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U/Th Separation by Counter-Current Liquid–Liquid Extraction with Tri-*sec* Butyl Phosphate by Using an Ejector Mixer–Settler

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ABSTRACT

Tri-*n*-butyl phosphate (TBP) and tri-*sec* butyl phosphate (TsBP) have been compared for U/Th separation by batch extraction studies and also by carrying out counter-current liquid–liquid extraction runs with a 16-stage air-pulsed ejector mixer–settler under identical conditions. The mixer–settler runs were initially carried out utilizing all stages for extraction and scrubbing (10 stages for extraction and 6 stages for scrubbing)

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and later integrating extraction, scrubbing, and stripping. Integral runs consisted of five stages for extraction, four stages for scrubbing, and seven stages for stripping. Data obtained from these studies are provided in this paper and indicate that TsBP is superior to TBP for U/Th separation.

Key Words: U/Th separation; Tri-*n*-butyl phosphate; Tri-*sec* butyl phosphate; Ejector mixer–settler; Distribution ratio; Separation factor.

INTRODUCTION

Tri-*n*-butyl phosphate (TBP) diluted with aliphatic hydrocarbons is a versatile solvent in nuclear technology for the recovery and purification of uranium and plutonium from spent fuels by the Purex process and also for the separation of uranium from irradiated thorium.[1,2] In the U/Th separation process (Thorex process), use of higher concentrations of TBP, such as 30% TBP, leads to the coextraction of uranium and thorium, and the loaded organic solvent has to be contacted with dilute nitric acid (0.2 M) to scrub thorium from the loaded organic phase.[3] But scrubbing with 0.2 M HNO_3 can lead to the loss of a significant amount of uranium into the scrub raffinate stream. The typical composition of the Thorex feed solution is about 200 mg Th/mL and about 240 μg U/mL in 4 M HNO_3; another limitation of TBP is the third phase formation due to the limited solubility of the $Th(NO_3)_4 \cdot 3TBP$ adduct in the nonpolar diluent. As a consequence, for process flowsheets designed with the aim of recovering only U(VI) from the solution of irradiated thorium, the TBP concentration used would normally be 5% to restrict Th(IV) extraction.[4] Nevertheless, the product uranium is always contaminated by coextracted thorium, which needs several stages of scrub for its removal, and the product uranium needs to be purified further by ion exchange or precipitation.[5–7]

This has influenced the need to develop novel extractants to improve the performance of the Thorex process.[8,9] Extensive studies on *N*,*N*-dialkyl amides for actinide separations have been carried out by several workers.[10–12] Pioneering work on the potential of alternate organophosphorus extractants for the separation of U(VI) from Th(IV) was done by Siddall, Mason and Griffin.[13,14] It has been realized that, in the absence of steric effects, the extraction of both U(VI) and Th(IV) increases as the basicity of the coordinating P=O of the neutral extractant increases. However, among the homologous series of neutral phosphate, phosphonate, phosphinate, and phosphine oxide, phosphate that has the least basic phosphoryl oxygen of the series gives the best separation factor for U/Th separation. In this connection, several trialkylphosphates have been developed toward U/Th separation in our laboratory, and some of them have been tested by batch equilibration experiments.[15] Earlier, we had reported the effect of altering the alkyl substituents of trialkyl phosphates on the extraction of actinide ions such as U(VI), Pu(IV), and Th(IV).[16] Studies carried out in our laboratory have revealed that distribution ratios for the extraction of Th(IV) could be drastically altered by the introduction of branching at the first carbon atom of the alkyl group.[15] The drastic reduction in the extraction of Th(IV) with branching in the carbon chain is due to the formation of trisolvate for Th extraction compared with the disolvate, which commonly is observed in the U(VI) extraction systems.[17] But branching at the first carbon atom of the alkyl group can enhance the distribution ratios for the extraction of U(VI) due to higher electron-donating power of the secondary carbon compared with that of primary carbon. Hence tri-*sec* butyl phosphate (TsBP) has been found to give a higher separation factor for U/Th separation compared with TBP in batch equilibration experiments. It also has been reported that TsBP can load more thorium without third-phase formation compared with TBP.[15]

To compare the extraction behavior of TBP and TsBP for large scale U/Th separations, counter-current liquid–liquid extraction runs that use TBP and TsBP as extractants have been carried out with a 16-stage ejector mixer–settler. A feed solution of around 200 mg Th/mL and 240 μg U/mL in 4 M HNO_3 and 0.183 M phosphate/heavy normal paraffin, which corresponds to 5% TBP (v/v), has been used to simulate the process conditions. These runs provided a comparison of the number of stages required for the extraction and scrubbing for U/Th separation by TBP and TsBP. On the basis of these runs, a new flow sheet integrating extraction, scrubbing, and stripping for U/Th separation by 0.183 M TsBP/HNP has been designed and applied. The results of U/Th separation by TsBP based on this new flow sheet are reported in this paper.

EXPERIMENTAL

Chemicals

$UO_2(NO_3)_2 \cdot 6H_2O$ obtained from BDH, Poole, England, was used as received. Nuclear grade thorium nitrate obtained from Indian Rare Earths Ltd., Mumbai, India, was used without any further purification. HNP was obtained from Tamil Nadu Petroproducts Ltd., Chennai, India. The TsBP was synthesized by the reaction between $POCl_3$ and a stoichiometric equivalent of *sec*-butanol in the presence of pyridine, using *n*-heptane as solvent. After synthesis, the product was washed with 0.2 M sodium carbonate solution and water. It was further purified by distillation under reduced pressure. The TsBP was characterized by phosphorous-31 nuclear magnetic resonance (^{31}P NMR) spectroscopy, IR spectroscopy, and elemental analysis. The TBP was obtained from M/s. Fluka (FLUKA Chemie GmbH, Buchs, Switzerland) (>97% pure) was used after washing with dilute sodium carbonate solution (0.2 M) after by water wash. The absence of acidic impurities, such as dialkyl and monoalkyl phosphoric acids, in TBP and TsBP was ascertained by measuring the *D* values for the extraction of U(VI) from 0.01 M HNO_3 solution into 0.183 M solution of phosphate in HNP. All other chemicals were analytical reagent (AR) grade.

Instruments and Equipment

High-efficiency air-pulsed ejector mixer–settler was originally developed by Koganti et al.[18] for reprocessing applications. Further development of the device with capacities as low as 5 mL/min were reported by Rajagopalan et al.[19] In the high-efficiency air-pulsed ejector mixer–settler[18], each cylindrical mixer is fitted with a liquid–liquid ejector with a short diffuser, fixed at the bottom of the mixer compartment, and the mixing device is isolated from the rest of the mixer volume except through the diffuser. This ensures that both continuous and dispersed phases pass through the diffuser so that good dispersion is achieved in the rest of the mixer section. The motive end of each ejector is independently connected through a pipe to a common header, which, in turn, is connected to a pressure and vacuum source through a 2-way 3-port Ross solenoid valve. A timer varies the frequency of the pulse, and varying the pressure and vacuum to the solenoid can change the amplitude of the pulse. Once the pulsing starts, the bottom portion of the mixer will develop a few inches of negative pressure, and the free level in the feed lines are lowered so that the aqueous and organic phases flow over their weirs to the corresponding mixer, thereby, eliminating the need for interstage pumps. The original paper[18] describes the efficiency runs in detail, and the unit is found to give near theoretical mass transfer efficiency at pulse frequencies as low as 40 cycles/min and even with low residence times as low as 12 sec in a mixer with HNO_3–30% TBP/*n*-dodecane system. The unit used for the present runs has 16 stages with a mixer, having a volume of 10 mL and a settler, having a volume of 30 mL. The settler is similar in construction except for the size and is made of a monolithic block of polypropylene nozzle and diffuser are 1.5 and 2 mm in diameter. The counter-current flow of organic and aqueous solutions in the mixer–settler is represented in Fig. 1.

Mass transfer efficiency of a stage can be defined as the ratio of the amount of solute transferred in the actual operating stage to the solute

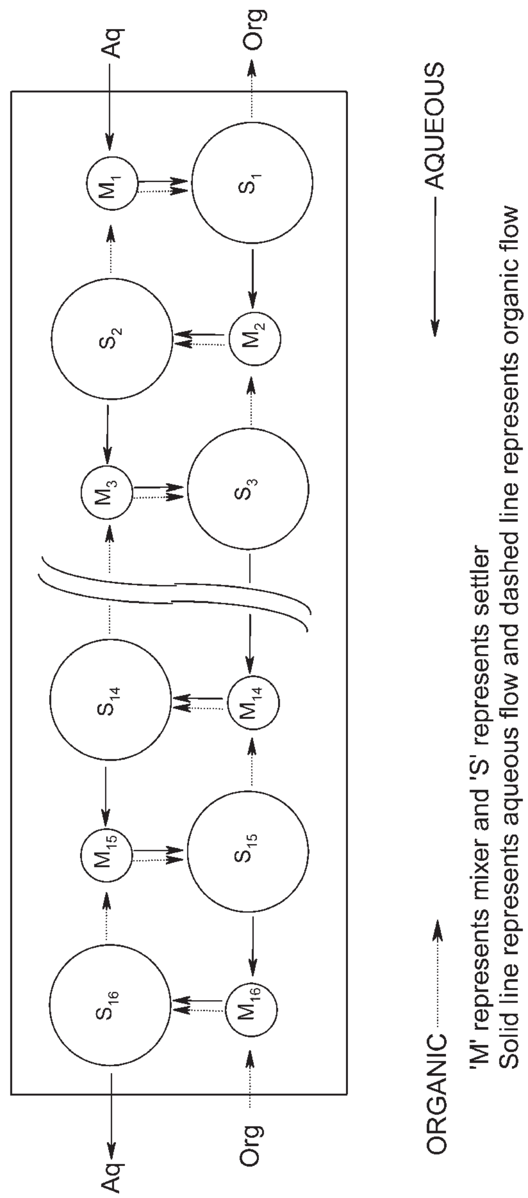

Figure 1. Typical counter-current flow of organic and aqueous phases in the mixer–settler.

transferred in an equilibrium stage under identical conditions. Therefore, stage efficiencies can be defined based on both aqueous and organic phases, as given below for the *n*th stage; the numbering is from 1 to *n* in the direction of aqueous flow.

$$\eta_{\mathrm{aq}} = \left(\frac{X_n - X_{n-1}}{X_{\mathrm{e}} - X_{n-1}}\right) \tag{1}$$

$$\eta_{\mathrm{org}} = \left(\frac{Y_{n+1} - Y_n}{Y_{n+1} - Y_{\mathrm{e}}}\right) \tag{2}$$

where X and Y are the aqueous and organic concentrations of the leaving streams from the given settler, and X_{e} and Y_{e} are the corresponding equilibrium concentrations obtained after remixing the settler phases in the flowsheet flow-rate ratio.

Valveless metering pumps of Fluid Metering Inc., USA, were used for precisely pumping the feed, scrub, organic, and strip solutions after prior calibration.

A SHIMADZU model UV-2100 spectrophotometer was used for absorbance measurements for the analysis of uranium and thorium.

Procedure for the Measurement of Distribution Ratio in Batch Studies

In batch equilibration studies, the extraction of U(VI) and Th(IV) was carried out to study the U/Th separation by equilibrating equal volumes of organic and aqueous solutions in equilibration tubes by using a mechanical shaker at room temperature (~298 K). Equilibration was carried out for the required length of time and after which the phases were allowed to settle by gravity. Suitable aliquots were withdrawn from the phases for analysis to calculate the distribution ratio (D_{M}) of solute (M), which is defined as

$$\mathrm{D}_M = \frac{[M]_{\mathrm{org}}}{[M]_{\mathrm{aq}}} \tag{3}$$

where $[M]_{\mathrm{org}}$ is the concentration of solute in organic phase and $[M]_{\mathrm{aq}}$ is the concentration of solute in the aqueous phase.

To compare the D values for the extraction of U(VI) by TBP and TsBP in the absence of Th(IV), 16 mL of 0.183 M TBP/HNP and 0.183 M TsBP/HNP (pre-equilibrated with 4 M HNO_3) were equilibrated with 16 mL of a solution containing ~125 μg/mL U(VI) in 4 M HNO_3 and the D values after $\frac{1}{2}$, 2, 6, and 23 hr were measured. At the same intervals, 3 mL of the extract (loaded organic) was removed from the equilibration tube (equivalent amount of aqueous also removed to maintain the 1 : 1 O/A ratio for extraction), and uranium was stripped from the extract with 3 mL of 0.01 M HNO_3, and D values for stripping also were measured.

To simulate extraction, scrubbing, and stripping properties of TBP and TsBP with a solution of uranium and thorium in HNO_3, when they are contacted with U/Th mixture in mixer–settler, 11 mL of 0.183 M TBP/HNP and 0.183 M TsBP/HNP were contacted with 11 mL of a solution containing 160 mg/mL Th and 180 μg/mL U in 3 M HNO_3 for $3\frac{1}{2}$ hr at ambient temperature and analyzed for acidity, uranium, and thorium to measure D values that were used to calculate the separation factor. An equilibration time of $3\frac{1}{2}$ hr was given to ensure the attainment of equilibrium, even though the kinetics is known to be fast.[20] Loaded organic phases (TBP and TsBP), 7 mL, were scrubbed with 7 mL of 3 M HNO_3 for the removal of thorium. Uranium from scrubbed organic phases was stripped with 0.01 M HNO_3. The separation factor (β) for the separation of two metal ions M_1 and M_2 is defined as:

$$\beta_{M1/M2} = D_{M1}/D_{M2} \tag{4}$$

where D_{M1} and D_{M2} are the distribution ratios of M_1 and M_2.

Counter-Current Liquid–Liquid Extraction Experiments with Using Ejector Mixer–Settler

In the first run (run no. 1), a Thorex feed solution containing 200 mg Th/mL and 240 μg U/mL in 4 M HNO_3 (4 mL/min), a scrub of 2 M HNO_3 (2.66 mL/min), and the solvent of 0.183 M TBP/HNP (8 mL/min) were fed into the 7th, 1st and 16th stage mixer inlet ports of the mixer–settler, respectively, at the predetermined rates by using calibrated metering pumps (see the flow-sheet diagram, Fig. 2). The loaded organic and raffinate were collected from the 1st and 16th stage settler outlet ports. After running the equipment for ~7 hr (after attainment of steady state), organic and aqueous stage samples were collected from settlers while in operation. After washing the equipment several times with distilled water, a second run (run no. 2) was carried out by using 0.183 M TsBP/HNP under identical conditions. In the first integral run (run no. 3), the Thorex feed solution, 0.183 M TsBP/HNP (solvent), 2 M HNO_3 (scrub), and 0.01 M HNO_3 as strippant were fed into the 12th, 16th, 8th and the 1st mixer inlet ports, respectively, by using calibrated metering pumps with predetermined flow rates (see the flow-sheet diagram, Fig. 3). Raffinate, lean organic and aqueous products were collected from the 16th, 1st and 7th settlers, respectively. After confirming the attainment of steady state (after running the equipment for ~7 hr),

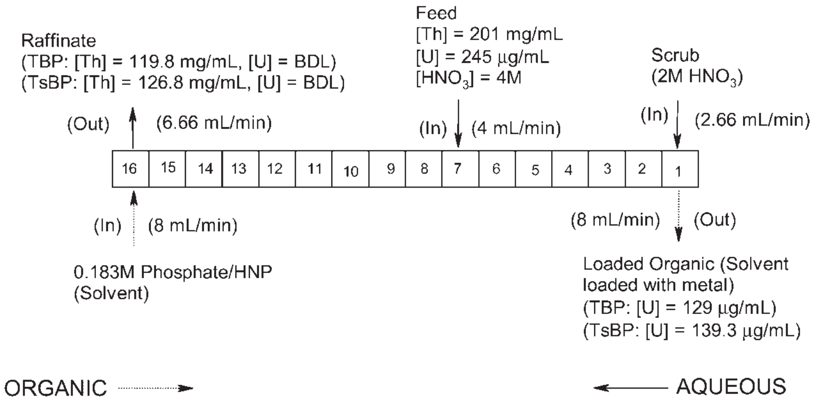

Figure 2. Flow sheet for U/Th separation runs (run no. 1 and 2) with 0.183 M TBP/HNP and 0.183 M TsBP/HNP.

organic and aqueous stage samples were collected from settlers. In the fourth run (run no. 4), the integral run was duplicated to validate the performance of TsBP for U/Th separation. The TsBP solution used in the run no. 2 has been reused for the two integral runs after stripping the solvent completely from uranium and thorium. A pulse frequency of 60 cycles min^{-1} and a pulse amplitude of 100–150 mm in the pulse probe (i.d. = 6 mm) were maintained during all mixer–settler runs. All organic and aqueous stage samples were analyzed for free acidity, uranium, and thorium.

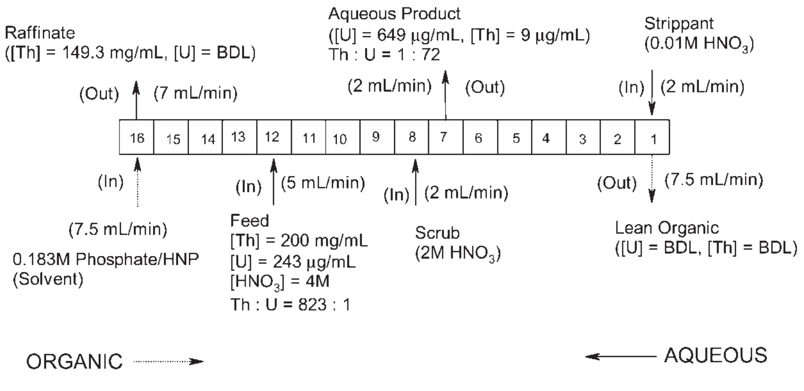

Figure 3. Flow sheet for the integral U/Th separation runs (run no. 3 and 4) with 0.183 M TsBP/HNP (Composition of feed, raffinate, and aqueous product given in the flowsheet are from the results obtained from run no. 3).

Analytical Procedures

Free HNO_3 in the aqueous and organic samples was estimated by titration with standardized NaOH solution by using phenolphthalein as an indicator after complexing the thorium and uranium, with saturated preneutralized potassium oxalate solution. Macro quantities of thorium were estimated by complexometry by using diethylenetriaminetetraacetic acid (DTPA) as a titrant and xylenol orange as an indicator at pH 1. Thorium in ppm concentrations was estimated by spectrophotometry by using thoron as a chromogenic agent. Uranium in ppm concentrations (with and without thorium) was estimated by spectrophotometry by using 2-(5-bromo-2-pyridyazo)-5-(diethylamino phenol) (Br-PADAP) as a chromogenic agent at a wavelength of 577 ± 1 nm.[21] The detection limit for the spectrophotometric analysis of uranium is about 1 ppm and that of thorium is about 5 ppm.

RESULTS AND DISCUSSION

Studies on U/Th Separation by TBP and TsBP by Batch Equilibration Method

The D values for the extraction of U(VI) by 0.183 M TBP/HNP and 0.183 M TsBP/HNP from uranyl nitrate solution (125 μg/mL in 4 M HNO_3) in the absence of Th(IV) by batch studies are given in Table 1. In both the cases, there is no appreciable change in the D_U values (average $D_U = 4.54$ for TBP and average $D_U = 6.09$ for TsBP) with time. The higher D values for the extraction of U(VI) by TsBP compared with that of TBP is due to the fact that electron donating ability of the *sec*-butyl group is higher than that of the *n*-butyl group, resulting in the higher basicity of TsBP compared with TBP. The HNO_3 loading in the case of TBP (0.147 M) and that in the case of TsBP (0.151 M) are comparable. The D_U values for the stripping do not change significantly with time (average $D_U = 0.027$ for TBP and average $D_U = 0.050$ for TsBP). This also indicates that both TBP and TsBP are chemically stable with 4 M HNO_3 under the conditions adopted for mixer–settler experiments.

Table 2 shows the data on U/Th separation by TBP and TsBP by batch equilibration studies. The influence of the presence of thorium on U(VI) extraction also is reflected in the data. Since each thorium ion is associated with 4 NO_3^- ions, $Th(NO_3)_4$ can act as a salting-out agent in the extraction of U(VI). But the D value for the extraction of U(VI) in the presence of Th(IV) by 0.183 M TBP/HNP decreased to 3.13; but, for TsBP, it is increased to 10.17 compared with those values in the absence of Th(IV). However, the D value for the extraction of Th(IV) by 0.183 M TBP/HNP is 0.043 with a

Table 1. Variation of D_U for the extraction and stripping of U(VI) by 0.183 M TBP/HNP and 0.183 M TsBP/HNP with time in the absence of Th(IV).

	D_U							
	0.5 hr		2 hr		6 hr		23 hr	
Extractant	Extraction	Strip	Extraction	Strip	Extraction	Strip	Extraction	Strip
TBP	4.46	0.024	4.77	0.027	4.40	0.027	4.53	0.029
TsBP	6.15	0.046	6.21	0.051	6.07	0.050	5.92	0.054

Table 2. Extraction, scrubbing and stripping behavior of 0.183 M TBP/HNP and 0.183 M TsBP/HNP with a solution of U(VI) and Th(IV) in HNO_3—batch studies.

	TBP			TsBP		
	Extraction	Scrub	Strip	Extraction	Scrub	Strip
$[H^+]$ (mol/L)						
Org.	0.056	0.128	0.015	0.147	0.255	0.019
Aq.	2.99	2.94	0.123	3.01	2.91	0.146
D_H	0.019	—	—	0.049	—	—
$[Th^{4+}]$ (mg/mL)						
Org.	6.63	0.61	—	2.39	0.061	—
Aq.	152.8	6.06	—	156.0	2.28	—
D_{Th}	0.043	—	—	0.015	—	—
$[UO_2^{2+}]$ (µg/mL)						
Org.	141.4	111.7	8.34	168.0	144.4	40.47
Aq.	45.23	31.43	103.0	16.52	26.79	103.5
D_U	3.13	—	—	10.17	—	—
$\beta_{U/Th} = D_U/D_{Th}$		72			665	

loading of 6.63 mg Th/mL in the organic phase. On the other hand, TsBP shows a D_{Th} value of 0.015, with an organic loading of 2.39 mg Th/mL. Hence, it is clear that the *D* value for the extraction of Th(IV) is decreased when the oxygen atom of the alkoxy group of phosphate is bonded to a secondary carbon atom as in the case of TsBP. This is because the introduction of branching at the first carbon atom causes steric hindrance in the vicinity of the coordination site during the formation of a thorium complex that contains three molecules of trialkyl phosphate compared with the extraction of U(VI), where the solvate is known to be disolvate. Earlier, we have reported that the steric effect in the extraction of Th(IV) by TsBP also is accentuated in the presence of higher concentrations of nitric acid.[15] From the *D* values, it is found that the U/Th separation factor for TBP is 72 and that of TsBP is 665 for the extraction from 3 M HNO_3. In nitric acid extraction, loading of HNO_3 in the organic phase is 0.147 M in the case of TsBP, and in the case of TBP, reduced to 0.056 M. Higher loading of thorium in TBP phase compared with TsBP (three extractant molecules are associated with each thorium) reduces the concentration of free extractant and might result in the reduction in the loading of HNO_3 and a lower *D* value for the U(VI) extraction in the case of TBP compared with TsBP. In the scrubbing step, in the case of TBP, the *D* value for the thorium removal is found to be 0.1007 (90% of Th scrubbed), whereas, TsBP has shown a very low *D* value of 0.0268 with a thorium recovery of 97%. It is found that in the case of TBP, 92% uranium is stripped, while in the case of TsBP, uranium recovery was 72%. The difference in U stripping is due to the fact that in the case of TsBP, the higher amount of nitric acid extracted in TsBP phase increases the equilibrium aqueous acidity during stripping of U(VI) from TsBP compared with that in the case of TBP.

The separation of U(VI) and Th(IV), therefore, can be more effectively accomplished by using TsBP as the extractant. The thorium extraction behavior observed with TsBP suggests that it might be possible to use higher concentrations of TsBP for U/Th separations, but still operate at low thorium loadings in the organic phase. This would have the advantages such as higher recovery of U(VI) in lesser number of stages of extraction.

U/Th Separation Runs by 0.183 M TBP/HNP and 0.183 M TsBP/HNP with Mixer–Settler (Run No.1 and 2)

The data on the separation of uranium and thorium by 0.183 M TBP/HNP and 0.183 M TsBP/HNP (run no. 1 and 2) are shown in Table 3, which provides a comparison of extraction behavior of TBP and TsBP. From the HNO_3 extraction profile (Fig. 4), it is clear that the loading of nitric acid in

Table 3. Comparison of data on U/Th separation by TBP and TsBP (run no. 1 and 2).

Stage no.	TBP				TsBP			
	[Th^{4+}] (mg/mL)		[UO$_2^{2+}$] (μg/mL)		[Th^{4+}] (mg/mL)		[UO$_2^{2+}$] (μg/mL)	
	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.
1	—	—	129	48.4	—	—	139.3	30.88
2	—	—	140.2	75	—	—	154.9	38.74
3	—	—	142.5	75	—	—	152.8	39.32
4	—	0.187	139.7	73.4	—	—	151.6	39.34
5	0.359	4.49	140.2	75	0.095	0.73	152.2	38.74
6	1.43	18.7	143.1	68.9	0.206	6.95	155.6	33.2
7	5.8	122.9	139.9	52.3	2.05	169.8	146.8	63.1
8	6.01	130.8	43.1	18.3	2.05	148.3	19.2	14.41
9	6.06	131.1	12.5	2.55	2.04	138.5	2.24	3.73
10	6.54	130.5	4.83	BDL	2.02	131.7	BDL	BDL
11	5.99	130.8	BDL	BDL	1.93	129.4	BDL	BDL
12	6.14	130.6	BDL	BDL	1.93	129.9	BDL	BDL
13	6.08	132.1	BDL	BDL	1.97	129.4	BDL	BDL
14	5.94	132	BDL	BDL	1.88	131.2	BDL	BDL
15	6.05	132.7	BDL	BDL	1.89	128.6	BDL	BDL
16	5.99	119.8	BDL	BDL	1.92	126.8	BDL	BDL

Note: BDL: below detectable limit (extraction stages: 7–16, scrub stages: 1–6).

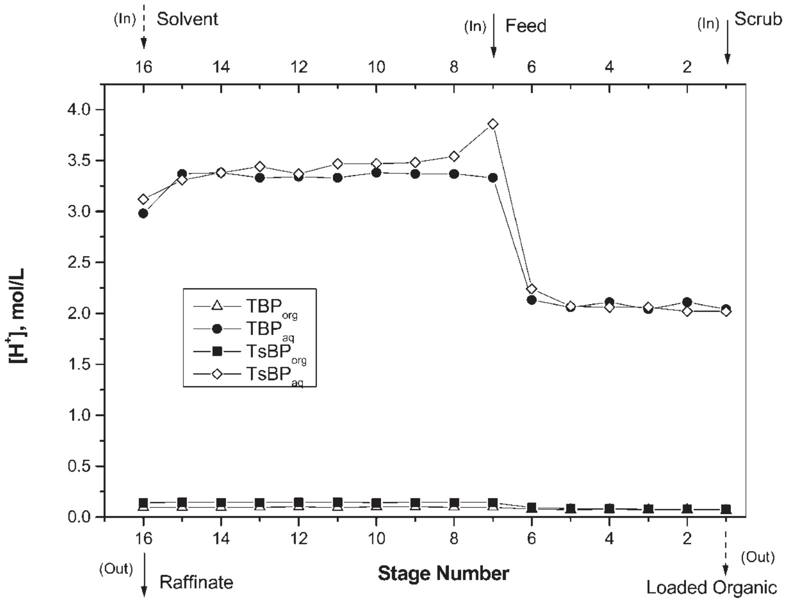

Figure 4. Stage profiles for the extraction of HNO_3 by 0.183 M TBP/HNP and 0.183 M TsBP/HNP in run no. 1 and 2.

the TBP phase is about 0.096 M with ~3.3 M HNO_3 in the aqueous phase for the extraction section (7–16 stages) and that in the scrub section (1–6 stages) is ~0.072 M with about 2.1 M HNO_3 in the aqueous phase. On the other hand, the loading of nitric acid in the TsBP phase is about 0.143 M in the extraction section and that in the scrub section is around 0.08 M.

In TBP system, thorium loading in the organic phase of the extraction section is about 6 mg/mL with around 130 mg/mL thorium in the aqueous phase. But the thorium concentration in the raffinate is about 120 mg/mL. In the case of TsBP, the thorium loading is about 2 mg/mL and the raffinate concentration is about 127 mg/mL. Poor extraction of thorium by TsBP is confirmed from the thorium loading in the scrub section. A small amount of thorium is present in the 6th and 5th stages. In both the cases, the organic loading of thorium in the scrub section decreases as the stage number decreases.

The data also indicate that in run no. 1 with TBP, uranium in the organic phase is present until the 10th stage and the aqueous uranium is below the detectable limit in the 10th stage and goes below detectable limit from the 11th stage onward. This also indicates that only four stages are required for the extraction of uranium. Hence, the raffinate can be treated as a pure solution of thorium nitrate in HNO_3, with a very high decontamination from uranium.

The organic loading of uranium in the scrub section is about 140 μg/mL. In run no. 2 with TsBP, uranium is present only up to the 9th stage and is not detectable from the 10th stage onward, and, hence, only three stages are required for the extraction of uranium. In this case, the organic loading of uranium in the scrub section is about 152 μg/mL.

The higher affinity of TBP for thorium compared with TsBP is evident from the data. It is clear from Table 3 that TsBP requires a fewer number of stages for scrubbing for a given decontamination factor compared with TBP. The extraction of uranium by TsBP is higher compared with that by TBP. Hence, U/Th separation factor (β) achieved in the case of TsBP is higher than that of TBP. For example, for the first extraction stage (7th stage) and the first scrub stage (6th stage), the β values work out to 56.7, 27.1 for TBP, and 192.3, 158.4 for TsBP, respectively. These differences also highlight the influence of the structure of the extractant on extraction behavior.

Integral U/Th Separation Runs with 0.183 M TsBP/HNP (run no. 3 and 4)

The profiles for the extraction of thorium and uranium in the integral U/Th separation run (run no. 3) by using 0.183 M TsBP/HNP are shown in Fig. 5. The data indicate that concentration of thorium in the organic phase in the extraction section (from 12th to 16th stage) is less than 2 mg/mL and thorium concentration in the scrub section decreases with stage number toward the strip section. The concentration of thorium in the raffinate is about 149.3 mg/mL and uranium was found to be below detectable limit and, hence, can be considered to be a pure thorium nitrate solution, highly decontaminated from uranium. Concentration of uranium in the 8th stage organic phase leaving the scrub section is about 163 μg/mL with a very small amount of thorium (8 μg/mL). In the strip section, concentration of uranium in the aqueous product is about 649 μg/mL with a small amount of thorium (9 μg/mL). Hence, thorium and uranium present in the feed solution with a ratio of 823 : 1 get separated into the product of uranium with a small amount of thorium (Th : U = 1 : 72) and $Th(NO_3)_4$ solution with negligible amount of uranium, as shown in Fig. 3. The uranium product is decontaminated from thorium by a factor of 2.2×10^4. It also is seen that the concentration of uranium in the lean organic is below detectable, indicating negligible loss. The data on the integral run (run no. 4) by using 0.183 M TsBP/HNP are provided in Table 4. Also in this run the uranium product is seen to achieve a decontamination factor of 2.9×10^4 from thorium. It is found that the profiles for the extraction of HNO_3, thorium, and uranium in this run are similar to the profiles observed in the run no. 3.

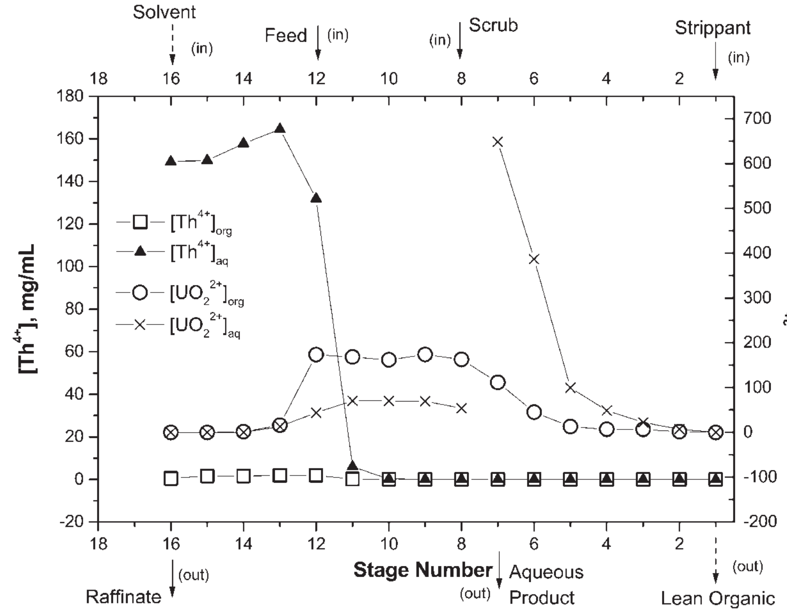

Figure 5. Stage profiles for the extraction of U(VI) and Th(IV) by 0.183 M TsBP/HNP in the integral run (run no. 3).

These results are compared with the data on U/Th separation studies carried out by Balasubramaniam et al.[4] with a feed solution comprising 200 mg/mL Th and 240 μg/mL U in 4 M HNO_3, a scrub acid of 2 M HNO_3, and 5% TBP/SST (shell sol-T) by using a 20 stage mixer–settler (with air pulsing as a mixing device and an air lift for interstage fluid transfer). They reported that with 12 stages provided for extraction and 8 stages for scrubbing, the concentration of Th in the organic product is 4.2 μg/mL. But with reduced stages for scrubbing (6 nos), concentration of Th in the organic product increased to 24 μg/mL. But in the present study, the Th concentration in the loaded organic (organic phase leaving the 8th stage) in the integral run with TsBP (run no. 4) is only 7 μg/mL just with four stages for scrubbing. It is clear that decontamination factor achieved in these runs with TsBP would have been much higher if the number of stages for scrubbing is increased to 6 or 8.

For the run no. 4, the equilibrium concentrations of uranium in both aqueous and organic phases after remixing the stage samples in the same flow-rate ratios are 106.8, 64.85, and 9.76 μg/mL in the aqueous phase and 9.78, 212.6, and 25.1 μg/mL in the organic phase, respectively, for the stage no. 5 (stripping section), 9 (scrubbing section), and 13 (extraction

Table 4. Data on U/Th separation by the second integral run (run no. 4).

Stage no.	$[H^+]$ (mol/L)		$[Th^{4+}]$ (mg/mL)		$[UO_2^{2+}]$ (μg/mL)	
	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
1	—	0.019	BDL	BDL	BDL	BDL
2	—	0.012	BDL	BDL	—	7.45
3	—	0.014	BDL	BDL	1.87	20.61
4	—	0.013	BDL	BDL	6.68	46.69
5	—	0.015	BDL	BDL	9.86	107.5
6	0.0027	0.057	BDL	BDL	24.44	514.9
7	0.011	0.41	—	0.007	137.3	714.7
8	0.061	2.00	0.007	0.005	200.5	56.88
9	0.058	1.96	0.009	0.057	211.9	65.12
10	0.064	1.97	0.037	0.275	204.7	73.21
11	0.078	2.14	0.073	5.35	216.9	72.88
12	0.133	3.23	1.68	131.1	189.1	42.43
13	0.135	3.58	1.87	144.5	25.50	9.97
14	0.159	3.51	1.76	158.2	3.20	—
15	0.13	3.34	1.68	155.6	BDL	BDL
16	0.039	3.40	0.537	151.1	BDL	BDL

Note: BDL: Below detectable limit (extraction stages: 12–16, scrub stages: 8–11, strip stages: 1–7).

section). By using these equilibrium concentrations and the stage profile data given in Table 4, stage efficiencies work out to 101%, 103.3%, and 99.3% based on aqueous phase concentrations and 99.4%, 91.1%, and 101% based on the organic phase concentrations, respectively.

These results confirm high-stage efficiencies even with the low residence times of about 50 sec. Since kinetics of mass transfer for uranium, thorium, and nitric acid in TBP and TsBP are known to be faster, low residence times may not be a problem, provided nonidealities such as bypass of the phases through mixer, etc., are eliminated from the unit.

Mass Balance

For run no. 1 and 2, mass balance for thorium and uranium can be calculated by using Eq. (5) and for the integral runs by using Eq. (6), given below;

$$S \times X_S + F \times X_F - R \times X_R = O \times Y_O - O \times Y_i \tag{5}$$

$$F \times X_F + S \times X_S + St \times X_{St} - R \times X_R - P \times X_P = O \times Y_O - O \times Y_i \tag{6}$$

where S, F, R, St, P, and O stand for the flow rates of scrub, feed, raffinate, strippant, aqueous product, and organic (solvent) streams, respectively. X and Y refer to the concentrations in aqueous and organic phases, respectively, and the corresponding subscripts refer to the respective streams. Subscripts i and o refer to the solvent in and out of the extractor bank.

All the runs show a very good material balance for thorium (within 5%). Small differences might be due to the errors associated with analysis of metal ions and flow-rate variations. In run no. 1 and 3, material balance for uranium is within 5%. But for run no. 2, the material balance deviation for uranium solute is about 13%, and for run no. 4, it is about 17%. The aqueous stage profile data presented in Fig. 4 and Table 3 for the case of TsBP (run no. 2) reveal that refluxing of uranium, thorium, and nitric acid is occurring at feed stage (stage no. 7), thereby, lowering the D_U value, whereas, in the case of TBP (run no. 1) no reflux is observed, and the material balance for TBP run is within the analytical error range. Though the process can be operated steadily under reflux condition, reflux can be avoided by increasing the scrub acidity or by increasing the percentage of extractant. From the identical runs (run no. 3 and 4), run no. 3 material balance results for uranium are excellent, whereas, in the case of run no. 4, the reason for large deviation in material balance observed is not very clear.

CONCLUSIONS

The trialkyl phosphate isomers TBP and TsBP have been explored for U(VI)/Th(IV) separation both by batch equilibration studies and countercurrent runs by using a novel ejector mixer–settler. The results indicate superior performance of TsBP over TBP. Hence, TsBP can be used for U/Th separation with a fewer number of stages. It is found that in the integral runs, the uranium product achieved a decontamination factor of about 2.5×10^4 from thorium. Hence, the present study has proven that TsBP is a promising extractant for the processing of irradiated ^{232}Th for the recovery of ^{233}U and also for the processing of certain ores of thorium-containing uranium.

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