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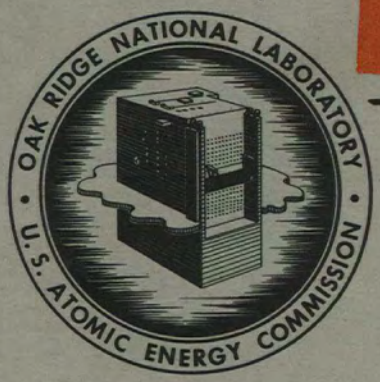


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## ABSTRACT

Zirconium is extracted readily by tri-n-octylphosphine oxide (TOPO) from acidic chloride and nitrate solutions, to a lesser extent from perchlorate, but only slightly from sulfate or fluoride media. Complete extraction of zirconium from sulfate, fluoride, and tartrate solutions can be achieved with multiple equilibrations when chloride or nitrate ions, especially as $AlCl_3$ or $Al(NO_3)_3$, are added to the aqueous solutions.

In chloride and nitrate systems, the extraction coefficient increases from $< 10$ in 1 M acids to $> 1000$ in 7 M HCl or $HNO_3$. Similar enhancement is obtained by the addition of chloride or nitrate as the salts of mono-, di-, or trivalent metals. Extraction coefficients, $> 100$, are achieved in 1 M acid systems that also are $> 3$ M with respect to chloride or nitrate. The amount of zirconium that can be extracted to $> 99$ per cent in a single, 10-minute equilibration period is 40 mg from chloride and 30 mg from nitrate solution per millimole of TOPO. The efficiency of the extraction is not impaired when the aqueous to organic phase ratio is varied between 1 and 20. The extracted species are $ZrCl_4 \cdot 2[n\text{-}(C_8H_{17})_3PO]$ and $Zr(NO_3)_4 \cdot 2[n\text{-}(C_8H_{17})_3PO]$, respectively.

# THE USE OF TRI-n-OCTYLPHOSPHINE OXIDE IN THE SOLVENT EXTRACTION OF ZIRCONIUM

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## INTRODUCTION

In previous reports[7,3] the authors have investigated the solvent extraction of chromium and iron from acidic solutions with tri-n-octylphosphine oxide (TOPO) dissolved in inert hydrocarbon solvents. This report involves a similar study of the solvent extraction of zirconium from acidic solutions with TOPO.

The authors reported in their survey test program[6] that zirconium was readily extracted by TOPO from the common acidic solutions. Indeed, from spectrographic data, it was indicated that zirconium can be extracted satisfactorily from acidic sulfate solutions. The results of a quantitative investigation of the solvent extraction characteristics of zirconium are reported herein.

Hafnium-free zirconium was used in this study, so the data reported apply specifically to zirconium. Although quantitative investigation of the extraction of hafnium under similar conditions has not been made, on the basis of qualitative tests[6] there appear to be no significant differences between the two similar elements in their extraction behavior with TOPO.

## REAGENTS

Standard solution of zirconium nitrate, approximately 10 mg per ml. The standard solution of zirconium was prepared by dissolving about 8.5 g of zirconium nitrate, $Zr(NO_3)_4$, in 250 ml of 2 M $HNO_3$. The zirconium nitrate was a specially prepared hafnium-free compound that was about 98 per cent $Zr(NO_3)_4$. The solution was standardized by analyzing it for zirconium gravimetrically.

Tri-n-octylphosphine oxide (TOPO), 0.1 M solution. The solution was prepared by dissolving 38.6 g of TOPO in one liter of cyclohexane. The purity of the TOPO exceeded 99 per cent; it is available from Eastman Organic Chemicals, EK 7440.

## GENERAL PROCEDURE

The extractions were performed in glass containers, that were described in an earlier report,[7] as well as in separatory funnels of various capacities. When the total volume of both liquid phases was less than 20 ml, the specially made containers were used, and agitation was achieved with a Kahn shaker. All extractions that were carried out in separatory funnels were performed manually.

Synthetic test solutions were prepared by combining the desired amount of zirconium, as aliquots of standard solutions of zirconium nitrate, and sufficient acid, salt, or both to form a solution in which each of these components had a predetermined concentration. In most tests the volume of the aqueous phase was 5 ml. The desired volume of TOPO-cyclohexane extractant, usually 5 ml of 0.1 M solution, was then transferred by pipet to the extraction vessel, following which the mixture was agitated for a set period of time.

Following equilibration, the mixture was allowed to stand until the phases were separated completely. Test portions of the two phases were then removed by pipet, after which the zirconium content was determined colorimetrically. The determination of zirconium in aqueous solutions was performed, in most cases, by the alizarin method[1] that had been modified[2] to yield a molar absorbancy index of $6 \times 10^3$. The pyrocatechol violet method[9] (molar absorbancy index of $33 \times 10^3$) was substituted for the alizarin method when the solution contained sulfate or less than 10 μg of zirconium. All analyses of the organic phases were performed by an adaption of the alizarin method.[2] In this non-aqueous colorimetric method the zirconium-alizarin color was formed and the intensity of the color measured in a solution of ethanol-acetone-cyclohexane-TOPO (molar absorbancy index of $7 \times 10^3$). This non-aqueous determination of zirconium afforded the only method for measuring the degree to which zirconium was extracted from solutions that contained aluminum, calcium, and magnesium since these ions interfered with both the aqueous alizarin and pyrocatechol violet methods. In the analyses of systems that contained fluoride, determinations of zirconium were carried out directly in the organic phase; however, the fluoride had to be removed from aqueous solutions (through fuming with perchloric acid) before either the alizarin or pyrocatechol violet methods could be applied.

The extraction coefficient, $E_a^o$, in the following discussion is defined as

$$E_a^o = \frac{\text{concentration of zirconium in organic phase}}{\text{concentration of zirconium in aqueous phase}},$$

after equilibration under the conditions that are listed for each series of tests.

Effect of Concentration of Acid

The effect of acid concentration on the extraction of zirconium with TOPO was established by two series of extractions. In the first series of tests, the results of which are given in Table I, solutions that contained 16.8 mg of zirconium in five ml of various concentrations of either nitric, hydrochloric, or perchloric acid were equilibrated for 10 minutes with five ml of 0.1 M TOPO in cyclohexane. Solutions that contained 5.8 mg of zirconium were used to study the effect of sulfuric acid since preliminary results had indicated that much smaller extraction coefficients were to be expected in sulfate systems than in nitrate, chloride, or perchlorate media.

The extraction coefficients were calculated after determining the amounts of zirconium that remained in the aqueous phase.

Table I

Extraction of Zirconium with 0.1 M Tri-n-Octylphosphine Oxide
Effect of Type and Concentration of Acid

| | |
|---|---|
| Zirconium, mg | 16.8 |
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Phase ratio | 1 |
| Equilibration time, minutes | 10 |

| Acid | | Zirconium, mg | | $E_a^o$ |
|---|---|---|---|---|
| Type | Molarity | Organic | Aqueous | |
| HCl | 1 | 13.0 | 3.83 | 3.4 |
| | 3 | 15.5 | 1.28 | 12 |
| | 5 | 16.5 | 0.33 | 50 |
| | 7 | 16.7 | 0.075 | 220 |
| $HNO_3$ | 1 | 13.5 | 3.25 | 4.2 |
| | 3 | 14.8 | 1.95 | 7.6 |
| | 5 | 15.2 | 1.63 | 9.3 |
| | 7 | 15.2 | 1.63 | 9.3 |
| $HClO_4$ | 1 | 11.5** | 5.30 | 2.2* |
| | 3 | 12.9** | 3.85 | 3.4* |
| | 5 | 13.9 | 2.90 | 4.8 |
| | 7 | 14.8 | 2.00 | 7.4 |
| $H_2SO_4$*** | 1 | 3.6 | 2.2 | 1.7 |
| | 3 | 2.2 | 3.6 | 0.6 |
| | 5 | 1.0 | 4.8 | 0.2 |

* Three phases present after equilibration.
** Zirconium in two upper phases.
*** 5.8 mg Zr present.

The extraction of zirconium is at a maximum in 7 M HCl. At this high concentration the extraction is greater than 99 per cent complete. In nitric acid, the maximum extraction is about 90 per cent complete. Essentially this same degree of extraction was observed for perchloric acid solutions. In both 1 and 3 M $HClO_4$, a third phase, insoluble in either the organic or the aqueous phase, was encountered. No third phase formed at higher concentrations of perchloric acid, however.

Extraction of zirconium from sulfuric acid is much less than from the other mineral acids. The maximum extraction is only 62 per cent complete.

The extraction coefficient of zirconium in chloride, nitrate, and perchlorate systems increases as the concentration of acid is increased. The reverse effect, however, is observed in sulfuric acid. Extraction of zirconium from sulfuric acid is undoubtedly depressed because of the high stability constants of the negatively charged complexes that are formed between zirconium and sulfate ions in aqueous solution. Such complexes decrease the availability of zirconium for solvation by the extractant and, therefore, reduce the extent to which zirconium is extracted.

A second series of extractions was performed with hydrochloric and nitric acid solutions that contained only 9.35 mg of zirconium. By reducing the zirconium content to an amount that corresponds essentially to complete extraction under optimum conditions, a more exact determination of the effect of acid concentration was obtained. These results are shown in Table II.

Table II

Extraction of Zirconium with 0.1 M Tri-n-Octylphosphine Oxide
Effect of Acid Concentration

| | |
|---|---|
| Zirconium, mg | 9.35 |
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Phase ratio | 1 |
| Equilibration time, minutes | 10 |

| Acid | | Zirconium, mg | | $E_a^o$ |
|---|---|---|---|---|
| Type | Molarity | Organic | Aqueous | |
| HCl | 1 | 4.93 | 4.42 | 1.1 |
| | 2 | 6.54 | 2.81 | 2.3 |
| | 3 | 6.94 | 2.41 | 2.9 |
| | 5 | 7.63 | 1.72 | 4.4 |
| | 6 | 9.03 | 0.315 | 29 |
| | 7 | 9.33 | .015 | 610 |
| | 10 | 9.35 | .002 | 4700 |
| $HNO_3$ | 1 | 6.98 | 2.37 | 3.0 |
| | 2 | 9.11 | 0.242 | 38 |
| | 3 | 9.20 | .146 | 63 |
| | 5 | 9.31 | .042 | 222 |
| | 7 | 9.33 | .024 | 390 |
| | 10 | 9.33 | .016 | 570 |

From these results, it is evident that 9.35 mg of zirconium can be completely extracted over a rather wide range of nitric acid concentration. Even at 2 M $HNO_3$ the extraction is 98.5 per cent complete.

In hydrochloric acid, complete extraction is not obtained until the HCl concentration exceeds six molar.

Effect of Extraction Time

Upon close examination of the effect of acid concentration on the extraction coefficient of zirconium (Table I and Table II), it would appear that equilibrium probably had not been obtained in the 10-minute equilibration period, particularly in the range of two to five molar acid. To check this point, a series of tests was conducted in which the phases were equilibrated

for longer periods. The results are presented in Table III and plotted in Figure 1.

Table III

Extraction of Zirconium with 0.1 M Tri-n-Octylphosphine Oxide
Effect of Extraction Time

| | |
|---|---|
| Zirconium present, mg | 9.35 |
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Phase ratio | 1 |

| Extraction Time, Minutes | Acid | | Zirconium, mg | | $E_a^o$ |
|---|---|---|---|---|---|
| | Type | Molarity | Organic | Aqueous | |
| 20 | HCl | 1 | 5.65 | 3.70 | 1.5 |
| | | 3 | 9.00 | 0.35 | 26 |
| | | 5 | 9.30 | .051 | 184 |
| | | 7 | 9.34 | .005 | 1870 |
| | | 10 | 9.35 | .004 | 2320 |
| 30 | HCl | 1 | 7.65 | 1.70 | 4.5 |
| | | 3 | 9.22 | 0.130 | 71 |
| | | 5 | 9.33 | .015 | 630 |
| | | 6 | 9.34 | .008 | 1170 |
| 30 | $HNO_3$ | 1 | 8.08 | 1.27 | 6.4 |
| | | 2 | 9.18 | 0.170 | 54 |
| | | 3 | 9.24 | .114 | 81 |
| | | 5 | 9.30 | .045 | 207 |
| | | 7 | 9.33 | .020 | 478 |

These results clearly confirm the premise that a period of 10 minutes is not sufficient for equilibrium to be attained. The peculiar curve for HCl at a 10-minute extraction period, which resembles a strong base-strong acid titration curve, becomes essentially a straight line function when the extraction is carried out for a period of 20 or 30 minutes (see Figure 1). The effect of increased equilibration time is most pronounced for the extraction from 3 M HCl where the corresponding coefficients for 10, 20, and 30 minute equilibration periods are 3, 26, and 71 respectively. It should be noted

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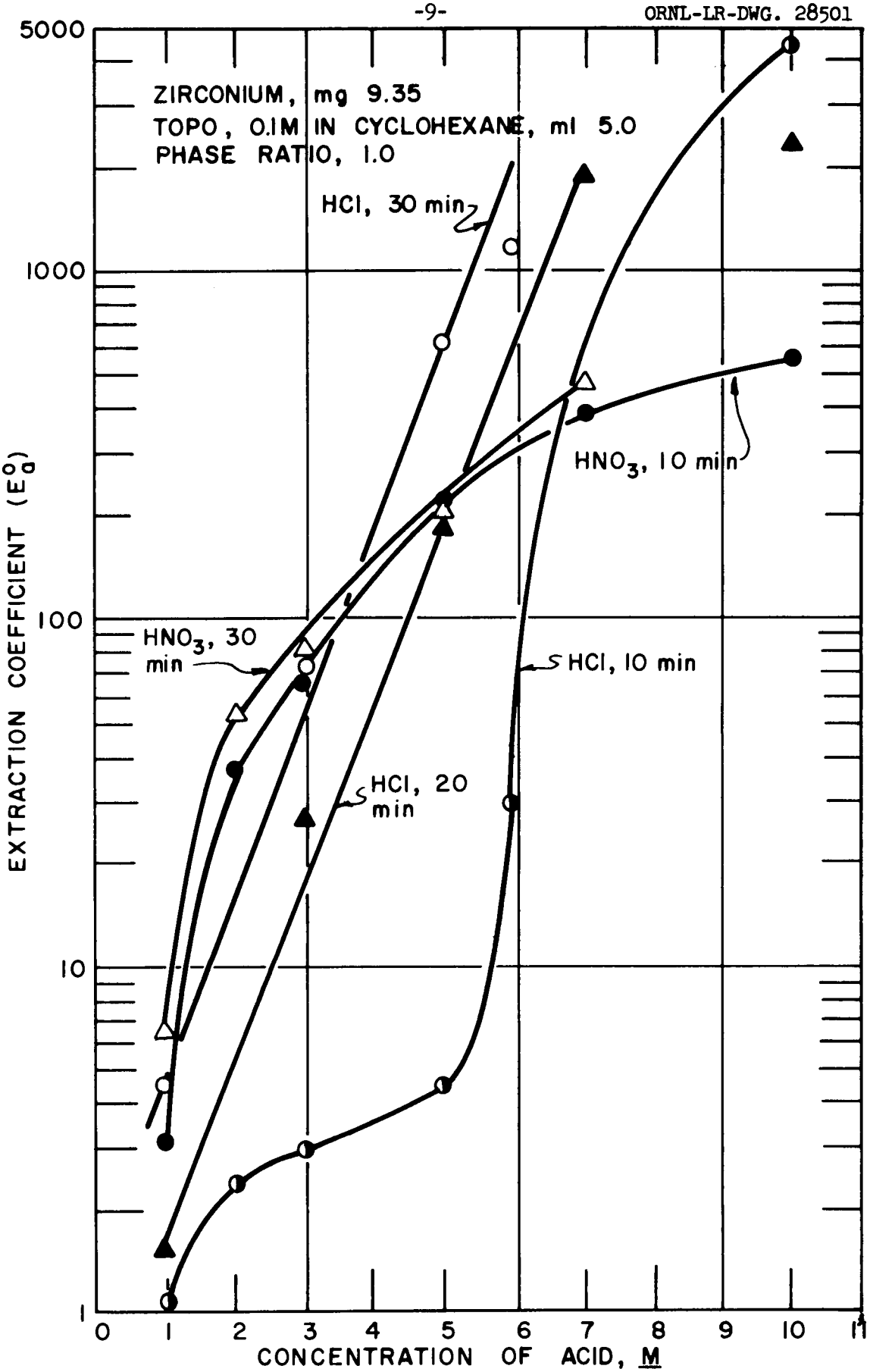



FIGURE 1. EFFECT OF ACID CONCENTRATION AND EXTRACTION TIME ON THE EXTRACTION OF ZIRCONIUM WITH 0.1 M TRI-n-OCTYLPHOSPHINE OXIDE

however, that, for HCl concentrations, approximately five molar and higher, complete extraction is achieved in 20 minutes and, furthermore, at 7 M HCl, in only 10 minutes.

This anomalous behavior is probably due to the slow rate of formation of the extractable zirconium species in 2 to 5 M HCl. The equilibrium for this formation is disturbed by the extraction of the zirconium species with TOPO, which explains the eventual high extraction from these concentrations after 30 minutes. The rate of formation of the extractable species in aqueous solution is apparently accelerated also by a larger zirconium concentration. The effect of increased equilibration time is not so evident in nitric acid systems where the curves for 10 and 30 minute periods are essentially identical.

Effect of Phase Ratio

The degree to which zirconium is concentrated from aqueous solution into small volumes of TOPO solution was evaluated. The effect of variation of the aqueous/organic ratio on the extraction coefficient of zirconium was determined in 7 M HCl and 7 M $HNO_3$ systems. The results in Table IV show that excellent extraction is obtained in systems which contain 9 mg of zirconium even when the phase ratio is 20. Concentration of this amount of zirconium from relatively large volumes of aqueous solution is readily attained in chloride systems and only to a slightly lesser degree in nitrate media.

Table IV

Extraction of Zirconium with 0.1 M Tri-n-Octylphosphine Oxide
Effect of Phase Ratio

| | |
|---|---|
| Zirconium present, mg | 9.35 |
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Equilibration time, minutes | 10 |

| Va/Vo | Acid | Zirconium, mg | | Per Cent Extracted |
|---|---|---|---|---|
| | | Organic | Aqueous | |
| 1 | HCl, 7 M | 9.35 | 0.009 | >99 |
| 5 | | 9.35 | .009 | >99 |
| 10 | | 9.34 | .013 | >99 |
| 20 | | 9.32 | .026 | >99 |
| 1 | $HNO_3$, 7 M | 9.33 | 0.024 | >99 |
| 5 | | 9.29 | .055 | >99 |
| 10 | | 9.26 | .089 | 99 |
| 20 | | 9.24 | .108 | 99 |

A second series of extractions was performed with five ml of 0.1 M TOPO and solutions of various volumes that contained the maximum amount of zirconium that is extracted completely at a phase ratio of one. The results given in Table V reveal that even at ratios as high as 10, at least 95 per cent of the zirconium is extracted from 7 M HCl. In 7 M $HNO_3$, however, 89 per cent of the 16 mg of zirconium is extracted at a phase ratio of 10. The extraction coefficients are, nevertheless, sufficiently large for efficient extraction.

Table V

Extraction of Zirconium with 0.1 M Tri-n-Octylphosphine Oxide
Effect of Phase Ratio

| | |
|---|---|
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Equilibration time, minutes | 10 |

| Va/Vo | Acid | Zirconium, mg | | | Per Cent Extracted |
|---|---|---|---|---|---|
| | | Present | Organic | Aqueous | |
| 1 | 7 M HCl | 23.3 | 22.7 | 0.63 | 97 |
| 2 | | | 22.6 | 0.68 | 97 |
| 5 | | | 22.1 | 1.2 | 95 |
| 10 | | | 22.1 | 1.2 | 95 |
| 1 | 7 M $HNO_3$ | 16.3 | 15.7 | 0.59 | 96 |
| 2 | | | 15.2 | 1.1 | 93 |
| 5 | | | 14.9 | 1.4 | 91 |
| 10 | | | 14.5 | 1.8 | 89 |

Effect of Concentration of Tri-n-Octylphosphine Oxide

A series of extractions was performed with various concentrations of TOPO to determine the combining ratio of zirconium and TOPO in the extracted complex and also to establish the saturation, or loading, value of 0.5 millimole of TOPO. The results of this series are given in Table VI.

Table VI

Extraction of Zirconium with Tri-n-Octylphosphine Oxide
Effect of Concentration of Tri-n-Octylphosphine Oxide

| | |
|---|---|
| Zirconium, mg | 40.8 |
| TOPO, ml | 5 |
| HCl, M | 5 |
| Phase ratio, aqueous/organic | 7/5 |

| TOPO, Molar | Zirconium, mg | | $C_{TOPO}/C_{Zr}$ |
|---|---|---|---|
| | Organic | Aqueous | |
| 0.05 | 12.1 | 28.7 | 1.9 |
| .10 | 25.1 | 15.7 | 1.8 |
| .15 | 35.6 | 5.2 | 1.9 |

The molar ratio of TOPO and zirconium in the organic phase is approximately two. As shown in Figure 2, the saturation value of 0.5 millimole of TOPO is 25.1 mg of zirconium in 7 M HCl systems. Inasmuch as 20 mg of zirconium is extracted by 0.5 millimole of TOPO to an extent greater than 99 per cent and as much as 23 mg of zirconium is extracted to an extent that exceeds 95 per cent, it is evident that very little mineral acid is extracted in such systems and that the saturation of 0.5 millimole of TOPO can nearly be achieved with stoichiometric amounts of zirconium. The effect of decreasing the concentration of both the phosphine oxide and the zirconium to be extracted was evaluated by making extractions of 0.1 to 1 mg of zirconium from 7 M $HNO_3$ and 7 M HCl with 0.01 M TOPO and extractions of 1 to 7 mg with 0.05 M TOPO. The results are shown in Tables VII and VIII.

Table VII

Extraction of Zirconium with 0.05 M Tri-n-Octylphosphine Oxide

| | |
|---|---|
| TOPO, 0.05 M in cyclohexane, ml | 5 |
| Phase ratio | 1 |
| Equilibration time, minutes | 20 |

| Acid | Zirconium, mg* | | | $E_a^o$ |
|---|---|---|---|---|
| | Present | Organic | Aqueous | |
| 7 M HCl | 0.986 | 0.982 | 0.0038 | 260 |
| | 2.97 | 2.96 | .0055 | 540 |
| | 4.95 | 4.94 | .011 | 490 |
| | 6.93 | 6.90 | .031 | 315 |
| 7 M $HNO_3$ | 0.986 | 0.982 | 0.0040 | 260 |
| | 2.97 | 2.95 | .019 | 160 |
| | 4.95 | 4.87 | .080 | 61 |
| | 6.93 | 6.50 | .427 | 21 |

* Zirconium in aqueous phase determined by pyrocatechol violet method.

Table VIII

Extraction of Zirconium with 0.01 M Tri-n-Octylphosphine Oxide

| | |
|---|---|
| TOPO, 0.01 M in cyclohexane, ml | 5 |
| Phase ratio | 1 |
| Equilibration time, minutes | 20 |

| Acid | Zirconium, μg* | | | $E_a^o$ |
|---|---|---|---|---|
| | Present | Organic | Aqueous | |
| 7 M HCl | 99 | 98 | 1.4 | 70 |
| | 197 | 195 | 2.0 | 98 |
| | 394 | 392 | 2.0 | 196 |
| | 591 | 588 | 3.3 | 180 |
| | 788 | 781 | 6.5 | 120 |
| | 985 | 974 | 11 | 89 |
| 7 M $HNO_3$ | 99 | 92 | 6.8 | 14 |
| | 197 | 176 | 21 | 8.4 |
| | 394 | 361 | 33 | 11 |
| | 591 | 521 | 70 | 7.5 |
| | 788 | 667 | 121 | 5.5 |
| | 985 | 811 | 172 | 4.7 |

* Zirconium in aqueous phase determined by pyrocatechol violet method.

Up to 7 mg of zirconium can be extracted completely from 7 M HCl by 0.25 millimoles of TOPO (see Table VII). From 7 M $HNO_3$ the upper limit of complete extraction is only 5 mg of zirconium.

This difference in extraction between nitric and hydrochloric acids is more evident in the tests on the extraction of 0.1 to 1 mg of zirconium by 0.05 millimoles of TOPO. The extraction is complete in 7 M HCl, incomplete in 7 M $HNO_3$. It is evident that the extraction of the stoichiometric amount of zirconium, based on the Zr/TOPO molar ratio of 0.5, is more nearly achieved in 7 M HCl than in 7 M $HNO_3$. Complete extraction is achieved in 7 M HCl with only a two molar ratio excess of TOPO. This excess is in sharp contrast to the 20-fold excess in 7 M $HNO_3$ in which only about 92 per cent

of the 100 μg of zirconium is extracted. To attain complete extraction of zirconium at this concentration from 7 M $HNO_3$, the molar ratio excess should be at least 25.

Effect of Concentration of Zirconium

A series of extraction tests was conducted to establish the maximum amount of zirconium that is extracted by 0.5 millimole of TOPO in a single equilibation.

These tests were performed with 7 M solutions of HCl and $HNO_3$ by varying the amount of zirconium present and determining the zirconium that remained in the aqueous phase. The results, as presented in Table IX and Figure 2, reveal that as much as 23 mg of zirconium is extracted from 7 M HCl to an extent that exceeds 95 per cent, while, in 7 M $HNO_3$ media, the corresponding value is 17 mg of zirconium. Removal of 99 per cent of the zirconium in the aqueous phase can be achieved with as much as 20 mg of zirconium in 7 M HCl or 14 mg of zirconium in 7 M $HNO_3$.

When the zirconium present in 7 M HCl systems was increased to 40 mg only 25 mg was extracted. This limiting value, approximately 0.25 millimole of zirconium per 0.5 millimole of TOPO, apparently represents the maximum amount of zirconium that can be extracted by 0.5 millimole into TOPO under these conditions and is equivalent to a molar ratio of two for TOPO:Zr in the extracted species. The efficiency of TOPO as an extractant for zirconium is evident from the fact that extraction of $>$90 per cent of the limiting value is achieved in 7 M HCl.

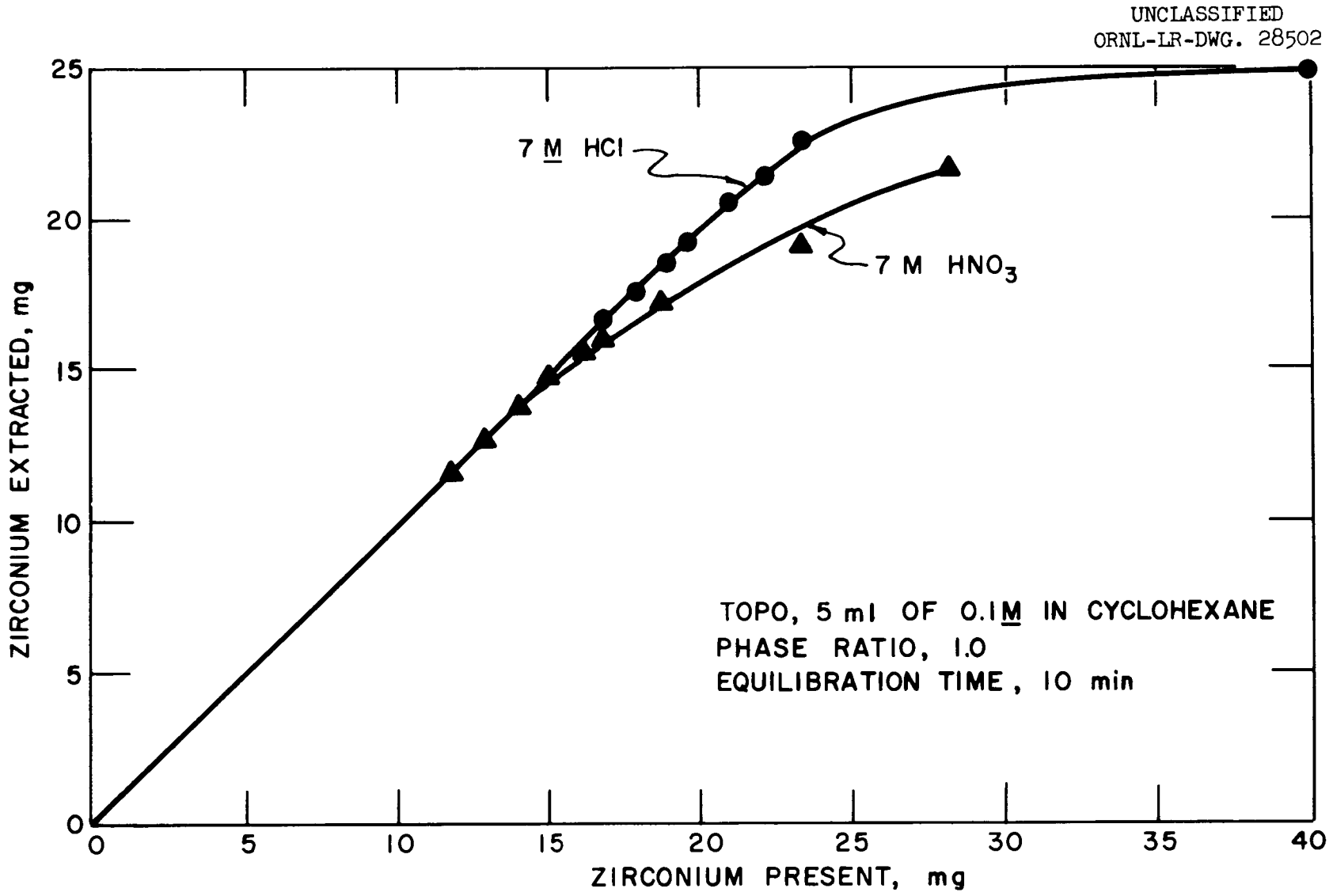



FIGURE 2. EXTRACTION OF ZIRCONIUM WITH TRI-n-OCTYLPHOSPHINE OXIDE

Table IX

Extraction of Zirconium with 0.1 M Tri-n-Octylphosphine Oxide
Effect of Concentration of Zirconium

| | |
|---|---|
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Phase ratio | 1 |
| Equilibration time, minutes | 10 |

| Acid | Zirconium, mg | | | $E_a^o$ |
|---|---|---|---|---|
| | Present | Organic* | Aqueous** | |
| 7 M HCl | 16.8 | 16.7 | 0.075 | 220 |
| | 17.8 | 17.7 | .117 | 152 |
| | 18.7 | 18.6 | .125 | 148 |
| | 19.6 | 19.4 | .239 | 81 |
| | 20.9 | 20.6 | .265 | 78 |
| | 22.1 | 21.5 | .620 | 35 |
| | 23.3 | 22.7 | .631 | 36 |
| | 40.8 | 25.1 | 15.7 | 2 |
| 7 M $HNO_3$ | 11.6 | 11.6 | 0.032 | 363 |
| | 12.8 | 12.7 | .051 | 249 |
| | 14.0 | 13.9 | .130 | 107 |
| | 15.1 | 14.8 | .306 | 48 |
| | 16.3 | 15.7 | .589 | 27 |
| | 16.8 | 16.2 | .620 | 26 |
| | 18.7 | 17.3 | 1.41 | 12 |
| | 23.4 | 19.2 | 4.19 | 5 |
| | 28.1 | 21.9 | 6.19 | 4 |

* By difference.
** Analyzed by alizarin method.

Effect of Anion Concentration

The data in Tables I and II are evidence that the extraction of zirconium with TOPO is enhanced by increasing the concentration of HCl or $HNO_3$ in the aqueous solution. Tests were performed to elucidate the effect of chloride and nitrate ions on this enhancement. These tests consisted of extracting zirconium from a solution in which the hydrogen ion concentration was held constant at one molar and the nitrate and chloride concentrations were varied by addition of univalent, divalent and trivalent metal chloride and nitrate

salts. The effect of the anion concentration is shown by the data presented in Tables X and XI and Figures 3 and 4.

Table X

Effect of Chloride Concentration on the Extraction of Zirconium with Tri-n-Octylphosphine Oxide

| | |
|---|---|
| Zirconium, mg | 9.35 |
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Phase ratio | 1 |

| Molarity | | | | | Extraction Coefficient ($E_a^o$) Extraction Time, Minutes | |
|---|---|---|---|---|---|---|
| HCl | NaCl | $MgCl_2$ | $AlCl_3$ | Total Cl | 10 | 30 |
| 1 | - | - | - | 1 | 1.1 | 4.5 |
| 1 | - | - | 0.17 | 1.5 | 3.5 | 20 |
| 1 | 1 | - | - | 2 | 1.1 | 23 |
| 1 | - | 0.5 | - | 2 | 1.0 | 61 |
| 2 | - | - | - | 2 | 2.4 | - |
| 1 | 2 | - | - | 3 | 1.5 | 143 |
| 1 | - | 1 | - | 3 | 1.5 | - |
| 1 | - | - | 0.67 | 3 | 10.5 | 56 |
| 3 | - | - | - | 3 | 2.9 | 71 |
| 1 | - | - | 1 | 4 | 93 | 142 |
| 1 | 4 | - | - | 5 | 1.7 | 830 |
| 1 | - | 2 | - | 5 | 2.5 | 310 |
| 1 | - | - | 1.5 | 5.5 | >1000 | >1000 |
| 5 | - | - | - | 5 | 4.4 | 630 |
| 1 | 5 | - | - | 6 | 5.0 | - |
| 6 | - | - | - | 6 | 29 | 1170 |
| 1 | 6 | - | - | 7 | 9.5 | 1640* |
| 1 | - | 3 | - | 7 | 4.1 | >1000 |
| 7 | - | - | - | 7 | 610 | >1000 |

* Saturated solution.

Table XI

Effect of Nitrate Concentration on the Extraction of Zirconium with 0.1 M Tri-n-Octylphosphine Oxide

| | |
|---|---|
| Zirconium, mg | 9.35 |
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Phase ratio | 1 |

| Molarity | | | | | Extraction Coefficient ($E_a^o$) Extraction Time, Minutes | |
|---|---|---|---|---|---|---|
| $HNO_3$ | $NaNO_3$ | $Ca(NO_3)_2$ | $Al(NO_3)_3$ | Total $NO_3$ | 10 | 30 |
| 1 | - | - | - | 1 | 3.0 | 6.4 |
| 1 | 1 | - | - | 2 | 9.8 | 84 |
| 1 | - | 0.5 | - | 2 | 11 | - |
| 2 | - | - | - | 2 | 61 | 54 |
| 1 | 2 | - | - | 3 | 30 | 126 |
| 1 | - | 1.0 | - | 3 | 30 | - |
| 1 | - | - | 0.67 | 3 | >1000 | - |
| 3 | - | - | - | 3 | 63 | 81 |
| 1 | 4 | - | - | 5 | 190 | 278 |
| 1 | - | 2.0 | - | 5 | 93 | - |
| 1 | - | - | 1.5 | 5.5 | >1000 | - |
| 5 | - | - | - | 5 | 222 | 207 |
| 1 | 6 | - | - | 7 | 270 | 504 |
| 1 | - | 3.0 | - | 7 | >1000 | - |
| 7 | - | - | - | 7 | 390 | 478 |

The anion concentration, either chloride or nitrate, is obviously the controlling factor in the extraction of zirconium. The same dependence of the extraction on equilibration time was observed in two to five molar chloride solution as for hydrochloric acid alone.

The effect of aluminum in increasing the extraction coefficient to a marked degree and in accelerating the extraction of zirconium is striking. The ability of aluminum ions to attract and hold water molecules probably accounts for this enhancing effect in that the net result is to free zirconium

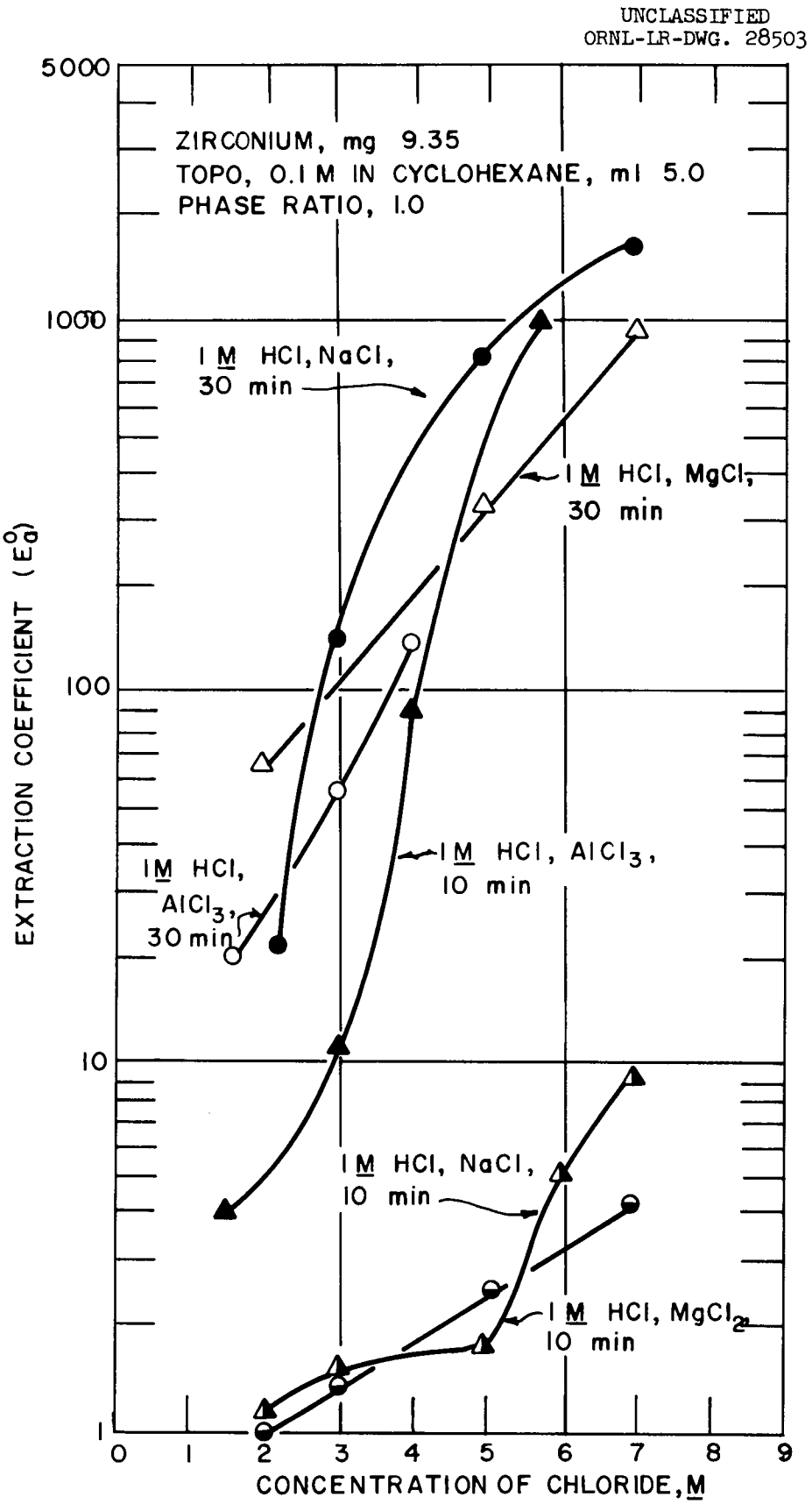
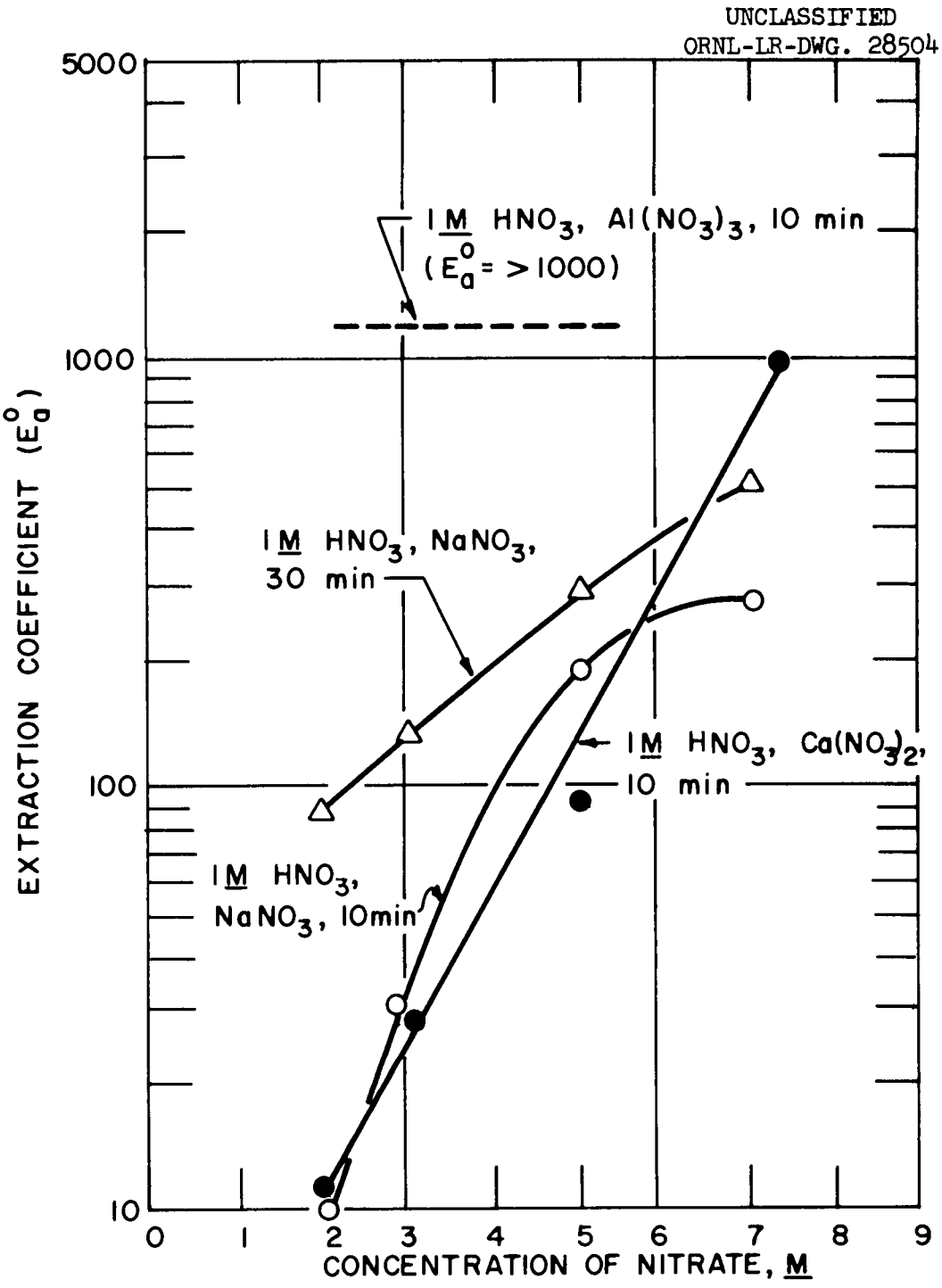



FIGURE 3. EXTRACTION OF ZIRCONIUM BY 0.1M TRI-N-OCTYLPHOSPHINE OXIDE AS A FUNCTION OF THE CONCENTRATION OF CHLORIDE SALTS OF UNI-, DI-, AND TRI-VALENT METALS.




ZIRCONIUM, mg 9.35. TOPO, 1 M IN CYCLOHEXANE, ml 5.0. PHASE RATIO, 1.0

FIGURE 4. EXTRACTION OF ZIRCONIUM BY 0.1 M TRI-N-OCTYLPHOSPHINE OXIDE AS A FUNCTION OF THE CONCENTRATION OF NITRATE SALTS OF UNI-, DI-, AND TRI-VALENT METALS

ions of solvation by water and thereby release the zirconium for extraction into the organic phase.

Effect of Chloride and Nitrate on the Extraction of Zirconium From Sulfate Solutions

From the data in Table I, it is established that the presence of sulfate in the aqueous phase has a detrimental effect on the extraction of zirconium by TOPO. This effect is thought to be due to the formation of stable complexes between zirconium and sulfate which are not extractable with a consequent reduction in the concentration of extractable zirconium species. In previous studies[2,3] this detrimental effect of sulfate complexes was alleviated to a great extent by adding chloride or nitrate to the aqueous solution prior to extraction. In this manner, analogous to mass-action reactions, the formation of extractable chloride or nitrate species is enhanced with a corresponding increase in the extraction coefficient.

The effect of chloride and nitrate on the extraction of zirconium from sulfate solutions was determined by adding HCl, $HNO_3$, $AlCl_3$, or $Al(NO_3)$ to 0.5 to 3 M $H_2SO_4$ solutions of zirconium. Zirconium is readily extracted from each of these chloride or nitrate solutions in the absence of sulfate. The results are presented in Table XII.

Table XII

Effect of Chloride and Nitrate on the Extraction of Zirconium from Sulfate Solutions

TOPO, 0.1 M in cyclohexane, ml 5
Equilibration time, minutes 10

| $H_2SO_4$ Molarity | Chloride Type | Chloride Molarity | Nitrate Type | Nitrate Molarity | Va/Vo | Zirconium, mg Present | Zirconium, mg Organic | Zirconium, mg Aqueous | $E_a^o$ | Per Cent Extracted |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.5 | $AlCl_3$ | 1 | - | - | 2 | 9.35 | 5.20 | 4.15 | 2.6 | 56* |
| 1.0 | | 1 | - | - | | | 3.44 | 5.91 | 1.2 | 37* |
| 2.0 | | 1 | - | - | | | 3.10 | 6.25 | 1.0 | 33* |
| 1.0 | HCl | 6 | - | - | 1.2 | 4.95 | 4.83 | 0.116 | 50 | 98* |
| 1.0 | | 6 | - | - | | 23.3 | 17.8 | 5.5 | 3.9 | 77 |
| 2.0 | | 6 | - | - | | | 17.6 | 5.7 | 3.7 | 76 |
| 3.0 | | 6 | - | - | | | 17.3 | 6.0 | 3.5 | 74 |
| 1 | - | - | $HNO_3$ | 6 | 1.2 | 4.95 | 4.39 | 0.564 | 10 | 89* |
| 1 | - | - | | 7 | 1.0 | 15.1 | 11.2 | 3.9 | 2.9 | 73 |
| 1 | - | - | $Al(NO_3)_3$ | 0.17 | 2 | 9.35 | 1.96 | 7.39 | 0.5 | 21 |
| 1 | - | - | | 1.0 | | | 4.55 | 4.80 | 2.0 | 49 |
| 2 | - | - | | 0.17 | | | 1.01 | 8.34 | 0.2 | 11 |
| 2 | - | - | | 1.0 | | | 3.04 | 6.31 | 1.0 | 33 |
| 3 | - | - | | 0.17 | | | 0.83 | 8.52 | 0.2 | 9 |
| 3 | - | - | | 1.0 | | | 3.10 | 6.25 | 1.0 | 33* |

* Extraction time - 30 minutes.
** Precipitate formed during extraction.

The extraction of zirconium from sulfate solutions is obviously enhanced by the addition of either chloride or nitrate in some cases. In none of the above tests was the zirconium extracted completely; however, maximum extraction was achieved for 5 mg of zirconium in 6 M hydrochloric acid solution at a concentration of sulfate of 1 M. In general, the extraction coefficient is decreased as the concentration of sulfate is increased; however, in 3 M sulfate solutions, the coefficients are very much greater than those obtained in the absence of chloride or nitrate and are sufficiently large to enable complete extraction to be attained in two or three equilibrations.

The extraction coefficients that are obtained after the addition of aluminum salts are considerably less than those in purely acidic solutions. The reverse had been expected, because it was thought that aluminum ions would reduce the concentration of zirconium sulfate complexes to a greater extent than that caused by hydrogen ions through the formation of weakly ionized $Al_2(SO_4)_3$.

Effect of Fluoride

Zirconium and fluoride form several types of complexes in acidic solutions which have stability constants of such magnitude as to preclude the existence of uncomplexed zirconium ions.[4] Previous tests have shown that the formation of such tightly bound complexes also inhibits the extraction of the metal by TOPO. This effect is evident from the results that are presented in Table XIII wherein the separation of zirconium by TOPO from fluoride solutions is observed to be very slight even in 0.6 M hydrofluoric acid systems.

Table XIII

Extraction of Zirconium from Fluoride Solutions with 0.1 M Tri-n-Octylphosphine Oxide

| | |
|---|---|
| Zirconium, mg | 5.8 |
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Phase ratio | 1 |
| Equilibration time, minutes | 10 |

| HF, M | Zirconium, mg | | $E_a^o$ |
|---|---|---|---|
| | Organic | Aqueous | |
| 0.6 | 0.3 | 5.5 | 0.06 |
| 1.1 | .2 | 5.6 | .04 |
| 1.7 | .2 | 5.6 | .04 |
| 2.2 | .2 | 5.6 | .04 |

Inasmuch as a method for separating zirconium from fluoride solutions was considered to be highly desirable, several techniques were applied to enhance the extraction of zirconium by TOPO. All of these tests, as shown in Table XIV, included the addition of mineral acid, aluminum nitrate, or both in an effort to shift the equilibria among the zirconium fluoride complexes in favor of an ionized, i.e. extractable, species of zirconium. The data reveal that the addition of nitric acid and aluminum nitrate enhanced the extraction to a greater extent than that achieved with the salt alone, while the addition of mineral acid alone had little effect. This trend was expected since the aluminum ions tend to remove fluoride ions from the solution through formation of complexes. The removal of 88 per cent of the zirconium from 0.1 M fluoride solutions and 66 per cent from 0.5 M fluoride media is considered very significant because these results indicate that fluoride is being removed from zirconium complexes to form new complexes with aluminum, although the stability of the former is reported to be greater than that of the latter. The extraction coefficients

are sufficiently high to enable a complete separation of zirconium from 0.1 M fluoride solution to be performed with two equilibrations. The number of equilibrations required for complete extraction would have to be increased in systems of higher fluoride concentration.

Table XIV

Effect of Chloride and Nitrate on the Extraction of Zirconium from Fluoride Solutions

TOPO, 0.1 M in cyclohexane, ml 5
Equilibration time, minutes 10

| HF Molarity | HCl Molarity | Nitrate Type | Nitrate Molarity | Va/Vo | Zirconium, mg Present | Zirconium, mg Organic | Zirconium, mg Aqueous | $E_a^o$ | Per Cent Extracted |
|---|---|---|---|---|---|---|---|---|---|
| 0.6 | 7 | - | - | 1 | 5.8 | 0.6 | 5.2 | 0.11 | 10 |
| 0.6 | - | $HNO_3$ | 7 | 1 | 5.8 | <0.1 | 5.8 | <0.01 | <2 |
| 0.1 | - | $Al(NO_3)_3$ | 1 | 2 | 9.35 | 7.13 | 2.22 | 6 | 76 |
| 0.5 | - | | | | | 6.27 | 3.08 | 4 | 67 |
| 1.0 | - | | | | | 4.56 | 4.79 | 2 | 49 |
| 0.1 | - | $Al(NO_3)_3$ + 1M $HNO_3$ | 1 | 2 | 9.35 | 8.13 | 1.22 | 13 | 87 |
| | | | | | | 7.75 | 1.60 | 10 | 83* |
| 0.1 | | $Al(NO_3)_3$ + 4M $HNO_3$ | 1 | 2 | 9.35 | 8.22 | 1.13 | 15 | 88* |
| 0.5 | - | $Al(NO_3)_3$ + 1M $HNO_3$ | 1 | 2 | 9.35 | 6.15 | 3.20 | 4 | 66 |

* Equilibration time - 30 minutes.

Effect of Hydroxy Acids

Zirconium also forms stable complexes with various hydroxy and polyhydroxy organic acids. A series of extractions that involved the extraction of zirconium from solutions of tartaric acid was performed to determine if the stability of zirconium tartrate was of such a character that the extraction of zirconium by TOPO was adversely affected. In Table XV are given the

results of these extractions which were carried out in 7 M HCl and 7 M $HNO_3$ systems that contained various concentrations of tartaric acid.

Table XV

Effect of Tartrate on the Extraction of Zirconium from Chloride and Nitrate Solutions

| | |
|---|---|
| HCl ($HNO_3$), M | 7 |
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Equilibration time, minutes | 10 |
| Phase ratio | 1 |

| Acid | Tartrate, Molarity | Zirconium, mg | | | $E_a^o$ |
|---|---|---|---|---|---|
| | | Present | Organic | Aqueous | |
| HCl | 0.10 | 23.3 | 21.7 | 1.61 | 14 |
| | 0.25 | | 21.6 | 1.68 | 13 |
| | 0.50 | | 21.1 | 2.22 | 10 |
| | 1.0 | | 20.8 | 2.52 | 8 |
| $HNO_3$ | 0.10 | 15.1 | 14.5 | 0.613 | 24 |
| | 0.25 | | 14.3 | 0.804 | 18 |
| | 0.50 | | 14.2 | 0.861 | 17 |
| | 1.0 | | 14.0 | 1.07 | 13 |

The extraction of zirconium from 7 M HCl or 7 M $HNO_3$ solutions that contain 0.1 M tartrate is only slightly less than in systems that do not contain tartrate. Tartrate does impair the extraction of zirconium to a certain extent, however, and this detrimental effect increases as the concentration of tartrate is increased. The extraction coefficients of zirconium can be maintained sufficiently high, even in 1 M tartrate solutions, to attain separation of zirconium from such media with multiple extractions.

Extraction from Solutions of Ethylenediaminetetraacetic Acid (EDTA)

The application of EDTA, as well as other similar complexones, as a solvent for many types of compounds has received widespread attention in the past few years. A cursory investigation of TOPO as an extractant for

zirconium from solutions of EDTA was made, although in previous tests the extraction coefficient of zirconium was diminished by decreasing the acid concentration of the aqueous phase. This investigation consisted of equilibrating TOPO with (1) solutions of zirconium that were 0.2 M with respect to $HNO_3$ (such acid as was in the standard solution of zirconium) and that contained 25 to 100 mg of EDTA, and (2) similar solutions that also contained $Al(NO_3)_3$.

Table XVI

Extraction of Zirconium from Solutions of EDTA* with 0.1 M Tri-n-Octylphosphine Oxide

TOPO, 0.1 M in cyclohexane, ml 5
Equilibration time, minutes 10

| EDTA, mg | $HNO_3$ Molarity | $Al(NO_3)_3$ Molarity | Va/Vo | Zirconium, mg Present | Organic | Aqueous | $E_a^o$ |
|---|---|---|---|---|---|---|---|
| 25 | 0.2 | - | 1 | 5.8 | 0.4 | 5.4 | 0.07 |
| 50 | | | | | 0.4 | 5.4 | 0.07** |
| 100 | | | | | 0.3 | 5.3 | 0.05** |
| 25 | 1 | 1 | 2 | 9.35 | 4.86 | 4.49 | 2 |
| 100 | | | | | 0.03 | 9.32 | < 0.01 |

* Ethylenediaminetetraacetic acid.
** Organic phase turbid.

These data reveal that only very slight separation of zirconium is achieved unless the conditions are made more favorable by increasing the hydrogen ion and nitrate ion concentration. The great stability of the zirconium-EDTA complex in the aqueous phase is evidenced by the sharp decrease in extraction that occurs under the best conditions when the EDTA concentration is increased to 10 mg per ml.

Identification of the Species That are Extracted from Chloride and Nitrate Solutions

Chloride. The stoichiometry of the zirconium species that is extracted by 0.1 M TOPO from 1 to 6 M HCl solutions was established from analyses of the organic phases of these systems. In each extraction test, the aqueous phase contained 158 mg of zirconium, as zirconyl chloride, an amount that was approximately seven times the loading capacity of 0.5 millimoles of TOPO. This excessive amount of zirconium was used in an effort to minimize the extraction of free HCl by TOPO.

The data in Table XVII represent the molar ratios of the constituents of the organic phase. The zirconium in this phase was calculated by difference after analysis of the aqueous phase for zirconium by gravimetric methods. Chloride was determined directly in the organic phase by titration with a standard solution of $AgNO_3$.

Table XVII

Molar Ratios of the Components of the Organic Phase of Zirconium-Chloride-TOPO Systems

| | |
|---|---|
| Zirconium present, mg | 158 |
| TOPO, 0.1 M in cyclohexane, ml | 5 |
| Extraction time, minutes | 30 |
| Phase Ratio | 1 |

| HCl, M | Extracted, Millimoles | | Ratio | |
|---|---|---|---|---|
| | Zirconium | Chloride | Cl / Zr | TOPO / Zr |
| 1 | 0.039 | 0.22 | 6 | 13 |
| 2 | .15 | 0.64 | 4.3 | 3.3 |
| 3 | .21 | 0.89 | 4.2 | 2.7 |
| 4 | .22 | 0.98 | 4.4 | 2.3 |
| 5* | .23 | 1.00 | 4.3 | 2.2 |
| 6* | .21 | 1.00 | 4.8 | 2.4 |

* Saturated with $ZrOCl_2$.

It is evident from the non-integral characteristics of the molar ratios, chloride to zirconium and TOPO to zirconium, that the stoichiometry of the extracted species cannot be specified exactly.

It has been observed in other extraction studies with TOPO[8] that the loading capacity of one millimole of TOPO with respect to HCl varies from 0.2 millimole of acid in 0.5 M HCl systems to two millimoles of acid in 6 M HCl media. The extraction of varying amounts of HCl is indicated in the data of Table XVII, even though the system is saturated with zirconium, since the maximum extraction of zirconium in these tests is less than that found previously in chloride solutions of zirconium that also contained a small amount of nitrate (Table IX).

The molar ratios that were obtained in 3 to 6 M HCl systems are postulated to represent the extraction of $ZrCl_4 \cdot 2(TOPO)$ as well as lesser amounts of X HCl·(TOPO), where the coefficient (X) is between one and two.

The extraction of both the zirconium species and HCl is decreased when the concentration of HCl in the aqueous phase is decreased from 3 to 2 M. This impairment is even greater when the acid concentration is further reduced to 1 M. The data obtained in 1 and 2 M HCl systems is indicative of an unsaturated organic phase caused by a decrease in the availability of extractable species in the aqueous phase. In 1 and 2 M HCl media only 0.05 and 0.2 millimoles of HCl are extracted by 0.5 millimole of TOPO.[8] Zirconium is reported to be increasingly polymerized and hydrolyzed in chloride solutions as the acidity is decreased below 5 M. These two effects of decreasing acidity are thought to reduce the availability of both HCl and zirconium for extraction in 1 and 2 M HCl systems and, thus, account for the higher TOPO to zirconium ratios in these two systems.

Nitrate. The stoichiometry of the extracted species of zirconium in nitrate-TOPO systems has been investigated only in 7 M $HNO_3$ media. In these tests zirconium was added to the acidic solution as $ZrO(NO_3)_2$ and was present in an amount equivalent to about five times the loading capacity of the TOPO present.

The components of the organic phase were determined after an equilibration period of 30 minutes. Nitrate was determined from spectrophotometric measurements of the organic phases at 274 mμ. At this wavelength, the concentration of nitrate in a cyclohexane solution of TOPO follows Beer's law with a molar absorbancy index of 10. Zirconium in the organic phase was again calculated by difference after analysis of the aqueous phases for zirconium by gravimetric methods. The molar ratios of the constituents are presented in Table XVIII.

Table XVIII

Identification of the Zirconium Species That is Extracted From 7 M Nitric Acid by Tri-n-Octylphosphine Oxide

| | |
|---|---|
| $HNO_3$, M | 7 |
| Zirconium present, mg | 159 |
| TOPO, M, in cyclohexane | 0.1 |
| Extraction time, minutes | 30 |
| Phase ratio | 1 |

| TOPO, Millimoles | Extracted, Millimoles | | Ratio | |
|---|---|---|---|---|
| | Zirconium | Nitrate | Nitrate / Zirconium | TOPO / Zirconium |
| 0.5 | 0.20 | 1.1 | 5.5 | 2.5 |
| | .22 | 1.0 | 4.6 | 2.3 |
| | .20 | 1.1 | 5.5 | 2.5 |
| | .20 | 1.1 | 5.5 | 2.5 |
| 0.7 | 0.30 | 1.5 | 5.0 | 2.3 |
| | .30 | 1.7 | 5.7 | 2.3 |

The data in Table XVIII are very similar to that obtained in 3 to 6 M HCl systems and the non-integral relationships of the ratios - nitrate to zirconium and TOPO to zirconium - can be explained on the same basis as in chloride systems.

The nitrate to zirconium ratios are slightly larger than the chloride to zirconium ratios reported in Table XVII. This is indicative of greater extractability of $HNO_3$ than HCl and is in agreement with the known extraction characteristics of these two acids. One millimole of TOPO extracts one millimole of acid from 1 M $HNO_3$ solutions and two millimoles of acid from 7 M $HNO_3$ media.(8)

It is postulated, therefore, that the species that are extracted by TOPO from 7 M $HNO_3$ solutions of zirconium are $Zr(NO_3)_4 \cdot 2(TOPO)$ and a lesser amount of Y $HNO_3 \cdot (TOPO)$, where the coefficient (Y) approximates 3.

In the analysis of the data that was obtained in both chloride and 7 M $HNO_3$ systems the assumption has been made that no oxygenated species of zirconium is extracted by TOPO. The basis for this assumption is obtained primarily from the known loading capacity of TOPO when equilibrated with various concentrations of HCl and $HNO_3$. If an oxygenated species of zirconium is postulated to be extracted by TOPO, the concentration of free HCl or $HNO_3$ must also be assumed to be greater than twice the concentration of the zirconyl species. This deduction arises from the presence of four to five times as much anion in the organic phase as zirconium. Such a concentration of free acid as X HCl·(TOPO) or Y $HNO_3 \cdot (TOPO)$, where X and Y are 5 to 7, is inconsistent with the known coefficients for such adducts in 1 to 7 M HCl or $HNO_3$ systems.

The postulation that only a non-oxygenated species of zirconium is extractable by TOPO implies that an equilibrium exists in 1 to 7 M HCl and in 7 M solutions between oxygenated and non-oxygenated species of zirconium since it is recognized that zirconium salts are readily hydrolyzed in such media.

Effect of Diluent

The effect of type of diluent on the extraction of zirconium with TOPO was investigated through the substitution of a polar solvent (nitrobenzene) and another non-polar solvent (carbon tetrachloride) for cyclohexane. The extraction coefficient that was obtained with carbon tetrachloride was practically the same as with cyclohexane and twice as large as that in the nitrobenzene system. A white solid formed in the organic phase of the nitrobenzene system. This solid was presumed to be hydrolyzed zirconium that was formed through an insufficiency of extracted acid.

## SUMMARY

Zirconium is extracted exceedingly well from either nitric or hydrochloric acid using TOPO in cyclohexane. The extraction is decidedly acid-dependent; for example, the extraction coefficient increases sharply from about 2 in 1 M acid to around 1000 in 7 M acid. Similar enhancement is also achieved in chloride or nitrate systems by increasing the concentration of the anion and maintaining the acid concentration constant at 1 M. The loading value of 0.5 millimole of TOPO is 25 mg of zirconium. The molar ratio of TOPO to Zr is 2; the formula of the extracted species from chloride solutions is $ZrCl_4 \cdot 2TOPO$. As much as 20 mg of zirconium can be extracted completely in five minutes from 7 M HCl, whereas 15 mg is separated to an extent that exceeds 99 per cent in acidic solutions (1 M) that contain 7 M nitrate. The extraction from chloride and nitrate solutions remains essentially complete at a phase ratio, Va/Vo, of 20. Relatively little extraction of zirconium occurs in systems that contain substances which form stable complexes with zirconium. By the addition of chloride or nitrate to give 7 M solutions and adjustment of the acidity to at least 1 M, separation of zirconium from solutions of certain anions, such as sulfate and tartrate, can be made essentially complete. No such effect was observed on the addition of chloride or nitrate to fluoride solutions of zirconium. If aluminum salts are added, however, the extraction of zirconium can be made quantitative after several equilibrations. Extraction of zirconium from perchlorate systems is readily achieved; however, the resulting extract frequently consists of two immiscible organic phases which thereby reduce the possibility of recovering the extracted metal completely.

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