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SOLVENT EXTRACTION CHEMISTRY AND KINETICS OF ZIRCONIUM

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ABSTRACT

The solvent extraction behavior of zirconium in the HNO_3-tributyl phosphate (TBP) system can be explained based on the existence of four principal aqueous species, Zr^{4+}, $ZrOH^{3+}$, $Zr_3(OH)_4^{8+}$, and oxo-polymers. The Zr^{4+} and $ZrOH^{3+}$ species are extractable and are in equilibrium with inextractable $Zr_3(OH)_4^{8+}$. The oxo-polymers are formed by heat, are inextractable, and are not in equilibrium with the other species. The aqueous equilibria and their equilibrium quotients have been previously determined. In the present study, these equilibria were used along with both tracer and macro zirconium concentrations (oxo-polymers excluded by extraction and back scrubbing) to determine the distribution equilibrium constants for both the Zr^{4+} and $ZrOH^{3+}$ ions. The four equilibrium constants give excellent fits to both tracer and macrozirconium distribution data.

The concentrations of the extractable zirconium species which are calculated from the equilibria have been used to begin examining the extraction kinetics of zirconium in the HNO_3-TBP system. In relatively concentrated nitric acid, approximately 3 $\underline{M}$ and greater, Zr^{4+} ion predominates, and the rate of extraction of zirconium increases as approximately the second power of the TBP concentration. In low acid (1 $\underline{M}$ and less) $ZrOH^{3+}$ ion predominates, and the rate of extraction of zirconium increases as approximately the third power of the nitrate concentration. This is in significant contrast with the behavior of uranium, which shows only a small dependence of the extraction rate on TBP concentration, and no dependence on nitrate concentration. This suggests that operation of a kinetic separations system at low TBP and nitrate concentrations will significantly improve separations over those achieved at equilibrium.

INTRODUCTION

The solvent extraction chemistry of zirconium has been studied by numerous investigators (1-10) using both tracer and macro zirconium concentrations. The tracer work showed that zirconium distribution depends on the tributyl phosphate (TBP) concentration to the second power (1, 2) and the HNO_3 concentration to about the third power (1,2,6). Studies that used macro zirconium concentrations demonstrated that certain "nonequilibrating" species could be separated by extracting the zirconium with TBP solutions and then back-scrubbing with nitric acid (4). The aqueous species remaining after this treatment behaved as an equilibrium mixture. $ZrNO_3^{3+}$ has been reported as a species in nitrate solutions (11); however, more recent studies (9, 10) indicate that this species is not present in significant concentrations. For this reason it will not be considered in subsequent discussions.

The aqueous hydrolytic behavior of zirconium has been summarized (12), and hydrolysis and polymerization constants for zirconium have been estimated. Based on these data and the expected distribution behavior of zirconium, the reactions of zirconium are as follows:

$$Zr^{4+} + H_2O \overset{K_1}{\rightleftarrows} ZrOH^{3+} + H^+ \tag{1}$$

$$3Zr^{4+} + 4H_2O \overset{K_2}{\rightleftarrows} Zr_3(OH)_4^{8+} + 4H^+ \tag{2}$$

$$Zr_3(OH)_4^{8+} \xrightarrow{\text{Heat}} \text{oxo-polymers [proposed reaction]} \tag{3}$$

$$Zr^{4+} + 4NO_3^- + 2TBP \overset{K_3}{\rightleftarrows} Zr(NO_3)_4 \cdot 2TBP \tag{4}$$

$$ZrOH^{3+} + 3NO_3^- + 2TBP \overset{K_4}{\rightleftarrows} Zr(OH)(NO_3)_3 \cdot 2TBP. \tag{5}$$

These reactions assume that only the monomeric species of zirconium are extractable. Obviously, other reactions are possible; these are the minimum number that adequately represent the experimental data.

EXPERIMENTAL

Reagents

The following is a typical preparation technique for zirconium stock solutions. "Zirconium dinitrate oxide" was obtained from Alfa

Division, Ventron Corporation, Danvers, Mass. About 140 g of this material was dissolved in 500 ml of 7 M HNO_3. After filtration, the solution was contacted with 30% tributyl phosphate (TBP) in normal paraffin hydrocarbon (NPH). The extracted zirconium was then stripped using 500 ml of 0.5 M HNO_3. In order to achieve a high concentration of zirconium in the strip acid, the organic was recontacted with the original zirconium solution and stripped with the same 0.5 M HNO_3 solution three more times. At the end of this treatment, the strip acid was about 2.5 M in HNO_3 and contained about 35 g of Zr per ℓ. This and similar solutions were used in all zirconium tests. During the first two acid-organic extractions, two organic phases were observed; these were stripped simultaneously.

The TBP--NPH organic phase was prepared by diluting TBP with NPH (both obtained from the Savannah River Plant, Aiken, S.C.) and then purifying the solution from possible TBP degradation products by scrubbing twice with sodium carbonate solution, followed by multiple water washes.

Apparatus and Procedure

Aqueous-organic equilibrations were performed by contacting the aqueous phase with the organic phase (pre-equilibrated with the proper acid except in the thermal stability tests) in an erlenmeyer flask vigorously stirred by a magnetic stirrer for 15 min. Tests at shorter mixing times showed that equilibrium was attained in less than 5 min under these conditions.

In the tests examining the thermal stability of the prepared zirconium stock, the following four solutions of varying zirconium concentration were made by dilution with acid:

(1) 0.518 M Zr in 3.8 M HNO_3,
(2) 0.433 M Zr in 2.1 M HNO_3,
(3) 0.096 M Zr in 3.3 M HNO_3, and
(4) 0.085 M Zr in 1.3 M HNO_3.

These solutions were placed in three neck round-bottom flasks equipped with refluxing condensers, thermometers, and a sampling port. Samples were taken periodically, quenched, and the zirconium distribution measured using 30% TBP-NPH pre-equilibrated with either 3 M HNO_3 (two highest acid solutions) or 1 M HNO_3 (two lower acid solutions).

All kinetic studies used a simple two-phase apparatus (Lewis cell) in which each phase is mixed by a paddle, but with a minimal disturbance of the interface. A typical Lewis cell is shown in Fig. 1. The cell is essentially a cylindrical glass vessel (this may be jacketed for temperature control) having a double-bladed paddle (one paddle in each phase) to mix the individual phases without dispersing one phase in the other. Where it is applicable, the Lewis cell gives excellent results with a minimal investment of equipment and experimental time. In all cases, the organic phases were pre-equilibrated with nitric acid solutions to prevent extraction of nitric acid during the test. A Lewis cell test is begun by placing the aqueous phase and pre-equilibrated organic phase in the cell and then starting the mixing. At this point no zirconium is present in either phase. The upper paddle is positioned about 3 to 4 mm above the interface to give the best possible stirring of the organic phase; this possibly minimizes the concentration gradient in the relatively viscous organic phase. A concentrated solution of the element under study is then introduced (spiked) into one or the other phases. When the aqueous phase is to be spiked, the solution is introduced by means

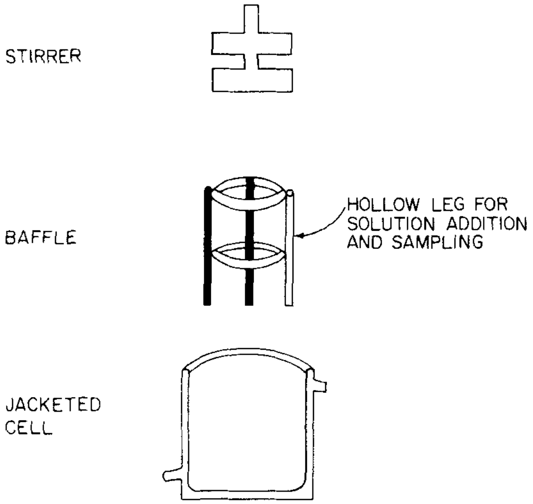

FIGURE 1. Lewis cell.

of a hypodermic needle through a hollow leg in the stainless steel baffle shown in Fig. 1. This method of introducing the element being studied does not disturb the interface, and the added material is observed to mix completely within a few seconds with the barren solution. Samples of the phase into which transfer is occurring are taken as a function of time using vacuum-containing tubes (Vacutainer brand) with a puncturing needle and a teflon capillary positioned in the proper phase of the Lewis cell. Samples are taken over a short time period to minimize diffusion and mixing problems in the organic phase. If the data are then plotted as a function of time (Fig. 2), a distinct curvature is seen in some cases. When this is observed, it is an indication of either a change of mechanism or a near approach to equilibrium; in this case (Fig. 2) the distribution at the last sampling is only about 7% of the equilibrium distribution leading to the conclusion that the system is becoming diffusion controlled. At initial time, when a diffusion gradient has not been developed, the rate (slope of line in Fig. 2) is determined by reaction

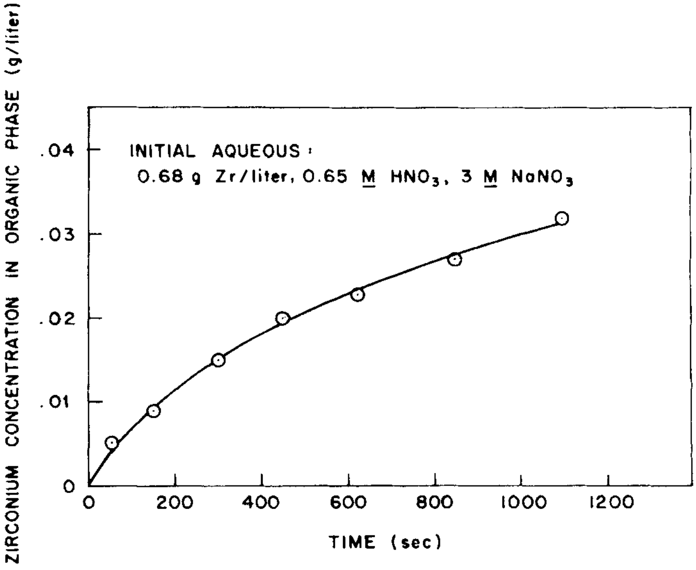

FIGURE 2. Experimental transfer kinetics data.

kinetics. The initial slope has been determined by calculating the apparent rate constant between the initial point (0,0) and each subsequent data point and graphically extrapolating back to zero time. This technique has been shown previously (13) to give good agreement between Lewis cell, drop, and Kenics mixer data.

Analyses of zirconium were by x-ray fluorescence.

Mathematical Equations

In the transfer kinetics studies, the concentrations of the various species were first calculated from the various equilibria (Eqs. 1-5). The transfer is then described by the pseudo-first-order rate equations:

$$\frac{dc'}{dt} = -\frac{k'c'a}{v'} + \frac{kca}{v'} \text{ (change in aqueous phase concentration)} \qquad (6)$$

$$\frac{dc}{dt} = -\frac{kca}{v} + \frac{k'c'a}{v} \text{ (change in organic phase concentration)} \qquad (7)$$

At equilibrium,

$$\frac{k'}{k} = D = \frac{c}{c'} \ . \qquad (8)$$

In these equations c is the molar concentration of the zirconium species, a is the interfacial area, v is the phase volume, k is a rate constant, D is the distribution coefficient, and t is time; the primed symbols refer to the aqueous phase, and the unprimed symbols refer to the organic phase.

As a guide to inspecting the rate data, it is observed that since the ratio of the forward to the reverse rate constants should be equal to the equilibrium constant (the distribution coefficient, D, in this case), it follows that the power effect of a variable on the forward rate constant minus the power effect on the reverse constant must be equal to the power effect on the equilibrium constant.

For aqueous to organic transfer in the Lewis cell, near time = 0 where $c' \sim c'_o$ (the "o" subscript indicates initial concentration), the equation is:

$$k' = -\frac{vD}{at} \ln \left[1 - \frac{c}{c'_o D}\right]. \qquad (9)$$

Equilibrium Studies

Considerable distribution data for tracer-level zirconium exist in the literature; for fitting the distribution equations we have chosen the data of Alcock (2) because these data cover the largest range of nitric acid concentrations. Other literature data (1,3,5,6,8) are in good agreement above 2 or 3 $\underline{M}$ HNO_3 but, in general, show greater extractability at the lower acid concentrations. The equilibrium equations for reactions (1), (2), (4), and (5) are, respectively:

$$K_1 = \frac{[ZrOH^{3+}][H^+]}{[Zr^{4+}]} = 0.28, \qquad (10)$$

$$K_2 = \frac{[Zr_3(OH)_4^{8+}][H^+]^4}{[Zr^{4+}]^3} = 2.5 \times 10^5,\ 5 \times 10^5 \qquad (11)$$

$$K_3 = \frac{[Zr(NO_3)_4 \cdot 2TBP]}{[Zr^{4+}][NO_3^-]^4[TBP]^2} = 0.002, \qquad (12)$$

$$K_4 = \frac{[Zr(OH)(NO_3)_3 \cdot 2TBP]}{[ZrOH^{3+}][NO_3^-]^3[TBP]^2} = 0.38, \qquad (13)$$

where terms in brackets are molar concentrations. It is recognized that, if known, activities should be used in the quotients. In the studies with nitric acid solutions the hydrogen and nitrate ion activities of Davis (14) gave better agreement with experimental results and were used; in all other cases molar concentrations were used. TBP concentrations in the organic phase were taken as the initial TBP concentration minus the HNO_3 extracted into the organic phase (assumed as the 1:1 TBP:HNO_3 complex). The values of the equilibrium quotients K_1 and the first value of K_2 are from Ref. 11; the second value of K_2 is from fitting of zirconium distribution data shown later in this report. The values of K_3 and K_4 are from trial-and-error fitting of distribution data using both tracer-level data (2) and data obtained using macro concentrations of zirconium.

The data of Alcock and our low concentration data are shown in Fig. 3, with all data corrected to a hypothetical 30% total TBP solution by assuming a second-power dependence (2) on TBP concentration. The line is calculated from the equilibria of Eqs. (10), (12), and

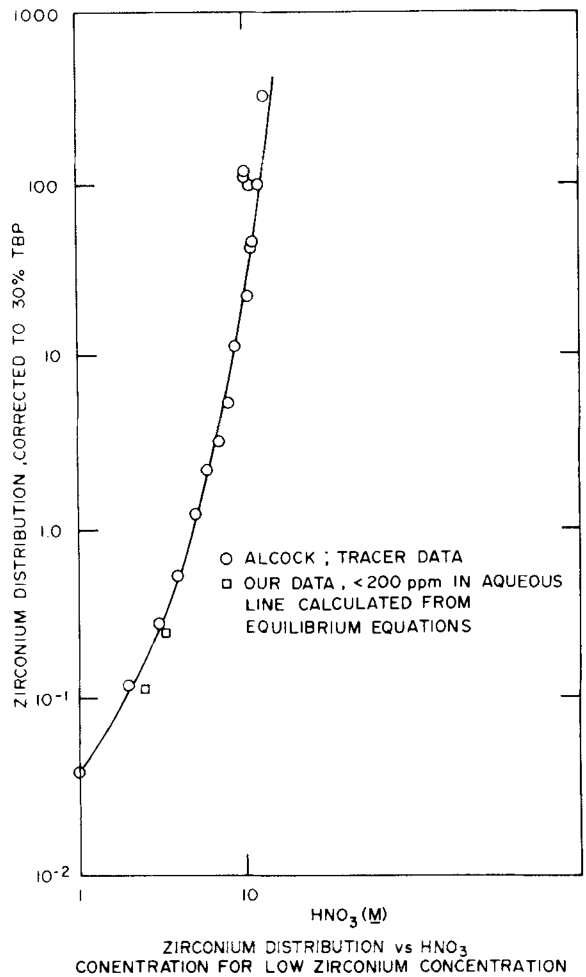

FIGURE 3. Zirconium distribution vs HNO_3 concentration for low zirconium concentrations.

(13); no polymeric species are possible at these low zirconium concentrations. The agreement is excellent.

In our studies of the behavior of macro concentrations of zirconium, we found that the zirconium solutions prepared by extraction and back-scrubbing were much more extractable than solutions prepared using the as-supplied zirconium. This enhanced extractability did not change in 30 days at room temperature, so the refluxing experiments described in the "Apparatus and Procedures" section were performed. The results of these tests are plotted in Fig. 4. No change in extractability occurred in up to 5 hr at the refluxing temperatures. Examination of the distribution coefficients shows that extractability of zirconium increases with increasing nitric acid concentration and decreasing zirconium concentration. This is in agreement with Eqs. (1) to (5). The extraction behavior of zirconium in 2.5 M HNO_3 as a function of the aqueous zirconium concentration is shown in Fig. 5. The agreement between the experimental and calculated distribution coefficients for zirconium is significantly improved by increasing the value of K_2 to 5×10^5. This value is used in subsequent calculations.

The equilibria can be used to calculate the concentrations of the various zirconium species at specified conditions (e.g., Fig. 6 shows the concentrations in 3 M HNO_3 as a function of increasing total zirconium concentration). In this acid the $ZrOH^{3+}$ concentration is always small, and as the total zirconium increases, the Zr^{4+} concentration falls and the $Zr_3(OH)_4^{8+}$ concentration rises.

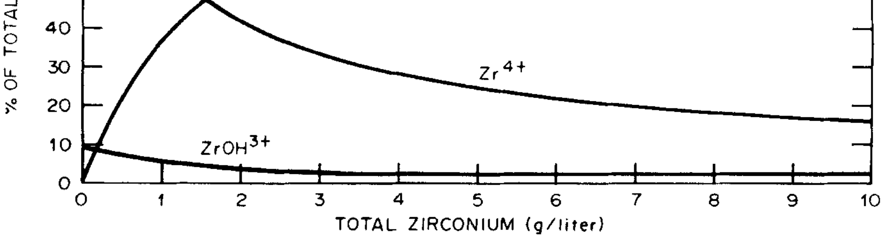

FIGURE 4. Zirconium distribution vs time of refluxing.

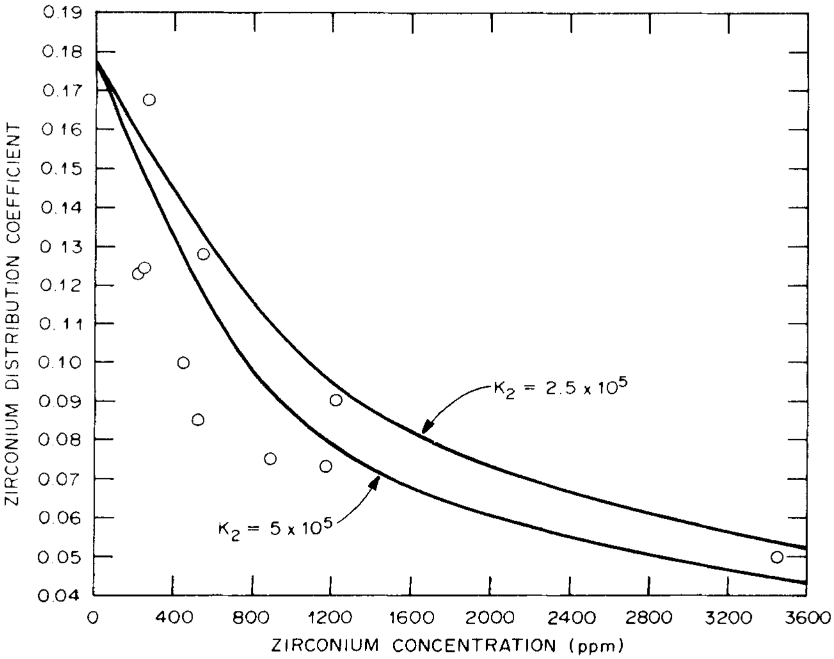

FIGURE 5. Effect of aqueous zirconium concentration on zirconium distribution; 2.5 M HNO_3--30% TBP in normal paraffin diluent. Lines are calculated from Eqs. (10)-(13).

Transfer Kinetics Studies

Since the concentration of the extractable Zr^{4+} and $ZrOH^{3+}$ ions can be calculated for solutions free of oxo-polymers, it is possible to study the extraction kinetics of these ions. However, since two extractable species exist in the aqueous phase (Zr^{4+} and $ZrOH^{3+}$), interpretation of the kinetic results can be difficult. In the two cases to be presented, the experimental conditions were chosen such that a single species should dominate the extraction behavior of zirconium. Figure 7 shows the effect of TBP concentration on the aqueous-to-organic rate constant for Zr^{4+} at 3.5 M HNO_3 (Zr^{4+} predominates over $ZrOH^{3+}$ under these conditions). The power effect is shown as 2 to be consistent with the combining ratio with TBP although the data are consistent with either a second or third power

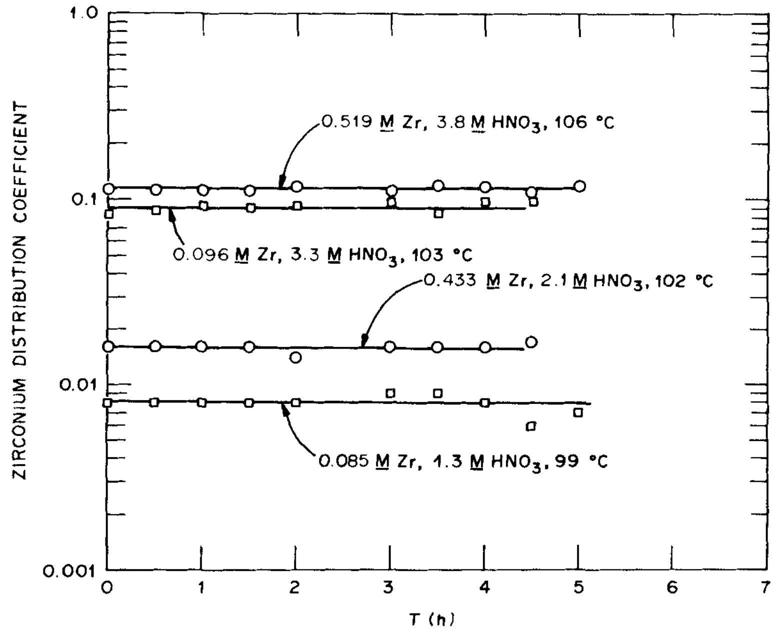

FIGURE 6. Fraction of zirconium as various species as a function of total zirconium in 3 M HNO_3.

effect. Figure 8 shows the effect of neutral nitrate on the aqueous-to-organic rate constant for $ZrOH^{3+}$ from mixtures containing 0.5 M HNO_3 and added $NaNO_3$ ($ZrOH^{3+}$ predominates over Zr^{4+} under these conditions). The slope of about three is consistent with the pickup of three nitrates required for transfer of $ZrOH^{3+}$ into the organic phase.

DISCUSSION

The solution equilibria and the plausible extraction equilibria for zirconium fit experimental data well. Nonequilibrating zirconium species were present in the as-received zirconium oxy-nitrate, but after these were removed no nonequilibrating species were produced by refluxing in nitric acid for up to 5 hr. This suggests that these

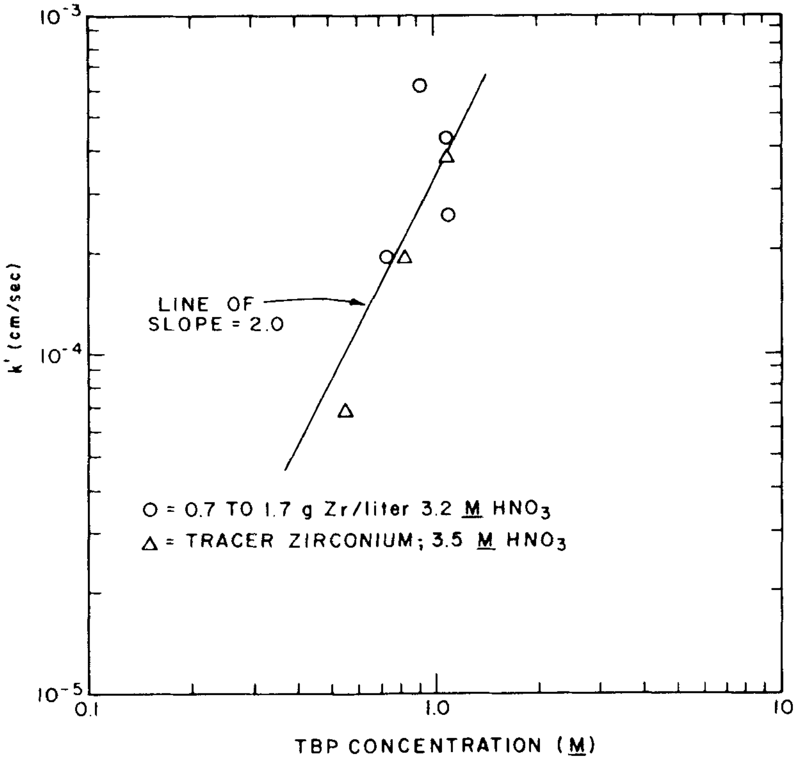

FIGURE 7. Zr^{4+} aqueous-to-organic rate constant vs TBP concentration; 3.5 M HNO_3.

species may be formed when the material is taken to dryness and subjected to substantial heating.

Transfer kinetics studies of zirconium indicate substantial effects of TBP and nitrate on the aqueous-to-organic transfer rate. This is in significant contrast to the behavior of uranium where the effect of TBP is small (about 0.5 power) and no effect of nitrate was observed (13). Studies at Argonne National Laboratory (15) have shown that a modest (about 20%) improvement in the U-Zr separation factor is attained by nonequilibrium extraction from 3 M HNO_3 using 30% TBP solutions; based on the differences in the kinetic behavior of

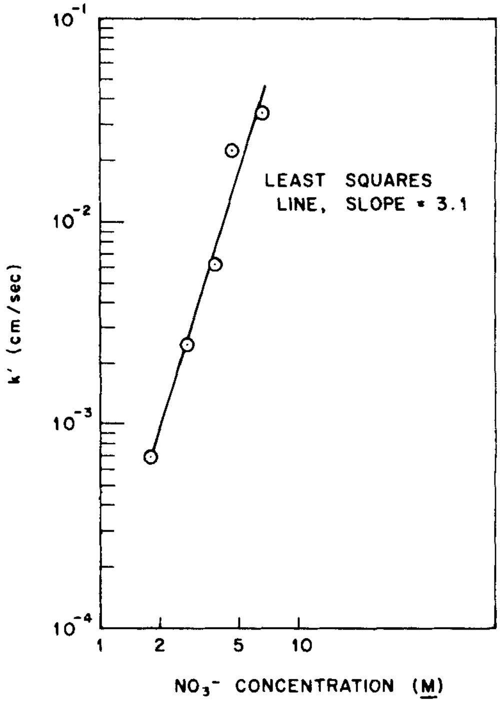

FIGURE 8. $ZrOH^{3+}$ aqueous-to-organic rate constant vs nitrate concentration at 1 M free TBP (corrected for HNO_3 complexing of TBP).

uranium and zirconium seen in the present studies, the operation of a kinetic separation system at low TBP and nitrate concentrations should achieve a single-stage separation substantially better than that which would be found at equilibrium.

Substantially more study of the transfer kinetics of zirconium is possible using the equilibria presented here to calculate the concentrations of extractable species and choosing conditions which favor only one extractable species. Particular studies of interest include the effect of TBP on the extraction kinetics of $ZrOH^{3+}$ and the effects of the variables (HNO_3, NO_3^-, and TBP) on the organic-to-transfer rates of both Zr^{4+} and $ZrOH^{3+}$.

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