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M. Alex Brown[a]; Peter Tkac[b]; Alena Paulenova[a]; George F. Vandegrift[c]
[a] Department of Nuclear Engineering & Radiation Health Physics, Oregon State University, Corvallis, OR, USA [b] Radiation Center, Oregon State University, Corvallis, OR, USA [c] Argonne National Laboratory, Argonne, IL, USA

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Influence of Temperature on the Extraction of Pu(IV) by Tri-*n*-butyl Phosphate from Acidic Nitrate Solutions

M. Alex Brown,[1] Peter Tkac,[2] Alena Paulenova,[1] and George F. Vandegrift[3]
[1]*Department of Nuclear Engineering & Radiation Health Physics, Oregon State University, Corvallis, OR, USA*
[2]*Radiation Center, Oregon State University, Corvallis, OR, USA*
[3]*Argonne National Laboratory, Argonne, IL, USA*

The influence of temperature on the extraction of Pu(IV) into 30 vol.% tri-*n*-butyl phosphate in *n*-dodecane from acidic nitrate solutions has been investigated at temperatures ranging from T = (294 to 313) K. Temperature was found to decrease the distribution of Pu(IV). Three species of plutonium were considered present in the aqueous solution: Pu^{4+}, $Pu(NO_3)^{3+}$, and $Pu(NO_3)_2^{2+}$. The enthalpy and entropy of the extraction, calculated using Van't Hoff plots, are $-60.4 \pm 3.34\,kJ \cdot mol^{-1}$ and $-120 \pm 10.6\,J \cdot mol^{-1} \cdot K^{-1}$, respectively.

Keywords plutonium; TBP; nitrate; solvent extraction; Van't Hoff; PUREX

INTRODUCTION

Solvent extraction has come to be one of the most important separation processes in the reprocessing of radioactive waste. The PUREX process (Plutonium-Uranium-Extraction), which utilizes the neutral extractant tri-*n*-butyl phosphate (TBP), is currently the most established and widely used technology for the recovery of uranium and plutonium from used nuclear fuel. In order to facilitate large-scale industrial applications of liquid-liquid separation processes, knowledge of the thermodynamic constants associated with the distribution of metal ions between immiscible media is necessary. The enthalpy and entropy constants derived for the distribution reaction of metal neutral complexes give important information about hydration and organic phase solvation (1); however, very few investigations have been dedicated to this problem.

To date, the data reported (2–4) concerning the effect of temperature on extraction of plutonium under PUREX conditions has been contradictory. Table 1 compares selected distribution data. Rozen et al. (2) found that increasing temperature decreases the distribution of Pu(IV) while Kolarik (3) and Ramanujan et al. (4) argue the opposite trend at acid concentrations below 6 M. Danesi et al. (5) studied the effect of temperature on the extraction of plutonium nitrates into long chain amines and found the distribution to decrease with temperature. Also, the extraction of Pu(VI) from nitric acid into TBP was found to decrease with temperature according to Sajun et al. (6)

Numerous studies conducted on the distribution of plutonium into TBP from nitric acid did not incorporate the chemistry of plutonium in solution. The majority of the mentioned authors neglected the effect of hydrolysis and disproportionation. With advances in analytical instrumentation techniques over the past two decades, the chemistry of actinoids in acidic solution is better understood. It is now known that elevated temperatures enhance hydrolysis and disproportionation and can greatly affect the calculation of constants for extractions at lower acid concentrations.

We attempted to develop a comprehensive database of experimental values related to the distribution of plutonium. The partitioning of Pu(IV) in the extraction system consisting of TBP, nitric acid, and lithium nitrate was investigated with regard to variations in temperature and nitrate concentrations. Thermodynamic and stability constants for plutonium extraction from acidic nitrate solutions by TBP are discussed and calculated in the present work.

EXPERIMENTAL

^{239}Pu was obtained from the Argonne National Laboratory as a chloride, dissolved in nitric acid, and adjusted to tetravalent oxidation state using H_2O_2 and solid $NaNO_2$. The ^{241}Am impurity was removed by anion exchange chromatography (Dowex 1X-4). The americium was washed from the column with 7 M HNO_3 and Pu(IV) was eluted with 0.36 M HCl. The Pu(IV) chloride solution was evaporated and dissolved in 4 M HNO_3 and used as a working stock solution. Purity of the tetravalent oxidation state was confirmed to be approximately 99% by

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Address correspondence to Alena Paulenova, Radiation Center, Oregon State University, Corvallis, OR 97331-5903. Tel.: 541-737-7070. E-mail: alena.paulenova@oregonstate.edu

TABLE 1
Comparison of selected literature on the distribution of Pu into TBP from ~1M HNO_3 at various temperatures

Ref. (1)		Ref. (2)		Ref. (3)		This work	
T/K	D_{Pu}	T/K	$D_{Pu(IV)}$	T/K	$D_{Pu(IV)}$	T/K	$D_{Pu(IV)}$
293	1.4	293	2.8	283	2.3	294	1.4
303	1.3	303	3.0	298	2.8	303	0.6
323	1.2	313	3.2	333	3.7	313	0.3

both absorption spectroscopy and extraction with thenoyl trifluoroacetone (TTA) in xylene which is specific to Pu(IV). The presence of nitrite ions and 4 M acidity was able to stabilize the oxidation state over the course of the experiments. TBP (98%, Alfa Aesar) was dissolved in *n*-dodecane (+99%, Alfa Aesar) to 30 vol.%. Prior to extraction, the TBP solutions were pre-equilibrated at room temperature (294 ± 1 K) with nitric acid and lithium nitrate solutions of the desired nitrate concentrations for all trials. Equal volumes of pre-equilibrated TBP and fresh nitrate solutions were spiked with 20 μL of Pu(IV) stock, heated to the desired temperature, rigorously agitated in extraction vials for one minute, and heated again. This procedure was repeated six times for each extraction. During agitation, extraction vials were insulated to maintain the temperature of the system at ± 1 K as previously determined by using samples absent of Pu. The samples were then centrifuged and separated. Aliquots from both the organic and aqueous phases were taken for analysis. The remaining organic phase was then subject to a back extraction with fresh portions of nitrate solution and the extraction process was repeated. Each aliquot was mixed with a scintillation cocktail (Ultima Gold) and counted using liquid scintillation (Perkin Elmer). The distribution ratios were calculated as the ratio of organic to aqueous activity concentration.

RESULTS AND DISCUSSION

The complexation of Pu(IV) by nitric acid and TBP has been extensively studied and reviewed in multiple publications [2–4,7] and is generally accepted as the formation of the neutral solvate adduct complex of Pu^{4+} with four nitrate anions:

$$Pu^{4+} + 4NO_3^- + 2TBP \rightarrow Pu(NO_3)_4 \cdot TBP_2 \qquad (1)$$

The speciation of plutonium in both the aqueous and organic phases is very important; all possible aqueous equilibria must be considered in order to distinguish between species in the aqueous solution. Factors to consider are hydrolysis, disproportionation and nitrate complexation.

The Hydrolysis and Disproportionation of Pu(IV)

Plutonium, particularly in its tetravalent state, is the most susceptible to hydrolysis in relation to the actinoids Th, U, and Np (8). The hydrolysis reaction can be written as:

$$Pu^{4+} + xH_2O \rightarrow Pu(OH)_x^{4-x} + xH^+ \qquad (2)$$

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

The hydrolysis of plutonium is important to consider because hydrolyzed plutonium is not readily extracted by TBP. The mechanism of hydrolysis has been studied under acidic and non-acidic conditions and has been described as very rapid, irreversible, and enhanced at elevated temperatures (9). Although recent studies have shown the presence of extracted hydrolyzed species (10), the present work assumes the hydrolyzed species extraction to be negligible under the chosen conditions. At low acidic conditions the chemistry of plutonium becomes more complicated because Pu^{4+} can also disproportionate to form trivalent and hexavalent oxidation states.

$$3Pu^{4+} + 2H_2O \rightarrow 2Pu^{3+} + PuO_2^{2+} + 4H^+ \qquad (4)$$

These various oxidation states are known to co-exist in solutions. The Nernst equation verifies that Pu^{4+} is unstable with respect to disproportionation at $pH > 0$ under standard conditions.

$$E^o = -0.02V$$
$$E = E^o + 2(59.4mV)pH - \frac{RT}{\upsilon F}\ln\frac{[PuO_2^{2+}][Pu^{3+}]^2}{[Pu^{4+}]^3} \qquad (5)$$

Costanzo et al. (9) reported significant concentrations of multiple oxidation states as well as hydrolyzed species at concentrations below 0.6M HNO_3. Elevated temperatures were found to have a considerable effect on the disproportionation of Pu(IV) and polymerization from 25°C to 50°C. Therefore, in the present work, acid concentrations in the range of 2 M – 5 M were selected.

Aqueous Speciation

Spectroscopic studies show evidence of various tetravalent plutonium-nitrate complexes in aqueous solutions. Veirs et al. (11) identified mono-, di- and tetranitrate complexes of Pu(IV) at nitric acid concentrations less than 6 M. At higher concentrations, hexanitrate complexes can exist. Incorporating formation constants, the total plutonium concentration in the aqueous phase can be written as:

$$[Pu(IV)]_{aq} = [Pu^{4+}(H_2O)_n] \begin{pmatrix} 1+\frac{K_H}{\{H^+\}}+\beta_1\{NO_3^-\}+\beta_2\{NO_3^-\}^2 \\ +\beta_4\{NO_3^-\}^4+\beta_6\{NO_3^-\}^6 \end{pmatrix} \tag{6a}$$

$$= [Pu^{4+}(H_2O)_n]+[Pu(OH)_x^{4-x}]+[Pu(NO_3)^{3+}] + [Pu(NO_3)_2^{2+}]+[Pu(NO_3)_4]+[Pu(NO_3)_6^{2-}] \tag{6b}$$

where K_H represents the hydrolysis constant, β the formation constant of the plutonium-nitrate complexes (the subscript symbol is the number of nitrates in the plutonium complex) and n ($n = 7$–12) the number of aqua ligands bound to the plutonium cation. Taking into account the hydrolysis constant for Pu(IV) studied by Metivier et al. (12), the hydrolyzed species of Pu(IV) can be considered negligible at acid concentrations > 2 M. It should also be noted that Metivier et al. (12) reported multiple hydrolyzed species of plutonium. The formation constants β_4 and β_6 are not well understood and have seldom been studied. Despite the slight presence of tetra- and hexanitrate complexes reported for the acid range of 2 M – 5 M (11), this work assumes their formation to be negligible and the aqueous speciation consists of mono-, dinitrate complexes and Pu^{4+}.

The Extraction of Nitric Acid

In addition to metals, TBP is able to extract other components from aqueous solution. Chaiko and Vandegrift (13) studied the thermodynamics of the distribution of nitric acid into 1.095 M TBP in kerosene. The speciation of nitric acid in TBP was found as $HNO_3 \cdot TBP$, $HNO_3 \cdot TBP_2$ and $(HNO_3)_2 \cdot TBP$. The majority of the extracted nitric acid existed as $HNO_3 \cdot TBP$ and the dinitric acid complex did not exist below acid concentrations of 6 M. The TBP_f concentration (TBP unbound to nitric acid) decreased with increasing nitric acid. Adamskii et al. (14) also studied the speciation of extracted nitric acid by 0.736 M TBP in kerosene with similar results and calculated the concentration of TBP_f in the presence of plutonium and uranium. The authors (14) extended the research into the effect of temperature and concluded that temperature had a negligible effect on the distribution and speciation of nitric acid.

Chemical Equilibria

The mechanism by which Pu(IV) is extracted into TBP was assumed to be similar to that of hexavalent uranium described by Rydberg et al. (15) The plutonium in aqueous solutions is complexed with neutral aqua ligands. The nitrate ions then fill the four valence shells as bidentate ligands and two TBP molecules form the adduct complex $Pu(NO_3)_4 \cdot TBP_2$. Previously (7), it was found that the complex $Pu(NO_3)_4 \cdot TBP_2 \cdot HNO_3$ is also extracted at ambient temperature. However, since the extraction constant was determined to be much smaller than that of the complex formation shown in Eq. (1), this adduct was not included in the calculations reported in the present work. Therefore, the rate determining step is the transfer of the plutonium complex from the aqueous phase into the organic phase.

$$Pu(NO_3)_4 \cdot TBP_{2,aq} \rightarrow Pu(NO_3)_4 \cdot TBP_{2,or} \tag{7}$$

The equilibrium constant at specific temperatures, $K_{ex}(T)$, for the complexation of Pu(IV) by TBP is:

$$K_{ex}(T) = \frac{[Pu(NO_3)_4 \cdot TBP_2][H_2O]^n}{[Pu^{4+}(H_2O)_n][NO_3^-]^4[TBP_f]^2} \frac{\gamma_{Pu(NO_3)_4 \cdot TBP_2}\gamma_{H_2O}^n}{\gamma_{Pu^{4+}(H_2O)_n}\gamma_{NO_3^-}^4\gamma_{TBP_f}^2} \tag{8}$$

The distribution coefficient of Pu(IV) is defined as the concentration ratio of plutonium in the organic and aqueous phases, or

$$D_{Pu(IV)} = \frac{[Pu(IV)]_{or}}{[Pu(IV)]_{aq}}. \tag{9}$$

Substituting Eq. (6a) into Eq. (8), the equilibrium constant, $K_{ex}(T)$, can be defined as:

$$K_{ex}(T) = \frac{D_{Pu(IV)}[H_2O]^n}{[NO_3^-]^4[TBP_f]^2}(1+\beta_1\{NO_3^-\}+\beta_2\{NO_3^-\}^2) \frac{\gamma_{Pu(NO_3)_4 \cdot TBP_2}\gamma_{H_2O}^n}{\gamma_{Pu^{4+}(H_2O)_n}\gamma_{NO_3^-}^4\gamma_{TBP_f}^2} \tag{10}$$

where γ represents the activity coefficients of each species and T is the absolute temperature (K) of the extraction reaction. The activity coefficients of plutonium in the organic phase and TBP_f are assumed to be one. The activity coefficients of Pu^{4+} were estimated using the specific ion interaction theory (SIT) and the approach of chemical analogs and similar behavior of tetravalent thorium and plutonium. The SIT interaction parameter, $\Delta\varepsilon$, was chosen to be 0.31 as reported by Neck et al. (16) for thorium solutions. The influence of temperature on the stability constants β_1 and β_2 should be considered. Numerous studies (17–25) have been conducted on the plutonium-nitrate

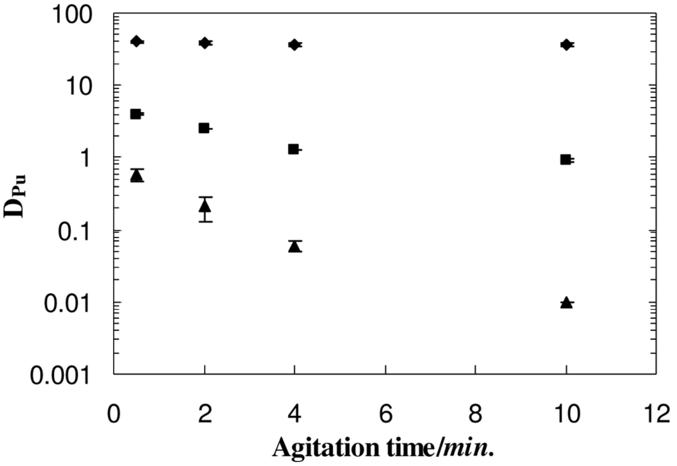

FIG. 1. The effect of agitation on the distribution of plutonium at 294 K: (◆) 7M HNO_3; (■) 1M HNO_3; (▲) 0.1M HNO_3.

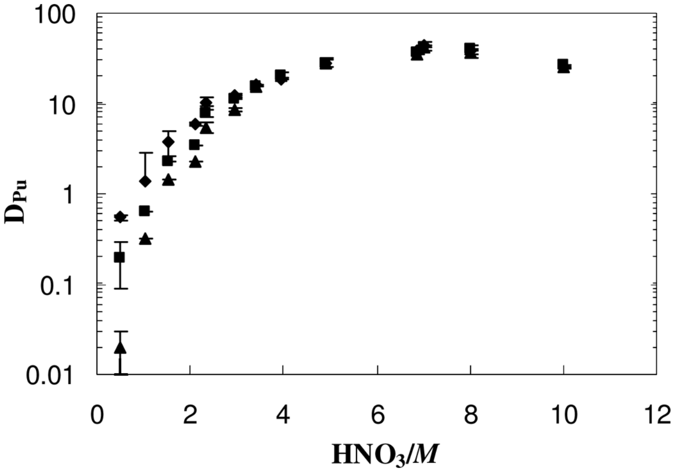

FIG. 2. The distribution of plutonium at various temperatures for a system containing nitric acid: T = (◆) 294 K; (■) 303 K; (▲) 313 K.

system but to our knowledge, none have investigated the effects of temperature on the nitrate complexation with Pu(IV). This work assumes β_1 and β_2 to be dependent on ionic strength but independent of temperature as well as the concentration of water and the dehydration energy of Pu(IV). Eq. (10) can then be written as:

$$K_{ex}(T) = \frac{D_{Pu(IV)}}{[NO_3^-]^4[TBP_f]^2}\left(1 + \beta_1\{NO_3^-\} + \beta_2\{NO_3^-\}^2\right)\frac{1}{\gamma_{Pu^{4+}}\gamma^4_{NO_3^-}} \qquad (11)$$

To calculate the thermodynamic characteristics, equilibrium constants were determined at different temperatures. Using the equation for Gibbs energy

$$\Delta G^o = -RT \ln K_{ex}(T) \qquad (12)$$

and:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (13)$$

a Van't Hoff plot of the natural logarithm of K_{ex}(T) versus the inverse temperature will yield a slope proportional to the enthalpy and an intercept proportional to the entropy.

Experimental data show that the distribution of Pu(IV) is a complex process. Figure 1 plots the distribution as a function of agitation time at various nitric acid

TABLE 2
The distribution of Pu(IV) for nitrate concentrations between 2M – 5M. (D^{I}_{Pu}) forward extractions; (D^{II}_{Pu}) back extractions

			T/K = 294			T/K = 303			T/K = 313		
HNO_3/M	$LiNO_3$/M	Total NO_3^-/M	D^{I}_{Pu}	D^{II}_{Pu}	$D^{Avg.}_{Pu}$	D^{I}_{Pu}	D^{II}_{Pu}	$D^{Avg.}_{Pu}$	D^{I}_{Pu}	D^{II}_{Pu}	$D^{Avg.}_{Pu}$
2.0	–	2.0	6.1	5.7	5.9 ± 0.3	3.7	3.7	3.7 ± 0.0	2.4	2.2	2.3 ± 0.2
2.4	–	2.4	11.3	9.6	10.5 ± 1.2	8.5	7.3	7.9 ± 0.8	6.6	4.3	5.4 ± 1.7
2.9	–	2.9	12.1	12.5	12.3 ± 0.3	11.2	11.5	11.4 ± 0.2	8.3	8.8	8.5 ± 0.4
3.4	–	3.4	16.2	16.0	16.1 ± 0.1	15.9	15.5	15.7 ± 0.3	14.7	16.5	15.6 ± 1.3
3.9	–	3.9	19.1	18.6	18.9 ± 0.3	18.9	21.3	20.1 ± 1.7	18.7	21.3	20.0 ± 1.8
4.9	–	4.9	26.3	30.5	28.4 ± 3.0	26.1	29.5	27.8 ± 2.4	25.1	31.3	28.2 ± 4.4
2.0	0.5	2.5	12.3	9.4	10.9 ± 2.0	8.0	6.1	7.1 ± 1.4	5.3	2.6	4.0 ± 1.9
2.0	1.0	3.0	18.4	16.0	17.2 ± 1.7	15.1	13.1	14.1 ± 1.4	9.6	8.1	8.9 ± 1.0
2.0	1.5	3.5	27.8	26.2	27.0 ± 1.1	22.8	19.1	20.9 ± 2.7	17.9	15.9	16.9 ± 1.5
2.0	2.0	4.0	38.2	39.0	38.6 ± 0.6	34.5	32.0	33.3 ± 1.7	28.8	32.1	30.4 ± 2.4
2.0	3.0	5.0	68.5	89.8	79.2 ± 15.1	59.5	84.1	71.8 ± 17.4	57.0	88.9	72.9 ± 22.5

TABLE 3
Parameters used to calculate equilibrium constants and Gibbs free energies for various nitric acid concentrations

				$\ln K_{ex}(T)$					
HNO_3/M	TBP_t/M	γPu^{4+}	$\{NO_3^-\}^*$	T/K = 294	T/K = 303	T/K = 313	T/K = 294	T/K = 303	T/K = 313
2.0	0.45	0.0010	1.75	12.0	11.4	11.0	$\ln K_{ex}^0(T)$		
2.3	0.35	0.0012	2.06	12.7	12.4	12.0			
2.9	0.24	0.0016	2.86	12.8	12.7	12.4	10.1	9.4	8.7
3.4	0.18	0.0020	3.59	13.2	13.2	13.2	$\Delta G(T)/kJ\cdot mol^{-1}$		
3.9	0.13	0.0024	4.54	13.7	13.7	13.7			
4.9	0.07	0.0033	6.68	14.9	13.6	14.9	−24.8	−23.8	−22.6

$^*\{NO_3^-\}$ indicates nitrate activity.

concentrations. D_{Pu} decreases with agitation time at 1 M HNO_3 and below whereas 7 M is able to maintain consistent values. At low acid concentrations, longer contact times result in the production of inextractable species such as Pu(III) and hydrolyzed plutonium. These reactions are shown in Eqs. (2) and (4). It was measured that 6 min. extraction time was sufficient to achieve equilibrium at acid concentrations $\geq$2 M. Values of D_{Pu} as a function of nitric acid concentration are shown in Fig. 2. As the concentration of nitric acid increases, the distribution of Pu(IV) increases until a maximum of approximately 7 M HNO_3. Beyond 7 M, the distribution of Pu(IV) begins to decrease as the majority of the TBP is complexed with nitric acid. Table 2 specifically lists the forward and back extraction values at nitrate concentrations between 2 M – 5 M for each temperature. From the distribution data, the equilibrium constants at each temperature can be calculated using Eq. (11). Bromley's method (26) was used to calculate the activities of nitrates in solution; SIT found the variations in activities with temperature. The concentration of TBP_f, β_1 and β_2 as a function of nitrate concentration were reported in the recent work (7) and employed in calculation of the equilibrium constant at a given temperature.

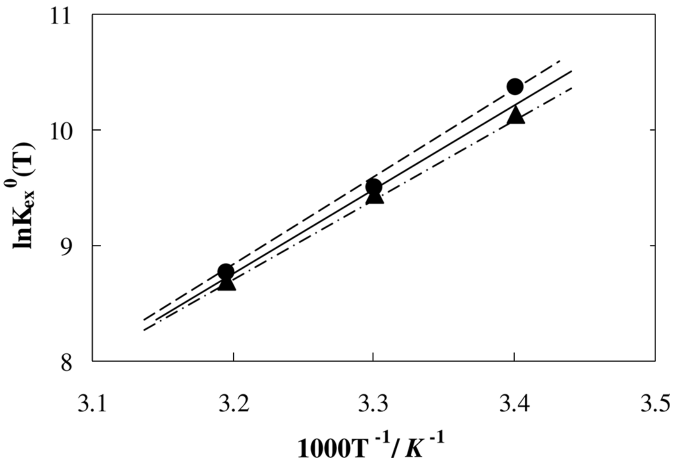

FIG. 3. Van't Hoff plots for systems containing (▲-·-·-) nitric acid: slope = 6.99, y-intercept = −13.6; (●- - -) 2M $HNO_3 + LiNO_3$: slope = 7.56, y-intercept = −15.4; (—) average linear regression.

Table 3 lists the activities of Pu^{4+}, nitrate, TBP_f concentrations and the calculated equilibrium constants at different temperatures. It can be seen that the extraction equilibrium constants change with nitrate concentration. This behavior was also reported by Rozen et al. (2) The gradient is likely associated with some error in the activity coefficient assumptions, such as assuming the organic solution activities of TBP_f and $Pu(NO_3)_4 \cdot TBP_2$ to be set equal to one. As it was mentioned before, no sufficient literature exists on the values of plutonium-nitrate stability constants at different temperatures; therefore, all β were assumed independent of temperature. The behavior of $\ln K_{ex}$(T) with nitrate concentration, however, is linear and can be extrapolated to $[NO_3^-] = 0$ M where the activity coefficient is equal to one. Using computer software, linear trends can be fit to give the extrapolated equilibrium constants for each temperature. The extrapolated $\ln K_{ex}^0(T)$ values are listed in Table 3. Plotting the natural logarithm of $K_{ex}^0(T)$ versus inverse temperature, as in Fig. 3, reveals a line ($R^2 = 0.99$) with a slope and intercept of 6.99 and −13.6, respectively. These parameters yield $\Delta H = -58.1$ kJ · mol^{-1} and $\Delta S = -113$ J · mol^{-1} · K^{-1} which suggest an exothermic reaction that should be, according to Eq. (13), less spontaneous with increasing temperature. This trend is in agreement with the decreasing distribution values at higher temperatures. The values calculated for $\Delta G(T)$ are listed in Table 3. Rozen et al. (2) reported an enthalpy of -25.1 kJ · mol^{-1} without an entropy value for a similar system containing 20 vol.% TBP in kerosene.

Salting-out agents can vastly increase the distribution of plutonium. The addition of an inextractable nitrate salt, in this case lithium nitrate, lowers the concentration of nitric acid while keeping the total nitrate concentration high. Systems containing 2 M HNO_3 and 1 M – 3 M $LiNO_3$ were

TABLE 4

Parameters for calculating equilibrium constants and Gibbs energy for systems containing 2 M HNO_3 and $LiNO_3$; equilibrium constants are plotted in Fig. 4

		γPu^{4+}			$\{NO_3^-\}^*$					
NO_3^-/M	TBP_t/M	$T/K = 294$	$T/K = 303$	$T/K = 313$	$T/K = 294$	$T/K = 303$	$T/K = 313$	$T/K = 294$	$T/K = 303$	$T/K = 313$
2.0	0.45	0.0009	0.0008	0.0006	1.62	1.62	1.63		$\ln K_{ex}^0(T)$	
2.5	0.36	0.0011	0.0010	0.0007	2.32	2.30	2.27			
3.0	0.29	0.0013	0.0012	0.0009	3.18	3.15	3.11	10.4	9.5	8.7
3.5	0.19	0.0017	0.0015	0.0011	4.17	4.14	4.10		$\Delta G(T)/kJ \cdot mol^{-1}$	
4.0	0.24	0.0020	0.0018	0.0014	5.25	5.21	5.16			
5.0	0.13	0.0031	0.0027	0.0022	7.74	7.69	7.63	−25.2	−24.0	−22.7

$^*\{NO_3^-\}$ indicates nitrate activity.

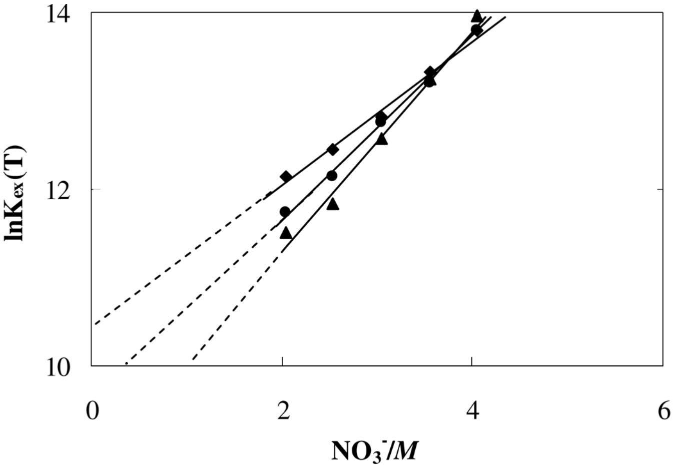

FIG. 4. The equilibrium constants at various temperatures calculated by Eq. (11) for a system containing 2M HNO_3 and $LiNO_3$. Values for $\ln K_{ex}^0(T)$ were found at the extrapolated point $[NO_3^-] = 0M$. T = (◆) 294 K; (●) 303 K; (▲) 313 K.

used to analyze the distribution of Pu(IV). Table 2 lists values of $D_{Pu(IV)}$ for systems containing lithium nitrate. The equilibrium constants at each nitrate concentration and temperature were calculated using Eq. (11) and are listed in Table 4. Plotting the natural logarithm of the equilibrium constants as a function of nitrate concentration, as in Fig. 4, produces three isothermal trends that can be extrapolated to $[NO_3^-]=0\,M$ ($R^2 = 0.99$ for all temperatures). The Van't Hoff plot for this system is shown in Fig. 3 ($R^2 = 0.99$). The enthalpy and entropy were calculated to be $-62.8\,kJ \cdot mol^{-1}$ and $-128\,J \cdot mol^{-1} \cdot K^{-1}$, respectively. It should be restated that the distribution ratios at a constant nitrate concentration are much higher for systems with added nitrate than those with nitric acid only on account of the increased nitrate and TBP_f concentrations. The thermodynamic characteristics, however, should be similar. Therefore, an average enthalpy and entropy can be calculated from the two systems: $\Delta H = -60.4 \pm 3.34\,kJ \cdot mol^{-1}$ and $\Delta S = -120 \pm 10.6\,J \cdot mol^{-1} \cdot K^{-1}$.

CONCLUSIONS

The influence of temperature on the extraction of Pu(IV) by 30 vol.% tri-*n*-butyl phosphate in *n*-dodecane from acidic nitrate solutions has been investigated at temperatures ranging from $T = (294$ to $313)$ K. When evaluating the extraction behavior of Pu(IV) at elevated temperatures, the intricate behavior of plutonium in aqueous solutions must be considered. Although the concentrations of nitrate and TBP_f have an overwhelming influence on the extraction of Pu(IV), it is evident that the distribution decreases with temperature. The largest changes in D_{Pu} values were seen at nitric acid concentrations $<2\,M$ due, in part, to the enhanced hydrolysis and disproportionation. Therefore, only the extraction data for the nitrate concentration range of $2\,M - 5\,M$ were considered. The three species of plutonium present in the aqueous solution (Pu^{4+}, $Pu(NO)^{3+}$ and $Pu(NO)_2^{2+}$) were used for the estimation of thermodynamic characteristics. The enthalpy and entropy of Pu(IV) extraction into TBP from acidic nitrate solutions were calculated to be $-60.4 \pm 3.34\,kJ \cdot mol^{-1}$ and $-120 \pm 10.6\,J \cdot mol^{-1} \cdot K^{-1}$. The decrease in the distribution of Pu(IV) with temperature can be explained by the increase of $\Delta G(T)$.

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