INCREASED STABILITY OF SILVER NANOPARTICLES IN SALINE AND OXIDIZING MEDIA IN THE PRESENCE OF BIOGENIC AMINES

E. A. Kurskaya,* A. A. Askadskii, O. A. Serenko, and N. A. Samoilova

Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, str. 1, Moscow, 119334 Russia

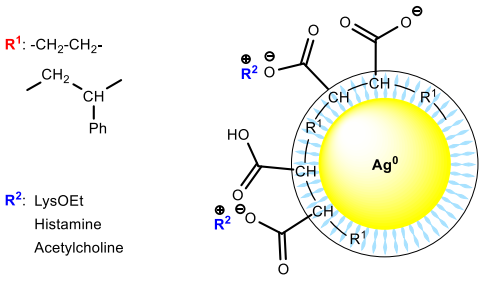
Cite this: *INEOS OPEN*, **2022**, *5 (5)*, 138–143
DOI: 10.32931/io2225a

Received 14 June 2023,
Accepted 29 July 2023

http://ineosopen.org

Abstract

The research has been carried out to increase the stability of silver nanoparticles stabilized by maleic acid copolymers in saline and oxidizing media. It is shown that the stability of silver nanoparticles in NaCl and H_2O_2 solutions increases upon complexation with biocompatible amines, namely, histamine, Lys-OEt, and acetylcholine. The additional steric and electrochemical stabilization allows for maintaining significantly the stability of nanocomplexes in solutions of salts and oxidizing agents at 40 °C. The destruction of the nanocomplexes was studied by UV-vis spectroscopy, transmission electron microscopy, and gel permeation chromatography.



Key words: maleic acid copolymer, silver nanoparticles, stability in saline and oxidizing media.

Introduction

It is known that nanoparticles of some metals, including silver nanoparticles (AgNPs), display bactericidal properties and, as a rule, do not cause addiction of pathogenic microorganisms [1]. Various forms and modifications of silver, in particular, nanosized particles are used as antimicrobial agents or diagnostic tools owing to pronounced plasmon resonance. Nanosilver-based preparations can be used in biomedical applications: for treatment and drug delivery, as coatings for medical devices from various materials, *etc.* [2]. The main problem that arises when using AgNPs in biomedicine is the lack of stability under physiological conditions and in an oxidizing environment. In dilute systems, silver nanoparticles are in equilibrium with atmospheric oxygen, but the presence of electrolytes (for example, NaCl) contributes to the oxidation of nanoparticles with the formation of silver cations and a number of insoluble compounds according to the following schemes.

$$2Ag^0 + ½O_2 = Ag_2O\downarrow$$
$$Ag_2O + H_2O = 2Ag^+ + 2OH^-$$
$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

At a large excess of chloride ions relative to silver nanoparticles, various soluble coordination complexes of the general formula $[AgCl_x]^{(1-x)}$ can be formed. Their compositions depend on the Cl^-/Ag^0 molar ratio [3].

It is known that in electrolyte solutions, due to a decrease in the zeta potential of AgNPs, the rate of particle aggregation changes according to the Derjaguin–Landau–Verwey–Overbeek (DLVO) coagulation theory. For example, at low concentrations of sodium chloride in solution (10–40 mM), the aggregation rate of 0.05 mM silver nanoparticles stabilized by fulvic acid increases with an increase in the electrolyte concentration and, after reaching the maximum value (at a NaCl concentration of about 40 mM), changes insignificantly. To evaluate the aggregation kinetics of nanoparticles in solutions of different electrolytes (NaCl, $NaNO_3$, $CaCl_2$) depending on their concentrations, dynamic light scattering was used [4]. The critical coagulation concentrations were found to be 30, 40, and 2 mM for $NaNO_3$, NaCl, and $CaCl_2$, respectively. At the initial stage of aggregation, the size of AgNPs with an initial value of 82 nm gradually increased, and as the NaCl concentration increased to 100 mM, the nanoparticle diameter decreased due to the formation of soluble complexes between silver cations and chloride anions.

Existing literature provides information both on the kinetics of aggregation of silver nanoparticles in aqueous salt solutions and on the effectiveness of the antiaggregating activity of various stabilizers, including electrostatic (for example, sodium citrate), steric (poly(ethylene glycol), polyvinylpyrrolidone, poly(vinyl alcohol), or nonionic surfactant Tween-80), as well as electrosteric (polyethyleneimine, polyacrylic and polymethacrylic acids, ionic surfactants, and proteins) [5–9]. To stabilize AgNPs, we have used earlier maleic acid copolymers of a regular structure, which offer the following advantages [10, 11]:

– commercial availability or simple synthesis by the radical copolymerization (in the form of maleic anhydride copolymers);

– the possibility of controlling the hydrophilic–hydrophobic balance by selecting the appropriate maleic acid comonomer or by the chemical modification of carboxy groups of maleic acid residues; diphilic nature, linear shape of the macromolecules with a high density of negatively charged groups in the pH range from 4 to 12 at 0–100 °C, which provide good solubility and

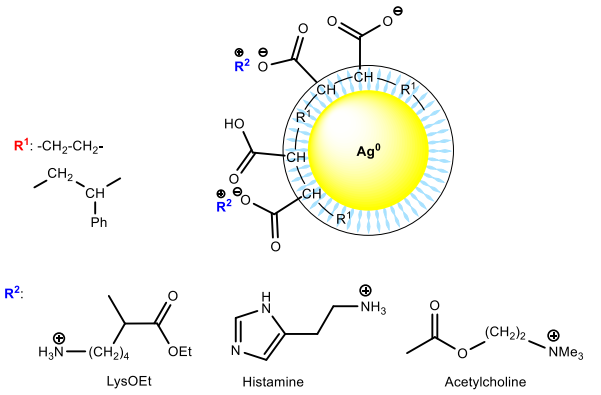
surfactant properties of maleic acid copolymers in an aqueous medium;

– the possibility of redissolving dry samples of AgNPs without loss of properties;

– the lack of toxicity for a number of these copolymers [12].

We have established the noncooperative nature of binding between silver cations and maleic acid copolymer macromolecules and characterized the shape and sizes of AgNPs formed by the chemical reduction of Ag^+ complexes with maleic acid copolymer macromolecules [10, 11].

The goal of this work was to study the effect of a sodium chloride solution and an oxidizing medium on the stability of colloidal solutions of silver nanoparticles stabilized by amphiphilic macromolecules of an ethylene–maleic acid copolymer (EM) or a styrene–maleic acid copolymer (SM). To reduce the destructive effect of the salt and oxygen on the copolymer-stabilized silver nanoparticles, low molecular weight biogenic amines (acetylcholine, histamine, and lysine ethyl ester) were used as additional stabilizers of nanoparticles, which are capable of forming electrostatic complexes of various compositions and, consequently, various charges with ionized carboxy groups of the maleic acid copolymer (Scheme 1).



Scheme 1. Structures of the complexes of copolymer-stabilized silver nanoparticles with low molecular weight biogenic amines: R^1—maleic acid comonomers, R^2—biogenic amines.

Results and discussion

The stability of silver nanoparticles stabilized by ethylene–maleic acid copolymer macromolecules in normal saline was studied by gel permeation chromatography (GPC) and colorimetry using the cationic dye methylene blue (MB). The concentration of stabilizing copolymer macromolecules separated from the surface of AgNPs under the action of the salt was determined in chromatographic fractions free of nanoparticles and NaCl ions (see the Experimental section) [13, 14]. The stabilizing macromolecules, desorbed from the surface of the nanoparticles, interacted with the dye molecules, which led to a change in its absorption spectrum in the visible region: the maximum absorbance characteristic of free single dye molecules at a wavelength of 665 nm decreased, while absorbance at 608 nm, which is characteristic of the bound dimerized MB molecules, increased [15–17].

When comparing the concentrations of stabilizing macromolecules in the samples treated with sodium chloride solution and the untreated sample, it was found that, if AgNPs were not treated with sodium chloride, then the concentration of stabilizing macromolecules was virtually zero. In a solution of NaCl (154 mM) containing, for example, 2 μmol of nanoparticles, the content of separated stabilizing macromolecules was 0.154 μmol for the EM copolymer and 0.220 μmol for the SM copolymer. At the same time, the absorption maximum shifted to shorter wavelengths, which indicated an increase in the molar fraction of MB dimers upon binding with the desorbed stabilizer macromolecules. The partial desorption of stabilizing macromolecules from the surface of nanoparticles in saline leads to the aggregation of AgNPs (Fig. 1).

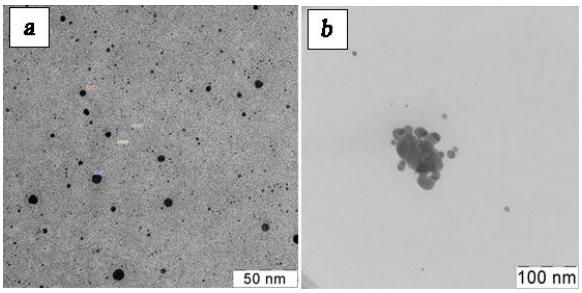


Figure 1. TEM images of silver nanoparticles stabilized by the ethylene–maleic acid copolymer (AgEM) macromolecules in aqueous (***a***) and saline (***b***) solutions. AgEM particles were kept in a physiological solution for 1 day.

Figure 2 shows the absorption spectra of AgEM (***a***) and AgSM (***c***) nanoparticles in a solution of sodium chloride at 40 °C (these conditions simulate the physiological ones) during 7 days of observation, and Table 1 summarizes their spectral characteristics. In a physiological solution, a significant change in the spectra of nanoparticles in time is observed.

Thus, in a week, approximately one third of the initial number of nanoparticles remains in the solution of AgEM, while in the case of AgSM, the analogous value amounts to 14% (Table 1, IV). Therewith, both absorbance and character of the spectra change: the absorption maximum of AgEM nanoparticles ($D\ \lambda_{max}$) shifts from 412 to 398 nm and that for AgSM nanoparticles shifts from 419 to 399 nm (Table 1, II), the absorbance at 500 nm (typical for larger particles [18]) also increases. This leads to a decrease in the ratios of absorbances at $D\ \lambda_{max}$ and $D\ \lambda_{500}$ (Table 1, IV/V).

On the one hand, the hypsochromic shift (Table 1, III) indicates a decrease in the sizes of nanoparticles, while an increase in the absorbance at λ = 500 nm, on the contrary, points to the formation of larger aggregates in the solution. Consequently, the destabilization of AgEM and AgSM in aqueous NaCl solutions is accompanied by oppositely directed processes of agglomeration, caused by the partial desorption of stabilizing copolymer macromolecules from the surface of nanoparticles, and the dissolution due to the formation of soluble Ag^+ compounds in the presence of an excess of chloride ions [3].

One of the methods to increase the stability of AgNPs with a surface polymer layer in electrolyte solutions is to prevent the desorption of a polymeric stabilizer from the surface of nanoparticles by forming an additional protective layer. As additional stabilizers, we used low molecular weight biogenic amines, namely, acetylcholine, lysine ethyl ester, and histamine.

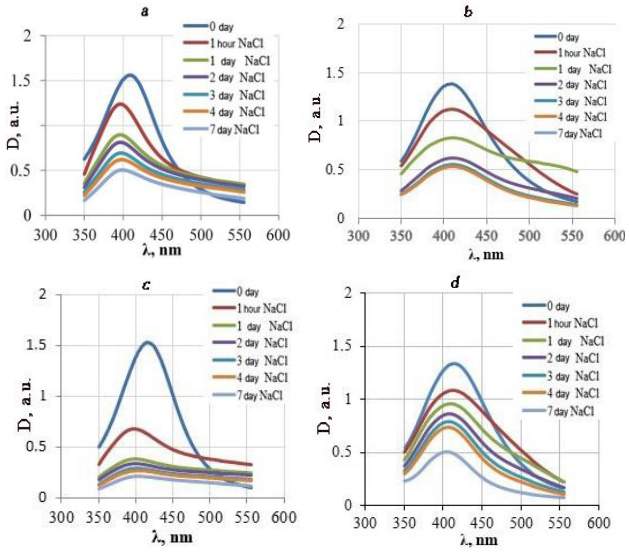


Figure 2. Changes in the absorption spectra of AgEM and AgSM in the absence (***a***, ***c***) and presence of acetylcholine (***b***, ***d***) (solution composition: 1 μmol of nanoparticles in 3 mL of saline at 40 °C).

Table 1. Changes in the absorption spectra of AgEM and AgSM nanoparticles in a physiological solution without additional stabilization

AgEM					
24 h	λ_{max}, nm	Δ*	Dt λ_{max}, nm	Dt λ_{500}, nm	IV/V
I	II	III	IV	V	
0	412	0	1.56	0.25	6.2
1/24	399	13	1.23	0.40	3.1
1	398	14	0.90	0.39	2.3
2	398	14	0.81	0.35	2.3
3	398	14	0.69	0.32	2.2
4	398	14	0.62	0.32	2.1
7	398	14	0.50	0.26	1.9
AgSM					
1	419	0	1.53	0.25	6.1
0	400	19	0.68	0.38	1.8
1/24	399	20	0.38	0.25	1.8
1	399	20	0.34	0.22	1.6
2	399	20	0.26	0.20	1.4
3	399	20	0.26	0.19	1.4
4	399	20	0.21	0.15	1.4
7	399	20	0.21	0.15	1.4

Δ* = $\lambda_{max}(0)$–$\lambda_{max}(t)$ is the hypsochromic shift of the plasmon resonance peak of AgEM and AgSM nanoparticles.

Figure 2 shows the absorption spectra of AgEM (***b***) and AgSM (***d***) nanoparticles in a physiological solution in the presence of acetylcholine (1 μmol of nanoparticles in 3 mL of saline at 40 °C). As can be seen, there is almost no shift in the maximum of the plasmon resonance peak of AgEM nanoparticles, while for AgSM the value of the hypsochromic shift is 6 nm, which is significantly lower than the value of Δ for AgSM without the additional stabilizing agent (Table 2, III).

Figure 3 demonstrates the changes in the absorption maximum wavelength of an aqueous solution of AgEM (D λ_{max}) in the presence of histamine, lysine ethyl ester, and acetylcholine during dynamic titration of nanoparticles with a NaCl solution. The low molecular weight amines, taken in certain molar proportions relative to nanoparticles, in a neutral medium can form electrostatic complexes of various compositions with ionized carboxy groups of maleic acid in the copolymer macromolecules (Scheme 1). A partial decrease in the negative charge upon complexation with the amines leads to some weakening of the negative effect of the ionic strength of NaCl and, at the same time, increases the steric protective layer, weakening the agglomeration of nanoparticles. Thus, in the presence of acetylcholine, the wavelength of the absorption peak (D λ_{max}) of AgEM shifted from 412 nm to 400 nm with an increase in the amount of NaCl to 140 μmol in 3 mL of the solution. At the same time, in the presence of histamine and lysine ester, the value of D λ_{max} of nanoparticles shifted to 397–398 nm already at the lower content of the salt in the system (Fig. 3). Over a short time of titration, a further increase in the concentration of NaCl almost did not affect the peak position.

Table 2. Changes in the absorption spectra of AgEM and AgSM nanoparticles in a physiological solution in the presence of an equimolar amount of acetylcholine

AgEM					
24 h	λ_{max}, nm	Δ*	Dt λ_{max}, nm	Dt λ_{500}, nm	IV/V
I	II	III	IV	V	
0	410	0	1.56	0.25	6.2
1/24	410	13	1.23	0.4	3.1
1	410	14	0.9	0.39	2.3
2	410	14	0.81	0.35	2.3
3	410	14	0.69	0.32	2.2
4	410	14	0.62	0.32	2.1
7	410	14	0.50	0.26	1.9
AgSM					
0	415	0	1.34	0.34	3.9
1/24	414	1	1.09	0.52	2.1
1	411	4	0.96	0.45	2.1
2	411	4	0.86	0.34	2.5
3	410	5	0.79	0.23	3.4
4	409	6	0.73	0.22	3.3
7	409	6	0.50	0.13	3.8

Δ* = $\lambda_{max}(0)$–$\lambda_{max}(t)$ is the hypsochromic shift of the plasmon resonance peak of AgEM and AgSM nanoparticles in the presence of the amine.

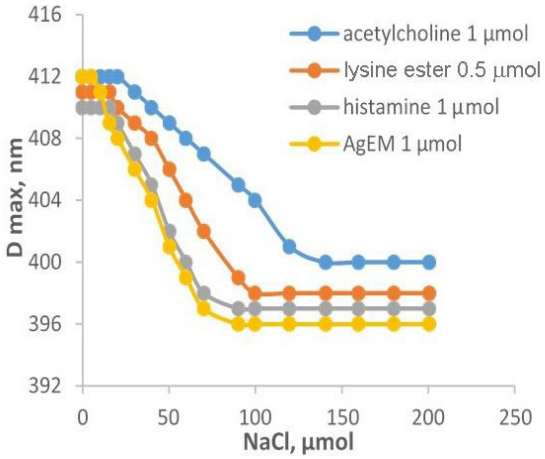


Figure 3. Shift of the absorption maximum wavelength (D λ_{max}, nm) in the AgEM spectra (1 μmol in 3 mL of water) in the presence of different amines depending on the salt content in the system during dynamic titration with the addition of 1 M NaCl solution in 5–10 μL portions every 3 min.

The resulting data may imply relatively higher efficiency of acetylcholine as an additional stabilizing agent for nanoparticles in a physiological solution.

The oxidative degradation of nanoparticles was studied under the action of a dilute hydrogen peroxide solution (simulating the oxidative effect of water-soluble oxygen with a certain degree of reliability) on AgEM nanoparticles. As an example, Fig. 4 shows the kinetic dependences of the change in the absorption maximum of AgEM nanoparticles under the action of hydrogen peroxide in the presence and absence of the low molecular weight amines in the system. The change in the absorption intensity of the solution in the presence of H_2O_2 was related to the initial absorbance $D\ \lambda_{max}$ (412 nm) of silver nanoparticles without an oxidizing agent, neglecting some shift of the maximum of a plasmon resonance peak in the presence of an oxidizing agent [19].

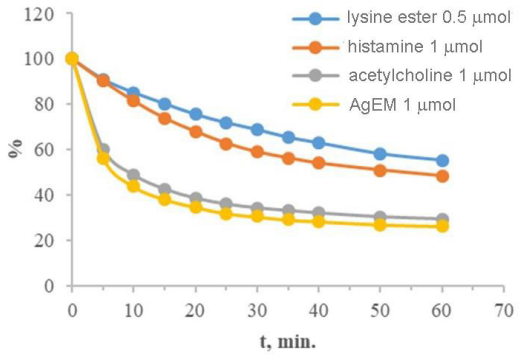


Figure 4. Kinetics of the change of absorbance ($D\ \lambda_{max}$, nm) of a solution of AgEM nanoparticles (1 μmol) under the influence of H_2O_2 (1 μmol) in the presence and absence of biogenic amines in a total volume of 4 mL at pH = 7 (expressed as a percentage of the initial absorbance $D\ \lambda_{max}$ 412 nm in the absence of H_2O_2).

The introduction of acetylcholine into the system reduces the effect of the oxidizing agent in 1.14 times; for histamine and lysine ester, this change composes 1.8 and 2.1, respectively. Thus, it can be concluded that the complexation of AgEM with the primary amine, namely, lysine ethyl ester, protects nanoparticles from the oxidative effect of hydrogen peroxide more effectively than that with the quaternary amine acetylcholine. It should be noted that, in the absence of a stabilizing amine in the composite, the discoloration of the AgEM colloidal solution occurs in 60 min.

It is known that all amines undergo oxidation. Tertiary amines are oxidized to oxides most readily, and the oxidation process can be catalyzed by the presence of a noble metal in the system [20]. Primary amines are least susceptible to oxidation [21]. These properties of amines are due to the difference in their electrode potentials [22]. Based on this and the experimental results presented above, it can be concluded that primary amines are more preferable as additional stabilizers for nanoparticles in an oxidizing medium than quaternary amines.

Thus, in aqueous solutions of NaCl and H_2O_2, silver nanoparticles stabilized by the amphiphilic copolymers of maleic acid can undergo both dissolution and agglomeration due to the desorption of the stabilizing polymer, resulting in the formation of a range of inorganic compounds of silver. However, the addition of fixed amounts of low molecular weight biogenic amines to the system gives rise to the complexes with ionized carboxy groups of maleic acid residues, affording an additional steric protective layer that increases the resistance of nanoparticles to the destructive effect of these media.

Experimental section

Materials

The following reagents were purchased from commercial sources and used without further purification: $AgNO_3$, HCl, H_2O_2 (Reakhim, reagent grade), NaCl (Sigma, USA), NaOH (Panreac, Spain), methylene blue (Sigma Aldrich, USA), $NaBH_4$ (Panreac Sintesis, Spain), acetylcholine, histamine, and lysine ethyl ester (Aldrich, USA). The colloidal solutions of silver nanoparticles AgSM and AgEM were obtained according to the published procedure [11]. The copolymers of maleic anhydride with ethylene and styrene (Monsanto, USA) had the following characteristics: $M_w = 25\times10^3$ and 50×10^3, the molar masses of the EM and SM units M = 144 and 220, respectively. The solutions were prepared using double distilled water. The synthesis of stabilized silver nanoparticles [11] is described in the Electronic supplementary information (ESI).

Methods

Measurement of the absorption spectra of stabilized silver nanoparticles in aqueous NaCl solutions. Solutions containing 1 μmol of nanoparticles in double distilled water (3 mL) were supplemented with the calculated amount of a 1 M NaCl solution. The NaCl concentration was 100 and 154 μmol/mL for the AgEM and AgSM solutions, respectively. The absorption spectra were measured in 5 mm cuvettes with a Specord M40 spectrophotometer (Carl Zeiss, Germany) at room temperature before the addition of the salt, in 1 h after the addition, and then every day for a week. The confidence interval of the optical density of the solutions did not exceed ±4%.

Measurement of the absorption spectra of AgEM upon addition of H_2O_2 in the presence of amines. Solutions containing 1 μmol of AgEM in double distilled water (pH = 7) and the calculated amount of one of the amines (in a total volume of 4 mL) were supplemented with 1 μmol of H_2O_2 (11 μL of a 0.3% solution). The change in the absorbance value $D(t)$ was fixed in 1–2 min. The results were presented as a percentage of the ratio $D(t)/D(0)$ at λ_{max} = 412 nm in the absence of H_2O_2.

Determination of the desorption of stabilizing copolymer macromolecules from the surface of nanoparticles in a physiological solution by GPC. To determine the stability of silver nanoparticles in a physiological solution by GPC (Fig. 5), a thermostated column with Sepharose CL-6B (1.5×50 cm) was used. An eluent was 0.01 M bicarbonate buffer (pH = 9) at 40 °C. 2 mL samples bearing EM or SM copolymer (2 μmol/mL) as well as silver nanoparticles stabilized by these copolymers were applied to the column. The absorbance of the eluate was determined spectrophotometrically using a Specord M40 spectrophotometer (Carl Zeiss, Germany) at λ = 230 nm.

Column calibration. The column free volume V_0 = 14 mL (the volume in which the main part of stabilized silver nanoparticles leaves the column) was determined using blue

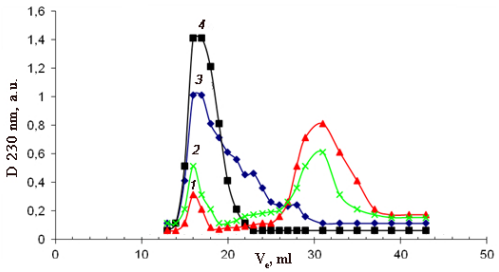


Figure 5. Chromatograms for EM (***1***), SM (***2***), Ag–EM (***3***), and Ag–SM (***4***) in 0.01M bicarbonate buffer (pH = 9) at 40 °C.

dextran, MM ≥ 2000 kDa. The total column volume V_t = 39 mL was defined using glycine. V_e = 29–37 mL is the average elution fraction of EM or SM, in which the content of desorbed copolymer macromolecules was determined by the colorimetric method with the cationic dye methylene blue.

When studying the effect of NaCl, 1 M sodium chloride solution was added to the colloidal solutions of AgEM and AgSM in 0.01 M bicarbonate buffer (pH = 9) so that the final salt concentration was 154 μmol/mL. In 30 min, the resulting precipitate was separated by centrifugation at 5000 rpm for 10 min. A 2 mL sample (2 μmol/mL) was applied to the chromatographic column. The elution was carried out with a 0.01 M bicarbonate buffer solution. A fraction of nanoparticles was released from the column in a volume of 14–28 mL. Since nanoparticles interfere with the determination of the concentration of desorbed copolymer macromolecules, their concentration was determined in an average fraction of 29–37 mL, which does not contain nanoparticles and low molecular weight ions.

Determination of the EM or SM stabilizing copolymer concentrations in aqueous solutions using the methylene blue dye. To detect desorbed macromolecules of EM or SM copolymers in the average GPC fraction with V_e = 29–37 mL, we used a colorimetric method based on the change in the absorption spectrum of the methylene blue dye in water upon its transition from the monomeric form to the dimeric state: a decrease in the absorbance at λ = 665 nm (characteristic of monomeric molecules of this dye) and the corresponding increase in the absorbance at λ = 608 nm (characteristic of dimeric MB molecules [17]).

For this purpose, an initial solution of MB in water with the concentration of 0.90 μmol/mL was prepared. For a 4 mL sample, 0.09 mL of the MB solution (C = 0.02 μmol/mL) and 3.91 mL of the aqueous copolymer solution were taken in the concentration range of 0.005–0.020 μmol/mL. The ratio of the molar concentrations of the components did not exceed 1 (EM or SM/MB ≤ 1). At 665 nm, the absorbance value ($D(\lambda_{665})$) of the MB solution without the addition of copolymer macromolecules was 1.47 ± 0.01. In 10 min after mixing the components, $\Delta D(\lambda_{665}) = 1.47 - D(\lambda_{665})$ × (MB + EM or SM) was determined, where $D(\lambda_{665})$ × (MB + EM or SM) is the absorbance of the MB solution in the presence of copolymer macromolecules. A decrease in the absorption intensity associated with a change in the blue color is caused by the interaction of MB with copolymer macromolecules to form dimers of the dye molecules [16]. A shift in the MB absorption maximum to shorter wavelengths is indicative of an increase in molar fraction of the dimeric molecules. Hence, a decrease in the absorbance of MB solutions at λ = 665 nm due to the dimerization of the dye molecules when they are bound with the copolymer macromolecules can be used to evaluate their amount under conditions of separation from stabilized nanoparticles under the action of a salt.

Conclusions

The results of the investigations aimed at increasing the stability of silver nanoparticles stabilized by amphiphilic copolymers of ethylene or styrene with maleic acid in the media containing sodium chloride or an oxidizing agent (hydrogen peroxide) were presented. The chosen media simulate physiological conditions. It was shown that silver nanoparticles undergo simultaneously agglomeration and oxidative destruction in sodium chloride solutions, which are caused by the partial desorption of stabilizing copolymer macromolecules from the surface of nanoparticles.

It was established that an increase in the stability of stabilized silver nanoparticles in NaCl solutions is achieved due to the complexation with low molecular weight biocompatible amines. The results obtained indicate that the quaternary amine acetylcholine at an equimolar ratio with AgEM most effectively stabilizes nanoparticles against the salt destructive action. For an oxidizing environment, on the contrary, the primary amine lysine ethyl ester protects nanoparticles from hydrogen peroxide more effectively than acetylcholine.

The additional electrosteric stabilization allows for maintaining significantly the stability of the copolymer-stabilized nanoparticles in saline solutions at 40 °C as well as in solutions with a low concentration of the oxidizing agent for several days.

The modified nanocomplexes are promising objects for use in biomedicine, for example, for incorporation in antiseptic compositions. For nanosilver-containing composites, the application scope of aerobic and NaCl-containing microbial culture media test systems used in the investigations of drugs against opportunistic pathogenic microorganisms [23, 24] and *Mycobacterium tuberculosis* [25] is expanding.

Acknowledgements

This work was performed with financial support from the Ministry of Science and Higher Education of the Russian Federation (agreement no. 075-03-2023-642) using the equipment of the Center for Molecular Composition Studies of INEOS RAS.

We are grateful to Dr. S. S. Abramchuk for help with TEM studies.

Corresponding author

* E-mail: kurskaya_e@mail.ru (E. A. Kurskaya)

Electronic supplementary information

Synthesis of silver nanoparticles stabilized by the maleic acid copolymers with ethylene and styrene. For ESI, see DOI: 10.32931/io2225a.

References

1. B. Shivaramakrishnan, B. Gurumurthy, A. Balasubramanian, *Int. J. Pharm. Sci. Res.*, **2017**, *8*, 985. DOI: 10.13040/IJPSR.0975-8232.8(3).985-00
2. S. J. Amina, B. Guo, *Int. J. Nanomed.*, **2020**, *15*, 9823–9857. DOI: 10.2147/IJN.S279094
3. C. Levard, S. Mitra, T. Yang, A. D. Jew, A. R. Badireddy, G. V. Lowry, G. E. Brown, *Environ. Sci. Technol.*, **2013**, *47*, 5738–5745. DOI: 10.1021/es400396f
4. X. Li, J. J. Lenhart, H. W. Walker, *Langmuir*, **2010**, *26*, 16690–16698. DOI: 10.1021/la101768n
5. B. Mukherjee, J. W. Weaver, *Environ. Sci. Technol.*, **2010**, *44*, 3332–3338. DOI: 10.1021/es903456e
6. A. M. El Badawy, T. P. Luxton, R. G. Silva, K. G. Scheckel, M. T. Suidan, T. M. Tolaymat, *Environ. Sci. Technol.*, **2010**, *44*, 1260–1266. DOI: 10.1021/es902240k
7. K. A. Huynh, K. L. Chen, *Environ. Sci. Technol.*, **2011**, *45*, 5564–5571. DOI: 10.1021/es200157h
8. S. A. Al-Thabaiti, F. M. Al-Nowaiser, A. Y. Obaid, A. O. Al-Youbi, Z. Khan, *Colloids Surf., B*, **2008**, *67*, 230–237. DOI: 10.1016/j.colsurfb.2008.08.022
9. N. Akaighe, S. W. Depner, S. Banerjee, V. K. Sharma, M. Sohn, *Sci. Total Environ.*, **2012**, *441*, 277–289. DOI: 10.1016/j.scitotenv.2012.09.055
10. N. Samoilova, E. Kurskaya, M. Krayukhina, A. Askadsky, I. Yamskov, *J. Phys. Chem. B*, **2009**, *113*, 3395–3403. DOI: 10.1021/jp806683m
11. N. A. Samoilova, I. V. Blagodatskikh, E. A. Kurskaya, M. A. Krayukhina, O. V. Vyshivannaya, S. S. Abramchuk, A. A. Askadskii, I. A. Yamskov, *Colloid J.*, **2013**, *75*, 409–420. DOI: 10.1134/S1061933X1304008X
12. K. Banshoya, Y. Kaneo, T. Tanaka, S. Yamamoto, H. Maeda, *Int. J. Pharm.*, **2019**, *572*, 118719. DOI: 10.1016/j.ijpharm.2019.118719
13. M. Vanaja, K. Paulkumar, M. Baburaja, S. Rajeshkumar, G. Gnanajobitha, C. Malarkodi, M. Sivakavinesan, G. Annadurai, *Bioinorg. Chem. Appl.*, **2014**, 742346. DOI: 10.1155/2014/742346
14. Sh. Sohrabnezhad, M. A. Zanjanchi, M. Razavi, *Spectrochim. Acta, Part A*, **2014**, *130*, 129–135. DOI: 10.1016/j.saa.2014.02.188
15. T. Fujita, H. Watanabe, S. Tanaka, *Chem. Phys. Lett.*, **2007**, *434*, 42–48. DOI: 10.1016/j.cplett.2006.11.112
16. D. Heger, J. Jirkovský, P. Klán, *J. Phys. Chem. A*, **2005**, *109*, 6702–6709. DOI: 10.1021/jp050439j
17. E. Morgounova, Q. Shao, B. J. Hackel, D. D. Thomas, S. Ashkenazi, *J. Biomed. Opt.*, **2013**, *18*, 056004. DOI: 10.1117/1.JBO.18.5.056004
18. K.-C. Lee, S.-J. Lin, C.-H. Lin, C.-S. Tsai, Y.-J. Lu, *Surf. Coat. Technol.*, **2008**, *202*, 5339–5342. DOI: 10.1016/j.surfcoat.2008.06.080
19. A. Henglein, *Chem. Mater.*, **1998**, *10*, 444–450. DOI: 10.1021/cm970613j
20. M. Colladon, A. Scarso, G. Strukul, *Green Chem.*, **2008**, *10*, 793–798. DOI: 10.1039/B805404E
21. M. Largeron, *Eur. J. Org. Chem.*, **2013**, *24*, 5225–5235. DOI: 10.1002/ejoc.201300315
22. A. K. V. Mruthunjaya, A. A. J. Torriero, *Molecules*, **2023**, *28*, 471. DOI: 10.3390/molecules28020471
23. N. Samoilova, M. Krayukhina, A. Naumkin, N. Anuchina, D. Popov, *New J. Chem.*, **2021**, *45*, 14513–14521. DOI: 10.1039/D1NJ02478G
24. N. A. Samoilova, M. A. Krayukhina, N. M. Anuchina, D. A. Popov, *Appl. Biochem. Microbiol.*, **2021**, *57*, 377–383. DOI: 10.1134/S000368382103011X
25. N. A. Samoilova, M. A. Krayukhina, K. B. Majorov, P. Yu. Ivanov, V. S. Velezheva, *INEOS OPEN*, **2022**, *5*, 21–26. DOI: 10.32931/io2205a