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PHYSICAL METHODS OF INVESTIGATION

Reaction between Silver Trifluoroacetate and Quercetin in Low-Polarity Organic Media

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Abstract— CF_3COOAg–Qr–P systems, where Qr is quercetin and P is an organic solvent, have been studied by spectroscopic methods. The reaction between silver trifluoroacetate and quercetin has been shown to produce colloid solutions, whose destruction terminates with the precipitation of a silver phase.The kinetic characteristics of the reaction between silver trifluoroacetate and quercetin in ethyl acetate have been determined.

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Colloid solutions of metals and their compounds have unordinary physical and chemical properties. They are applied in the chemical synthesis of metal powders, metallic film coatings, and functional materials [1–3]. The stability, size, and size distribution of colloid particles and the direction of their further transformations depend to a considerable degree on the properties of a dispersion medium. The use of dispersion media based on optical monomers and polymers allows one to combine the synthesis of nanosized metal particles and metal compounds with the synthesis of optically transparent metal-containing polymer materials and, among other things, to obtain quantum dots immobilized in optically transparent polymer matrices [4–6]. Complexation, redox, and colloidation processes play an important part in these syntheses, but they are very poorly studied in low-polarity organic solvents.

Here our task is to perform the spectroscopic study of the reaction between silver trifluoroacetate and quercetin in organic media that are close to optical monomers by their polarity.

Our choice of silver-containing systems is directly due to the properties of silver and silver-containing functional materials [4, 6]. The use of silver trifluoroacetate is caused by its high solubility in low-polarity solvents without additional components [7]. Quercetin has a moderate reducing activity with respect to silver ions in organic media [8].

EXPERIMENTAL

Silver trifluoroacetate was synthesized by the reaction between freshly precipitated $Ag_2O \cdot nH_2O$ and trifluoroacetic acid in an aqueous medium. The crystalline salt was separated via slow evaporation of its acidified solution on a water bath and subsequent drying in air. The salt was identified by IR spectroscopy using literature data [9, 10] and the spectrum of sodium trifluoroacetate, which was preliminary synthesized by the reaction between trifluoroacetic acid and sodium hydroxide.

The quercetin $C_{15}H_{10}O_7$ used in our work was of pure grade (LACHEMA).

The IR spectra of compounds were recorded on an Infralum FT 801 spectrophotometer in the region of 4000–400 cm^{-1}. The electronic absorption spectra of solutions were recorded on a Specord UV Vis spectrophotometer in the region of 200–800 nm. The absorbance at absorption band maxima was measured on an SF-46 spectrophotometer with reference to ethyl acetate at a temperature of 296 K. The photometric scale of the SF-46 spectrophotometer was calibrated as described in [11].

RESULTS AND DISCUSSION

Solutions of silver trifluoroacetate, quercetin, and their mixtures were prepared in trichloromethane, ethyl acetate, methylmethacrylate, and acetonitrile with concentrations of 1.00×10^{-3} mol/L and lower.

Silver trifluoroacetate solutions are colorless. The long-wave absorption band in the spectra of solutions recorded with reference to the solvent is located in the region of 250 nm. It is assigned to the $n \rightarrow \sigma^*$ electron transition. This band is due to the carboxyl group of trifluoroacetate ions. Silver trifluoroacetate solutions are transparent in the spectral region of >270 nm.

Quercetin solutions are light-yellow.In the region of wavelengths >250 nm, the spectra contain two absorption bands of quercetin at 272 and 377 nm (Fig. 1). The apparent molar extinction coefficients at the maxima of these bands are $\sim 6 \times 10^3$ and $\sim 2 \times 10^4$ L/(mol cm), respectively. The absorption bands are related with the $\pi \rightarrow \pi^*$ electron transitions in the chromophore systems of quercetin.

After quercetin solutions were added to silver salt solutions or vice versa, the mixtures gradually acquired

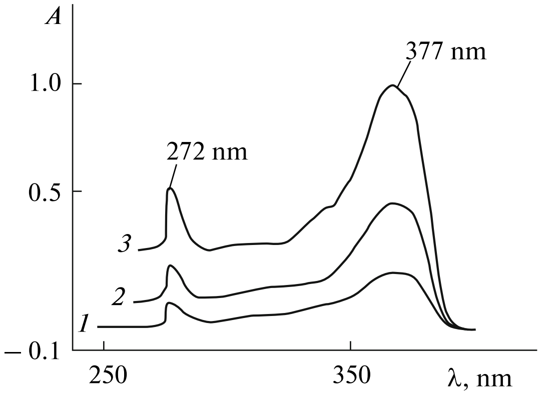

Fig. 1. Absorption spectra of quercetin solutions in ethyl acetate with reference to ethyl acetate at a quercetin concentration of (*1*) 1.00 × 10^{-5}, (*2*) 2.00 × 10^{-5}, and (*3*) 4.00 × 10^{-5} mol/L.

a light pink color. With time, they became purple-red. The rate of the change in color, color intensity, and shade depended on the concentrations and concentration ratios of dissolved compounds. In the region of 450–600 nm, the spectra of solutions contained an absorption band with a maximum at 529 nm (Fig. 2). Its intensity grew with time (Fig. 3). The position of the long-wave edge of this absorption band remained unchanged. No shift of the absorption band maximum was observed in the spectrum upon the replacement of a solvent. Reasoning from the obtained results and the literature data [8, 12–15], this band was assigned to the absorption of colloid particles formed in the reaction between silver trifluoroacetate and quercetin. This band shifted towards long wavelengths with respect to the absorption bands of elemental silver colloids in the spectra of aqueous solutions, low-temperature oxide matrices, and inverted aqueous micelles in hydrocarbon systems [8, 12–15]. We relate this shift to the effect of an organic medium, including a probable interaction of silver ions with quercetin on the surface of colloid particles. This interaction may also be one of the factors that stabilize colloid solutions.

The colloid solutions were stable during the time period from several minutes to several days. The process of their destruction terminated with the formation of a "silver mirror" on the walls of a reaction vessel and the settlement of a black elemental silver precipitate. The colloid solutions in the systems prepared from equal amounts of reagents up to ~4 × 10^{-4} mol/L had the highest stability. When the concentration of compounds in solutions was increased (at the same equimolar ratios), the formation of a "silver mirror" predominated. The excess concentration of one reagent eventually led to the predominant settlement of elemental silver in the form of a black precipitate on the bottom of a reaction vessel. A considerable effect on the rate of the formation and destruction of colloid solutions was produced by the temperature.

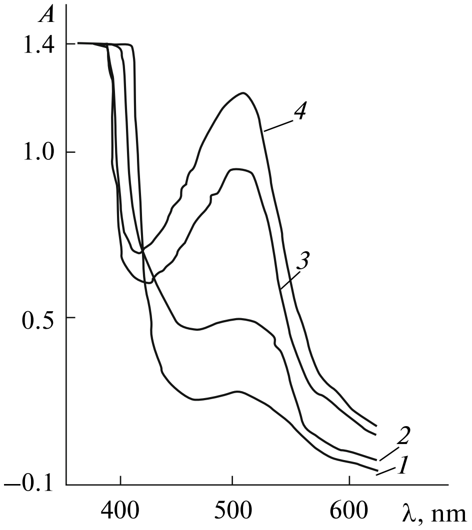

Fig. 2. Absorption spectra recorded for the CF_3COOAg–Qr–P system, where P stands for (*1*) acetonitrile, (*2*) trichloromethane, (*3*) methylmethacrylate, and (*4*) ethyl acetate, in 6 min beginning from the moment the solutions were prepared.

The kinetic of the reaction between silver trifluoroacetate and quercetin was studied in an ethyl acetate medium. The reaction was monitored by the change in the absorbance of solutions. The experimental conditions (analytical wavelength, concentrations and concentration ratios of reagents, and temperature) were selected from the obtained spectral information. They allowed us to record the absorbances of solutions with the

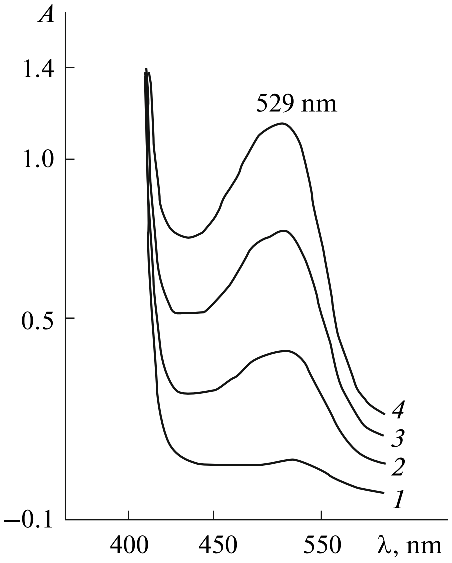

Fig. 3. Absorption spectra recorded for the CF_3COOAg–Qr–ethyl acetate system with reference to ethyl acetate in in different time intervals beginning from the moment the solutions were (*1*–*4*) were prepared. c_{Ag} = 5.00 × 10^{-5} mol/L, c_{Qr} = 1.00 × 10^{-3} mol/L.

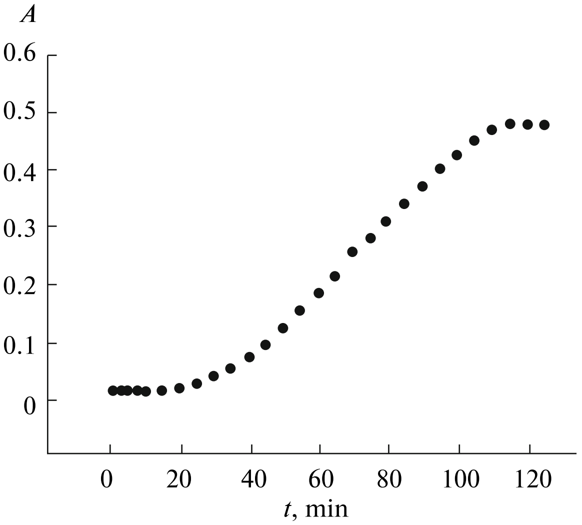

Fig. 4. $A = f(t)$ for the CF_3COOAg–Qr–ethyl acetate system. $c_{\mathrm{Ag}}/c_{\mathrm{Qr}} = 2$, $c_{\mathrm{Ag}} = 4.00 \times 10^{-4}$ mol/L, $c_{\mathrm{Qr}} = 2.00 \times 10^{-4}$ mol/L.

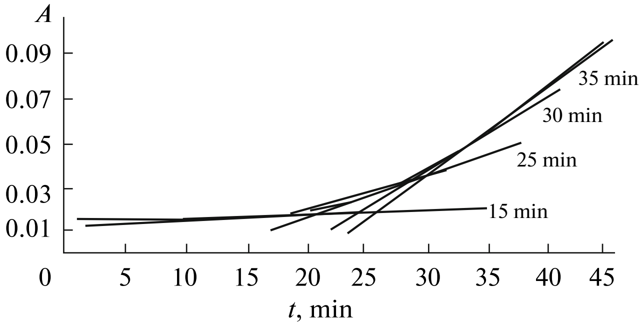

Fig. 5. Initial region of the dependence $A = f(t)$ for the CF_3COOAg–Qr–ethyl acetate system. $c_{\mathrm{Ag}}/c_{\mathrm{Qr}} = 2$, $C_{\mathrm{Ag}} = 4.00 \times 10^{-4}$ mol/L, $c_{\mathrm{Qr}} = 2.00 \times 10^{-4}$ mol/L.

lowest error and perform the reaction for 60–120 min. The rate constants and orders of the reactions with respect to reagents were determined by the method of excess concentrations [16]. In this case, we assumed that a formally simple chemical reaction proceeds in the systems.

Solutions with a constant excess quercetin concentration (1.00×10^{-3} mol/L) and a decreasing silver trifluoroacetate concentration were prepared. Molar ratios $c_{\mathrm{Qr}}/c_{\mathrm{Ag}}$ in the solutions of this series were varied from 1 : 1 to 150 : 1. The second series of solutions was prepared with a constant excess silver trifluoroacetate concentration (4.00×10^{-4} mol/L) and a decreasing quercetin concentration. Molar ratios $c_{\mathrm{Ag}}/c_{\mathrm{Qr}}$ in these solutions were varied from 1 : 1 to 4 : 1. The absorbances of solutions were recorded at 529 nm.

The obtained data were used to plot $A_{529} = f(t)$ plots that reflected the change in the absorbance of solutions with reaction time. Each curve may nominally be divided into three regions: the region of the accumulation of a product with a gradual increase in reaction rate, the linear region with a constant rate, and the region corresponding to a decrease in the reaction rate and the termination of the reaction. The reaction rate (w^*, min^{-1}) was determined via graphical differentiation by drawing tangent lines at different points of a kinetic curve. The reaction rate constants and orders with respect to reagents were determined logarithmically [16]. The procedure of estimating the reaction rate and plotting the dependence $w^* = f(t)$ for one of the solutions is illustrated in Figs. 4–8 and Table 1. The data for plotting a $\ln(w^*) = f(\ln c)$ plot of the logarithmic function $\ln w^* = \ln k_i^* + n_i \ln c_i$, where i is silver or quercetin according to the studied series of solutions and k_i^* is the rate constant found from w^*; the equations of these plotd, and linearity coefficients are given in Tables 2 and 3. The rate constant $k_{\mathrm{Ag}}^* = 0.90\ \mathrm{L}^{0.56}/(\mathrm{mol}^{0.56}\ \mathrm{min})$ and the reaction order with respect to silver $n_{\mathrm{Ag}} = 0.56$ were calculated from the equation that describes the dependence at an excess quercetin concentration and a variable silver trifluoroacetate concentration. The rate constant $k_{\mathrm{Qr}}^* = 8.2 \times 10^2\ \mathrm{L}^{1.44}/(\mathrm{mol}^{1.44}\ \mathrm{min})$ and the reaction order with respect to quercetin $n_{\mathrm{Qr}} = 1.44$ were calculated from the equation that describes the dependence at an excess silver trifluoroacetate concentration and a variable quercetin concentration.

The calculation of the total reaction order $n = n_{\mathrm{Ag}} + n_{\mathrm{Qr}}$ gives 2. The reaction rate constant was calculates as $k^* = \frac{k_i^*}{a_i c_j^{n_j}}$, where i is silver and j is quercetin for the series of solutions with excess quercetin and vice versa for the series of solutions with excess silver trifluoroacetate, a_i and a_j are the stoichiometric coefficients in the equation of the reaction between silver trifluoroacetate and quercetin, $a_i = a_j = 1$. The assumption on the equality of the stoichiometric coefficients to unity fol-

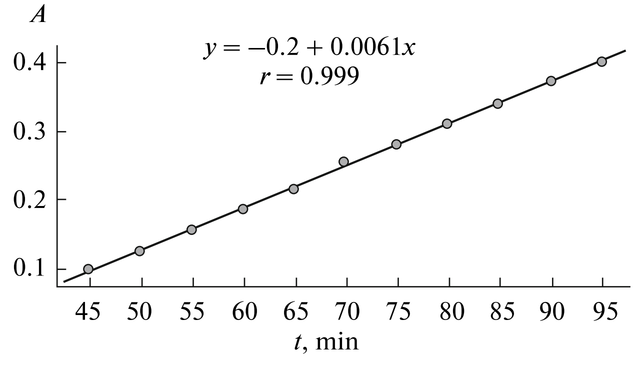

Fig. 6. Middle region of the $A = f(t)$ plot for the CF_3COOAg–Qr–ethyl acetate system. $c_{\mathrm{Ag}}/c_{\mathrm{Qr}} = 2$, $c_{\mathrm{Ag}} = 4.00 \times 10^{-4}$ mol/L, $c_{\mathrm{Qr}} = 2.00 \times 10^{-4}$ mol/L.

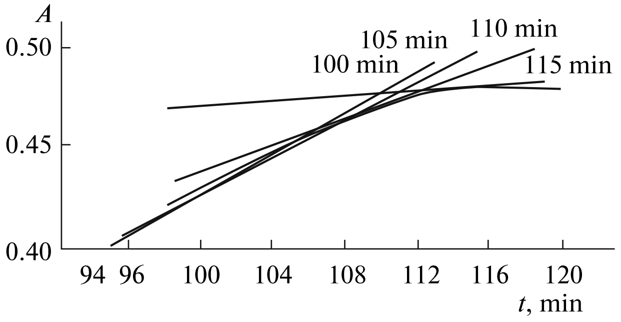

Fig. 7. End region of the $A = f(t)$ plot for the CF_3COOAg–Qr–ethyl acetate system. $c_{Ag}/c_{Qr} = 2$, $c_{Ag} = 4.00 \times 10^{-4}$ mol/L, $c_{Qr} = 2.00 \times 10^{-4}$ mol/L.

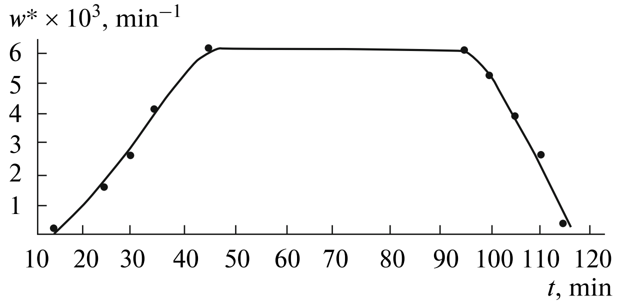

Fig. 8. $w^* = f(t)$ for the CF_3COOAg–Qr–ethyl acetate system. $c_{Ag}/c_{Qr} = 2$, $c_{Ag} = 4.00 \times 10^{-4}$ mol/L, $c_{Qr} = 2.00 \times 10^{-4}$ mol/L.

lows from the single-electron exchange in the redox reaction between silver ions and quercetin and is based on the character of the interaction of metals with quercetin [9]. As a result, the average reaction rate constant amounted ~4×10^4 $L^2/(mol^2$ min). Noninteger reaction orders with respect to compounds and partial reaction rate constant ratios indicate a complex character of the process and its high sensitivity to the changing quercetin concentration in solution.

The conversion to the reaction rate (w, mol/(L min)), the partial reaction rate constants (k_{Ag}, $mol^{0.44}/(L^{0.44}$ min); k_{Qr}, $L^{0.44}/(mol^{0.44}$ min)), and the total reaction rate constant (k, L/(mol min)) can be performed using the Bouguer–Lambert–Beer law and knowing the molar extinction coefficient at an analytical wavelength in the absorption band of colloid particles as $w = \frac{w^*}{\varepsilon l}$ and $k = \frac{k^*}{\varepsilon l}$, where w^* and k^* are the reaction rate (min^{-1}) and the reaction rate constant which are determined from $A = f(t)$, ε is the molar extinction coefficient, L/(mol cm), and l is the thickness of an analytical cell, cm. The estimation of ε in similar systems is a very complicated problem. For example, it variates from 7×10^3 to 1×10^4 L/(mol cm) for colloid elemental silver particles [8]. The average molar extinction coefficient calculated for colloid particles from the rates of the reaction w^*, the time until its termination, and the concentrations of a reagent on the basis of the data for the entire series of studied solutions both with excess silver trifluoroacetate and

Table 1. Data for plotting $w^* = f(t)$ for the CF_3COOAg–Qr–ethyl acetate system. $c_{Ag}/c_{Qr} = 2$, $c_{Ag} = 4.00 \times 10^{-4}$ mol/L, and $c_{Qr} = 2.00 \times 10^{-4}$ mol/L

t, min	15	25	30	35	45	95	100	105	110	115
$w^* \times 10^3$, min^{-1}	0.18	1.60	2.67	4.13	6.10	6.10	5.33	4.00	2.67	0.54

Table 2. Data for plotting a $\ln w^* = f(\ln c)$ plot for the CF_3COOAg–Qr–ethyl acetate system at a constant excess quercetin concentration of 1.00×10^{-3} mol/L

c_{Ag}, mol/L	6.00×10^{-5}	5.00×10^{-5}	4.00×10^{-5}	2.00×10^{-5}	0.68×10^{-5}
$\ln c_{Ag}$ [mol/L]	–9.72	–9.90	–10.1	–10.8	–11.9
w^*, min^{-1}	0.0040	0.0038	0.0036	0.0019	0.0013
$\ln w^*$ [min^{-1}]	–5.52	–5.57	–5.63	–6.27	–6.65
Equation, linearity coefficient			$\ln w^* = -0.102 + 0.556 \ln c_{Ag}$, $r = 0.980$		

Table 3. Data for plotting a $\ln w^* = f(\ln c)$ plot for the CF_3COOAg–Qr–ethyl acetate system at a constant excess silver trifluoroacetate concentration of 4.00×10^{-4} mol/L

c_{Qr}, mol/L	4.00×10^{-4}	3.00×10^{-4}	2.00×10^{-4}	1.00×10^{-4}
$\ln C_{Qr}$ [mol/L]	–7.82	–8.11	–8.52	–9.21
w^*, min^{-1}	0.0060	0.0099	0.0061	0.0010
$\ln w^*$ [min^{-1}]	–5.12	–4.62	–5.10	–6.91
Equation, linearity coefficient	$\ln w^* = 6.71 + 1.44 \ln c_{Qr}$, $r = 0.863$			

quercetin is ~6×10^3 L/(mol cm) that is close to the data [8].

Hence, as a result of our study, we have detected the formation of colloid silver particles in the reaction between silver trifluoroacetate and quercetin in organic media that are close to optical monomers in their polarity. The kinetic characteristics of the reaction of the components in an ethyl acetate medium have been determined.

REFERENCES

1. S. P. Gubin and I. D. Kosobudskii, Usp. Khim. **52**, 1350 (1983).
2. A. D. Pomogailo, A. S. Rozenberg, and I. E. Uflyand, *Metal Nanoparticles in Polymers* (Khimiya, Moscow, 2000) [in Russian].
3. S. N. Shtykov and T. Yu. Rusanova, Ros. Khim. Zh. (Zh. Ros. Khim. O–va im. D.I. Mendeleeva) **52** (2), 92 (2008).
4. M. V. Galkin, E. V. Ageeva, D. A. Nedosekin, et al., Vestn. Mosk. Univ, Ser. 2: Khim. **51**, 115 (2010).
5. A. A. Biryukov, Candidate's Dissertation in Chemistry (TGU, Tomsk, 2010).
6. P. A. Muzalev, I. D. Kosobudskii, D. M. Kul'batskii, and N. M. Ushakov, Materialovedenie, No. 5, 48 (2011).
7. V. P. Smagin, R. A. Maier, G. M. Mokrousov, and R. A. Chupakhina, Patent RU 1806152, Byull. Izobret., No. 12 (1993).
8. E. M. Egorova, Extended Abstract of Doctoral Dissertation in Chemistry (MGATKhT im. M.V. Lomonosova, Moscow, 2011).
9. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley-Interscience, 1986; Mir, Moscow, 1991).
10. E. V. Karpova, Candidate's Dissertation in Chemistry (Moscow, 2000).
11. A. J. Gordon and R. A. Ford, *The Chemist's Companion: A Handbook of Practical Data, Techniques and References* (Wiley, New York, 1972; Mir, Moscow, 1976).
12. G. B. Sergeev, *Nanochemistry* (Moscow Univ. Press, Moscow, 2003) [in Russian].
13. A. A. Eliseev and A. V. Lukashin, *Physical Properties of Materials in Nanocrystalline State. Methodical Materials* (Izd-vo MGU, Moscow, 2007) [in Russian].
14. E. V. Anishchenko, G. V. Lyamina, N. M. Korshikova, and G. M. Mokrousov, *Izv. Politekh. Tomsk. Univ.*, No. 1, 56 (2006).
15. S. B. Brichkin, Extended Abstract of Doctoral Dissertation in Chemistry (IPKhF RAN, Chernogolovka, 2010).
16. A. G. Stromberg, *Physical Chemistry*, Ed. by A. G. Stromberg and D. P. Semchenko (Vysshaya Shkola, Moscow, 1999) [in Russian].

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