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Modeling of Pu(IV) Extraction from Acidic Nitrate Media by Tri-*n*-butyl Phosphate

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A thermodynamic model of the distribution of Pu(IV) between aqueous solutions of nitric acid and lithium nitrate and 30 % (by volume) TBP in *n*-dodecane was developed. The mean activity coefficients of the hydrogen ion, nitrate ion, and water were calculated using Bromley's method of activity coefficients. The computation of the distribution ratios is based on a critical evaluation of the speciation of Pu(IV) under the solution conditions used. Five Pu(IV) species, Pu^{4+}, $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(NO_3)^{3+}$, and $Pu(NO_3)_2^{2+}$, were considered to be present in (0.1 to 4) $mol \cdot L^{-1}$ aqueous solutions of HNO_3. Because of the various extraction capabilities of the different oxidation states of Pu, disproportionation of Pu(IV) is the main factor controlling the distribution of Pu at low acidity. Two different Pu(IV) solvate adducts $Pu(NO_3)_4 \cdot TBP_2$ and $Pu(NO_3)_4 \cdot TBP_2 \cdot HNO_3$ were considered as extracted species over a wide range of experimental conditions, and their extractions constants were determined. The correlation between experimental and calculated data produced a reasonable fit. To determine the extraction constant of hydrolyzed Pu(IV) species for low acid concentrations, additional experimental data on the kinetics of disproportionation of tetravalent plutonium in two phase systems would be necessary.

Introduction

Over the past the two decades, various reprocessing schemes have been proposed for extraction of actinides from fission products and other elements present in spent nuclear fuel. Most current reprocessing schemes operate using a tri-*n*-butyl phosphate-based (TBP) extraction process: the PUREX process (plutonium and uranium recovery by extraction). Knowledge of stoichiometric and distribution relationships for tetravalent plutonium in solvent extraction systems related to the PUREX process, together with knowledge of Pu speciation over a wide range of experimental conditions, is important for the separation process design. Measured values of distribution ratios serve as a database for the development of computing codes for modeling and simulation of extraction processes.

Several modeling approaches of extraction processes developed in the U.S. were recently reported in the literature; for example, AMUSE (Argonne model for universal solvent extraction), SX Solver,[1] and SXLSQI.[2] The models differ mainly by the way that species activities in the aqueous and organic phase are evaluated, including the activities of water and the organic solvent. AMUSE is a process modeling tool, whereas SX Solver and SXLSQI are equilibrium modeling programs. The latter two applications differ in the way that the aqueous activities are calculated. SX Solver and AMUSE use the same methodology for calculation of aqueous-phase activities.

Modeling of distribution ratios for Pu(IV) from nitric acid by TBP is very important for the prediction of extraction behavior under various initial conditions without requiring additional experiments. To calculate the distribution ratio of Pu(IV), all metal species present in the aqueous and organic phases must be taken into account. To determine the speciation distribution of Pu(IV) in aqueous solutions containing nitric acid from low to moderate concentrations, at least the first two stability constants of hydroxo complexes and nitrate complexes of Pu(IV) must be applied. Determination of the stability constants for ternary hydroxonitrate complexes of Pu(IV) is complicated because of very complex chemistry of plutonium. Also, the previously reported values of stability constants for the $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(NO_3)^{3+}$, and $Pu(NO_3)_2^{2+}$ complexes must be applied with care.

In the present work, we report our attempt to develop a computational model of distribution ratios of Pu(IV) evaluating the speciation of Pu(IV) in the HNO_3/TBP extraction system and applying the mean aqueous activity coefficients of species and critically evaluated stability constants. Comparison of the calculated values with the experimental results and previously reported data[3,4] for the distribution ratios of Pu(IV) for a set of various concentrations of HNO_3 and $LiNO_3$ are discussed.

Experimental Section

Safety Notes. Pu-239 is an alpha-emitting radioactive isotope. Working with radioactive isotopes requires appropriate precautions and experimental procedures developed for operations with ionizing radiation.

Materials and Methods. Pu-239, obtained from Argonne National Laboratory in the chloride form, was dissolved in nitric acid and adjusted to the tetravalent oxidation state by the addition of acidified H_2O_2 and a few crystals of solid $NaNO_2$. Impurities of Am-241 were removed by anion exchange chromatography (Dowex 1X-4). Am was washed out with 7 $mol \cdot L^{-1}$ HNO_3, and Pu(IV) was eluted with 0.36 $mol \cdot L^{-1}$ HCl. The solution of Pu(IV) in HCl was evaporated to dryness and

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converted to nitrate form. The purity of the tetravalent oxidation state of Pu was found to be greater than 99.5 %, which was confirmed by absorption spectroscopy and extraction by thenoyl trifluoroacetone (TTA) in xylene from 1 $\text{mol}\cdot\text{L}^{-1}$ nitric acid.

Solvent Extraction. A solution of 30 % (by volume) TBP in *n*-dodecane was used as the solvent for all extraction experiments. Before its use, TBP was pre-equilibrated with an aqueous phase containing HNO_3 and $LiNO_3$ in the same concentration as that used in the extraction experiment. Distribution ratios for Pu(IV) (initially at $\sim 1\cdot 10^{-7}$ $\text{mol}\cdot\text{L}^{-1}$) were measured in batch experiments; samples were rigorously agitated in plastic extraction vials using a vortex mixer at a 1/1 organic/aqueous volume ratio for 4 min (if not stated otherwise) under ambient temperature conditions (22 ± 2) °C. After agitation, phases were separated after a short centrifugation, and aliquots from both organic and aqueous phases were taken to measure equilibrium concentrations of the metal using liquid scintillation counting with an Ultima Gold scintillation cocktail. For the second (back) extraction, the extraction procedure was repeated with the organic phase from the first extraction (forward) with an addition of a fresh portion of the aqueous phase containing no Pu. Distribution ratios of plutonium were calculated as the ratio of the total equilibrium analytical concentrations of Pu in the organic and aqueous phase.

Results and Discussion

Experimental distribution ratios for tetravalent Pu ($D_{\text{Pu(IV)}}$) for extraction with 30 % (by volume) TBP were measured over the range of (0.1 to 12) $\text{mol}\cdot\text{L}^{-1}$ HNO_3 and various concentrations of additional nitrate ($LiNO_3$). Relevant extraction data for Pu(IV) by 30 % (by volume) TBP collected by Petrich and Kolarik[3] and data determined by Karraker[4] are included for comparison.

Evaluation of the Pu(IV) extraction data confirms that they are greatly affected by the speciation of the metal in the aqueous phase; therefore, all aqueous plutonium species whose concentrations depend mostly on the concentration of the mixed aqueous electrolyte of HNO_3 and $LiNO_3$ must be considered. The only major discrepancies between experimental (4 min extraction time) and the literature data are in the range of lower nitric acid (< 1 $\text{mol}\cdot\text{L}^{-1}$), which is the most difficult region for acquiring reliable data because of hydrolysis and disproportionation reactions of tetravalent plutonium. Therefore, all distribution ratios for Pu(IV) for nitric acid concentration less than 1 $\text{mol}\cdot\text{L}^{-1}$ must be considered to be very uncertain.

Speciation of Pu(IV) in the Aqueous Phase. The highly charged cation Pu^{4+} hydrolyzes more readily than any other of the plutonium species and undergoes hydrolysis in aqueous solution, even under relatively high acidic conditions. The hydrolysis constant for the tetravalent actinides increases in the order of decreased ionic radius and increasing Lewis acidity from Th(IV) to Pu(IV):[5] Th(IV) < U(IV) < Np(IV) < Pu(IV). The hydrolysis reaction of Pu(IV) can be written as

$$Pu^{4+} + xH_2O \Leftrightarrow Pu(OH)_x^{4-x} + xH^+ \qquad (1)$$

The apparent constant of hydrolysis, K_H, is given by

$$K_{H,x} = \frac{[Pu(OH)_x^{4-x}]\cdot[H^+]^x}{[Pu^{4+}]} \qquad (2)$$

with the corresponding formation constants, β, of plutonium(IV) hydroxo-complex

$$\beta_x = \frac{[Pu(OH)_x^{4-x}]}{[Pu^{4+}]\cdot[OH^-]^x} \qquad (3)$$

Reliable thermodynamic data for Pu(IV) are difficult to obtain because of the complicated redox chemistry of plutonium; that is, Pu(III), Pu(IV), Pu(V), and Pu(VI) are known to coexist in aqueous solutions. The determination of thermodynamic data of Pu(IV) is further complicated by hydrolysis, even at low pH (pH 1), and the formation of polymeric/colloidal species. A number of studies on the hydrolysis constants for mononuclear species, $Pu(OH)_x^{4-x}$ ($x = 1$ to 4), have been performed over recent decades and are well summarized by Lemire et al.[6] and later updated by Guillaumont et al.[7] The methods frequently used for determination of the hydrolysis constant are vis−NIR spectroscopy, solvent extraction, and potentiometry. Because the solubility of Pu(IV) hydroxide is low, the ability to investigate its aqueous speciation by spectroscopic techniques is rather poor.[8] As the Pu^{4+} ion undergoes hydrolysis reactions, even at low pH, the solubility product evaluated from experimental solubility data directly depends on the hydrolysis constants applied to calculate the Pu^{4+} concentration.[9]

The Pu(IV) hydrolysis in weakly acidic solutions leads to polynucleation, which grows further to colloidal aggregation.[10] As demonstrated by Kim and Kanellakopulos,[11] colloidal Pu(IV) can be produced, even at pH 0 to 1 at Pu concentrations below 10^{-3} $\text{mol}\cdot\text{L}^{-1}$. Colloids may be considered to be long-lived metastable amorphous particles. They remain stable in solution, devoid of precipitation from oversaturated solutions, and lead to apparent Pu(IV) concentrations significantly exceeding the thermodynamic solubility. Investigation of plutonium chemistry by conventional absorption spectroscopy requires a concentration of (10^{-4} to 10^{-3}) $\text{mol}\cdot\text{L}^{-1}$, which considerably exceeds the solubility limit of the Pu(IV) hydrous oxides at pH 1 to 2.[5] When the concentration exceeds the solubility limit, the formation of Pu(IV) colloids, which remain in solution without precipitation, is the predominant reaction.[8] The formation of colloids at higher Pu concentrations and higher pH can lead to inaccurate interpretation of experimental results. Therefore, more satisfactory data on hydrolysis constants can be obtained by solvent extraction using trace concentrations of Pu. Metivier and Guillaumont[12] applied solvent extraction with Pu-238 to measure all four constants of plutonium hydrolysis: $K_{H1} = 0.355$; $K_{H2} = 0.178$; $K_{H3} = 5.01\cdot 10^{-4}$, and $K_{H4} = 5.01\cdot 10^{-7}$. As can be seen from Table 1, where several earlier literature data are summarized, their constants differ by an order of magnitude from the others reported; however, the solubility of amorphous $Pu(OH)_4$ in the range of pH 0 to 12 determined by Knopp et al.[9] agrees very well with the pH dependence predicted by the hydrolysis constants determined by Metivier and Guillaumont.[12]

To obtain a complete set of formation constants for mononuclear species $An(OH)_n^{4-n}$, Neck and Kim[8] estimated the

Table 1. Review of Pu(IV) Hydrolysis Constants

ionic strength $\text{mol}\cdot\text{L}^{-1}$	medium	$\log K_{H1}$	$\log K_{H2}$	ref
1	$HClO_4/LiClO_4$	−0.45	−1.2	12
2	$HClO_4/LiClO_4$	−1.26		13
2	$HClO_4/NaClO_4$	−1.73	−1.94	14
0.5	HCl/NaCl	−1.65		15
0.5	$HClO_4/NaClO_4$	−1.60		15
1	$HClO_4/NaClO_4$	−1.51		16
0.5	$HClO_4/NaClO_4$	−1.57		17
0.1	$HClO_4/NaClO_4$	−1.2		17
0.19	$HClO_4$	−1.96		18
0.06	$HClO_4$	−1.48		18

unknown constants by applying two different methods based on: (i) an empirical intercorrelation between hydrolysis constants of actinide ions at different oxidation states and (ii) a semiempirical approach in which the decrease in stepwise complexation constants for a given metal−ligand system is related to the increasing electrostatic repulsion between the ligands. For Pu(IV), the estimated values[8] were close to experimental values determined by Metivier and Guillaumont,[12] which are considered to be the most reliable data on hydrolysis of tetravalent plutonium by these and other authors now.[5,7,9] Therefore, the speciation and extraction model of Pu(IV) in the mixed electrolyte $HNO_3/LiNO_3$ presented in this article employs the first two hydrolysis constants determined by Metivier and Guillaumont.[12]

Increasing the nitric acid concentration, addition of nonextractable nitrate salts to the aqueous phase, or both suppresses hydrolysis of Pu(IV) and favors formation of nitrate complexes. Determination of formation constants for weak complexes, such as Pu nitrate complexes, is limited because it is difficult to maintain constant ionic strength (I) because of the necessity to use high concentrations of the ligand.[19] It is also important to note that at $I > 0.1\ \mathrm{mol \cdot L^{-1}}$, activity coefficients depend not only on the ionic strength but also on the composition of the electrolyte medium,[19] so the earlier assumption that the equilibrium constant at the same ionic strength but in different background electrolytes is the same is not valid.

A number of speciation studies reporting the application of various modern methods (vis−NIR, NMR, EXAFS, and computer modeling) to investigate the complexation between tetravalent plutonium and nitrate in aqueous solutions were recently published.[19−23] Only four major species of tetravalent plutonium, the mono-, di-, tetra-, and hexanitrate complexes ($Pu(NO_3)^{3+}$, $Pu(NO_3)_2{}^{2+}$, $Pu(NO_3)_4$, $Pu(NO_3)_6{}^{2-}$) were identified as the major species present over a wide range of concentration of nitric acid.[20] However, only the presence of $Pu(NO_3)_6{}^{2-}$ at nitric acid concentrations above $10\ \mathrm{mol \cdot L^{-1}}$ may be considered to be well established. Numerous studies provided evidence for the existence of Pu(IV)−nitrate complexes with coordination numbers lower than six, particularly plutonium mono- and dinitrate species. The stability constants for the first two Pu(IV)−nitrate complexes determined by simultaneous analysis of spectra at multiple wavelengths in the ionic strength range of $I = (0.3\ \text{to}\ 19)\ \mathrm{mol \cdot kg^{-1}}$ are discussed in the paper of Berg et al.[22] In that work, each formation constant was corrected for the incomplete dissociation of nitric acid using the specific ion interaction theory (SIT).[24] According to literature data, no good values for the higher Pu−nitrate complexes exist, and it is assumed that in the considered concentration range of (0.1 to 4) $\mathrm{mol \cdot L^{-1}}$ $NO_3{}^-$, only mono- and dinitrate species of Pu(IV) are present in aqueous solution

$$\mathrm{Pu^{4+} + NO_3^- \Leftrightarrow Pu(NO_3)^{3+}} \tag{4}$$

$$\mathrm{Pu^{4+} + 2NO_3^- \Leftrightarrow Pu(NO_3)_2^{2+}} \tag{5}$$

As a result of all of the issues identified for interpretation of the hydrolysis constants of Pu(IV) and the formation constants of Pu(IV) nitrates, we attempted to estimate the speciation of Pu(IV) in aqueous solutions by selecting the critically evaluated and best available values of the constants employed in the calculations. The stability constants $\log \beta^0{}_1 = 2.12$ and $\log \beta^0{}_2 = 3.66$ for the $Pu(NO_3)^{3+}$ and $Pu(NO_3)_2{}^{2+}$ complexes reported by Berg et al.,[22] together with thermodynamic hydrolysis constants $\log K^0{}_{\mathrm{H1}} = 0.6$ and $\log K^0{}_{\mathrm{H2}} = 0.63$ obtained by Metivier and Guillaumont,[12] were selected for our modeling work. Both hydrolysis and complexation constants were adjusted for changing ionic strength by the SIT[24] approach.

Extraction of Hydrolyzed Pu(IV) Species. Distribution ratios for Pu(IV) from low concentrations of nitric acid $< 1\ \mathrm{mol \cdot L^{-1}}$ are difficult to evaluate because of hydrolysis and disproportionation of Pu(IV). As can be seen later in Table 2, a prolonged extraction time leads to a drop in the distribution ratio because of a decrease in the Pu(IV) concentration by the formation of nonextractable Pu(III) and partially extractable Pu(VI) in the aqueous phase. In the earlier literature,[25,26] it was proposed that hydrolyzed Pu species should also be considered to be extracted species; however, their presence in the TBP organic phase was just recently confirmed spectrophotometrically.[27] Comparison of the vis−NIR absorption spectra of Pu in the TBP-extraction phase contacted with $0.1\ \mathrm{mol \cdot L^{-1}}$ HNO_3 and $2\ \mathrm{mol \cdot L^{-1}}$ HNO_3 reveals that the Pu(IV) species extracted from low nitric acid concentration were Pu(IV)-hydrolyzed species.[27] As reported, the disproportionation of Pu(IV) can be partially stabilized by the formation of the extractable solvate complex of Pu(IV) with TBP. However, to determine their extraction constant and fit the experimental and calculated values of the plutonium distribution ratio for low acid concentrations, additional experimental data on the kinetics of disproportionation are necessary.

Extraction of Nitric Acid by Tri-n-butyl. A very important factor in the modeling of the extraction of metals is the calculation of the free extractant concentration available for the metal complexation. TBP extracts a significant amount of HNO_3; hence, speciation of HNO_3 in the organic phase was extensively studied, and several models were proposed by various authors.[28,29] Equilibrium of HNO_3 between aqueous and organic TBP-*n*-dodecane phases was successfully modeled by Chaiko and Vandegrift.[28] Extraction of nitric acid by TBP can be expressed by the following reaction equilibria (eqs 6, 7, and 8)

$$\mathrm{H^+ + NO_3^- + \overline{TBP} \overset{\mathit{KT}_1}{\Leftrightarrow} \overline{TBP{\cdot}HNO_3}} \tag{6}$$

$$\mathrm{H^+ + NO_3^- + 2\overline{TBP} \overset{\mathit{KT}_2}{\Leftrightarrow} \overline{TBP_2{\cdot}HNO_3}} \tag{7}$$

$$\mathrm{H^+ + NO_3^- + \overline{TBP{\cdot}HNO_3} \overset{\mathit{KT}_3}{\Leftrightarrow} \overline{TBP{\cdot}2HNO_3}} \tag{8}$$

where the overbars represent species in the organic phase. Depending on the total nitrate and hydrogen ion concentrations, three complexes between TBP and HNO_3 can be formed (eqs 6, 7, and 8) with extraction equilibrium constants determined:[28] ($KT_1 = 0.185$; $KT_2 = 0.444\ \mathrm{L \cdot mol^{-1}}$, and $KT_3 = 1 \cdot 10^{-4}$), respectively. At various concentrations of HNO_3 and $NO_3{}^-$ in the aqueous phase, different species in the organic phase are formed. Formation of the $TBP \cdot 2HNO_3$ complex in a considerable amount is relevant to only a nitric acid concentration above $6\ \mathrm{mol \cdot L^{-1}}$. TBP_f, the fraction of TBP noncomplexed with HNO_3 and available for metal extraction, will be much lower in the system with a high nitrate concentration. The mass balance of TBP can be defined as follows

$$\begin{aligned}\overline{[\mathrm{TBP}]}_\mathrm{f} &= \overline{[\mathrm{TBP}]}_\mathrm{T} - \overline{[\mathrm{TBP{\cdot}HNO_3}]} - 2\overline{[\mathrm{TBP_2{\cdot}HNO_3}]} - \\ &\quad \overline{[\mathrm{TBP{\cdot}2HNO_3}]} = \overline{[\mathrm{TBP}]}_\mathrm{T} - KT_1{\cdot}\overline{[\mathrm{TBP}]}_\mathrm{T}{\cdot}\{\mathrm{HNO_3}\} - \\ &\quad KT_2{\cdot}\overline{[\mathrm{TBP}]}_\mathrm{T}^2{\cdot}\{\mathrm{HNO_3}\} - KT_3{\cdot}\overline{[\mathrm{TBP}]}_\mathrm{T}{\cdot}\{\mathrm{HNO_3}\}^2\end{aligned} \tag{9}$$

where $[\mathrm{TB\bar{P}}]_\mathrm{T}$ denotes the total concentration of TBP in the organic phase, $[\mathrm{TB\bar{P}}]_\mathrm{f}$ is the equilibrium concentration of TBP noncomplexed with HNO_3, and $\{HNO_3\}$ is the aqueous activity of nitric acid.

Modeling the Distribution Ratio of Pu(IV). Speciation diagrams for Pu(IV) species in nitric acid solutions generated

Table 2. Distribution Ratios of Pu(IV) with 30 % (by Volume) TBP

HNO_3 mol·L^{-1}	$LiNO_3$ mol·L^{-1}	total NO_3^- mol·L^{-1}	$D_{Pu(IV)}$ ref 3; 4	$D_{Pu(IV)}$ forward (4 min)	$D_{Pu(IV)}$ backward (4 min)	$D_{Pu(IV)}$ average	$D_{Pu(IV)}$ calculated
0.1		0.1		0.26	0.17	0.21 ± 0.06	0.0074
0.1			0.023	0.03[a]			
0.2		0.2		0.80	0.27	0.53 ± 0.37	0.069
0.2		0.2	0.070	0.08[a]			
0.4		0.4		1.72	0.96	1.34 ± 0.53	0.40
0.4		0.4		0.40[a]			
0.5		0.5	0.64; 0.85				0.61
0.6		0.6		2.49	1.83	2.16 ± 0.46	0.92
0.6		0.6	1.4	1.15[a]			
0.7		0.7	1.5				1.23
0.8		0.8		3.08	3.87	3.48 ± 0.55	1.56
0.8		0.8		1.67[a]			
0.93		0.93	3.0				1.96
1.0		1.0	3.0; 2.7	2.12[a]		2.32 ± 0.28	2.4
1.0		1.0		2.52[a]			
2.0		2.0	7.15; 8.06	8.06	9.46	8.8 ± 1.0	7.1
3.0		3.0	16.0; 16.0	16.4	15.3	15.9 ± 0.8	15.2
4.0		4.0	23.6; 25.0	23.2	25.2	24.2 ± 1.5	27.4
5.0		5.0	30.0	38.9	36.4	37.6 ± 1.8	
6.0		6.0	35.0	49.4	39.3	44.3 ± 7.2	
7.0		7.0	23.5	48.7	44.9	46.8 ± 2.7	
8.0		8.0		48.2	44.5	46.3 ± 2.6	
9.0		9.0		31.0	31.8	31.4 ± 0.6	
10.0		10.0		30.9	31.2	31.0 ± 0.3	
11.0		11.0		15.57	15.79	15.7 ± 0.16	
12.0		12.0		11.75	12.50	12.1 ± 0.53	
0.1	1.0	1.1		2.82	0.48	1.65 ± 1.4	4.01
0.2	1.0	1.2		4.76	1.27	3.01 ± 2.1	4.9
0.4	1.0	1.4		7.75	3.13	5.44 ± 2.7	6.7
0.6	1.0	1.6		9.38	4.9	7.14 ± 2.7	8.2
0.8	1.0	1.8		11.6	6.8	9.20 ± 3.0	8.4
1.0	1.0	2.0		13.3	10.1	11.7 ± 2.5	10.4
2.0	1.0	3.0		27.0	21.8	24.37 ± 3.7	19.5
3.0	1.0	4.0		39.2	30.8	35.0 ± 6.0	34.3
4.0	1.0	5.0		51.9	36.9	44.4 ± 10.6	
5.0	1.0	6.0		65.1	56.0	60.6 ± 6.4	
6.0	1.0	7.0		70.3	56.9	63.6 ± 9.4	
7.0	1.0	8.0		57.9	59.6	58.8 ± 1.2	
8.0	1.0	9.0		42.0	44.0	43.0 ± 1.4	
9.0	1.0	10.0		28.3	30.5	29.4 ± 1.5	
10.0	1.0	11.0		19.5	19.1	19.3 ± 0.25	
11.0	1.0	12.0		13.5	14.1	13.8 ± 0.44	
12.0	1.0	13.0		10.4	10.6	10.5 ± 0.17	
0.5	0.48	0.98		6.3	3.1	4.7 ± 1.9	2.8
0.5	1.45	1.95		13.5	6.6	10.1 ± 4.1	13.8
0.5	2.43	2.93		25.73	14.1	19.9 ± 7.2	36.9
0.5	3.41	3.91		108.7	80.8	94.7 ± 18.4	94.7
0.5	4.39	4.89		762.4	380.0	571 ± 255	
1.0	0.98	1.98		12.10	10.55	11.3 ± 1.1	10.2
1.0	1.95	2.95		22.50	20.45	21.5 ± 1.5	26.0
1.0	2.92	3.92		60.00	47.86	53.9 ± 8.6	66.2
1.0	3.89	4.89		77.47	95.77	86.6 ± 12.9	
1.0	4.87	5.87		61.03	59.74	60.4 ± 0.92	
2.0	0.96	2.96		19.85	17.19	18.5 ± 1.9	17.7
2.0	1.93	3.93		47.21	41.71	44.5 ± 3.9	44.6
2.0	2.91	4.91		109.84	97.62	103.7 ± 8.6	
2.0	3.89	5.89		191.74	183.22	187.5 ± 6.0	

[a] Data acquired after 10 min of contact time.

using the HySS[30] modeling program are displayed in Figure 1. Calculated results suggest that at 0.1 mol·L^{-1} HNO_3, more than 90 % of Pu (Figure 1a), and in the presence of 1 mol·L^{-1} lithium nitrate, about 55 % of Pu (Figure 1b) is present as hydrolyzed plutonium. Even at 0.6 mol·L^{-1} HNO_3, more than 10 % of total Pu(IV) is still hydrolyzed. However, the increase in nitrate and acid concentration lead to the formation of Pu(IV) mono- and dinitrate species that predominate at ≥ 0.4 mol·L^{-1} HNO_3. According to this speciation model based on the literature data, to determine the distribution by TBP of all Pu(IV) species present in aqueous solutions over a wide range of nitric acid and lithium nitrate concentrations, five Pu(IV) species must be considered to be present: Pu^{4+}, $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(NO_3)^{3+}$, and $Pu(NO_3)_2^{2+}$. The formation constants for ternary Pu−hydroxonitrate complexes and higher Pu−nitrate species ($Pu(NO_3)_4$ and $Pu(NO_3)_6^{2-}$) remain to be unknown; hence, only the first two nitrate complexes were included in this model, and the calculated values were compared with the values of the distribution ratios measured for the range of (0.1 to 4) mol·L^{-1} HNO_3 and total nitrate ≤ 4 mol·L^{-1}.

We performed the calculation of the distribution ratio of Pu(IV) assuming the extraction of the $Pu(NO_3)_4$ species coordinated with two molecules of TBP[31] to be an anhydrous solvate adduct

$$Pu^{4+}(H_2O)_n + 4NO_3^- + \overline{2TBP} \overset{K_1}{\Leftrightarrow} \overline{[Pu(NO_3)_4 \cdot TBP_2]} + nH_2O \tag{10}$$

where n represents the hydration number of the cation, which refers to the number of waters of hydration lost during complexation with TBP. For simplicity, we assumed that a single hydration number is satisfactory to describe the extraction behavior of tetravalent plutonium over the whole range of conditions sufficiently. According to Allen et al.,[21] the hydration number for $Pu(NO_3)_2^{2+}$ (predominant species in the range of (0.2 to 4) mol·L^{-1} HNO_3, Figure 1) determined by EXAFS was 7.

Predicting distribution ratios of Pu(IV) by TBP from the proton/metal−nitrate electrolyte medium is strongly dependent on the calculation of activities of all species present in the extraction system together with providing reasonable values for their complexation constants. The extraction constant for the Pu−tetranitrate species can be expressed as follows

$$K_1 = \frac{\overline{[Pu(NO_3)_4 \cdot TBP_2]} \cdot [H_2O]^n}{[Pu^{4+}(H_2O)_n] \cdot [NO_3^-]^4 \cdot \overline{[TBP]}^2} \frac{\overline{\gamma_{Pu(NO_3)_4 \cdot TBP_2}} \cdot (\gamma_{H_2O})^n}{\gamma_{Pu^{4+}} \cdot (\gamma_{NO_3^-})^4 \cdot \overline{(\gamma_{TBP})}^2} \tag{11}$$

where $\gamma(Pu^{4+})$ and $\gamma(NO_3^-)$ are the activity coefficients of the aqueous species and $\gamma(Pu(NO_3)_4 \cdot TBP_2)$ and $\gamma(TBP)$ are the activity coefficients of the species in the organic phase; it was assumed that the activity coefficients of neutral species in the organic phase were equal to one. Because of a low solubility of TBP in aqueous solution, the activities of aqueous species are not affected. Because the concentration of Pu(IV) (~1·10^{-7} mol·L^{-1}) is negligible compared with the concentration of TBP (1.1 mol·L^{-1}), the calculation of free TBP was based on the distribution ratio of nitric acid[28] using eq 9. The mean activity coefficients of H^+, NO_3^-, and H_2O were calculated by the method of Bromley.[32]

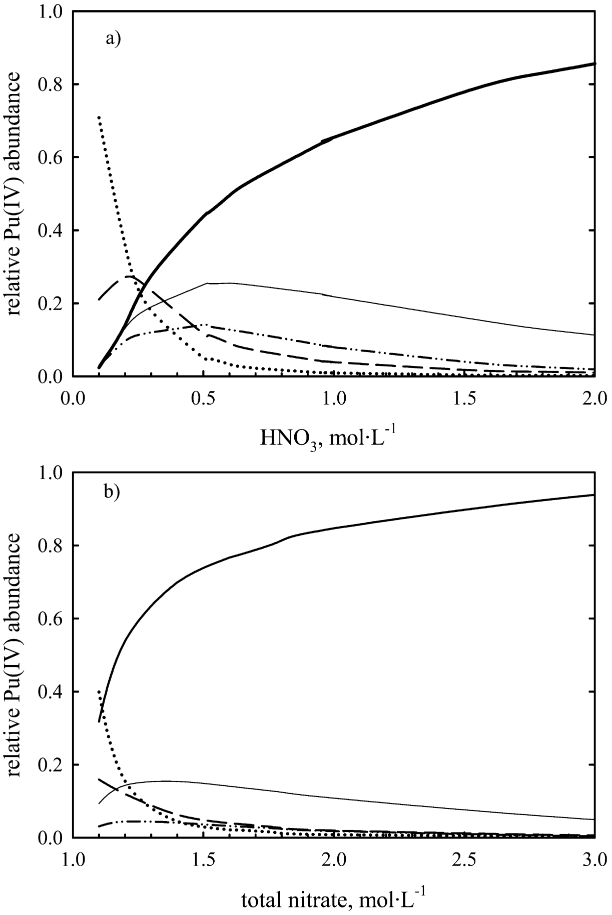

Figure 1. Speciation distribution diagram of Pu(IV) in aqueous solution containing (a) (0.1 to 2) mol·L^{-1} HNO_3 and (b) 1 mol·L^{-1} $LiNO_3$ and various HNO_3 concentration: −··−, Pu^{4+}; −−−, $Pu(OH)^{3+}$; ······, $Pu(OH)_2^{2+}$; −, $Pu(NO_3)^{3+}$; bold line, $Pu(NO_3)_2^{2+}$.

There are large discrepancies between values of the activity coefficients reported for plutonium and those of other actinide metals. Berg et al.[22] reported the values of interaction parameters for $Pu(NO_3)^{3+}$ and $Pu(NO_3)_2^{2+}$ complexes but not for Pu^{4+}. Finally, Neck et al.[33] determined the interaction parameter $\Delta\varepsilon(Pu^{4+}, NO_3^-) = 0.31$ by using the approach of chemical analogs and the similar behavior of tetravalent Th and Pu. The reported value,[33] $\Delta\varepsilon(Th^{4+}, NO_3^-) = 0.31 \pm 0.12$, gives a better linear correlation between $\varepsilon(M^{Z+}, NO_3^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$ or $\varepsilon(M^{Z+}, Cl^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$ than other values[18] reported earlier. Therefore, in this work, the activity coefficients of Pu^{4+} in the nitrate system were calculated by the SIT approach using the interaction parameter $\Delta\varepsilon(Pu^{4+}, NO_3^-) = 0.31$, adopting the value recently determined for Th^{4+} in nitrate media by Neck et al.[33]

By simply assuming that one hydroxo group replaces one molecule of water and each nitrate group replace two molecules of water in the hydration shell associated with the plutonium cation, the concentration of total aqueous $[Pu(IV)]_T$ can be described as

$$[Pu(IV)]_T = [Pu^{4+}(H_2O)_n] \cdot \left(1 + K_{H1}\frac{1}{\{H^+\} \cdot \{H_2O\}} + K_{H2}\frac{1}{(\{H^+\} \cdot \{H_2O\})^2} + \beta_1\frac{\{NO_3^-\}}{\{H_2O\}^2} + \beta_2\frac{\{NO_3^-\}^2}{\{H_2O\}^4}\right) \tag{12}$$

where K_{H1}, K_{H2}, β_1, and β_2 are the first two constants of hydrolysis and nitrate complexation, respectively, and terms in {} are activities of the species. Therefore, when the only extractable species is plutonium tetranitrate coordinated with two molecules of TBP, the distribution ratio for Pu(IV) can be expressed by a combination of eqs 11 and 12 as follows

$$D_{Pu(IV)} = \frac{\overline{[Pu(IV)]_T}}{[Pu(IV)]_T} = \frac{\gamma_{Pu^{4+}} \cdot \{TBP\}_f^2 \cdot K_1 \cdot \{NO_3^-\}^4}{\left(1 + K_{H1}\frac{1}{\{H^+\} \cdot \{H_2O\}} + K_{H2}\frac{1}{(\{H^+\} \cdot \{H_2O\})^2} + \beta_1\frac{\{NO_3^-\}}{\{H_2O\}^2} + \beta_2\frac{\{NO_3^-\}^2}{\{H_2O\}^4}\right) \cdot \{H_2O\}^n} \tag{13}$$

The comparison of the values of the distribution ratio of Pu(IV) calculated by eq 13 ($K_1 = 1.77 \cdot 10^5$) with the experimental data and literature data,[3,4] as displayed in Figure 2, does not provide a satisfactory fit ($R^2 = 0.884$) for concentrations higher than 1 mol·L^{-1} HNO_3, and suggests a need for reevaluation of the species and constants included in the model. An alternative view is not only that Pu−nitrate can be solvated by two molecules of free TBP but also that the $TBP_2 \cdot HNO_3$ adduct is capable of plutonium extraction. To the best of our knowledge, the formation of the $Pu(NO_3)_4 \cdot TBP_2 \cdot HNO_3$ species has not been confirmed experimentally; however, the hypothesis

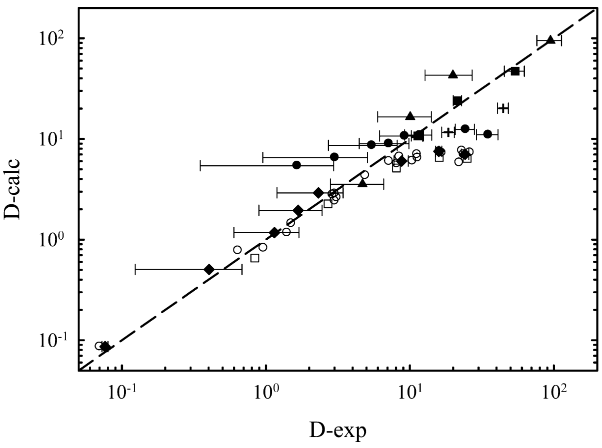

Figure 2. Plot of experimental versus calculated data for Pu(IV) distribution ratio determined using eq 13 and a value of $K_1 = 1.77 \cdot 10^5$. The line represents theoretical correlation between experimental and calculated data: ◆, (0.2 to 4) mol·L^{-1} HNO$_3$; ▲, 0.5 mol·L^{-1} HNO$_3$, various LiNO$_3$; ■, 1 mol·L^{-1} HNO$_3$, various LiNO$_3$; +, 2 mol·L^{-1} HNO$_3$, various LiNO$_3$; ●, 1 mol·L^{-1} LiNO$_3$, various HNO$_3$; ○, (0.2 to 4.2) mol·L^{-1} HNO$_3$, ref 3; □, (0.5 to 4) mol·L^{-1} HNO$_3$, ref 4.

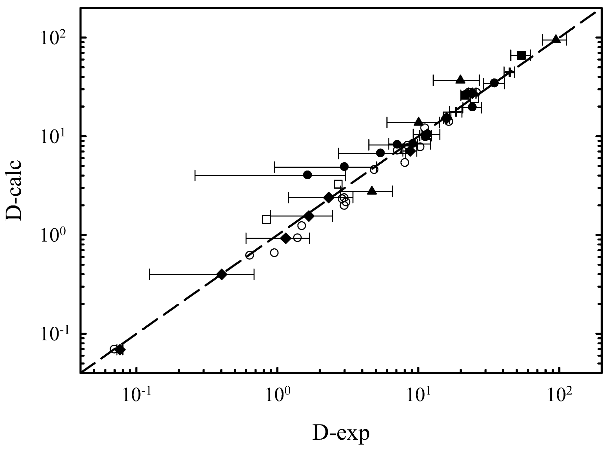

Figure 3. Plot of experimental versus calculated data for Pu(IV) distribution ratio determined using eq 15 and values of $K_1 = 1.06 \cdot 10^5$ and $K_2 = 2.12 \cdot 10^4$. The line represents theoretical correlation between experimental and calculated data: ◆, (0.2 to 4) mol·L^{-1} HNO$_3$; ▲, 0.5 mol·L^{-1} HNO$_3$, various LiNO$_3$; ■, 1 mol·L^{-1} HNO$_3$, various LiNO$_3$; +, 2 mol·L^{-1} HNO$_3$, various LiNO$_3$; ●, 1 mol·L^{-1} LiNO$_3$, various HNO$_3$; ○, (0.2 to 4.2) mol·L^{-1} HNO$_3$, ref 3; □, (0.5 to 4) mol·L^{-1} HNO$_3$, ref 4.

that either $TBP_2 \cdot HNO_3$ alone or two species TBP and $TBP \cdot HNO_3$ together are capable of coordinating plutonium tetranitrate is widely accepted. A similar mechanism was also proposed for other neutral extractants, for example, for extraction of uranium from nitric acid by amides.[34] Accepting this approach, the formation of two organic plutonium species containing four and five nitrate molecules solvated with TBP is considered in the present model (eqs 10 and 14)

$$\mathrm{Pu^{4+}(H_2O)}_n + 4\mathrm{NO_3^-} + \overline{\mathrm{TBP}} + \overline{\mathrm{TBP{\cdot}HNO_3}} \overset{K_2}{\Leftrightarrow} \overline{\mathrm{Pu(NO_3)_4{\cdot}TBP_2{\cdot}HNO_3}} + n\mathrm{H_2O} \qquad (14)$$

Adding the equilibrium constant K_2 representing the extraction of Pu−tetranitrate associated with $TBP_2 \cdot HNO_3$, distribution ratios can be calculated by eq 15, where the index n over the activity of water represents the number of hydration molecules released after complexation of Pu with TBP. The best fit was obtained for $n = 7$, and this is in excellent agreement with the hydration number reported by Allen[21]

$$D_{\mathrm{Pu(IV)}} = N \cdot \gamma_{\mathrm{Pu^{4+}}} \cdot (K_1 \cdot \{\mathrm{NO_3^-}\}^4 + K_2 \cdot \{\mathrm{NO_3^-}\}^5 \cdot \{\mathrm{H^+}\}) \qquad (15)$$

where $N =$

$$\frac{\{\mathrm{TBP}\}_f^2}{\left(1 + K_{H1} \cdot \dfrac{1}{\{\mathrm{H^+}\} \cdot \{\mathrm{H_2O}\}} + K_{H2} \cdot \dfrac{1}{(\{\mathrm{H^+}\} \cdot \{\mathrm{H_2O}\})^2} + \beta_1 \cdot \dfrac{\{\mathrm{NO_3^-}\}}{\{\mathrm{H_2O}\}^2} + \beta_2 \cdot \dfrac{\{\mathrm{NO_3^-}\}^2}{\{\mathrm{H_2O}\}^4}\right) \cdot \{\mathrm{H_2O}\}^n} \qquad (16)$$

A correlation plot of experimental data and values of $D_{\mathrm{Pu(IV)}}$ calculated using eq 15 is displayed in Figure 3. Because the extraction constants $K_1 = 1.06 \cdot 10^5$ and $K_2 = 2.12 \cdot 10^4$ are expressed in activities, they are dimensionless thermodynamic equilibrium constants.

Examining the calculated values of extraction constants, two different sets of hydrolysis constants from ref 12 and 14, which differ by one order of magnitude, were applied; however, both sets of data provided very similar results, which differed by less than 5 %. Including the K_2 extraction constant for the $Pu(NO_3)_4 \cdot TBP_2 \cdot HNO_3$ species and optimization of the K_1 and K_2 values using the MS Excel Solver plug-in provided a reasonable fit between calculated and experimental data ($R^2 = 0.971$). The Solver was set to find optimal values of extraction constants with minimum differences between the calculated and experimentally observed distribution ratios. Introducing the second extraction constant, K_2, produced very good results, even for data with low nitric acid concentrations (acquired after 10 min of contact time) and in the presence of additional $LiNO_3$. The better fit for the data at low acid concentration is due to the lower value of the K_1 extraction constant.

Table 2 summarizes a comparison of the experimental, calculated (eq 15), and literature[3,4] data on the distribution ratios for Pu(IV) over a wide range of nitric acid and lithium nitrate concentrations. On the basis of the calculated data, it can be estimated that the formation of the $Pu(NO_3)_4 \cdot TBP_2 \cdot HNO_3$ adduct is predominant at $HNO_3 \geq 2$ mol·L^{-1}. Accepting two TBP adducts (TBP_2 and $TBP_2 \cdot HNO_3$) capable of coordinating $Pu(NO_3)_4$ produced a very good fit, and eq 15 can be used for calculating the distribution ratios of Pu(IV) over a wide range of nitric acid and additional nitrate concentrations.

Despite extensive research of the extraction of tetravalent plutonium from nitric acid by TBP, there are only a few papers reporting the plutonium extraction constants. The significant differences in the previous data are mainly caused by the calculation method of the complexation constants and the activity coefficients of all relevant species. For example, Moiseenko and Rozen[35] determined the extraction constant of $2.6 \cdot 10^4$ at 20 °C. They applied a simplified approach to the calculation of the apparent distribution constant assuming that the $Pu(NO_3)_4 \cdot 2TBP$ adduct is the only extractable species over a wide range of (0.1 to 10) mol·L^{-1} HNO_3. On the contrary, Rubisov and Solovkin[26] concluded that three hydrolyzed species are present in the aqueous solutions and are extractable as neutral adducts with nitrates and two molecules of TBP. Surprisingly, the largest extraction constant ($4.17 \cdot 10^4$) they reported was for the monohydroxo species of Pu(IV), whereas the constant calculated for $Pu(NO_3)_4 \cdot 2TBP$ was only $1.9 \cdot 10^2$. The other two constants were $1.19 \cdot 10^3$ for the TBP adduct with dihydroxo and 9.4 for the adduct with trihydroxo species. Moreover, it seems likely that Rubisov and Solovkin[26] did not evaluate the nitrate speciation of Pu(IV) in aqueous solutions. Also, the activity of water or the association of Pu(IV) with the $TBP_2 \cdot HNO_3$ adduct was considered in neither of these papers.

In summary, it can be concluded that calculation of the extraction constants strongly depends on the concept of how all of the assumptions regarding Pu disproportionation, hydrolysis, and complexation with nitrate were made. Because the activity coefficients for Pu^{4+} implied in this work are very small ($\sim 10^{-3}$), even small changes in the interaction parameter $\Delta\varepsilon(Pu^{4+}, NO_3^{-})$ can considerably affect the values of K_1 and K_2 extraction constants. For example, just assuming the activity coefficients for Pu^{4+} over the whole range of experimental conditions to be equal to one, the best fit between the experimental and calculated data ($R^2 = 0.89$) was obtained for extraction constants $K_1 = 51.1\ \text{mol}\cdot\text{L}^{-1}$ and $K_2 = 45.2\ \text{mol}\cdot\text{L}^{-1}$.

This model should not be used indiscriminately. Because of processes involving disproportionation and extraction at the same time and difficulties in obtaining consistent data for the extraction of Pu(IV) from low nitric acid concentration, the determination of the extraction constant for Pu-hydrolyzed species is more complicated and cannot be solved in this article. Although the presence of hydrolyzed species in the organic extraction phase of 30 % (by volume) TBP in *n*-dodecane was confirmed spectroscopically,[27] additional experimental data on the kinetics of disproportionation of Pu are necessary for correct estimation of the extraction constants of hydrolyzed plutonium species.

Conclusions

A rich chemistry of plutonium in aqueous solutions makes predicting Pu speciation a multifaceted task and designing extraction flowsheets more complicated. After a detailed review and critical evaluation of previously published data, five Pu(IV) species were considered to be present in aqueous solution containing (0.1 to 4) $\text{mol}\cdot\text{L}^{-1}$ HNO_3: Pu^{4+}, $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(NO_3)^{3+}$, and $Pu(NO_3)_2^{2+}$. Distribution ratios for Pu(IV) from low concentrations of nitric acid < 1 $\text{mol}\cdot\text{L}^{-1}$ are difficult to evaluate because of disproportionation of Pu(IV). To determine their extraction constant and fit the experimental and calculated values of the plutonium distribution ratio for low acid concentrations, additional experimental data on the kinetics of disproportionation are necessary. Although only two extractable species of Pu(IV) were included in the model, the calculated and experimental values of $D_{Pu(IV)}$ for (1 to 4) $\text{mol}\cdot\text{L}^{-1}$ HNO_3 fit very well, and the thermodynamic extraction constants determined for $Pu(NO_3)_4 \cdot 2TBP$ and $Pu(NO_3)_4 \cdot 2TBP \cdot HNO_3$ were $K_1 = 1.06 \cdot 10^5 \pm 1.1 \cdot 10^4$ and $K_2 = 2.12 \cdot 10^4 \pm 5 \cdot 10^3$, respectively.

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