PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Kinetics of Dissolution of Silver Nanoparticles inside Triton N-42 Reversed Micelles

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Abstract—Our spectrophotometric study of the kinetics of dissolution of silver nanoparticles by nitric acid inside inverted micelles of Triton N-42 (a nonionic surfactant) verified the universal character of the mechanism for this type of process, which includes the interaction of surface metal atoms with an oxidizer in two routes: either with (autocatalysis) or without newly formed ionic species of the oxidized metal. Effective rate constants for both routes are independent of the value of solubilization capacity (V_s/V_o is the ratio of the volume of the dispersed aqueous phase to the volume of the micellar solution); the solubilization capacity is useful to control the micelle and particle sizes: $k_1 = 0.018 \pm 0.003$, 0.010 ± 0.003 , and $0.012 \pm 0.003 \text{ s}^{-1}$ and $k_2 = 2.5 \pm 0.8$, 1.5 ± 1.1 , and $1.4 \pm 0.4 \text{ L/(mol s)}$ for $100V_s/V_o = 1$, 2, and 3%, respectively.

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Precious metal nanoparticles, particularly silver, are important for advanced materials design and technologies [1, 2]. Efficient syntheses of particles with desired properties and ascertaining of their utility in particular materials and processes need data on the laws governing chemical reactions of nanoparticles. The oxidative dissolution of nanoparticles is of interest for synthesis (for correcting particle sizes and shapes via controlled etching), predicting the resistance of nanoparticles to various oxidizers, and gaining new data on the reactivity of nanodisperse metallic particles whose properties differ from the properties of compact metals and molecular metallic clusters.

Our studies concern the synthesis and reactions of nanoparticles inside polar cavities of inverted micelles, which themselves are nanosized objects (nanoreactos) [3–6]. In this context, the nature of the surfactant and the structure (size and shape) of micelles can influence the reactions of nanoparticles. This work was intended to determine the kinetic laws for the dissolution of silver particles by nitric acid inside micelles of Triton N-42 (a nonionic surfactant) with diverse solubilization capacities of the micellar solution and to compare the results with similar data for the oxidative dissolution of silver particles in AOT (an anionic surfactant) [5] and gold particles in Triton N-42 [6].

EXPERIMENTAL

The following chemicals were used: crystalline AgNO₃, concentrated aqueous HNO₃, *n*-decane, (all of chemically pure grade), solid KBH₄ (95%), and liquid Triton N-42 (from Sigma) [6].

A 0.25 M organic solution of Triton N-42 in decane, standard aqueous solutions of AgNO₃ and 2 M HNO₃, and initial micellar solutions of silver nanoparticles (solution I) and nitric acid (solution II) were prepared and the kinetic experiment was carried out as described elsewhere [5]. The sizes of micelles and nanoparticles synthesized were varied via varying solubilization capacity V_s/V_o (the ratio of the dispersed aqueous phase to the volume of the micellar solution).

The dissolution kinetics at a fixed temperature $(25.0 \pm 0.5)^{\circ}$ C were studied spectrophotocolorimetrically. The reaction timezero (τ) was the moment when solutions I and II were mixed in the volume ratio 1 : 1 after they were each prethermostated at the set temperature (both solutions had the same solubilization capacities). UV/Vis absorption spectra and absorbances of solutions during kinetic experiments were recorded on a Shimadzu UV-1700 spectrophotometer; the reference cell was filled with a micellar solution of water having a set solubilization capacity. Preliminary experiments showed that micellar solutions of Triton N-42, AgNO₃, HNO₃ and its reduction products, as well as KNO₃ and B(OH)₃ (byproducts of nanoparticle synthesis; <10⁻⁴ mol/L), do not absorb in the visible ($\lambda > 350$ nm).

In checking whether the Beer law holds for solutions I, we diluted the micellar solution of nanoparticles $(c_{Ag}^* = 6.56 \times 10^{-4} \text{ mol/L})$ with the micellar solution of water, and the silver concentration was determined by atomic absorption on Hitachi Z-8000 after silver nanoparticles were dissolved in nitric acid.

RESULTS AND DISCUSSION

Triton N-42 is a mixture of oxyethylated para-nonylphenols where the average degree of oxyethylation is four. When Triton N-42 dissolves in decane, its molecules are aggregated as spherical micelles of equal sizes. The hydrodynamic radius of such dry micelles $r_0 \approx 2.8$ nm and is close to the average length of surfactant molecules that form monolayered shells of micelles [7]. Data on the structure of micelles in the HNO₃-H₂O-Triton N-42decane system are lacking. Judging from the data on a similar system (HCl-H2O-Triton N-42-decane), the hydrodynamic radius (r_h) of micelles upon the solubilization of aqueous acid solutions increases with increasing solubilization capacity and acid concentration, and the micelle shape changes from spherical to ellipsoidal or spherocylindrical. The changing shape indicates the elasticity of shells of Triton N-42 micelles, as distinct from rigid AOT micelles (sodium bis(2-ethylhexyl)sulfosuccinate), which retain spherical shapes [8]. According to [7], the upper boundary of the diameter of the micellar cavity for Triton N-42 micelles is estimated at $2(r_h - r_0) < 9$ nm as applied to the conditions of our study $(100V_s/V_o \le 3 \%)$ and $\leq 1 \text{ mol/L}$ acid in the dispersed aqueous phase). Presumably, the sizes of silver nanoparticles initially formed inside micellar cavities and the more so the sizes of nanoparticles formed during dissolution also do not exceed this value. The surface plasmon resonance (SPR) spectrum of spherical particles with diameters smaller than 20 nm is known to weakly depend on the particle size, and the absorbance A of their solutions in a fixed external medium is proportional to the overall silver concentration in the solution [8, 9]. Violations of the Beer law are caused by specific interactions of particles with one another or with components of the medium [10, 11].

Check-up for the set of initial solutions I prepared by dilution and having common silver concentrations $c_{Ag} = c_{Ag}^* / N$ (where $c_{Ag}^* = 6.56 \times 10^{-4}$ mol/L, N is dilution) showed that the law $A = l \varepsilon_{Ag}$ (where l is the cell length, cm) strictly holds for the maximum wavelength of the SPR band ($\lambda_{max} = 406 \text{ nm}$) and for a limited range of concentrations ($c_{Ag} < 2 \times 10^{-4}$ mol/L; Fig. 1a). The molar extinction coefficient of silver has $\varepsilon_{max} = (2.04 \pm$ $(0.07) \times 10^4$ L/(mol cm). The pattern of the spectra of dilute solutions (the symmetry and peak position of the SPR band and ε_{max} value) is typical of metallic silver nanoparticles with spherical shapes and narrow particle-size distributions [8-12]; therefore, such particles are formed in Triton N-42 micelles. The deviation from the Beer law for $c_{Ag} > 2 \times 10^{-4}$ mol/l is likely because of the interactions between silver particles. This is evidenced by the decrease of extinction coefficient in the region of 406 nm and the increase in the region of 470 nm, which is made clear by the comparison of the relative spectra of solutions: $\varepsilon_i/\varepsilon_{10} = A_i N_i/(\bar{A}_{10}N_{10})$, where *i* is the solution no. and i = 10 corresponds to the most dilute solution (Fig. 1b).



Fig. 1. (a) Absorbance and (b) relative extinction coefficient of the micellar solution of silver nanoparticles upon dilution with water. $100V_s/V_o = 2\%$, l = 0.2 cm. N = (I) 1 ($c_{Ag} = 6.56 \times 10^{-4}$ mol/L), (2) 1.1, (3) 1.2, (4) 1.4, (5) 1.7, (6) 2.0, (7) 2.5, (8) 3.3, (9) 5.0, and (10) 9.9. Inset: the fulfillment of the Beer law at $\lambda_{max} = 406$ nm.

Kinetic experiments use a large excess of HNO₃ for the dissolution of silver particles, and the reaction produces Ag⁺ ions. Although NO₃⁻ and Ag⁺ ions themselves do not absorb light with $\lambda > 350$ nm, they can influence the SPR spectrum of the particles. The spectrum of the micellar solution of nanoparticles remains unchanged while less than 1 mol/L of NaNO₃ is added to the dispersed aqueous phase; small additional absorption on account of NO₃⁻ is observed only in the region of 300 nm (Fig. 2). No influence of Ag⁺ is noted while AgNO₃ concentrations added are [Ag⁺]' $\leq 5 \times 10^{-3}$ mol/L in the dispersed aqueous phase or [Ag⁺] = [Ag⁺]'V_s/V_o $\leq 1 \times 10^{-4}$ mol/L in the micellar solution.



Fig. 2. Effect of the composition of the dispersed aqueous phase on the spectrum of the micellar solution of silver nanoparticles. $100V_s/V_o = 2\%$. $c_{Ag} = (1) 1 \times 10^{-4}$ mol/L Ag⁰ (l = 0.5 cm) and (2–8) 5×10^{-5} mol/L Ag⁰ (l = 1 cm) in the micellar solution. Aqueous phase: (1, 2) H₂O, (3) 1 mol/L NaNO₃, (4) 2.5×10^{-3} mol/L AgNO₃, (5) 5×10^{-3} mol/L AgNO₃, (5) 5×10^{-3} mol/L AgNO₃, (5) 5×10^{-3} mol/L AgNO₃, (6) 2.5×10^{-2} mol/L AgNO₃ immediately after the micellar solution was prepared, (7) the same 5 min later, and (8) the same 15 min later.

For $[Ag^+]' = 2.5 \times 10^{-2}$ mol/L or $[Ag^+] = 5 \times 10^{-4}$ mol/L, however, the spectrum of the particles acquires another pattern, and some time is required for the new spectrum to stabilize (Fig. 2; curves 6–8).

In view of the aforesaid, we studied the dissolution kinetics at $\lambda_{\text{max}} = 406$ nm using micellar solutions of silver nanoparticles with $c_{\text{Ag}} < 1 \times 10^{-4}$ mol/L. Interactions of the particles with one another and with Ag⁺ ions (the reaction product) violating the proportionality between the measured absorbance and the concentration of metallic silver are expected to nonsexist in these solutions.

In all cases, mixing of the micellar solutions of nanoparticles (solution I) and HNO₃ (solution II) is immediately followed by some narrowing of the SPR band and an increase in absorbance compared to the spectrum of the initial solution I. These distinctions, insignificant for $100V_s/V_o = 1\%$ (Fig. 3; curves 1, 2), strengthen with increasing solubilization capacity. For example, the difference between the extinction coefficients $\Delta \varepsilon_{max}/\varepsilon_{max}$ for $100V_s/V_o = 3\%$ is ~10%. Thus, the spectrum of the reaction mixture for τ_0 is related to the micelle size and the occurrence of H⁺ in the dispersed aqueous phase, because NO₃⁻, does not influence the SPR of the particles (see above). Proton effects can arise from various causes: direct nanoparticle–H⁺ interactions, effects of H⁺–surfactant interactions (via the



Fig. 3. Evolution of the spectrum of the micellar solution during dissolution of silver nanoparticles. $100V_s/V_o = 1\%$ (l = 1 cm). Reaction time τ , min: (I) 0, (2) 1, and (3-24) 11–221 in 10-min steps.

donor oxygen atoms of -CH2-O-CH2- and -CH2-O-H fragments in surfactant molecules) on nanoparticlesurfactant interactions inside micellar cavities, and/or variations in the properties of the medium of the dispersed aqueous phase (and the micellar solution as a whole). The size of the micellar cavity, which is controlled by V_s/V_o , also influences the quality of the medium of the dispersed aqueous phase [5]. It is impossible to resolve these effects, but all of them can be assigned to the integral medium effect; this effect is fixed in each experiment because of the constancy of V_s/V_o and HNO₃ concentrations ($c_{\rm HNO_3} \ge c_{\rm Ag}$). In view of the above considerations, the absorbance of initial solution I (A_{I}) was not used to estimate the initial value A_0 (for $\tau = 0$) in processing rate curves; the A_0 values corresponding to the real reaction medium were calculated as one parameter along with the observed rate constants.

As the dissolution of nanoparticles progresses, the SPR intensity decreases monotonically (Fig. 3). In the final state ($\tau \rightarrow \infty$), the micellar solution has no spectrum, but its absorbance A_{∞} remains at a level of 10^{-1} to 10^{-2} opt. un. depending on the wavelength. Experimental values of A_{∞} for $\lambda_{\text{max}} = 406$ nm were determined in each experiment and taken into account in processing rate curves whose representative trends for various solubilization capacities are shown in Fig. 4.

Substitution of the kinetic scheme of the process and the data processing procedure are described in [5]. The dissolution of nanoparticles by nitric acid occurs inside the cavities of inverted surfactant micelles via the interaction of Ag^0 with the oxidizer (NO_3^-) on the surface of nanoparticles in two routes: either with (autocatalysis)

lations.

or without Ag⁺. For the pseudo-first-order reaction $(c'_{\rm HNO_3} = 1 \text{ mol/L}, c'_{\rm HNO_3} = c'_{\rm HNO_3} V_s / V_o \ge c_{\rm Ag})$, the process can be represented by conventional reactions (1) and (2) below (the products of NO₃⁻ reduction are omitted) with the relevant rate law equation (3) and auxiliary equation (4) for calculating constants.

$$Ag^0 \longrightarrow Ag^+,$$
 (1)

$$Ag^0 + Ag^+ \longrightarrow 2Ag^+,$$
 (2)

$$d[Ag^{0}]_{\tau}/d\tau = -k_{1}V_{s}/V_{o}[Ag^{0}]_{\tau} - k_{2}[Ag^{0}]_{\tau}(c_{Ag} - [Ag^{0}]_{\tau}), (3)$$

$$\ln(A_{\tau} - A_{\infty}) = a_0 + a_1 x_1 + a_2 x_2, \tag{4}$$

Here, c_{Ag} and $[Ag^0]_{\tau}$ are the initial and current concentrations of metallic silver in the micellar solution, mol/L; A_0 and A_{τ} are the initial and current absorbances of the micellar solution for $\lambda_{\text{max}} = 406 \text{ nm}$; $x_1 = \tau$; $x_2 =$ $\int_{0}^{\tau} (A_{\tau} - A_{\infty}) d\tau, a_{0} = \ln(A_{0} - A_{\infty}), a_{1} = -\{k_{1}V_{s}/V_{o} + k_{2}(A_{0} - A_{\infty}), a_{2} = -\{k_{1}V_{s}/V_{o} + k_{2}(A_{0} - A_{\infty}),$ A_{∞} /($l\epsilon_{\max}^{\varnothing}$)}, $a_2 = k_2/(l\epsilon_{\max}^{\varnothing})$; and k_1 and k_2 are the effective rate constants for reactions (1) and (2). Such constants in combination with the targeted selection of initial and boundary conditions radically simplify the model (in the case at hand, this is the model of the oxidation kinetics of silver particles inside micelles), despite the complexity of the system studied [13]. The initial concentration of metallic silver and the extinction coefficient for nanoparticles in experiments were estimated at $c_{Ag} = A_{I}/(2l\epsilon_{max})$ and $\epsilon_{max}^{\varnothing} = (A_{0} - k_{max})$ $A_{\infty})/(lc_{Ag})$, where \emptyset signifies the conformity of ε_{max} to certain fixed parameters of the medium (solvent, surfactant, c_{surf} , c_{HNO_2} , V_s/V_o).

The values found for the constants k_1 and k_2 were characterized by confidence ranges (P = 0.95) and are satisfactorily reproduced in replica experiments (table). The rate curves calculated with the use of these constants adequately fit experimental data (Fig. 4). Average values of each constant (k_1 or k_2) obtained for various solubilization capacities of the micellar solution are close to each other with account for experimental errors and are in fact independent of V_s/V_o in the range from 1 to 3% (Fig. 5).

For the previously studied dissolution of silver nanoparticles by nitric acid in AOT micelles [5] and gold nanoparticles (with HCl + H₂O₂ as oxidizer) in Triton N-42 micelles [6], slightly different qualitative effects of V_s/V_o on k_1 and k_2 are observed. For silver and AOT, k_1 tends to decrease as $100V_s/V_o$ increases from 2 to 4%; $k_2 \approx$ const for $100V_s/V_o = 2$ and 3% and increases about twofold when $100V_s/V_o = 4\%$. For gold and Triton N-42, a change in solubilization capacity from 0.25 to 1.5% induces an about tenfold monotonic decrease in k_1 , whereas $k_2 \approx$ const for $100V_s/V_o \le 1.2\%$ and increases about eightfold when $100V_s/V_o = 1.5\%$.

* The mean value of the constant; the error is evaluated as the variation range of partial values of the constant.

Effective rate constants of silver nanoparticle dissolution for various solubilization capacities of the micellar solution

100V _s /V _o , %	k_1, s^{-1}	<i>k</i> ₂ , L/(mol s)
1	0.017 ± 0.001	2.1 ± 0.2
	0.020 ± 0.003	2.9 ± 0.7
	$\langle 0.018 \pm 0.003 \rangle^*$	$\langle 2.5 \pm 0.8 \rangle^*$
2	0.009 ± 0.001	2.0 ± 0.2
	0.011 ± 0.001	2.0 ± 0.3
	0.011 ± 0.003	1.1 ± 0.8
	0.010 ± 0.001	1.2 ± 0.1
	0.009 ± 0.002	1.8 ± 0.2
	0.012 ± 0.001	0.9 ± 0.1
	$\langle 0.010 \pm 0.003 \rangle^*$	$\langle 1.5 \pm 1.1 \rangle^*$
3	0.014 ± 0.002	1.2 ± 1.1
	0.011 ± 0.004	1.6 ± 1.8
	$\langle 0.012 \pm 0.003 \rangle^*$	$\langle 1.4 \pm 0.4 \rangle^*$



Fig. 4. (a) Representative rate curves for various solubilization capacities of the micellar solution: (1) 1, (2) 2, and

(3) 3%. l = 1 cm. Markers: experimental data; lines: calcu-

In general, variations in solubilization capacity (an

equivalent parameter is $w_o = c_{\rm H_2O}/c_{\rm surf}$, which is related

to V_s/V_o as $w_o = (c'_{\rm H_2O} V_s/V_o)/c_{\rm surf}$ or $w_o \approx 220 V_s/V_o$ when



Fig. 5. Effect of the solubilization capacity of the micellar solution on effective rate constants (1) k_1 and (2) k_2 .

 $c'_{\rm H_{2}O} \approx 55$ mol/L and $c_{\rm surf} = 0.25$ mol/L) changes not only the micelle size but also the properties of the reaction medium inside micellar cavities. This primarily pertains to the major component of the solubilized aqueous solution, i.e., water, for which two states can roughly be distinguished: water structured on account of interactions of its molecules with one another and with polar fragments of surfactant molecules and free (bulk) water inside the cavities (cores) of micelles. Comprehensive analysis of the literature on the structure of inverted surfactant micelles and the state of water inside them is found in Bulavchenko's dissertation [14]. Estimates of the limiting V_s/V_o value above which the properties of bulk water are observed depend on the nature of the surfactant, solvent, property measured, and the sensitivity of the measurement technique. In micelles of nonionic surfactant Triton N-42, free water appears when $100V_s/V_o > 1\%$ as judged from characteristic IR bands [7]. Ionic surfactant AOT binds water more strongly. Therefore, aqueous cores appear at higher values of the solubilization capacity (>4%); when $100V_s/V_o < 4\%$ ($c_{surf} = 0.25$ mol/L) or $w_o < 10$, all solubilized water is structured due to hydrogen bonds stabilized by high dipole moments of the sulfo groups of AOT [15].

Comparison of the laws governing the influence of V_s/V_o on effective rate constants and the state of the medium inside micellar cavities for silver and AOT and for gold and Triton N-42, shows that the integral medium effect is significant for k_1 , whereas k_2 is less responsive to medium effects but responds to the appearance of free water. The latter is likely due to the fact that, unlike in route (1), the products of nanoparticle dissolution (Ag⁺ and [AuCl₄]⁻) are involved in autocatalytic route (2) apart from the oxidizer. In the absence of free water, these product ions are to some

degree bound by the surfactant to form ion pairs (Ag⁺, $^{-}O_3S$ –) for AOT and [AuCl₄] $^{-}...H^{+}...O<$ hydrogen bonds for Triton N-42. Free water that appears inside micellar cavities enhances the dissociation of these bonds, making Ag⁺ and [AuCl₄] $^{-}$ free to participate in reaction (2).

The dissolution of silver particles by nitric acid in the system with Triton N-42 was studied for $100V_s/V_o \ge$ 1%, the conditions providing the occurrence of free water inside micellar cavities; this water likely largely cancels out the change in the properties of the medium in response to V_s/V_o variations. Moreover, Triton N-42 cannot bind silver(I) cations to form ion pairs or hydrogen bonds. Apparently, these features of the system under consideration are responsible for the noninfluence of V_s/V_o on the effective rate constants k_1 and k_2 .

In summary, our new data support that the oxidative solubilization of nanoparticles, regardless of the metal (silver or gold), oxidizer (nitric acid or hydrated chlorine), and surfactant (ionic AOT or nonionic Triton N-42), follows the same kinetic mechanism, which involves the interaction of surface metal atoms with the oxidizer in two routes: either with (autocatalysis) or without ionic species of the oxidized metal as reaction products. The reaction medium changes, following variations in solubilization capacity, on account of a change in the state of water inside polar cavities of micelles. The process kinetics are influenced by both the integral medium effect and specific interactions between water, metal ions, and the surfactant. The medium effect is more significant for the noncatalytic route, whereas the autocatalytic route is more susceptible to the occurrence of free water in micelles if there are relatively strong specific interactions between newly formed metal atoms and the surfactant. In the absence of such interactions and given that an aqueous core exists, effective rate constants for both routes are independent of $V_{\rm s}/V_{\rm o}$, as observed for silver and Triton N-42.

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