Extraction of Zirconium with Tributyl Phosphate from Nitric Acid Solutions


Khlopin Radium Institute, Research and Production Association, Federal State Unitary Enterprise,
St. Petersburg, Russia

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Abstract—The extraction of zirconium with tributyl phosphate (TBP) in organic diluent was studied. The dependence of the distribution ratio of Zr on the TBP concentration in the organic phase and also the IR spectra of Zr–TBP extracts obtained at different concentrations of Zr and HNO₃ in the aqueous phase show that at least two kinds of extractable zirconium nitrate solvates with TBP are formed in extraction with 30% TBP. The solvate formed at HNO₃ concentration not exceeding 3 M contains water molecules. The extractable species formed at higher nitric acid concentration in the aqueous phase is anhydrous zirconium nitrate disolvate with TBP.

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The extraction of zirconium with tributyl phosphate (TBP) in reprocessing of spent nuclear fuel (SNF) is a complex process, because the speciation of Zr in solutions is dependent, all factors being the same, on procedures used for dissolving SNF and on the SNF kind [1–4]. The similar problems arise in extraction of zirconium from model solutions prepared by procedures simulating the industrial treatment of ore concentrates. Another complication is caused by the fact that the extractable Zr–TBP complexes are capable of additional extraction of uranium under dynamic conditions, which is not observed in static laboratory experiments [5].

Earlier studies of the stoichiometry of Zr extraction with TBP [1–4], based solely on extraction methods, did not allow unambiguous determination of the composition of the extractable species. It was found that, along with the hydroxy solvate Zr(OH)₂(NO₃)₄(TBP)₂ and anhydrous neutral solvate Zr(NO₃)₄(TBP)₃, acidic solvates Zr(NO₃)₄(HNO₃)₂(TBP) and Zr(NO₃)₄(HNO₃)₄(TBP) are also formed. It was also found [6] that, in separation of zirconium extract into two organic phases, the organic phase enriched in TBP (80–90%) contains the acidic solvate Zr(NO₃)₄(HNO₃)(TBP).

The results of IR studies of Zr–TBP extracts were reported in [7, 8]. Unfortunately, Zr–TBP extracts examined in these studies were obtained either at very high HNO₃ concentrations (≥8 M), or neat TBP was used [8]. These conditions strongly differ from those of the PUREX process where the solvent is 30% TBP in organic diluent and the HNO₃ concentration in the aqueous phase ranges from 1 to 6 M.

It was reported recently [9–11] that, in extraction of actinides with TBP, along with anhydrous solvates, hydrated extractable solvates containing cationic and anionic actinide complexes are also formed.

In this study we examined the formation of hydrated extractable Zr–TBP complexes in extraction of Zr with TBP from aqueous nitric acid solutions. We also attempted to reveal excess extraction properties of Zr in 30% TBP.

EXPERIMENTAL

The initial solution of zirconyl nitrate in 10 M HNO₃ was preliminarily boiled for 2 days to stabilize zirconium in the cationic form Zr⁴⁺. The resulting solution was separated from the insoluble residue and diluted with water to an HNO₃ concentration of 6–7 M just before the extraction. This procedure simulates the conditions of dissolving SNF from nuclear power plants.

All the organic reagents were subjected to additional purification. TBP was subjected to alkaline permanganate treatment and then was distilled in a vacuum.
The experiments on extraction of Zr, Np(IV), and U(VI) from nitric acid solutions with TBP were carried out in test tubes at 20±1°C. Before analysis Zr was purified by alkaline precipitation on U(VI), the zirconium-containing residue was dissolved in HCl, and Zr was determined spectrophotometrically with Alizarin Red S [12]. Neptunium was determined radiometrically. Uranium was determined spectrophotometrically with Arsenazo III [13].

The IR spectra of zirconium-containing organic solutions were recorded on an FTIR-8700 spectrometer (CaF$_2$ optical widows, layer thickness 50 μm).

RESULTS AND DISCUSSION

It is known that, in extraction of actinides with TBP, the slope (tan α) of the log-log plot of the actinide distribution ratio vs. TBP concentration in the organic phase deviates from 2.0 with increasing TBP concentration. This deviation is attributed to growing contribution of hydrated extractable complexes, forming along with anhydrous metal nitrate solvates with TBP, with an increase in the TBP concentration [9–11]. Figure 1 shows the log-log plot of the distribution ratio of Zr(IV) vs. TBP concentration, together with the similar plots for U(VI) and Np(IV). It can be seen that the slope of all these curves progressively deviates from 2 with increasing TBP concentration. The similarity of these curves for actinides, on the one hand, and zirconium, on the other hand, suggests that, with increasing TBP concentration, the hydrated extractable Zr–TBP complexes are formed.

Figure 2 shows that, at an HNO$_3$ concentration of 6 M, the slope of the log-log plot of the Zr distribution ratio vs. TBP concentration becomes equal to 2. These results suggest that, at high acidity, the anhydrous Zr nitrate solvate with TBP is formed instead of hydrated extractable Zr–TBP complexes.

We believe that the increase in the HNO$_3$ concentration in the aqueous phase cannot by itself affect the slope of the plots under consideration, because the extraction constants of actinides and Zr with TBP much exceed the HNO$_3$ extraction constant. It is also known [14] that, at constant composition of the extractable metal complex, the simultaneous formation of TBP monosolvate with HNO$_3$ does not noticeably affect the slope of the curves but only somewhat shifts them along X-axis. The Zr-containing extraction systems are more complex since, with increasing HNO$_3$ concentration, the speciation of Zr changes not only in the aqueous phase due to suppression of hydrolysis but also in the organic phase due to formation of anhydrous zirconium nitrate solvate with TBP. That is why in our extraction system the slope changes with increasing TBP concentration.

To elucidate how the HNO$_3$ concentration affects the composition of extractable Zr–TBP complexes, we recorded the IR spectra of Zr–TBP extracts obtained at various Zr and HNO$_3$ concentrations (Figs. 3–5).

In the PUREX process, the HNO$_3$ concentration in the organic phase considerably exceeds that of Zr. Therefore, the absorption band of the P=O stretching vibrations belonging to Zr nitrate solvate with TBP is overlapped by the absorption band of the P=O stretching vibrations of TBP HNO$_3$ solvate. To resolve the P=O absorption bands of the extractable Zr–TBP complex from those of TBP HNO$_3$ solvates, we used the technique suggested by Stoyanov [8]. In this method, the absorption spectrum of TBP–HNO$_3$ is subtracted from the spectrum of Zr–TBP extract.