBP in $[Me_3BuN][NTf_2]$ (butyltrimethylammonium bis(trifluoromethylsulfonyl) imide). Similarly, CMPO-functionalized TSILs [28] have been used by us for the extraction of UO_2^{2+}, which also showed higher extraction than a solvent comprising of CMPO in C_4mim (1-*n*-butyl-3-methylimidazolium)·NTf_2. Bonnaffé-Moity et al. [29] used malonamide-functionalized TSILs for the extraction of UO_2^{2+} which was found to be superior to solvents containing DMDBTDMA (*N*,*N*′-dimethyl-*N*,*N*′-dibutyltetra decyl malonamide) or DMDOHEMA (*N*,*N*′-dimethyl-*N*,*N*″-dioctyl-2-(2-hexyloxyethyl)malonamide) in RTILs [25]. Recently, we have reported the synthesis and extraction behaviour of a diglycolamide (DGA)-functionalized TSIL [30], which exhibited an exceptionally high extractability for Am^{3+} and Eu^{3+}. It was of interest to use this TSIL for a detailed investigation of the extraction of other relevant actinides which are present in the high level waste (HLW).

The present work deals with a systematic investigation on the extraction of various actinide ions such as UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+}, Np^{4+}, Pu^{4+}, and Am^{3+} from nitric acid medium using the DGA-TSIL (Chart 1). The nature of the extracted species was ascertained and the thermodynamic parameters were determined. Stripping studies were carried out using a variety of strippants, while radiolytic degradation studies were performed by solvent extraction and EPR spectroscopy. To our knowledge, this is the first report on a detailed investigation of actinide extraction using a DGA-functionalized TSIL.

2. Experimental

2.1. Materials

2.1.1. Reagents

DGA-TSIL was prepared as per a previous report [30] by first synthesizing the DGA-imidazole-propanamide-butyl bromide, which was subsequently converted into the NTf_2-form by reacting with the bis(trifluoromethane)sulfonimide lithium salt. The ionic liquid C_4mim·NTf_2 (99%) was procured from IoliTec, Germany, and was used as received. Suprapur® nitric acid (Merck, Germany) was used for preparing the aqueous feed solutions for the solvent extraction studies and the final strength of the dilute acid solutions was determined by acid–base titration using standard NaOH solution and phenolphthalein (Merck) as indicator. EDTA (ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid), DTPA (diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid), and guanidine carbonate were obtained from Alfa Aeser, USA, while formic acid, hydrazine hydrate, and citric acid were procured from SD Fine Chem, Mumbai. All other reagents were of AR grade. MiliQ water (Millipore) was used for the preparation of all solutions used in the present work.

2.1.2. Radiotracers

The radiotracers ^{241}Am, Pu (mainly ^{239}Pu), and ^{233}U tracers were used from laboratory stock solutions after purification prior to their use by ion-exchange methods as reported earlier [31], while ^{239}Np was obtained by irradiating natural U in a nuclear reactor at a neutron flux of 1×10^{13} n/cm^2/s followed by separation according to a method reported previously [32]. Assaying of ^{241}Am and ^{239}Np was done by gamma counting using a NaI(Tl) scintillation counter (Para Electronics, India) inter phased to a multi-channel analyzer (ECIL, India), while nuclides such as ^{239}Pu and ^{233}U were assayed by liquid scintillation counting (Hidex, Finland) using an Ultima Gold scintillator cocktail (Sisco Research Laboratory, Mumbai).

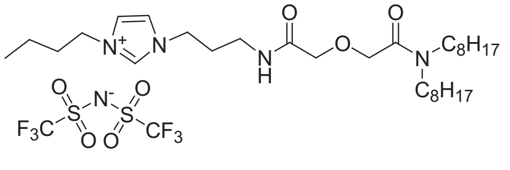

Chart 1. Structure of DGA-TSIL.

2.1.3. EPR Spectroscopic studies

The spectra were recorded on a Bruker Biospin EMX EPR spectrometer (Germany) in X-band, having phase sensitive detection to obtain a first derivative signal. Diphenyl picrylhydrazyl (DPPH) was used for the calibration of the g-values of paramagnetic species. The EPR spectra were recorded with the modulation amplitude 5 Gauss. The final signal was obtained by performing a convolution of each transition line, adding all contributions and calculating the first derivative signal. The line width of each component was optimized to obtain the best fit with the observed experimental values.

2.2. Methods

2.2.1. Distribution studies

DGA-TSIL was diluted with C_4mim·NTf_2 to yield a 3.6×10^{-2} M solution, which was used throughout this study. The distribution studies were carried out by equilibrating 1 mL of the diluted DGA-TSIL solution with an equal volume of the requisite aqueous phase containing the radiotracers at a particular concentration of HNO_3 in Pyrex tubes in a thermostated water bath at 25 ± 0.1 °C for about 3 h, which was optimized by an experiment with varying equilibration time. For the temperature variation studies, the tubes were equilibrated at varying temperatures in the range of 20–40 °C. Usually, the studies involving Am, U, and Pu were carried out using about 10^{-7}, 10^{-5}, and 10^{-6} M concentrations of the respective metal ions, while the concentration of Np was at the tracer level ($<10^{-10}$ M). After equilibration, the tubes were centrifuged followed by phase separation and assayed radiometrically as mentioned above.

The valency of Pu was adjusted to the +4 state by using a few drops of 1×10^{-2} M $NaNO_2$, which was checked by the TTA extraction method [33]. On the other hand, Pu was oxidized to the +6 state by the use of AgO followed by mild warming under an IR lamp. The Np valency state was adjusted to the +4 state by ferrous sulphamate and hydroxylamine hydrochloride [34], while NpO_2^{2+} was prepared using potassium dichromate [34].

The distribution ratio of the metal ions (D_M) was defined as the ratio of the activity per unit volume in the ionic liquid phase to that in the aqueous phase. As the ionic liquid phases were of reasonably higher viscosity than the aqueous phases, sampling errors may be significant. Therefore the D_M values in the ionic liquid phase were determined by the difference of the initial and final counts in the aqueous phase as follows:

$$D_M = (C_i - C_f)/(C_f) \tag{1}$$

where C_i and C_f are the initial and final concentrations of the metal ion, respectively. All experiments were carried out in duplicate and the precision of the experimental data points was within ±5%.

The radiolytic degradation studies were carried out using a ^{60}Co irradiation source at a dose rate of 1.6 kGy/h. Stripping studies were carried out in a manner similar to the forward extraction studies with the difference that the activity loaded organic phases were equilibrated with an equal volume of the aqueous phase containing either 0.05 M DTPA/EDTA in 1 M guanidine carbonate or a buffer mixture containing 0.1 M citric acid +0.4 M formic acid +0.4 M hydrazine hydrate.