

Mass Spectrometric Detection of Charged Silver Nanoclusters with Hydrogen Inclusions Formed by the Reduction of AgNO_3 in Ethylene Glycol

O. A. Boryak^a, M. V. Kosevich^{a, *}, V. V. Chagovets^{a, b}, and V. S. Shelkovsky^a

^aVerkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine, Kharkov, 61103 Ukraine

^bResearch Center for Obstetrics, Gynecology and Perinatology, Ministry of Healthcare of the Russian Federation, Moscow, 117997 Russia

*e-mail: mvkosevich@ilt.kharkov.ua

Received May 24, 2016; in final form, July 12, 2016

Abstract—In the problem of the production silver nanoparticles, mass spectrometry allows one to identify nanoclusters as nuclei or intermediates in the synthesis of nanoparticles and to understand the mechanisms of their formation. Using low-temperature secondary emission mass spectrometry, we determined the cluster composition of a system formed in the microwave treatment of a solution of AgNO_3 in ethylene glycol (M).

Along with silver ion–ethylene glycol associates $M_m \cdot \text{Ag}^+$ ($m = 1–5$) and small silver clusters Ag_n^+ ($n = 1–9$), unusual silver clusters with one hydrogen atom $[\text{Ag}_n\text{H}]^+$ ($n = 2, 4$) were observed. Possible pathways for the formation of silver nanoparticles taking into account hydrogen-containing cluster intermediates are discussed.

Keywords: low-temperature secondary emission mass spectrometry, silver nanoclusters, ethylene glycol

DOI: 10.1134/S1061934817130032

INTRODUCTION

The development and improvement of methods for the synthesis of silver nanoparticles as a material useful for various engineering, pharmacological, biomedical, and environmental applications [1–7] remain to be one of topical problems of modern nanotechnology. Silver nanoparticles are synthesized by different chemical, physical, and biological methods [1, 4]. Wide literature data suggests that the formation of Ag_n nanoparticles from silver salts in the reduction of Ag^+ ions by different organic reductants proceeds both spontaneously and on exposure to physical factors, such as ultrasonic, microwave, laser, and γ irradiation, and heat. The selection of reaction conditions is governed by the search for methods for the control of the composition and shape of nanoparticles to be synthesized [8].

As a part of the solution of this problem, mass spectrometry is applied both to the determination of the composition of nanosilver [9–11] synthesized outside of a mass spectrometric instrument and the understanding of chemical and physical mechanisms and pathways to the formation of silver nanoparticles and nanoclusters [12–14]. One of physical methods for the preparation of silver clusters consists in their laser or

ion-beam sputtering from a metal or a salt in the ion source of a mass spectrometer [15–18]. In recent years, unique procedures for the chemical synthesis of small silver clusters directly in a mass spectrometric instrument using technical capabilities provided by electrospray ionization (ESI) have been proposed [19–21]. For example, silver metal clusters Ag_n^+ and Ag_n^- were obtained in [20] by heating ESI-sprayed microdroplets of silver organic salt solutions in a long capillary. In several works [21–25], silver clusters and their gas-phase reactions were studied under specific conditions of multistep collision-induced dissociation (CID) applied to ESI-generated multicomponent associates of silver ions with different organic ligands.

In our previous studies of the formation of silver nanoclusters in organic media, the laser desorption/ionization (LDI) [11] and fast atom bombardment (FAB) [12] mass spectrometric techniques were used to study the formation of silver nanoparticles in the medium of polyether, viz., polyethylene glycol (PEG). To clarify some questions arose in these works, we decided to study the corresponding processes in a solution of the PEG monomer, ethylene glycol. Note that, in contrast to the spontaneous formation of silver nanoparticles in the polyether medium, the initiation

of this process in an ethylene glycol medium requires an external impact.

The syntheses of silver nanoparticles from silver salts in an ethylene glycol medium [26–30] on exposure to heat, γ radiolysis [28], microwave treatment [29], and catalysts [30] have been described. In the present work, silver nanoparticles were synthesized by the microwave treatment of a solution of AgNO_3 in ethylene glycol. It is known that, in the synthesis in liquid samples, a polydisperse set of silver nanoclusters and nanoparticles was produced, as well as reaction intermediates remained in different charge states, which has been found earlier by spectroscopic and structural analysis [1, 6]. Using LDI mass spectrometry, we showed the presence of Ag_n nanoclusters with n up to 50 in dried samples [31]. To establish the pathways for the formation of silver nanoclusters under such conditions, we analyzed a system including ethylene glycol as a solvent highly volatile under vacuum conditions, using the low-temperature version of FAB secondary emission mass spectrometry. In a series of detected clusters, some peculiar associates $[\text{Ag}_n + 1]^+$ ($n = 2, 4$), formally corresponding to hydrogen-containing silver clusters were discovered; the discussion of these associates is the main subject of this report.

At the time of writing this paper, there were no literature data on the observation of silver–hydrogen associates Ag_nH^+ directly in organic media in the synthesis of silver nanoparticles. However, Ag_nH^+ clusters were detected recently along with Ag_n^+ using the above-mentioned multistep CID procedure for the gas-phase (vacuum) decomposition of silver ion associates with glycine (**Gly**) and *N,N*-dimethylglycine $[(\text{Gly} + \text{Ag} - \text{H})_m + \text{Ag}]^+$ [21]. The results of our studies can favor bridging between the chemical physics of ion-molecular reactions of silver in the gas phase and physicochemical processes in solutions resulting in the formation of silver nanoclusters.

EXPERIMENTAL

For the synthesis of silver nanoparticles, a test portion of AgNO_3 was preliminarily dissolved in a small amount of deionized water and mixed with ethylene glycol. The salt concentration in ethylene glycol was 9.4×10^{-2} M and the volume ratio of water to ethylene glycol was 1 : 50. The resulting solution in an Eppendorf plastic tube was heated in a domestic microwave oven over 3 min periods at intervals of several minutes to avoid overheating for a total time of 15 min until the solution became light-yellow, which, according to the literature data [1, 32], corresponded to the formation of nanoparticles with sizes of about 10–30 nm.

The application of the low-temperature method in FAB mass spectrometric experiments was due to the need in cooling the ethylene glycol sample to decrease saturated vapor pressure, whose value at room tem-

perature under vacuum conditions results in the rapid evaporation of the substance [33]. Measurements were performed using an MI 1201E sector-type magnetic mass spectrometer (Electron, Sumy, Ukraine) with a secondary ion source modified for low-temperature studies. The bombarding agent was argon with an energy of 4 keV. The switch between the ion (secondary ion mass spectrometry, **SIMS**) and neutral atom bombardment modes resulted in about a two-fold decrease in the intensities of the sprayed ions, but had no effect on the qualitative composition of the mass spectrum.

A droplet of a reaction mixture (5 μL) was applied to a metal support and frozen in liquid nitrogen vapors. Then, the sample was inserted into the secondary ion source of the instrument through the direct inlet lock until heat contact with a cryo unit through which the cooling agent was fed externally to maintain the specified temperature of the sample. Mass spectra were recorded on warming up the sample.

Earlier, we have shown [31] by LDI that Ag_n nanoclusters with n up to 50 were present in the system under study. In the present work, the research objects were small silver nanoclusters containing up to ten atoms. The table with the calculated isotopic ratios in the peak packages for Ag_n clusters with $n = 1–10$ is given in [11]. The FAB mass spectra were interpreted in terms of the concept of that charged particles present in solutions of ionic compounds underwent direct spraying [34].

RESULTS AND DISCUSSION

The microwave-treated sample of a solution of AgNO_3 in ethylene glycol (**M**) was studied by low-temperature FAB. The mass spectra were recorded at a slow increase in the temperature of the frozen sample. The temperature dependences of the resulting mass spectra were in agreement with our earlier developed model for the interpretation of low-temperature secondary-emission mass spectra [34–37], as well as with the earlier obtained dependences for solutions of salts [38] and amino acids [33] in ethylene glycol. Upon warming up the sample, an information-bearing mass spectrum (Fig. 1a) containing a high-intensity series of protonated ethylene glycol clusters $\text{M}_m \cdot \text{H}^+$ ($n = 1–6$) was obtained after a liquid phase has appeared in the sample, i.e., under the implementation of conditions corresponding to usual conditions for the FAB method with a liquid matrix. Such a spectrum was recorded in the temperature range from about -80 to -20°C . For the system with the silver salt, similar to other metal ion-containing ethylene glycol solutions, the mass spectrum displayed silver cation–ethylene glycol clusters $\text{M}_m \cdot \text{Ag}^+$ ($m = 1–5$). However, in contrast to the systems containing alkali metal salts [38] at the same initial concentration as in our initial solution of AgNO_3 , the peak intensity of the

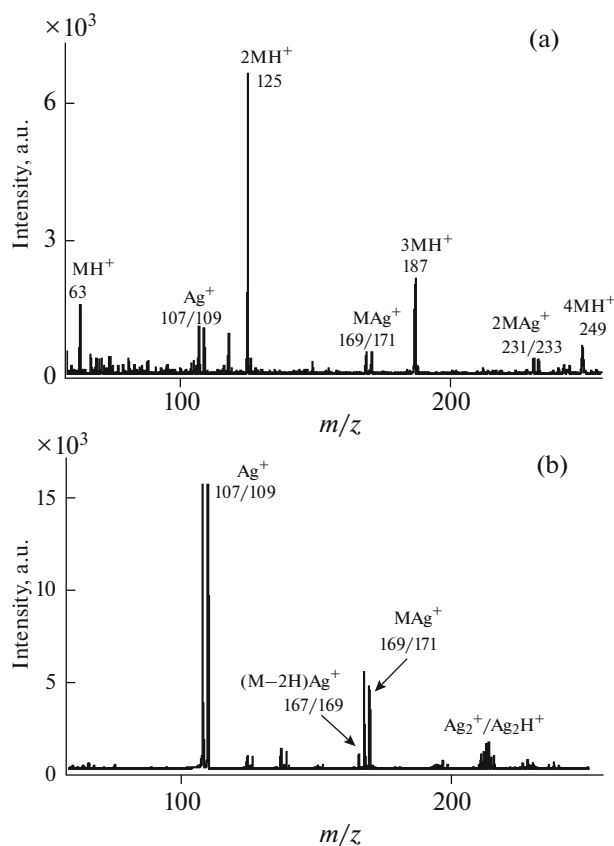


Fig. 1. Low-temperature FAB mass spectra for the microwave-treated (AgNO_3 + ethylene glycol) system at (a) -20°C and (b) -5°C ; M is the ethylene glycol molecule.

$\text{M}_m \cdot \text{Ag}^+$ clusters was much lower than that of $\text{M}_m \cdot \text{H}^+$. The relative intensity of Ag^+ peaks (m/z 107/109) was also low, which suggests a slight amount of silver ions in the solution. Both facts suggest the inclusion of most of silver into nanoparticles formed in the microwave treatment of the sample.

With a further increase in temperature, the rate of ethylene glycol evaporation increased, which resulted in a decrease in the amount of “solvent” and, consequently, in an increase in the concentration of dissolved substances. Such a process appeared in the mass spectra as a gradual redistribution of intensities of cluster series: while the total intensity of the $\text{M}_m \cdot \text{H}^+$ series decreased, the intensity of the $\text{M}_m \cdot \text{Ag}^+$ series increased; the intensity of Ag^+ also increased (Fig. 1b). In addition, on the depletion of the liquid up to a thin film on the support, particles which, earlier, were in the bulk of the liquid concentrated in a thin film and cropped out. This allowed us to detect a series of Ag_n^+ silver nanoclusters ($n = 1-9$) (Fig. 2). The remarkable fact was that the dependence of cluster intensity on the n value was governed by a known rule of intensity alternation for even and odd clusters which, along with

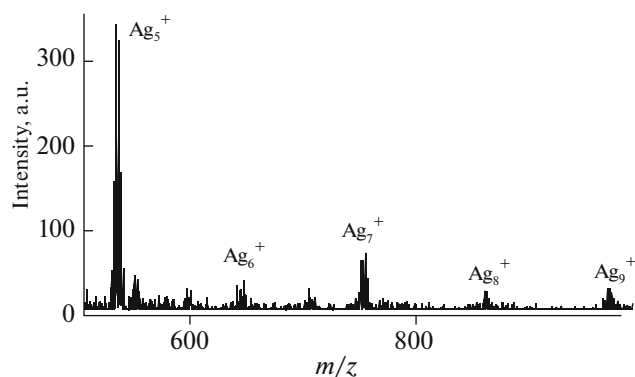


Fig. 2. Mass spectrum for Ag_n^+ ($n = 5-9$) silver nanoclusters recorded upon FAB of a thin ethylene glycol film with an increased concentration of therein dissolved components obtained during liquid evaporation. $T = -5^\circ\text{C}$.

the existence of the so called “magic numbers”, has been established earlier for the mass spectra of silver clusters [39–42], namely: the intensity of signals for positively charged clusters with odd numbers of atoms $n = 3, 5, 7, 9$ was higher than that for neighboring clusters with even numbers of atoms.

Along with the above-mentioned expected phenomena, a new experimental fact was detected. In the verification of isotope distribution in the peak groups corresponding to Ag_n^+ clusters, the typical distributions in the peak packages for clusters with even $n = 2, 4$ were found to superimpose on the peak package with the same distribution, but with mass value higher by unity [$\text{Ag}_n + 1$] (Fig. 3). For all peak packages for clusters with odd n , no such superimposition was observed. Thus, the [$\text{Ag}_n + 1$] series was also governed by the rule of intensity alternation for clusters with $2n$ and $(2n + 1)$. The intensities of isotopic peaks in the groups of [$\text{Ag}_2 + 1$] and [$\text{Ag}_4 + 1$] were about 1.5- and 2-fold higher than those of corresponding peaks in the Ag_2^+ and Ag_4^+ series. Formally, in this case the contribution of clusters with odd numbers of atoms was higher than that of clusters with even numbers of atoms.

Because of the above-mentioned features of the alternation of signal intensities for clusters (see Fig. 2), we failed to reliably determine the ratio of low-intensity peaks of [$\text{Ag}_n + 1$] being observed in peak groups for clusters with higher even values of $n = 6, 8$. We cannot use the accumulation mode for certain peak groups in this temperature range because of the fast depletion of the sample. However, the presence of [$\text{Ag}_n + 1$] species with $n = 2, 4$ in the system under study is a reliable and reproducible fact.

An increase in the mass of silver clusters by unity corresponds to the incorporation of one hydrogen atom or ion into the cluster composition. One can assume that the silver–hydrogen clusters are interme-

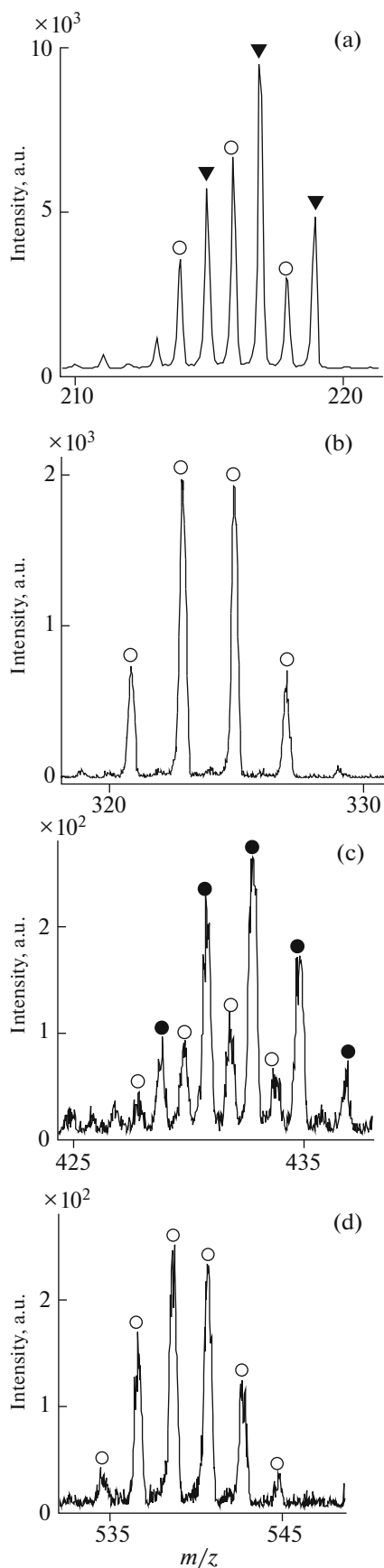


Fig. 3. Fragments of low-temperature FAB mass spectra for the microwave-treated (AgNO_3 + ethylene glycol) system containing groups of peaks corresponding to silver nanoclusters: (a) superposition of the groups of peaks for Ag_2^+ and Ag_2H^+ ; and (b) Ag_3^+ ; (c) superposition of the groups of peaks for Ag_4^+ and Ag_4H^+ ; and (d) Ag_5^+ .

Notation: \circ is Ag_n^+ , \blacktriangledown is Ag_2H^+ ; and \bullet is Ag_4H^+ .

diate products in the synthesis of silver nanoparticles under our experimental conditions and we succeeded in their detection by the analysis of the entire reaction mixture, while most of analytical works studied nanoparticles that were either already isolated from the reaction mixture or obtained by physical methods, such as laser sputtering.

As was noted in Introduction, the $[\text{Ag}_n\text{H}]^+$ clusters (with even n) under the mass spectrometric experimental conditions have been obtained earlier only in one work [21] as species resulting from the fragmentation of the initial clusters of glycine associated with silver ions $[(\text{Gly} + \text{Ag} - \text{H})_m + \text{Ag}]^+$ by the gas-phase multistep CID (or MS^n with n up to 5). Thus, we detected the $[\text{Ag}_n\text{H}]^+$ clusters for the first time directly in the reaction system.

In our previous work dedicated to the preparation of silver nanoparticles in polyethers [11], no $[\text{Ag}_n\text{H}]^+$ clusters were detected; however, their formation in these systems remains an open question, since the quite severe LDI method used earlier could induce the destruction of such intermediates.

Of interest was the nature of silver–hydrogen clusters, namely, could they be considered as either protonated neutral associates of silver atoms $(\text{Ag}_n) \cdot \text{H}^+$ or intermediates of silver reduction by a hydrogen atom as the source of electrons. The correct answer to this question can be obtained by quantum-chemical calculations [43–45], which showed that, in the positively charged $[\text{Ag}_n\text{H}]^+$ clusters, one neutral hydrogen atom replaced the silver atom in the spatial structure equivalent to the structure of the Ag_{n+1}^+ cluster. The electronic structural features of clusters with even and odd numbers of silver atoms, determining a higher stability of clusters with odd n were also responsible for the possible supplementation of clusters with even n with one hydrogen atom. Note that we failed to find literature data on the protonation of neutral metal clusters under mass spectrometric experimental conditions.

With regard to establishing possible mechanisms for the formation of silver nanoparticles, in the most of works dedicated to the discussion of this problem, emphasis was on the reduction of silver ions under the action of reductants and organic media were considered predominantly as a source of electrons generated under any external action [6, 46]. The next step was the formation of primary nucleating species, associates of several silver atoms and ions which then aggregated into larger formations. The role of organic sub-

stances in the synthesis medium at this step consisted in providing steric constraints determining the shape of the growing nanoparticles [8, 32, 47], as well as their aggregation [48] and stabilization [49]. However, in the chemistry of organometallic compounds, a sufficiently great number of works [50–58], including review [50] were published in recent years, in which the formation of associates of two, three, and more silver ions surrounded by organic ligands was considered. A core of silver ions bound to a hydrogen atom formed in some structures [54–58], which was proved by structural methods [54, 55]. Just these “ready” associates, which can act as primary building blocks for Ag_2^{2+} , Ag_2^+ , Ag_3^+ , and Ag_2 , as well as unusual Ag_nH^+ , being released from the organic environment on external exposure (UV, laser, thermal, microwave, and ultrasonic irradiation and CID). That is, in this case, organic anions or ligands serve to provide contacts between several silver ions, which determines the following steps in nucleation in the synthesis of silver nanoclusters. Note that, in our previous work [12] dedicated to the formation of silver nanoclusters in the medium of organic polyethers, we proposed a similar mechanism, involving inorganic NO_3^- ions, whose excess also favors the closer approximation of several silver ions to form a primary nucleus. The involvement of neutral hydrogen atoms in certain reduction steps of the silver ion has been discussed in recent work [59].

Thus, the detection of hydrogen-containing $[\text{Ag}_n\text{H}]^+$ clusters in the liquid reaction system (ethylene glycol– AgNO_3) points to the necessity of considering new pathways for the formation of silver nanoparticles, involving these hydrogen-containing subunits, but not only Ag^+ ions or Ag^0 atoms. Also, the question arises whether such intermediates occur in other organic media used for the synthesis of silver nanoparticles, which will be the subject of the future studies.

The discovered possibility of the direct preparation of hydrogen-containing Ag_nH^+ clusters using the FAB secondary-emission mass spectrometric technique provides an easier method for the generation of such clusters for their subsequent study as compared to multistep CID [21]. This method can be implemented on any instrument with a source of ions for liquid SIMS.

Silver compounds with hydrogen are in themselves interesting because of the problems of the improvement of voltaic cells and hydrogen power engineering; however, the literature search suggests that silver hydride as an individual compound, whose isolation in preparative scales is a disputable problem of classical inorganic chemistry [60, 61], still remains understudied. For example, the NIST database [62] contains very few data for the compound AgH , most of which were obtained by mass spectrometric techniques [63, 64]. Note that the properties of small clus-

ters, sometimes referred to as the fifth state of matter, differ from those of macroscopic volumes of corresponding substances, because of which $[\text{Ag}_n\text{H}]^+$ clusters are of interest as an individual subject of research.

CONCLUSIONS

The application of mass spectrometry, namely, a low-temperature version of FAB mass spectrometry, to the synthesis of silver nanoparticles by the microwave treatment of a solution of AgNO_3 in ethylene glycol allowed us to determine the composition of the resulting silver nanocluster products directly in their formation medium, viz., ethylene glycol.

Along with the expected silver ion–ethylene glycol associates $\text{M}_m \cdot \text{Ag}^+$ ($m = 1–5$) and small silver clusters Ag_n^+ ($n = 1–9$), hydrogen-containing silver clusters $[\text{Ag}_n\text{H}]^+$ ($n = 2, 4$) were detected in the reaction medium. Since, at the time of writing this paper, we found no data on the observation of $[\text{Ag}_n\text{H}]^+$ clusters directly in organic media in the synthesis of silver nanoparticles, one can consider that silver compounds with hydrogen as intermediates in the synthesis of Ag_n^+ were discovered for the first time by mass spectrometry.

The mass spectra for the cluster series showed their intensity to depend on the n value: the Ag_n^+ series was characterized by a known effect of higher intensities for the clusters with odd n compared to those with even n ; and the $[\text{Ag}_n\text{H}]^+$ series included only clusters with even n number.

The detection of hydrogen-containing clusters $[\text{Ag}_n\text{H}]^+$ in the reaction system points out the necessity of considering new alternative pathways and mechanisms for the formation of silver nanoparticles in organic media involving such hydrogen-containing subunits.

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Translated by K. Utegenov