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Interpretation of the Extraction Mechanism of the Purex and Thorex Processes from Kinetics Data

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ABSTRACT

The rate of transfer of species between phases in solvent extraction is expected to be controlled by chemical reaction kinetics, diffusion, or a combination of these steps. Transfer kinetics data for uranium(VI), thorium(IV), and zirconium(IV) indicate that the chemical reaction is the rate-controlling step for most dispersed systems. The evidence for this conclusion is: (1) the transfer rate constants for the extraction of uranium were the same for Lewis cell, single drop, and Kenics mixer tests; (2) the forward transfer rate constants increase with increasing TBP concentration (the viscosity of the organic phase also increases) in all cases; (3) the reverse transfer rate varies dramatically with changes in nitrate concentration in the aqueous phase (same phase viscosities); and (4) the difference in the activation energies of the forward and reverse reactions for uranium(VI) transfer is equal to the heat of reaction of uranium with TBP. A proposed mechanism for the solvent extraction kinetics which is consistent with the experimental results includes the formation or decomposition of a charged interfacial complex as the rate-controlling step and equilibration of the interfacial complex with the bulk organic complex as the rapid step.

Introduction

The solvent extraction kinetics of uranium(VI) (1), thorium(IV) (2), and zirconium(IV) (3) in the HNO_3—tri-n-butyl phosphate (TBP)—normal paraffin hydrocarbon diluent

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(NPH) system have been studied to examine the effects of process variables and to aid in understanding the mechanism involved in these extractions. Uranium(VI) extraction kinetics were extensively studied using the drop method, the Lewis cell, and the Kenics mixer (4) (Kenics Corporation, Danvers, Mass.)/H-10 centrifugal separator (Metallextraktion AB, Sweden). Thorium(IV) extraction kinetics were studied in a similar manner using both the drop and Lewis cell methods. Zirconium(IV) extraction kinetics received only a brief examination using the Lewis cell, but these limited data give additional support to the mechanism developed primarily from the results of the studies on U(VI) and Th(IV). The Lewis cell data were taken during the initial stages of the experiment before diffusion gradients had completely developed in the receiving phase to minimize diffusion effects. Details of the experimental techniques and discussions of earlier literature are contained in references 1–3. The evidence developed in these studies can be grouped into the following categories:

1. Comparing the extraction rate constants obtained using different experimental techniques;
2. Examining the effect of the concentrations of reacting species on the transfer rate constants; and
3. Comparing the difference in the activation energies of the forward and reverse transfers of U(VI) to the heat of reaction of uranium with TBP.

Additionally, the ratio of the forward (aqueous-to-organic) to the reverse (organic-to-aqueous) transfer rate constants was shown to be equal to the equilibrium constant. This evidence is included to support the validity of the experimental results.

In all the extraction kinetics studies, the transfer is described by the pseudo-first-order rate equations:

$$\frac{dc'}{dt} = -\frac{ak'c'}{V'} + \frac{akc}{V'} \text{ (change in aqueous phase concentration)} \tag{1}$$

$$\frac{dc}{dt} = -\frac{akc}{V} + \frac{ak'c'}{V} \text{ (change in organic phase concentration) .} \tag{2}$$

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At equilibrium,

$$\frac{k'}{k} = D = c_e/c_e' \ . \tag{3}$$

In these studies, c is the molar concentration of the metal ion being extracted at time t, a is the interfacial area, V is the phase volume, k is a transfer rate constant, and D is the equilibrium distribution coefficient. The subscript e denotes equilibrium conditions, whereas the primed symbols refer to the aqueous phase and the unprimed symbols to the organic phase. In this treatment, the effects of system variables such as nitrate concentration, TBP concentration, and temperature are included in the rate constants and are evaluated, except in the case of temperature effects, by log-log plots of the rate constant vs the appropriate variable.

DISCUSSION

Determination of Transfer Rate Constant by Differing Techniques

The forward transfer rate constant for U(VI) was determined from measurements by the Lewis cell, falling-rising drop, and

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10^{-3} cm/s for the Lewis cell, drop method, and Kenics mixer/H-10 centrifugal separator tests, respectively. The estimated standard deviation for all of the methods was about $\pm 2.4 \times 10^{-3}$ cm/s. Thus, within experimental error, all three experimental techniques yielded the same value for the rate constant. The agreement of the forward rate constants for uranium transfer by these three very different techniques is a convincing argument for chemical reaction as the controlling transfer mechanism.

The Effect of the Concentration of Reacting Species on the Transfer Rate Constants

Log-log plots of the transfer rate constants vs the free TBP concentration for U(VI), Th(IV), and Zr(IV) are shown in Figs. 1–3, respectively. Free TBP is defined as the TBP in the organic phase that is not bound to extracted metal ion. The U(VI) and Th(IV) plots contain data points obtained either by the drop method or by the Lewis cell; since the results by both methods were essentially identical, individual data points were not identified as to experimental technique. In all three cases, the forward transfer rate constants increase with increasing TBP concentration. The viscosity of the organic phase also increases with the TBP concentration so that the rate of diffusion of species in that phase would be expected to decrease. The overall transfer rate, if it is diffusion-controlled, should be limited by the organic phase which is more viscous than the aqueous phase. The fact that system changes which result in a decrease in the diffusion rate actually increase the experimentally measured transfer rates is evidence for chemical reaction control of the transfer for U(VI), Th(IV), and Zr(IV). The reverse transfer rates for U(VI) and Th(IV) [that for Zr(IV) was not determined] both decrease with increasing TBP concentration. This negative dependence of the reverse transfer rate constants on TBP concentration is evidence for a complex reaction mechanism; other evidence to be discussed later also supports a complex reaction mechanism.

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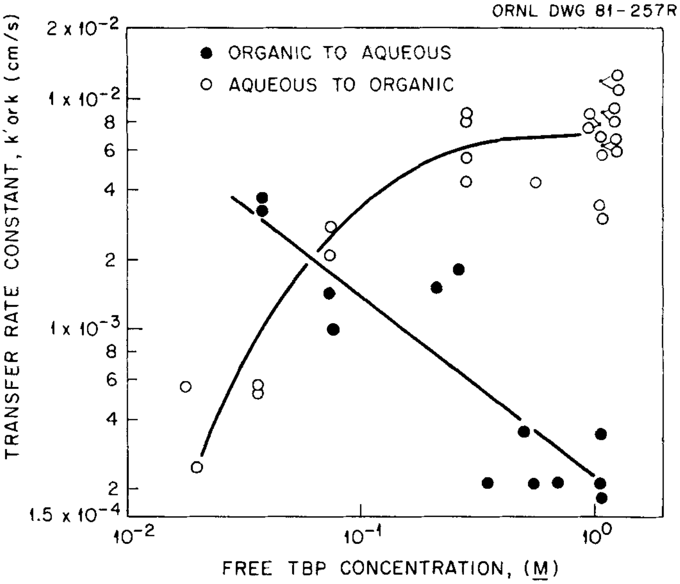

FIGURE 1. Uranium(VI) transfer rate constants vs free TBP concentration. Aqueous phase, 3.5 M HNO_3.

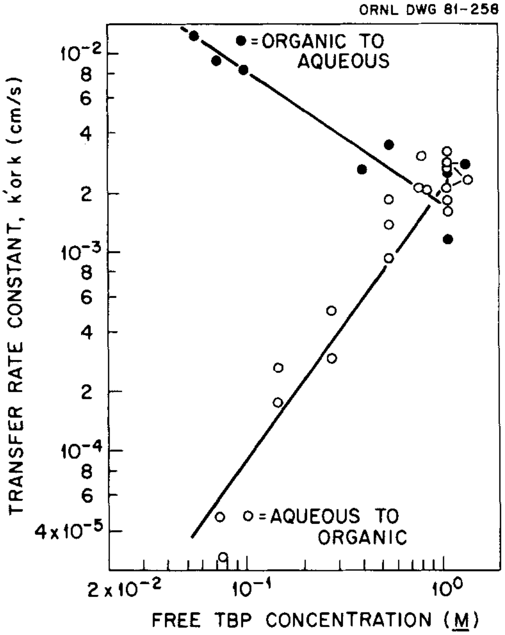

FIGURE 2. Thorium(IV) transfer rate constants vs free TBP concentration. Aqueous phase, 2 M HNO_3.

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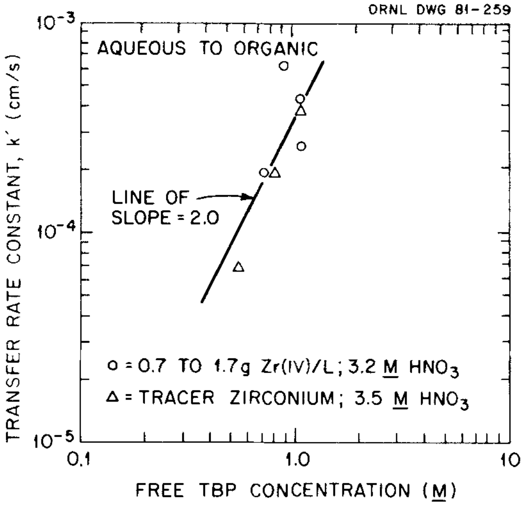

FIGURE 3. Zr(IV) transfer rate constant vs free TBP concentration. Aqueous phase, 3.2 to 3.5 $\underline{M}$ HNO_3.

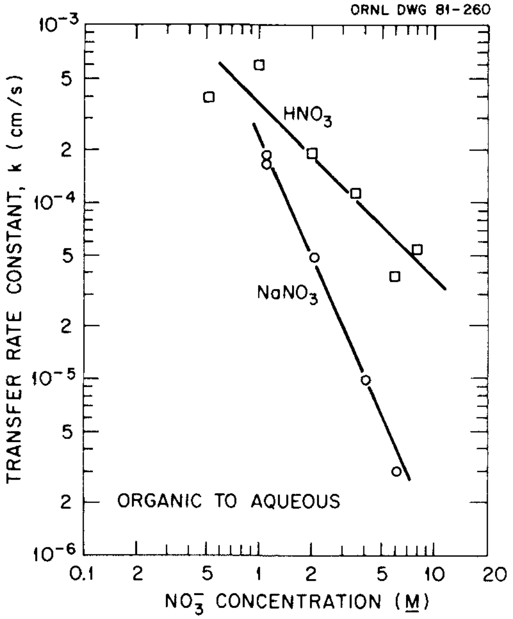

FIGURE 4. Uranium(VI) transfer rate constant vs HNO_3 and $NaNO_3$ concentrations. Organic phase, 30% TBP.

The effects of nitric acid and sodium nitrate on the transfer rate constants of U(VI), Th(IV), and Zr(IV) are shown in Figs. 4–7. The forward rate constant of U(VI) was not affected, within the accuracy of the experiments, by changes in the concentrations of nitrate or nitric acid, in contrast to the pronounced effects observed on the forward rate constant for Th(IV) and, particularly, for Zr(IV). The addition of nitric acid or sodium nitrate to the aqueous phase is without major effect on the viscosity of either phase; thus, neither should have a direct effect on the diffusion rate in either direction. However, increasing the nitrate concentration in the aqueous phase will increase the fraction of the metal ion present as nitrate complexes in the aqueous phase and could conceivably increase the overall forward transfer rate by increasing the concentration of the transferring species in the aqueous phase. No such argument can explain the major decrease in the reverse rate constants with increasing nitrate concentration observed for both uranium and thorium. The negative effects on the transfer rate constants are taken as additional evidence for chemical reaction control of the transfer and as evidence for a complex reaction mechanism. Such an effect argues that the controlling reaction includes pickup of nitrate during extraction and loss of nitrate during stripping.

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Comparison of the Difference in Activation Energies with the Heat of Reaction

The activation energy for the forward transfer of U(VI) was found to be 13.4 kJ/mol; for the reverse transfer the activation energy was 28.9 kJ/mol. The difference in these two values,

-15.5 kJ/mol, is the heat of reaction for a system in which the chemical reaction controls the rates of transfer. The heats of reaction of uranyl nitrate with TBP determined by evaluation of equilibrium data (1) and by direct thermal measurement (9) are -15.9 and -15.1 kJ/mol, respectively. The excellent agreement of the difference in the activation energies with independent values

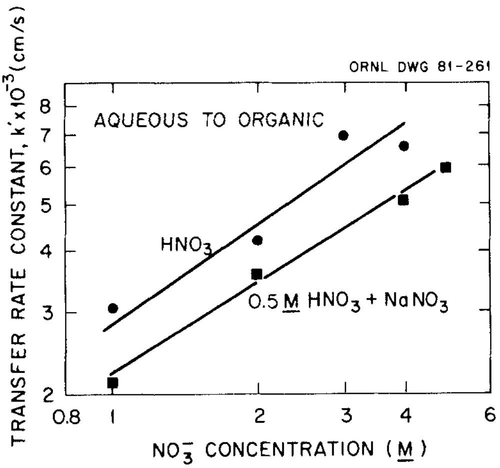

FIGURE 5. Thorium(IV) transfer rate constant vs nitrate concentration. Organic phase, 30% TBP.

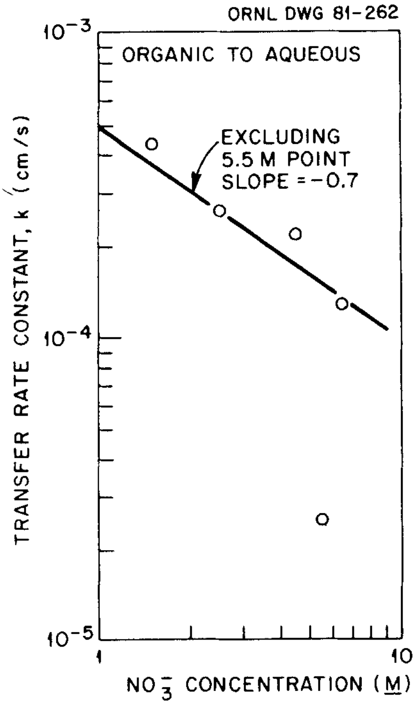

FIGURE 6. Thorium(IV) transfer rate constant vs nitrate concentration. Aqueous phase, 0.5 M HNO_3 + $NaNO_3$. Organic phase, 30% TBP total.

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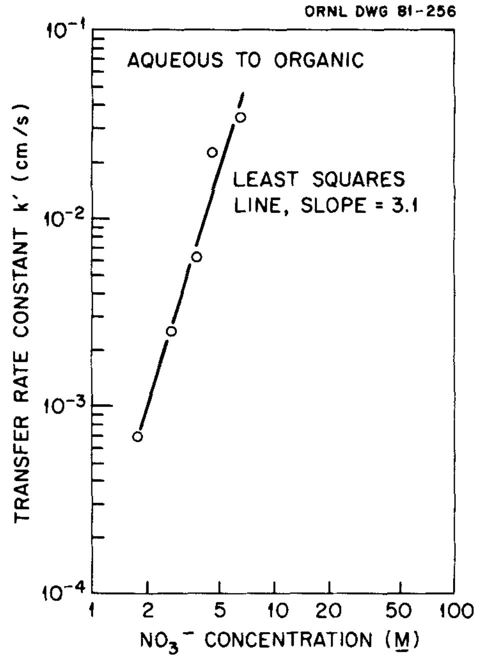

FIGURE 7. $Zr(OH)^{3+}$ transfer rate constant vs nitrate concentration. Aqueous phase, 0.5 M HNO_3 + $NaNO_3$. Organic phase, 1 M TBP uncomplexed (corrected for TBP complexed with Zr(IV) and nitric acid).

of the heat of reaction is additional evidence for chemical reaction control of the transfer rate.

Comparison of the Ratio of the Forward to the Reverse Rate Constants with the Equilibrium Constant

The ratio of the forward to the reverse transfer rate constants should be equal to the equilibrium constant and in this case the distribution coefficient, D, [Eq. (3)] for a transfer controlled by either chemical reaction kinetics or diffusion. Plots of k'/k and D vs free TBP concentration for U(VI) and Th(IV) (Figs. 8 and 9) show that within the accuracy of the experiments, the agreement between k'/k and D is good. This demonstrates consistency in the data and lends credence to the experimental techniques.

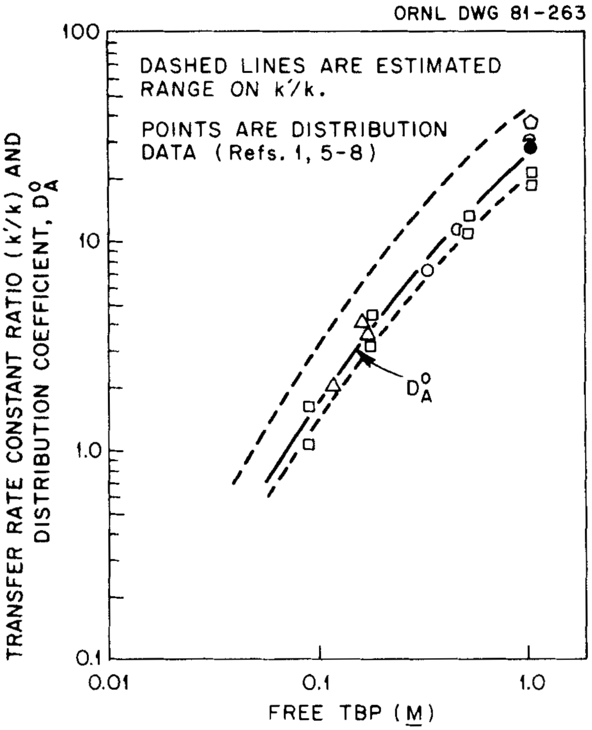

FIGURE 8. Uranium(VI) transfer rate constant ratios and equilibrium distribution coefficients vs free TBP concentration. Aqueous phase, 3.5 M HNO_3.

Proposed Mechanism

The proposed mechanism for solvent extraction kinetics in the Purex and Thorex processes in the sequence of reactions (a tetravalent ion is used as an example)

$$M(NO_3)_m^{(4-m)+}\ (A) + nNO_3^- + PTBP \rightleftarrows [M(NO_3)_{m+n}^{(4-m-n)+} \cdot pTBP]_i (B) \qquad (4)$$

and

$$[M(NO_3)_{m+n}^{(4-m-n)+} \cdot pTBP]_i + (4-m-n)NO_3^- + (2-p)TBP \rightleftarrows M(NO_3)_4 \cdot 2TBP\ (D)\ , \qquad (5)$$

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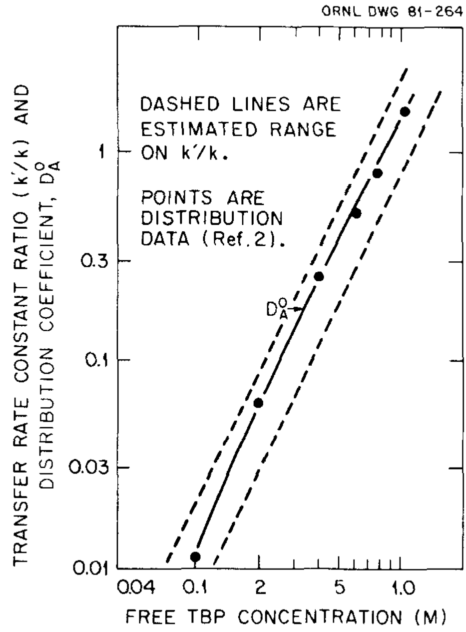

FIGURE 9. Thorium(IV) transfer rate constant ratios and equilibrium distribution coefficients vs free TBP concentration. Aqueous phase, 2 $\underline{M}$ HNO_3.

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where (A), (B), and (D) represent the aqueous metal-nitrate ion, the charged interfacial complex, and the bulk organic complex, respectively.

The rate-controling reaction is the formation or decomposition of the charged interfacial complex according to Eq. (4). The equilibrium between the interfacial complex and the bulk organic species, Eq. (5), is assumed to be established rapidly.

The rate equation for the aqueous-to-organic transfer in Eq. (4) is

$$\frac{dC_A}{dt} = -\frac{a}{V} k_f C_A C^n_{NO_3} C^p_{TBP} + \frac{a}{V'} k_2 C_B \ , \qquad (6)$$

where the charge on the nitrate ion is omitted. The equilibrium constant (K) for Eq. (5) is

$$K = \frac{C_D}{C_B C_{NO_3}^{4-m-n} C_{TBP}^{2-p}} \qquad (7)$$

The term C_B in Eq. (6) is eliminated by use of Eq. (7) and then the term k_2/K is replaced by k_r so that the rate equation becomes

$$\frac{dC_A}{dt} = - \frac{a}{V'} k_f C_A C_{NO_3}^{n} C_{TPB}^{p} + \frac{a}{V'} k_r \frac{C_D}{C_{NO_3}^{4-m-n} C_{TBP}^{2-p}} , \qquad (8)$$

where C is the molar concentration of the subscripted species, a is the interfacial area, V' is the aqueous phase volume, k_f and k_r are the forward and reverse transfer rate constants, respectively, and k_2 is is the reverse transfer rate contsant for Eq. (6). The pseudo-first-order rate equation for the change in aqueous concentration commonly used in extraction kinetics studies, Eq. (1), as discussed earlier, incorporates the explicit nitrate and TBP concentration terms of Eq. (8) in the rates constants, k' and k,

$$\frac{dC_A}{dt} = - \frac{a}{V'} k'C_A + \frac{a}{V'} kC_D . \qquad (9)$$

The following series of equations are obtained at equilibrium:

$$\frac{dC_A}{dt} = 0 , \qquad (10)$$

$$\frac{a}{V'} k_f C_A C_{NO_3}^{n} C_{TBP}^{p} = \frac{a}{V'} \frac{k_r C_D}{C_{NO_3}^{4-m-n} C_{TBP}^{2-p}} \quad \text{[from Eq. (8)] (10)} \qquad (11)$$

$$\frac{k_f}{k_r} = \frac{C_D}{C_A C_{NO_3}^{4-m} C_{TBP}^{2}} = K_D \text{ (equilibrium constant) (10)} \qquad (12)$$

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and

$$\text{Distribution coefficient (10)} = C_D/C_A = K_D C_{NO_3}^{4-m} C_{TBP}^2 .$$

The distribution coefficient at equilibrium predicts a second power dependence on the TBP concentration and a (4-m) power dependence on the nitrate concentration, where m is the number of nitrate ions associated with the metal ion in the aqueous phase. In addition, the power effect of a variable on the forward transfer rate minus the power effect on the reverse transfer rate must be equal to the power effect on the equlibrium distribution coefficient. This relationship is approximately true for cases where data are available. The values of the power effects of the concentration variables which have been determined are shown in Table 1.

Of particular interest is the lack of uniformity in the effect of a particular variable on the transfer rate, forward or reverse. For instance, for U(VI) the nitrate affects only the reverse transfer rate while for Th(IV) and $ZrOH^{3+}$ there are effects on the forward transfer rates. The TBP concentration affects both the forward and reverse transfer rates for U(VI) and Th(IV) while the only effect in the case of Zr^{4+} is apparently on the forward rate since there is an approximately second power effect of the TBP concentration on the forward rate constant and on the distribution coefficient for Zr^{4+}.

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SUMMARY

There is substantial evidence that the transfer rate in the Purex and Thorex systems is limited by chemical reaction. This evidence includes the observations that the same transfer rate constants are found for experimental techniques which give different area-to-volume ratios and different mixing efficiencies, that the difference in the activation energies for the forward and reverse transfer of U(VI) is equal to its heat of reaction with TBP, and that the effects of concentration variables do not conform to expectations for diffusion control. The mechanism must be

TABLE 1

Concentration Effects in Solvent Extraction Kinetics

		Concentration exponent[a]			
				Distribution coefficient	
Species	Concentration variable	Forward transfer	Reverse transfer	Value	Reference
U(VI)	HNO_3	0	-1	1	(8)
	NO_3	0	-2	2	
	TBP	0.5[b]	-0.8	1.38	(1)
Th(IV)	HNO_3	1	Small	1.35	(11)
	NO_3	0.6	-0.7	2	(2)
	TBP	1.3	-0.7	2	(2)
$Zr(OH)^{3+}$	HNO_3	-	-	-	
	NO_3	3.2	-	3[c]	
	TBP	-	-	-	
Zr^{4+}[d]	HNO_3	-	-	-	
	NO_3	-	-	-	
	TBP	2	-	2	

[a] For example, distribution coefficient $\propto$ (conc. variable)$^{\text{conc. exponent}}$.

[b] The power effect on the forward transfer rate of U(VI) varies with TBP concentration.

[c] Assumed to be 3 since $Zr(OH)^{3+}$ must add three nitrates during extraction.

[d] Both $Zr(OH)^{3+}$ and Zr^{4+} are extractable.

complex since negative effects of TBP and nitrate concentration were found for the reverse transfer rate constants of U(VI) and Th(IV). Although a number of mechanisms could give such a dependence, the assumption that an interfacial complex is in rapid equilibrium with the bulk organic species leads to relatively simple rate and equilibrium expressions which are consistent with the experimental data and do not violate any of the known behavioral requirements for the two-phase system.

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