

Article

Synthesis of Silver Nanoparticles with Gemini Surfactants as Efficient Capping and Stabilizing Agents

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Abstract: The scientific community has paid special attention to silver nanoparticles (AgNPs) in recent years due to their huge technological capacities, particularly in biomedical applications, such as antimicrobials, drug-delivery carriers, device coatings, imaging probes, diagnostic, and optoelectronic platforms. The most popular method of obtaining silver nanoparticles as a colloidal dispersion in aqueous solution is chemical reduction. The choice of the capping agent is particularly important in order to obtain the desired size distribution, shape, and dispersion rate of AgNPs. Gemini alkylammonium salts are named as multifunctional surfactants, and possess a wide variety of applications, which include their use as capping agents for metal nanoparticles synthesis. Because of the high antimicrobial activity of gemini surfactants, AgNPs stabilized by this kind of surfactant may possess unique and strengthened biocidal properties. The present paper presents the synthesis of AgNPs stabilized by gemini surfactants with hexadecyl substituent and variable structure of spacer, obtained via ecofriendly synthesis. UV-Vis spectroscopy and dynamic light scattering were used as analyzing tools in order to confirm physicochemical characterization of the AgNPs (characteristic UV-Vis bands, hydrodynamic diameter of NPs, polydispersity index (PDI)).

Keywords: silver nanoparticles; gemini surfactant; green synthesis



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1. Introduction

Over the past twenty years, silver nanoparticles (AgNPs) have become increasingly popular due to their special physical, chemical, and biological properties. It is characteristic that, depending on the surface to volume ratio, the properties of nanosilver change, and they have been exploited for different purposes [1,2]. AgNPs offer promising prospects for a wide range of applications, such as antimicrobials against bacteria [3–12], fungi [10,13–17], and viruses [9,18–23]. Silver nanoparticles can also be helpful in managing the ongoing pandemic of COVID-19 (Coronavirus Disease 2019) caused by the SARS-CoV-2 (severe acute respiratory syndrome coronavirus 2) [24,25]. AgNPs have been tested as biomedical device coatings [12,26–28], combating multidrug-resistant cancer [12,29], drug-delivery carriers [12,30], and imaging probes in ultrasensitive analysis [26,31–34]. They may also find applications in sensing [27,31,35,36] and chemical catalysis [32,35,37–39]. Due to the great interest of AgNPs, different synthetic methods have been developed, such as physical, chemical, and biological approaches [26,40,41]. Among them, chemical reduction is the most frequently used synthesis method of silver nanoparticles, with high productivity and low costs [39,41]. In this approach, stable colloids in water or non-aqueous solvents can be obtained. Generally, synthesis of AgNPs in solution requires three particular components: metal precursors (silver nitrate, perchlorate, chloride, trifluoroacetate or $(\text{PPh}_3)_3\text{AgNO}_3$), reducers, and stabilizers [42]. Several reductants are commonly used for the preparation of the AgNPs: sodium borohydride, sodium citrate, glucose, *N,N*-dimethylformamide, hydrazine, polyols, (e.g., ethylene glycol, diethylene glycol), formaldehyde [42]. One important factor is to apply capping agents to stabilize dispersive NPs, thus protect them

against their agglomeration [41]. In general, the shape and size distribution of the synthesized nanoparticles are controlled by altering the method and conditions of the synthesis, reducing and stabilizing agents, their concentrations, and molar ratios [43]. Recently, different types of surfactants started to be used as stabilizing agents for AgNPs. We should mention that a proper stabilizer and/or reaction time is crucial for the obtaining of stable and small size Ag nanoparticles [44].

Dimeric quaternary alkylammonium salts, named by Menger and Littau as gemini, are modern type of surfactants [45]. These compounds consist of two long alkyl substituents and two cationic headgroups connected by a linker. The connector may have various structures: short, long, flexible, stiff, polar (e.g., functionalized by heteroatoms), and nonpolar (e.g., hydrocarbon chains or rings) [46–50]. Spacer and hydrophobic chain are very important units in gemini surfactant architecture. They are a keystone in the adsorption of dimeric surfactants on surfaces and interfaces, in creation of micelles of different shapes [48,49,51–54]. Considering the structure of gemini surfactants, they exhibit a higher efficacy in contrast to monomeric (conventional) surfactants, such as decreased critical micelle concentration (CMC), greater ability to reduce surface tension, or promote antimicrobial activity [48,50,55–57]. From an ecological point of view, dimeric alkylammonium salts are considerably less toxic to marine organisms than quaternary ammonium salts [58,59], and can be biodegradable [48,60–62]. Considering the above properties, and the fact that the use of gemini surfactant provides the desired effect at a lower concentration in comparison to monomeric analogues, the use of dimeric alkylammonium salts is correlated with the greenolution idea in chemistry [63,64]. Gemini surfactants, due to their antimicrobial properties against bacteria [48,55,56,65–70] and fungi [47,48,56,66,71], can be used as microbicides or biofilm eradication agents in many areas of life and industries [66,72–74].

In reference to the growing interest in silver nanoparticles and gemini surfactants, we focused on the different procedures for obtaining silver nanoparticles capped with gemini surfactants, having a different structure in spacer unit, obtained in easy, low-cost, and green synthesis. Detailed spectroscopic analysis and surface activity of the gemini surfactants, as well as analysis of AgNPs based on a UV-Vis, and dynamic light scattering (DLS) study were presented.

2. Materials and Methods

2.1. Material Used

N,N-Dimethyl-*N*-hexadecylamine, bis(2-bromoethyl)ether, 1,6-dibromohexane, silver nitrate, and sodium borohydride, were obtained from Sigma-Aldrich (Poznan, Poland). Acetonitrile and diphosphorus pentoxide were purchased from VWR Chemicals (Gdansk, Poland). Reagent purity was at least 95%. All materials were used without prior purification.

2.2. Synthesis

2.2.1. Synthesis of Gemini Surfactants

The 16-6-16 (1,6-hexamethylene-bis(*N*-hexadecyl-*N,N*-dimethylammonium bromide)): the *N,N*-dimethyl-*N*-hexadecylamine (10 g; 37 mmol) and 1,6-dibromohexane (4.5 g; 18.8 mmol) were placed in a 250 mL round-bottom flask. Reaction mixture was stirred without the solvent at room temperature for 2 h. Then, the reaction mixture was left to solidify completely. The crude product was purified by crystallization from acetonitrile, filtered, and dried in a vacuum desiccator over P₂O₅ and in an oven at 60 °C. Reaction yield was over 98%.

The 16-O-16 (3-oxa-1,5-pentane-bis(*N*-hexadecyl-*N,N*-dimethylammonium bromide)): the *N,N*-dimethyl-*N*-hexadecylamine (10 g; 37 mmol) and bis(2-bromoethyl)ether (4.36 g; 18.5 mmol) were placed in a 250 mL round-bottom flask. Reaction mixture was stirred without the solvent at room temperature for 2 h. Then, the reaction mixture was left to solidify completely. The crude product was purified by crystallization from acetonitrile,

filtered, and dried in a vacuum desiccator over P_2O_5 and in an oven at 60 °C. Reaction yield was over 95%.

2.2.2. Synthesis of Silver Nanoparticles

Experiments 1–6: 40 mL of 0.75 mM silver nitrate was mixed with 10 mL of specific amount of gemini surfactant (16-6-16 or 16-O-16) corresponding to three different molar ratio $nAg/nGemini = 2.5; 5; 10$. The mixture was stirred for 5 min, and then 5 mL of 1 mM sodium borohydride cold solution was added dropwise. Color changed to intense orange. After adding all of the solution, stirring occurred for another 20 min.

Experiment 7: 15 mL of 4 mM $NaBH_4$ and 10 mL of 0.2 mM 16-6-16 solutions were placed in a 100 mL Erlenmeyer flask and stirred for 5 min. Then 5 mL of 2 mM $AgNO_3$ was added dropwise to the flask. Stirring continued for another 20 min.

Experiment 8: 5 mL of 12 mM $NaBH_4$ was placed in a 100 mL Erlenmeyer flask with 20 mL of water. Solution of 10 mL of 1 mM $AgNO_3$ and 10 mL of 0.2 mM 16-6-16 was prepared separately and added dropwise into $NaBH_4$. After adding all of the solution, stirring occurred for another 20 min.

All of the experiments were repeated three times in order to confirm the reproducibility of the synthetic procedures. The AgNPs stabilized by gemini surfactants were stable for at least three months, during which no changes in the UV-vis and DLS were observed.

2.3. Experimental Methods

2.3.1. Analysis of Dimeric Alkylammonium Salts

The melting point of the synthesized gemini surfactants was measured on Stuart SMP30 apparatus (Staffordshire, UK), using capillary with one sealed side. The measurements give the values with resolution of 1.0 °C. The elemental analysis measurements were performed on a FLASH 2000 elemental analyzer (Delft, The Netherlands) with a thermal conductivity detector. The nuclear magnetic resonance (NMR) spectra were measured with a Varian VNMR-S 400 MHz (Oxford, UK), operating at 403 and 101 MHz for 1H and ^{13}C respectively, attendant with software Vnmr VERSION 2.3 REVISION A (Varian, Oxford, UK). The chemical shifts were performed in $CDCl_3$ relative to an internal standard—TMS (tetramethylsilane). The Fourier Transform Infrared Spectroscopy (FTIR) spectra were performed on FT-IR Bruker IFS 66v/S (Poznan, Poland) apparatus. All of the samples were tested in solid state in the form of tablets with potassium bromide.

The critical micelle concentration values were determined by conductivity analysis using a Conductivity Meter Elmetron CC-505 (Zabrze, Poland). The apparatus was calibrated by a standard (147 $\mu S/cm$ in 298.15 K). All samples were obtained using deionized water. Conductivity measurements were carried out at 25 °C. The titration was repeated at least three times for each compound.

2.3.2. Analysis of Silver Nanoparticles

UV-Vis absorption spectra of all the AgNPs solutions capped with dimeric ammonium salts were recorded on Varian Cary 50 Scan UV-Vis spectrophotometer (Varian, Oxford, UK) at 25 °C, operated with Cary WinUV software (Varian, Oxford, UK) with quartz cuvettes of 1 cm path length. In all cases, samples were diluted 5-fold with deionized water, to decrease the absorbance to the range suitable for UV-Vis measurements.

Dynamic light scattering measurements and polydispersity index (PDI) were performed at 25 °C using Zetasizer, Nano-ZS Malvern Instruments (Malvern, UK) with a He-Ne laser (633 nm, 4 mW) equipped with a built-in thermo-controller. Ten repeated measurements were conducted for each sample.

3. Results and Discussion

3.1. Synthesis and Spectroscopic Characterization of Gemini Surfactants

Gemini surfactants tested in this paper as capping agents for AgNPs were received by alkylation of *N,N*-dimethyl-*N*-hexadecylamine with 1,6-dibromohexane or bis(2-bromoethyl) ether, for 16-6-16, and 16-O-16 respectively (Figure 1). A synthetic procedure developed in our laboratory assumes carrying out the reaction without a solvent at room temperature [50,75]. These reactions proceed according to the nucleophilic substitution mechanism S_N2 . The rate of these reactions depends on the substrates concentrations. In case of the reaction without a solvent, the concentration of the reactants is the highest possible. Such reactions take place with high efficiency without waste. These reactions are in accordance with the greenolution approach, because they reduce the use of solvent to a minimum and minimize costs.

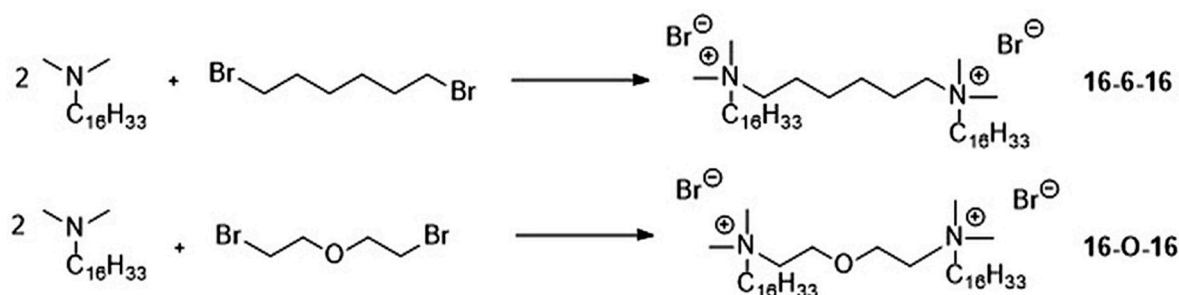


Figure 1. Synthesis of 16-6-16 and 16-O-16.

The structure and purity of gemini surfactants obtained were confirmed by ^1H NMR, ^{13}C NMR, FTIR, and elemental analysis.

The 16-6-16: mp 222–223 °C; elemental analysis (%) calcd. for $\text{C}_{42}\text{H}_{90}\text{Br}_2\text{N}_2$: C 64.43, H 11.58, N 3.58; found C 64.72, H 11.68, N 3.40; ^1H NMR (403 MHz, CDCl_3) 3.73 (bs, 4H, $\text{N}^+\text{CH}_2(\text{spacer})$), 3.49 (m, 4H, $-\text{N}^+\text{CH}_2-$), 3.39 (s, 12H, $-\text{N}^+(\text{CH}_3)_2$), 2.01 (bs, 4H, $-\text{N}^+\text{CH}_2\text{CH}_2-(\text{spacer})$), 1.72 (bs, 4H, $-\text{N}^+\text{CH}_2\text{CH}_2-$), 1.57 (bs, 4H, $-\text{N}^+\text{CH}_2\text{CH}_2-\text{CH}_2(\text{spacer})$), 1.36–1.25 (m, 52H, $-\text{CH}_2(\text{CH}_2)_{13}\text{CH}_3$), 0.88 (t, 6H, $-\text{CH}_2\text{CH}_3$); ^{13}C NMR (101 MHz, CDCl_3): 65.9 ($-\text{N}^+\text{CH}_2\text{spacer}$), 64.06 ($-\text{N}^+\text{CH}_2-$), 50.98 ($-\text{N}^+\text{CH}_3$), 31.89 ($-\text{CH}_2\text{CH}_2\text{CH}_3$), 29.61, 29.59, 29.56, 29.34, 29.27, 29.45, 29.37, 29.12 ($-\text{N}^+(\text{CH}_2)_2(\text{CH}_2)_{11}-$), 26.86 ($-\text{N}^+\text{CH}_2\text{CH}_2-$), 24.37 ($-\text{N}^+\text{CH}_2\text{CH}_2-(\text{spacer})$), 22.6 ($-\text{N}^+\text{CH}_2\text{CH}_2-\text{CH}_2(\text{spacer})$), 21.61 ($-\text{CH}_2\text{CH}_3$), 14.11 ($-\text{CH}_2\text{CH}_3$).

The 16-O-16: mp 240–242 °C; elemental analysis (%) calcd. for $\text{C}_{40}\text{H}_{86}\text{Br}_2\text{N}_2\text{O}$: C 62.32, H 11.24, N 3.63; found C 61.41, H 11.68, N 3.20; ^1H NMR (403 MHz, CDCl_3) 4.36 (bs, 4H, OCH_2), 4.05 (bs, 4H, $\text{N}^+\text{CH}_2\text{CH}_2\text{O}-$), 3.67–3.62 (m, 4H, $-\text{N}^+\text{CH}_2-$), 3.46 (s, 12H, $-\text{N}^+(\text{CH}_3)_2$), 1.73 (bs, 4H, $-\text{N}^+\text{CH}_2\text{CH}_2-$), 1.47–1.10 (m, 52H, $-\text{CH}_2(\text{CH}_2)_{13}\text{CH}_3$), 0.88 (t, 6H, $-\text{CH}_2\text{CH}_3$); ^{13}C NMR (101 MHz, CDCl_3): 65.92 ($-\text{N}^+\text{CH}_2\text{CH}_2\text{O}-$), 64.59 ($-\text{OCH}_2-$), 64.03 ($-\text{N}^+\text{CH}_2-$), 51.57 ($-\text{N}^+\text{CH}_3$), 31.82 ($-\text{CH}_2\text{CH}_2\text{CH}_3$), 29.61, 29.58, 29.56, 29.54, 29.45, 29.37, 29.25, 26.25 ($-\text{N}^+(\text{CH}_2)_2(\text{CH}_2)_{11}-$), 22.83 ($-\text{N}^+\text{CH}_2\text{CH}_2-$), 22.58 ($-\text{CH}_2\text{CH}_3$), 14.00 ($-\text{CH}_2\text{CH}_3$).

FTIR spectra for tested dimeric alkylammonium salts (Figure 2) show regular bands for the asymmetric (ν_{as}) and symmetric (ν_{s}) stretching vibrations of methyl and methylene groups at 2916–2846 cm^{-1} , as well as bands for the deformation vibration (δ) of methyl groups at 1472–1464 cm^{-1} . The 16-O-16 spectra shows usual peaks of C–O stretching vibration at 1146 cm^{-1} . Due to hydrophilicity (ability to absorb water) of gemini surfactants the strong absorption at the 3500–3350 cm^{-1} region from the $-\text{OH}$ stretching vibrations of water molecule is detected in FTIR spectra.

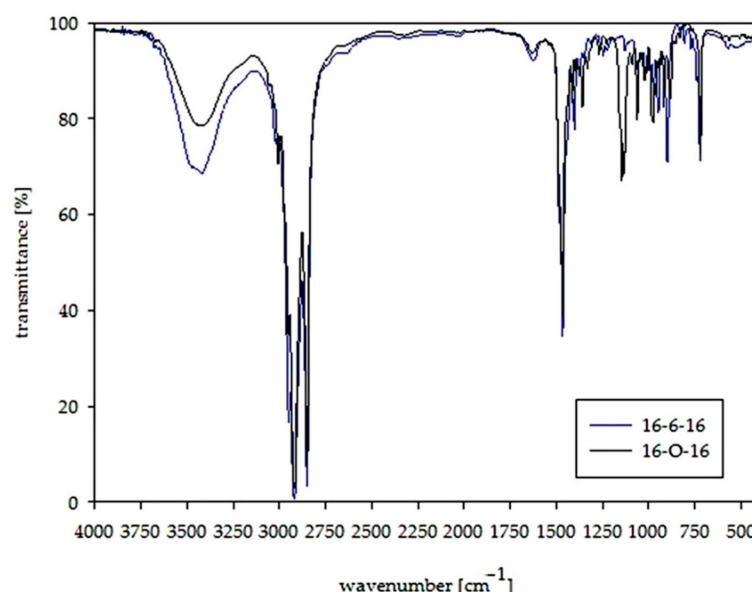


Figure 2. FTIR spectra for 16-6-16 and 16-O-16.

3.2. Surface Properties of Gemini Surfactants

The basic ability of surface active agents is their tendency to be adsorbed at interfaces. Mechanism of surface action of dimeric surfactants based on the adsorption of ammonium cations into a polar phase, and hydrocarbon chains in a nonpolar phase [48]. The keystone of all surfactants research is determination of their critical micelle concentration [49], the lowest concentration at which particles rapidly aggregate into micelles. The fact that dimeric alkylammonium salts have much lower CMC values than monomeric ones, creates great application possibilities for them [52,63,76–79]. The determination of CMC is also important, because toxicity of gemini rises when their concentration surpasses CMC [80].

The CMC was determined using a conductometric titration, creating dependency graphs of the characteristic conductivity in water of the obtained compounds as a function of the concentration. This relationship generates two lines with different slopes. The straight line with higher inclination illustrates behavior before micellization, whereas the line with a smaller slope indicates the process of micellization (Figure 3). The intersection of lines formed as a result of linear regression defines CMC [50,59].

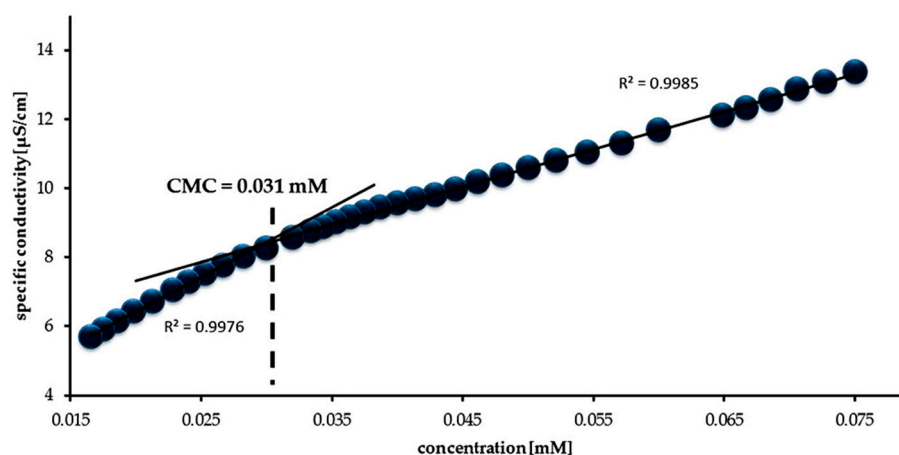


Figure 3. Specific conductivity versus surfactant concentration in water for 16-O-16.

The values for the slope ratios of linear regression in pre- and post-micellization regions allow estimating the degree of ionization (α) and the degree of counterion binding parameter (β). These parameters demonstrate the capability of the counterion binding on

the micelles [50,59]. Knowing the values of CMC and β allow for calculation of Gibbs free energy of micellization ($\Delta G^{\circ}_{\text{mic}}$) [81]. The experimental values of CMC, α , β and $\Delta G^{\circ}_{\text{mic}}$ for the investigated gemini surfactants are given in Table 1.

Table 1. Critical micelle concentration, degree of ionization, counterion binding parameter, and Gibbs free energy of micellization in 25 °C.

Surfactant	CMC (mM)	α	β	$\Delta G^{\circ}_{\text{mic}}$ (kJ/mol)
16-6-16	0.034	0.55	0.45	−50.16
16-O-16	0.031	0.40	0.60	−58.32

Critical micelle concentration of dimeric surfactants depends on many structural elements: length and structure of spacer and substituents and type of anion. It is well known that gemini surfactants with long (hexadecyl, octadecyl) substituents possess lower CMC values than analogues with shorter hydrocarbon chain [48–50,77,82–86]. CMCs of dimeric alkylammonium salts tested in this work are over thirty times lower, than CMC of 12-6-12 (1,6-hexamethylene-bis(*N*-hexadecyl-*N,N*-dimethylammonium bromide)) which is 0.98 (mM) [57]. Surface activity of our gemini surfactants, although they have different spacer structure, is comparable. This result are in good correlation to our previous result—that an element of the structure, which essentially affects the surface activity, is the length of the substituent, not the structure of the linker [50].

The 16-O-16 possesses a lower degree of ionization value than 16-6-16. The small α is caused by the stronger binding of the counterion to the aggregates, suggesting better packing of the head groups and higher surface charge density at the interface [50,51]. Both obtained gemini surfactants have negative $\Delta G^{\circ}_{\text{mic}}$, indicating that the micellization process is spontaneous [50,55]. Surfactant with oxygen-functionalized spacer (16-O-16) shows greater tendency to form micelles, because in this case $\Delta G^{\circ}_{\text{mic}}$ is lower.

3.3. Preparation and Characterization of Silver Nanoparticles

AgNPs were prepared by chemical synthetic procedure under different conditions. We used: silver salt (AgNO_3) as a metal precursor, sodium borohydride (NaBH_4) as a reductant and gemini surfactants (16-6-16 in experiments 1–3 and 7–8, 16-O-16 in experiments 4–6) as stabilizing agents (Figure 4). Experiments 1–6 were performed according to preparation described by Pisárčik [87]. Different molar ratios of AgNO_3 and gemini surfactants were applied to study the formation of AgNPs (Table 2). In these cases, $n\text{AgNO}_3$ was taken in excess of 6-fold to $n\text{NaBH}_4$. Experiments 7 and 8 were carried out by another procedure, with 16-6-16 as stabilizing agent in silver-gemini surfactants molar ratio 5 (Table 2). In these cases, $n\text{NaBH}_4$ was taken in excess of 6-fold to $n\text{AgNO}_3$.

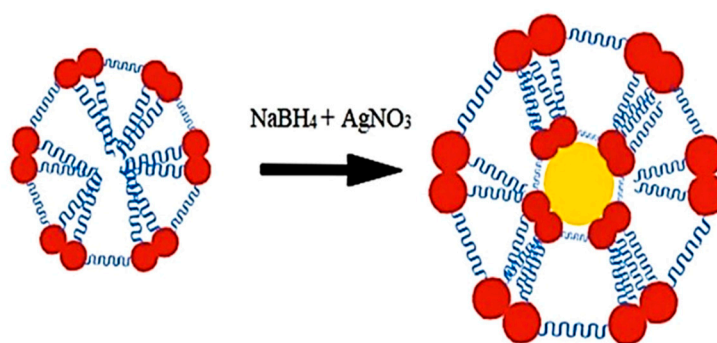


Figure 4. Schematic representation of the formation of layer of gemini surfactants, surrounding the Ag nanoparticles.

Table 2. Experimental data of different procedures for AgNPs obtaining.

Experiment	Gemini Surfactant	Molar Ratio nAg/nGemini	Concentration of AgNO ₃ [mM]
1	16-6-16	2.5	0.75
2	16-6-16	5	0.75
3	16-6-16	10	0.75
4	16-O-16	2.5	0.75
5	16-O-16	5	0.75
6	16-O-16	10	0.75
7	16-6-16	5	2
8	16-6-16	5	1

The color of AgNPs solution depends on the degree of dilution of the colloids, starting from yellow and going to intense orange with the increase of colloids concentration. Gemini surfactant allows for keeping the nanodispersion homogeneous, with a color depending on the nanodispersion dilution. In our work, in all experiments, the intense orange color was formed, showing that the reaction was followed by the formation of nanoparticles [87–90]. The color of AgNPs solution is suggested to appear due to localized surface plasmon resonance (LSPRs). LSPR is a collective excitation of the free electrons in the conduction band around the surface of the nanoparticles. The electrons are specified to particular vibration modes, which depend on particle size and shape. Therefore, AgNPs could be detected and characterized by UV-Vis. With increasing of particle size, the absorption wavelength shifts to longer wavelengths [91].

UV-Vis spectroscopic analysis is an essential technique for observation of AgNPs formation and stability in solution. The absorbance peak of silver nanoparticles usually occurs at wavelength range of 350–450 nm, and moves to longer wavelengths with progressive particle size [91]. In Figure 5a, the UV-Vis spectra of AgNPs, which were stabilized with 16-6-16 is presented. The spectra were measured for three various Ag-to-gemini surfactant molar ratios: nAg/n16-6-16 = 2.5; 5; 10. We can see that from the highest gemini concentration (experiment 1) to the lowest (experiment 3), the peak of absorbance increases gradually: 0.286, 0.332 and 0.359. As it is known, the absorbance is directly connected with the concentration, thus, since the difference is not significant, it can be concluded that 16-6-16 has a strong stabilizing effect on AgNPs in the extensive range of nAg/n16-6-16 molar ratio values. However, the nAg/n16-6-16 molar ratio at 2.5 indicates a slightly weak stabilizing effect since the concentration of AgNPs is not high.

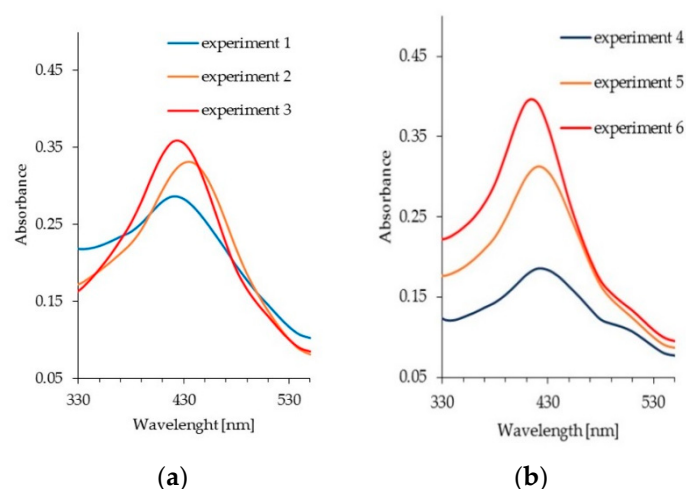
**Figure 5.** UV-Vis spectra of silver nanoparticles stabilized with gemini surfactants (a) 16-6-16; (b) 16-O-16 at different nAg/nGemini values.

Figure 5b shows the UV-Vis absorption spectra of nanoparticles stabilized with 16-O-16. These AgNPs were synthesized similar to the previous ones, but 16-O-16 was taken as capping agent (experiment 4–6). We observe that the peak of absorbance gradually increases with the decrease of gemini surfactant concentration as well, as in the case of experiments 1–3. The peaks of absorbance for experiments 4, 5, and 6 are 0.185, 0.313, and 0.397, respectively. The stabilizing effect of 16-O-16 on AgNPs is stronger for molar ratios of $n\text{Ag}/n16\text{-O-16} = 5$ and 10, whereas it has weaker effect for reaction with $n\text{Ag}/n16\text{-O-16}$ molar ratio of 2.5. Same trend was observed for 16-6-16.

UV-Vis absorption spectra of AgNPs obtained in experiments 7 and 8 are shown in Figure 6. Strong absorption peaks at approximately 410 and 419 nm come from the surface plasmon absorption of nanosized silver particles. These spectra stand out; the good symmetric absorption peaks with a nearly unaltered width, suggesting that the size of the nanoparticles is very homogenous [89,92].

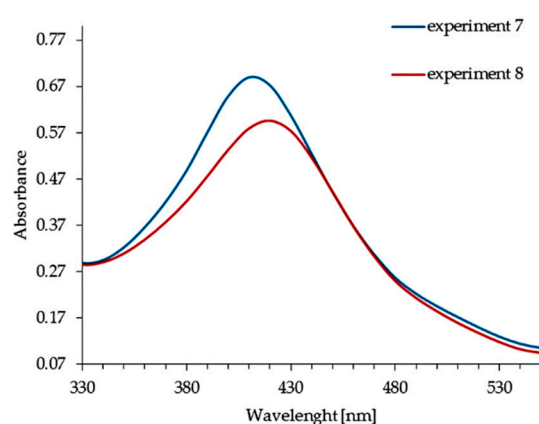


Figure 6. UV-Vis spectra of silver nanoparticles stabilized with 16-6-16 obtained in procedure with excess of reductant.

All UV-Visible absorption spectra exhibit the absorbance peaks in the range of 410–435 nm (Table 3), which is typical feature for colloidal silver nanoparticles [93], confirming our statement that gemini surfactants in the Ag nanodispersion ensures a stabilizing effect on the nanoparticles. These results are in good correlation with what was described previously [87,94,95].

Table 3. The wavelength and absorbance data obtained from UV-Vis spectra.

Experiment	Wavelength [nm]	Absorbance
1	420	0.286
2	435	0.332
3	425	0.359
4	420	0.185
5	420	0.313
6	415	0.397
7	410	0.690
8	419	0.596

Consequently, the colloidal stability is also confirmed by the polydispersity index (PDI), which is given in DLS analysis and should be less or about 0.3. If the PDI is equal or higher than 1, the observable precipitation may occur [96]. The PDI values were between 0.2 and 0.4 in experiments 1–3 and 7–8, illustrating good colloidal features, and PDI values around 0.5 were found to be for the experiments 4–6. Higher PDI values in experiments 4–6 supports relatively broad and slightly distorted width of the UV-Vis spectra (Figure 5b) as well as the visual minor nanodispersions, which were of white color.

3.4. Effect of Spacer Structure on the Size of Silver Nanoparticles

The size of AgNPs capped with gemini and their particle size distributions were obtained using DLS measurements. The Figure 7 shows hydrodynamic diameter of nanoparticles stabilized with gemini surfactants 16-6-16 and 16-O-16, which is plotted as a function of the nAg/nGemini molar ratio. The nanoparticle diameter values illustrate an average value of the particle size distribution.

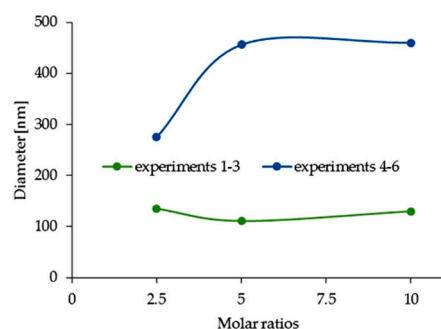


Figure 7. Size of silver nanoparticles capped with 16-O-16 and 16-6-16 as a function of nAg/nGemini molar ratio.

For experiments 4–6 we can observe, that with decreasing of 16-O-16 concentration the silver nanoparticles diameter size increase. However, in the case of 16-6-16 (experiments 1–3) the opposite trend is noticed—we monitor the almost constant diameter size in the range of all molar ratios. Construction of the spacer of gemini surfactants have a considerable impact on nanoparticles size. Compounds with more hydrophobic linker stabilizes more efficiently and gives smaller AgNPs than analog with spacer functionalized by ether group.

Hydrodynamic diameter of silver nanoparticles, stabilized with 16-6-16 from synthetic procedure with excess of reductor, are 110 and 220 nm for experiments 7 and 8, respectively. These results clearly show that synthetic procedure applied in experiment 7 gives the smallest AgNPs with the best stabilizing effect of gemini bilayer. Figure 8 represents the particle size distribution histograms of AgNPs synthesized in the experiments 7 and 8.

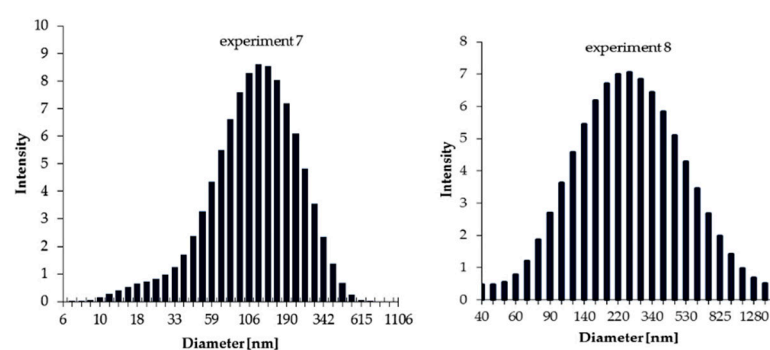


Figure 8. Particle size distribution histograms of AgNPs obtained by DLS measurements.

In fact, the particle sizes of AgNPs measured by DLS is the whole conjugate size, with countslayer of capping agents too [88]. This explains the relatively big diameters. He et al. explained that the gemini cationic surfactants can be adsorbed on the particle surface due to electrostatic interactions between surfactant positive charge head group and counterions attached onto the nanoparticle surface. This causes the formation of coating layers, which lowers the aggregation of particles [90]. Pisárčik et al. demonstrates that gemini surfactants with dodecyl substituent and different spacer length from two to twelve carbon atoms are able to efficiently stabilize silver nanoparticles [87]. Our results indicate that gemini surfactants with longer substituent can also be applied as efficient stabilizer for AgNPs.

Introduction of oxygen atom to spacer results in an increase of hydrophilicity of surfactant molecule. This caused increasing of formed silver nanoparticles size, indicating that the stabilizing effect of gemini bilayer is less efficient. We also demonstrate that, not only the kind of stabilizing agent is crucial, but also synthetic procedures and silver to gemini surfactant molar ratios are very important factors in AgNPs synthesis. These results are in good correlation with what was described previously [87].

4. Conclusions

The 1,6-hexamethylene-bis(*N*-hexadecyl-*N,N*-dimethylammonium bromide) and 3-oxa-1,5-pentane-bis(*N*-hexadecyl-*N,N*-dimethylammonium) bromide) were obtained via solvent-free green synthetic procedure. The products structures have been confirmed by ^1H and ^{13}C NMR, FTIR, and elemental analysis. The critical micelle concentrations were specified by conductivity measurement. Silver nanoparticles were obtained via chemical reduction, using gemini surfactants as stabilizing agent. Physicochemical investigations were done by using UV-Vis spectroscopy and DLS measurements. We demonstrated that the structure of the gemini surfactant and conditions of the silver nanoparticles preparation determine their shape and size distribution. It was shown that the hydrophilicity of the dimeric alkylammonium salts can affect the size distribution of AgNPs. The best stabilization, which is represented by a small nanoparticle size, was received in experiment with 16-6-16 as a stabilizing agent, molar ratio $n\text{Ag}/n\text{Gemini} = 5$, and with excess of reductant. Results of our research show that application of gemini surfactants is a prospective field of study, which may provide an easy-to-follow green method for the synthesis of nanoparticles.

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