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The oxidation of neptunium(IV) by nitric acid in 100% TBP and diluted TBP/*n*-dodecane solutions

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Abstract

For the accurate computer simulation of the Purex process the kinetics of important chemical reactions occurring in both the aqueous and solvent phases in the process must be included in the model. One important species in the Purex process is Np(IV), and so the kinetics of the oxidation of Np(IV) by HNO_3 in TBP phases have been determined experimentally to aid the efficient modelling of Np(IV) in Purex process flowsheets. It was found that in 100% TBP solutions the oxidation is autocatalytic, with a mechanism proceeding predominantly via Np(V) reproportionation. The rate equation and rate constants have been determined for both the non-catalysed and autocatalysed components. However, there are significant departures from these kinetics as the TBP solution is diluted by *n*-dodecane. These differences include the retardation of the reaction and a change from an autocatalytic reaction to first-order kinetics, particularly at lower temperatures. Although this data is suitable for inclusion into computer models, the slow reaction in 30% TBP solutions means that the solvent-phase oxidation of Np(IV) will be a minor effect.

Keywords: Neptunium (IV); tri-Butyl phosphate; Nitric acid; Kinetics; Spectrophotometry

1. Introduction

Neptunium control in the Purex process is usually achieved by chemical reduction–oxidation reactions, such as reduction by hydroxylamine. However, efficient Np control is difficult since Np has several oxidation states in solution which leads to a complex process chemistry [1]. It is well known that the distribution of Np valence states can be affected by nitric and nitrous acids and the kinetics of these reactions in aqueous solution have been studied in detail [2,3]. However, redox reactions in the organic TBP phase will also occur and whilst these are likely to be less significant than aqueous-phase reactions the kinetics of solvent-phase reactions need to be determined to allow the accurate computer modelling of the Purex process.

2. Experimental methods

The experimental methods have been described elsewhere [4]. Briefly, $Np(NO_3)_4 \cdot 2TBP$ stock solution was prepared by reduction of Np to Np(IV) by hydrazine followed by solvent extraction of Np(IV) from HNO_3 into TBP. Concentrations of HNO_3 and H_2O in TBP were determined by titrations and HNO_2 was analysed colorimetrically. Total Np concentration was analysed radiometrically, and the concentrations of different Np oxidation states were determined spectrophotometrically. During the kinetic experiments the rate of decrease of the Np(IV) concentration was followed spectrophotometrically using the Np(IV) absorption band at 709 nm.

3. Results and discussion

3.1. Kinetics and mechanism of the oxidation of Np(IV) by HNO_3 in 100% TBP solution (Eq. (1))

$$Np(NO_3)_4 + HNO_3 + H_2O = NpO_2(NO_3)_2 + HNO_2 + 2HNO_3 \quad (1)$$

Fig. 1 shows that this reaction (Eq. (1)) is autocatalytic, i.e. the rate of reaction is increased by products of the Np(IV) oxidation (catalysed component), and there is an induction period (non-catalysed component). This autocatalysis could be due to either HNO_2 (Eq. (2)) or Np(VI). Calculations and experiments where additional HNO_2 and Np(VI) were introduced into the initial solution

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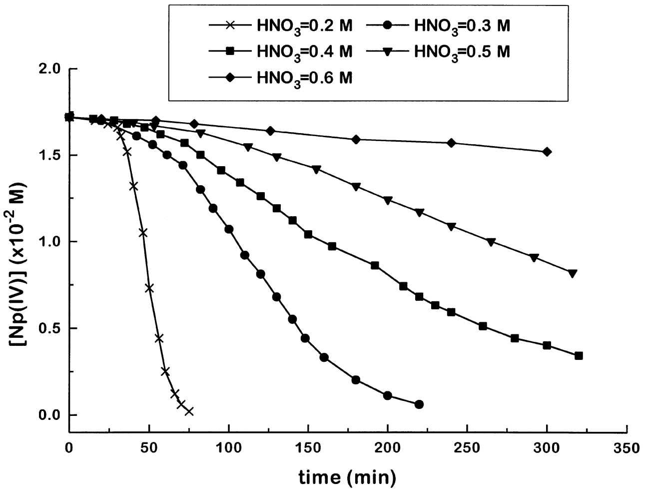

Fig. 1. Kinetic curves for the reaction in 100% TBP solutions at 60.2°C, $[H_2O]=2.45$ M and $[HNO_3]=0.2$–0.6 M.

of Np(IV) showed that the reaction mechanism via Np(V) reproportionation (Eq. (4)) dominated the reaction.

$$Np^{4+} + HNO_2 + H_2O = NpO_2^+ + NO + 3H^+ \tag{2}$$

$$2Np^{4+} + HNO_3 + 3H_2O = 2NpO_2^+ + HNO_2 + 6H^+ \tag{3}$$

$$Np^{4+} + NpO_2^{2+} + 2H_2O = 2NpO_2^+ + 4H^+ \tag{4}$$

The general form of the rate equation therefore is a combination of the non-catalysed reaction (3) and the two autocatalytic reactions (2 and 4). After integration this takes the form of Eq. (5), where $a=[\mathrm{Np(IV)}]_o$; $(a-x)=[\mathrm{Np(IV)}]$; $k_3'=k_3[HNO_3]^n$; $K=k_3'/k_8'$; and $k_8'=k_2'+k_5'$.

$$\ln[(a-x)/(K+x)] = \ln(a/K) - k_8'(a+K)t \tag{5}$$

It was shown that Eq. (5) described the experimental data well and so k_8' and the rate constant k_3' of reaction (3) were determined (see Table 1). The data shows that k_3' reaches a maximum value at $[HNO_3]\approx 0.4$ M and then decreases. k_8' is significantly decreased with increasing acidity and the order relative to HNO_3 is equal to -4. It was then shown that the order of reaction with respect to $[H_2O]$ for the catalytic route was 3 and that the order of the non-catalysable reaction (3) was -10. The rate constants are listed in Table 2. Therefore, the manipulation of the experimental data ultimately led to the derivation of the overall kinetic equation for the Np(IV)–HNO_3 reaction in 100% TBP solutions (Eq. (6)):

$$-\frac{d[\mathrm{Np(IV)}]}{dt} = \frac{k_3''[\mathrm{Np(IV)}]}{[H_2O]^{10}} + \frac{k_8[\mathrm{Np(IV)}][\mathrm{Np(VI)}][H_2O]^3}{[HNO_3]^4} \tag{6}$$

The rate constant for the non-catalysable reaction route is

Table 1
Variations of rate constants k_3' and k_8' with $[HNO_3]$ at 60.2°C

$[HNO_3]$ (M)	k_3' ($\times 10^{-3}$ min^{-1})	k_8' (l mol^{-1} min^{-1})[a]	k_8'' ($\times 10^{-2}$ mol^3 l^{-3} min^{-1})[b]
0.1	0.01	~42	—
0.2	0.1±0.01	8.90±0.09	1.42
0.3	0.8±0.1	1.81±0.08	1.47
0.4	1.4±0.2	0.59±0.03	1.41
0.5	1.1±0.3	0.23±0.03	1.44
0.6	0.25±0.08	0.12±0.04	1.55
Mean			1.48±0.07

$[H_2O]=2.45$ M and $[\mathrm{Np(IV)}]_o=1.72\times 10^{-2}$ M.
[a] $k_8'=k_2'+k_5'$ where $k_2'=k_2[H_2O]$ and $k_5'=k_5[H_2O]$.
[b] $k_8''=k_8'[HNO_3]_4$ when defined for experiments to determine the order of reaction with respect to $[HNO_3]$; i.e. at constant $[H_2O]$.

Table 2
Variation of rate constants k_3' and k_8' with $[H_2O]$ at 60.2°C

$[H_2O]$ (M)	k_3' ($\times 10^{-3}$ min^{-1})[a]	k_8' (l mol^{-1} min^{-1})	k_3'' (mol^{10} l^{-10} min^{-1})[b]	k_8'' (l^4 mol^{-4} min^{-1})[c]	k_8 ($\times 10^{-4}$ min^{-1})[d]
1.89	0.9±0.06	3.31±0.05	0.52	0.49	7.9
2.15	0.5±0.1	4.96±0.67	1.05	0.50	8.0
2.45	0.1±0.01	8.90±0.09	0.78	0.60	9.7
2.93	0.01±0.005	13.7±0.34	0.47	0.55	8.7
Mean			0.70±0.43	0.53±0.04	8.6±1.3

$[HNO_3]=0.2$ M and $[\mathrm{Np(IV)}]_0=1.72\times 10^{-2}$ M.
[a] $k_3'=k_3[HNO_3]^n$ (non-catalysed reaction route).
[b] $k_3''=k_3'[H_2O]^{10}$ (non-catalysed reaction route).
[c] $k_8''=k_8'/[H_2O]^3$.
[d] $k_8=k_8''[HNO_3]^4$ when defined for experiments to determine the order of reaction with respect to $[H_2O]$; i.e. at constant $[HNO_3]$.

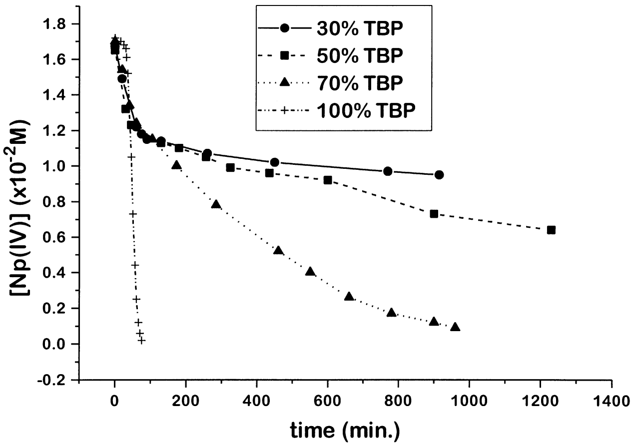

Fig. 2. Kinetic curves for the reaction in diluted TBP solutions at 60.2°C and $[HNO_3]=0.2$ M compared to 100% TBP.

$k_3''=0.70\pm0.43$ mol^{10} l^{-10} min^{-1} at 60.2°C and $[HNO_3]=0.2$ M. k_3'' varies slightly with $[HNO_3]$, corresponding to the change in the rate constant k_3'. The rate constant of the autocatalytic reaction route (k_8) is equal to the sum of k_2 and k_5 rate constants (reactions 2 and 4) and is independent of $[HNO_3]$. The mean value of k_8 calculated over all our experiments is equal to $(9.5\pm0.8)\times10^{-4}$ min^{-1} at 60.2°C.

To determine the activation energy of the reaction, the temperature dependence of the rate constants k_3' and k_9' was studied between 43.0 and 73.2°C ($[HNO_3]=0.2$ M, $[H_2O]=2.45$ M). It was found that the activation energy (E_8) calculated from the data for the catalytic reaction route governed by the rate constant k_8' is 90 ± 2 kJ mol^{-1}. The activation energy for the non-catalysed reaction (E_3) was less accurately determined, but is approximately equal to 63 ± 6 kJ mol^{-1}.

3.2. Kinetics of the oxidation of Np(IV) by HNO_3 in diluted TBP solutions

The oxidation in diluted TBP/*n*-dodecane solutions showed significant departures from the characteristics of the reaction in 100% TBP described previously (see Fig. 2). These included the disappearance of the induction period and a change from an autocatalytic reaction mode to a first-order reaction (relative to Np(IV)). The rate of Np(IV) oxidation was also drastically decelerated with increasing TBP dilution. For instance, in 0.2 M HNO_3 at 60.2°C the half-life of the reaction ($t_{1/2}$) in 30% TBP/*n*-dodecane is increased by a factor of 20 compared to 100% TBP. The kinetic data calculated from these experiments are listed in Table 3. Table 3 shows that K increases substantially as TBP is diluted. Since $K=k_3'/k_8'$ this is a consequence of either an increase of the rate constant for the non-catalytic route of the reaction (k_3') or a decrease of the catalytic rate constant (k_8'), or even changes of both rate constants. One plausible reason for this increase is that if, in dilute TBP solutions, the order of the non-catalysed reaction relative to water is still equal to -10 then even a slight decrease in $[H_2O]$ in this series of experiments[1] will lead to a large increase in k_3' when changing from 100 to 30% TBP solutions, despite the constant HNO_3 concentration (0.2 M).

In 70% TBP/*n*-dodecane K (0.022) is of a similar magnitude to x, which was $\leq1.7\times10^{-2}$ M. Therefore, Eq. (5) is still valid and can be solved as for the 100% TBP case. This leads to $k_3'=1.9\times10^{-3}$ min^{-1}, which is close to an estimated value of k_3' (1.85×10^{-3} min^{-1}) obtained from the (post-induction period) gradient of the linear kinetic graph based on the experimental data.

It can be seen from Table 3 that the rate constant k_8' is decreased by a factor of ~35 on reducing the TBP concentration from 100 to 70%. It is apparent that, as distinct from 100% TBP, in dilute solutions the contribution of reaction (2), i.e. HNO_2 autocatalysis, to the overall oxidation of Np(IV) is much higher and, consequently, the fraction of the rate constant k_2' in the sum $k_8'=k_2'+k_5'$ is greater. Further information on the kinetics of reaction (2) is needed; particularly to understand how the contribution of the HNO_2 autocatalytic reaction route to the overall oxidation of Np(IV) changes with dilution of the TBP solution.

For 30 and 50% TBP/*n*-dodecane solutions calculations based on Eq. (5) are not really meaningful since there is a deviation from the reaction route described by kinetic Eq. (5) to first-order kinetics (at 60.2°C). This deviation increases with increasing dilution (Fig. 2). This transformation from an autocatalytic reaction to a first-order reaction can be explained by the fact that, in these

Table 3
Reaction rate constants k_3', k_8', k' and the half-life of the oxidation of Np(IV) by HNO_3 in TBP solutions at 60.2°C

[TBP] (%)	$[H_2O]$ (M)	$t_{1/2}$ (min)	K ($\times10^{-3}$ M)	k_3' ($\times10^{-3}$ min^{-1})	k_8' (l mol^{-1} min^{-1})	k' ($\times10^{-3}$ min^{-1})
100	2.45	48	0.01	0.1	8.9	—
100	1.89	75	0.35	1.1	3.2	—
70	1.66	280	22	1.9	0.09	3.4
50	1.44	650	—	—	—	3.4
30	1.36	~1500	—	—	—	0.22

$[HNO_3]=0.2$ M and $[Np(IV)]_o=1.72\times10^{-2}$ M.

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[1] For various reasons, particularly due to the limited solubility of water in dilute TBP solutions, the concentration of water was not kept constant in this series of experiments.

experiments, since K is large and so $K \gg x$ the rate Eq. (5) reduces to a first-order Eq. (7):

$$\ln[(a - x)/(K + x)] = \ln(a/K) - k'_8(a + K)t \text{ Eq. (7)}$$

$$\ln(a - x) = \ln a - k't \tag{7}$$

where $k' = k'_3 + k'_8 a = k'_8(a + K)$. Finally, due to the very low rate of reaction at 60°C the oxidation of Np(IV) in 30% TBP/*n*-dodecane was studied at 80°C. According to the activation energy E_3, this 20°C temperature rise will accelerate the reaction rate by a factor of ~4. However, even at this temperature with a relatively high HNO_3 content (>0.3 M) Np(IV) oxidation was still very slow although, as in 100% TBP, the reaction is accelerated by reducing $[HNO_3]$. At 80°C, unlike the experiments at 60.2°C, the autocatalytic mode of the reaction is partially retained, i.e. the reaction route obeys the kinetic Eq. (5). After processing the experimental data using this equation the results at various HNO_3 concentrations are given in Table 4. It can be seen from the data that the rate constant k'_8 for the catalytic route of the reaction increases with decreasing $[HNO_3]$ in the same manner as for 100% TBP, where the order of reaction relative to HNO_3 is -4. The change in K is in a qualitative agreement, i.e. its value increases with increasing acidity. The dependence of the rate constant of the non-catalysed reaction route k'_3 on $[HNO_3]$ has not been ascertained, since values of k'_3 have not been determined with sufficiently high accuracy. The most probable cause of this uncertainty is varying and uncontrollable amounts of HNO_2 present in low concentrations in the TBP stock solutions.

4. Conclusions

In 100% TBP solution, the oxidation of Np(IV) by HNO_3 is autocatalysed by the reaction products, HNO_2 and Np(VI). The reaction route via Np(V) reproportionation was shown to be the dominant mechanism. The rate equation and rate constants for both non-catalysed and autocatalytic reactions have been determined. As TBP is diluted the rate of Np(IV) oxidation is decreased and the autocatalytic reaction mode, which is still evident in 70% TBP/*n*-dodecane solution, becomes a first-order reaction as the dilution increases (at 60.2°C). However, in diluted 30% TBP/*n*-dodecane at 80°C, the autocatalysis is still observable. Although such observations can be explained from the kinetics, further work is needed to properly understand the changing reaction mechanisms as 100% TBP is progressively diluted to a 30% TBP solution.

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Table 4

Kinetic data at varying $[HNO_3]$ for the oxidation of Np(IV) by HNO_3 in 30% TBP/n-dodecane at 80°C and $[H_2O] = 1.36$ M

$[HNO_3]$ (M)	K ($\times 10^{-3}$ M)	k'_3 ($\times 10^{-3}$ min^{-1})	k'_8 (l mol^{-1} min^{-1})	k''_8 ($\times 10^{-4}$ mol^3 l^{-3} min^{-1})[a]
0.2	15	1.1	0.076	1.21
0.1	10	9.5	0.95	0.95
0.07	1	4.0	4.0	0.96
mean	—	—	—	1.04±0.37

[a] $k''_8 = k'_8[HNO_3]$.