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Redox Reactions of Arabinogalactan with Silver Ions and Formation of Nanocomposites

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Abstract—Formation of silver nanoparticles in the course of chemical reduction of $AgNO_3$ with arabinogalactan in aqueous alkaline solution was studied by electronic absorption spectroscopy and X-ray diffraction analysis. The pH of the solution was found to be the major factor affecting the degree of reduction of Ag^+ ions. The probable reaction mechanism was discussed. Composites containing up to 58% Ag, with the metal particle size of 7–16 nm, were prepared. The nanoparticle size can be controlled by varying the reactant ratio $AgNO_3$: arabinogalactan. Chemical modification of arabinogalactan was confirmed by IR and ^{13}C NMR spectroscopy and by TLC.

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Interest in composites containing silver nanoparticles is due to prospects for their wide use as new antibacterial and antiviral agents [1–3], functional nonlinear optical materials [3–5], and catalytic systems for organic synthesis.

Stable silver nanoparticles are prepared now by various procedures, e.g., by chemical reduction [3–7], thermolysis [1, 5], photolysis, and radiation chemistry [8, 9], using various materials for stabilization of nanoparticles: solid zeolite matrices [1], aqueous-organic emulsions [10], and solutions of macromolecules [2–5, 7, 8]. The possibility of using polysaccharide matrices as a stabilizing macromolecular component of nanocomposites attracts steady researchers' attention but is as yet insufficiently examined.

For example, Kotel'nikova et al. [11, 12] demonstrated the possibility of silver intercalation into the polysaccharide matrix of cellulose. The polysaccharide showed a weak reducing power with respect to silver ions. These studies are an example of the synthesis of nanoparticles in the bulk and on the surface of a spatially organized polysaccharide in which the reduction is limited by hindered diffusion of the reagents into the structure, so that additional reductants are required.

We showed that formation of nanocomposites by processes occurring in aqueous alkaline solutions with metal ions in the presence of a natural water-soluble polysaccharide, arabinogalactan, is a facile route to unique polyfunctional nanosize compounds with a broad spectrum of activity [13, 14]. A combination of silver nanoparticles with a physiologically active macromolecule, arabinogalactan, participating in cell biorecognition, is of great interest for the development of bactericidal and virucidal systems of directional intracell effect.

Here we studied the formation of silver-containing composites of arabinogalactan, their composition, and dispersity of metal particles formed by reactions of silver ions with arabinogalactan in aqueous alkaline solution. The reaction of silver ions with arabinogalactan in alkaline solutions yields water-soluble silver compounds containing from 1 to 58% metal depending on the reaction conditions.

An X-ray diffraction analysis of the product reveals the presence of an amorphous polysaccharide phase of arabinogalactan and a nanodisperse phase of metallic silver, which confirms that the product is a composite. The diffraction patterns contain strong peaks from planes of the crystalline phase of zero-valent silver with the unit cell parameter a 4.050–4.080 Å and from 7–16-nm metal particles.

The reaction of arabinogalactant with Ag(I) is accompanied by acidification of the solution and appear-

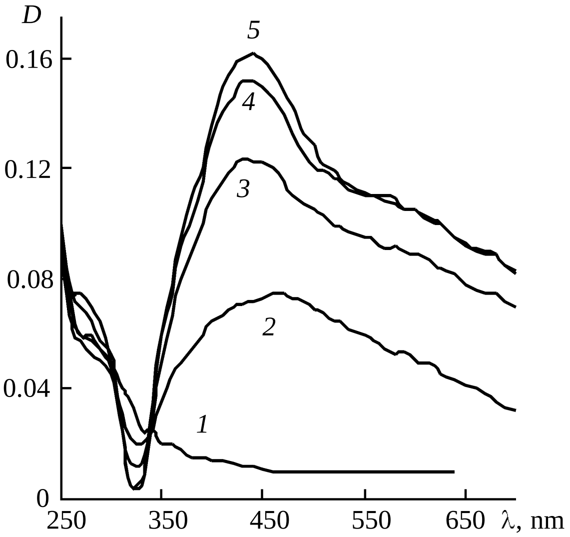


Fig. 1. Absorption spectra of aqueous solutions containing $AgNO_3$ (8.8×10^{-3} M) and arabinogalactan (0.8%) at pH 4.5 and various reaction times, h: (*1*) 0.16, (*2*) 24, (*3*) 48, (*4*) 72, and (*5*) 96.

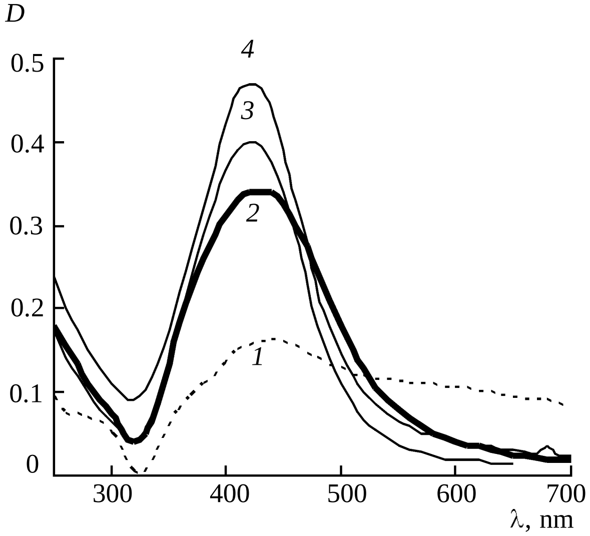


Fig. 2. Absorption spectra of aqueous solutions containing $AgNO_3$ (8.8×10^{-3} M) and arabinogalactan (0.8%) at various pH: (*1*) 4.5 (reaction time 96 h), (*2*) 6.1 (35 h), (*3*) 6.7 (27 h), and (*4*) 7.5 (10 h).

ance of a color; the color and its intensity depend on the initial pH of the reaction mixture. Therefore, for direct monitoring of the formation of the composites we used electronic absorption spectroscopy. The initial pH was varied from 4.5 to 11.0. On adding the silver salt to an aqueous solution of arabinogalactan at pH 4.5, a weak asymmetric absorption band with a broad maximum at λ 420–470 nm appears in the spectrum; the intensity of this band increases with the reaction time (Fig. 1).

As the solution pH increases, the electronic absorption spectra of the solutions also undergo appreciable changes (Fig. 2). In going from pH 4.5 to pH 6.1, the absorption band becomes stronger and narrower, and its long-wave wing disappears. It is interesting that the observed asymmetric absorption bands broadened from the long-wave side are preserved only in a narrow pH range of weak acidities. In going to the range of pH 6.7–7.5, the band becomes strong and symmetrical, with a pronounced bell shape and λ_{max} 420 nm; this band can be assigned to the plasmon resonance of silver nanoparticles [3, 5, 15].

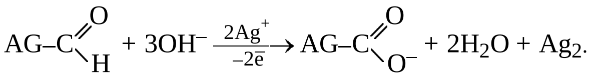
The development of the color in the dark and the pH dependence of the spectral characteristics rule out the photochemical pathway as the major mechanism of the formation of metallic silver. The changes observed in the character of the electronic spectra with variation of pH apparently reflect the progress of nucleation and an increase in the number of silver particles due to redox reactions in an aqueous solution of arabinogalactan and silver ions.

The weak band with a broad maximum at λ 420–470 nm, appearing in the range of pH 4.5–6.1, is due to the formation of primary centers of metallic silver [12]. Apparently, the reduction of Ag^+ does occur even under these conditions, but to a small extent, and the number of the reduced Ag(0) centers formed is insignificant. In more concentrated solutions and on heating, the reduction rate (experimentally estimated from the growth of the absorption intensity) increases, but the degree of reduction of silver ions does not exceed 9% (which corresponds to 0.9% silver content in the composite).

The stabilized silver metal nanoparticles are mainly formed in the range of pH 6.7–11.0. An increase in pH in this range leads to an increase in the content of metallic silver in the composites from 0.9 to 9.7% (which corresponds to 100% conversion of silver cations in aqueous solution) and is accompanied by an increase in the characteristic plasmon absorption of silver. The reduction at pH > 10 is accompanied not only by an increase in the absorption, corresponding to an increase in the number of metal particles, but also by changes in their size, which is manifested in a short-wave shift of the plasmon peak [15] from 420 to 410 nm (Fig. 3).

The decisive effect of pH on the efficiency of the silver reduction suggests that hydroxide ions directly participate in the redox transformations in the system.

Silver ions are reduced to the zerovalent state by aldehyde groups of arabinogalactan. Their content in arabinogalactan, determined by the Somogyi–Nelson method [16], is as low as 0.4%, which, in accordance with the scheme given below, can provide only 3% content of reduced silver in the composite. This scheme accounts for the acidification of the reaction mixture observed during the experiment.



$$\mathrm{AG{-}C}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \setminus\mathrm{H}\end{smallmatrix} + 3\mathrm{OH}^- \xrightarrow[-2\bar{e}]{2\mathrm{Ag}^+} \mathrm{AG{-}C}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \setminus\mathrm{O}^-\end{smallmatrix} + 2\mathrm{H_2O} + \mathrm{Ag_2}.$$

The possibility of preparing composites with a considerably higher content of metallic silver (up to 58%) suggests the participation of new reducing (aldehyde) centers in the reaction. The pronounced pH dependence of the process suggests a two-step mechanism of the redox transformations in aqueous solution of arabinogalactan and silver ions, in which the metal reduction is preceded by base degradation of the polysaccharide macromolecule followed by the formation of reducing fragments. The occurrence of the degradation is confirmed by gel permeation chromatography. It shows that the formation of the composite containing 58% silver is accompanied by changes in the molecular weight and polydispersity (ratio of the weight-average and number-average molecular weights) of the macromolecule from 20 700 to 14 500 and from 1.7 to 1.9, respectively (Fig. 4).

According to the existing views [17], base cleavage of polysaccharides (peeling) is accompanied by gradual elimination of monosaccharide units starting from the reducing terminus, which gives rise to an additional aldehyde group. The presence of a 1→3 bond labile in base hydrolysis facilitates the degradation of the macromolecule [18].

The development of the reaction at the aldehyde center is indirectly confirmed by the sensitivity of the reduction processes to the content of aldehyde groups. In particular, a decrease in the content of aldehyde groups of arabinogalactan from 0.4 to 0.04%, attained by their reduction to alcoholic groups with sodium borohydride, leads to a fourfold decrease in the intensity of the plasmon absorption upon reaction with silver ions at pH 11.

The oxidation of terminal carbonyl groups to carboxy groups with the progress of the metal reduction blocks the development of the base hydrolysis at these sites. Therefore, the contribution of the degradation to the overall process should depend on the nature of the base and oxidative activity of Ag(I) compounds.

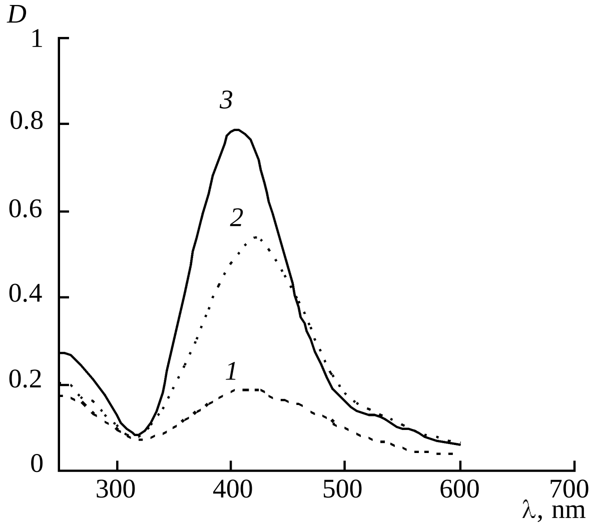


Fig. 3. Absorption spectra of aqueous solutions containing $\mathrm{AgNO_3}$ (8.8×10^{-3} M) and arabinogalactan (0.8%) at pH 10.1 and various reaction times, h: (*1*) 0.4, (*2*) 2.5, and (*3*) 19 (*l* 0.05 cm).

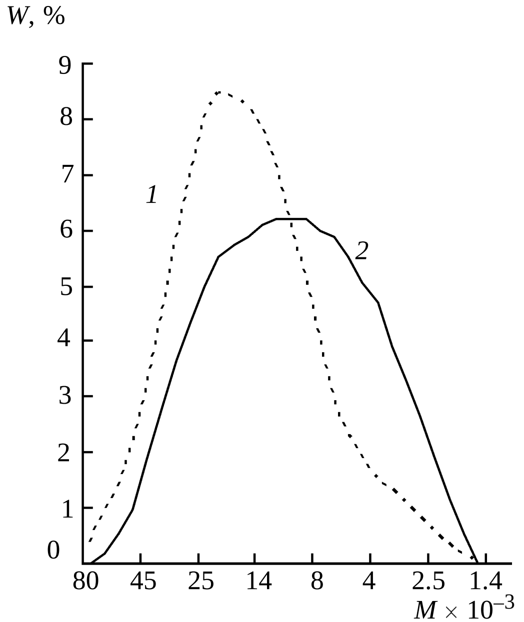


Fig. 4. Normalized molecular-weight distribution curves: (*1*) free arabinogalactan and (*2*) arabinogalactan in the complex. (*W*) Weight fraction.

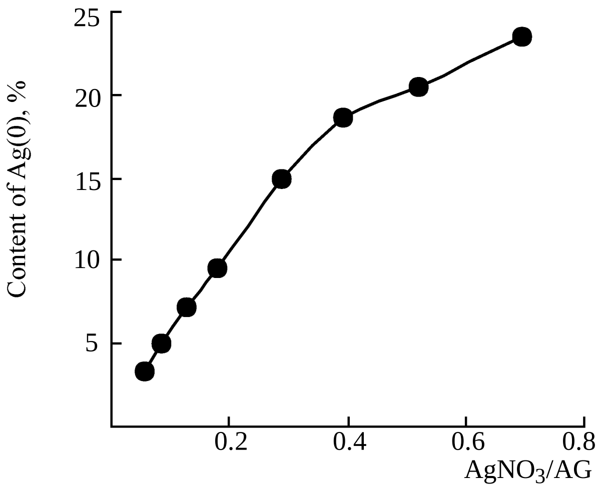


Fig. 5. Influence of the weight ratio of the metal salt to arabinogalactan (AG) on the Ag(0) content in the composites.

A brilliant manifestation of the effect exerted on the degradation by the nature of the base is the difference observed between the reactions performed in aqueous NaOH and aqueous ammonia, at the same OH^- concentration. With aqueous ammonia used as the base, a composite containing 3% silver is obtained, which confirms the well-known properties of an ammonia solution of Ag(I) (Tollens' reagent) as a reagent for aldehyde groups. The poor reducing properties of the cellulose macromolecule with respect to Ag(I) ions, noted in [11], are apparently due to the use of ammonium hydroxide.

At the same time, in an alkali solution, the hydrolysis and formation of finely dispersed silver(I) oxide will presumably lead to deceleration of the reactions of Ag(I) with aldehydes, so that the polysaccharide degradation leading to an increase in the number of reducing centers will prevail in the initial period of the reaction.

On the whole, the formation of water-soluble silver-containing arabinogalactan composites is provided, along with the redox reactions, by the colloid-stabilizing properties of arabinogalactan as a polymer [13, 19]. The formation of a stabilizing polysaccharide shell around the nanosized silver metal core can be represented as a result of surface interaction between zerovalent silver and polar groups of the macromolecule (hydroxy groups and forming carboxy groups). This interaction is provided not only by van der Waals forces [5, 20], but also by specific features of chemistry of nanoparticles [15]. The stability of the disperse system can be provided by hydrophilization of the particle surface due to adsorption of arabinogalactan molecules and by steric protection preventing the particle aggregation at collisions. Taking into account the formation of ionized carboxy groups in the process, it is reasonable to suggest also the participation of electrostatic forces in the particle stabilization. However, the latter factor is hardly decisive, since no destabilization of the dispersions is observed in acidic solutions in which the dissociation of carboxy groups is weak.

The efficiency of the stabilization processes, evaluated by the composition and yield of silver-containing composites, depends on the weight ratio of the metal salt to arabinogalactan in the reaction mixture (Fig. 5). An increase in this ratio from 0.01 to 0.39 leads to an increase in the silver content in the composite from 1 to 19%, at 95.0 to 99.0% yields. With a further increase in the silver salt to arabinogalactan ratio, a bend corresponding to the onset of coagulation is observed; separation of the insoluble metal phase causes a decrease in the yield of the water-soluble products from 95.0 to 84.2%, at a slight increase in the amount of silver (to 23.4%) in the composite.

The size of the forming particles, evaluated from the reflection broadening in the diffraction patterns, is also controlled by the initial weight ratio of the metal salt to arabinogalactan in the reaction mixture: At a ratio of 0.01–0.12, the particle size is within 7–8 nm, whereas at a ratio of 0.19–0.39 coarser particles (12–13 nm) are formed. Apparently, the ratio of the metal salt to arabinogalactan in the reaction medium can be considered as one of the factors controlling the size characteristics of metal nanoparticles in the course of their formation. At lower silver salt to arabinogalactan ratios, the nucleation of the new metal phase in the bulk of solution apparently prevails. With an increase in the silver content, the observed increase in the metal content in the composite is due, among other factors, to the growth of the nanoparticles as a result of predominant reduction of the metal ions on the surface of the already formed nuclei [5].

By performing the reaction in the mode of multiple successive treatments of the composite with the silver salt in alkaline solution, it is possible to extend the concentration range of the existence of the stable water-soluble composites and to prepare compounds containing 20–58% metal, with a particle size of 14–16 nm.

This high silver content in the composite leads to noticeable changes in its spectral characteristics. With an increase in the metal content, an absorption band at 1600 cm^{-1} originating from the stretching vibrations of the C=O bond in ionized carboxy group appears and grows in the intensity. The formation of carboxy groups in the course of silver reduction is also confirmed by ^{13}C NMR spectroscopy: The spectrum of the sample containing 58% silver has a new signal at 173.4 ppm belonging to the COO group. The specific features of polymer spectra (line broadening), along with the irregular structure of the arabinogalactan macromolecule, allow us to analyze changes only in the relatively “empty” part of the spectrum in which the signals of the anomeric C^1 atom (about 104 ppm) and C^6 atom bearing the primary OH group (about 60 ppm) are observed [21]. The possibility of the oxidation of primary alcoholic hydroxyls at the C^6 atom of the galactose unit to carboxy groups is ruled out by the constant ratio of the integral intensities of the C^6 and C^1 signals in the ^{13}C NMR spectra of the composites and free arabinogalactan.

The formation of low-molecular-weight fragments with carboxy groups by the developing degradation of arabinogalactan is confirmed by thin-layer chromatography. The development of the chromatograms of the composites, in contrast to the initial arabinogalactan, revealed the presence of carboxyl-containing compounds above the start line.

Thus, the reduction of silver ions in aqueous solutions of arabinogalactan is accompanied by the formation of silver metal nanoparticles stabilized by the polymeric matrix of the polysaccharide. These particles give rise to the plasmon resonance effect. The degree of reduction of silver ions in arabinogalactan solution is largely determined by pH and nature of the base. In a NaOH solution, the reductive properties of arabinogalactan are substantially enhanced owing to the base hydrolysis with the formation of low-molecular-weight reducing fragments. The redox reaction of silver ions with arabinogalactan does not involve primary alcoholic groups of the polysaccharide.

Using the regular trends revealed, it is possible to efficiently stabilize the nanoparticles and control their size in the range 7–16 nm.

The results obtained may be of interest for the development of new antimicrobial systems and materials with controlled nonlinear-optical properties.

EXPERIMENTAL

The IR spectra were recorded on a UR-10 spectrophotometer using KBr pellets or mulls in mineral oil. X-ray diffraction studies were performed with a DRON-3.0 diffractometer. The particle size was calculated from the reflection broadening in the diffraction patterns according to the procedure described in [22]. The ^{13}C NMR spectra of the composites in a D_2O solution were recorded on a Bruker AV-400 spectrometer. The quantitative NMR analysis was performed with an addition of a relaxant (chromium acetylacetonate).

The TLC analysis was performed with Silufol UV-254 plates in the system 96% ethanol–4% water–25% ammonia. Acids were detected with a 0.04% alcoholic solution of Bromocresol Green [23].

Arabinogalactan was isolated from aqueous extract of larch wood and purified by percolation through the polyamide sorbent with the subsequent reprecipitation into ethanol.

$AgNO_3$, NaOH, and $NaNO_3$ were of chemically pure grade.

Synthesis of silver-containing arabinogalactan composites. To 1 g of arabinogalactan in 2 ml of water, we added 2 ml of a solution containing 0.017–0.700 g of $AgNO_3$. The solution was vigorously stirred for 15 min at room temperature. Then 30% aqueous NaOH was added to pH 10.0–11.0, and the mixture was heated on a boiling water bath for 15 min and filtered. The reaction was accompanied by a rapid decrease in pH from 10–11 to 7–8. The target product was isolated from the solution and purified to remove low-molecular-weight impurities by twofold reprecipitation into ethanol. Then the samples were dried in a vacuum over $CaCl_2$. The yields of the powdered products varied in the range 0.97–1.22 g (84.2–96.0%), and their silver content, from 1.1 to 23.4%.

The reaction of arabinogalactan with $AgNO_3$ was studied in an aqueous solution in the range of pH 4.5–11.0. To a 0.8% solution of arabinogalactan we added $AgNO_3$ to a concentration of 8.8×10^{-3} M. The acidity was adjusted with 0.1 NaOH; the pH was monitored with an EV-74 pH meter. The electronic absorption spectra were recorded on an SF-26 spectrophotometer in the range 230–600 nm for solutions obtained at pH 4.5–8.0 and 10.0–11.0 in 1- and 0.05-cm cells, respectively, against solutions containing arabinogalactan and $AgNO_3$ in the same concentrations (% and M) as in the test solution.

The silver content in the composites was determined by titration with ammonium thiocyanate after dissolving the metallic silver in nitric acid [24], and also by atomic absorption analysis.

Reduction of arabinogalactan with sodium borohydride. To a solution of 1 g of arabinogalactan (0.4% aldehyde groups) in 200 ml of water, we added with stirring 1.5 g of sodium borohydride and kept at 23°C for 10 h. Excess sodium borohydride was removed by adding 0.1 N HCl. The neutral solution was dialyzed and concentrated in a vacuum at 40°C [25]. The target product was isolated by precipitation into ethanol.

Yield of reduced arabinogalactan 75.0%, content of aldehyde groups 0.04%. The reaction with silver nitrate was performed under the conditions described above for the preparation of silver composites.

The molecular-weight distribution of arabinogalactan was studied by gel chromatography as described in [19], with a solution containing 0.036 M H_3PO_4, 0.035 M LiBr, and 0.5 M CH_3OH as a mobile phase.

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