ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2014, Vol. 59, No. 9, pp. 998–1003. © Pleiades Publishing, Ltd., 2014. Original Russian Text © V.P. Smagin, O.V. Larina, 2014, published in Zhurnal Neorganicheskoi Khimii, 2014, Vol. 59, No. 9, pp. 1231–1236.

## PHYSICAL METHODS OF INVESTIGATION

# The Effect of Stabilizers on Reduction of Silver(I) Ions in Ethyl Acetate

V. P. Smagin and O. V. Larina

Altai State University, Barnaul, Russia e-mail: smaginV@yandex.ru Received February 17, 2014

Abstract—The effects of polyethylene glycol and polymethyl methacrylate on reduction of silver(I) ions in the  $CF_3COOAg-Q_r-EA$  system (where  $Q_r$  is quercetin and EA is ethyl acetate) were studied spectrophotometrically. The introduction of these stabilizers to the system inhibits the redox process. The inhibition of reduction of silver(I) ions is attributed to the predominance of complexation or to the diffusion factor at high molecular weights and concentrations of compounds.

**DOI:** 10.1134/S0036023614090216

Metal nanoparticles and functional materials modified by them play a significant role in modern technology. They are distinguished by unique physical and chemical properties and used to manufacture catalysts, magnetic and electric materials, and optical elements [1–4]. Metal (in particular, silver) nanoparticles show promise for biology and medicine [5, 6]. Metal nanoparticles can be manufactured chemically. Under certain conditions, the synthesis is accompanied by formation of colloidal solutions. Colloidal solutions of metals are either used directly or as precursors for powder, film, and other materials, in particular, optical quantum dots immobilized in solid organic matrices [7–9]. Significant problems associated with colloidal systems are due to their low stability, which can be enhanced using stabilizers. Stabilizers inhibit degradation of colloidal systems, thus having a direct effect on the formation of colloidal particles and considerably modifying the technological processes of synthesizing the products. Hence, searching for efficient stabilizers and optimal conditions for the stabilization of colloidal systems is quite topical.

This study was aimed at elucidating the effect of stabilizers of colloidal solutions on the reduction of silver(I) ions in ethyl acetate.

Silver-containing systems were selected due to the properties of silver and silver-containing functional materials [6, 9–11]. Silver trifluoroacetate is well soluble in low-polarity organic solvents (in particular, in ethyl acetate whose physical properties are similar to those of acrylic monomers and polymers) [12]. Quercetin has moderate reducing properties with respect to silver ions in organic mixtures [11]. Polyethylene glycol and polymethyl methacrylate are used as stabilizers of colloidal solutions of elemental metals and their derivatives [8, 13, 14].

#### EXPERIMENTAL

Silver trifluoroacetate was synthesized by interaction of freshly precipitated Ag<sub>2</sub>O · nH<sub>2</sub>O with trifluoroacetic acid in water, isolated by evaporation of the solvent, dried, and identified by IR spectroscopy using data from [15, 16] as described in [17]. Quercetin of pure grade (C<sub>15</sub>H<sub>10</sub>O<sub>7</sub>, Lachema), commercial standardized polyethylene glycol samples of chemically pure grade with molecular weight 1500 (PEG<sub>1500</sub>) and 6000 amu (PEG<sub>6000</sub>), and polymethyl methacrylate (PMMA) synthesized by thermal radical polymerization in the presence of benzoyl peroxide at 70°C ( $M_r \sim$ 1 × 10<sup>6</sup> amu, viscometry) were also used in this study.

The IR spectrum of the salt was recorded on an Infralum FT 801 Fourier-transform spectrometer in the range  $4000-400 \text{ cm}^{-1}$ . Electronic absorption spectra were recorded on a Specord UV Vis spectrophotometer in the range 200–800 nm. Absorbance at the maximum of the absorption band was measured on an SF-46 spectrophotometer with respect to ethyl acetate. The photometric scale of SF-46 was calibrated using the procedure described in [18].

## **RESULTS AND DISCUSSION**

Stock solutions of silver trifluoroacetate and quercetin (at a concentration of  $1.00 \times 10^{-3}$  mol/L) in ethyl acetate were prepared using weighed portions of the compounds. The working solutions of silver trifluoroacetate and quercetin were prepared by diluting the stock solutions. Concentrations of the compounds were  $4.00 \times 10^{-4}$  mol/L. The concentrations and the equimolar ratio correspond to the conditions for fabrication of the most stable colloidal solutions in this system [17]. When the quercetin solution was added to the silver trifluoroacetate solution (or vice versa), the resulting solution gradually became pink. The elec-



Fig. 1.  $A = f(\tau)$  for the CF<sub>3</sub>COOAg-Q<sub>r</sub>-EA system,  $c_{Ag}: c_{Qr} = 1:1, c_{Ag} = c_{Qr} = 4.00 \times 10^{-4} \text{ mol/L}.$ 



**Fig. 2.**  $A = f(\tau)$  for the CF<sub>3</sub>COOAg-Q<sub>r</sub>-PEG<sub>1500</sub>-EA system,  $c_{Ag}: c_{Qr}: c_{PEG} = 1:1:1: (c_{Ag} = c_{Qr} = c_{PEG} = 4.00 \times 10^{-4} \text{ mol/L})$  with PEG<sub>1500</sub> added before the reaction was started (the compounds were added to the system in the following order: CF<sub>3</sub>COOAg, PEG<sub>1500</sub>, Q<sub>r</sub>).

tronic absorption spectrum featured a band with the maximum at 529 nm. Its intensity increased with time. The solution was gradually becoming red. The function  $A = f(\tau)$  obtained for this system (Fig. 1) is similar to that reported in [17]. It consists of three regions. The first one (1, Fig. 1) corresponds to product accumulation with gradually increasing reaction rate. A ~5-min-long induction period can be distinguished in this region. The second region is ~50 min long and features a linear rise of absorbance with time (2, Fig. 1). The run of the function indicates that the reaction rate is constant in this region. The third region (3, Fig. 1) characterizes the completion of the redox process with a gradual decrease in reaction rate due to the elimination of reagents from the system.

The effect of  $PEG_{1500}$ ,  $PEG_{6000}$ , and PMMA on the reduction of silver(I) ions was detected as changes that occur in kinetic curves after these compounds had been added to the systems. Polyethylene glycol and polymethyl methacrylate were preliminarily dissolved in a minimal amount of the corresponding solvent and

added to the solutions containing silver trifluoroacetate and quercetin at different stages of the redox process.

Figure 2 shows an exemplary curve recorded after PEG<sub>1500</sub> was added to the system at the molle ratio 1 : 1 : 1 before the redox reaction was started. This curve is significantly different from the original function. The duration of the induction period increased to ~30 min. The third region, typical of the initial curve (3, Fig. 1), did not appear during the time that absorbance was measured. Another order of adding the reagents and the stabilizer to the system (e.g., silver trifluoroacetate-stabilizer-quercetin or quercetin-stabilizersilver trifluoroacetate) had no effect on the reaction course.

Figure 3 shows an exemplary curve recorded for the system with  $PEG_{1500}$  added 20 min after the redox reaction had been started. This moment corresponds to the end of the induction period and of the period when the reaction rate increases and reaches the linear region of the  $A = f(\tau)$  function. The resulting depen-



Fig. 3.  $A = f(\tau)$  for the CF<sub>3</sub>COOAg-Q<sub>r</sub>-PEG<sub>1500</sub>-EA system,  $c_{Ag}: c_{Qr}: c_{PEG} = 1:1:1$  ( $c_{Ag} = c_{Qr} = c_{PEG} = 4.00 \times 10^{-4}$  mol/L) with PEG<sub>1500</sub> added 20 min after the reaction was started.



**Fig. 4.**  $A = f(\tau)$  for the CF<sub>3</sub>COOAg-Q<sub>r</sub>-PEG<sub>1500</sub>-EA system,  $c_{Ag}: c_{Qr}: c_{PEG} = 1:1:1$  ( $c_{Ag} = c_{Qr} = c_{PEG} = 4.00 \times 10^{-4}$  mol/L) with PEG<sub>1500</sub> added on the 55th min after the reaction was started.

dence is a combination of the curves shown in Fig. 1 (before 20 min) and Fig. 2 (after 20 min). The difference is in that the reaction rate decreases within the period of time corresponding to the linear region of the curve, which is indicated by a decreased slope ratio in the equation.

Figure 4 shows an exemplary curve for the system with PEG<sub>1500</sub> added 55 min after the reaction was started. This time corresponds to the end of the region of the function  $A = f(\tau)$  that is characterized by a constant rate of the redox reaction (2, Fig. 1). The result is a combination of the curves shown in Fig. 1 (before PEG<sub>1500</sub> was added to the system) and Fig. 3 (after PEG<sub>1500</sub> was added to the system).

The systems containing PEG<sub>1500</sub> and PEG<sub>6000</sub> in concentrations of  $1.00 \times 10^{-4}$ ,  $8.00 \times 10^{-4}$ , and  $16.00 \times 10^{-4}$  mol/L, which corresponds to the molar ratio CF<sub>3</sub>COOAg: Q<sub>r</sub>: PEG = 1 : 1 : 0.25, 1 : 1 : 2, and 1 : 1 : 4 were further studied in a similar manner.

Figures 5 and 6 show the functions obtained for the systems where  $PEG_{1500}$  was added at different ratios with respect to the reagents before the redox reaction and 20 min after it had been started. An increase in the reagents :  $PEG_{1500}$  molar ratio to 1 : 4 increased the induction period to ~50 min. The reaction rate increased at the second stage in accordance with the slope ratio in the function  $A = f(\tau)$  (Fig. 6).

Comparison of the resulting dependences (Figs. 1– 6) shows that the strongest effect on reduction of silver(I) ions with quercetin in the system containing the reagents and PEG<sub>1500</sub> was observed after polyethylene glycol had been added before the reaction started at a 1:1:4 CF<sub>3</sub>COOAg: Q<sub>r</sub>: PEG molar ratio. A similar effect was observed in the system with the 1:1:1 molar ratio between the components. In our opinion, the effect observed at an equimolar ratio between the components can be caused by the predominant complexation of polyethylene glycol with silver trifluoroacetate in low-polarity ethyl acetate. Increasing poly-



**Fig. 5.**  $A = f(\tau)$  for the CF<sub>3</sub>COOAg-Q<sub>r</sub>-PEG<sub>1500</sub>-EA system,  $c_{Ag}: c_{Qr}: c_{PEG} = 1:1:2$  ( $c_{Ag} = c_{Qr} = 4.00 \times 10^{-4} \text{ mol/L}; c_{PEG} = 8.00 \times 10^{-4} \text{ mol/L}$ ) with PEG<sub>1500</sub> added (*I*) before the reaction was started and (*2*) 20 min after the reaction was started.



**Fig. 6.**  $A = f(\tau)$  for the CF<sub>3</sub>COOAg-Q<sub>r</sub>-PEG<sub>1500</sub>-EA system,  $c_{Ag}: c_{Qr}: c_{PEG} = 1:1:4$  ( $c_{Ag} = c_{Qr} = c_{PEG} = 4.00 \times 10^{-4}$  mol/L;  $c_{PEG} = 16.0 \times 10^{-4}$  mol/L) with PEG<sub>1500</sub> added (*1*) before the reaction was started and (*2*) 20 min after the reaction was started.

ethylene glycol concentration increases the viscosity of solutions; the diffusion factor starts having an additional effect at 1 : 1 : 4 molar ratio between the reagents and polyethylene glycol, which enhances the effect observed.

Figure 7 shows the curves recorded for the systems containing  $PEG_{6000}$  a different PEG-reagent ratios

for PEG added to the solutions before the redox reaction was started. Increasing molecular weight of PEG is expected to enhance the effect of the diffusion factor. Increasing PEG<sub>6000</sub> concentration in the solutions (the reagents : PEG<sub>6000</sub> molar ratio from 1 : 1 : 0.25 to 1 : 1 : 4) led to an almost complete attenuation of the induction period and reduced the reaction rate. The

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**Fig. 7.**  $A = f(\tau)$  for the CF<sub>3</sub>COOAg-Q<sub>r</sub>-PEG<sub>6000</sub>-EA system when PEG<sub>6000</sub> was added before the reaction was started. (1)  $c_{Ag}$ :  $c_{Qr}$ :  $c_{PEG} = 1:1:0.25$  ( $c_{Ag} = c_{Qr} = 4.00 \times 10^{-4}$  mol/L;  $c_{PEG} = 1.00 \times 10^{-4}$  mol/L); (2)  $c_{Ag} = c_{Qr} = c_{PEG} = 1:1:1$  ( $c_{Ag} = c_{Qr} = c_{PEG} = 4.00 \times 10^{-4}$  mol/L); and (3)  $c_{Ag}$ :  $c_{PEG} = 1:1:4$  ( $c_{Ag} = c_{Qr} = 4.00 \times 10^{-4}$  mol/L),  $c_{PEG} = 16.0 \times 10^{-4}$  mol/L).



**Fig. 8.**  $A = f(\tau)$  for the CF<sub>3</sub>COOAg-Q<sub>r</sub>-PMMA-EA system when PMMA was added before the reaction was started.  $C_{Ag}: C_{Qr} = 1:1$  ( $C_{Ag} = C_{Qr} = 4.00 \times 10^{-4} \text{ mol/L}$ ); weight of PMMA, g/25 mL: (1) 0.240 and (2) 0.015.

result shows good agreement with the proposed interpretation of the effects observed. However, it follows from the slope ratios (Figs. 6, 7) that addition of PEG<sub>1500</sub> to the system causes a more significant decrease in the reaction rate than addition of PEG<sub>6000</sub> under identical conditions. Hence, a conclusion can be drawn that complexation plays a rather significant role.

To verify this assumption, weighed portions of PMMA (0.015 and 0.240 g) were added to 25.00 mL graduated flasks before the redox reaction was started. The role of complexation in this case was less significant than when polyethylene glycol was added. The resulting curves are shown in Fig. 8.

Thus, the effect of PEG and PMMA on the formation of colloids of elemental silver in low-polarity ethyl acetate has been demonstrated. The effects observed are caused by complexation of the compounds with silver trifluoroacetate and increasing viscosity of solutions when their concentrations and molecular weights were increased.

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Translated by D. Terpilovskaya