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Mendeleev Commun., 2017, **27**, 186–187
Mendeleev Communications

One-step synthesis of a magnetoactive compound

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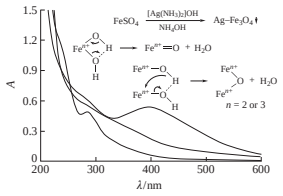
DOI: 10.1016/j.mencom.2017.03.027

The synthesis of stable silver-containing aqueous solution with magnetoactive particles (26–90 nm) based on the redox reaction of Fe^{II} cations with diammine silver(I) hydroxide in the presence of lignosulfonate and tetraethylammonium hydroxide has been developed.



The nanosized noble metals (Ag, Au and Pd) possessing unique properties can be used in catalysis, microelectronics and data storage, for drug delivery and in biosensors.[1–18] The most popular method for producing metal nanoparticles is the recovery of metals from solutions in the presence of stabilizers. Hydrogen,[19] lithium aluminum hydride and borohydrides,[20] alcohols and amines[21] are commonly used as reducing agents. Nanoscale catalysts are difficult to separate from the reaction medium because filtration and centrifugation are not suitable for these purposes. This problem can be solved with the use of magnetoactive catalysts, which can be easily removed from the reaction mixture by a magnetic field. The synthesis of materials with $Ag–Fe_3O_4$ compositions is typically multistage and time-consuming.[22–25]

The aim of this work was to develop a one-step synthesis of a water-soluble magnetoactive compound (MC).

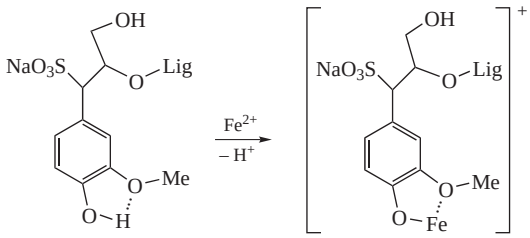
The described synthesis of materials with $Ag–Fe_3O_4$ compositions results in the original production of magnetite from Fe^{II} and Fe^{III} salt solution and the subsequent recovery of Ag^{I} cations to Ag^0 in the presence of the formed magnetite particles. The one-step method includes a redox reaction when a part of the Fe^{II} cations is oxidized by diammine silver(I) hydroxide;[26] then, an MC is formed in an alkaline medium. However, the reaction product in this method is a precipitate (Scheme 1).

$$FeSO_4 \xrightarrow[NH_4OH]{[Ag(NH_3)_2]OH} Ag–Fe_3O_4\downarrow$$

Scheme 1

We found that, during the synthesis of MC in the presence of lignosulfonates and TEA hydroxide, a dark brown solution having magnetic activity is formed.† The results of experiments with widely varied solution volumes revealed the following consumption of reagents for the production of the MC solutions: LS, 0.56–0.70 g per gram of Fe; $AgNO_3$, 0.12–0.58 g of Ag per gram of Fe; TEA hydroxide, no less than 12.6 g per gram of Fe. These solutions were stable for a month. The formation of magnetic activity occurred gradually during the storage of solution (Figure 1).

In the absence of TEA hydroxide and the LS, the $Ag–Fe_3O_4$ MC was formed only as a compact sediment. On the addition of $FeSO_4$ to a solution of sodium lignosulfonates **1**, complex **2** was formed due to the phenolic OH groups (Scheme 2).



1 **2**

Scheme 2

The mixing of this solution with NH_3 solution of silver nitrate caused a redox reaction that occurred almost instantaneously where a part of Fe^{II} was oxidized. Electron transfer from the Fe^{II} cation to the Ag^{I} cation was mediated by the oxygen atoms of iron cation hydration shells, and Ag^0 was formed. The hydroxo complex of Fe^{II} and Fe^{III} was precipitated in an alkaline medium. LS and silver were included in the complex, and Ag particles

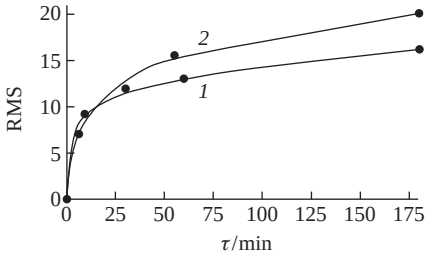
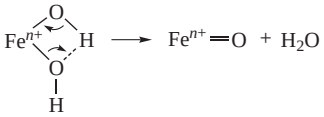


Figure 1 Dynamics of magnetic activity formation. $AgNO_3$, 0.35 g of Ag per gram of Fe; TEA hydroxide, 65 g per gram of Fe; LS, (*1*) 0.7 and (*2*) 0.18 g per gram of Fe.

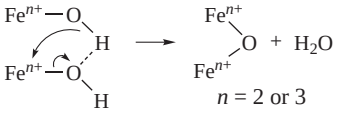
† The following reagents were used: $FeSO_4·7H_2O$, $AgNO_3$, powder sodium lignosulfonates (LS) and 35% tetraethylammonium (TEA) hydroxide and 25% NH_3 solutions. Initially, 2 ml of 0.1 M $FeSO_4$ was added to 10 ml of an aqueous LS solution (0.74 mg $ml^{–1}$). An oxidant solution was prepared by mixing 0.2 M $AgNO_3$, 25% NH_3 and 35% TEA hydroxide solutions. Then, both of the above solutions were mixed. At regular intervals, the relative magnetic susceptibility (RMS) was measured[27] after mixing the solutions.

initiated the MC formation. Apparently, the role of TEA hydroxide was to stabilize electrostatically the MC particle.

Unlike the redox step, the formation of magnetic activity proceeds gradually during the storage of solution that is associated with oxolation and olation, which result in the formation of an MC phase. Oxolation occurs as a dehydration process by electron redistribution involving two OH groups forming hydrogen bonds in an iron cation (Scheme 3) and olation – two iron cations (Scheme 4).



Scheme 3



Scheme 4

At the same time, dependences of the RMS on lgτ for different series of experiments are linear (R^2 = 0.971–0.993). The MC solutions synthesized at the consumption of TEA hydroxide 65 g per gram of Fe have the highest magnetic activity.

In contrast to the UV-VIS spectra of LS and a magnetic fluid synthesized by a published method[27] based on nitrosated LS, in the spectra of MC solutions, there is a broad absorption band at 400 nm (Figure 2), which is apparently related to the absorption of silver.[28]

The particle size of the synthesized MC in solution was determined by dynamic light scattering (DLS) and atomic force microscopy (AFM) (Figure 3).‡ The particle size distribution was unimodal. At various dilutions, the average particle size was 30–42 nm with a standard deviation of 1.5 nm. AFM showed that the MC particles have a spherical shape. The majority of these particles has the sizes close to those specified by DLS.

In conclusion, the reduction of diammine silver(I) by iron(II) in the presence of lignosulfonate and TEA hydroxide leads to the formation of stable silver-containing magnetoactive nanoparticles.

This study was supported by the Ministry of Education and Science of the Russian Federation (project no. 1321) and performed with the use of the equipment of the Arktika Centre of Collective Use at the Northern (Arctic) Federal University.

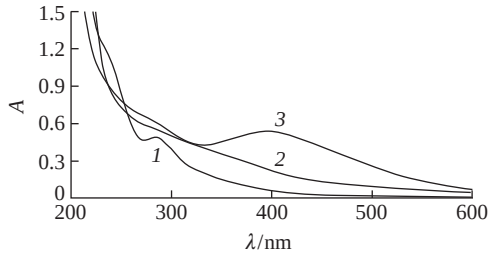


Figure 2 UV-VIS spectra of (*1*) LS solution, (*2*) magnetic fluid synthesized with nitrosated LS and (*3*) MC solution.

‡ The MC particle size was determined by DLS on a Horiba LB-550 nanoparticle size analyzer. The AFM measurements were carried out with an MC sample evaporated on mica from highly diluted solution using a Multimode 8 atomic force microscope (Bruker) with PeakForce tapping mode (Veeco Sb doped Si cantilever; stiffness probe, 62 N m^{-1}; resonance frequency, 354 kHz). The SEM measurements were performed using a Sigma VP scanning electron microscope (Zeiss) with an In Lenc detector at an accelerating voltage of 10 kV. The UV-VIS spectra were recorded with a Shimadzu UV-1650pc spectrophotometer.

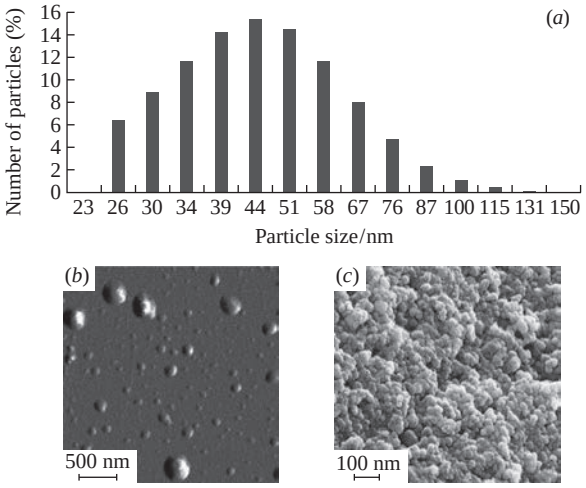


Figure 3 MC particles size determined by (*a*) DLS, (*b*) AFM and (*c*) SEM.

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Received: 7th July 2016; Com. 16/4989