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Extraction of uranyl ion from nitric acid medium using solvent containing TOPO and its mixture with D2EHPA in room temperature ionic liquids

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Studies on the extraction of uranyl ion were carried out from nitric acid feed solutions using solutions of tri-*n*-octyl phosphine oxide (TOPO) in several room temperature ionic liquids (RTIL), viz. [C$_4$mim][PF$_6$], [C$_6$mim][PF$_6$], [C$_8$mim][PF$_6$], [C$_4$mim][NTf$_2$], [C$_6$mim][NTf$_2$], [C$_8$mim][NTf$_2$]. All solvent extraction studies used 0.05 M TOPO in the respective RTILs. Out of the RTILs studied, those containing C$_8$mim$^+$ as the cationic part showed significantly higher extraction efficiency. The ionic liquids with PF$_6^-$ as the counter anion showed faster extraction kinetics as well as higher extraction efficiency as compared to those containing NTf$_2^-$ as the counter anion. The extraction studies carried out at varying concentrations of nitric acid indicated solvation mechanism of extraction similar to that displayed with molecular diluents such as *n*-dodecane. The extracted species were ascertained from the slope analysis method which indicated 1:2 (metal:ligand) ratio in the complex which displayed variations with the feed nitric acid concentration. UV–visible and fluorescence spectroscopic studies were also carried out to understand the nature of the extracted species.

Solutions of D2EHPA and its mixture with TOPO in the RTILs were also used for the extraction of U(VI) from both HNO$_3$ as well as H$_3$PO$_4$ medium. While the solvent system containing D2EHPA + TOPO in RTILs do not show appreciable variation with HNO$_3$ concentration, a sharp decrease was seen with increasing H$_3$PO$_4$ concentration.

1. Introduction

Nuclear energy is going to be one of the major sources of energy in the twenty first century due to the ever increasing power demands. The nuclear fuel containing fissile material makes use of enriched uranium in most of the currently operating reactors world wide. Keeping in mind the very high energy needs and long term perspectives with limited uranium resources, it is of paramount importance to recover uranium from various sources including lean sources. The most common methods of uranium recovery from acidic feeds include solvent extraction using neutral donor ligands such as TBP (tri-*n*-butyl phosphate), TOPO (tri-*n*-octylphosphine oxide), and CMPO (carbamoylmethylphosphine oxide) while there are other extraction methods using acidic extractants such as D2EHPA (di-2-ethylhexylphosphoric acid), PC-88A (di-2-ethylhexylphosphonic acid) and Cyanex 272 (di-2-ethylhexylphosphonic acid) [1]. TOPO has also been used as an auxiliary ligand in a synergistic extraction system containing D2EHPA as the primary ligand [2]. Wet process phosphoric acid (WPPA) method uses the extraction of very low concentrations of U from phosphoric acid feeds using mixtures of TOPO and D2EHPA [3]. Though these extraction methods are by and large efficient, there is a need to develop more efficient extraction methods.

Traditional liquid–liquid extraction methods using molecular diluents, though have been widely used, suffer from disadvantages such as use of inflammable and volatile organic compounds (VOC) which generate large volumes of secondary wastes. Recently, room temperature ionic liquids (RTIL) have been used as alternative diluents due to several advantages such as high boiling point, negligible vapour pressure, and tunable solvent characteristics [4–7]. There have been numerous applications of RTILs as diluents for the extraction of metal ions, quite a few of those involving uranium(VI). Giridhar et al. evaluated several RTIL based solvent systems containing TBP for the extraction of uranium(VI) [8]. Subsequently, the mechanism of extraction was investigated by Dietz and Stepinski and the extracted species were determined from mass spectrometric analyses, subsequently [9]. Though the

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extraction mechanism varied based on the nature of the RTIL, i.e., those containing a lower alkyl group followed the cation-exchange mechanism while the solvation mechanism was found to be operative in RTILs containing bulkier alkyl substituents such as *n*-octyl or *n*-decyl. Similar extraction behaviour was also seen while using solvents containing CMPO or diglycolamides in RTILs [10–12]. Similarity in the extraction mechanism was reported by Cocalia et al. [13] while using Cyanex 272 for the extraction of uranyl ion in an RTIL and a molecular diluent.

Though TOPO has been extensively used for uranium extraction using molecular diluents, to our knowledge no report is available on the extraction of U using RTILs as the diluent. On the other hand, the solvent system has been used for the extraction of divalent metal ions [14] and rare earth ions [15] very recently. Furthermore, a mixture of TOPO and D2EHPA (di-2-ethylhexylphosphoric acid) has been used for the recovery of uranium from phosphoric acid solutions, considered as a lean source of U, which is well known as the Wet Process Phosphoric Acid (WPPA). However, use of ionic liquid based separation method using a mixture of TOPO and D2EHPA as the extractants is not known to date. It was thought of interest, therefore, to carry out a detailed investigation on the extraction of U using either TOPO or D2EHPA alone or their mixture in ionic liquids from phosphoric acid medium as well.

In the present paper, studies on U extraction are carried out using TOPO in several room temperature ionic liquids. The nature of the ionic liquid (with varying cationic as well as anionic substituents) on the extraction of the metal ion, the kinetics of extraction have been carried out on the basis of which two RTILs viz. $[C_8mim][PF_6]$ and $[C_8mim][NTf_2]$ have been used for all subsequent studies. Other studies included the role of aqueous nitric acid concentration and TOPO concentration variation in the RTIL phase which were helpful in elucidating the extraction mechanism and predicting the nature of the extracted species. The extraction equilibrium constants have also been calculated based on the solvent extraction data. UV–visible and fluorescence spectroscopic studies were also carried out and compared for analogous systems containing *n*-dodecane as the diluent.

2. Experimental

2.1. Materials

The ionic liquids used in present work were procured from IoliTec, Germany at a purity of >99% and were used as obtained. TOPO (>99%) was procured from E. Merck, Germany while D2EHPA (98%) was obtained from Rare Earth Development Section, BARC and were used as such. Suprapur nitric acid (Merck, Germany) was used for preparing dilute acid solutions and the strength of the acid solutions was ascertained by volumetric titrations using phenolphthalein (Fluka) indicator. Phosphoric acid (85%, Aldrich) was used after dilutions and standardization using volumetric titrations. ^{233}U (in house stock) was used as the tracer for all studies after ascertaining its radiochemical purity. Uranyl nitrate hexahydrate, obtained from Uranium Extraction Division, BARC was used for all studies involving macro-concentrations of U.

2.2. Liquid–liquid extraction

Solvent extraction studies were carried out in airtight polypropylene tubes procured from Tarsons Products Pvt. Ltd., with 5 mL capacity. The solvent extraction studies were carried out by equilibrating equal volumes of the organic and aqueous phases (usually 0.5–1 mL) in a thermostated bath at 25 ± 0.1 °C for about 3 h which was optimized as detailed in the next section. The organic phases contained either a solution of TOPO, D2EHPA or their mixture in the ionic liquid while the aqueous phase contained the radiotracer spiked solutions at a given acidity. After equilibration of the two phases, the tubes were centrifuged and 100 μL aliquots were removed for subsequent assaying by radiometry using a liquid scintillation counting system (Hidex, Finland) using toluene based scintillation cocktail (SISCO). The distribution ratio (D_U) was calculated as the ratio of the concentration of uranium (expressed in terms of counts per unit time per unit volume) in the ionic liquid phase to that in the aqueous phase. All results were reproducible and found to be within an error limit of ±5% error. The errors in the distribution ratio data are from variations in triplicate measurements and also from counting statistics (usually <1%). Typically, the concentration of U in the tracer studies was about 10^{-5} M.

2.3. Spectroscopic studies

UV–visible spectroscopic studies were carried out using a JASCO V 530 double beam spectrophotometer using quartz cells and suitable reference solutions. The emission studies were carried out using a fluorescence spectrometer (Edinburgh Analytical Instruments, UK) controlled by a CD 920 controller and Xe flash lamp with excitation wavelength as 330 nm, while emission spectra were recorded in the range of 450–650 nm.

3. Result and discussion

3.1. Extraction from nitric acid medium

3.1.1. Studies with different ionic liquids

The ligand solubility was tested in various ionic liquids prior to the solvent extraction studies. A known weight of the ligands (TOPO, D2EHPA or their mixture) was taken in a given volume of the ionic liquid and the mixture was sonicated for several hours to get homogeneous solutions. Usually, 0.05 M TOPO or 0.1 M D2EHPA or their mixture in the ionic liquids were used for the U extraction studies involving nitric acid feeds. As mentioned below, a mixture of TOPO and D2EHPA in ionic liquids was used for the extraction of U from phosphoric acid as the extraction of the metal ion was negligible with solutions containing either TOPO or D2EHPA alone. Out of the different ionic liquids used in the present work, $[C_4mim][PF_6]$ was not used as it was difficult to prepare a solution of TOPO in it. On the other hand, all the other ionic liquids could dissolve TOPO without much hassle and 0.05 M solutions were prepared using $[C_6mim][PF_6]$, $[C_4mim][NTf_2]$, and $[C_6mim][NTf_2]$ after sonicating for about 30 min while those using both $[C_8mim][PF_6]$, $[C_8mim][NTf_2]$ were prepared almost instantaneously after sonication. The relative solubility data with TOPO are included in Table 1. Though there were conflicting reports on the solubility of D2EHPA in ionic liquids, i.e., difficult dissolution of the ligand (40 mM was the reported solubility) was reported by one research group [16] while rather free dissolution (at least up to 1 M) was reported by another group [17], we have faced little problem while preparing 0.1 M D2EHPA in $[C_8mim][NTf_2]$ while it was not possible to prepare equivalent solutions with $[C_8mim][PF_6]$ as the diluent even after 3 h of sonication.

The extraction of U(VI) was performed with 0.05 M TOPO solutions in these ionic liquids. Table 1 also lists the extraction data in these ionic liquids. For comparison purpose, extraction data with 0.05 M TOPO in *n*-dodecane are also included in the table. As shown in the table, the trend of U(VI) extraction at 3.0 M HNO_3 was found to be: *n*-dodecane > $[C_8mim][PF_6]$ > $[C_8mim][NTf_2]$ > $[C_4mim][NTf_2]$. This is rather unusual as most of the ionic liquid based solvent systems display more efficient extraction of the metal ions as compared to the molecular diluents [17]. Furthermore, the PF_6^- anion based ionic liquids show better extractability