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Synthesis of High-Pure Bismuth Citrate Using the Solid-Liquid Reactions

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Abstract

The interaction of oxohydroxobismuth (III) nitrate trihydrate having the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ with the aqueous solutions of citric acid were studied by means of X-ray phase analysis, thermogravimetry, IR spectroscopy and chemical analysis. The effect of the concentration of citrate ions, pH of the medium and process temperature on the rate of nitrate ion exchange for citrate ions was studied. The conditions for the formation of bismuth citrate with the composition $BiC_6H_5O_7$ were determined. The reasonability of the synthesis of high-purity bismuth citrate through the interaction of oxohydroxobismuth (III) nitrate trihydrate was demonstrated.

Key words: bismuth citrate, high-purity compounds, chemical synthesis, X-ray phase analysis, IR spectroscopy

INTRODUCTION

Bismuth (III) citrate having the composition $BiC_6H_5O_7$ is used to prepare efficient antiulcerants (De-Nol, Tribimol, Gastronorm, Pilorid), nutrient media for the production of bacterial preparations, and in the synthesis of bismuth-containing high-temperature superconducting materials. It was proposed to obtain this compound by adding the solution of citric acid to bismuth-containing lactic-acetic [1] or glycerol-containing [2] solutions, as well as by boiling freshly precipitated bismuth hydroxide or basic carbonate with the solution of citric acid [3, 4]. Bismuth (III) citrate can also be obtained by adding the nitrate solution of bismuth (III) into the solution of ammonium citrate [5] or by adding the solution of citric acid to bismuth nitrate solution within pH range 0.1–0.7 at the process temperature of (60±5) °C [6]. However, the final product of this interaction can be substantially contaminated with the major accompanying metals (lead, iron, silver *etc.*) that get co-precipitated with bismuth. During the recent years, in view of the increasing amount of bismuth compounds consumed, especially in medicine, development of sufficiently simple and reliable synthesis methods providing high purity and reactivity of the synthesized compounds becomes increasingly important.

Synthesis of bismuth compounds is usually carried out through precipitation from bismuth-containing nitrate solutions that are prepared by dissolving the granules of metal bismuth in nitric acid [7]. It was demonstrated [8] that preliminary oxidation of metal bismuth with oxygen of the air allows one to decrease the consumption of nitric acid by a factor of two and to eliminate the evolution of nitrogen oxides at the stage of preparation of bismuth nitrate solutions.

It is also known [9] that the precipitation of bismuth from nitrate solutions in the form of oxohydroxobismuth (III) nitrate trihydrate having the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$

allows one to carry out efficient purification of bismuth from extrinsic metals (impurity content not more than 10^{-3}–10^{-7} %). In this respect, investigation of the interaction of solid oxohydroxobismuth (III) nitrate trihydrate with the solutions of citric acid is practically essential for obtaining high-purity bismuth citrate.

In the present work we report on the results obtained in the investigation of the effect of citrate ion (Cit) concentration, pH of the medium and temperature on the rate and extent of the exchange reaction in the system: solid oxohydroxobismuth (III) nitrate trihydrate–citric acid solution, and also on the composition and purity of reaction products.

EXPERIMENTAL

Oxohydroxobismuth (III) nitrate trihydrate having the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ with the mass concentration of bismuth 72.28 % and nitrate ions 17.38 % was obtained at a temperature of (20±2) °C diluting the solution of bismuth (III) nitrate having the composition, g/L: Bi(III) 210, free HNO_3 35, with water at the volume ratio of 1 : 40 (pH ~ 1.0). The precipitate was carefully separated by filtering under vacuum, washed with distilled water and dried in the air. The weighted portion of basic bismuth nitrate with a mass of 10 g was treated with 100 mL of the solution of citric acid of os. ch. 8–4 reagent grade and different concentrations. The molar ratio of citric acid to basic bismuth nitrate (n) increased from 0 to 3. Precipitates after the treatment of oxohydroxobismuth (III) nitrate trihydrate with citric acid were separated from the mother solution by filtering, washed with distilled water and dried in the air. Bismuth content in solutions and products was determined by means of photocolorimetry in the presence of KI with KFK-2 instrument. Precipitated products were preliminarily dissolved in nitric acid (1 : 1). Determination of citric and nitric acids in the solid reaction products was performed after having transferred them into solution by means of preliminary treatment of the precipitates with the 2 M NaOH solution at 70–90 °C. We measured the concentration of nitrate ions using voltammetry with the copper renewable electrode [10], citrate ions by means of permanganatometric titration [11]. X-ray phase analysis (XPA) of reaction products was made with DRON-3 diffractometer using CuK_α radiation. The rate of counter rotation was 0.5 deg/min. The curves of differential thermal analysis (DTA) and mass change (TG) of the samples under investigation were recorded with a derivatograph (MOM, Hungary) in the air at the heating rate of 10 °C/min. Absorption spectra in the IR region (400–4000 cm^{-1}) were recorded with a Specord 75 IR spectrophotometer. The samples were prepared as tablets with calcined KBr. The pH of solution was measured with PB-20 pH meter using a glass or renewable solid electrode.

RESULTS AND DISCUSSION

Investigation of the interaction of oxohydroxobismuth (III) nitrate trihydrate with the solutions of citric acid at a temperature of (23±2) °C showed (Fig. 1) that at first, with an increase in the concentration of citric ions in solution, the molar ratio of nitrate ions to bismuth (III) A in the precipitate decreases from 0.81 at $n = 0$ to 0.46 at $n = 0.5$. A regular decrease in pH of the medium from 1.5 to 0.9 is observed. However, at $n > 0.5$ the A value starts to increase; a maximum corresponding to $A = 0.57$ is observed on the curve of $A - n$ dependence at $n = 0.75$. Along with this, within the indicated region we observe an increase in pH of the medium, which reaches its maximum equal to 2.3 at $n = 0.75$. Further increase in the

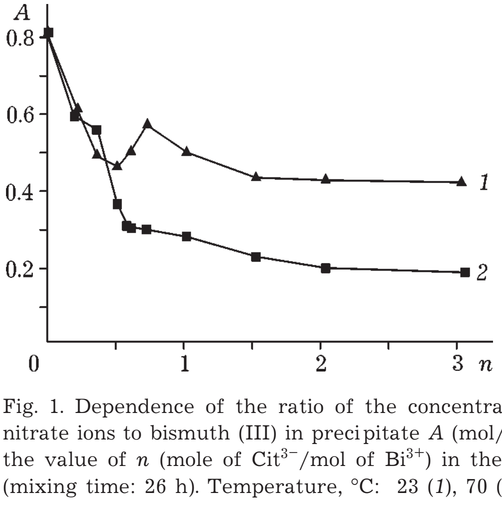

Fig. 1. Dependence of the ratio of the concentrations of nitrate ions to bismuth (III) in precipitate A (mol/mol) on the value of n (mole of Cit^{3-}/mol of Bi^{3+}) in the system (mixing time: 26 h). Temperature, °C: 23 (*1*), 70 (*2*).

concentration of citric acid in the solution to $n = 1$ again leads to an increase in the acidity of solution (pH decreases to 1.0) and a decrease in the molar ratio of nitrate ions to bismuth (III) to 0.435 at $n = 3$, which is the evidence of the exchange reaction. However, complete substitution of nitrate ions by citrate ions does not occur even in the case of three-fold excess of the latter with respect to bismuth (III) in solution and mixing time 26 h. An increase in the process temperature to (70±2) °C causes a more substantial decrease in the molar ratio of nitrate ions to bismuth (III) in the precipitate from 0.81 at $n = 0$ to 0.21 at $n = 3$, which is the evidence of an increase in the extent of exchange reaction progress. With an increase in the concentration of citric acid in the system from 0 to 1.25 mol/L, bismuth (III) content varies between 0.2 and 0.01 g/L, depending on pH of the medium and does not exhibit substantial dependence on the process temperature.

Oxohydroxobismuth (III) nitrate trihydrate having the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ (monoclinic crystal structure, space group $P2_1/C$) is composed of nitrate ions, water molecules and polycations in which two $[Bi_6O_5(OH)_3]^{5+}$ groups are connected with each other through two bridging oxygen atoms [12]. According to the data of X-ray phase analysis (Fig. 2), with an increase in the concentration of citric ions in the reaction mixture and the corresponding decrease of the ratio of nitrate ions to bismuth in the precipitate, the intensities of diffraction maxima with d/n equal to 13.51, 3.55 and 2.11 Å that are characteristic of the compound $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ (see Fig. 2, curve *1*) decrease. Their position remains almost the same, while the diffraction patterns at $n = 0.25$ clearly exhibit the appearance of additional maxima with d/n equal to 10.28, 5.15, 4.48, 3.88, 3.35, 1.69 Å ($T = (25\pm2)$ °C) (see Fig. 2, curve *2*); their intensities increase and then start to decrease sharply; at $n = 1.5$ they almost disappear. We did not find any data in the literature stating what compound these values correspond to. However, we tried to isolate this compound in the individual form (93–95 %) by treating oxohydroxobismuth (III) nitrate trihydrate with the solution containing 0.2 mol/L citric acid and 0.5 mol/L chloric acid. Chemical analysis shows that the isolated product contains, mass %: Bi 51.8, $C_6H_5O_7^{3-}$ 35.1, NO_3^- 1.25. Bismuth content in the mother solution is 9.8 %.

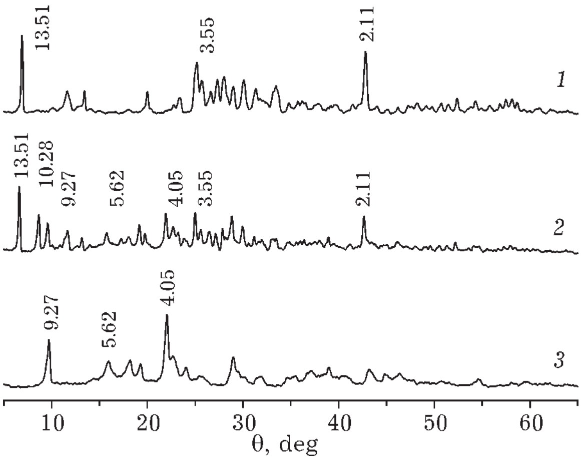

Fig. 2. Diffraction patterns of oxohydroxobismuth (III) nitrate trihydrate (*1*) and the products of its interaction with citric acid solutions (*2*, *3*).

Along with the listed products, for $n = 0.5$ the diffraction patterns exhibit the appearance of new diffraction maxima with d/n equal to 9.27, 5.62, 4.05 Å that correspond to the neutral bismuth (III) citrate with the composition $BiC_6H_5O_7$ (see Fig. 2, curve *3*). Precipitates obtained for $n = 1.5$ are mixtures of oxohydroxobismuth (III) nitrate trihydrate and neutral bismuth (III) citrate, which is confirmed by the data of X-ray phase analysis and chemical analysis. With an increase in the process temperature to 70 °C, the domain of existence of the intermediate compound gets more narrow, and for $n = 0.75$ the precipitates are only mixtures of oxohydroxobismuth (III) nitrate trihydrate and neutral bismuth citrate, the amount of the latter compound being strongly prevalent.

It is known [6] that bismuth citrate having the composition $BiC_6H_5O_7$ can be obtained by precipitation from nitrate bismuth-containing solutions after the addition of citric acid solution to them. Bismuth precipitation occurs almost completely in the acidic medium at pH ~ 0.6 and mixing time 30 min. In this connection, it was reasonable to investigate the effect of pH of the medium on the extent of the exchange reaction progress and product composition in the case when nitric acid was added to the reaction mixture of oxohydroxobismuth (III) nitrate trihydrate with citric acid at the molar ratio of citrate ions to bismuth equal to 1 : 1.

It follows from the analysis of data shown in Fig. 3 that the exchange of nitrate ions for citrate proceeds slowly without the additional introduction of nitric acid into the system (curves *1*, *2*); even at the process temperature increased to 70 °C, the yield of bismuth citrate after 4 h from the start of reaction does not exceed 50 %. The concentration of the acid in the mother solution is 0.1 mol/L. At the process temperature of 25 °C in the case when nitric acid is added to the system at a concentration of 0.25 mol/L (curve *3*), the quantitative formation of bismuth citrate is observed after 4 h; with an increase in the acid content to 0.5 mol/L (curve *4*) the exchange process is complete in 1 h after the start of the reaction. An increase in the process temperature to 0.5 mol/L (curves *5*, *6*) causes a sharp increase in the exchange rate. According to XPA data, the product of the exchange reaction is neutral bismuth (III) citrate with the composition $BiC_6H_5O_7$ even after 15 min from the start of the reaction. So, with an increase in the concentration of nitric acid in the system, the rate of the exchange reaction increases. The residual concentration of bismuth (III) in solution is ~5 g/L.

The authors of [5] studied the solubility of bismuth oxonitrate in the solutions of nitric acid and showed that the equilibrium constant of reaction

$$BiONO_3(s) + 2H^+ = Bi^{3+} + NO_3^- + H_2O$$

is equal to $(1.2\pm0.2)\cdot10^{-2}$. This is an evidence of substantial solubility of bismuth oxonitrate. Indeed, during its treatment with water at a temperature of 23 °C, bismuth content in solution is 1.09 g/L. So, during the treatment of oxohydroxobismuth (III) nitrate trihydrate with aqueous solutions of citric acid, its dissolution proceeds with the formation of bismuth ions in solution; they interact with citrate ions to form bismuth citrate in precipitate. The reaction of the exchange decomposition of oxohydroxobismuth (III) nitrate trihydrate with the formation of bismuth citrate may be represented in the following form:

$$[Bi_6O_5(OH)_3](NO_3)_5\cdot3H_2O + 6H_3C_6H_5O_7$$
$$= 6BiC_6H_5O_7 + 5HNO_3 + 11H_2O$$

Analysis of the IR absorption spectra of bismuth (III) citrate and the intermediate product allows us to drive definite conclusions concerning the possible composition and structure of the latter compound. In Fig. 4, in addition to the IR spectra of the indicated compounds (curves *3*, *4*), for comparison we show the spectra of citric acid monohydrate and its triple-substituted sodium salt (curves *1*, *2*). It follows from the IR spectrum of citric acid (see Fig. 4, curve *1*) that, while its two carboxyl groups

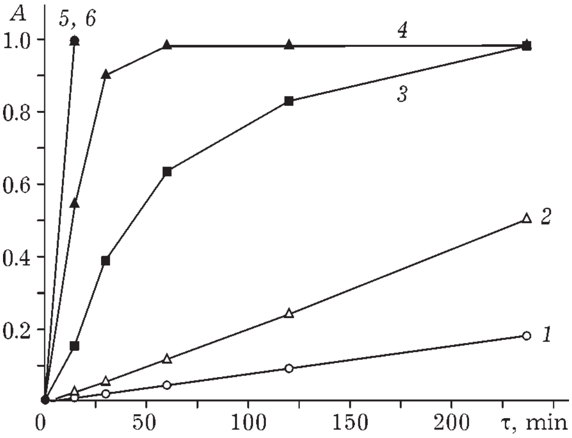

Fig. 3. Dependence of the ratio of the concentrations of citrate ion to bismuth (III) *A* (mol/mol) in the precipitate on time τ. Temperature, °C: 23 (*1*, *3*, *4*), 50 (*5*), 70 (*2*, *6*); HNO_3 concentration, mol/L: 0 (*1*, *2*), 0.25 (*3*), 0.5 (*4*–*6*).

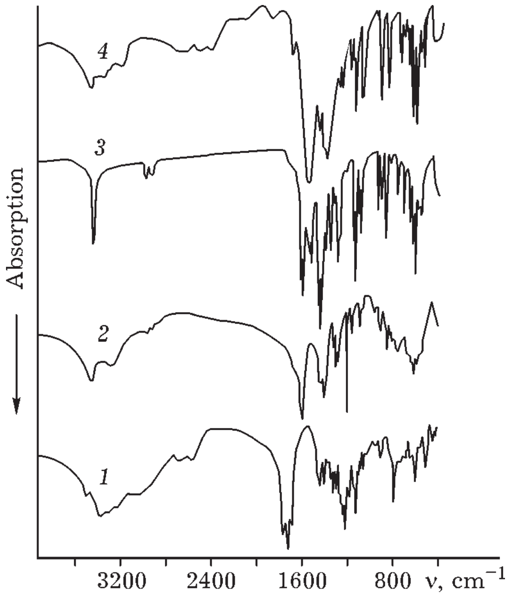

Fig. 4. IR absorption spectra of citric acid monohydrate (*1*), triply substituted sodium citrate (*2*), bismuth (III) citrate (*3*) and the intermediate product (*4*).

are involved in hydrogen bonding, the third carboxyl group and the oxo group are free functional groups. In addition to these frequencies, the spectrum of citric acid $H_3Cit \cdot H_2O$ is characterized by a weak band of the mixed vibration of water (2565 cm^{-1}) and a strong broad band of stretching vibrations of OH group in water in the region 3370–3299 cm^{-1}. Considering the IR spectrum of triple-substituted sodium salt of citric acid (see Fig. 4, curve *2*) it is necessary to stress that the band of stretching vibrations of OH group (3450 cm^{-1}) is conserved in it, but the bands with the characteristic wavenumbers of carboxylic groups disappear. The spectrum is now characterized only by the bands with the wavenumbers of COO^- group with 1.5-fold carbon-oxygen bonds: 1595 cm^{-1} (asymmetrical stretching vibrations), 1400 cm^{-1} (symmetrical stretching vibrations), which is an evidence of the transformation of carboxylic groups into the anion form. A definite amount of associated water is also present, which is confirmed by a broad band of the stretching vibration of OH group in the region 3300–3200 cm^{-1}. So, in the sodium salt of citric acid, substitution of hydrogen by sodium ions proceeds only at the carboxylic groups; oxo group remains intact.

A similar picture is observed also in the IR spectrum of bismuth citrate, which is precipitated, as it follows from the data shown in Fig. 4, curve *3*, in the form of anhydrous neutral salt $Bi(C_6H_5O_7)$. This composition is confirmed by the absence of broad absorption bands below 3000 cm^{-1} that are due to the presence of hydrogen bonds. The IR spectrum of the compound contains a very narrow band with a maximum at 3460 cm^{-1}, which is an evidence of the presence of free OH group in the compound. This group belongs to the citrate residue and (similarly to triply substituted sodium citrate) instead of the characteristic vibrations of carboxylic group we observe the appearance of the bands with the maxima at 1595 and 1430 cm^{-1}, which corresponds to the transformation of carboxylic groups into the anion form.

The spectrum of the intermediate compound (see Fig. 4, curve *4*) is characterized by the absence of the band of stretching vibrations of the free OH group (3460 cm^{-1}) and the appearance of the bands that allow us to suppose the presence of the free carboxyl group in the compound: a broad band with several maxima within the range 3200–2400 cm^{-1}, corresponding to the stretching vibrations of OH groups of carboxylic acids that participate in the formation of hydrogen bonds, and a small absorption band corresponding to the stretching vibrations of C=O bond of the carboxylic group (1720 cm^{-1}). In addition, the spectrum clearly contains a band with the maximum at 520 cm^{-1} that may be assigned to the stretching symmetrical vibrations of Bi–O bond [14]. So, the character of the IR spectrum of the intermediate product allows us to assume that there is some analogy between its structure and the structure of oxohydroxobismuth (III) nitrate trihydrate. Bismuth polycation is very likely to be conserved in the structure of this compound (this is confirmed by the presence of the absorption band at 520 cm^{-1}), and the acid residue should contain free carboxylic groups. This compound may be represented in the general form as $[Bi_xO_y(OH)_z]^{n+}(C_6H_7O_7)_n$. The possibility of the formation of these compounds was reported in [15].

The DTA and TG data for the samples of oxohydroxobismuth (III) nitrate trihydrate in the air (Fig. 5, *a*) provide evidence of the occurrence of a number of consecutive endothermic stages connected with progressive detachment of three water molecules (endo-effects at 125, 180 and 220 °C). Then, after the removal of one water molecule from the internal sphere of the complex (endo-effect at 270 °C) dehydroxylation process starts; the next five endo-effects at 330, 375, 440, 520 and 560 °C are connected with its completion, destruction of five nitrate ions and the formation of α-Bi_2O_3 phase [16]. The endothermic effect at 729 °C is connected with the polymorphous transformation of α-Bi_2O_3 into the high-temperature modification δ-Bi_2O_3, while the endothermic effect at 824 °C corresponds to melting of bismuth oxide [17]. The character of the derivatogram of bismuth citrate (see Fig. 5, *c*) is the evidence of the decomposition of citrate ions (exo-effects at 300 and 390 °C) and subsequent formation of bismuth oxide (endo-effects at 730 and 820 °C). It follows from the data shown in Fig. 5, *a* that bismuth oxide can be synthesized through thermal decomposition of oxohydroxobismuth (III) nitrate trihydrate at

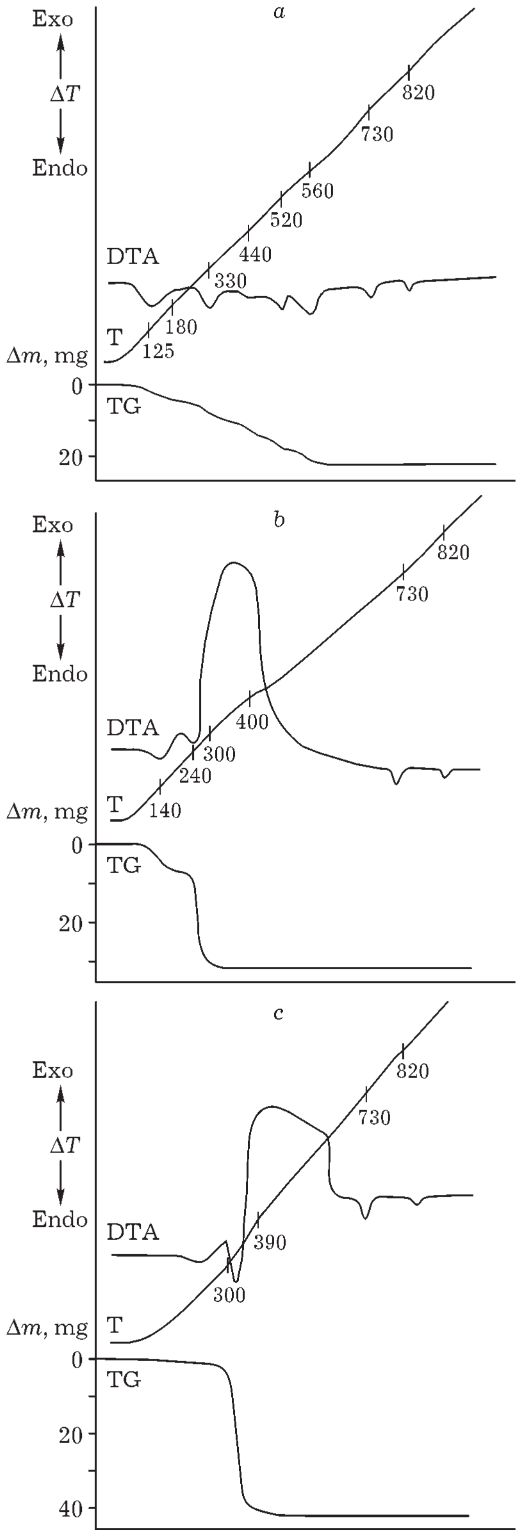

Fig. 5. Curves of thermal analysis of oxohydroxobismuth (III) nitrate trihydrate samples (*a*), its mixture with bismuth (III) citrate (*b*), and bismuth (III) citrate (*c*) in the air. Sample mass: 200 mg.

600 °C. One can see (see Fig. 5, *b*) that the decomposition of its mixture with bismuth (III) citrate occurs at much lower temperatures, and this fact may be used for the synthesis of fine-crystalline powders of bismuth oxide because the process may be performed at low temperature and thus it is possible to avoid agglomeration of the product.

Analysis of electron microscopic images shows (Fig. 6, *a*) that the initial oxohydroxobismuth (III) nitrate trihydrate is composed of elongated plain prismatic crystals with the size in the basal plane 10–30 μm and thickness about 1–3 μm. In the case of its treatment with the solution of citric acid at a temperature of 23 and 50 °C, the exchange decomposition reaction proceeds with the formation of bismuth citrate, which is composed of the concretions of plate-like crystals 10–20 μm in size. The plate-like crystals of bismuth citrate obtained at a temperature of 23 °C have a size of about 0.5 μm and thickness of 0.1 μm (see Fig. 6, *b*), while at a temperature of 50 °C the corresponding values are 1 and 0.2 μm, respectively.

Our investigation and the data obtained previously on obtaining the solutions of bismuth nitrate from metal bismuth [8] and hydrolytic purification of bismuth from accompanying metals during precipitation in the form of oxohydroxobismuth (III) nitrate trihydrate [9] allowed us to propose a scheme of the synthesis of high-purity bismuth citrate from the Vi 1 metal grade, which is usually used as the initial raw material. Metal bismuth (10 kg) having the composition (mass concentrations, %): Bi 98.5, Pb 1.20, Cu $9.5 \cdot 10^{-3}$, Ag $5.6 \cdot 10^{-2}$, Fe $6.2 \cdot 10^{-3}$, Zn $6.4 \cdot 10^{-4}$, Cd $3.0 \cdot 10^{-3}$ was preliminarily transformed into oxide and purified from the accompanying metals by precipitation in the form of oxohydroxobismuth (III) nitrate trihydrate according to [18]. The synthesis of bismuth citrate was carried out through the interaction of oxohydroxobismuth (III) nitrate trihydrate with the solution of citric acid at the molar ratio of citrate ions to bismuth equal to 1.06, concentration of the free nitric acid in solution 0.5 mol/L and process temperature 50 °C. The precipitate was washed three times with distilled water and dried at a temperature of 100 °C. Bismuth (III) citrate obtained in

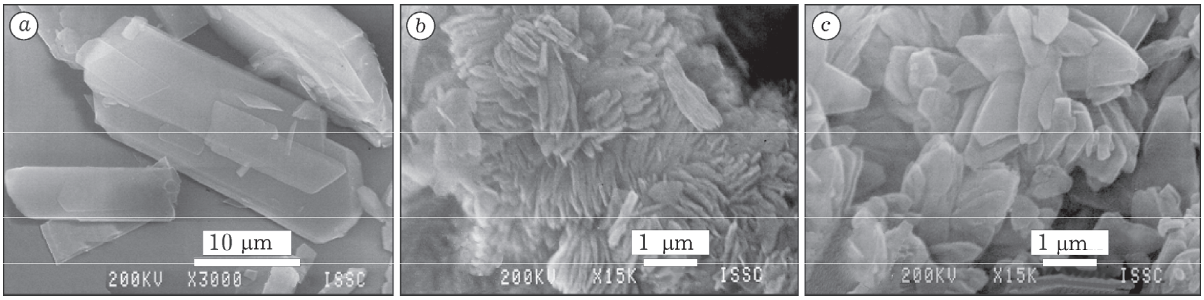

Fig. 6. Microphotographs of oxohydroxobismuth (III) nitrate trihydrate (*a*) and bismuth (III) citrate, taken after the exchange decomposition at the process temperature of 23 (*b*) and 50 °C (*c*).

larger-scale tests had the following composition (mass concentration, %): Bi 52.4, Pb $5 \cdot 10^{-5}$, Cu $2 \cdot 10^{-6}$, Ag $2 \cdot 10^{-5}$, Fe $1 \cdot 10^{-4}$, Zn $3 \cdot 10^{-5}$, Cd $5 \cdot 10^{-6}$. The yield of bismuth into the final product was 95.6 %.

CONCLUSION

Thus, it is reasonable to carry out the synthesis of high-purity bismuth citrate from metal bismuth *via* the following route: 1) carry out the oxidation of metal bismuth with atmospheric oxygen preliminarily, 2) purify bismuth from accompanying metals by its precipitation from nitrate solutions in the form of oxohydroxobismuth (III) nitrate trihydrate, and 3) transform it into bismuth citrate by treating it with the aqueous solution of citric acid within the pH range 0.5–0.7 at the process temperature (60±10) °C.

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