

# Task-specific ionic liquid tetraalkylammonium hydrogen phthalate as an extractant for U(VI) extraction from aqueous media

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**Abstract** In this paper a quaternary ammonium based room temperature ionic liquid (IL) trioctylmethylammonium hydrogen phthalate has been reported as promising extractant for separation of U(VI) from other metal ions from aqueous media. The IL was synthesized via metathesis route and characterized using various techniques such as hydrogen nuclear magnetic resonance, electron spray ionization mass spectrometry and infra red etc. The newly synthesized IL was evaluated for extraction of U(VI), Th(IV), La(III), Y(III), Nd(III) and Fe(III) from aqueous solutions and follow the order: U(VI) > Th(IV) > Fe(III) > Y(III) >> Nd(III) ~ La(III).

**Keywords** Ionic liquid · Solvent extraction · Separation · Uranium · Thorium

## Introduction

Separation, recovery and purification of metal ions by liquid–liquid extraction from various aqueous media play an important role in separation science and purification technology [1–4]. The main advantages of the process are their processing capability of a large volume of aqueous

solutions in a very small time using well established industrial scale equipments such as pulse column and mixer–settler unit [5–10]. However, the conventional liquid–liquid extraction using organic solvents have a large number of limitations in connection with environmental safety issues [11, 12]. The conventional organic extractants in combination with different diluents are toxic in nature and their disposal to the environment is of great concern [13, 14]. Ionic liquids (ILs), a class of low melting organic salt have become alternative extractants for metal ions removal from various aqueous media, since the first report published by scientist [15]. ILs can be considered as organic salt containing bulky organic cations with a wide variety of anions that are liquid at room temperature. Whereas, classical solvents are neutral organic compounds, ILs are made up of large ions which are held together by electrostatic forces. Because of these interactions, the properties of ILs are different from the classical organic solvents. They have a wide liquid range, very low vapor pressure, environmental friendly nature and wide chemical and electrochemical windows. Their excellent properties make them alternative solvent for recovery of valuable metal ions from different waste streams [16–20]. Generally liquid–liquid extraction of valuable metal ions using ILs can be carried out in two ways. First option is based on the use of conventional organic extractants in ILs media and extraction of metal ions from aqueous phase to ILs phase [21–24]. Second route is based on the use of functionalized ILs which can extract metal ions from aqueous media to ILs phase [25–30]. The second types of ILs are often known as task-specific ILs (TSILs). A large number of ILs as well as TSILs containing disulfide-, thioether-, urea-, or hydroxyl benzyl amine group as extracting agent for metal ions have been reported in literature [31–33]. Luo et al. [34]

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synthesized a imidazolium cation based TSIL containing a monoaza-crown ether fragment for extraction of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  from aqueous solutions with enhance selectivity. Separation of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  ions from aqueous medium has been studied using imidazolium based IL [28]. Various parameters such as effect of anions type and effect of their structure on extraction efficiency of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  has been evaluated in detail [28]. Separation of heavy metal ions such as  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  from aqueous medium has been investigated using imidazolium cation based TSILs containing different functional groups [30]. Harijani et al. have evaluated extraction and complexation properties of Cu(II), Ni(II) and Co(II) in aqueous medium with imidazolium cation based TSILs containing appended aninodiacetic acid moieties as di-tert-butyl ester as functional group [35, 36]. Liquid–liquid extraction of non ferrous metal ions has been investigated in detail using TSILs [37]. In addition to that, tetraalkyl ammonium cation based TSILs having different functionalized anions as counter ions draw attention as emerging solvents for metal ion recovery in recent past [38–46]. Further, various types of anions such as aromatic and aliphatic carboxylate anions, thiosalicylate anions as well as unsaturated aliphatic carboxylate are incorporated to prepare tetraalkyl ammonium cation based TSILs of desired functionality [31, 32, 37]. Literature survey indicated that there are very little work available tetraalkyl ammonium hydrogen phthalate based IL [47]. Further, no literatures are available on extraction of metal ions such as U(VI), Th(IV) and Ln(III) ions from aqueous medium using tetraalkyl ammonium hydrogen phthalate based TSIL.

In the present paper we report on synthesis and characterization of TSIL, trioctylmethyl ammonium hydrogen phthalate (TOMAHP) and its application on recovery of metal ions from various aqueous media using liquid–liquid extraction method for the first time. The TOMAHP was synthesized by metathesis route using Aliquat<sup>®</sup>336 and potassium hydrogen phthalate as starting material in water–toluene mixture at room temperature. The TSIL was purified and characterized using hydrogen nuclear magnetic resonance (<sup>1</sup>H-NMR), electron spray ionization mass spectrometry (ESI-MS) techniques. The TSIL was evaluated for extraction of metal ions U(VI), Th(IV), Y(III), Nd(III), La(III) and Fe(III) from various aqueous streams using liquid–liquid extraction technique and it was observed that TOMAHP is a better extractant for U(VI) than other metal ions. The presence of one free carboxylic acid in TOMAHP is acts as a functional group to bind with metal ions at various aqueous phase acidities. Based on the liquid–liquid extraction studies it is observed that the extraction order of different metal ions varies with the following order: U(VI) > Th(IV) > Fe(III) > Y(III) >> Nd(III) ~ La(III).

## Experimental

### Chemicals and solutions

Aliquat<sup>®</sup>336 (S.D.Fine Chemicals; trioctylmethylammonium chloride, MW: 404.17), potassium hydrogen phthalate (Aldrich; >99 % purity), toluene (Analytical grade) were used without further purification. Transition metal salt,  $\text{Fe}_2(\text{SO}_4)_3$  was prepared by dissolving required amount of salt in distilled water. Nuclear grade pure  $\text{U}_3\text{O}_8$  (Obtained from Uranium Extraction Division, Mumbai, India) was dissolved in  $\text{HNO}_3$  and converted to sulphate and phosphate medium by fuming with  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ . Rare Earths (REEs) oxides ( $\text{Y}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  >99 % purity) were procured from Indian Rare Earths Ltd. India. The REEs solutions were prepared by dissolving oxides in  $\text{HNO}_3$  medium and diluting to required concentration with distilled water.  $\text{Th}(\text{NO}_3)_4$  (A.R. grade, obtained from S. D. Fine Chemicals) was dissolved in distilled water to prepare its stock solution.

### Synthesis

IL i.e. TOMAHP was synthesized by metathesis route. Equimolar amount of Aliquat<sup>®</sup>336 and potassium hydrogen phthalate were dissolved in 1:1, water/toluene mixture and stirred for a period of 5 h at room temperature. A viscous pale yellow liquid was obtained after purification of organic phase. Detailed synthesis of TOMAHP can be found in the Electronic supplementary information (ESI).

### Analysis

Analysis of IL synthesized in our laboratory was performed using a 200 MHz Bruker nuclear magnetic resonance (NMR) spectrometer for <sup>1</sup>H NMR. The molecular weight and structure of the IL was determined using mass spectrometric technique, ESI-MS. ESI-MS spectra was recorded using micrOTOF II Electrospray Ionization Mass Spectrometer from Bruker. In the ESI-MS spectra, cationic peak at mass number 368.41 is due to trioctylmethylammonium cation and anionic peak at mass number 165.01 is due to phthalate anion. The Infrared spectrum of IL was recorded with JASCO FTIR 4100 Infrared Spectrometer using KBr pallet as window. The nature of cations and anions present including impurities such as  $\text{Cl}^-$  were determined using Dionex make ion chromatography (IC, Model No. DIONEX, ICS-1600). The sample was prepared in 40 % acetonitrile–water mixture at room temperature. The density and viscosity of the IL were measured using an Anton Paar SVM 3000/G2 type stabinger viscometer with an uncertainty of  $\pm 0.0005$  g/cc for density,  $\pm 0.005$  mPa.s for the viscosity and  $\pm 0.01$  K for temperature. The melting

temperature measurement was carried out using differential scanning calorimeter (DSC) Mettler Toledo make (Software DSC 823 e-Services), with a scan rate of 10 °C/min, a sensitivity of 0.1 mW and temperature precision of  $\pm 0.1$  °C. Similarly decomposition temperature was measured with a Mettler Toledo make thermogravimetric analysis (TGA) with a scan rate of 10 °C/min. The  $pK_a$  value as well as water content of IL was determined by potentiometric and Karl Fischer titration using Metrohm make potentiometer with Karl Fischer as attachment, Model 798 MPT tritrino. The  $pK_a$  value was found to be 3.2.

#### Solvent extraction experiments

The solvent extraction experiments were performed by equilibrating 1 mL aqueous and 1 mL pre-equilibrated IL in a 5 mL extraction vial for a period of 20 min. This time was found to be sufficient to reach the equilibrium. The organic phase and aqueous phase were separated by centrifuge, (REMI, research centrifuge) for a period of 10 min. The aqueous phases were analyzed for metal ion content using Horiba, Jobin–Yvon make inductively couple plasma spectrophotometer (ICP-AES), model No. JY238. The ICP-AES has a detection limit of 3 ppb for transition metal and 2 ppb for REEs and uranium with an uncertainty of 2–5 % below 50 ppm. The concentrations of metal ions in organic phase were calculated by the difference of the metal ions concentrations in the aqueous phase before and after extraction. The distribution ratio ( $D_M$ ) of metal ions was calculated as:

$$D_M = \frac{[M]_{\text{org,eq}}}{[M]_{\text{aq,eq}}} \quad (1)$$

where,  $[U]_{\text{org,eq}}$  and  $[U]_{\text{aq,eq}}$  refer metal ion concentrations in organic and aqueous phases, respectively, under equilibrium condition.

Percentage extraction (%E) of metal ions was defined as:

$$\%E = \left( \frac{([M]_{\text{aq,in}} - [M]_{\text{aq,eq}})}{[M]_{\text{aq,in}}} \right) \times 100, \quad (2)$$

where,  $[M]_{\text{aq,in}}$  initial metal ion concentration in the aqueous phase,  $[M]_{\text{aq,eq}}$  metal ion concentration in the aqueous phase at equilibrium.

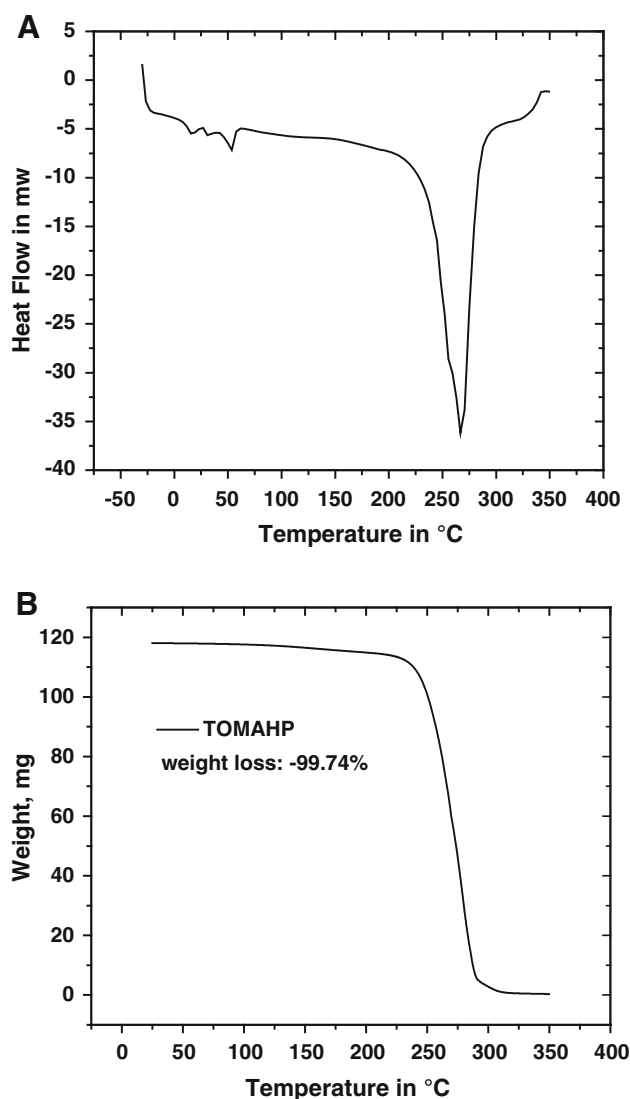
**Table 1** Density ( $\rho$ ), dynamic viscosity ( $\eta$ ), and kinematic viscosity ( $\nu$ ) at 25 °C, melting temperature ( $T_m$ ), decomposition temperature ( $T_d$ ) and water content ( $W_{\text{H}_2\text{O}}$ ) of the ionic liquid, TOMAHP

$\rho$ (g/cm <sup>3</sup> )	$\eta$ (mPa.s)	$\nu$ (mm <sup>2</sup> /s)	$T_m$ (°C)	$T_d$ (°C)	$W_{\text{H}_2\text{O}}$ (ppm)
0.974	542.75	557.06	7.08	251.35	3,000

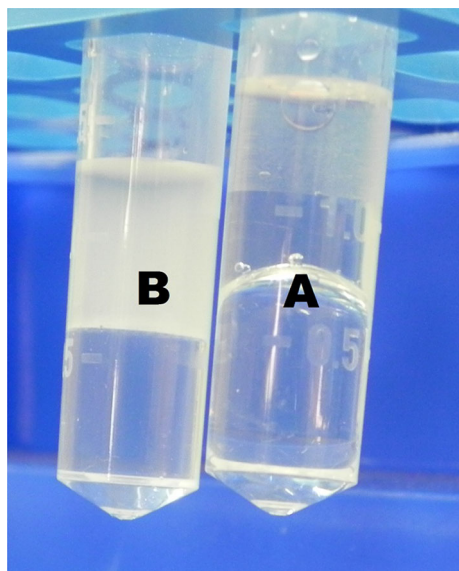
## Results and discussion

### Evaluation of physicochemical properties of IL

For the synthesis of IL i.e. TOMAHP, potassium hydrogen phthalate and Aliquat<sup>®</sup>336 were used in a metathesis reaction. The synthesis of IL was carried out at room temperature (25 °C) by just mixing the reactants in water–toluene mixture and stirred for a period of 5 h. The physical properties of IL were listed in Table 1. Literature survey indicated that the most of the tetraalkylammonium based IL with carboxylic acid as anion have viscosity ( $\eta$ ) in the range 100–1,500 mPa.s and it is mostly a function of cationic structures [43, 44]. The present studies indicate that the IL (TOMAHP) has lower viscosity (542.75 mPa.s) and density (0.974 g/cm<sup>3</sup>) as compared to other tetraalkyl



**Fig. 1** a Differential scanning calorimetric (DSC) curve of IL. b Thermogravimetric (TG) curve of IL

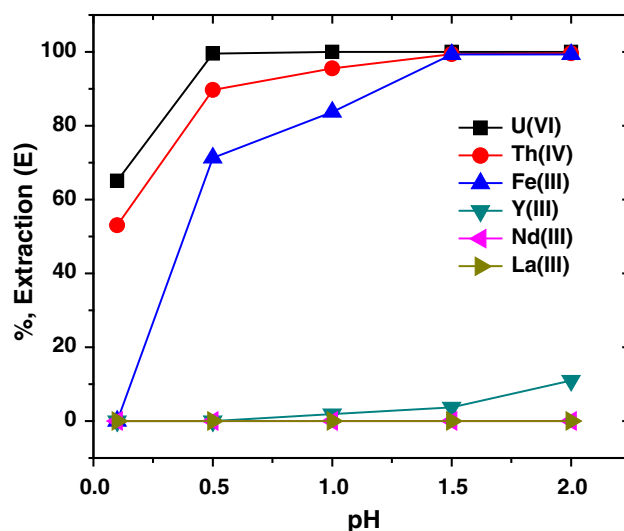


**Fig. 2** Color change observed during extraction of U(VI) from HNO<sub>3</sub> medium; pH 0.1. The tube marked as **a** shows the IL with aqueous phase before extraction and the tube marked as **b** shows the same after extraction

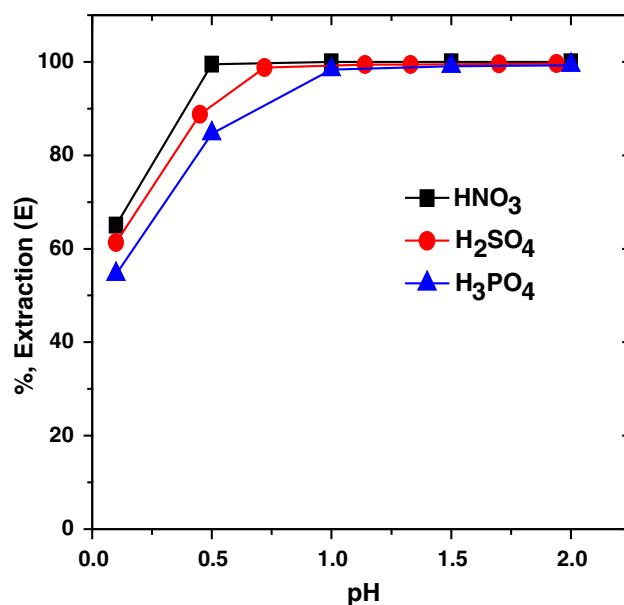
ammonium cation based IL containing various anions as counter ions. The decrease in viscosity is due to presence of potassium hydrogen phthalate anion in TOMAHP. Presence of impurities such as water, chloride anion in IL can alter the physical properties drastically [45]. In the present case the water content of IL before and after equilibration with water are 3,000 and 6,550 ppm but chloride content is <5 ppm. Based on differential scanning calorimetry (DSC) the melting point of IL was evaluated as 7.08 °C (Fig. 1a). Further, Fig. 1b showed the thermal gravimetric analysis (TGA) curve of the IL. The decomposition temperature ( $T_d$ ) was determined from the intersection of the base line and tangent line in the TGA curve [46] and the  $T_d$  value was found to be 251.35 °C (Table 1).

#### Extraction of various metal ions using IL

The synthesized IL was evaluated for metal ion extraction such as actinides (U(VI), Th(IV)), lanthanides (La(III), Nd(III)), Y(III) and transition metal ions Fe(III) from a HNO<sub>3</sub> solution at various pH. The concentration of each metal ion was maintained at  $2 \times 10^{-3}$  M. During the extraction of U(VI) from aqueous phase, a distinct color change was observed in the organic (IL) phase (Fig. 2). Figure 3 showed the pH isotherm of extraction of different metal ion from HNO<sub>3</sub> acidic aqueous media. With increase in pH of the aqueous phase there is an increase in extraction efficiency of U(VI), Th(IV) and Fe(III) where as very little or no extraction was observed in case of Y(III), Nd(III), and La(III) metal ions. These results indicate that



**Fig. 3** Extraction profile of different metal ions with IL at different pH (HNO<sub>3</sub> medium);  $[M] \sim 2 \times 10^{-3}$  M



**Fig. 4** Extraction profile of U(VI) from different acidic media at different pH;  $[U(VI)] \sim 2 \times 10^{-3}$  M

the IL could be a potential green solvent for selective separation of U(VI) from an aqueous solution containing Th(IV), Fe(III), Ln(III) as impurities.

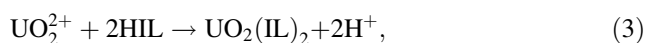
#### Extraction of U(VI) from various acidic medium

Further, extraction of U(VI) using IL was investigated from different acidic media (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) in the pH range of 0.1–2 and the results are listed in Fig. 4. With increase in pH of the aqueous phase there is an increase in

**Table 2** Effect of metal ion concentration on extraction of U(VI) from HNO<sub>3</sub> medium; pH 0.1

[U(VI)] (g L <sup>-1</sup> )	<i>D<sub>U</sub></i>	% <i>E</i>
0.50	1.86	65.03
1.54	1.59	61.39
3.71	1.46	59.35
5.71	1.39	58.16
10.99	1.28	56.14
23.05	1.18	54.13

U(VI) extraction for all the three acidic media indicating the cation exchange nature of extraction mechanism where cation is exchanged with proton present in carboxylic group of the IL according to the following equation:



where HIL represents the TOMAHP.

Similar mechanism was reported on extraction of transition metal ions using trioctyl methyl salicylate as extractant [33]. At lower pH (<1) the extraction of U(VI) from different acidic media using IL varies with the nature of acids (HNO<sub>3</sub> > H<sub>2</sub>SO<sub>4</sub> > H<sub>3</sub>PO<sub>4</sub>) where as at higher pH (>1) more than 99 % extraction was observed from all acidic solutions. This could be explained in terms of complexing ability of corresponding anions with UO<sub>2</sub><sup>2+</sup> in aqueous media. Further experiments were carried out to investigate the effect of U(VI) concentration in aqueous (HNO<sub>3</sub>) solution on *D<sub>U</sub>* using IL. It was observed that with increase in U(VI) concentration in aqueous solution from 0.5 to 23 g/L there is a decrease in *D<sub>U</sub>* from 1.86 to 1.18 as well as in %*E* from 65.03 to 54.13 (Table 2). With increase in U(VI) concentration in aqueous medium there is an increase of U(VI) concentration in IL phase, but the ratio of U(VI) concentration decrease due to increase in U(VI) concentration in denominator.

#### Separation of U(VI), Th(IV), Fe(III) and lanthanides

The selectivity of IL for U(VI) extraction from HNO<sub>3</sub> medium over other actinides, lanthanides and transition metal ions such as Th(IV), La(III), Nd(III), Y(III) and Fe(III) has been investigated from an aqueous solution of pH: 0.1. The concentration of each metal ion was kept constant at  $2 \times 10^{-3}$  M. Table 3 showed the extraction of binary mixture using U(VI) as a common metal ions using IL. It is observed that except U(VI) and Th(IV) no other metal ions get extracted under that conditions. Similar results were obtained for separation of U(VI) from an aqueous solution of pH: 0.1 over a multi-mixture of U(VI), Th(IV), La(III), Nd(III), Y(III) and Fe(III) using IL as extractant (Table 4).

**Table 3** Separation of U(VI) from binary mixture using IL; pH 0.1

Sr. no.	Binary mixture	<i>D<sub>U</sub></i>	<i>D<sub>M</sub></i>	% <i>E</i> (U)	% <i>E</i> (M)
1	U(VI), Th(IV)	1.60	1.02	61.54	50.49
2	U(VI), La(III)	1.68	0	62.68	0
3	U(VI), Nd(III)	1.33	0	57.06	0
4	U(VI), Y(III)	1.42	0	58.68	0
5	U(VI), Fe(III)	1.50	0	60.00	0

**Table 4** Separation of U(VI) from multi-component system; pH 0.1

Sr. no.	Elements	<i>D<sub>M</sub></i>	% <i>E</i> (M)
1	U(VI)	1.75	63.6
2	Th(IV)	0.86	46.30
3	La(III)	0	0
4	Nd(III)	0	0
5	Y(III)	0	0
6	Fe(III)	0	0

## Conclusions

TOMAHP was synthesized from Aliquat<sup>®</sup>336 and potassium hydrogen phthalate via metathesis route. The IL was characterized using <sup>1</sup>H-NMR, ESIMS spectrometry. The IL synthesized has a lower viscosity and water content compared to the other Aliquat<sup>®</sup>336 based IL reported in literature. These make the new IL attractive for faster mass transfer during extraction of metal ions. The newly synthesized IL was evaluated for liquid–liquid extraction of transition, lanthanides and actinides metal ion from aqueous solutions. The extraction data indicate that the TOMAHP is a green solvent for selective extraction of U(VI) from aqueous medium containing Th(IV), Fe(III) and Ln(III) as impurities.

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