SOLVENT EXTRACTION BEHAVIOUR OF TRACER ZIRCONIUM IN TTA-XYLENE SYSTEM*

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The solvent extraction behaviour of tracer zirconium in the TTA-xylene system has been studied. By studying the effect of TTA concentration, extraction time, and acid concentration for HNO₃ and HCl, optimum conditions of zirconium extraction are determined. It is found that zirconium is 98% extracted in one minute of extraction with 0.5M TTA in xylene from an 8M HNO₃ solution. A plot of lg D versus lg [TTA] gives a straight line with a slope of 2. This suggests that the zirconium ion is hydrolyzed and is present as ZrO²⁺, zirconyl ion, in aqueous solutions.

Introduction

Liquid-liquid extraction techniques are often used for rapid radiochemical separations of many fission products. The separation of zirconium from other elements with 2-thienoyltrifluoroacetone (TTA) in xylene was first developed by Moore.¹ Fundamental studies on the extraction of zirconium with TTA have been made by a number of workers.⁴-⁶ In concentrated acid solutions in the absence of complexing anions, one possible equation for the extraction of zirconium is:

\[ \text{Zr}^{4+} (\text{aq}) + 4 \text{HL} (\text{a}) \rightleftharpoons \text{ZrL}_4 (\text{a}) + 4 \text{H}^+ (\text{aq}) \]  

(1)

At constant hydrogen ion concentration, the equilibrium constant of the above reaction is given by the equation:

\[ \lg K' = \lg D - 4 \lg [\text{HL}] \]  

(2)

where \( K' \) - equilibrium constant at constant hydrogen ion concentration
\( D \) - distribution coefficient = \([\text{ZrL}_4]/[\text{Zr}^{4+}]\)

*Based on work done while the author was at the Massachusetts Institute of Technology, Cambridge, Mass. 02139, USA.
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If Eq. (2) holds, then a plot of $\lg D$ vs. $\log [HL]$ at constant hydrogen ion concentration should give a straight line of slope 4. It has been found, however, that zirconium ion both hydrolyzes and polymerizes at high concentrations of zirconium ion and at low acidity. From extraction experiments with TTA in benzene, Connick and McVey found that at low zirconium concentrations the average zirconium species in 2M perchloric acid has somewhere between zero and one hydroxide group attached to it. Cotton and Wilkinson consider that no true hydroxide $[\text{Zr(OH)}_4]^\text{2-}$ exists, the hydroxide rather being in the form $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$. They hold that hydrolysis of zirconium occurs and it is very doubtful indeed if $\text{Zr}^{4+}$ aqua ions exist even in strongly acid solutions. The hydrolyzed ion is often referred to as the "zirconi" ion and is written $\text{ZrO}_2^{2+}$. However, they point out that there is little, if any, reliable evidence for the existence of such an oxo ion either in solution or in crystalline salts.

In this study we present the results of tracer experiments performed to determine optimum conditions of zirconium extraction using the TTA-xylene system. The effects of TTA concentration, extraction time, and acid concentration for $\text{HNO}_3$ and for $\text{HCl}$, on the extraction of zirconium, as well as the extraction behavior of likely contaminants were studied. The results and their implications on the state of the zirconium ion in aqueous media are discussed.

Experimental

Purification of $^{95}\text{Zr}$ tracer and TTA

In all the experiments carrier-free radioactive tracers were used. The $^{65}\text{d}^{95}\text{Zr}$ tracer was obtained from the Operations Division of the Oak Ridge National Laboratory. It was in the form of a $^{95}\text{Zr}-^{95}\text{Nb}$ mixture in 0.5% oxalic acid. Pure $^{95}\text{Zr}$ tracer was obtained from this mixture by the following method. The $^{95}\text{Zr}-^{95}\text{Nb}$ mixture was diluted twentyfold with 6M $\text{HCl}$. This solution was extracted for 10 min with an equal volume of 0.5M TTA in xylene. The organic phase containing the zirconium was washed three times for 5 min periods with equal volumes of 6M HCl. The organic phase was next diluted tenfold or more, and reextracted with equal volumes of 8M $\text{HNO}_3$ or conc. HCl, depending on the nature of the subsequent experiments. The purity of the $^{65}\text{d}^{95}\text{Zr}$ tracer was established by observing its spectrum with a Ge(Li) detector. The purified $^{95}\text{Zr}$ tracer was used for about two days before repurification.

The TTA used was a product of Eastman Organic Chemicals. It was purified by crystallizing twice from xylene solution.

Extraction experiments

Equal volumes of aqueous and organic phases were introduced into an erlenmeyer flask. Extraction was achieved by using a mechanical shaker. Aliquots were taken.