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Catalytic Reduction of Np(VI) with Formic Acid in the Presence of Platinum Nanoparticles

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Abstract—The kinetics of catalytic reduction of Np(VI) with formic acid in the presence of Pt nanoparticles of different types ("brown" colloid stabilized with sodium polyacrylate and nonstabilized "gray" colloid) was studied. In both cases in the examined range of conditions ($[\mathrm{Np(VI)}]_0 = 2.80 \times 10^{-4}$–$9.03 \times 10^{-4}$ M; [HCOOH] = 0.03–1.0 M; [Pt] = 4×10^{-7}–2×10^{-5} M; T = 18–60°C) the reaction is zero-order with respect to [Np(VI)] and first-order with respect to [HCOOH]. The catalytic activity of the nonstabilized "gray" colloid exceeds by almost an order of magnitude that of the "brown" colloid, due to the blocking effect of stabilizing polyelectrolyte molecules on the active catalytic centers. The dependence of the reaction rate on the sodium polyacrylate concentration in the range 1×10^{-4}–1×10^{-2} M is nonmonotonic, due to deflocculation of the nanoparticles. The mechanism of the catalytic reduction of Np(VI) with formic acid in the presence of Pt colloids is discussed; it involves a slow step of dissociative chemisorption of HCOOH molecules on the nanoparticle surface.

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Metal nanoparticles, primarily those of platinum-group metals, actively and selectively catalyze many redox processes [1–5]. Nanoparticles prepared by different methods noticeably differ in the catalytic activity [5]. Elucidation of the mechanism of the catalytic effect and its correlation with the structure and nature of nanocolloids is an urgent problem.

The catalytic effect of platinum-group metal colloids on redox processes involving actinide ions was observed for the first time in reduction of Pu(IV) with formic acid on colloidal particles of Pd metal, formed in the course of exhaustive denitration with formic acid of process solutions from spent nuclear fuel reprocessing [6]. The observations were only qualitative; no data on the kinetics and mechanism of the process were reported. Catalytic reactions of actinide ions with HCOOH in the presence of heterogeneous supported platinum catalysts were studied in sufficient detail. However, no data are available on the course of these processes in the presence of Pt nanoparticles occupying an intermediate position between heterogeneous and homogeneous catalytic systems. At the same time, such data are of considerable scientific and practical interest for elucidating the mechanism of charge transfer between an actinide ion and a redox reagent in the presence of platinum-group metal nanoparticles and for understanding regular trends in variation of actinide valence forms in real systems from reprocessing of irradiated nuclear materials.

This study concerning the reduction of Np(VI) with formic acid in the presence of Pt nanoparticles opens a series of papers on the redox behavior of actinide ions under catalysis with nanoparticles of platinum-group metals.

EXPERIMENTAL

Preparation and Characteristics of Pt Nanoparticles

The catalytic reduction of Np(VI) was studied in the presence of two types of Pt colloids prepared by different procedures.

The Pt colloid of the first type was prepared by the standard procedure [5] involving the reduction of H_2PtCl_6 or K_2PtCl_4 in 10^{-2} M NaOH with hydrogen in the presence of a stabilizer, sodium polyacrylate (NaPA). As a result, a brown colloidal solution stable in time ("brown" colloid) was obtained.

In the course of the studies we found that heating on a water bath of a 0.1–0.5 M HCOOH solution containing 10^{-4}–10^{-6} M H_2PtCl_6 causes the reduction of Pt with the formation of a gray colloidal solution. The "gray" colloid thus obtained remains stable (until

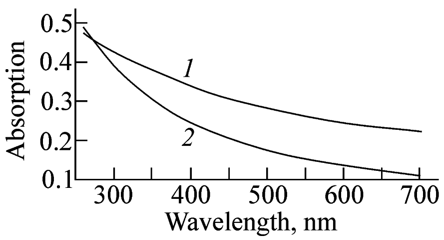

Fig. 1. Optical spectra of 1×10^{-4} M solutions of Pt nanoparticles in 0.5 M HCOOH: (*1*) in the absence of a stabilizing polyelectrolyte ("gray" colloid) and (*2*) in the presence of 2×10^{-3} M sodium polyacrylate ("brown" colloid).

precipitation of platinum black) at 25–60°C for several hours and can be used in kinetic experiments on reduction of Np(VI).

The size distribution of nanoparticles of the "gray" and "brown" colloids was studied by atomic force microscopy. The size distribution of the Pt particles in the "brown" colloid is close to monodisperse, with the mean nanoparticle size of 6 nm. The size distribution of the particles in the "gray" colloid is nonuniform. Along with a large amount of 4–8-nm particles, there are relatively coarse aggregates 20–40 nm in diameter. The gray color of the solution is caused by the light scattering on the coarse particles.

The optical absorption spectra of both types of colloids are shown in Fig. 1. The "brown" colloid exhibits specific absorption in the near-UV range, monotonically descending with increasing wavelength. Such a pattern is characteristic of fine particles with a size of up to 10 nm and is determined by intraband electronic transitions [8]. The colloid prepared without stabilizer ("gray" colloid) exhibits increased optical density in the long-wave range, indicative of the prevalent contribution of scattering on coarse particles to the total light absorption of the solution. It should be noted that the features of formation and mechanism of stabilization of the "gray" Pt colloid in HCOOH solutions are of independent scientific and practical interest and will be considered in a separate paper.

Experimental Procedure

Neptunium-237 used in the study was purified by an anion-exchange procedure. Perchloric acid solution of Np(VI) was prepared as described in [9]. A solution of Np in HNO_3 from the ion-exchange column was evaporated with $HClO_4$ to dryness. The residue was dissolved in double-distilled water. A spectrophotometric analysis showed that the solution contained 1% Np(V) and 99% Np(VI). The solution was ozonized to oxidize Np(V). Excess ozone was removed by air bubbling. The Np concentration in the stock solution was determined gravimetrically after drying a solution aliquot and calcining the dry residue to NpO_2 at 800°C. In the experiment we used chemically pure grade chemicals and double-distilled water.

Kinetic experiments were performed in a temperature-controlled 1-cm quartz cell arranged in the cell compartment of a Shimadzu UV-3110 spectrophotometer. In experiments with the "brown" Pt colloid, solutions of required compositions were prepared by mixing in the cell the calculated amounts of solutions (brought to the required temperature) of HCOOH, 1×10^{-4} M Pt + 2×10^{-3} M NaPA, and 2.8×10^{-2} M Np(VI). The order of mixing the solutions, i.e., the method of "initiating" the reaction, was varied if necessary. In experiments with the "gray" Pt colloid, it was prepared just before the kinetic experiment. To do this, an aliquot of an H_2PtCl_6 solution was injected into a test tube placed on a water bath at 80–90°C and containing the required volume of HCOOH of the required concentration. After keeping for 10 min (time required for complete reduction of Pt to zero oxidation state, as determined in a separate series of preliminary experiments), the solution was quickly cooled and transferred into a cell kept at the experimental temperature. The reduction of Np(VI) was initiated by injecting into the cell an aliquot of a 2.8×10^{-2} M Np(VI) solution. The kinetics of the Np(VI) reduction was monitored by a decrease in the solution absorption at $\lambda = 300$ nm [strong charge-transfer band of Np(VI)] in the automatic mode at 0.1-min intervals. The rate constants were calculated from the results of three independent kinetic runs.

RESULTS AND DISCUSSION

Neptunium(VI), being quite stable in 0.1–1.0 M HCOOH, starts to be reduced at a noticeable rate at room temperature in the presence of 2×10^{-6} M Pt nanoparticles stabilized with sodium polyacrylate ("brown" colloid). The threshold concentration of the nonstabilized "gray" colloid is $\sim 10^{-7}$ M. In the presence of the "brown" Pt colloid, Np(VI) is reduced to Np(V). With the nonstabilized "gray" colloid, the reduction proceeds further. Upon prolonged (several hours) storage of the reaction solution, small amounts of Np(IV) appear, as judged from the spectrum. The rate of the reduction of Np(V) to Np(IV), however, is very low under the conditions used. Therefore, we will not consider in this paper the kinetic features of this process.

Catalytic Reduction of Np(VI) in the Presence of the "Brown" Colloid

Preliminary experiments showed that the rate of Np(VI) reduction with formic acid in the presence of Pt nanoparticles depends on the order of mixing the reactants, i.e., on the mode of the reaction initiation. When the process is initiated by quick addition of an aliquot of the catalyst solution to the spectrophotometric cell, the reaction appears to be considerably faster than when Np(VI) is added last. The rate of the Np(VI) reduction is the lowest when HCOOH is added last (Fig. 2). All the subsequent kinetic experiments were performed with initating the reaction by adding an aliquot of the Np(VI) solution to a solution containing HCOOH and the catalyst.

The catalytic reduction of Np(V) with formic acid was studied in parametric kinetic experiments in which we varied the concentrations of Np, HCOOH, colloidal Pt, and stabilizer (NaPA) and the temperature in the following ranges: $[\mathrm{Np(VI)}]_0 = 2.80 \times 10^{-4}$–$9.03 \times 10^{-4}$ M; [HCOOH] = 0.1–0.9 M; [Pt] = 3×10^{-6}–2×10^{-5} M; [NaPA] = 1×10^{-4}–1×10^{-2} M; and T = 18–40°C. The volume of the reaction solution was 3.0 ml.

Typical kinetic curves of the catalytic reduction of Np(VI), obtained at different HCOOH concentrations, are shown in Fig. 3. The initial portions of the kinetic curves can be roughly approximated by a zero-order equation with respect to the Np(VI) concentration. Then, as the running Np(VI) concentration decreases, the reaction order grows, gradually approaching unity by the end of the reaction. Computer processing of the kinetic curves using the Table Curve 2D program (Jandel Scientific) showed that the whole curves can be satisfactorily described by a rate equation of the order n with respect to the Np(VI) concentration: $-d[\mathrm{Np(VI)}]/dt = k_n[\mathrm{Np(VI)}]^n$. However, the experimental reaction order with respect to [Np(VI)] is not constant and varies depending on the Np(VI) concentration in the solution. The fractional order with respect to [Np(VI)] is an apparent quantity. It reflects the adsorption nature of the catalytic process. Actually the reaction occurs along zero- and first-order pathways with respect to [Np(VI)]. The contribution of each of these pathways to the overall process is generally determined by the running concentration of Np(VI) and amount of the catalyst in the solution. To determine the true reaction order with respect to [Np(VI)], we performed a series of kinetic experiments with different initial concentrations of Np(VI) (Fig. 4). The initial rates ω_0 of the Np(VI) reduction in 0.33 M HCOOH in the presence of 1×10^{-5} M Pt at 40°C, determined from the initial linear portions of the kinetic curves at different [Np(VI)], are as follows:

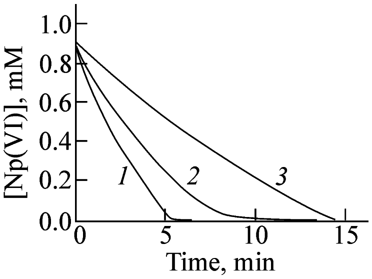

Fig. 2. Influence of the order of mixing the reactants on the rate of catalytic reduction of 9.03×10^{-4} M Np(VI) in 0.33 M HCOOH in the presence of 1×10^{-5} M Pt ("brown" colloid) at 25°C. Component added last: (*1*) catalyst, (*2*) Np(VI), and (*3*) HCOOH.

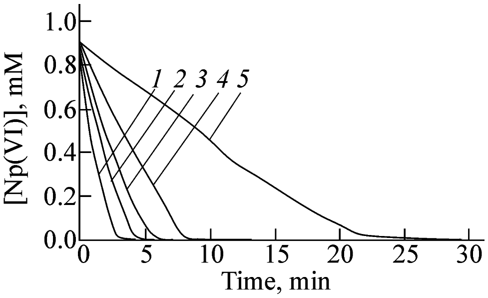

Fig. 3. Kinetic curves of reduction of Np(VI) with formic acid at 25°C in the presence of 1×10^{-5} M Pt ("brown" colloid) at different HCOOH concentrations. [HCOOH], M: (*1*) 0.9, (*2*) 0.7, (*3*) 0.5, (*4*) 0.33, and (*5*) 0.1.

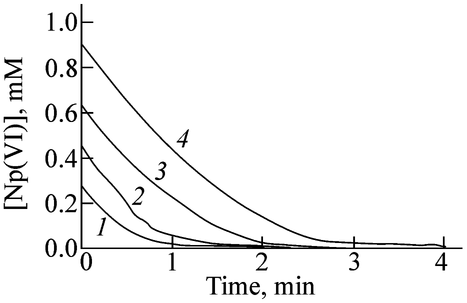

Fig. 4. Influence of the initial concentration of Np(VI) on the rate of its catalytic reduction in 0.33 M HCOOH in the presence of 1×10^{-5} M Pt ("brown" colloid) at 40°C. $[\mathrm{Np(VI)}]_0$, M: (*1*) 2.80×10^{-4}, (*2*) 4.60×10^{-4}, (*3*) 6.38×10^{-4}, and (*4*) 9.03×10^{-4}.

[Np(VI)], M	ω_0, mol l^{-1} min^{-1}
2.80×10^{-4}	5.20×10^{-4}
4.60×10^{-4}	5.25×10^{-4}
6.38×10^{-4}	5.22×10^{-4}
9.03×10^{-4}	5.23×10^{-4}

Table 1. Catalytic reduction of Np(VI) with formic acid in the presence of Pt nanoparticles ("brown" colloid)

$[Np(V)]_0$	[Pt]	[NaPA]	[HCOOH]	T, °C	k_0,* mol l^{-1} min^{-1}
M					
2.80×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.33	40	5.20×10^{-4}
4.60×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.33	40	5.25×10^{-4}
6.38×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.33	40	5.22×10^{-4}
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.33	40	5.23×10^{-4}
9.03×10^{-4}	3×10^{-6}	6.7×10^{-5}	0.33	40	1.32×10^{-4}
9.03×10^{-4}	2×10^{-5}	4.0×10^{-4}	0.33	40	9.25×10^{-4}
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.10	25	$(5.0 \pm 0.1) \times 10^{-5}$
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.33	25	$(1.62 \pm 0.05) \times 10^{-4}$
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.50	25	$(2.39 \pm 0.04) \times 10^{-4}$
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.70	25	$(3.6 \pm 0.2) \times 10^{-4}$
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.90	25	$(4.94 \pm 0.08) \times 10^{-4}$
9.03×10^{-4}	1×10^{-5}	1.0×10^{-4}	0.33	25	1.9×10^{-4}
9.03×10^{-4}	1×10^{-5}	2.0×10^{-3}	0.33	25	1.2×10^{-4}
9.03×10^{-4}	1×10^{-5}	4.0×10^{-3}	0.33	25	8.2×10^{-5}
9.03×10^{-4}	1×10^{-5}	6.7×10^{-3}	0.33	25	1.2×10^{-4}
9.03×10^{-4}	1×10^{-5}	1.0×10^{-2}	0.33	25	1.4×10^{-4}
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.33	18	$(6.34 \pm 0.04) \times 10^{-5}$
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.33	30	$(2.64 \pm 0.07) \times 10^{-4}$
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.33	36	$(5.0 \pm 0.1) \times 10^{-4}$
9.03×10^{-4}	1×10^{-5}	2.0×10^{-4}	0.33	46	$(7.3 \pm 0.1) \times 10^{-4}$

* The k_0 values given without errors were obtained from a single kinetic experiment; the same for Table 2.

The fact that the initial reaction rate is essentially independent of the Np(VI) concentration means that the reaction is zero-order with respect to [Np(VI)]. This allows us to use the equation $-d[Np(VI)]/dt = k_0$ for quantitative description of the kinetics of the Np(VI) reduction with formic acid in the presence of Pt nanoparticles. Data on the kinetics of catalytic reduction of Np(VI) with formic acid in the presence of the "brown" Pt colloid at varied experimental conditions are listed in Table 1.

Table 1 shows that, with an increase in the catalyst concentration in the reaction mixture, the reduction rate virtually proportionally increases, which is typical of heterogeneous catalytic processes. The reaction rate constant increases with an increase in the HCOOH concentration in the range 0.1–0.9 M. In the logarithmic coordinates, this dependence is well approximated by a straight line with a slope of ~1 (Fig. 5a), indicating that the reaction is first-order with respect to [HCOOH].

The temperature dependence of k_0 in the Arrhenius coordinates cannot be approximated by a straight line throughout the examined range 18–46°C (Fig. 6a). This fact reflects a transition from kinetic to diffusion control of the process with increasing temperature and is typical of heterogeneous catalytic reactions. The apparent activation energy calculated from the

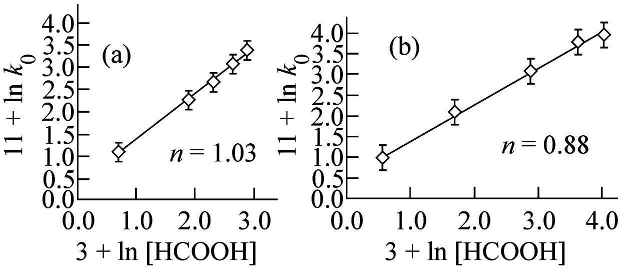

Fig. 5. Influence of the HCOOH concentration on the rate of the catalytic reduction of Np(VI) in the presence of (a) 1×10^{-5} M Pt ("brown" colloid) at 25°C and (b) 6.44×10^{-7} M Pt ("gray" colloid) at 40°C.

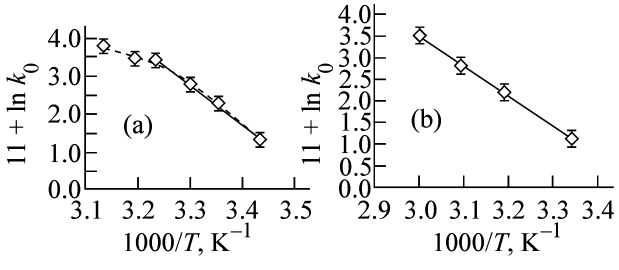

Fig. 6. Temperature dependences of the rate constant of the catalytic reduction of Np(VI) in 0.33 M HCOOH in the presence of (a) 1×10^{-5} M Pt ("brown" colloid) and (b) 4.13×10^{-7} M Pt ("gray" colloid).

Table 2. Catalytic reduction of 9.03×10^{-4} M Np(VI) with formic acid in the presence of Pt nanoparticles ("gray" colloid)

[Pt]	[NaPA]	[HCOOH]	T, °C	k_0, mol l^{-1} min^{-1}
M				
4.13×10^{-7}	0	0.33	26	$(5.15 \pm 0.04) \times 10^{-5}$
6.44×10^{-7}	0	0.33	26	7.95×10^{-5}
8.20×10^{-7}	0	0.33	26	1.0×10^{-4}
1.60×10^{-6}	0	0.33	26	2.3×10^{-4}
4.13×10^{-6}	0	0.33	26	5.9×10^{-4}
8.20×10^{-6}	0	0.33	26	8.2×10^{-4}
1.0×10^{-5}	0	0.33	22	8.15×10^{-4}
6.44×10^{-7}	0	0.033	40	$(4.4 \pm 0.2) \times 10^{-5}$
6.44×10^{-7}	0	0.10	40	$(1.36 \pm 0.08) \times 10^{-4}$
6.44×10^{-7}	0	0.33	40	$(3.6 \pm 0.2) \times 10^{-4}$
6.44×10^{-7}	0	0.67	40	$(7.11 \pm 0.03) \times 10^{-4}$
6.44×10^{-7}	0	1.0	40	$(8.6 \pm 0.1) \times 10^{-4}$
4.13×10^{-7}	0	0.33	40	$(1.5 \pm 0.1) \times 10^{-4}$
4.13×10^{-7}	0	0.33	50	$(2.80 \pm 0.06) \times 10^{-4}$
4.13×10^{-7}	0	0.33	60	$(5.58 \pm 0.08) \times 10^{-4}$
1×10^{-5}	4.0×10^{-4}	0.33	22	5.3×10^{-4}
1×10^{-5}	8.0×10^{-4}	0.33	22	4.7×10^{-4}
1×10^{-5}	2.0×10^{-3}	0.33	22	4.2×10^{-4}
1×10^{-5}	4.0×10^{-3}	0.33	22	$(3.61 \pm 0.05) \times 10^{-4}$
1×10^{-5}	6.0×10^{-3}	0.33	22	4.7×10^{-4}

linear portion of the Arrhenius plot in the range 18–36°C is 85.4 kJ mol^{-1}.

Our experiments revealed a relatively unusual and significant influence of the stabilizer (NaPA) concentration on the rate of the Np(VI) reduction with HCOOH. Initially, an increase in [NaPA] in the range $(1.0-4.0) \times 10^{-4}$ M (Fig. 7) leads to the expected decrease in the reaction rate due to adsorption blocking of active catalytic centers [10]. Further increase in the stabilizer concentration to 10^{-2} M causes a noticeable monotonic growth of the rate of Np(VI) reduction. A control experiment showed that Np(VI) was stable in the absence of HCOOH at 25°C in a solution containing 2×10^{-2} M NaPA and 1×10^{-5} M colloidal Pt, i.e., NaPA did not reduce Np(VI) under these conditions. No reduction of Np(VI) was observed, either, in a solution containing 0.33 M HCOOH and 2×10^{-2} M NaPA in the absence of Pt nanoparticles. Thus, acceleration of the Np(VI) reduction with formic acid with increasing [NaPA] is not caused by certain impurities that could be present in commercial NaPA and could initiate the reaction of Np(VI) with HCOOH by a homogeneous catalytic mechanism.

Catalytic Reduction of Np(VI) in the Presence of the "Gray" Colloid

The catalytic reduction of Np(V) with formic acid in the presence of nonstabilized Pt nanoparticles ("gray" colloid) was studied under the following conditions: $[\mathrm{Np(VI)}]_0 = 9.03 \times 10^{-4}$ M; [HCOOH] = 0.033–1.0 M; [Pt] = 4×10^{-7}–8.2×10^{-6} M; [NaPA] = 1×10^{-4}–8×10^{-3} M; and T = 25–60°C. The volume of the reaction solution was 3.0 ml.

Typical kinetic curves of the catalytic reduction of Np(VI) in 0.33 M HCOOH at 26°C, obtained at different concentrations of the nonstabilized Pt colloid, are shown in Fig. 8. As in the case of the "brown" colloid, the reaction is zero-order with respect to [Np(VI)]. The rate constants k_0 of the catalytic reduction of Np(VI) with HCOOH in the presence of the "gray" Pt colloid are given in Table 2.

Comparison of the rates of the Np(VI) reduction with HCOOH in the presence of "gray" and "brown"

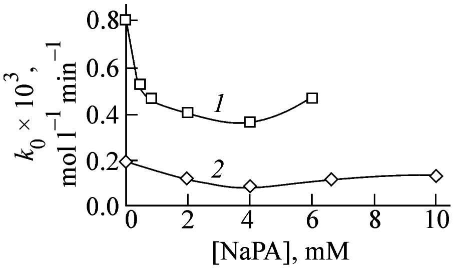

Fig. 7. Influence of the sodium polyacrylate concentration on the rate of the catalytic reduction of Np(VI) in 0.33 M HCOOH in the presence of 1×10^{-5} M Pt: (*1*) "gray" and (*2*) "brown" colloid.

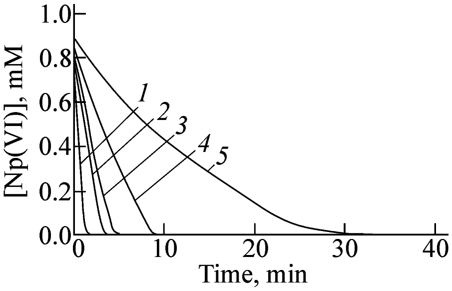

Fig. 8. Kinetic curves of the catalytic reduction of Np(VI) in 0.33 M HCOOH at 26°C in the presence of different concentrations of Pt nanoparticles ("gray" colloid). [Pt], M: (*1*) 8.20×10^{-6}, (*2*) 4.13×10^{-6}, (*3*) 1.60×10^{-6}, (*4*) 8.20×10^{-7}, and (*5*) 4.13×10^{-7}.

colloids (Tables 1, 2) reveals the following facts. Despite smaller size of nanoparticles and hence more developed surface of the "brown" colloid, its catalytic activity is lower by almost an order of magnitude than that of the "gray" colloid. A decrease in the catalytic activity of the "brown" colloid is due to blocking of the active surface of the catalyst with the stabilizer (NaPA) molecules, hindering the access of the reactants to the catalyst surface. A similar pattern was observed in experiments on catalytic reduction of Methyl Viologen with molecular H_2 on Pt nanoparticles [10]. However, this phenomenon is not fully understood. On the whole, the decreased catalytic activity of the "brown" colloid may be attributed to specific features of formation of the catalytic centers on the nanoparticle surface in the presence of NaPA and to the dependence of the concentration of these centers on the size and structure of the colloids.

As with the "brown" colloid, the rate of the catalytic reduction of Np(VI) with HCOOH grows in proportion with an increase in the concentration of the nonstabilized Pt nanoparticles. The experimental reaction order with respect to [HCOOH], found from the dependence $\ln k_0$–$\ln$[HCOOH] approximated by a straight line, is ~0.9 (Fig. 5b). Certain decrease in the reaction order compared to the "brown" colloid is apparently due to coarsening of the Pt nanoaggregates with increasing [HCOOH] in the absence of the stabilizing polyelectrolyte.

The temperature dependence of the rate of the Np(VI) reduction in the presence of the "gray" colloid in the coordinates $1/T$–$\ln k_0$ in the range 25–60°C is a straight line (Fig. 6b) with a slope corresponding to the apparent activation energy of 57.6 kJ mol^{-1}, which is appreciably lower than the value obtained for the catalytic reduction of Np(VI) on the Pt nanoparticles stabilized with sodium polyacrylate (85.4 kJ mol^{-1}). This significant difference between the apparent activation energies of the Np(VI) reduction in the presence of the "gray" and "brown" Pt colloids is obviously caused by the effect of the polyelectrolyte on the heat of adsorption of the reacting species. It follows from the Brønsted–Polanyi equation [11] that the apparent (experimentally determined) activation energy of the heterogeneous catalytic process E^* is related to the true activation energy by $E^* = E_{\text{true}} - \lambda$, where λ is the heat of adsorption. As the catalyst surface is energetically nonuniform, it can be expected that the integral heat of adsorption will depend on the degree of filling of the active centers. In the stabilized "brown" colloid, NaPA is adsorbed on the surface of Pt nanoparticles. Apparently, the polyelectrolyte molecules mainly occupy the most energetically favorable active sites, which leads to a decrease in the heat of adsorption of the reactants and increase in the apparent activation energy. The polyelectrolyte also increases the contribution of the diffusion constituent of the reaction rate, which makes narrower the temperature range of the chemically controlled process in the presence of the "brown" colloid and gives rise to an inflection in the temperature dependence of the rate constant (Fig. 6a).

As in the case of the "brown" colloid, addition of NaPA to a solution of the "gray" colloid leads first to a decrease in the rate of the Np(VI) reduction with HCOOH and then to its increase. With both types of the nanocolloids, the minimum in the k_0–[NaPA] curves corresponds to the polyelectrolyte concentration of approximately 4.0×10^{-3} M (Fig. 7). It is interesting that with the "gray" colloid the influence of [NaPA] on the reaction rate is more pronounced than with the "brown" colloid stabilized in advance. As shown above, an increase in the Np(VI) reduction rate with an increase in the NaPA concentration above 4.0×10^{-3} M is associated neither with the reducing effect of NaPA nor with the catalytic properties of the possible impurities. A reasonable explanation is associated with the flocculation of Pt nanoparticles in aqueous solution. With addition of NaPA and increase in its concentration, the polyelectrolyte molecules are sorbed on open areas of the surface of the colloidal particles, which results in blocking of the catalytic centers and in the observed decrease in the rate of the catalytic reaction. When the "critical" concentration of NaPA is attained, the flocculation gives way to deflocculation, i.e., breakdown of the associates. This is accompanied by a decrease in the size of the nanoparticles and hence in an increase in the total surface area of the catalyst under the action of the polyelectrolyte. A serious argument in favor of this assumption is the trend in variation of the optical spectra of the "gray" colloid in the presence of increasing amounts of NaPA (Fig. 9). It is seen that an increase in the NaPA concentration from 8×10^{-4} M to the "critical" level of 4×10^{-3} M leads to characteristic changes in the shape of the optical spectrum: The absorption intensity increases in the UV range and decreases in the long-wave region ("isobestic point" at about 750 nm). This trend is definitely indicative of the breakdown of floccules and increase in the number of separate nanoparticles. An increase in the optical density in the UV range is caused by an increase in the intrinsic absorption of platinum nanoparticles, and a decrease in the long-wave absorption is indicative of a decrease in the contribution of the light scattering factor due to breakdown of coarse scattering particles (floccules). Thus, a decrease in the catalytic activity of Pt nanoparticles due to blocking of the active centers with the polyelectrolyte can be compensated by an increase in the total surface area of the colloid. Starting from a certain concentration of the stabilizer (in our case, $\sim 4.0 \times 10^{-3}$ M), the latter trend becomes prevalent, leading to an increase in the rate of the catalytic reduction of Np(VI) with HCOOH.

The stability of Pt nanoparticles in the stabilized "brown" colloid is determined not only by the presence of the stabilizing agent, but also by the ionic strength of the medium. Addition of electrolytes (neptunyl perchlorate, HCOOH) to such systems alters the electrostatic equilibria in the colloidal solution, which results in coarsening of the nanoparticles and, as a consequence, in a decrease in the catalytic activity of the colloid. In the nanosystem stabilized with the polyelectrolyte, the colloid degrades relatively slowly, but this process is the faster and its extent is the greater, the higher the degree of dissociation of the electrolyte added. This trend is reflected in the dependence of the rate of the catalytic reaction on the order of mixing the reactants in the case when the reaction rate is higher than the rate at which the colloid attains the equilibrium state. Therefore, the catalytic reduction of Np(VI) with HCOOH occurs faster when the reaction is initiated by adding an aliquot of the pure stabilized Pt colloid to a formate solution of Np(VI) (Fig. 2). If the reaction is initiated by adding HCOOH to a solution containing Pt nanoparticles and Np(VI) perchlorate, the Np(VI) reduction is considerably slower, because an increase in the ionic strength of the colloidal solution due to addition of a strong electrolyte, Np(VI) perchlorate, caused a decrease in the active surface area of the colloid. Furthermore, access of HCOOH molecules to active centers of the catalyst is blocked by NaPA molecules. When the reaction is initiated by adding Np(VI) to a solution containing the stabilized colloid and a weak electrolyte, HCOOH, an intermediate pattern is observed.

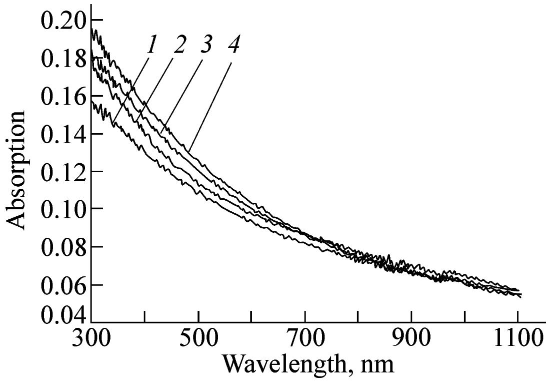

Fig. 9. Effect of NaPA additions on the absorption spectra of 1×10^{-5} M "gray" Pt colloid. [NaPA], M: (*1*) 0, (*2*) 8.0×10^{-4}, (*3*) 4.0×10^{-3}, and (*4*) 6.0×10^{-3}.

The above kinetic relationships allow certain assumptions concerning the mechanism of the catalytic reduction of Np(VI) with HCOOH in the presence of Pt nanoparticles. The independence of the reaction rate from the concentration of Np(VI) {zero reaction order with respect to [Np(VI)]} indicates that Np(VI) is reduced by a fast reaction with active species, possibly radicals, generated by chemisorption of HCOOH molecules on the catalytic centers of the platinum colloid. Generation of the active species is the rate-determining step of the overall process:

$$\mathrm{HCOOH_{sol}} \rightleftarrows \mathrm{HCOOH_{ads}}, \qquad (1)$$

$$\mathrm{HCOOH_{ads}} \rightleftarrows \mathrm{(H\cdots COOH)_{ads}} \rightleftarrows \mathrm{H^{*}_{ads}} + \mathrm{COOH^{*}_{ads}} \quad \text{(slow step)}. \qquad (2)$$

The concentration of adsorbed HCOOH is proportional to the concentration of HCOOH in the solution, which determines the first order of the reaction with respect to [HCOOH]. Then Np(VI) rapidly reacts with the chemisorbed HCOOH molecule:

$$\mathrm{NpO_2^{2+}} + \mathrm{(H\cdots COOH)_{ads}} \rightarrow \mathrm{NpO_2^{+}} + \mathrm{COOH^{\bullet}_{ads}} + \mathrm{H^{+}}, \qquad (3)$$

$$\mathrm{NpO_2^{2+}} + \mathrm{COOH^{\bullet}_{ads}} \rightarrow \mathrm{NpO_2^{+}} + \mathrm{CO_2} + \mathrm{H^{+}}, \qquad (4)$$

or with radicals:

$$\mathrm{NpO_2^{2+}} + \mathrm{H^{\bullet}_{ads}} \rightarrow \mathrm{NpO_2^{+}} + \mathrm{H^{+}}, \qquad (5)$$

$$\mathrm{NpO_2^{2+}} + \mathrm{COOH^{\bullet}_{ads}} \rightarrow \mathrm{NpO_2^{+}} + \mathrm{CO_2} + \mathrm{H^{+}}. \qquad (6)$$

Unfortunately, pathways (3), (4) and (5), (6) are kinetically indiscernible. However, the latter step seems preferable because of the following facts. It is known that the catalytic dehydrogenation of HCOOH in aqueous solution in the presence of palladium black at 30–70°C occurs by the chemisorption mechanism with the intermediate formation of the $COOH^{\bullet}$ and $H^{\bullet}$ radicals [12]. Data on the occurrence of this reaction on platinum catalysts under similar conditions are lacking. We found that the concentration of HCOOH (initial concentration 0.5 M) does not decrease on contact with the "brown" Pt colloid (1×10^{-4} M) at 70°C for 3 h; however, a chromatographic analysis of the gas phase over the solution revealed the presence of traces of H_2 and CO_2. This fact indicates that the dissociative chemisorption of HCOOH does occur in the presence of Pt nanoparticles, although its equilibrium (2) is strongly shifted to the left. An assumption that atomic hydrogen and formate radical are more active chemically than the adsorbed HCOOH molecule allows us to choose the pathway of the Np(VI) reduction via steps (5) and (6) as the most probable.

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