Zirconium Transport Dynamics in the Purex Solvent Extraction Process

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The primary objective of this study was to develop and validate experimental and mathematical procedures that can be used to determine the fundamental mechanisms of the Purex (plutonium and uranium) extraction process. The mechanisms of this solvent extraction process have been established by classical chemical engineering principles.

In the past, modeling of transport phenomena for the solvent extraction of spent nuclear fuel by the Purex process has typically (1) relied solely on diffusion, (2) relied solely on chemical reaction, (3) combined diffusion and chemical reaction in a semiempirical fashion, or (4) combined diffusion and chemical reaction in a nonclassical chemical engineering manner.

This study was conducted with the single Purex species, aqueous Zr^{4+}, to simplify the chemistry and modeling mathematics. The validated procedures and model are applicable to most all Purex species.

Introduction

Objectives and relevance

Optimizing the fission product and waste actinide decontamination will be the focus for future nuclear fuel reprocessing development. Successful efforts to minimize the radioactivity of reprocessed fuel will decrease radioactive exposure during handling of recycled uranium and plutonium and decrease poisoning (neutron adsorption) of fuel fabricated from recycled uranium and plutonium. In addition, separation of short-lived highly radioactive fission products from long-lived lower-activity waste actinides can significantly improve waste handling and storage techniques. Actinides could then be transmuted by way of neutron bombardment to short-lived fission products. In response to these future reprocessing needs, the proper application of fundamental mass-transfer and simultaneous chemical reaction principles to the Purex (plutonium and uranium extraction) solvent extraction process could lead to the development of an advanced modeling tool for optimizing decontamination of spent nuclear fuels.

Most methods for reprocessing spent nuclear reactor fuel are based on solvent extraction. The most common processes are: (1) the Redox process based on methyl isobutyl ketone as the extractant and alumina nitrate as the salting agent; (2) the Purex process based on tri-*n*-butyl phosphate (TBP) as the extractant and nitric acid as the salting agent. The aqueous fission product Zr^{4+} was selected for this study because it has a relatively high concentration in spent nuclear fuel as compared to other fission products, and it is readily available as a nonradioactive species. Because it is more commonly used by industry, the Purex process was selected for this study rather than the Redox process.

Significant prior work

Much of the existing literature concerning Purex solvent extraction deals primarily with defining the chemical complexation reaction. Little effort has been made to describe the mass-transfer process, because it depends on the contacting vessel. However, without understanding the mass-transfer process for the contacting vessel, it is not possible to estimate accurately the chemical complexation reaction rate constants.

The aqueous chemistry of zirconium in a nitric acid medium has been studied by many experimenters and is discussed in detail by Baes and Mesmer (1976) and summarized by Siczek

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and Steindler (1978) and Lo et al. (1983). They conclude that at zirconium concentrations below 0.0001 to 0.001 M and nitric acid concentrations above 3 to 5 M, concentrations of polymerized and hydroxylated zirconium are much less than those of the Zr^{4+} species. These concentrations are similar to data in sections of actual fuel reprocessing flow sheets.

A large number of publications have discussed proposed chemical complexation reactions for the solvent extraction of zirconium by the Purex process (see DeMuth, 1989 for the list). Some of the more noted publications include Tsvetkova et al. (1961), Adamskii et al. (1980), Alcock et al. (1957), Egorov et al. (1960), Benedict et al. (1981), Nikitina and Pushlenkov (1962), and Reznik et al. (1963). They all give Eq. 1 as the generalized zirconium-Purex complexation reaction, where n depends on the degree of hydrolysis:

$$Zr^{4+} + n(OH^-) + (4-n)(NO_3^-) + 2TBP \rightleftharpoons Zr(OH)_n(NO_3)_{4-n} \cdot 2TBP \quad (1)$$

None of the above-mentioned publications indicate whether Eq. 1 is an aqueous phase, organic phase, or interfacial reaction.

The test vessel selected for this study was a stirred cell for which generalized mass-transfer coefficient correlations had been previously developed by numerous investigators. Lewis (1954), Bulicka and Prochazka (1976), McManamey (1961), and Mayers (1961) reported various forms of a mass-transfer coefficient correlation for the stirred cell. Lewis' expression depends only on the Reynolds number and consequently assumes only eddy diffusion, not molecular diffusion. Other expressions depend on the Reynolds number and Schmidt number, which incorporates the molecular diffusion effect. The mass-transfer correlation selected for this study was that of Bulicka and Prochazka, which utilizes a Schmidt number dependency of 1/2 in accordance with penetration and surface renewal theories. Equation 2 is the expression of Bulicka and Prochazka, where the parameters z_o and z_1 are constants selected to fit the test vessel of this study. The parameter j refers to the phase of interest.

$$N_{Sh,j} = z_o (N_{Re,j})^{z_1} (N_{Sc,j})^{1/2}. \quad (2)$$

Major results and conclusions

This study focused on demonstrating and validating a method for determining the complexation reaction rate constants for the extraction of Zr^{4+} by the Purex process. With known reaction rate constants, extraction in almost any contacting vessel with known mass-transfer coefficients can be predicted. The techniques used are directly applicable to most other fission products and actinides.

To estimate reaction rate constants, we had to develop an extraction model for Zr^{4+} in the Purex system. This was done by incorporating chemical reaction and simultaneous mass-transfer principles as applied to the specific process conditions and the test vessel. The chemical complexation reaction expression and rate constants have been applied to a continuous stirred-tank reactor (CSTR) model, which is similar to nuclear fuel reprocessing equipment such as mixer-settlers and centrifugal contactors.

Using statistical methods, mass-transfer coefficient estimates, and analysis of existing data in the literature, we concluded for the system of this study that the Zr^{4+} extraction rate was controlled predominantly by (1) the chemical complexation reaction rate in the aqueous phase and (2) diffusion of the complexed Zr^{4+} species in the organic phase. The chemical reaction and mass-transfer differential equations describing this process were simultaneously solved using Laplace transforms. Complexation reaction rate constants were regressed from the nonlinear solution to the differential equations by a weighted least-squares method. The regression analysis used stirred-cell transient zirconium concentration data.

It has long been understood that the slower kinetics of fission product extraction, as compared to the more rapid kinetics of uranium or plutonium extraction, could be utilized to aid decontamination; however, past efforts have been generally qualitative. The model presented here could be utilized to provide a quantitative tool for optimization of flowsheets and equipment.

Experimental Studies

Determination of the complexation reaction rate constants was the primary objective of the experimental portion of this study. The following steps were required to obtain these rate constants.

1. Select an appropriate mass-transfer test vessel.
2. Characterize the mass-transfer coefficient correlation for the test vessel and estimate mass-transfer coefficients for the zirconium-Purex species of interest.
3. Determine the equilibrium constants for the Zr^{4+}-Purex system, that is, the distribution coefficients and complexation reaction equilibrium constant.
4. Ascertain the significant components of mass transfer for the zirconium-Purex process in the test vessel and develop an extraction model.
5. Utilize the extraction model to regress the complexation reaction rate constants from zirconium-Purex transient data collected in the test vessel.

A stirred cell was selected for the mass-transfer tests of this study. The design was modeled after that originally used by Lewis (1954). The stirred cell selected was operated as a closed system (rather than a flow-through), as shown in Figure 1. It consisted of a 1-L glass vessel in which each phase was stirred by a single-shafted central paddle. The paddle diameter could be changed, allowing independent control of the Reynolds number in each phase. Stainless steel vertical wall baffles were placed circumferentially along the vessel wall to minimize cavitation. The interfacial area was adjustable by means of a circular teflon block. The entire stirred cell was immersed in a water bath to control temperature.

A mass-transfer coefficient correlation was selected and characterized for the test vessel of this study. The correlation selected (Eq. 2) was that of Bulicka and Prochazka, in which the constants z_o and z_1 represent the unique hydrodynamic characteristics of the test vessel. The constants z_o and z_1 were regressed from acetic acid/water/isobutanol mass-transfer data collected in the selected test vessel. Acknowledging data in the literature and data collected during this study, we determined that the Marangoni effect (DeMuth, 1989, p. 19), ionization (Barrow, 1972, p. 418), and dimerization (Olander, 1980) had

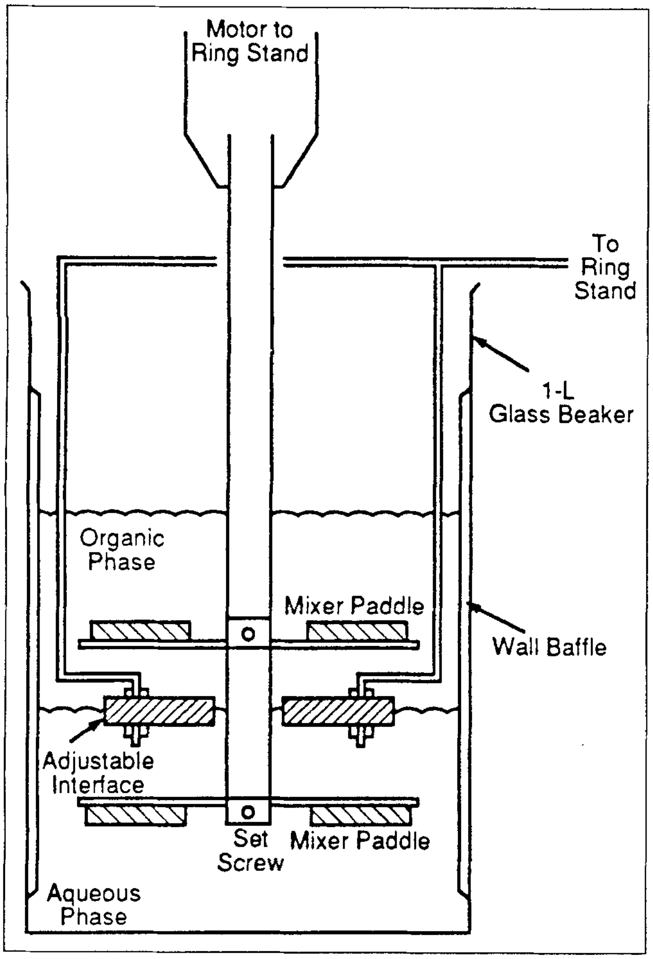

Figure 1. Stirred cell.

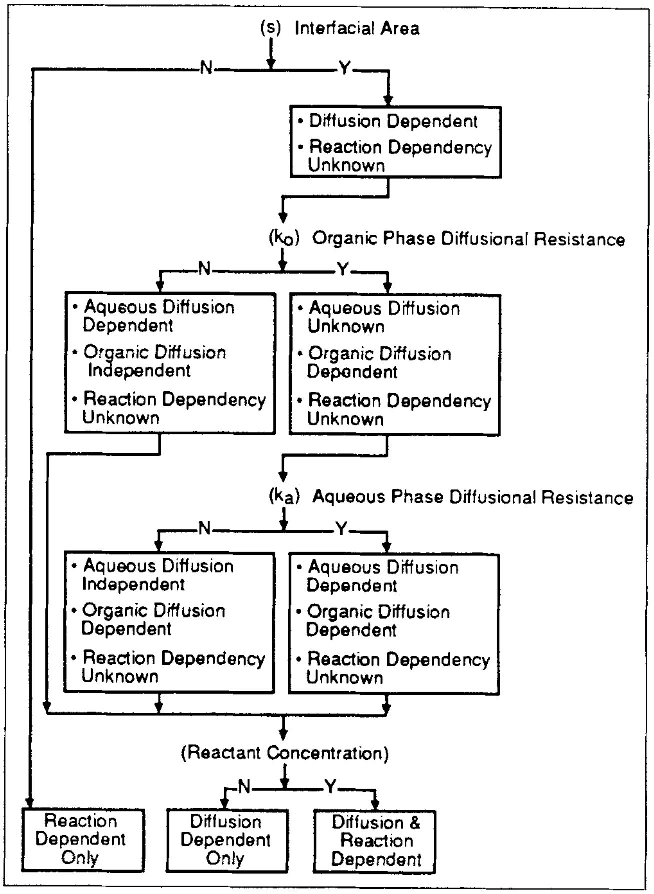

Figure 2. Selection of mass-transfer components.

negligible effects on the mass transfer of acetic acid from water to isobutanol, or the reverse, for the conditions of this study.

The zirconium-Purex equilibrium constant of Eq. 1 (where $n = 0$) was determined by zirconium distribution shake tests, which consisted of equal phases of nitric acid and TBP/dodecane mixed at constant temperature. The zirconium concentration was measured spectrophotometrically by the color indicator Arsenazo III. See DeMuth (1989) for details of these analyses.

Significant components of Zr^{4+} mass transfer for the Purex conditions of the study were determined from stirred-cell zirconium-Purex mass-transfer data. Distribution of zirconium in the aqueous and organic phases was measured with time and was statistically analyzed to determine the mass-transfer behavior. Figure 2 shows how such parameters as interfacial area, mixer diameter or consequent mass-transfer coefficient, and concentrations were used to ascertain the controlling mechanisms of mass transfer. Statistical methods were used to determine if the interfacial area and mass-transfer coefficient significantly affected the zirconium mass-transfer rate.

Each zirconium mass-transfer test began by equilibrating the aqueous nitric acid and TBP/dodecane before introducing zirconium. Following equilibration, a known amount of zirconium was added to the aqueous phase in the Zr^{4+} form with a pipet. Zirconium samples collected for the analysis were removed from the stirred cell at selected times. At 1- to 5-mL pipet was used for collecting the samples. The total cumulative samples per test never exceeded 5% of the original phase volume. Organic samples were back-extracted with dilute nitric acid before the spectrophotometric analysis with Arsenazo III. Details of these analyses are discussed by DeMuth (1989).

The complexation reaction rate constants were regressed from zirconium-Purex stirred-cell mass-transfer data. This was the same data used to determine significant components of mass transfer.

Results and Discussion

Mass-transfer coefficient correlation

Estimation of both mass-transfer coefficients and reaction rate constants from the zirconium data of this study would introduce too many degrees of freedom for reliable regression. Many mass-transfer coefficient models for stirred cells can be found in the literature. The model selected for this study was presented in the Introduction section, Eq. 2. It was necessary to use a nonreacting system to characterize the mass-transfer coefficient model. The transfer of acetic acid from water to isobutanol was selected because of the well-behaved chemical nature of acetic acid and isobutanol, and a solid literature database established by J. B. Lewis.

To determine the mass-transfer coefficient for the acetic acid/water/isobutanol system, we had to:

- Prove the Marangoni effect was insignificant
- Ascertain the vessel hydrodynamics were well-behaved such

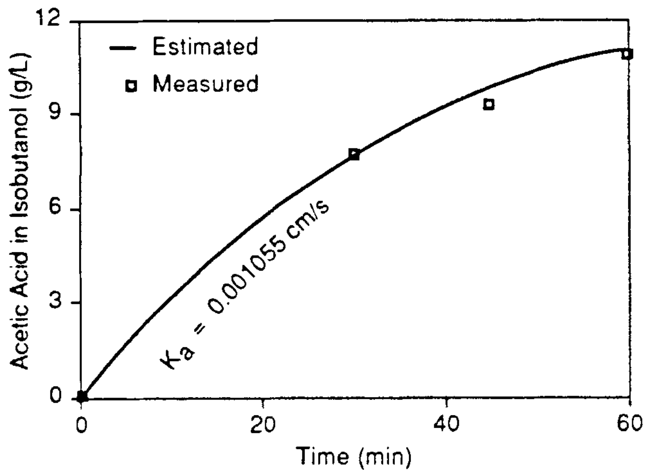

Figure 3. Acetic-acid mass-transfer test for S_2, V_{a2}, V_{02}, d_{a2} and d_{01}.

that phase volume and interfacial area did not affect the Reynolds number and consequent mass-transfer coefficient

- Determine which phase or phases controlled mass transfer.

Marangoni Effect. The significance of the Marangoni effect was determined by comparing Lewis' forward and reverse acetic acid mass-transfer coefficients in water and isobutanol. We judged from the data, as detailed by DeMuth (1989, p. 19), that the mass-transfer coefficient for acetic acid was not significantly different when transferring from water to isobutanol or the reverse with identical operating conditions. Hence, we concluded that the Marangoni effect was insignificant.

Vessel Hydrodynamics. The test conditions selected for the acetic-acid mass-transfer data were based on a half factorial experimental design. The half factorial design provided for determination of the single and the 1 × 1 interaction effects of interfacial area, phase volume, and mixer diameter on the mass-transfer coefficient. Figure 3 shows the aqueous-phase overall mass-transfer coefficient regression for conditions of large interfacial area, large aqueous and organic-phase volumes, and large aqueous-phase mixer diameter, and small organic-phase mixer diameter. Table 1 shows the aqueous-phase overall mass-transfer coefficients for the entire half factorial experimental design. Initial conditions of the tests were 0.5 M aqueous acetic acid at 25°C and mixed at 150 rpm.

Table 1. Acetic-Acid Aqueous-Phase Overall Mass-Transfer Coefficient

Area	Phase Vol.	Overall Mass Transfer Coefficient (cm/s) Mixer Diameter d_{a1},d_{o1}	d_{a2},d_{o1}	d_{a1},d_{o2}	d_{a2},d_{o2}
S_1	V_{a1},V_{o1}	0.000036	—	—	0.000956
	V_{a2},V_{o1}	—	0.000604	0.000925	—
	V_{a1},V_{o2}	—	0.000215	0.000771	—
	V_{a2},V_{o2}	0.000057	—	—	0.001151
S_2	V_{a1},V_{o1}	—	0.000083	0.000878	—
	V_{a2},V_{o1}	0.000092	—	—	0.001019
	V_{a1},V_{o2}	0.000034	—	—	0.000774
	V_{a2},V_{o2}	—	0.001055	0.000872	—

Mass-transfer controlling phase(s)

The aqueous-phase overall mass-transfer coefficient was regressed from the acetic-acid mass-transfer data (acetic acid transferred from water to isobutanol) based on integration of Eq. 3, which yields Eq. 4. The acetic-acid distribution coefficient was measured as 1.28 (DeMuth, 1989).

$$\frac{-V_a}{S}\frac{dC_a}{dt}=K_a(C_a-C_a^*) \tag{3}$$

where

$$m=C_o/C_a^*$$

$$V_a[C_a(t=0)]=V_aC_a+V_oC_o$$

$$K_a=\frac{-V_a}{(1+A)St}\ln\left\{\frac{(1+A)C_a-A[C_a(t=0)]}{C_a(t=0)}\right\}, \tag{4}$$

where

$$A=V_a/(mV_o).$$

The half factorial experimental design shown in Table 1 was evaluated by using a half normal plot. A half normal plot is used to ascertain significance in much the same way as an analysis of variance. The half factorial design is evaluated by a half normal plot when significance of interaction effects is sought with a minimum of data. The half normal plot utilizes a pooled error estimated by assuming the data to be normally distributed. The assumption of normally distributed data allows the degrees of freedom, otherwise consumed by estimating the pooled error, to be used for estimating interaction effects. For a discussion of half normal plots, see Johnson and Leone (1964).

Figure 4 shows the half normal plot produced from data in Table 1, from which the following conclusions can be drawn.

1. Statistically, in more than 95 out of 100 tests the organic-phase mixer diameter should significantly affect the mass-transfer rate. Each of the other effects would be significantly less than 80 times out of 100.

2. Acknowledging conclusion 1, it follows that for the op-

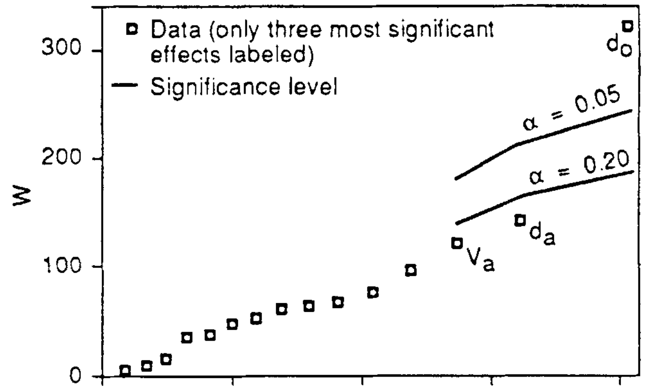

Figure 4. Acetic-acid half normal plot.

erating conditions of this study, the acetic-acid mass-transfer rate from water to isobutanol was predominantly controlled by mass-transfer resistance in the organic phase.

3. It also follows from conclusion 1 that the vessel hydrodynamics were not affected significantly by the range of interfacial areas and phase volumes used in this study. This is desirable for a controlled experiment.

Based on predominant organic-phase mass-transfer resistance, the aqueous-phase overall mass-transfer coefficient can be related to the organic-phase individual mass-transfer coefficient by Eq. 5:

$$1/K_a = 1/(mk_o). \tag{5}$$

Equation 5 can be combined with Eq. 2 to provide a correlation between the organic-phase mixer diameter and aqueous-phase overall mass-transfer coefficient as shown by Eq. 6:

$$K_a = 0.0000934(mD/d_o)(N_{Re,o})^{1.38}(N_{Sc,o})^{1/2}. \tag{6}$$

The constants 0.000093 and 1.38 of Eq. 6 were determined by linear regression of the aqueous-phase overall mass-transfer coefficients in Table 1 (see DeMuth, 1989, p. 31).

Zirconium-Purex equilibrium constant

Because we wanted to demonstrate the objective of the study with a single Purex species, we selected Zr^{4+}. For a 3-M HNO_3 and 0.001-M zirconium aqueous solution, the parameter n in Eq. 1 is essentially zero (no hydrolysis), as shown by Eq. 7.

$$Zr^{4+}4(NO_3^-) + 2TBP \underset{K^r}{\overset{K^f}{\rightleftharpoons}} Zr(NO_3)_4 \cdot 2TBP. \tag{7}$$

For conditions described by Eq. 7, we can reason that the formation rate of $Zr(NO_3)_4 \cdot 2TBP$ is approximately proportional to $[NO_3^-]^4$ and $[TBP]^2$, and is supported by $Zr(NO_3)_3(OH)$ data of Mailen et al. (1980).

It has been reported by Marcus and Kertes (1969, p. 679), that HNO_3 is not significantly ionized in pure TBP or in a TBP hydrocarbon mixture (approximately 0.1 mol % NO_3^- of total HNO_3 in organic phase). The solubility of TBP in water, for a 30-vol. % TBP in dodecane organic mixture, has been reported by Benedict et al. (1981, p. 511), as approximately 0.27 g/L TBP at 25°C. Leroy (1967) reports that the solubility of TBP in water decreases approximately 7% with each 1-M increase in aqueous HNO_3 concentration to a minimum at 7-M HNO_3. Based on littlè HNO_3 ionization in TBP/dodecane, the TBP solubility, and Eq. 7, the probability of an aqueous-phase vs. organic-phase complexation reaction can be estimated as follows:

1. The NO_3^- aqueous-phase concentration at 3-M HNO_3 is approximately 5,000 times greater than the organic-phase concentration at 30 vol. % TBP in dodecane, due to an HNO_3 (organic/aqueous) distribution coefficient of 0.2 (see Benedict et al., 1981) and the NO_3^- ionization of 0.1 mol % of total HNO_3 in the organic phase.
2. The TBP aqueous solubility in 3-M HNO_3 is approximately 0.2 g/L, and the concentration in organic phase at 30 vol. % is 295 g/L.
3. Therefore,

$$\frac{[NO_3^-]_a^4[TBP]_a^2}{[NO_3^-]_o^4[TBP]_o^2} = \frac{[5{,}000]^4[0.2]^2}{[1]^4[295]^2} = 3 \times 10^8.$$

The rate of $Zr(NO_3)_4 \cdot 2TBP$ formation in the aqueous phase should be approximately 10^8 times greater than that in the organic phase. The conclusion and assumption for the remainder of this study are that the formation of $Zr(NO_3)_4 \cdot 2TBP$ is predominantly an aqueous-phase reaction. It will be shown later that the reaction is not instantaneous and, consequently, not interfacial.

Equation 8 displays the equilibrium expression based on Eq. 7.

$$\frac{K^f}{K^r} = K_{eq} = \frac{[Zr(NO_3)_4 \cdot 2TBP)]_a}{[Zr^{4+}]_a[NO_3^-]_a^4[TBP]_a^2}. \tag{8}$$

The following assumptions and consequent simplifications were made to express the equilibrium constant in terms of concentrations rather than activities. For a liquid-phase reaction at constant temperature and pressure, the equilibrium constant is defined in terms of activities:

$$K_{eq} = \Pi \bar{a}_i^{\beta i}.$$

The activitiy of species i in a mixture is defined in terms of fugacity:

$$\bar{a}_i = \frac{\bar{\mathfrak{f}}_i}{\mathfrak{f}_i^o}.$$

For a solute at low concentration, the fugacity can be approximated by Henry's Law:

$$\bar{\mathfrak{f}}_i = \mathcal{H}_i m_i, \text{ and } \mathfrak{f}_i^o = \mathcal{H}_i m_i^o$$

such that

$$\bar{\mathfrak{f}}_i = \mathfrak{f}_i^o m_i \text{ or } \bar{a}_i = \frac{\bar{\mathfrak{f}}_i}{\mathfrak{f}_i^o} = m_i \propto C_i$$

for m_i^o taken as one, and water the solvent.

For a solute high concentration, the activity coefficient can be approximated as one, in accordance with the Lewis-Randall rule, such that:

$$\gamma_i = \frac{\bar{\mathfrak{f}}_i}{x_i \mathfrak{f}_i}$$

and

$$\bar{a}_i = \gamma_i x_i(\mathfrak{f}_i/\mathfrak{f}_i^o) = x_i(\mathfrak{f}_i/\mathfrak{f}_i^o) = x_i \propto C_i$$

for an aqueous solution.

For the system of this study, zirconium and TBP are at low concentrations in the aqueous phase ($x_i < 10^{-6}$), and nitric acid is at a relatively high concentration ($x_i \cong 0.2$).

The aqueous-phase $Zr(NO_3)_4 \cdot 2TBP$ species is difficult to measure because the aqueous-phase cation Zr^{4+} also exists. However, the cation Zr^{4+} does not exist in significant concentration in the organic phase, so the organic-phase $Zr(NO_3)_4 \cdot 2TBP$ species predominates and is consequently measurable. The zirconium at the beginning of the test exists only in the aqueous phase and predominantly as the Zr^{4+} species.

Distribution coefficients reported in the literature for zirconium at chemical process conditions similar to this study must be defined by Eq. 9:

$$m_{Zr^{4+}} = \frac{[Zr(NO_3)_4 \cdot 2TBP]_o}{[Zr^{4+}]_a + [Zr(NO_3)_4 \cdot 2TBP]_a}. \qquad (9)$$

Equation 9 can be combined with the zirconium material balance and re-arranged to yield a linear form capable of regression, yielding the $[Zr^{4+}]_a$ and $[Zr(NO_3)_4 \cdot 2TBP]_a$ reaction equilibrium constant and $Zr(NO_3)_4 \cdot 2TBP$ distribution coefficient based on the equilibrium organic-phase total zirconium concentration.

$$\frac{1}{m_{Zr^{4+}}} = \frac{[Zr^{4+}\,(t=0)]_a + [Zr(NO_3)_4 \cdot 2TBP]_o}{[Zr(NO_3)_4 \cdot 2TBP]_o}$$

$$= \frac{[1/(m_{Zr}'K_{eq})]}{[NO_3]_a^4\{[TBP]_o/(m_{TBP})\}^2} + \frac{1}{(m_{Zr}')},$$

where

$$m_{Zr}' = \frac{[Zr(NO_3)_4 \cdot 2TBP]_o}{[Zr(NO_3)_4 \cdot 2TBP]_a}.$$

Zirconium equilibrium shake tests were performed over a range of HNO_3 and TBP concentrations. The data were regressed by Eq. 9, and the results are shown in Figure 5, where:

$$K_{eq} = 3.5 \times 10^{22}\ (\text{mol/mL})^6$$
$$m_{Zr}' = 0.35 \text{ and } R^2 > 0.95.$$

Zirconium-Purex significant components of mass transfer

As done with acetic acid, the effects of phase volume, mixer diameter, and interfacial area on the Zr^{4+} mass-transfer rate were ascertained by use of a half factorial experimental design evaluated with a half normal plot. Table 2 shows the mass of zirconium transferred from aqueous phase to organic phase at two, four and six hours. The initial test conditions (before equilibrium) for Table 2 were the following:

Aqueous Phase	Organic Phase
3.5 M HNO_3 in water	30 vol. % TBP
0.00137 M $Zr(NO_3)_4$	70 vol. % dodecane
25°C	25°C
150 rpm	150 rpm

The half normal plot corresponding to two hours in Table 2 is shown in Figure 6. It is evident from Figure 6 that only the organic-phase mixer diameter significantly affected the mass-transfer rate at greater than the 0.05 significance level, at up to two hours into each test. Conclusions from the half normal plot for zirconium mass transfer up to two hours are:

1. Mass-transfer resistance in the organic phase predominated up to two hours into each test; consequently, aqueous bulk and aqueous interfacial concentrations were approximately equal up to two hours.
2. Based on the first conclusion, the organic-phase $Zr(NO_3)_4 \cdot 2TBP$ diffusional resistance significantly affects the zirconium mass-transfer rate.

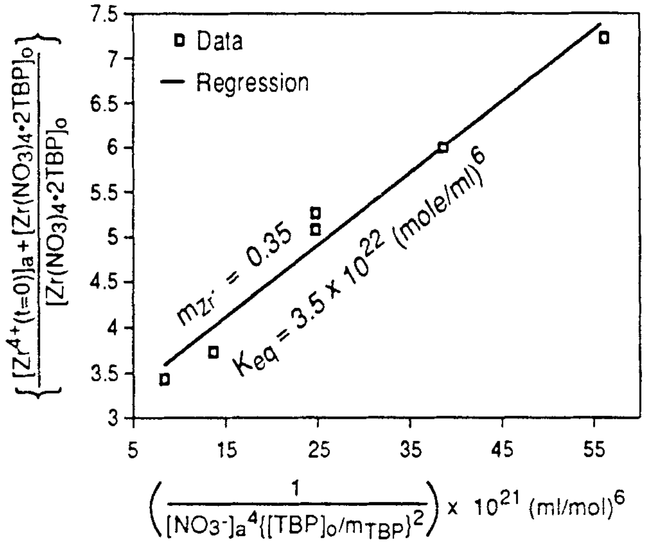

Figure 5. Complexed zirconium distribution coefficient and equilibrium constant.

The effect of each reactant concentration on the zirconium mass-transfer rate was used to demonstrate that the chemical complexation reaction significantly affected the mass-transfer

Table 2. Accumulated Zirconium in Organic Phase for Changes in Interfacial Area, Phase Volume, and Mixer Diameter

			Mass Transferred ($g \times 10^5$) Zr Mixer Diameter			
Area	Phase Vol.	h	d_{a1},d_{o1}	d_{a2},d_{o1}	d_{a1},d_{o2}	d_{a2},d_{o2}
S_1	V_{a1},V_{o1}	2	46			271
		4	88	X	X	403
		6	140			570
	V_{a2},V_{o1}	2		130	147	
		4	X	243	269	X
		6		321	356	
	V_{a1},V_{o2}	2		75	139	
		4	X	115	252	X
		6		166	337	
	V_{a2},V_{o2}	2	66			250
		4	115	X	X	454
		6	166			607
S_2	V_{a1},V_{o1}	2		177	389	
		4	X	306	531	X
		6		423	619	
	V_{a2},V_{o1}	2	137			280
		4	268	X	X	445
		6	281			612
	V_{a1},V_{o2}	2	76			319
		4	145	X	X	520
		6	206			632
	V_{a2},V_{o2}	2		194	240	
		4	X	373	421	X
		6		410	532	

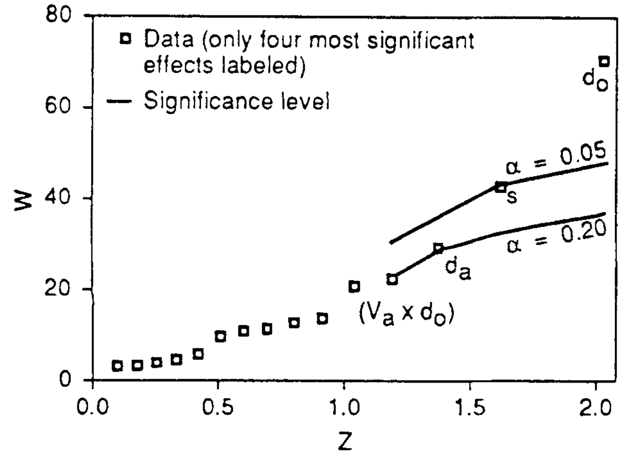

Figure 6. Zirconium half normal plot.

rate. Table 3 shows the range of test conditions used to investigate the reactant concentration effect.

Equations 10 through 12 define the zirconium mass transfer if it were assumed that the chemical reaction is instantaneous.

Chemical complexation reaction:

$$-V_a\frac{d[\mathrm{Zr}^{4+}]_a}{dt}=K^f[\mathrm{Zr}^{4+}]_a[\mathrm{NO_3^-}]_a^4\left(\frac{[\mathrm{TBP}]_o}{m_{\mathrm{TBP}}}\right)^2$$
$$-K^r[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_a,\ =0\ \text{(instantaneous reaction)}. \quad (10)$$

Diffusion:

$$\frac{-V_o}{S}\frac{d[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o}{dt}$$
$$=k_o\{[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o^*-[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o\}. \quad (11)$$

Material balance:

$$V_a[\mathrm{Zr}^{4+}(t=0)]_a=V_a[\mathrm{Zr}^{4+}]_a$$
$$+V_a[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_a+V_o[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o. \quad (12)$$

The solution to Eqs. 10 through 12 is shown as Eq. 13, in which the only unknown constant is the organic-phase individual mass-transfer coefficient for $\mathrm{Zr(NO_3)_4\cdot 2TBP}$. The interfacial concentration $[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o^*$ is eliminated by use of m_{Zr}':

$$k_o=(1/t)\ln[A'/(A'-B'C_{\mathrm{Zr},o})], \quad (13)$$

where

$$C_{\mathrm{Zr},o}=[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o$$
$$A'=\frac{S(m_{\mathrm{Zr}}')}{V_o}\{[\mathrm{Zr}^{4+}(t=0)]_aC_{NT}/(C_{NT}+1/K_{\mathrm{eq}})\}$$
$$B'=\frac{S}{V_o}\{[m_{\mathrm{Zr}}'(V_o/V_a)C_{NT}]/(C_{NT}+1/K_{\mathrm{eq}})+1\}$$
$$C_{NT}=[\mathrm{NO_3^-}(t=0)]_a^4\{[\mathrm{TBP}(t=0)]_o/(m_{\mathrm{TBP}})\}^2$$

and initial conditions are:

$$[\mathrm{Zr}^{4+}(t=0)]_a=\mathrm{Zr}^{4+}\ \text{introduced initially}$$
$$[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_a=0$$
$$[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o=0.$$

Table 3. Tests Demonstrating Concentration Effect

Reactant*	Time	Test 1	Test 2	Test 3	Test 4
		mol/L			
$[\mathrm{Zr}^{4+}]_a$	($t=0$)	1.4×10^{-6}	0.7×10^{-6}	1.4×10^{-6}	1.4×10^{-6}
$[\mathrm{NO_3^-}]_{a,\mathrm{eq}}$	($t=0$)	0.0029	0.0029	0.0015	0.0029
$[\mathrm{TBP}]_{o,\mathrm{eq}}$	($t=0$)	1.1×10^{-6}	1.1×10^{-6}	1.1×10^{-6}	0.6×10^{-6}
$[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o$		($\mathrm{g/L}\times10^5$)			
	2 h	399	133	70	136
	4 h	510	173	113	187
	6 h	629	240	133	216

* eq refers to aqueous-organic equilibrated concentrations before zirconium introduction.

Simplifications for two-hour data are:

$$[\mathrm{NO_3^-}(t)]_a=[\mathrm{NO_3^-}(t=0)]_a,$$
$$\text{since } [\mathrm{NO_3^-}(t=0)]_a \gg [\mathrm{Zr}^{4+}(t=0)]_a,$$

and

$$[\mathrm{TBP}(t)]_a=[\mathrm{TBP}(t=0)]_a,$$

since organic-phase mass-transfer resistance was predominant up to two hours.

Table 4 displays the k_o values regressed from Table 3 using Eq. 13, which assumes an instantaneous chemical complexation reaction. When reactant concentrations are reduced (except for $\mathrm{NO_3^-}$, test 3), the value of k_o decreases. Viscosity changes, due to reduction of the reactant concentrations, would either have a negligible effect on k_o or would actually increase k_o. The k_o calculated when reducing the $\mathrm{NO_3^-}$ concentration in test 3 was found to be highly sensitive to the fourth-power exponent in Eq. 10 and was consequently considered an uncertain data point. It was concluded from Table 4 that an additional resistance to mass transfer occurs when reducing reactant concentrations. This additional resistance to mass transfer is actually a result of the chemical reaction, implying a noninstantaneous complexation reaction. Therefore, during the initial two hours of each test, the mass-transfer rate of Zr^{4+} was predominantly controlled by the chemical complexation reaction in the aqueous phase and the mass-transfer resistance to the complexed species $\mathrm{Zr(NO_3)_4\cdot 2TBP}$ in the organic phase.

Components of the mass-transfer model describing the zirconium-Purex stirred-cell tests of this study (up to two hours) are based on: the chemical complexation reaction in the aqueous phase; insignificant diffusional resistance in the aqueous phase and hence, lack of position-related concentration gradients in

Table 4. Organic-Phase Individual Mass-Transfer Coefficient Assuming Instantaneous Complexation Reaction

	Test 1	Test 2	Test 3	Test 4
k_o (cm/s) $\times 10^4$	2.4	1.5	2.4	1.3

the aqueous phase; and the organic-phase diffusional resistance of the zirconium complex. These components of mass transfer can be modeled by Eqs. 10 through 12, where Eq. 10 does not equal zero (noninstantaneous complexation reaction).

Beyond two hours of each test, aqueous diffusion was significant, which required Eq. 10 to be nonlinear, and then required a numerical simultaneous solution to Eqs. 10 to 12. Consequently, only two-hour data were used to regress the complexation reaction rate constants. Two-hour data involved insignificant aqueous diffusion, which allowed Eq. 10 to be linear and permitted an exact simultaneous solution to Eqs. 10 to 12.

The simultaneous solution of Eqs. 10 through 12 was accomplished with Laplace Transforms to yield Eqs. 14 to 16.

$$[\mathrm{Zr}^{4+}]_a = b_2 + b_1 e^{-a_1 t} + b_o e^{-a_o t}. \tag{14}$$

$$[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]_a = \frac{1}{A_1}[A_2 b_2 + b_2(A_1 - a_1)e^{-a_1 t} + b_o(A_2 - a_o)e^{-a_o t}]. \tag{15}$$

$$[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]_o = \frac{V_a}{V_o}\left\{[Zr^{4+}(t=0)]_a - b_2\left(1+\frac{A_2}{A_1}\right) - b_1\left(1+\frac{A_2-a_1}{A_1}\right)e^{-a_1 t} - b_o\left(1+\frac{A_2-a_o}{A_1}\right)e^{-a_o t}\right\} \tag{16}$$

where

$a_o = \{-f_4 + [(f_4)^2 - 4(f_5)]^{1/2}\}/2$

$a_1 = \{-f_4 - [(f_4)^2 - 4(f_5)]^{1/2}\}/2$

$A_1 = K^r/V_a$

$A_2 = (K^f C_{NT})/V_a$

$A_3 = (S/V_o)k_o$

$A_4 = (S/V_o)k_o(m_{\mathrm{Zr}}')$

$A_5 = \{[\mathrm{Zr}^{4+}(t=0)]_a\}A_1$

$A_6 = A_1 + A_2$

$A_7 = (V_o/V_a)A_1$

$A_8 = \{[\mathrm{Zr}^{4+}(t=0)]_a\}A_4$

$A_9 = A_3 + (V_o/V_a)A_4$

$b_o = \dfrac{f_1(a_o)^2 + f_2(a_o) + f_3}{a_o(a_o - a_1)}$

$b_1 = \dfrac{f_1(-a_1)^2 + f_2(-a_1) + f_3}{-a_1(a_o - a_1)}$

$b_2 = f_3/(a_o a_1)$

$f_1 = -[\mathrm{Zr}^{4+}(t=0)]_a$

$f_2 = -(A_5 + A_9)$

$f_3 = A_7 A_8 - A_5 A_9$

$f_4 = -(A_6 + A_9)$

$f_5 = A_4 A_7 - A_6 A_9$

Equation 16 was used to regress the reaction rate constants because the zirconium cation and zirconium complex could not be easily distinguished in the aqueous phase. The regression was based on a single degree of freedom, that is, only one regression constant was unknown. The constants included in Eq. 16 were determined by the following procedures.

(1) Phase volumes V_a and V_o were measured directly.

(2) Interfacial area S was measured directly.

(3) Initial concentrations $[\mathrm{Zr}^{4+}(t=0)]_a$, $[\mathrm{NO_3^-}(t=0)]_a$, and $[\mathrm{TBP}(t=0)]_o$ were measured directly.

(4) The organic-phase complexed species $[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]_o$ mass-transfer coefficient was calculated by Eqs. 2 and 6. For the 3-cm-dia. paddle at 150 rpm and 25°C, k_o was calculated to be 0.000167 cm/s in 30 vol. % TBP and 70 vol. % dodecane. For the 6-cm paddle at similar conditions, k_o was calculated to be 0.000567 cm/s.

(5) The Zr^{4+} complexation equilibrium constant K_{eq} and $[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]$ distribution coefficient m_{Zr}' were determined from regression of equilibrium data using Eq. 9 as shown by Figure 5. The equilibrium constant was then used to eliminate either the forward or reverse Zr^{4+} complexation reaction rate constant, K^f or K^r.

Since the two reaction rate constants were related to the equilibrium constant by $K_{\mathrm{eq}} = K^f/K^r$, only one constant remained to be defined in Eq. 16, K^f or K^r. The regression analysis utilized a trial-and-error computer program to select the constant (K^f or K^r) based on the weighted least-square error between the measured and predicted $[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]_o$ value of Eq. 16 (see DeMuth, 1989, p. 206).

Data were selected for regression of reaction rate constants from Tables 2 and 3, such that one change of each parameter and reaction concentration was included. The two-hour data were exclusively used for regression, because aqueous mass transfer at four and six hours was more significant (see DeMuth, 1989, p. 96). The aqueous resistance at four and six hours was probably a result of TBP diffusion into the aqueous phase. Before zirconium introduction at the beginning of the test, the aqueous and organic phases were equilibrated. Judging from the solubility of TBP in the aqueous phase and the total amount of zirconium transferred to the organic phase at equilibrium, TBP was well in excess in the aqueous phase up to about two hours of mass transfer (see DeMuth, 1989, p. 184).

The value of the forward complexation reaction rate constant regressed from the data of Tables 2 and 3 was determined to be:

$$K^f = 6.5 \times 10^{21}\ [(\mathrm{mol/s})(\mathrm{mL/mol})^7].$$

The average error was 24% of the predicted $[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]_o$ value, with a variance of 1.1×10^{-14} $(\mathrm{mol/mL})^2$. The reverse rate constant was calculated from the forward rate constant and equilibrium constant to be:

$$K^r = 0.059\ (\mathrm{mL/s}).$$

Figure 7 shows the measured value of $[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]_o$ and predicted values of $[\mathrm{Zr}^{4+}]_a$, $[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]_a$ and $[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]_o$ as calculated from Eqs. 14 through 16 with the regressed distribution coefficient and rate constants. The approximate 95% confidence interval band is shown for data at only two hours. The data at four and six hours fall below the predicted curve as would be expected with additional aqueous-phase mass-transfer resistance. The approximate 95% confidence interval was estimated as two standard errors, in which one standard error equals the square root of the variance.

A standard error-propagation analysis was performed, which related the measured concentration variance to the predicted concentration variance. This was necessary because of the nonlinearity of the model (see DeMuth, 1989, p. 213).

Zirconium-Purex application to CSTR

Modern nuclear fuel reprocessing facility designers promote the use of mixer-settlers or centrifugal contactors for fission product decontamination. The short residence time of mixer-settlers and centrifugal contactors is useful when attempting to extract uranium and plutonium (with relatively fast complexation reaction kinetics) from fission products (with relatively slow complexation reaction kinetics). In addition, their short residence time reduces hydrolytic and radiolytic solvent (TBP and diluent) degradation.

A mixer-settler or centrifugal contactor interfacial-area/phase-volume ratio would be orders of magnitude greater than the same ratio for the stirred cell of this study (see DeMuth, 1989, p. 105). For mixer-settler or centrifugal contactor conditions, the mass-transfer rate of zirconium extraction via the Purex process is likely to be predominantly controlled by the complexation reaction. The large interfacial-area/phase-volume ratio would render diffusional resistance insignificant.

The complexation reaction for zirconium extraction as defined by Eq. 10 can be combined with the expression for a CSTR, Eq. 13 of Levenspiel (1972, p. 103), to yield Eq. 17.

$$t=\frac{[\mathrm{Zr}^{4+}(t=0)]_a-[\mathrm{Zr}^{4+}]_a}{-r}$$

or

$$t=\frac{[\mathrm{Zr}^{4+}(t=0)]_a-[\mathrm{Zr}^{4+}]_a}{K^f[\mathrm{Zr}^{4+}]_a C_{NT}-K^r[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_a}. \tag{17}$$

The degree of extraction can be defined in terms of initial zirconium concentration $[\mathrm{Zr}^{4+}(t=0)]_a$ and the zirconium transferred to the organic phase $[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o$, as shown in Eq. 18 by rearranging Eq. 17.

$$\frac{[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o}{[\mathrm{Zr}^{4+}(t=0)]_a}=\left\{\frac{(K^f C_{NT})t}{t\{K^f C_{NT}[1/(m_{Zr}')+V_o/V_a]+[K^r/(m_{\mathrm{Zr}}')]\}+[1/(m_{\mathrm{Zr}}')+V_o/V_a]}\right\}.$$

Equation 18 can be applied to most all of the Purex species, which would provide a modeling tool for optimization of decontamination in terms of contacting equipment residence time.

Conclusions

Literature comparison

The Zr^{4+} complexation equilibrium constant K_{eq} and complexation reaction rate constants K^f and K^r from this study can be compared with similar constants reported in the literature.

Benedict et al. (1981, p. 192) report a zirconium complexation equilibrium constant based on Eq. 19.

$$[\mathrm{Zr}^{4+}]_a+4[\mathrm{NO_3^-}]_a+2[\mathrm{TBP}]_o=[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o. \tag{19}$$

Equation 19 must be assumed to be interfacial, because aqueous

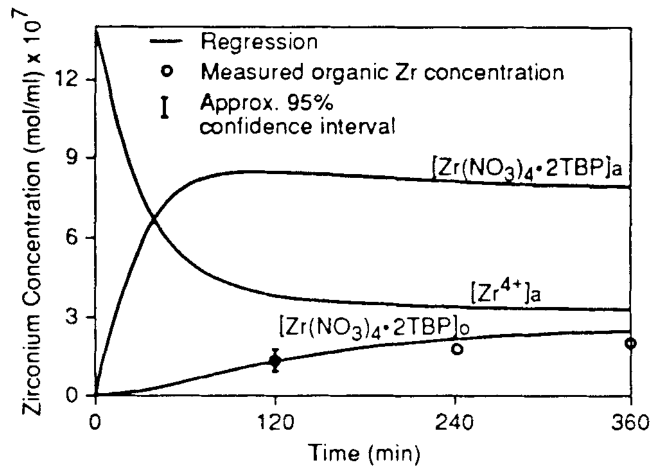

Figure 7. Zirconium mass transfer for S_1, V_{a1}, V_{01}, d_{a2} and d_{02}.

and organic reactants can coexist only at the interface. The equilibrium constant based on Eq. 19 is shown by Eq. 20.

$$K_{\mathrm{eq}}'=\frac{[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o}{[\mathrm{Zr}^{4+}]_a[\mathrm{NO_3^-}]_a^4[\mathrm{TBP}]_o^2}. \tag{20}$$

The equilibrium constant of Benedict differs from the equilibrium constant of this study by the $\mathrm{HNO_3}$ and TBP distribution coefficients, as shown by Eq. 21.

$$\frac{K_{\mathrm{eq}}}{K_{\mathrm{eq}}'}=\frac{(m_{\mathrm{TBP}})^2}{m_{\mathrm{Zr}}'}=\frac{(1{,}000)^2}{0.35}=2.9\times 10^6. \tag{21}$$

The ratio of the K_{eq} determined by this study and K_{eq}' reported by Benedict is:

$$\frac{K_{\mathrm{eq}}}{K_{\mathrm{eq}}'}=\frac{[2.7\times 10^{22}\ (\mathrm{mL/mol})^6](1\ \mathrm{L}/1{,}000\ \mathrm{mL})^6}{0.0032\ (\mathrm{L/mol})^6}=8.4\times 10^6.$$

The ratio of $K_{\mathrm{eq}}/K_{\mathrm{eq}}'$ determined from $\mathrm{HNO_3}$ and TBP distribution coefficients differs from the K_{eq} (of this study) and K_{eq}' (of Benedict) ratio by approximately a factor of three. This should be considered good agreement based on the complexity of controlling the zirconium species of interest, that is, $\mathrm{Zr(OH)}^x(\mathrm{NO_3})^{n-x}$ hydrolysis and polymerization.

The zirconium complexation rate constants K^f and K^r can be compared with similar constants determined by Mailen et al. (1980). Mailen performed mass-transfer tests with zirconium in the Purex system using a stirred cell similar to this study. Mailen's mass-transfer model is shown by Eq. 22.

$$\frac{-d[\mathrm{Zr}^{4+}]_a}{dt}=\frac{S}{V_a}(K^{f\prime})[\mathrm{Zr}^{4+}]_a-\frac{S}{V_o}(K^{r\prime})[\mathrm{Zr(NO_3)_4\cdot 2TBP}]_o. \tag{22}$$

The mass-transfer model of this study, Eq. 10, can be related to Mailen's as shown by Eq. 23.

$$S(K^{f'}) = K^{f}[NO_3^-]_a^4\{[TBP]_o/m_{TBP}\}^2. \tag{23}$$

By rearranging the equation, one can make a comparison of K^f (this study) and $K^{f'}$ (Mailen's) as follows:

$$K^f \text{ (this study)} = 6.5 \times 10^{21} \ [(\text{mol/s})(\text{mL/mol})^7],$$

$$\frac{S(K^{f'})}{[NO_3^-]_a^4\{[TBP]_o/m_{TBP}\}^2} = (4.2 - 5.4) \times 10^{21} \ [(\text{mol/s})(\text{mL/mol})^7].$$

Multiple values for Mailen's $K^{f'}$ exist because it depended on the interfacial area. Comparison of Mailen's forward rate constant with the forward rate constant of this study agrees within a factor of two. This should be considered good agreement.

Acknowledgment

Research was conducted at and sponsored by the Consolidated Fuel Reprocessing Program of Oak Ridge National Laboratory, under U.S. Government contract no. DE-AC05-840R21400.

Notation

$\bar{a}$ = activity in mixture
C = concentration
C_{NT} = $[NO_3^- (t=0)]_a^4\{[TBP(t=0)]_o/(m_{TBP})\}^2$
d = mixer diameter; $d_1 = 3$ cm, $d_2 = 6$ cm
D = diffusion coefficient
$\mathfrak{f}$ = fugacity of pure species
$\underline{\mathfrak{f}}^o$ = fugacity at standard state
$\mathfrak{f}$ = fugacity in a mixture
$\mathcal{H}$ = Henry's law constant
k = individual mass-transfer coefficient
K_{eq} = K^f/K^r, complexation reaction equilibrium constant
K = overall mass-transfer coefficient
K^f = forward complexation reaction rate constant
K^r = reverse complexation reaction rate constant
M = molar
m = C_o/C_a, equilibrium distribution coefficient
$\mathfrak{m}$ = molality
N_{Re} = $(\omega d^2/\nu)$, Reynolds number
N_{Sc} = (ν/D), Schmidt number
R = correlation coefficient
S = interfacial area; $S_1 = 62$ cm^2, $S_2 = 79$ cm^2
t = time
TBP = tributyl-phosphate
V = phase volume; V_1 = 350 mL, V_2 = 450 mL
W = half normal plot W-factor
x = mole fraction
$[y]$ = concentration of species y (mol/mL)
Z = half normal plot weighting factor

Greek letters

β = stoichiometric equivalent
γ = activity coefficient
ν = kinematic viscosity
ω = mixing speed (rpm)

Subscripts

a = aqueous phase
o = organic phase

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Manuscript received Mar. 21, 1991, and revision received Oct. 2, 1991.