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Reduction of Np(VI) with Hexamethylenetetraacetic Acid in $HClO_4$ Solution

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Abstract—Spectroscopic method was used to examine the stoichiometry of the reaction of No(VI) with hexamethylenediaminetetraacetic acid (HMDTA, H_4hmdta) in a 0.05 M $HClO_4$ solution. At an excess of Np(VI), 1 mole of complexon reduces about 4 moles of Np(VI) to Np(V). In 0.1–1.0 M $HClO_4$ solutions (the ionic strength of 1.0 was maintained with $LiClO_4$) containing 2–20 mM HMDTA, neptunium(VI) with concentration of 0.3–3.0 M decreases at 35–55°C by the first-order rate law until the instant when less than 20% Np(VI) remains. The initial reaction rate has the first order in [HMDTA] and –2 order in [H^+]. An activated complex is formed with loss of two H^+ ions. The activation energy is 102 ± 7 kJ/mol.

Keywords: neptunium(VI), hexamethylenediaminetetraacetic acid, reduction, kinetics

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In a systematic study of the stability of Np(VI) in complexon solutions, attention has been given to the influence exerted by the number of nitrogen atoms and carboxylate groups in a complexon molecule and to the structure of a carbon chain between nitrogen atoms. In the present study, we examined the behavior of an analog of EDTA, i.e., the complexon in which the carbon chain of six methylene groups replaced the ethylene group in the EDTA molecule. The molecule of hexamethylenediaminetetraacetic acid (HMDTA) differs from the EDTA molecule in its solubility in water and acid media and also in the value of the dissociation constants. It is difficult to predict the reducing capacity of HMDTA in comparison with EDTA. This problem can be only solved experimentally.

EXPERIMENTAL

A ^{237}Np preparation was used in experiments. Neptunium was purified and a stock solution of Np(VI) was prepared and normalized by the procedure reported in [1]. Hexamethylenediaminetetraacetic acid of pure grade (main-substance content no less than 99%) was used without additional purification. A weighed portion of HMDTA was mixed with a LiOH solution in a 1 : 2 molar ratio. The Li_2H_2hmdta solution was quantitatively transferred into a measuring flask. Chemically pure $HClO_4$ and $LiClO_4$ of pure grade were used. Lithium perchlorate was recrystallized from a bidistillate and dried in air. All the solutions were prepared with a bidistillate and normalized by the known procedures.

When studying the reaction stoichiometry, we introduced an aliquot of the Li_2H_2hmdta solution into a quartz cuvette (*l*c1 cm) with a solution of Np(VI) in $HClO_4$ and the optical absorption at 981 nm, where the main absorption band of Np(V) is peaked, was periodically recorded with a Shimadzu PC 3100 (Japan) or SF-46 LOMO (Russia) spectrophotometer. In kinetic studies, an aliquot of a Np(VI) solution was added to the $HClO_4$ + H_4hmdta solution in a thermostated cuvette and the increase in the Np(V) concentration was monitored. Each experiment was repeated 2–3 times.

RESULTS AND DISCUSSION

The stoichiometry of the reaction Np(VI) + H_4hmdta was examined in 0.01 M $HClO_4$ at 23°C and 0.05 M $HClO_4$ at 45°C. The initial concentrations of Np(VI) and H_4hmdta were 3 and 0.5 mM, respectively. The Np(V) concentration was calculated by using the molar absorption coefficient of 403 M^{-1} cm^{-1}. At room temperature, 1.58 mM of Np(V) was formed in 70 h, and 1.9 mM of Np(V) accumulated at 45°C in 8.7 h, i.e., Δ[Np(V)]/Δ[H4hmdta] is close to 4. Below, an example is presented of one of the runs.

Time, h	0.014	0.033	0.211	4.17	8.67
[Np(V)], M	0.54	0.82	1.44	1.70	1.90

Presumably, the reaction between Np(VI) and H_4hmdta occurs at a high rate because the stoichiometric coefficient reached a value of 1.6 already in 2 min. The further accumulation of Np(V) is due to the slow reaction of Np(VI) with decomposition products of HMDTA. The data obtained suggest that the following reactions occur in solutions containing $HClO_4$ and H_4hmdta.

$$\mathrm{Np(VI)} + \mathrm{H_4hmdta} \rightarrow \mathrm{Np(V)} + \mathrm{R_1}\,(\text{slowly}), \quad (1)$$

$$\mathrm{Np(VI)} + \mathrm{R_1} \rightarrow \mathrm{Np(V)} + \mathrm{R_2}\,(\text{rapidly}), \quad (2)$$

$$\mathrm{Np(VI)} + \mathrm{R_2} \rightarrow \mathrm{Np(V)} + \mathrm{R_3}\,(\text{slowly}), \quad (3)$$

$$\mathrm{Np(VI)} + \mathrm{R_3} \rightarrow \mathrm{Np(V)} + \text{low-activity products}. \quad (4)$$

The kinetics of the reaction Np(VI) + H_4hmdta was examined in 0.1–1.0 M $HClO_4$ solutions at a ionic strength $I = 1.0$ M, maintained by addition of $LiClO_4$. Figure 1 shows kinetic dependences plotted in the time–$\log(D_\infty - D)$ for 0.25 M $HClO_4$ + 0.75 M $LiClO_4$ solutions containing 10 mM of H4hmdta and 0.3, 1.0, and 3.0 mM of Np(VI) at 45°C.

$[H_4\mathrm{hmdta}]$, mM	2	3	5	10	20
$k' \times 10^4$, s^{-1}	3.60	4.80	9.50	19	40
k, $M^{-1} \cdot s^{-1}$	0.18	0.16	0.19	0.19	0.20

The kinetic dependences are linear until half or more of Np(VI) has reacted.

The linearity of the initial portions of the kinetic curves plotted in semilog coordinates is indicative of the first order of the reaction in Np(VI). The reaction rate is described by the equation

$$-\mathrm{d}\big[\mathrm{Np(VI)}\big]/\mathrm{d}t = k'\big[\mathrm{Np(VI)}\big]$$
$$= k'\Big(\big[\mathrm{Np(V)}\big]_\infty - \big[\mathrm{Np(V)}\big]\Big), \quad (5)$$

where k' is the first-order rate constant. In the integral form, equation (5) passes on replacing [Np(V)] with D proportional to the concentration into the equation

$$2.3\log\big(D_\infty - D\big) = -k't + \text{const}. \quad (6)$$

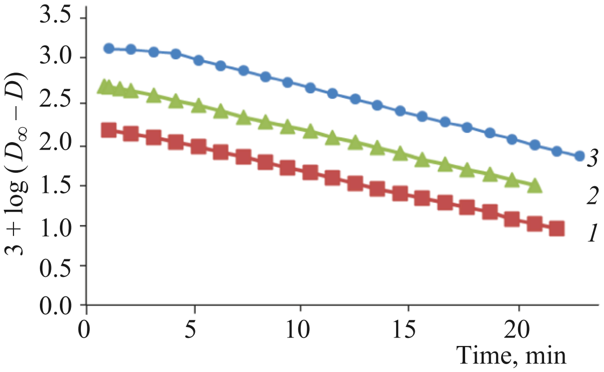

Fig. 1. Kinetic curves for the reduction of Np(VI) by H_4hmdta molecules at 45°C. 0.25 M $HClO_4$, 0.75 M $LiClO_4$, 10 mM H_4hmdta. [Np(V)], mM: (*1*) 0.3, (*2*) 1.0, (*3*) 3.0.

The first-order rate constant grows with increasing H_4hmdta concentration. This can be seen for the example of 0.25 M $HClO_4$ and 0.75 M $LiClO_4$ solutions containing 1 mM Np(VI) and 2–20 mM H_4hmdta at 45°C.

The bimolecular rate constant $k = k'/[H_4\mathrm{hmdta}]$ remains nearly constant in the range of H_4hmdta concentrations under study, which is indicative of the first order in the reducing agent. Table 1 lists k values obtained in different conditions.

It follows from the values listed in Table 1 that the rate of Np(VI) reduction sharply decreases with increasing concentration of perchloric acid. Figure 2 shows the dependence of k on $[H^+]$, plotted in the logarithmic coordinates. At 45°C, experimental points fall on the straight line with slope ratio of –2.0. Therefore, a conclusion can be made that the reduction occurs via formation of an activated complex with

Table 1. Effect of conditions on the bimolecular rate constant of the reaction Np)VI) + H_4hmdta. I = 1.0 M. [H4hmdta] = 3–10 mM, [Np(VI) = 1 mM.

T, °C	$[HClO_4]$, M	k, M^{-1} s^{-1}
45.0	0.10	1.520
	0.25	0.190
	0.50	0.050
	1.00	0.012
35.0	0.25	0.060
40.0	0.25	0.120
49.5	0.25	0.38
55.0	0.25	0.68

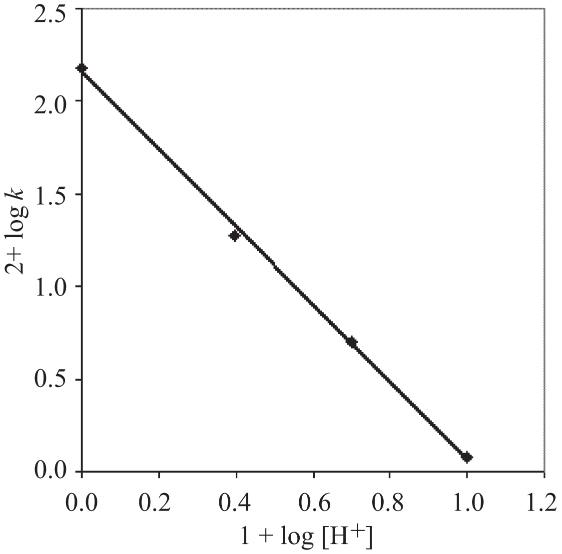

Fig. 2. Effect of the concentration of H^+ ions on the rate constant of Np(VI) reduction by H_4hmdta molecules in a solution with ionic strength of 1.0 at 45°C.

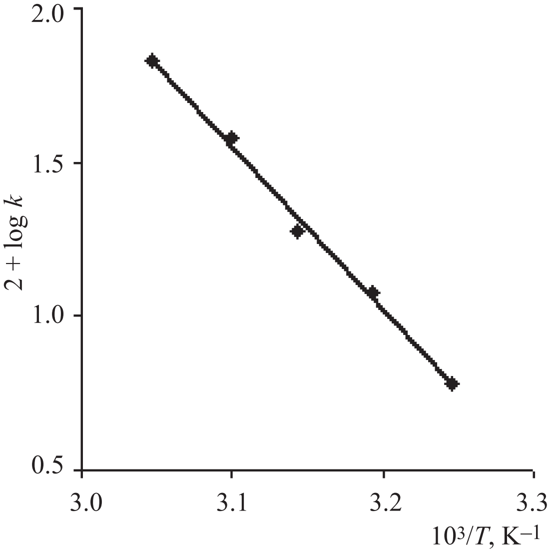

Fig. 3. Dependence of the logarithm of the rate constant of Np(VI) reduction on inverse temperature in 0.25 M $HClO_4$ + 0.75 M $LiClO_4$ solutions.

splitting of two protons, but it is not improbable that protons are separated in equilibrium reactions before the appearance of an activated complex.

Changing the ionic strength affects the rate of the reaction Np(VI) + H_4hmdta. In a 0.1 M $HClO_4$ solution, $k = 3$ M^{-1} s^{-1}, and in a 0.1 M $HClO_4$ + 0.9 M $LiClO_4$ solution, $k = 1.52$ M^{-1} s^{-1}. The decrease in the reaction rate with increasing ionic strength is characteristic of the interaction of oppositely charged species.

In solutions, there exist the equilibria

$$H_4\text{hmdta} = H_3\text{hmdta}^- + H^+,$$
$$H_3\text{hmdta}^- = H_2\text{hmdta}^{2-} + H^+.$$

The activated complex (AC) is formed by the reaction

$$NpO_2^{2+} + H_2\text{hmdta}^{2-} = AC.$$

Further, charge transfer occurs in the activated complex

$$AC \rightarrow NpO_2^+ + R_1.$$

The radical R_1 rapidly reacts with Np(VI), but it is not impossible that the radical activates the molecule or the ion of the reducing agent.

Figure 3 shows the temperature dependence of k in the Arrhenius coordinates. The activation energy found from this dependence 102 ± 7 kJ/mol.

Comparison of the kinetic patterns for the reactions of Np(VI) with H_4edta and H_4hmdta shows that the rate constants are markedly different under identical conditions, the reaction mechanisms involving these compounds being also different.

CONFLICT OF INTEREST

The authors state that they have no conflict of interest.

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