



Extraction of thorium employing N,N-dialkyl amide into room temperature ionic liquid followed by supercritical carbon dioxide stripping



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ABSTRACT

N,N-dialkyl aliphatic amides with varying alkyl groups viz. N,N-dibutyl-2-ethyl hexanamide (DBEHA), N,N-dibutyl-3,3-dimethyl butanamide (DBDMBA), N,N-dihexyl octanamide (DHOA), N,N-di-sec-butyl pentanamide (DBPA), N,N-dibutyl octanamide (DBOA), have been evaluated for solvent extraction of thorium from nitric acid medium into the hydrophobic ionic liquid phase, 1-butyl-3-methyl imidazolium hexafluorophosphate. Distribution ratio values were markedly higher for room temperature ionic liquids (RTIL) as compared to molecular diluent, n-hexane. DBOA yielded the highest extraction. The extraction behaviour of Th(IV) into RTIL was found to be different from n-hexane with respect to extraction kinetics, effect of molarity of nitric acid and stoichiometry of Th(IV)-amide complex. Thermodynamic studies revealed that the extraction was enthalpy driven. Mechanism of the extraction was found to be dependent on the nitric acid molarity of the aqueous phase. High stripping efficiency was obtained with supercritical carbon dioxide which also provided insight into the mechanism of extraction into RTIL phase. Extraction of Th(IV) from aqueous phase (having low acid molarity, 0.2 M) into RTIL employing DBOA followed by stripping with supercritical carbon dioxide modified with DBOA·HNO₃ adduct yielded the highest overall efficiency.

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1. Introduction

India possesses vast reserves of thorium in contrast to modest quantity of uranium [1] and there is a need to develop capabilities on all aspects of thorium fuel cycle, i.e. mining, fuel fabrication, reprocessing and waste management. In this context, development of processes for separation and purification of thorium from various matrices is of utmost importance.

N,N-dialkyl aliphatic amides have been proposed to be an alternative to TBP in the reprocessing of spent nuclear fuel [2–4] due to several attractive features like innocuous nature of degradation products (mainly carboxylic acids/amines) and possibility of complete incineration of the used extractant leading to reduction in volume of secondary waste. Also, physico-chemical properties of this class of extractants can be tuned by the judicious choice of alkyl groups. Extensive studies, carried out for the solvent extraction of actinides using N,N-dialkyl amides, have been reported

[5,6] and reviewed [7,8]. Studies have been reported on the extraction of Th(IV) into molecular diluents employing amides [9].

Room temperature ionic liquids (RTIL) are a novel class of low-melting semi-organic salts comprised entirely of ions. Various properties make them a potential alternative to molecular diluents for metal ion extraction [10–13]. They have no detectable vapour pressure as against traditional organic diluents, are non-flammable and exhibit high solubility for a variety of compounds. Also, many RTILs, due to the presence of aromatic rings, have higher radiation resistance than conventional molecular diluents [14] making them a lucrative choice for the nuclear industry [15]. In fact, recent studies have discussed the interesting role of sacrificial nature of ionic liquids, the aromatic cation part in particular, in protecting the extractant and also keeping the system intact for metal ion extraction as a whole [16].

There are a number of reports on the extraction of actinides into RTILs [12,13,17]. Various studies have been reported on the solvent extraction of Th(IV) into RTIL employing β -diketone, HTTA [18], diglycolamide, TODGA [19,20] and even diglycolamide based Task Specific Ionic Liquid (TSIL) [21].

However, to the best of our knowledge, no studies are reported on the extraction of thorium employing N,N-dialkyl amides into RTIL. In

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the present study, N,N-dialkyl aliphatic amides with varying alkyl groups viz. N,N-dibutyl-2-ethylhexanamide (DBEHA), N,N-dibutyl-3,3-dimethylbutanamide (DBDMBA), N,N-dihexyloctanamide (DHOA), N,N-disecbutylpentanamide (DBPA), N,N-dibutyloctanamide (DBOA), have been evaluated for solvent extraction of thorium from nitric acid medium into the hydrophobic ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]). Here we study and compare the extraction behaviour of thorium employing amides by conventional solvent extraction with molecular diluent (n-hexane) and next generation diluent (RTIL) and alternative separation process (SFE) [22]. n-hexane (~1.8) was chosen as the molecular diluent due to its similar dipole moment with Supercritical (SC) CO₂ (~1.5). Effect of acid molarity, amide molarity and extraction time was investigated. Mechanism of extraction into RTIL has been probed. An insight into the thermodynamic parameters for extraction of thorium from RTIL has been given. Stripping remains a challenge for extraction experiments with RTIL, low stripping efficiency and cross contamination being the major challenges. Here, we also compare the stripping behaviour of thorium from RTIL by conventional route as well as by employing SC CO₂. Successful stripping with SC CO₂ modified by DBOA-HNO₃ comprises unique strategy combining high extraction and stripping.

2. Materials and methods

2.1. Materials

High purity ThO₂ was used for preparation of standard solution. Room Temperature Ionic Liquid used, 1-Butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], was obtained from Sigma. Arsenazo III (Merck, Germany) was used in the spectrophotometric determination of thorium. Sulphamic acid (Merck, Germany) was of 99% purity. A.R. grade nitric acid, chloroform, methanol, ethanol, oxalic acid and n-hexane were used. Amides (listed in Table 1) were obtained from Department of Chemistry, Delhi University and were used as such. CO₂ gas employed for preparing supercritical fluid was of 99.9% purity. DBOA-HNO₃ adduct was prepared by thorough mixing of DBOA and 4 M HNO₃ (1:1 v/v) in a glass beaker for one hour using a magnetic stirrer. The organic portion (DBOA-HNO₃ adduct) was separated by separating funnel and used for stripping experiments.

2.2. Solvent extraction study

For solvent extraction, thorium solution (~100 µg mL⁻¹ in HNO₃) and amide solution (in ([bmim][PF₆])/n-hexane) were taken in 1:1 volume ratio and equilibrated on a mechanical shaker for required time. The solution was allowed to settle for 30 min. Subsequently, the aqueous phase was used for the determination of Th (IV) amount spectrophotometrically employing arsenazo III metal indicator [23]. Absorbance was measured at 655 nm wavelength.

Table 1
Comparison of extraction behaviour of thorium employing amides into n-hexane, [bmim][PF₆] and by SFE.

Amides (0.2 M)	Distribution ratio, <i>D</i>		Extraction efficiency (%) [22] Aq. phase 4 M HNO ₃ , SFE (%)
	Aq. phase 4 M HNO ₃ , organic phase n- hexane	Aq. phase 0.2 M HNO ₃ , organic Phase [bmim] [PF ₆]	
DBEHA	0.08	0.85	19
DBDMBA	0.19	6.30	36
DBPA	0.51	3.97	66
DHOA	0.21	7.07	37
DBOA	0.61	13.5	75

Results are average of triplicate runs.

The distribution ratio (*D*) is the ratio of concentration of Th(IV) in the organic phase to the concentration of thorium in the aqueous phase after solvent extraction. Thorium concentration in the organic phase was, in turn, calculated from the difference of initial concentration of thorium taken in aqueous phase and the thorium left in the aqueous phase after solvent extraction.

2.3. SFE set-up and procedure for stripping

The details of the SFE set-up have been described elsewhere [24]. The extraction vessel, containing 1 mL of the RTIL extract, was loaded in the SFE set-up and after achieving the desired temperature in thermostat, CO₂ from respective delivery pump was flown (2 mL min⁻¹) until desired pressure was attained. Modifier pump was operated at 10% of flow rate of CO₂ delivery pump. The system was allowed to remain at desired pressure (200 atm) and temperature (323 K) conditions for certain time (static time, 20 min). Subsequently, extraction was performed by flowing SC CO₂ for certain time (dynamic time, 20 min) and collecting the extract in collection tube. After extraction, system was depressurized to atmospheric pressure and the extraction vessel was unloaded. The collected liquid was analysed for Th(IV) by spectrophotometry (Section 2.2).

3. Results and discussion

3.1. Comparison of distribution ratio of various amides into RTIL and n-hexane

Study was carried out for solvent extraction of Th(IV) from nitric acid medium into the hydrophobic ionic liquid, [bmim][PF₆] containing various dialkyl amides (Table 1). The extraction behaviour of Th(IV) into the RTIL, [bmim][PF₆] as diluent was compared with that of molecular diluent, n-hexane and SFE [22]. It is noteworthy while comparing the three systems, mechanism of extraction, acid molarity are not same. Also, solvent extraction with RTIL and n-hexane are equilibrium processes at ambient pressure-temperature conditions while SFE is a non-equilibrium process at elevated temperature and pressure. For a given amide under optimum conditions for respective systems, extraction was higher for RTIL (see Fig. 1).

In case of molecular diluents and SC CO₂ extraction, the general structure of complex of Th(IV) with amides is given by Th(NO₃)₄·3Amide [8]. Since Th(IV) is surrounded by four nitrate ions and three amide moieties, steric considerations play a pronounced role in deciding the extraction efficiency of thorium. The extraction efficiency is lowest for the amide having branched alkyl group especially at C_α position, that is, DBEHA. Highest extraction was obtained with straight chain amide, DBOA. We need to examine the stoichiometry in case of RTIL, [bmim][PF₆]. Interestingly, the trend in extraction for all amides in the three cases is similar. All further experiments were carried out with DBOA.

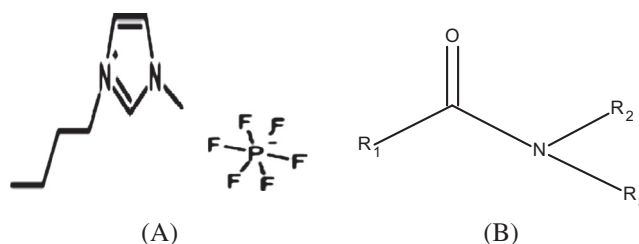


Fig. 1. (A) Room temperature ionic liquid used, 1-Butyl-3-methyl-imidazolium hexafluorophosphate, [bmim][PF₆]. (B) General structure of N,N-dialkyl amide.

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