Kinetics of reduction of hexavalent neptunium by nitrous acid in solutions of nitric acid

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Nitrous acid is a key redox controlling factor, affecting the speciation of neptunium in the reprocessing of used nuclear fuel by solvent extraction. The kinetics of the reduction of neptunium(VI) by nitrous acid in solutions of nitric acid was investigated spectrophotometrically by the method of initial rates. The reaction is first order with respect to Np(VI) while the order with respect to HNO_2 is 1.20 ± 0.04. The reaction rate is inversely proportional to the hydrogen ion concentration (corrected for incomplete dissociation of HNO_3 in strongly acidic solutions), indicating that the reaction proceeds primarily through the reaction of neptunium(VI) with the nitrate anion. The experimental value of the rate constant k for the rate law $-d[Np(VI)]/dt = k \cdot [Np(VI)] \cdot [HNO_2]^{1.2}/[H+]$ is of (0.163 ± 0.014) $M^{-0.2}s^{-1}$ in $I = 4$ M and at 20°C. The activation energy is (-57.3 ± 1.6) kJ/mol, which is in agreement with previous data on this reaction in perchloric acid.
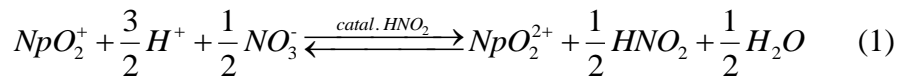
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Introduction

Extraction of hexavalent and tetravalent actinides with tributyl phosphate (TBP) from nitric acid solutions is the most widely used industrial process for the reprocessing of used nuclear fuel (UNF) and is the basis for the development of advanced reprocessing schemes like UREX and TRUEX. An unresolved issue of UNF reprocessing is the management of neptunium in the extraction system because of its not clearly defined redox speciation. Neptunium is present in both pentavalent (V) and hexavalent (VI) oxidation states that differ greatly in their extractability to the organic phase (hexavalent state being very well extracted by TBP, whereas pentavalent neptunium is almost not extracted). As a result,

neptunium is distributed in both organic and aqueous streams of the separation process.

Nitrous acid, the key redox controlling factor, is always present in these systems, as it forms during the dissolution of UNF and by the radiolysis of nitric acid. Low linear energy transfer radiation like β and γ have radiation yields of HNO_2 around 0.25 mM/kGy in 1M HNO_3, and the radiation yields of α particles are approximately two times lower [1].Nitrous acid HNO_2 is relatively well extracted by TBP (log $D \approx 1$) and is therefore distributed from the source raffinate solution in further stages of the separation system [2].The influence of nitrous acid on the redox state of neptunium is complex. If HNO_2 is present in a small concentration, it primarily acts as a catalyst of the oxidation of Np(V) by nitric acid. This reaction is an autocatalytic process, as additional HNO_2 is produced. However, if neptunium is initially present primarily in the hexavalent state, large concentrations of HNO_2 lead to reduction back to the pentavalent state. Both reactions are governed by an acidity-dependent equilibrium:

$$NpO_2^+ + \frac{3}{2}H^+ + \frac{1}{2}NO_3^- \xleftrightarrow{\text{catal. }HNO_2} NpO_2^{2+} + \frac{1}{2}HNO_2 + \frac{1}{2}H_2O \qquad (1)$$

The reaction equilibrium can be characterized by an apparent equilibrium constant K_{app} from measured concentrations of Np(VI), Np(V), nitric acid and nitrous acid in equilibrium:

$$K_{app} = \frac{[Np(VI)][HNO_2]^{1/2}}{[Np(V)][HNO_3]^2} \qquad (2)$$

The value of the constant and its dependence on ionic strength, acidity and temperature has been measured by many authors [3-7] and varies between $K_{app} = 3 \times 10^{-4} - 2 \times 10^{-3}$. Some of these authors have also investigated the kinetics of oxidation of Np(V) by HNO_3.[3-5,8] Both spectrophotometry and solvent extraction methods have been employed. The analysis of the system proved to be quite complex and the reported forms of the rate law and its associated rate constants vary greatly between the authors.

The rapid reduction of Np(VI) to Np(V) by the addition of nitrite to solutions of 1M HNO_3 was observed already during the initial studies on the redox properties of neptunium performed during the Manhattan Project by Magnusson et al.[9] Since then, the kinetics of reduction of Np(VI) by HNO_2 has attracted just a little

interest. To our best knowledge, only two in-depth studies about this issue have been undertaken [10,11].

Shilin and Nazarov [10] studied the Np(VI) reduction kinetics in the nitric/nitrate system in an excess of HNO_2 as an apparent first order reaction with respect to the concentration of Np(VI). However, their original proceeding paper is not available, and all information about their results was adopted from a secondary reference, a review paper by Koltunov and Marchenko [12].

A comparative study between the rates of oxidation of HNO_2 by Np(VI) and Am(VI) in a non-complexing perchlorate system has been analyzed by a spectrophotometric stopped-flow method by Woods et al. [11]. These researchers have utilized both first and second order kinetic relations to describe the progress of the reaction. Differences between the activation energy values and dependencies of the reaction rate on the concentration of HNO_2 and hydrogen ion reported by these two studies are discussed below. In order to clarify these discrepancies, the kinetics of the studied oxidation reaction was investigated using UV-VIS-NIR spectrophotometry.

Experimental

Chemicals

Distilled, deionized water (Barnstead Nanopure, 18 MΩ·cm resistivity) was used for all experiments. 68% nitric acid (EMD Chemicals GR ACS grade) was used for preparation of HNO_3 stock solutions. The concentration of the nitric acid stock solution was determined to ±0.3% precision by titration using sodium hydroxide standardized by potassium hydrogen phthalate (Analytical Reagent, Mallinckrodt). Solutions of lithium nitrate (Alfa Aesar, anhydrous, 99.999% pure - metals basis) in distilled water were used in experiments to control ionic strength. Stock solutions of sodium nitrate $NaNO_2$ (Mallinckrodt, analytical reagent) were dissolved in neutral distilled water and used as a source of nitrite anions.

Neptunium

^{237}Np ($t_{1/2}$ = 2.1 $\times 10^6$ y) was received as NpO_2 from Argonne National Laboratory and dissolved in a slight molar excess of H_2O_2 and 8 M HNO_3. Confirmation of the tetravalent oxidation state was determined using Vis-NIR

spectroscopy. In order to remove any transuranic impurities, the Np solution was added to a prepared BioRad AG-1 anion exchange column. The column was rinsed with a solution of 8 M HNO_3, 0.3 M hydrazine monohydrate, and 2 g/L hydroquinone. Np was stripped from the column using 0.36 M aq. HCl and its isotopic purity was confirmed using thin-window HPGe gamma spectrometry. Any organic impurities were destroyed by concentrated nitric acid and hydrogen peroxide. After re-evaporation with nitric acid, an approximate 15mM stock solution of the purified neptunium was made in 4 M HNO_3. The solution had its oxidation state adjusted in a glass H-cell by electrolysis on a Pt wire electrode at potential +1.3V vs. reference Ag/AgCl electrode. The electrochemical process was controlled by a BASi Epsilon[TM] e2 potentiostat.Following the electrolysis, Np existed in the hexavalent oxidation state in greater than 95% (the remainder existed as the pentavalent oxidation state).

Instrumentation

Absorption spectrophotometry in an open-air 1 cm path-length quartz cuvette was performed using two spectrometer instruments.

Near-infrared spectroscopy over a 900-1300 nm range was performed using an Olis[®] RSM 1000 Monochromator equipped with a double grating (600 lines/mm, 1μm blazed wavelength), an 800 nm high-pass filter, two InGaAs (sample and reference) detectors and a 300W tungsten halogen light source. A full spectral scan was collected over a 1 minute period; however, in this mode the instrument was not appropriate for the subsequent kinetic experiments, whose timescale was only a few minutes.

A wide UV-VIS-NIR range of 200-1000 nm was monitored by an OceanOptics[TM] QE65000 spectrometer (fiber optic system) with combined deuterium/halogen light source DH-2000 BAL. As opposed to the RSM 1000, the diode-array detector of the QE65000 spectrophotometer permitted the recording of absorbance on all selected wavelength within the 200-1000nm range simultaneously. To minimize noise, an integration interval of up to 5 seconds was employed for each absorbance measurement. The temperature of cuvette holder used during the kinetic experiments was controlled to ±0.02°C (Quantum Northwest). To assure a homogenous solution during the reactions, a magnetic stirrer was used to mix the contents of the cuvette.

Full spectral scans recorded before and after each experimental run were taken by both instruments. The spectra were then fitted to a digitized reference spectra published for $0.1 – 4.0$ M HNO_3 solutions by Friedman et al.[13] in order to determine the quantitative redox speciation of neptunium between Np(V) and Np(VI). The characteristic peaks at wavelengths 980nm for Np(V) and 1220 nm for Np(VI) were primarily observed. No absorption peaks characteristic of Np(IV) were observed during any experiments.

Observation of the kinetic progress

During kinetic experiments, the liquid content of the quartz cuvette was continuously stirred with a small magnetic stir bar; therefore, the desired initial concentrations of the reactants in the cuvette were achieved in several seconds after addition of a calculated solution of $NaNO_2$ to a prepared solution of Np(VI) in the cuvette. The extent of the reaction was monitored in 1 or 5 second intervals by recording the absorbance at 980 nm where the spectrum of Np(V) has a maximum (the molar absorption coefficient value of Np(V) at 980nm is $\varepsilon = 395$ $M^{-1}cm^{-1}$ [14]).

The baseline noise and the influence of initial turbulences, created by mixing during the first several seconds of the reaction, were observed at a side wavelength of 950 nm, at which none of the involved species (Np(V), Np(VI), HNO_2) have a significant absorption coefficient. Subtracting the absorbance at 950 nm from absorbance at 980 nm allowed observing the reaction during the mixing period. The rate of the reaction can be calculated from the change in the absorbance A at 980nm as follows:

$$\frac{d[Np(V)]}{dt} = -\frac{d[Np(VI)]}{dt} = \frac{1}{\varepsilon} \cdot \frac{dA}{dt} \quad (3)$$

Nitrous acid instability

The setup of the experiments and its analysis was complicated by the instability of nitrous acid in solutions exposed to air. The solution of HNO_2 was prepared by a direct addition of a spike of concentrated stock aqueous solution of sodium nitrite. Because HNO_2 is a relatively weak acid, almost all nitrite was immediately protonated. A decrease of the HNO_2 concentration was observed by monitoring its absorption peaks in the 340-400 nm UV region in a stirred cuvette. A

characteristic half-life of the HNO_2 was observed and quantified to be approximately 1 hour. $NaNO_2$ solutions in distilled water are not susceptible to decomposition/evaporation. This was verified by regular checking of the UV absorbance created by diluting a defined volume of the $NaNO_2$ stock solution in 1 M HNO_3.

The decomposition rate of nitrite in acid decreased significantly when the top of solutions in cuvette was protected [15] with a thin layer of a pure n-dodecane; however, this practice was eventually disregarded as the regeneration of neptunium after the experiment became exceedingly complicated.

Due to the short time available for assuming a quasi-stable concentration of excess amounts of HNO_2, the kinetic analysis was eventually performed through the method of initial reaction rates, as opposed to both studies by Shilin et al. and Woods et al. who assumed an apparent reversible first order kinetics for processing the data.

Data analysis

The initial rate was calculated from the slope of a least squares linear regression through the first 10% of data points for the reaction extent. Replicate experiments were not performed due to limited amount of neptunium stock solution; however, the reaction rate uncertainties were estimated to account for a 10% uncertainty range which is indicated by the error bars in all the figures. The influence of this uncertainty was taken in account in the estimation of uncertainty for slopes of dependencies on log-log plots. Rate constants have their uncertainty estimated by a single standard deviation.

Results and discussion

Determination of reaction orders with respect to Np(VI) and HNO_2

Both the observed reaction rate of the Np(VI) reduction and the equilibrium reaction extent increased with increasing initial concentration of the reducing agent, nitrous acid. The individual reaction orders with respect to both Np(VI) and HNO_2 were found from the slope of the log-log dependence of the initial reduction rates against the variation of reactant concentrations; see figure 1.
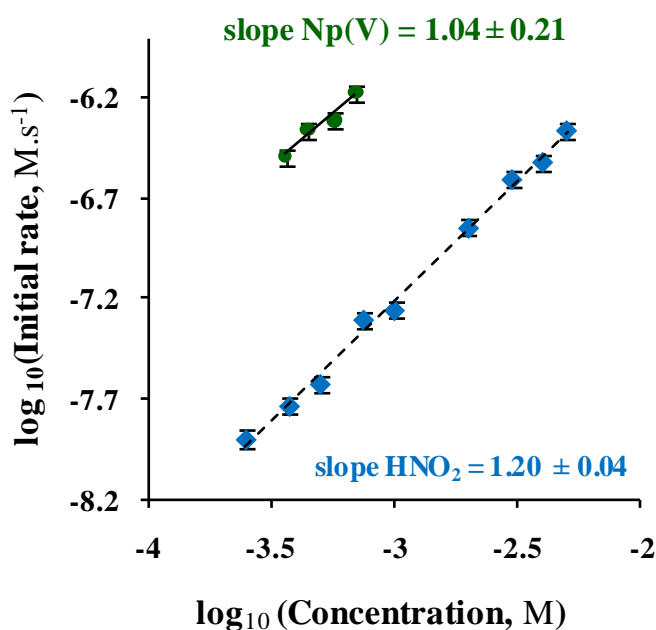
Fig. 1 Determination of reaction orders with respect to initial conc. of Np(VI) and HNO$_2$

(initial conditions: 4 M HNO$_3$, t = 20.0°C;

● C$_{HNO_2}$ = 5.0 mM, C$_{Np(VI)}$ = 0.36-0.70 mM; ♦ C$_{Np(VI)}$ = 0.44 mM, C$_{HNO_2}$ = 0.25 - 5.0 mM)

The slope for the Np variation was determined to be 1.04 ± 0.21, which indicates that the order with respect to Np(VI) is most likely to be one − as expected. However, the order of reaction with respect to HNO$_2$ was 1.20 ± 0.04, which is higher than 1.00 with a high degree of certainty.

Effect of H⁺ / HNO$_3$ concentration and ionic strength

In order to observe the influence of the hydrogen ion concentration on the initial rate, the kinetic experiments were performed with a set of aqueous solutions, where the concentration of nitric acid varied from 0.75 M to 4 M HNO$_3$, while maintaining the total ionic strength of solutions of μ = 4 M by the addition of LiNO$_3$ as a background salt, see figure 2. The initial rate significantly decreases with increasing acid concentration. The slope of the dependence of the initial rate on the analytical concentration of HNO$_3$ was equal to − 0.92 ± 0.06. However, the hydrogen ion concentration has to be corrected for incomplete dissociation of the nitric acid in strongly acidic solutions. After calculating the real H⁺ concentrations by applying dissociation constant pK_a = -1.44 [16] and ionic strength corrections (γ$_±$ = 1.15) [17], the calculated slope decreased to − 0.99 ± 0.06. This means that

the rate was found to be almost exactly inversely proportional to the hydrogen ion concentration.

As opposed to the effect of H⁺ concentration, no significant dependence of the initial rate was observed when the ionic strength μ (total nitrate concentration) was varied at a constant HNO₃ concentration of 1 M (fig. 2).
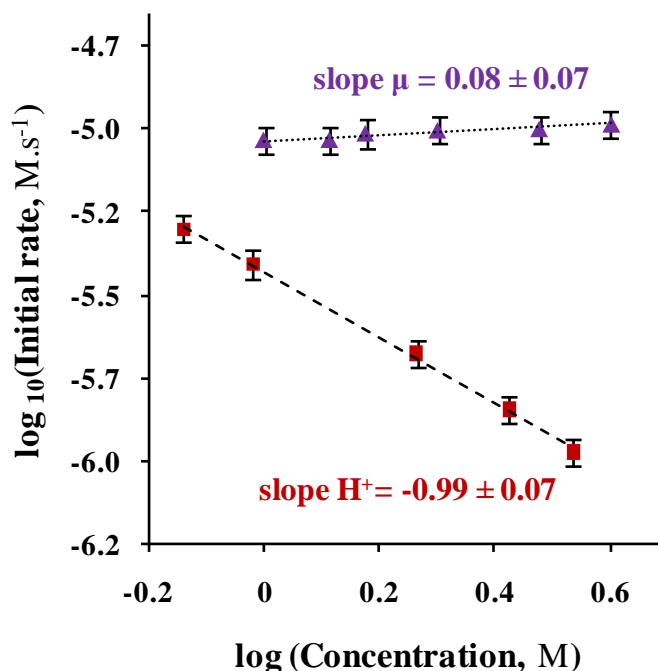

Fig. 2 Effect of the molar conc. of hydrogen ions H+ and ionic strength μ on the initial reaction rate (initial conditions: t = 25.0°C,
■ - effect of H⁺: C_{HNO_2} = 5.0 mM, $C_{Np(VI)}$ = 0.90 mM , μ = 4 M (Li/H)NO₃
▲ - effect of μ : C_{HNO_2} = 6.0 mM, $C_{Np(VI)}$ = 0.60 mM, 1 M HNO3 + 0-3 M LiNO₃)

Discussion on the form of the rate law

From the apparent experimental form of the rate equation derived above, the current investigation arrived at the following form:

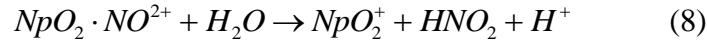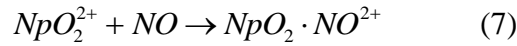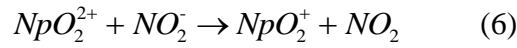$$-\frac{d[Np(VI)]}{dt} = k^* \frac{[Np(VI)][HNO_2]^{1.2}}{[H^+]} \qquad (4)$$

As calculated from the initial rate data for T = 20°C and μ = 4 M, the value of the apparent rate constant is $k^* = (0.163 \pm 0.014)$ M$^{-0.2}$s^{-1}. The findings are in approximate agreement with the previous findings Shilin and Nazarov [10] who have determined that the reaction orders with respect to Np(VI) were one and with respect to HNO₂ were somewhere between orders 1.0 and 1.5. The reaction order with respect to HNO₃ concentration was -0.85, and after correcting their data on

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incomplete HNO_3 dissociation, the apparent order with respect to H^+ increases to -0.94 ± 0.01. This is in close proximity to the value determined presently.

Shilin and Nazarov proposed that the reverse reaction (1) proceeds via two pathways in which there are two direct species responsible for the reduction of $Np(VI)$ [12]. The first is the nitrate ion NO_2^- produced by dissociation of nitrous acid (its concentration is therefore inversely proportional to the $[H^+]$ concentration). The second reductant is nitric oxide created by the disproportionation of HNO_2:

$$3HNO_2 \rightleftarrows 2NO + HNO_3 + H_2O \qquad (5)$$
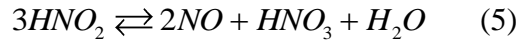
The mechanism of the reaction can then be expressed by the following scheme:

$$NpO_2^{2+} + NO_2^- \rightarrow NpO_2^+ + NO_2 \qquad (6)$$

$$NpO_2^{2+} + NO \rightarrow NpO_2 \cdot NO^{2+} \qquad (7)$$

$$NpO_2 \cdot NO^{2+} + H_2O \rightarrow NpO_2^+ + HNO_2 + H^+ \qquad (8)$$

Equations (6) and (7) are the rate limiting steps. The resulting form of the rate law then has two terms dependent on HNO_2:

$$-\frac{d[Np(VI)]}{dt} = [Np(VI)]\left(k_1 \frac{[HNO_2]}{[H^+]} + k_2 \frac{[HNO_2]^{1.5}}{[H^+]^{0.5}[NO_3^-]^{0.5}} \right) \quad (9)$$

The values of the constants k_1 and k_2 were reported by Shilin and Nazarov as 0.97 s^{-1} and 15.5 M$^{-0.5}$s^{-1}, respectively [12].

By modifying equation (9) for the case of the initial rate observation:

$$\frac{\left(-\dfrac{d[Np(VI)]}{dt} \right)_{init}}{[Np(VI)][HNO_2][H^+]^{-1}} = \left(k_1 + k_2 \frac{[H^+]^{0.5}}{[NO_3^-]^{0.5}} [HNO_2]^{0.5} \right) \quad (10)$$
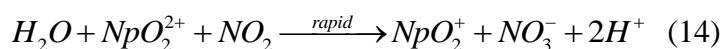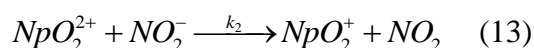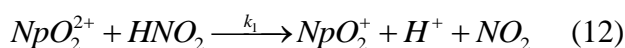
and plotting the left hand side against the variable initial concentration parameter $[H^+]^{0.5}[NO_3^-]^{-0.5}[HNO_2]^{0.5}$, the constants k$_1$ and k$_2$ can be received as an intercept and a slope of the resulting plot. In the case of the non-integer dependence of the reaction rate on the HNO_2 concentration, fitting data by equation 10 yielded the values of constants $k_1 = (0.29 \pm 0.03)$ s^{-1} and $k_2 = (5.43 \pm 0.79)$ M$^{-0.5}$s^{-1}. This is in general agreement with the identified experimental rate law (4). However, plotting of the data in the same manner for the dependence of the initial reaction rate on $[H^+]$ in a constant nitrate concentration , didn't provide constants with

approximately the same values. In the present investigation, no significant dependence on the nitrate concentration was identified (Fig. 2); the particular form of the dependence of the second term on H^+ and NO_3^- is the most probable reason.

On the contrary, for Np(VI) reduction by nitrous acid in perchlorate medium of lower concentrations (0.1 - 1.0 M $HClO_4$/$NaClO_4$), Woods et al. [11] reported first order with respect to both reactants. For the rate dependence on the H^+ concentration they have identified the rate law to be of a different form:

$$-\frac{d[Np(VI)]}{dt} = [Np(VI)][HNO_2]\left(k_1 + \frac{k_2}{[H^+]}\right) \qquad (11)$$

The values of the second order constants were $k_1 = 2.01 \pm 0.45$ $M^{-1}s^{-1}$ and $k_2 = 1.56 \pm 0.07$ s^{-1} for 25°C and 1 M ionic strength. The authors have proposed a mechanism plausible with this law:

$$NpO_2^{2+} + HNO_2 \xrightarrow{k_1} NpO_2^+ + H^+ + NO_2 \qquad (12)$$

$$NpO_2^{2+} + NO_2^- \xrightarrow{k_2} NpO_2^+ + NO_2 \qquad (13)$$

$$H_2O + NpO_2^{2+} + NO_2 \xrightarrow{rapid} NpO_2^+ + NO_3^- + 2H^+ \qquad (14)$$

where reactions (12) and (13) are the rate limiting steps.

In the present study, the rate the order with respect to the concentration of HNO_2 has been found to be greater than 1. Also, no term independent on H^+ concentration has been identified in the rate equation (4). Therefore, it is most likely that in a nitrate environment, the direct reaction (12) of the HNO_2 molecule with Np(VI) is either not possible or very slow.

Effect of temperature

The initial reaction rates are strongly dependent on temperature. Their thermal activation has been examined in 4 M HNO_3 in a temperature range of 10-40°C. Under the same initial reactant concentrations the initial rate would be proportional only to the change of rate constant(s). Therefore, the dependence of the initial rate was evaluated by an equation derived from the Arrhenius equation in order to determine the activation energy E_A:

$$R \cdot \ln\left(-\frac{d[Np(VI)]}{dt}\right)_{init.} = -\frac{E_A}{T} + const. \qquad (15)$$

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$R = 8.314$ J·K^{-1}mol^{-1} is the universal gas constant and T is the absolute temperature in kelvins. From the slope of the data points plotted in figure 3 the activation energy was determined as $E_A = (57.3 \pm 1.6)$ kJ/mol. This is in slight disagreement with the data by Shilin et al. [10] that activation energy is (62.0 ± 1.3) kJ/mol.

However, Woods et al. [11] have calculated activation energies of (51.5 ± 2.4) kJ/mol and (70.0 ± 4.4) kJ/mol for 1 M perchlorate system for the [H$^+$]-independent and [H$^+$]-inversely dependent rate constants k_1 and k_2 (eq. 11), respectively. Interestingly, using the data of Woods et al. with the assumption that [H$^+$] = 1.0 M, the effective value of activation energy calculated from the temperature variation of an observed second order rate constant k_{obs} in the rate law

$$-\frac{\mathrm{d}[Np(VI)]}{\mathrm{d}t} = k_{obs}[Np(VI)][HNO_2] \qquad (16)$$

in perchlorate medium would be (57.9 ± 2.0) kJ/mol, which is in very good agreement with the value for nitrate medium reported in the present paper.

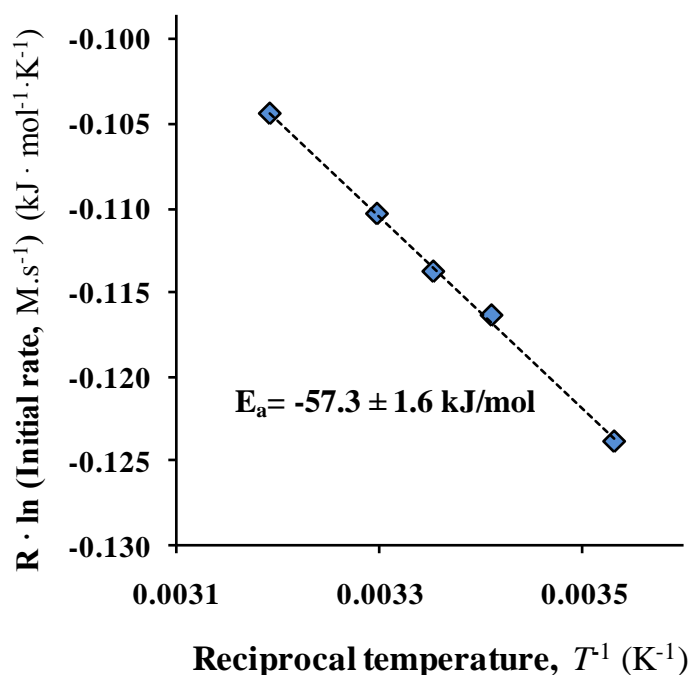**Fig. 3** Determination of activation energy of reduction of Np(VI) by HNO$_2$
(initial conditions: t = 10.0 - 40.0°C, C_{HNO_2} = 6.0 mM, $C_{Np(VI)}$ = 0.60 mM, 4 M HNO$_3$, errors of rate determination are smaller than the symbols)

Conclusion

For the reduction of Np(VI) by nitrous acid in a nitrate medium , the results of the present investigations of the reaction orders with respect to concentrations of Np(VI), HNO_2 and H^+ agree reasonably well with the previous investigations in the nitrate environment [10]. However, a significant difference was determined in the exact form of the rate law. As opposed to previous findings, no notable dependence on the NO_3^- concentration was observed. The currently determined value of the activation energy is slightly different, but agrees well with the apparent value determined for the reaction in 1 M $HClO_4$ environment [11].

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