# Synthesis and Characterization of Silver Nanoparticles in Reverse Micelles of Nonionic Surfactants and in Their Mixed Micelles with AOT

P. S. Popovetskiy\*

Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia \*e-mail: popovetskiy@niic.nsc.ru

Received October 11, 2019; revised November 5, 2019; accepted November 9, 2019

**Abstract**—Stable silver nanoparticles have been obtained in reverse micelles of known and available nonionic surfactants, sorbitan monooleate (Span 80) and tetraethoxylated dodecanol and *p*-nonylphenol (Brij 30 and Tergitol NP-4, respectively), in *n*-decane. The obtained nanoparticles have been characterized using a number of physicochemical methods. The stability, hydrodynamic diameter, and electrokinetic potential of the nanoparticles have been studied as depending on the amounts of added water; chloroform; and an anionic surfactant, sodium bis(2-ethylhexyl)sulfosuccinate (AOT). It has been shown that, for different surfactants, AOT should be introduced in different ways to provide the nanoparticles with the electrokinetic potential values sufficient for enhancing their stability and ensuring the possibility of concentrating them by nonaqueous electrophoresis. In the case of Brij 30, it is preferable to introduce AOT after the synthesis as a "charging additive," while, in the case of Tergitol NP-4, it should be added as a cosurfactant at the stage of the synthesis. The nanoparticles synthesized in Span 80 micelles have a rather high electrokinetic potential even in the absence of the additives. In this case, the use of AOT as a cosurfactant decreases the electrokinetic potential of the nanoparticles, while, being added after the synthesis, it increases the potential.

**DOI:** 10.1134/S1061933X2002009X

# INTRODUCTION

Stable sols of inorganic substances, such as metals, are attracting great interest on the part of researchers all over the world due to the wide possibilities of their use in electronics, especially in printing electronics [1]. Experts believe that the production of accessories for electronic devices by the printing method is a promising way to decrease the cost of final products [2]. Many formulations of inks for printed electronics have been proposed in spite of the severe requirements imposed on them [3-6]. Such inks are commonly based on silver, because it has the greatest electrical conductivity among metals and a rather high chemical stability [2].

Two main approaches to the production of nanoparticles are commonly distinguished between, i.e., "top-down" and "bottom-up." In the former case, nanoparticles are separated from a bulk metal by laser ablation, mechanical grinding, plasma evaporation, and some other methods [7-10]. The authors of reviews [1, 2] devoted to inorganic nanomaterials used in printing electronics have reported that this approach encounters difficulties associated with the control over the particle size distribution, which is of principle importance in this case. The latter approach consists in the preparation of nanoparticles by reduc-

ing or decomposing ionic precursors using the methods of "wet chemistry." Polymers—in particular, polyelectrolytes—and surfactants are widely used as stabilizers of nanoparticles. Both water and organic solvents may serve as dispersion media. Synthesis of nanoparticles in reverse micelles of surfactants yields very stable nanoparticles with narrow size distributions [11–13]; therefore, it seems to be a rather promising method of producing inks for printing electronics. The use of organic solvents has a negative effect on the cost and ecological compatibility of the inks but gives wide possibilities for varying their properties [14].

Sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol OT, AOT) is the most popular and thoroughly studied surfactant widely used for the synthesis of nanoparticles. Nanoparticles stabilized with anionic AOT often have a rather high electrokinetic potential ( $\zeta$ -potential). Therefore, AOT is also widely used as a "charging additive," when is necessary to increase the  $\zeta$ -potential of nanoparticles [15, 16]. This not only increases their stability, but also makes it possible to realize their electrophoretic concentration [17–19] with rather high concentration coefficients and almost quantitative degrees of extraction. The use of the electrophoretic concentration seems to be the most effi-

cient method for solving the main problem of the microemulsion synthesis—the low metal content in an obtained organosol.

However, AOT has a number of drawbacks, first of all, the presence of sodium and sulfur in its molecules, with these components being rather difficult to remove by thermal treatment of inks. A decrease in AOT concentration may improve the purity of a treated coating and its characteristics—primarily, its conductivity. It is evident that the partial or complete replacement of AOT by nonionic surfactants (NSs) with lower onset temperatures of thermal degradation and almost quantitative mass losses upon thermolysis is a possible way to solving this problem. However, the replacement of an ionic surfactant by an NS will, most probably, decrease the  $\zeta$ -potential of resulting particles and, accordingly, their stability.

The goal of this work was the synthesis and characterization of silver nanoparticles in reverse micelles of widely known commercial oil-soluble NSs. The hydrodynamic diameters of the nanoparticles and their optical properties (the pattern of the localized surface plasmon resonance (LSPR) spectrum, the position of the absorption maximum, and the molar extinction coefficient) were determined. Especial attention was focused on the  $\zeta$ -potential of the obtained nanoparticles: the effects of water, chloroform, and AOT on the magnitude of the  $\zeta$ -potential were studied, while monitoring the hydrodynamic diameter and stability of the nanoparticles. Water and chloroform were added after the synthesis, while AOT served as both an additive incorporated after the synthesis and a cosurfactant used at the stage of the svnthesis (in amounts up to 50 mol %). The  $\zeta$ -potential magnitudes obtained at different variants of the use of AOT for "charging" nanoparticles were compared.

## **EXPERIMENTAL**

#### **Reagents and Nanoparticle Synthesis**

*n*-Decane (99%) and chloroform (reagent grade, stabilized with 0.5-0.75% ethanol) were used as solvents in this work. Silver nitrate and hydrazine hydrate (both reagent grade) were used as initial substances for the synthesis of nanoparticles. Widespread oil-soluble NSs, namely, Span 80 (sorbitan monooleate, Sigma Aldrich), Brij 30, and Tergitol NP-4 (dodecanol and *p*-nonylphenol with an average degree of ethoxylation of 4 produced by Sigma Aldrich and Dow Chemical, respectively) and AOT (Sigma Aldrich, basic substance content of 97%), were used as stabilizers. All reagents were used as received.

Nanoparticles were synthesized by the common microemulsion method. The reagents (silver nitrate and reductant) taken in amount of 1 vol % were introduced into two portions of 0.1-1 M solutions of the surfactants in *n*-decane via injection solubilization. Silver nitrate was used as a 1 M solution, while hydra-

COLLOID JOURNAL Vol. 82 No. 2 2020

zine hydrate was applied without dilution (hydrazine concentration was about 20 M). After being intensely stirred, the reagent-containing microemulsions were mixed and allowed to stand for, at least, 12 h. When synthesizing nanoparticles in NS + AOT mixed micelles, the total surfactant concentration in a solution was chosen on the basis of the maximum molar extinction coefficient obtained after the synthesis in the absence of AOT. The molar fraction of AOT was varied from 10 to 50%. The synthesis was performed in a way similar to that described above.

#### Investigation Methods

Electronic absorption spectra of organosols were recorded using an UV-1700 spectrophotometer (Shimadzu, Japan) in quartz cells with a light path of 0.2 cm. When necessary, the organosols were diluted with initial surfactant solutions so that the maximum optical density was no higher than 1.5 optical units.

Effective hydrodynamic particle diameters were determined with a NanoBrook Omni dynamic light scattering spectrometer (Brookhaven Instruments, United States) using polymodal analysis based on the NNLS (Non-Negatively Constrained Least Squares) algorithm. Before the measurements, the organosols were cleared of dust by fivefold cyclic filtration through a Teflon membrane filter with a pore diameter of 0.2 µm (Sartorius, Germany) directly into a glass measuring cell. Photons scattered by the particles were detected at an angle of 90° to the radiation source—a solid-state laser operating at a wavelength of 640 nm and a power of 35 mW. Photon accumulation time during one measurement was 10 s, and a hydrodynamic diameter was determined as an average result of 20-30 measurements.

The electrokinetic ( $\zeta$ ) potential of the nanoparticles was also determined with the NanoBrook Omni spectrometer by laser electrophoresis using the phase analysis light scattering (PALS). The measurements were carried out in an SRR2 special cell (Brookhaven Instruments) resistant to the action of organic solvents. The cell was equipped with plane-parallel palladium electrodes having an area of nearly 45 mm<sup>2</sup>; the interelectrode gap was 3.45 mm. Photons scattered by the particles were detected at an angle of 15°. Before the measurements, the organosols were cleared of dust by tenfold cyclic filtration, while the electrodes were purified by continuously passing the solvent for 20 min using a BI-SFS filtering system (Brookhaven Instruments) at a solvent flow rate of 7.8 mL/min. The nanoparticle velocity was measured in a manual regime at an external field of 275-550 V/cm (in some cases, at lower strength magnitudes); the  $\zeta$ -potential was found as an average result of 10-20 measurements at different external field. No dependence of the  $\zeta$ -potential on the field was observed in the aforementioned range. The  $\zeta$ -potential was calculated using the Hückel–Onsager model [20, 21].

#### POPOVETSKIY

**Table 1.** The values of hydrodynamic diameter  $d_h$ , scattered light intensity *I*, absorption maximum wavelength  $\lambda_{max}$ , molar extinction coefficient  $\varepsilon_{max}$  at  $\lambda_{max}$ , and the full width at half maximum (FWHM) of the plasmon absorption peak of silver nanoparticles obtained in reverse micelles of NSs

C <sub>surf</sub> , mol/L	$d_{\rm h}$ , nm		Ι,	$\varepsilon_{\rm max} \times 10^{-4},$	λnm	FWHM nm					
	mode 1	mode 2	kcps*	L/(mol cm)	$n_{\rm max}$ , IIII	1 11111,1111					
Span 80											
0.1	—	20	520	0.92	414	97					
0.25	18	140	500	0.87	414	98					
0.5	28	140	1070	1.50	413	68					
0.75	—	92	920	0.80	411	67					
1.0	—	110	620	1.29	411	67					
Tergitol NP-4											
0.1	9.8	—	295	—	—	—					
0.25	8.3	140	690	—	—	—					
0.5	12	49	3430	0.74	408	57					
0.75	6.8	76	1990	0.25	409	55					
1.0	10.4	150	520	0.037	411	59					
Brij 30											
0.1	15	120	170	_	—	_					
0.25	—	32.9	177	2.10	403	50					
0.5	—	68	3920	1.60	408	48					
0.75	—	80	4800	0.73	409	53					
1.0	_	92	800	0.13	409	54					

\* Here and below, the units of scattered light intensity are denoted as kcps (kilo count per second).

Moreover, the electrokinetic phenomena and the sign of the  $\zeta$ -potential were preliminarily studied qualitatively by the moving boundary method for all of the systems. This method has been described in detail elsewhere [18, 19]. Copper electrodes with an area of 2 cm<sup>2</sup> and an interelectrode gap of 1 cm were used. In the absence of electrokinetic motion visible with the naked eye (the formation of an interface between a raffinate and an organosol with nanoparticles), a system was not further analyzed by the PALS method.

#### **RESULTS AND DISCUSSION**

#### Hydrodynamic Diameter and Optical Properties

Nanoparticles in micelles of nonionic surfactants. Table 1 shows the results of measuring hydrodynamic diameters  $d_h$  of nanoparticles obtained in reverse micelles of NSs. In addition, the Table 1 presents the scattered light intensities and the characteristics of the LSPR spectra.

The data presented in Table 1 show that the use of NSs in low concentrations (0.1 and 0.25 M in the case of Tergitol NP-4 and 0.1 M in the case of Brij 30) leads to a dramatic decrease in the stability of the formed nanoparticles and to the precipitation of silver metal. Organosols obtained at these NS concentrations were

colorless. Organosols obtained at all studied concentrations of Span 80 were strongly colored and exhibited an LSPR band, with the latter being, however, wider than that in the case of ethoxylated surfactants most likely due to a wider size distribution of the obtained particles.

For all synthesized organosols (with the exception of the colorless ones), the wavelength of the LSPR maximum was in a range of 400-415 nm typical of small silver nanoparticles-the hvdrodvnamic nanoparticle diameter was no larger than 150 nm in all cases. The following regularity was observed when using the ethoxylated NSs: an increase in their concentrations within ranges of 0.5-1 and 0.25-1 M for Tergitol NP-4 and Brij 30, respectively, led to an increase in the hydrodynamic diameters and a decrease in the stability of the obtained nanoparticles. It should also be noted that the mode attributed to surfactant micelles was recorded only in the case Tergitol NP-4. Their diameter was about 10 nm, thereby being somewhat larger than the size of anhydrous Tergitol NP-4 micelles (6–8 nm depending on concentration). In other cases, no modes assigned to surfactant micelles were recorded because of their low intensity caused by smaller sizes of Brij 30 and Span 80 micelles as compared with Tergitol NP-4 micelles.

For subsequent studies, we chose systems with the highest molar extinction coefficients calculated taking into account the total silver contents in them (5 mM as calculated per organic phase volume), i.e., the systems stabilized with 0.25 M Brij 30 and those stabilized with Span 80 and Tergitol NP-4 taken in a concentration of 0.5 M. In the cases of Span 80 and Tergitol NP-4, these systems (as might be expected) exhibited the strongest light scattering, while, in the case of Brij 30, the scattering was weakest (laser radiation was intensely absorbed by nanoparticles).

Nanoparticles in nonionic surfactant micelles with additives of water, chloroform, and AOT. When Brij 30 and Span 80 were used as stabilizers, the obtained organosols were miscible with a 1 M AOT solution in all ratios with no loss of stability. In the case of Tergitol NP-4, the addition of AOT in concentrations up to 0.05 M and above caused a relatively rapid loss of stability: the hydrodynamic nanoparticle diameter grew from 100 to 300 nm, while the scattered light intensity increased from 3000 to 7000 kcps over less than 5 min.

Organosol of nanoparticles stabilized with Tergitol NP-4 was also less stable upon the addition of chloroform. When chloroform was added in amounts of 9 vol % and above, the scattered light intensity first drastically decreased to 50 kcps due to the formation of aggregates, which intensely absorbed laser radiation: then, it increased to 1000 kcps because of their sedimentation. It is of interest that the measured hydrodynamic nanoparticle diameter remained almost unchanged in this case. Analogous aggregates were observed upon the addition of chloroform (12 vol %) to an organosol of nanoparticles stabilized with Brij 30: the scattered light intensity decreased from 1000 to 70 kcps due to the absorption of laser radiation. Neither sedimentation of aggregates nor variations in their hydrodynamic diameter were observed during the measurement. Organosol of nanoparticles stabilized with Span 80 was miscible with chloroform in all ratios with no stability loss.

Upon the addition of water to an organosol of nanoparticles stabilized with Tergitol NP-4, turbidity was observed only when  $H_2O$  was solubilized in amounts of more than 10 vol %. Organosols of nanoparticles stabilized with Span 80 and Brij 30 became turbid already upon the addition of water in amounts of 3 and 4 vol %, respectively. Variations in the hydrodynamic diameter of silver nanoparticles in these systems are illustrated in Fig. 1.

Nanoparticles in NS + AOT mixed micelles. Silver nanoparticles were synthesized in NS + AOT mixed micelles at a total surfactant concentration of 0.25 M, because the main idea of this work was to decrease the AOT concentration in the studied systems. In the cases of Span 80 and Tergitol NP-4, we also used systems with a total surfactant concentration of 0.5 M, at which the maximum values of the optical density and scattered light intensity were obtained in the absence

COLLOID JOURNAL Vol. 82 No. 2 2020



**Fig. 1.** Variations in the hydrodynamic diameter of silver nanoparticles obtained in reverse micelles of NSs in the presence of additives of (a) water, (b) chloroform, and (c) AOT.

of AOT. The characteristics determined for these systems are presented in Table 2.

In the case of Span 80, the addition of AOT does not affect significantly the characteristics of the LSPR spectra at all studied concentrations: the extinction coefficient, the wavelength of the maximum, and the width of the resonance peak remain almost unchanged. In other cases, a dramatic drop in the extinction coefficient is observed at some NS/AOT

#### POPOVETSKIY

**Table 2.** The values of hydrodynamic diameter  $d_h$ , scattered light intensity *I*, absorption maximum wavelength  $\lambda_{max}$ , molar extinction coefficient  $\varepsilon_{max}$  at  $\lambda_{max}$ , and FWHM of the plasmon absorption peak of silver nanoparticles obtained in NS + AOT mixed reverse micelles

$C_{\rm AOT}$ , mol %	d <sub>h</sub> , nm		Lkens	$\varepsilon_{\rm max} \times 10^{-4}$ ,	$\lambda_{\max}^*$ ,	FW/HM nm				
	mode 1	mode 2	<i>1</i> , керз	L/(mol cm)	nm	. **				
Span 80 + AOT (0.5 M)										
10	6	26	116	1.19	409	86				
20	17	110	147	1.21	409	90				
30	10	100	157	1.30	408	88				
40	30	160	160	1.34	407	86				
50	21	160	129	1.36	406	88				
Tergitol NP-4 + AOT $(0.5 \text{ M})$										
10	16	60	1330	1.28	408	63				
20	4	72	2870	0.55	407	71				
30	51	370	1710	0.87	407	69				
40	29	210	770	1.46	406	70				
50	90	580	450	1.52	406	68				
Brij 30 + AOT (0.25 M)										
10	8.5	88	6460	1.40	412	71				
20	12	91	5210	1.11	413	81				
30	15	112	9300	0.09	416 (650)	112				
40	52	320	5200	0.16	422 (640)	108				
50	41	230	920	0.32	412 (600)	101				
Span 80 + AOT (0.25 M)										
10	15	117	3480	0.91	406	68				
20	—	181	4650	0.97	405	80				
30	8.9	211	1270	0.92	405	74				
40	12.6	180	280	0.93	405	83				
50	6.2	24	225	0.95	406	92				
Tergitol NP-4 + AOT $(0.25 \text{ M})$										
10	12	62	7170	0.98	406	50				
20	13	67	7100	0.91	408	56				
30	34	145	1300	0.48	405 (630)	60				
40	18	90	6160	0.59	405 (650)	61				
50	22	67	4700	0.86	404	57				

\* The wavelengths of the absorption maxima of long-wave shoulders (when take place) in the LSPR spectra are presented in parentheses.

ratios, with the drop being, as a rule, accompanied by the appearance of a long-wave shoulder in a range 600–650 nm. This is most likely due to specific structural features of mixed micelles at these surfactant ratios. The above-described variations in the spectra are accompanied by the appearance of particle size distribution modes with hydrodynamic diameters of 100–300 nm for Brij 30/AOT mixtures and 110–210 and 200–600 nm for Tergitol NP-4/AOT mixtures with total surfactant concentrations of 0.25 and 0.5 M, respectively. These effects are less pronounced in the case of Span 80/AOT mixtures, for which the hydrodynamic diameter of this mode is 100-160 nm. The reasons for this may be aggregation and the formation of particles with a prolate shape.

## Electrokinetic Potential

**Initial systems.** As might be expected, no electrophoretic motion was recorded by the moving bound-

COLLOID JOURNAL Vol. 82 No. 2 2020



**Fig. 2.** Experimental (points) and calculated (solid lines) time dependences of the phase of light scattered by nanoparticles in the course of their electrophoretic motion for five parallel measurements. The data on silver nanoparticles stabilized with Span 80 are presented: field is 280 V/cm, silver concentration is 5 mM, and Span 80 concentration is 0.5 M; *n*-decane as a solvent.

ary method for silver nanoparticles stabilized with ethoxylated surfactants. Particles may have a nonzero electrokinetic potential, provided that the following conditions are met:

(1) the particles must have a nonzero surface charge;

(2) the surface charge must not be completely neutralized by the dense part of the electrical double layer (EDL); and

(3) free charge carriers forming a diffuse part of the EDL must be present in a system.

In reverse micellar systems, the role of the charge carriers may be played by ionic surfactant reverse micelles, which may have a fluctuation charge owing to the intermicellar ion exchange [22], or some ionizable additives of, e.g., a more polar solvating solvent, chloroform [23]. Such charge carriers must be absent in additive-free systems based on NSs. From the considerations of the electrical neutrality of the entire system, even when the surface charge of a nanoparticle is nonzero, it is completely compensated by the dense part of the EDL, which is, most probably, represented by the adsorption layer of the nanoparticle.

Nevertheless, in the case of silver nanoparticles stabilized with Span 80, a diffuse boundary was formed between a pale-yellow raffinate and a colored nanoparticle-containing organosol under the action of an electric field of 200 V/cm. For this system, the PALS method has yielded reproducible results, which indicate that the particles have a substantial  $\zeta$ -potential (+16.1 ± 0.2 mV). Figure 2 shows dependences for the phase shift of the light scattered by nanoparticles in the course of their electrophoretic motion. Very good agreement is observed between the calculated and experimental data. It is obvious that, by analogy with ionic surfactants, this system contains some charge carriers; however, at this stages of the studies, no unambiguous explanation is available for the nature of these charge carriers, while the study of the reasons for the existence of a nonzero  $\zeta$ -potential at the nanoparticles stabilized with typically nonionic surfactants was beyond the scope of this work and will be the goal of a separate investigation. The presence of ionizable impurities in commercial Span 80 seems to be the most probable reason.

Electrochemical potential in the presence of water, chloroform, and AOT. For silver nanoparticles stabilized with the studied ethoxylated surfactants, the differences in the patterns of the dependences and the obtained  $\zeta$ -potential values are small and will be discussed jointly.

The addition of water (up to 5 vol % or to the cloud point) had no effect on the nanoparticle  $\zeta$ -potential, which remained to be zero. An analogous situation was observed for ethanol. The obtained data lead us to assume that water and ethanol penetrate into polar cavities of reverse micelles and are not involved in the formation of the diffuse part of the EDL.

The addition of chloroform in an amount greater than 6 vol % led to the appearance of electrophoretic motion, which was recorded by the moving boundary method. The imposition of an electric field of 200 V/cm gave rise to the formation of a distinct boundary between a colorless raffinate, which was almost free of nanoparticles, and a colored organosol, with this boundary being seen with the naked eye. Nanoparticles moved toward the cathode, thereby indicating their positive charge. The attempts to measure the  $\zeta$ -potential by the PALS method did not yield reproducible data because of an increase in the electrical conductivity of the system due to nanoparticle coagulation. Thus, the use of chloroform for creating the diffuse part of the EDL does not seem to be reasonable in this case, because it leads to electrocoagulation.

The addition of AOT in the form of a 1 M solution also resulted in the charging of the nanoparticles, the electrophoretic motion of which was recorded by the moving boundary method. The electrocoagulationinduced increase in the conductivity was also observed for this systems, although to a lower extent, thereby enabling us to correctly determine the  $\zeta$ -potential by the PALS method using an electric field below 275 V/cm. The  $\zeta$ -potential values appeared to be about 6 mV for both surfactants. No dependence on AOT concentration was observed in a range of 0.02– 0.1 M.

In the case of Span 80, the addition of water (1 vol %) had no effect on the  $\zeta$ -potential of silver nanoparticles, while the addition of 2 vol % water did not lead to reproducible data. As has been mentioned above, the addition of water in concentrations of 3 vol % and

- Span  $80 + AOT(0.5 \text{ M}) \square \text{Tergitol NP4} + AOT(0.5 \text{ M})$
- Span 80 + AOT(0.25 M) □ Tergitol NP4 + AOT(0.25 M)



Fig. 3. Dependences of the  $\zeta$ -potential on AOT fraction at total surfactant concentrations of 0.25 and 0.5 M for nanoparticles obtained in NS + AOT mixed micelles.

above made the organosols turbid. The addition of AOT (0.02-0.1 M) or chloroform (3-15 vol %) increased the nanoparticle  $\zeta$ -potential to nearly 30 mV. No dependences on AOT concentration and chloroform volume were observed within the aforementioned ranges.

Thus, when AOT was used as a "charging additive," the measurements of the  $\zeta$ -potential by the PALS method yielded reproducible data for all surfactants.

Nanoparticles in NS + AOT mixed micelles. It should, first of all, be noted that, for Brij 30 + AOTmixtures, measurements of the  $\zeta$ -potential by the PALS method gave no reproducible results throughout the studied concentration range, although the electrophoretic motion of nanoparticles was recorded by the moving boundary method in systems with AOT molar fractions of 30% and above. It seems that the most probable reason is the low stability of the obtained nanoparticles (their aggregation): the LSPR peaks are wide and have long-wave shoulders, with the optical density of the organosols being low. In all other cases, the moving boundary method indicated the electrophoretic motion of nanoparticles, while the PALS method vielded reproducible values of the  $\zeta$ -potential. The dependences of the  $\zeta$ -potentials of nanoparticles on the molar fraction of AOT in the mixtures of the surfactants are presented in Fig. 3.

The use of the Tergitol NP-4 + AOT mixture showed an expectable linear increase in the  $\zeta$ -potential of the nanoparticles with the molar fraction of AOT as a result of the additional incorporation of possible charge carriers, i.e., ionizable AOT molecules, into the system. Another situation was observed for Span 80: an increase in the molar fraction of AOT caused a decrease in the  $\zeta$ -potential. Most probably, this was due to the ability of Span 80 to form the diffuse part of the EDL, which provides  $\zeta$ -potential values higher than those in the case of AOT.

#### CONCLUSIONS

In this work, silver nanoparticles stabilized with nonionic surfactants and mixtures thereof with an anionic surfactant, AOT, have been studied. It has been found that AOT is a more preferable "charging agent" than chloroform, while water cannot be used for this purpose at all. However the addition of AOT leads to the "contamination" of a system with sodium and sulfur, which can hardly be subsequently removed. Therefore, a goal of the work was to find a method that would make it possible to obtain nanoparticles with a maximum  $\zeta$ -potential at a minimum AOT concentration in a system. It has been shown that the preferable variants of AOT application may be different even for NSs having rather similar natures. In the case of Brij 30, the use of AOT as a cosurfactant at the stage of the synthesis has decreased the stability of nanoparticles, thereby making it impossible to obtain reproducible data on their  $\zeta$ -potential. However, the addition of AOT in small amounts after the synthesis makes it possible to obtain nanoparticles with a  $\zeta$ -potential that is relatively low but reliably measurable. In the case of Tergitol NP-4, small additives of AOT introduced after the synthesis have led to an analogous situation; however, the use of Tergitol NP-4 + AOT mixed micelles gives rise to the formation of nanoparticles with a high  $\zeta$ -potential. It should be noted that stabilization with a Tergitol NP-4 + AOT mixture may make it possible to obtain organosols with a high molar concentration of a metal by means of nonaqueous electrophoresis [24]. Both these approaches lead to a decrease in the AOT fraction in the systems, thereby giving grounds to expect an increase in the electrical conductivity of silver coatings obtained on their basis.

The results obtained for the case of Span 80 are most unusual. Nanoparticles stabilized with this NS have a relatively high  $\zeta$ -potential. The incorporation of AOT as a cosurfactant at the stage of the synthesis decreases the  $\zeta$ -potential of nanoparticles, while its addition after the synthesis increases it. This system needs undoubtedly to be studied in detail. The interest is primarily attracted by the nature of the charge carriers that form the diffuse part of an EDL. It may be expected that the use of Span 80 will make it possible to obtain concentrated organosols without application of any "charging additives." Such organosols will represent a promising variant of inks for printed electronics and enable one to produce silver coatings with increased purity and conductivity.

#### FUNDING

This work was supported by the Russian Foundation for Basic Research, project no. 18-33-00064 mol-a.

#### CONFLICT OF INTEREST

The author declare that he have no conflict of interest.

COLLOID JOURNAL Vol. 82 No. 2 2020

### REFERENCES

- 1. Wu, W., Nanoscale, 2017, vol. 9, p. 7342.
- Kamyshny, A. and Magdassi, S., *Small*, 2014, vol. 10, p. 3515.
- Shin, D.-H., Woo, S., Yem, H., Cha, M., Cho, S., Kang, M., Jeong, S., Kim, Y., Kang, K., and Piao, Y., *ACS Appl. Mater. Interfaces*, 2014, vol. 6, p. 3312.
- 4. Vassem, M., McKerricher, G., and Shamim, A., ACS Appl. Mater. Interfaces, 2016, vol. 8, p. 177.
- 5. Jason, N.J., Shen, W., and Cheng, W., ACS Appl. Mater. Interfaces, 2015, vol. 7, p. 16760.
- Lee, K.J., Jun, B.H., Kim, T.H., and Joung, J., Nanotechnology, 2006, vol. 17, p. 2424.
- Shinde, S.R., Banpurkar, A.G., Adhi, K.P., Limaye, A.V., Ogale, S.B., Date, S.K., and Marest, G., *Mod. Phys. Lett. B*, 1996, vol. 10, p. 1517.
- Begin-Colin, S., Wolf, F., and Le Caer, G., J. Phys. III, 1997, vol. 7, p. 473.
- 9. Ananthapadmanabhan, P.V., Sreekumar, K.P., Venkatramani, N., Sinha, P.K., and Taylor, P.R., *J. Alloys Compd.*, 1996, vol. 244, p. 70.
- 10. Lu, J., Yang, H., Yu, S., and Zou, G., *Mater. Chem. Phys.*, 1996, vol. 45, p. 197.
- 11. Pileni, M.P., J. Phys. Chem., 1993, vol. 97, p. 6961.
- 12. Eastoe, J., Hollamby, M.J., and Hudson, L., Adv. Colloid Interface Sci., 2006, vols. 128–130, p. 5.

- 13. Zhang, W., Qiao, X., Chen, J., and Wang, H., *J. Colloid Interface Sci.*, 2006, vol. 302, p. 370.
- 14. Popovetskiy, P.S., Shaparenko, N.O., Arymbaeva, A.T., and Bulavchenko, A.I., *Colloid J.*, 2016, vol. 78, p. 485.
- 15. Sainis, S.K., Merrill, J.W., and Duffresne, E.R., *Langmuir*, 2008, vol. 24, p. 13334.
- 16. Sainis, S.K., Germain, V., Mejean, C.O., and Duffresne, E.R., *Langmuir*, 2008, vol. 24, p. 1160.
- Popovetskiy, P.S., Bulavchenko, A.I., and Manakov, A.Yu., *Opt. Zh.*, 2011, vol. 78, no. 7, p. 67.
- 18. Bulavchenko, A.I. and Pletnev, D.N., *J. Phys. Chem. C*, 2008, vol. 112, p. 16365.
- 19. Bulavchenko, A.I. and Popovetskiy, P.S., *Langmuir*, 2010, vol. 26, p. 736.
- 20. O'Brien, R.W. and White, L.R., *J. Chem. Soc., Faraday Trans.*, 1978, vol. 74, p. 1607.
- Delgado, A.V., Gonzalez-Caballero, F., Hunter, R.J., Koopal, L.K., and Lyklema, J., *J. Colloid Interface Sci.*, 2007, vol. 309, p. 194.
- 22. Morrison, I.D., Colloids Surf. A, 2008, vol. 71, p. 1.
- 23. Popovetskiy, P.S., Bulavchenko, A.I., Demidova, M.G., and Podlipskaya, T.Yu., *Colloid J.*, 2015, vol. 77, p. 58.
- 24. Popovetskiy, P.S. and Beketova, D.I., *Colloids Surf. A*, 2019, vol. 568, p. 51.

Translated by A. Kirilin