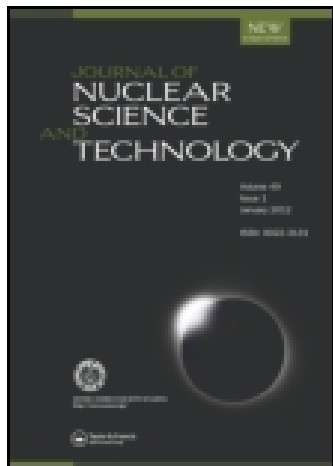


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Kinetics and Mechanisms of Np(VI) and Np(V) Reductions by U(IV) in TBP Solutions

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Spectrophotometric methods were used to study the kinetics of Np(VI) reduction to Np(V) and Np(IV) in 30% TBP solution in n-dodecane. The first reaction is limited by the stage in which solvated TBP molecules of $\text{NpO}_2(\text{NO}_3)_2$ interact with hydrolyzed forms of U(IV), i.e. $\text{U}(\text{OH})_2(\text{NO}_3)_2$ ions. Accordingly, the reaction rate is catalyzed by water and inhibited by nitric acid. The reaction proceeds at a much slower rate in a TBP solution than in an aqueous solution. The rate of Np(V) reduction with uranium(IV) in a TBP solution is independent of $[\text{HNO}_3]$ or $[\text{H}_2\text{O}]$ and proceeds at a substantially higher rate than in an aqueous solution. At the limiting stage, the transport of charge takes place between the reagents in their basic forms, NpO_2NO_3 and $\text{U}(\text{NO}_3)_4$. The reaction is affected by the formation of the non-reactive complex $[\text{NpO}_2\text{U}(\text{NO}_3)_5]$.

KEYWORDS: kinetics, mechanism, neptunium, U(IV), tributyl phosphate.

I. Introduction

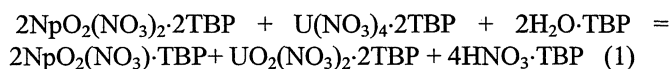
In the reprocessing of irradiated nuclear fuel, tetravalent uranous nitrate is commonly used to separate U and Pu. This is achieved by the reductive stripping of Pu(IV) from the solvent phase in to the aqueous phase as Pu(III). A stabilising agent such as hydrazine is also used to prevent Pu(III) reoxidising back to Pu(IV). Np ions are also usually present, as Np(VI) ions, in the solvent phase at the U/Pu partition stage. Np(VI) is also reduced by U(IV), initially to inextractable Np(V) and then further, to Np(IV). Np(IV) is extractable and so, in Purex flowsheets, Np is often routed with the U stream. These redox reactions occur in both aqueous and solvent phases, although the reactions in the aqueous phase have generally received greater attention. However, to fully understand the chemistry of the U/Pu partition and, in particular, the fate of Np within this contactor, data is needed on the rates of reactions in both aqueous and solvent phases. This is particularly important for process simulation and accurate flowsheet modelling.

Also RedOx reactions of actinides in organic solutions, TBP solutions included, are of interest as regards the comparison of their kinetics and mechanisms with the identical data on those reactions in aqueous solutions. In particular to elucidate the role played by water in those reactions.

This paper deals with the results acquired from studying the reductions of Np(VI) to Np(V) and Np(V) to Np(IV) with U(IV) in 30% TBP solution in n-dodecane.

II. Np(VI) – U(IV) Reaction

The overall stoichiometry of the Np(VI) – U(IV) reaction is given according to the equation:



This reaction was studied spectrophotometrically in 30% TBP solution in n-dodecane using the absorption band of the reaction product Np(V) at 980 nm. It turned out that the molar coefficient of Np(V) extinction decreases with an increase in $[\text{U}(\text{IV})]$, which is governed by the formation of cation-cation complexes of Np(V) with U(IV) (see Section III).

The rate of reaction (1) obeys the second order equation (2) where $k' = 35 \pm 3 \text{ M}^{-1}\text{min}^{-1}$ at 20°C, $[\text{HNO}_3] = 0.3\text{M}$ and $[\text{H}_2\text{O}] = 0.2\text{M}$.

$$-d[\text{Np(VI)}]/dt = k'[\text{Np(VI)}][\text{U(IV)}] \quad (2)$$

With an increase in $[\text{HNO}_3]$ the reaction is decelerated (Table 1); the order of the reaction in relation to HNO_3 changes from ~ -1 to ~ -2 as the concentration of HNO_3 increases from 0.062 M to 0.31 M (see Fig. 1). (The narrow ranges of the concentrations of the reagents, HNO_3 and H_2O , is due to the formation of a second organic phase in the U(IV) – HNO_3 – H_2O – TBP – n-dodecane system).

In this regard the reaction under study is similar to the oxidation of U(IV) with HNO_2 ¹⁾ in which the mechanism of the reaction involves the interaction of U(IV) as twice hydrolyzed ions, $\text{U}(\text{OH})_2^{2+}$, in the slow reaction stages. Hence, if this is true for this reaction we can write down (note that for the sake of clarity the forms of ions are written down without accounting for their complexes with TBP):

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$$-d[\text{Np(VI)}]/dt = \chi[\text{NpO}_2^{2+}][\text{U(OH)}_2^{2+}] \quad (3)$$

Table 1 Rate constants of Np(VI) – U(IV) reaction in 30% TBP at 20°C.

[HNO ₃] M	[H ₂ O] M	k' M ⁻¹ min ⁻¹	k* M ⁻¹ min ⁻¹
0.062	0.30	370	57.1
0.102	0.30	256	58.5
0.123	0.30	216	61.3
0.190	0.30	116	59.9
0.250	0.30	68	55.2
0.250	0.30	72	58.5
0.310	0.30	44	52.2
0.310	0.30	48	57
0.190	0.25	90	62.5
0.190	0.30	116	59.9
0.190	0.35	148	60.6
0.190	0.40	180	61.5
mean		58.7 ± 1.8	

$$^*) k = k'([\text{HNO}_3]^2 + \beta_1[\text{HNO}_3][\text{H}_2\text{O}] + \beta_2[\text{H}_2\text{O}]^2) / [\text{H}_2\text{O}]^2$$

Then, taking into account the constants of U(IV) hydrolysis at the first (β_1) and second (β_2) stages, the reaction rate can be described by equation (4) where $k = \chi\beta_2$.

$$\frac{d[\text{Np(VI)}]}{dt} = k \frac{[\text{Np(VI)}][\text{U(IV)}][\text{H}_2\text{O}]^2}{[\text{HNO}_3]^2 + \beta_1[\text{HNO}_3][\text{H}_2\text{O}] + \beta_2[\text{H}_2\text{O}]^2} \quad (4)$$

The data of Table 1 provide evidence that the dependence of the second order rate constant k' on both $[\text{HNO}_3]$ and $[\text{H}_2\text{O}]$ is actually conveyed by equation (4). Also Fig. 1 shows that the dependence of the reaction rate constant on $[\text{HNO}_3]$ calculated using Eq. (4) agrees with the experimentally observed dependence. The mean value of the overall rate constant in this equation is $k = 58.7 \pm 1.8 \text{ M}^{-1}\text{min}^{-1}$ at 20°C.

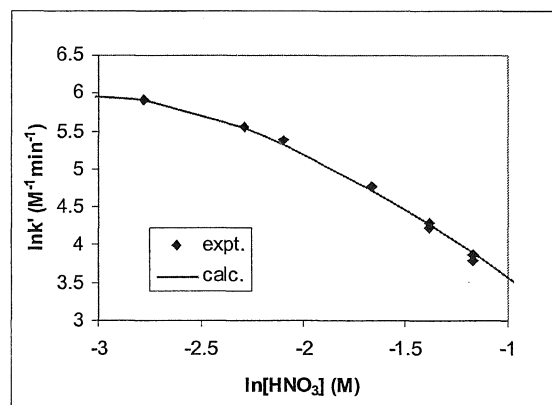


Fig.1 The experimental dependence of the Np(VI) – U(IV) reaction rate constant on $[\text{HNO}_3]$ compared with the calculated dependence from Eq. (4).

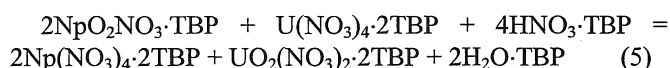
The temperature dependence of k' at $[\text{HNO}_3] = 0.31 \text{ M}$ and $[\text{H}_2\text{O}] = 0.30 \text{ M}$ was studied and the acquired results given are below:

T, °C	15.1	20.0	24.9	30.0	34.9
k', M ⁻¹ min ⁻¹	29	48	73	119	173

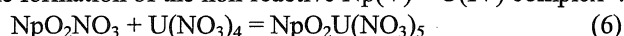
These are adequately expressed by the Arrhenius equation and the activation energy of the reaction is $E = 66.6 \pm 3.8 \text{ kJ/mole}$, which compares with 66.5 and 78.6 kJ/mole in $\text{HNO}_3^{2)}$ and $\text{HClO}_4^{3)}$ respectively.

III. Np(V) – U(IV) Reaction

Under comparable conditions the reduction of Np(V) with U(IV) in 30% TBP solution in n-dodecane, as given in Eq. (5), proceeds by approximately a factor of 40-50 times more slowly than the Np(VI) → Np(V) reduction.



The kinetics of reaction (5) were investigated by following the variations in Np(IV) concentration using its absorption band at 728 nm. The reaction is complicated by the formation of the non-reactive Np(V) – U(IV) complex³⁾:



This absorbs light at a wave length of ~1000 nm with an extinction coefficient of $\epsilon \approx 50 \text{ M}^{-1}\text{cm}^{-1}$. The equilibrium constant of the complex formation was assessed to be $K_1 = 360 \pm 40 \text{ M}^{-1}$ at 15 °C and $K_1 = 400 \text{ M}^{-1}$ at 35 °C. Assuming reaction (5) involves only non-complexed forms of Np(V) and, expressing their concentration via the analytic concentration of Np(V) and the equilibrium constant K_1 given in Eq. (6), leads to:

$$[\text{NpO}_2\text{NO}_3] = [\text{Np(V)}] / (1 + K_1[\text{U(IV)}]) \quad (7)$$

Accounting for the high excess of U(IV)], the reaction rate equation (8) is derived, from which after substituting $[\text{Np(V)}] = a-x$; $[\text{U(IV)}] = b - 0.5x$ and integrating we derive a linear function – Eq. (9).

$$\frac{d[\text{Np(IV)}]}{dt} = \frac{k[\text{Np(V)}][\text{U(IV)}]}{1 + K_1[\text{U(IV)}]} \quad (8)$$

$$(2+2bK_1 - K_1a) \ln(a-x) - 2\ln(2b-x) = (2 + 2bK_1 - K_1a)\ln a - 2\ln 2b + (a-2b)kt \quad (9)$$

This function adequately describes the experimentally acquired kinetic data under all conditions studied.

The values of the second order rate constants obtained are listed in Table 2. The data evidence that the “k” value is independent of the initial concentrations of Np(V) or U(IV) as well as $[\text{HNO}_3]$ (within the range 0.15 – 0.4 M) and H_2O (within the range 0.33 – 0.64 M). The mean value of the rate constant is $k = 24.6 \pm 1.3 \text{ M}^{-1}\text{min}^{-1}$ at 35 °C. The apparent increase in the rate constant observed at $[\text{HNO}_3] \geq 0.5 \text{ M}$ is not understood and needs to be investigated separately.

The temperature dependence of the rate constant was investigated at $[\text{HNO}_3] = 0.3 \text{ M}$ and $[\text{H}_2\text{O}] = 0.4 \text{ M}$. The results are given below and these give an activation energy calculated to be $E = 82 \pm 22 \text{ kJ/mole.}$:

T, °C	26	31	35	41	44	51
k, M ⁻¹ min ⁻¹	4.9	11.3	23.7	29.8	45.7	90.3

Table 2 Rate constants of Np(V) – U(IV) reactions in 30 % TBP solution at 35.0 °C.

[Np(V)] ₀ [*] x10 ⁻³ M	[U(IV)] ₀ [*] x10 ⁻³ M	[HNO ₃] M	[H ₂ O] M	k M ⁻¹ min ⁻¹
1.2	11.6	0.30	0.33	24.1
2.6	12.5	0.30	0.33	24.1
3.1	11.9	0.30	0.33	22.1
2.2	11.6	0.30	0.33	26.9
2.8	8.7	0.30	0.33	26.7
3.0	6.55	0.30	0.33	22.3
2.9	10.8	0.15	0.40	21
2.9	12.2	0.20	0.40	23.6
2.9	11.3	0.30	0.40	23.9
2.9	11.6	0.40	0.37	25.5
2.9	13.3	0.50	0.42	(32.0)
2.3	14.3	0.60	0.50	(37.7)
2.7	12.4	0.30	0.44	22.0
2.9	12.3	0.30	0.50	21.1
3.1	14.1	0.30	0.53	29.5
3.1	11.5	0.30	0.63	25.2
2.5	12.0	0.30	0.64	21.0
mean				24.6 ± 1.3

* "0" subscripts refer to initial concentrations.

It is of interest to note that uranyl nitrate introduced into the reaction solution retards the rate of Np(V) reduction with U(IV). This can be explained by the fact that part of the initial Np(V) becomes incorporated in to a complex with U(VI) – "NpO₂UO₂(NO₃)₃". This Np(V) – U(VI) "cationation" complex is well known²⁾ and has an absorption band at 993 nm. Accounting for the effect of this complex (where K₂ is estimated from spectral data), the rate constant vs. [U(VI)] is expressed via the ratio (10), which is corroborated by the data of **Table 3**.

$$k = k_1 / (1 + K_2[\text{U(VI)}]) \quad (10)$$

Table 3 Rate constant vs. concentration of UO₂(NO₃)₂ at [HNO₃] = 0.3 M, [H₂O] = 0.4 M and 35 °C.

[UO ₂ (NO ₃) ₂] x10 ⁻² M	k M ⁻¹ min ⁻¹	k ₁ [*] M ⁻¹ min ⁻¹
0	23.7	23.7
1.05	21.8	24.1
2.1	19.1	23.1
6.3	16.3	26.2
mean		24.2 ± 2.2

* k₁ = k(1+K₂[U(VI)])

Thus, with U(VI) present the rate of reaction (5) is described by:

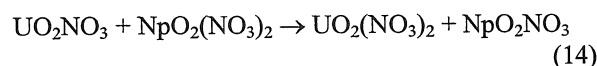
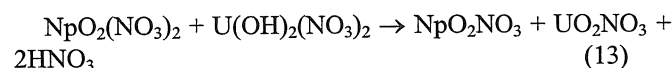
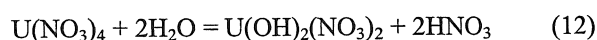
$$\frac{d[\text{Np(IV)}]}{dt} = k_1 \frac{[\text{Np(V)}][\text{U(IV)}]}{(1 + K_1[\text{U(IV)}])(1 + K_2[\text{U(VI)}])} \quad (11)$$

where $k_1 = 24.2 \pm 2.2 \text{ M}^{-1}\text{min}^{-1}$, $K_1 \approx 400 \text{ M}^{-1}$ and $K_2 \approx 10 \text{ M}^{-1}$ at 35°C.

IV. Discussion of Results

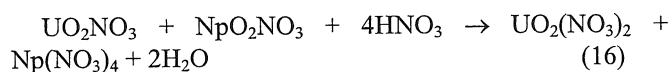
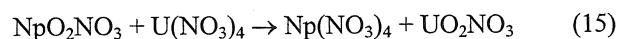
The results of these particular kinetic investigations can now be used in consideration of the actual mechanisms of the Np(VI) → Np(V) and Np(V) → Np(IV) reductions by U(IV) in TBP solution.

The former reaction apparently comprises the stages:



with stage (13) proceeding slowly and stages (12) and (14) proceeding quickly. By comparing this mechanism to that of the reaction in aqueous HClO₄⁽²⁾ and HNO₃⁽³⁾ solutions it can be seen that in both aqueous and TBP solutions hydrolyzed forms of U(IV) are involved. However, in aqueous solution the first hydrolysis product, U(OH)³⁺, proves to be more reactive to Np(VI), whilst in an organic TBP solution the second hydrolysis product, U(OH)₂²⁺, seems to be the more reactive form. It is to be noted that under comparable conditions (e.g. [HNO₃] = 1 M, 20 °C) the rate of reduction of Np(VI) in an aqueous solution proceeds 30-50 times faster than in 30 % TBP solution. This difference in the rates is probably explained by the ratio of the water concentrations in both environments.

As distinct from the Np(VI) – U(IV) reaction, the rate of the subsequent conversion of Np(V) to Np(IV) in TBP solution is independent of either HNO₃ or H₂O concentrations. It is a likely consequence that the mechanism of charge transport occurs between the reagents in their major forms in TBP solution (Eq. 15), followed by a quick oxidation of U(V) (Eq. 16), with part of the reagents combining to form a non-reactive Np(V)-U(IV) complex (Eq. 17).



It is of interest to mention that, unlike reaction (13), reaction (15) in TBP proceeds by a factor of 4000-3000

times more quickly than in aqueous HNO_3 ⁵⁾ or HClO_4 ⁶⁾ solutions (at $[\text{H}^+] = 1 \text{ M}$ and $35 \text{ }^\circ\text{C}$). Water in the reaction apparently has a strong inhibiting effect, the nature of which is not yet clear.

V. Conclusions

Rate equations for the reductions of Np(VI) and Np(V) ions by U(IV) ions in organic solutions of 30 % TBP, containing HNO_3 and H_2O have been determined. Interesting effects of water on their respective rates have been observed. In particular, the rate of Np(V) reduction has been shown to be much faster in 30 % TBP than in aqueous solution. Also the effects of cation-cation complexes of Np(V) with U(IV) and U(VI) on the reaction rates have been explored. These rate equations are suitable for use in process models for the simulation of Purex solvent extraction flowsheets.

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