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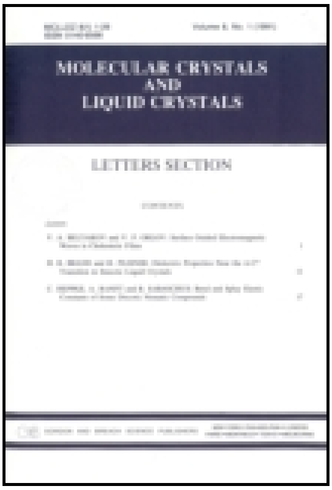

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Micelle Encapsulation of Silver Nanoparticles at Borohydride Reduction

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The present work demonstrates the encapsulation of silver nanoparticles into micellar structures of the diblock copolymer (DBC) consisting chemically complementary methoxypoly (ethylene oxide) and poly(acrylic acid). The reduction of silver ions to silver nanoparticles or nanoclusters is achieved by an excess of sodium borohydride in the DBC aqueous solutions with various pH. The formation of considerably more smallest and stable Ag-nanoparticles in the DBC micellar solution at pH = 3 compare with the test of an Ag^+ *solution without DBC micelles was revealed. The morphology of Ag-nanoparticles dispersed within DBC matrices and their average particle size were indicated by TEM images.*

Keywords Diblock copolymer; self-assembly; micelles; nanoparticles; nanoclusters; silver

Introduction

Last time, the silver-nanostructured polymeric materials, which can be used in biomedical areas such as tissue engineering and drug delivery [1–3], in sensitized solar cells [4], on semiconductor surfaces [5], and so on, are intensively studied. One of the most common methods to prepare silver nanoparticles is the reduction of silver salts by strong reducing agents such as sodium borohydride [6], sodium hydroxide [7], or sodium citrate [8], which ones can simultaneously be used as stabilizing agents. The syntheses are carried out in aqueous or non-aqueous media [9] using surfactants [10] or polymers [11–13] as stabilizing agents. Silver nanoparticles dispersed in polyvinylpyrrolidone [14], polymethyl methacrylate [15], polystyrene [16], and other polymer matrices were obtained. It was shown that homo- and block copolymers based on anionic polyelectrolytes such as poly(acrylic acid) (PAAc) or poly(methacrylic acid) (PMAAc) can be ideal templates to generate water-soluble fluorescent Ag-nanoclusters (AgNCs) [17] or highly stable Ag-nanoparticles (AgNPs) [18,19]. The aggregative stability of AgNPs in polymeric matrices with carboxylic functional groups was considered from the point of view of the processes of electrostatic interactions, steric stabilization, flocculation, and phase separation in a system. Additionally, PAAc and PMAAc conformations respond reversibly to environmental

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pH, ionic strength, and temperature. This makes it possible to study the influence of pH-dependent conformational changes in PAAc or PMAAc matrices on the AgNP generation.

In our previous study, we considered the AgNP formation at the borohydride reduction of silver ions in aqueous solutions of diblock copolymers contained methoxypoly(ethylene oxide) and poly(sodium acrylate) (MOPEO-*b*-PANa) as well as a partial reduction of silver ions up to AgNCs in the solutions of protonated DBCs (MOPEO-*b*-PAAc) [20]. At the same time, a possibility of the AgNP formation and stabilization in polymer-free solutions also exists [21]. Therefore, in this study, we compare the synthesis process, stabilization, and morphology of AgNPs, which were obtained at borohydride reduction in pure water and in DBC micellar solutions.

Experimental

Synthesis and Characterization of the Diblock Copolymer

According to our study [20], the rate of AgNP growth and their stability in DBC solutions strongly increase with a growth of the PAAc block length. Therefore, the DBC sample with a relatively small length of MOPEO block ($M_n = 5.3$ kDa) and an essentially higher length of PANa block ($M_n = 23.05$ kDa) was synthesized by the free radical block copolymerization of acrylic acid (AAc) ("Fluka," USA) with MOPEG from the same firm. Terminal hydroxyl groups of MOPEG were activated by cerium ammonium nitrate [20,22]. The detailed methodology of block copolymerization was described earlier [20]. The sample of DBC in H-form was rewashed by deionized water after the synthesis and transformed to Na-form by the dissolution in water with sodium hydroxide. The obtained DBC in Na-form was re-precipitated by the addition of hydrochloric acid up to pH = 2; then it was dissolved again in a sodium hydroxide solution and freeze dried.

Formation of Silver Nanoparticles by Borohydride Reduction

Syntheses of silver nanoparticles in pure water and DBC aqueous solutions were carried out by the addition of $NaBH_4$ (from China) to $AgNO_3$ solution or Ag^+/DBC blend ($C_{DBC} = 1\ kg{\cdot}m^{-3}$, $C_{AgNO_3} = 1.4{\cdot}10^{-2}\ kg{\cdot}m^{-3}$) at a molar ratio of $[Ag^+]/[COO^-] = 0.1$. The excess of the reducing agent is necessary to favor the formation of monodispersed metal nanoparticles through the fast nucleation process [21]. This process could be described by the stochiometric equation [19]

$$8Ag^+ + BH_4^- + 8OH^- = 8Ag + H_2BO_3^- + 5H_2O. \qquad (1)$$

In our experiments, the molar excess of $NaBH_4$ with respect to Ag^+ ions was 8 and 80 times. The AgNPs were identified using UV-Vis spectroscopy. Corresponding spectra of the reaction mixtures were recorded by a Cary 50 Scan UV-Visible Spectrophotometer from "Varian" (USA) in the range 200–1000 nm.

The Micelle and Nanoparticle Characterization by Transmission Electron Microscopy (TEM)

TEM images of DBC micelles were recorded with a JEM-I23O instrument ("JEOL," Japan) operating at an accelerating voltage of 90 kV. Small drops ($\sim 1{\cdot}10^{-4}\ cm^3$) of DBC solution

($C_{DBC} = 0.5$ kg·m^{-3}) at pH = 2.5 were deposited in copper grids coated with Formvar film and carbon and then were dried for ∼ 1–2 min at room temperature. Electron images were obtained in 24 h after the sample preparation.

In order to obtain the TEM images of AgNPs prepared in pure water and DBC solutions at the different pH ($C_{DBC} = 1$ kg·m^{-3}, $C_{AgNO_3} = 1.82{\cdot}10^{-2}$ kg·m^{-3}, $[NaBH_4]/[Ag^+] = 8$), the reaction mixtures were kept after the borohydride reduction in a dark box at room temperature for 10 days.

Results and Discussion

Parameters and Morphology of Copolymer Micelles

According to our previous work [20], the synthesized DBC sample was pH-sensitive, namely, its polyacid block at pH ≤ 4 was close to the fully protonated state and formed a intramolecular polycomplex with MOPEO block. Due to hydrophobic interactions between non-polar bound segments of both blocks, the intense micellization was developed in the pointed pH region [20]. In this case, the formation of “hairy-type” micelles with a relatively small hydrophobic “core” and a large “corona” could be expected. TEM image of DBC micelles is represented in Fig. 1. These micelles contained a dense “core” and a developed “corona,” due to which a micelle shape differs from the spherical one in many cases. A size of micelles was equal to 5 ÷ 32 nm.

Formation of Silver Nanoparticles in the Copolymer Solutions with Variable pH

Typical plasmon resonance bands, which were recorded during the process of AgNP formation in $AgNO_3/DBC_{PANa}$ mixtures at pH = 9, are shown in Fig. 2. We observed a steady increase in the intensity of the absorption bands with $\lambda_{max} = 381 \div 390$ nm during 120 min. When the reaction time exceeded 120 min, the maximum intensity of the plasmon band was reached (Note that, in both cases, the AgNP band intensity increases with the $[NaBH_4]/[Ag^+]$ molar ratio. It was revealed that the AgNP growth in pure water, especially in the case of $[NaBH_4]/[Ag^+] = 80$, occurred more quickly than that in DBC_{PANa} solutions at a selected DBC concentration (Fig. 2b, d). In our opinion, this fact could be explained by the slow diffusion of a reducing agent to Ag^+-ions, which are bonded with –COO– groups of DBC_{PANa} at the first stage of the reduction reaction and disposed in “cores” of special micellar structures [20,23]. The capability of connection of Ag^+-ions with –COO– groups of DBC_{PANa} was shown in our previous work [20]. This connection resulted in the formation of stable Ag^+/DBC_{PANa} micelles that was initiated by hydrophobic interactions between non-polar PANa segments bound with Ag^+-ions [1,20].

In both reaction media during the second stage of borohydrate reduction, the appearance of fully stable AgNP dispersions was fixed. At the same time, the effect of AgNP destabilization at the low-molecular-weight electrolyte addition (0.1 M KNO_3) was observed only in the copolymer-free solution. It is known [21] that increasing the plasmon resonance band intensity at practically constant values of its position (λ_{max}) could be attributed to the yield of AgNPs. This allows controlling the rate of AgNP formation. Kinetic peculiarities of AgNP growth in the DBC_{PANa} solution compared to the copolymer-free $AgNO_3$ solution (at pH = 9) are represented in Fig. 3 as the time evolution of λ_{max} (Fig. 3a , b) and the integral intensity of the band (Sq) (Fig. 3c, d), which is proportional to the AgNP yield at a constant λ_{max}.

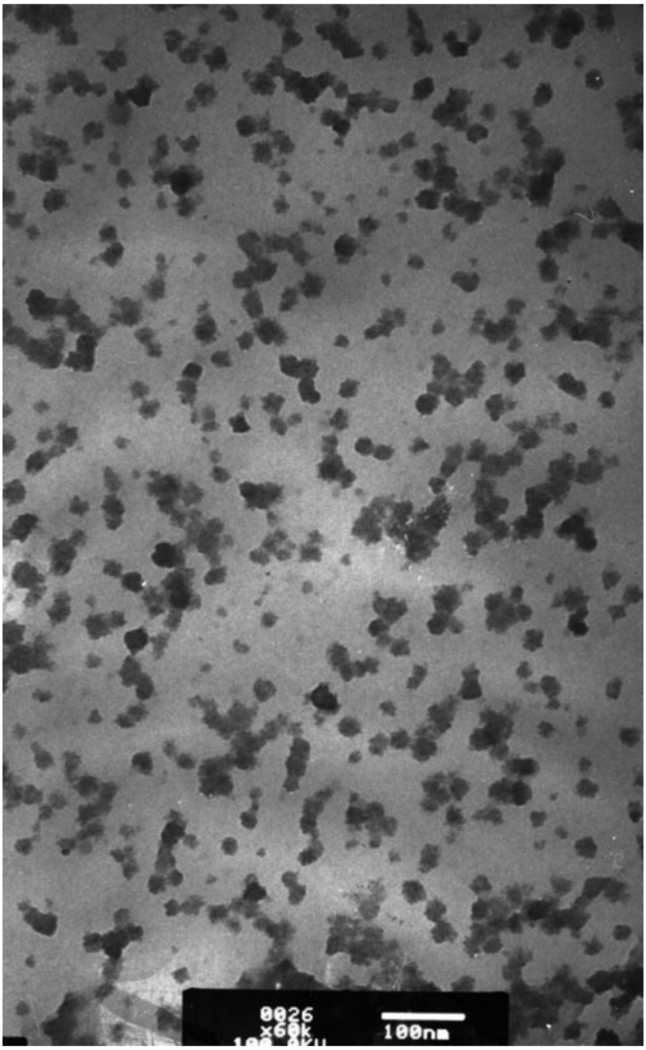

Figure 1. TEM image of DBC_{PAAc} micelles at pH = 2.5. $C_{DBC} = 0.5$ kg·m^{-3}.

It is seen that the main quantity of AgNPs arose in both the media during the first 3 min. The corresponding initial rates of AgNP formation calculated by the formula $v = dS/dt$ are shown in Table 1.

In accordance with the study [20,21], the AgNP formation in water and in DBC solution could be represented by two distinct processes. For the first process (up to 3 min), the quick reduction of Ag^+-ions and the formation of primary AgNCs and AgNPs with a high rate took place (Fig. 3, Table 1). But, for the second one (since 3 min), the coagulation or aggregation of primary clusters and nanoparticles occurred. The second process was displayed by a consequent increase in λ_{max} values at $t > 3$ min (Fig. 3a, b). It should be noted that the rate of AgNC/AgNP formation in the first process grew increases with the $[NaBH_4]/[Ag^+]$ ratio and at the transition from DBC solution to pure water (Table 1).

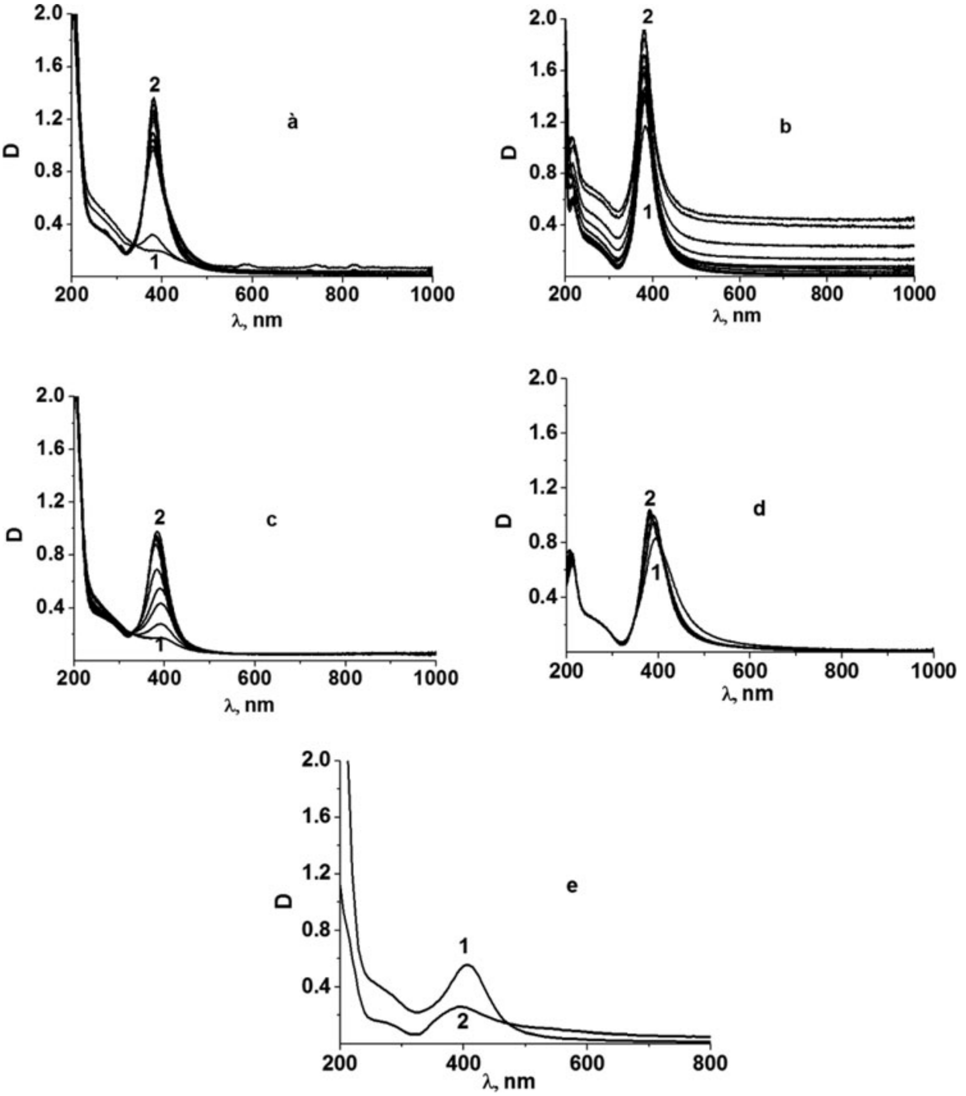

Figure 2. Absorption spectra of AgNPs obtained in DBC_{PANa} (a, c) and in $AgNO_3$ (b, d) solutions at $[NaBH_4]/[Ag^+] = 80$ (a, b) and $[NaBH_4]/[Ag^+] = 8$ (c, d) in different times after the reduction beginning: 2 -*1*, and 120 min –*2*; Scanning interval -10 min. Absorption spectra of AgNPs obtained in DBC_{PANa} –*1* and in $AgNO_3$ -*2* solutions in 30 days after the reduction beginning at $[NaBH_4]/[Ag^+] = 80$ (e). $C_{DBC} = 1$ kg·m^{-3}, $C_{AgNO_3} = 1.4 \cdot 10^{-2}$ kg·m^{-3}, pH = 9.

The main task of the last experimental series was to carry out the silver ion reduction in micellar structures of the copolymer, which were formed at pH ≤ 4 [20]. In this case, we carried out the Ag^+-ion reduction in water and DBC solutions with pH = 2.5. But, at the addition of the reducing agent to the acidic $AgNO_3$ solution or acidic $AgNO_3/DBC_{PAAc}$ mixture (at the $[NaBH_4]/[Ag^+] = 80$ ratio), the solution pH became equal to 6 that was accompanied by the destruction of DBC_{PAAc} micelles [20]. UV-Vis spectra for corresponding reaction mixtures at pH = 6 are shown in Fig. 4.

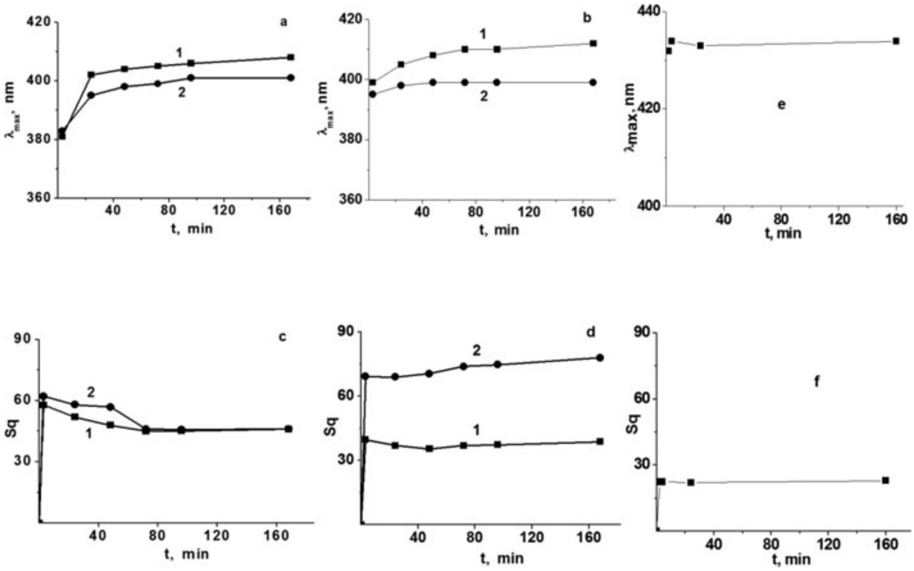

Figure 3. Time dependences of the position (λ_{max}) (a, b, e) and the integral intensity (c, d, f) of the plasmon resonance band for AgNPs formed in water solutions with and without DBC; DBC_{PANa} -*1*, $AgNO_3$ -2, $[NaBH_4]/[Ag^+] = 80$, pH = 9 (a, b, c, d) and DBC_{PAAc}, $[NaBH_4]/[Ag^+] = 8$, pH = 3 (e, f); $C_{DBC} = 1$ kg·m^{-3}, $C_{AgNO_3} = 1.4 \cdot 10^{-2}$ kg·m^{-3}.

The absorption bands near 400 nm were practically absent in the absorption spectra of the reaction mixtures. Instead those, the absorption band with $\lambda_{max} \sim 864$ nm together with a blue color of the mixtures appeared. According to the literature data [1], this result could be interpreted by the formation of very long sequences of AgNCs (and Ag^+-ions), which were bound with a polyacid block of DBC (the so-called "blue silver"). Therefore, the chemical reduction of Ag^+-ions in DBC solutions at pH $\sim$ 6 (unlike to pH $\sim$ 9) led to the formation of AgNCs and their complexes with polyacid blocks. The intensity of the "blue-silver" band was practically unchanged in time, while its position is shifted to the "red" region. An analogous band with essentially lower intensity appeared also in the copolymer-free solution at pH = 6, but it fully disappeared in 4 min after the $NaBH_4$

Table 1. Initial rate of the silver nanoparticle formation under different conditions

Medium	pH	C_{AgNO_3}, kg·m^{-3}	v, s^{-1}	
			$[NaBH_4]/[Ag^+] = 8$	$[NaBH_4]/[Ag^+] = 80$
DBC_{PANa} solution [1]	9	0.014	0.22	0.32
water	9	0.014	0.39	0.35
DBC_{PAAc} solution[1]	3	0.014	0.19	—

[1] $C_{DBC} = 1$ kg·m^{-3}.

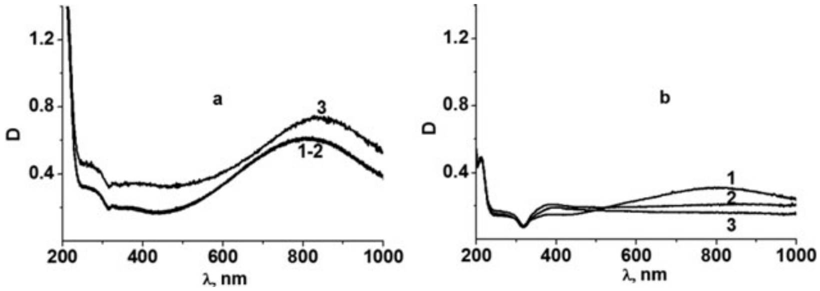

Figure 4. Absorption spectra of $Ag^+/DBC_{PANa/PAAc}$ (a) and $AgNO_3$ (b) solutions in different times after the $NaBH_4$ addition: 2 -*1*, 4 -*2*, 160 -*3* min. $C_{DBC} = 1$ kg·m^{-3}, $C_{AgNO_3} = 1.4 \cdot 10^{-2}$ kg·m^{-3}, $[NaBH_4]/[Ag^+] = 80$. pH = 6.

addition. Thus, the stabilization of AgNCs as products of the incomplete reduction of silver ions took place only in $DBC_{PANa/PAAc}$ solution.

In order to solve the problem of Ag^+ reduction in the DBC_{PAAc} micellar solution, we have decreased the $[NaBH_4]/[Ag^+]$ molar ratio in the reaction mixture by 10 times (up to 8). In this case, the solution pH equal to 3 was not changed. Results of these experiments are represented in Fig. 5.

At once after the $NaBH_4$ addition, the relatively broad absorption band with $\lambda_{max} =$ 431–433 nm arose in the Ag^+/DBC_{PAAc} micellar solutions due to the formation of AgNPs (Fig. 5a). The integral intensity of this band and their position were practically unchanged during some times (Fig. 3e, f) and then, in ~24 h after the $NaBH_4$ addition, disappeared because of the microphase separation in the system. It was shown that the formation of primary AgNCs and AgNPs in the DBC_{PAAc} micellar solution (pH = 3) was occurred with a smaller rate compared to that in DBC_{PANa} solution (pH = 9) (Fig. 3f , Table 1).

An analogous broad plasmon resonance band with low intensity appeared in 2 min after the $NaBH_4$ addition in the copolymer-free solution (Fig. 5b), but it fully disappeared in 160 min. So, AgNPs, which were obtained at the borohydride reduction in water at pH = 3 without copolymer micelles were instable. Note that the borohydride redox potential decreased with lowering the solution pH [1].

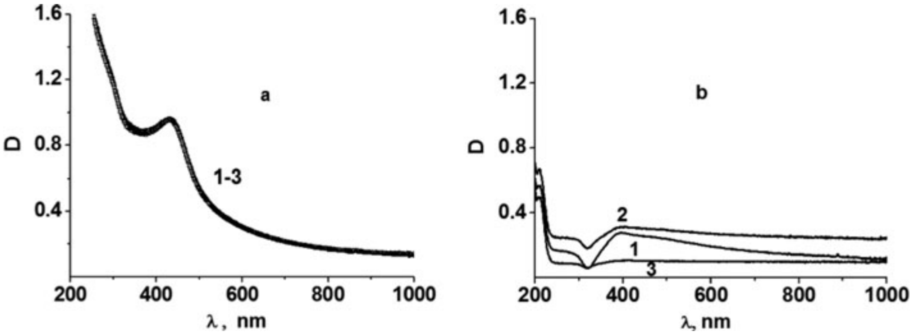

Figure 5. Absorption spectra of Ag^+/ DBC_{PAAc} micellar solution (a) and $AgNO_3$ solution (b) in 2 -*1*, 24 -*2* and 160 -*3* min after the $NaBH_4$ addition; $C_{PAAc} = 1$ kg·m^{-3}, $C_{AgNO_3} = 1.4 \cdot 10^{-2}$ kg·m^{-3}, $[NaBH_4]/[Ag^+] = 8$. pH = 3.

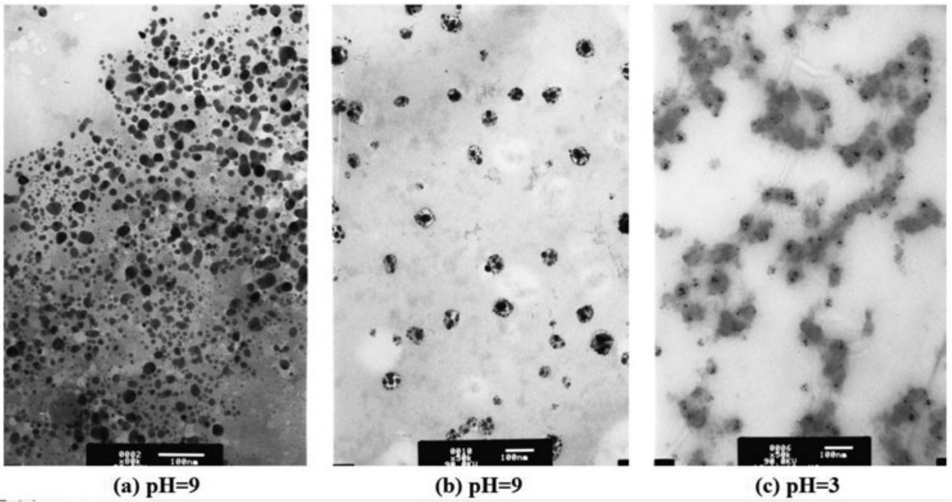
(a) pH=9 (b) pH=9 (c) pH=3

Figure 6. TEM images of AgNPs synthesized in water solution (a), DBC_{PANa} solution (b), DBC_{PAAc} solution (c). $C_{DBC} = 1$ kg·m^{-3}, $C_{AgNO_3} = 1.82 \cdot 10^{-2}$ kg·m^{-3}, $[NaBH_4]/[Ag^+] = 8$.

TEM images of AgNPs synthesized in water and DBC solutions at various pH are represented in Fig. 6.

They confirmed that AgNPs of a mainly spherical shape, but with different size, were generated in the presence and without DBC. The nanoparticles obtained in water without DBC demonstrated a relatively wide size distribution (from 2 to 33 nm); moreover, some aggregates of AgNPs of higher size were also present. Another situation was observed in the presence of DBC_{PANa} at pH = 9. In this case, AgNPs 2 ÷ 38 nm in size were produced and stabilized in the Ag^+/DBC_{PANa} micellar nanoreactors, whose dimension changed from 18 to 80 nm (Fig. 6b).

The smallest spherical AgNPs (2 ÷ 20 nm in diameter) were found inside the swelled and aggregated micellar structures of DBC_{PAAc} at pH = 3 (Fig. 6c). Thus, the reduction reaction proceeded exactly in these micellar nanoreactors.

Conclusion

It has been shown that the smallest spherical and stable AgNPs with a narrow size distribution (~2 ÷ 20 nm) can be synthesized in a DBC_{PAAc} micellar solution at pH = 3, where the lowest rate of borohydride reduction was fixed. Such effect can be explained by a deeper penetration of Ag^+-ions through the practically uncharged (at this pH) micellar "corona" in the micelle space at the first stage of chemical reduction (before the borohydride addition). Unlike this, in the copolymer-free solution at the same pH, the formation of stable AgNPs was not observed.

The similar spherical AgNPs stable in solution with a wider size distribution (~2 ÷ 38 nm) can be obtained in DBC_{PANa} solution at pH = 9. But, in this case, the reduction reaction developed in the special micellar structures, which appeared at the first stage of borohydride reduction due to the formation of a complex of Ag^+-ions with oppositely-charged PANa blocks. The existence of such micellar nanoreactors with a size of ~18 ÷ 80 nm was fully confirmed by TEM. The AgNPs obtained at pH = 9 in DBC_{PANa} solution demonstrated a high stability even to the addition of a low-molecular-weight electrolyte unlike to AgNPs, which were synthesized in the copolymer-free solution and were precipitated at the electrolyte addition.

The partial reduction of Ag^+ to the blue nanoclusters and its further stabilization in DBC solution at $pH = 6$ were revealed. An insignificant amount of AgNCs, which was obtained under the same experimental conditions in the copolymer-free solution, was not stabilized.

Thus, the functional capabilities of DBC solutions with different pH as templates for the silver nanoclusters/nanoparticles formation at the borohydride reduction compared to those of copolymer-free solutions were shown.

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