

Synthesis of High-Purity Bismuth (III) Tartratahydrotartrate Trihydrate

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Abstract

Bismuth (III) tartratahydrotartrate trihydrate $[\text{Bi}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_4\text{H}_5\text{O}_6)] \cdot 3\text{H}_2\text{O}$ was synthesized by the interaction of oxohydroxobismuth (III) nitrate trihydrate with the solutions of tartaric acid and investigated by means of X-ray phase analysis, thermogravimetry, electron microscopy, IR spectroscopy and chemical analysis. Expediency of obtaining high-purity bismuth (III) tartratahydrotartrate trihydrate from metal bismuth with preliminary oxidation of the latter by the oxygen of the air, dissolution of the resulting Bi_2O_3 in nitric acid (1 : 1) and purification of bismuth from extrinsic metals by means of its precipitation in the form of oxohydroxobismuth (III) nitrate trihydrate at $\text{pH} \sim 0.9$ by adding ammonium carbonate solution, followed by subsequent treatment of the formed oxohydroxobismuth (III) nitrate trihydrate with tartaric acid solution at a temperature of $(20 \pm 3)^\circ\text{C}$, tartrate ion to bismuth molar ratio of 2.1, and concentration of hydrogen ions 0.2–0.6 mol/l was demonstrated.

INTRODUCTION

Bismuth (III) compounds with tartaric acid and its salts are widely used in medicine to treat various diseases; they are also used to synthesize bismuth-containing oxide materials: superconductors, segnetoelectrics, piezoelectrics, catalysts, etc. [1–3]. These compounds are usually synthesized by bismuth precipitation from nitrate solutions with tartaric acid or its salts with alkaline metals [4]. Among the requirements to these materials, the major one is high purity. Because of this, development of synthesis methods for bismuth tartrate of increased purity is an urgent problem.

Bismuth (III) compounds are usually obtained from the metal of Bi1 grade (not less than 97.7 % Bi) by dissolving its granules in nitric acid (9 mol/l) and subsequent hydrolytic purification of bismuth from extrinsic metals at $\text{pH} 1.5\text{--}2.0$ [5]. Disadvantages of this method

are evolution of toxic nitrogen oxides into the gas phase at the stage of obtaining bismuth nitrate solutions and low degree of bismuth purification from extrinsic metals during the deposition of its compounds from solution. It was demonstrated [6] that preliminary oxidation of metal bismuth as a result of the introduction of bismuth (III) oxide $(20 \pm 5) \%$ into the melt at $(350 \pm 50)^\circ\text{C}$ under mixing allows one to decrease nitric acid consumption by a factor of 2 and to exclude emission of nitrogen oxides into the atmosphere at the stage of obtaining bismuth nitrate solution. This process is used in the production of bismuth compounds.

Synthesis of bismuth (III) compounds is carried out by its deposition from nitrate solutions [3, 5]. However, this method does not always allow obtaining a high-purity compound because major extrinsic metals precipitate together with bismuth. For instance, when pro-

cessing the Bi1 grade metal containing 1.2 % lead, bismuth (III) tartratahydrotartrate trihydrate obtained by precipitation from nitrate solutions contains 0.55 % lead [4]. Because of this, in order to synthesize high-purity bismuth tartrates, it is necessary either to use Bi00 grade metal (≥ 99.98 % Bi) or to carry out preliminary purification of bismuth from extrinsic metals. It was demonstrated [3] that bismuth precipitation from nitrate solutions in the form of a compound with the composition $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ allows one to purify it efficiently from extrinsic metals; this process is used in the synthesis of bismuth (III) oxide of special purity. For obtaining bismuth tartrate of high purity, it is important from the practical viewpoint to investigate the interaction of oxohydroxobismuth (III) nitrate trihydrate with aqueous solutions of tartaric acid. In the present paper we describe the results of investigation of the interaction of oxohydroxobismuth (III) nitrate trihydrate with aqueous solutions of tartaric acid resulting in the formation of bismuth (III) tartratahydrotartrate trihydrate.

EXPERIMENTAL

Oxohydroxobismuth (III) nitrate trihydrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (bismuth content: 72.28 %, nitrate ion content: 17.38 %) was obtained by adding ammonium carbonate solution ($c = 2.5$ mol/l) to the nitric solution of bismuth (380 g/l Bi, 110 g/l HNO_3) till pH ~ 0.9 . The precipitate was filtered, washed with distilled water and dried in the air. Weighed portions of oxohydroxobismuth (III) nitrate trihydrate 10 g ($5.72 \cdot 10^{-3}$ mol) were treated at (20 ± 3) and (60 ± 5) °C with 100 ml of the aqueous solution of tartaric acid with different concentrations for 3 h. Precipitates were filtered with the help of vacuum, washed on the filter with distilled water, and dried in the air. The X-ray phase analysis (XPA) of the resulting products was carried out with DRON-3 diffractometer using $\text{CuK}\alpha$ radiation, counter rotation frequency 2 deg/min, $I = 1000$. The curves of differential thermal analysis (DTA) and mass changes (TG) of the samples were recorded with a derivatograph of MOM com-

pany (Hungary) at the sample heating rate of 10 deg/min. Absorption spectra in the IR region ($400\text{--}4000$ cm^{-1}) were recorded with Specord 75-IR spectrophotometer. The samples were prepared as tablets with calcined KBr. The chromatographic method of thermal desorption of argon was used to measure specific surface of the samples. Macro amounts of bismuth (III) in the liquid and solid phases were determined by titration with a solution of complexone (III) using xylenol-orange as indicator, while micro amounts were determined by means of photolorimetry in the presence of potassium iodide or by atomic absorption. The interaction products were preliminarily dissolved in nitric acid (1 : 1). Permanganatometric titration was used for quantitative determination of tartrate and hydrotartrate ions [7]. The concentration of nitrate ions was measured by means of photometry with sodium salicylate [8] after transferring them into solution with the help of preliminary treatment of the precipitates with 2 mol/l sodium hydroxide solution at a temperature of 70–90 °C.

RESULTS AND DISCUSSION

Oxohydroxobismuth (III) nitrate trihydrate having the composition $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (crystal structure: monoclinic, space group: $P2_1/c$)

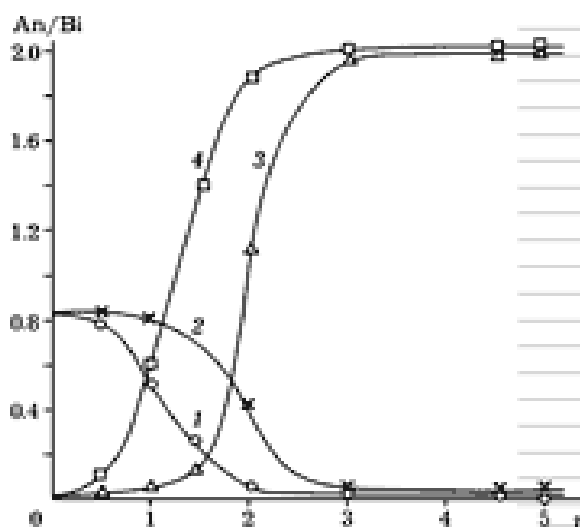


Fig. 1. Dependence of the ratio of nitrate ions (1, 2), tartrate ions (3, 4) and bismuth in the precipitate on n value in the system. T , °C: 23 (1, 4), 60 (2, 3).

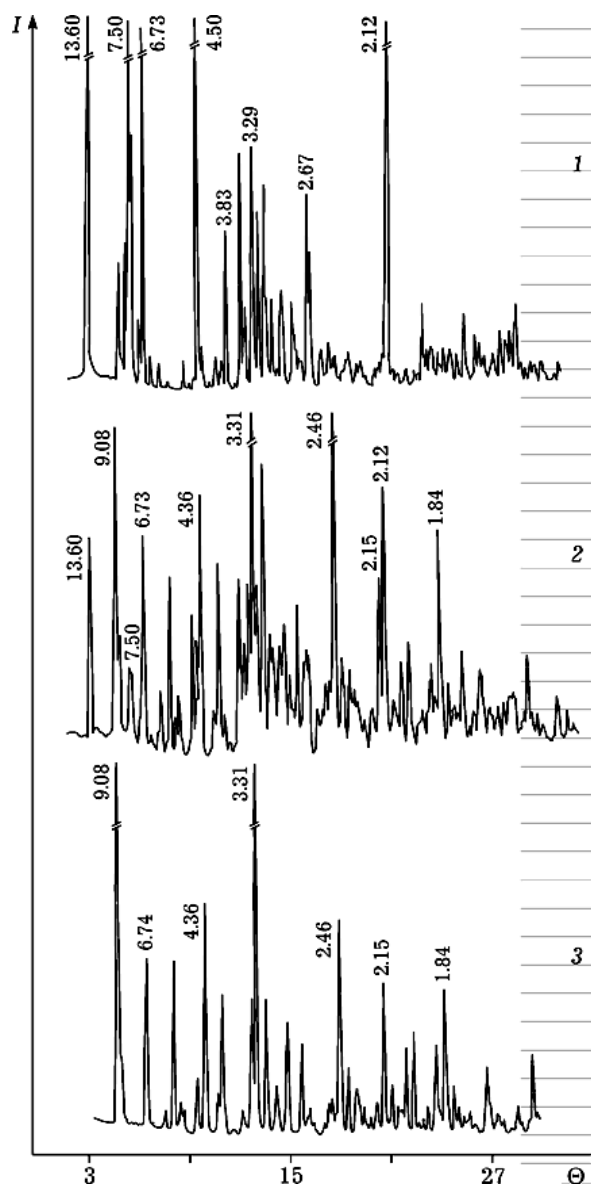


Fig. 2. Diffraction patterns of oxohydroxobismuth (III) nitrate trihydrate (1) and the products obtained as a result of its treatment with the solutions of tartaric acid at $n = 2$ (2) and 5 (3).

is composed of nitrate ions, water molecules and polycations in which two cage-like $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$ groups are connected with each other through the centre of symmetry by two bridging oxygen atoms [9].

Investigation of the interaction of oxohydroxobismuth (III) nitrate trihydrate with aqueous solutions of tartaric acid showed (Fig. 1) that the molar ratio of nitrate ions to bismuth decreases with an increase in the concentration of tartaric acid in the system under investiga-

tion (curves 1, 2), while the ratio of tartrate and hydrotartrate to bismuth decreases (curves 3, 4). For example, for the ratio of tartrate and hydrotartrate to bismuth in solution n equal to 2, the content of NO_3^- ions in the precipitate is 5.62% (60 °C) and 0.10% (20 °C), while the content of tartrate and hydrotartrate ions is 36.4 and 52.2%, respectively. For $n = 5$, the molar ratio of tartrate and hydrotartrate ions to bismuth (III) in the precipitate is equal to 2.0. The detected content (%) of the sum of tartrate and hydrotartrate ions is 53.2, Bi 37.4, nitrate ions 0.01. For $[\text{Bi}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_4\text{H}_5\text{O}_6)] \cdot 3\text{H}_2\text{O}$, the calculated content (%) of the sum of tartrate and hydrotartrate ions is 53.0, Bi 37.3.

According to X-ray data (Fig. 2), with an increase in the concentration of tartaric acid in solution, the intensity of diffraction maxima $d/n = 13.60; 7.50; 6.73; 4.50; 3.83; 3.29; 2.67$ and 2.12 Å (curve 1) which are characteristic of oxohydroxobismuth (III) nitrate trihydrate decreases sharply. Maxima with $d/n = 9.08; 6.74; 4.36; 3.31; 2.46; 2.15$ and 1.84 Å corresponding to the compound of the composition $[\text{Bi}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_4\text{H}_5\text{O}_6)] \cdot \text{H}_2\text{O}$ (crystal structure: orthorhombic, space group: $P2_12_12_1$) appear in the diffraction patterns. Two different tartrate ligands are present in this compound: $[\text{L}(+)\text{-tartrate}]^-$ and $[\text{L}(+)\text{-tartrate}]^{2-}$; the structure of the compound involves a three-dimensional net with bridging and chelate bonds of polydentate hydroxycarboxylate ligands [2]. The precipitate obtained with $n = 1$ (curve 2) is a mixture of these two compounds. For $n = 5$ (curve 3), complete substitution of nitrate ions by tartrate and hydrotartrate ions occurs, resulting in the formation of bismuth (III) tartratahydrotartrate trihydrate.

The data of TGA and TG in air for the samples of oxohydroxobismuth (III) nitrate trihydrate, as well as bismuth (III) tartrates obtained with $n = 1$ and 5 (Fig. 3) provide evidence for the occurrence of a series of sequential endothermic and exothermal stages. The TG curve of oxohydroxobismuth (III) nitrate trihydrate (see Fig. 3, a) is generally similar to that reported in [10] and is the evidence of sequential detachment of three water molecules (endothermic effects at 125, 180 and 220 °C). Then, after one water molecule is re-

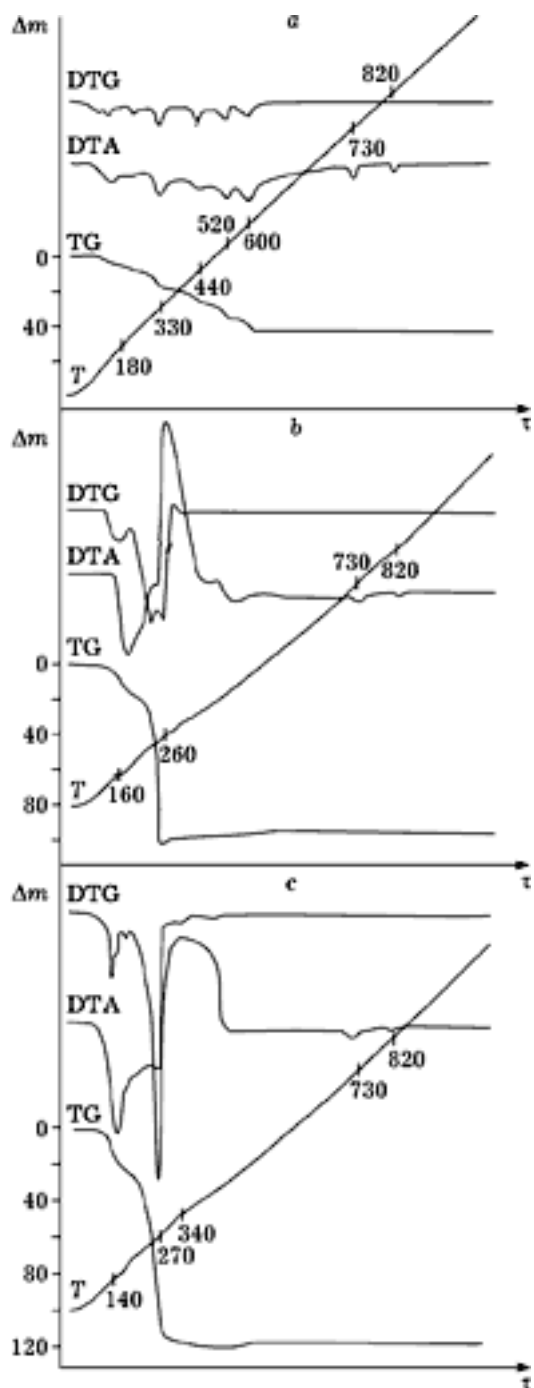


Fig. 3. Thermograms of oxohydroxobismuth (III) nitrate trihydrate (a) and the products obtained as a result of its treatment with the solutions of tartaric acid at $n = 1$ (b) and 5 (c). Weighed portion of sample: 200 mg.

moved from the internal sphere of the complex (endothermic effect at 270 °C), dehydroxylation process starts, and the next five endothermic effects at 330, 375, 440, 520 and 600 °C are connected with its completion and destruction of five nitrate ions. Comparative analysis

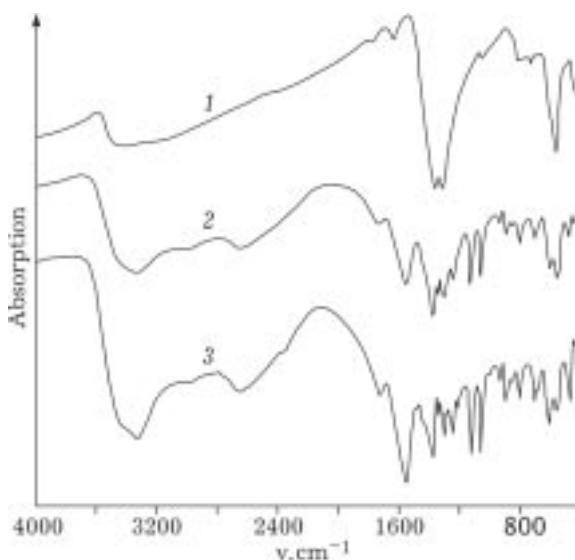


Fig. 4. IR absorption spectra of oxohydroxobismuth (III) nitrate trihydrate (1) and the products obtained as a result of its treatment with the solutions of tartaric acid at $n = 1$ (2) and 5 (3).

of the TG curves of samples obtained with $n = 1$ and 5 (see Fig. 3, b, c) showed that the process starts with water removal (endothermic effects on DTA curves at $T = 140$ and 160 °C), destruction of tartrate ions (endothermic effects at 260 and 270 °C and exothermic effect at 340 °C), and finishes with the formation of bismuth oxide. Endothermic effects at 729 °C which take place similarly to the case of oxohydroxobismuth (III) nitrate trihydrate, are connected with the polymorphous transformation of α - Bi_2O_3 into high-temperature modification δ - Bi_2O_3 , while endothermic effects at 824 °C correspond to bismuth oxide melting [11].

The analysis of the IR absorption spectra (Fig. 4) also allows one to track gradual transformation of the initial oxohydroxobismuth (III) nitrate trihydrate into bismuth (III) tartratahydroxotartrate trihydrate with an increase in the concentration of tartaric acid in solution. The spectrum of $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (see Fig. 4, curve 1) within the range 1400–700 cm^{-1} contains bands characteristic of nitrate ions with the symmetry not higher than C_{2v} [12]. These bands are ν_1 (1040 and 1030 cm^{-1}), which are prohibited in the IR spectrum of the free NO_3^- ion (D_{3h}), ν_2 (810 cm^{-1}), ν_4 (725 cm^{-1}), and a very intensive band with several maxima within the range 1420–1290 cm^{-1} correspond-

ing to the stretching antisymmetric vibration ν_3 of the free nitrate ion. A broad diffuse absorption band below 3600 cm^{-1} should be assigned to the stretching vibrations of crystallization water and OH groups participating in strong hydrogen bonds. A band at 1620 cm^{-1} corresponds to the deformation vibrations of crystallization water molecules. An intensive band with maxima at 600 and 565 cm^{-1} can be assigned to fanning vibrations of water molecules [13]. For the spectrum shown in Fig. 4, curve 2, in addition to a decrease in the intensity of the bands related to the absorption of nitrate ions, the appearance of absorption bands assigned to tartrate ions is characteristic. The IR spectrum of bismuth (III) tartratahydrotartrate nitrate trihydrate (see Fig. 4, curve 3), no bands related to oxohydroxobismuth (III) nitrate trihydrate were detected. In addition to absorption bands of the carboxylate group (1590 and 1390 cm^{-1}), band appear which allow assuming the presence of carboxylic group in the compound under investigation: a broad band in the region $3200\text{--}2400\text{ cm}^{-1}$ corresponding to the stretching vibrations of OH groups of carboxylic acids participating in the formation of hydrogen bonds, and an absorption band corresponding to the stretching vibrations of the C=O bond of carboxylic group (1720 cm^{-1}), which corresponds to the composition $[\text{Bi}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_4\text{H}_5\text{O}_6)] \cdot 3\text{H}_2\text{O}$.

Electron microscopic image provide evidence that the initial oxohydroxobismuth (III) nitrate trihydrate is composed of rather large crystals with indices of block structure, with the size in the basis plane $30\text{--}60\text{ }\mu\text{m}$ and thickness $\sim 10\text{ }\mu\text{m}$ (Fig. 5, a). The blocks are elongated flat-prismatic crystals with the size in the basis plane $3\text{--}20\text{ }\mu\text{m}$ and thickness $\sim 1\text{--}3\text{ }\mu\text{m}$. Treatment of oxohydroxobismuth (III) nitrate trihydrate with the solution of tartaric acid at $n = 3$, $T = 20$ and $60\text{ }^\circ\text{C}$ (see Fig. 5, b, c) causes splitting of the crystals into the blocks and their dispersion. Recrystallization of the product takes place, resulting in the formation of bismuth (III) tartratahydrotartrate trihydrate, which is composed of oriented attachments of elongated prismatic (nearly needle-shaped) crystals; their size depends on the process temperature. In the case when the process is carried out at $20\text{ }^\circ\text{C}$, the size of unit

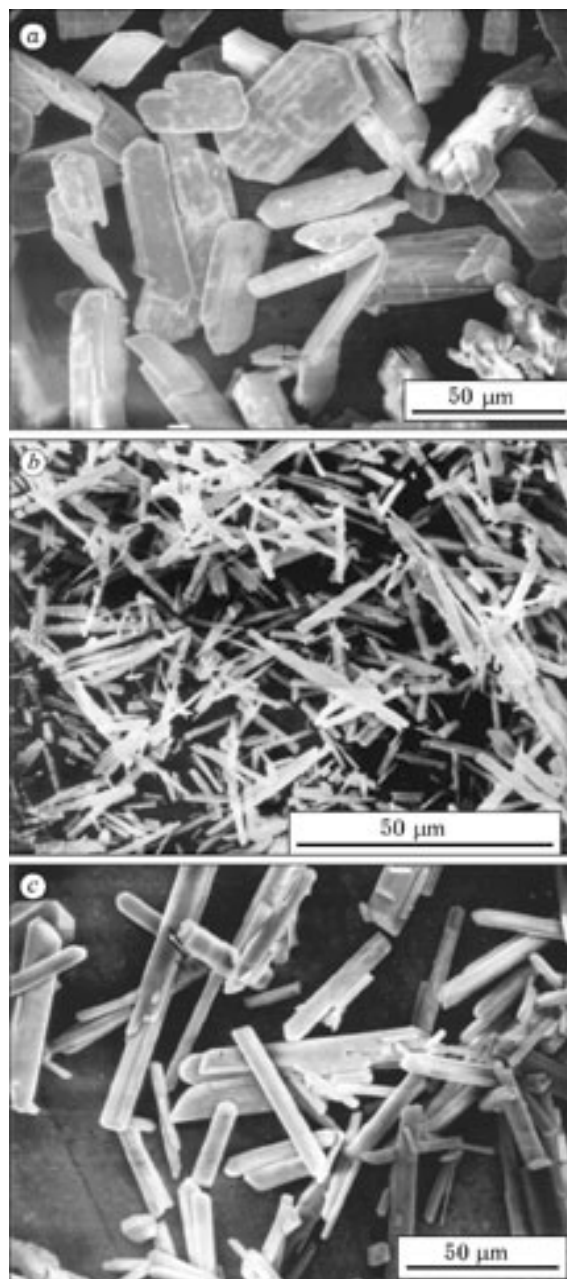


Fig. 5. Microphotographs of oxohydroxobismuth (III) nitrate trihydrate (a) and bismuth (III) tartratahydrotartrate trihydrate (b, c) obtained by treating it with the solutions of tartaric acid. T , $^\circ\text{C}$: 20 (b), 60 (c).

crystal is $10\text{--}20\text{ }\mu\text{m}$, while specific surface of the product is $0.80\text{ m}^2/\text{g}$. The size of crystals of the product obtained at a temperature of $60\text{ }^\circ\text{C}$ is $20\text{--}60\text{ }\mu\text{m}$, and its specific surface is equal to $0.17\text{ m}^2/\text{g}$.

Comparison of the results of interaction of oxohydroxobismuth (III) nitrate trihydrate with tartaric acid at 20 and $60\text{ }^\circ\text{C}$ (see Fig. 1)

showed that at elevated temperature substitution of nitrate ions by tartrate and hydrotartrate ions in the compound proceeds slower. In this connection, the effect of pH of the medium and mixing time on the reaction between oxohydroxobismuth (III) nitrate trihydrate and tartaric acid at $n = 2.1$ and $T = 60$ °C was studied. It was shown that the equilibrium is established in this system after 3 h; further increase in mixing time has no noticeable effect on the composition of reaction products, which are a mixture of oxohydroxobismuth (III) nitrate trihydrate and bismuth (III) tartratahydrotartrate trihydrate. The concentration of hydrogen ions in solution is equal to 0.26 mol/l. An increase in acid content of the solution causes a complete substitution of nitrate ions by tartrate and hydrotartrate ions. For instance, for hydrogen ion concentration in solution equal to 1.5 and 0.75 mol/l, bismuth concentration is 35.5 and 4.0 g/l, respectively; precipitate is bismuth (III) tartratahydrotartrate trihydrate. With further decrease in the hydrogen ion content of solution, the fraction of oxohydroxobismuth (III) nitrate trihydrate in the precipitate increases. At the process temperature of 20 °C and the molar ratio of tartrate and hydrotartrate ions to bismuth equal to 2.1, the equilibrium is established in the system within 1 h; complete substitution of nitrate ions by tartrate and hydrotartrate ions occurs. Hydrogen ion content of the solution is 0.30 g/l, and bismuth 0.42 g/l. A change in the hydrogen ion concentration from 0.2 to 0.6 mol/l causes an increase in bismuth content of solution from 0.18 to 2.9 g/l, that is, the yield of bismuth into the final product decreases. In both cases, the precipitate is bismuth (III) tartratahydrotartrate trihydrate. Thus, it is reasonable to carry out the synthesis of bismuth (III) tartratahydrotartrate trihydrate with the molar ratio of tartrate ions to bismuth equal to 2.1, the concentration of hydrogen ions in solution 0.2–0.6 mol/l and the process temperature (20 ± 3) °C.

On the basis of the above statements, the synthesis of high-purity bismuth (III) tartratahydrotartrate trihydrate was carried out as follows: metal bismuth of the Bi1 grade containing (%) 98.5 bismuth, 1.20 lead, $9.5 \cdot 10^{-3}$ copper, $5.6 \cdot 10^{-2}$ silver, $6.2 \cdot 10^{-3}$ iron, $6.4 \cdot 10^{-4}$

zinc and $3.0 \cdot 10^{-3}$ cadmium was fused at a temperature of 350 °C; under mixing, 20 % of bismuth oxide was added into solution. After that, temperature was increased to 600 °C, and the powder was mixed for 4 h. A part of the resulting bismuth oxide was consumed for the stage of oxidation of the next lot of metal bismuth, while the major part was dissolved in a 6 M HNO₃ solution. Bismuth was precipitated from the solution containing 380 g/l Bi and 110 g/l of free nitric acid by adding ammonium carbonate solution with the concentration 2.5 mol/l under mixing at the process temperature of 60 °C. The mother solution was separated by decanting two times, the precipitate was washed under mixing with distilled water and treated also under mixing with an aqueous solution of tartaric acid at a temperature of 20 °C and molar ratio of tartrate ions to bismuth equal to 2.1, for 2 h. Bismuth concentration in the mother solution was 0.60 g/l, and hydrogen ions 0.36 mol/l. The precipitate was washed and dried at 70 °C. Bismuth (III) tartratahydrotartrate trihydrate obtained in enlarged tests contained (in %): 37.1 bismuth, $2.0 \cdot 10^{-4}$ lead, $2 \cdot 10^{-6}$ copper, $3 \cdot 10^{-6}$ silver, $1 \cdot 10^{-4}$ iron, $1.3 \cdot 10^{-5}$ zinc and $1.4 \cdot 10^{-5}$ cadmium. Specific surface of the product was 0.78 m²/g.

CONCLUSION

Thus, it is reasonable to carry out the synthesis of high-purity bismuth (III) tartratahydrotartrate trihydrate from metal bismuth according to the following procedure: preliminary oxidation of metal bismuth with oxygen of the air, purification of bismuth from extrinsic metals by its precipitation from nitrate solutions in the form of oxohydroxobismuth (III) nitrate trihydrate, and transformation of the latter under the treatment with the aqueous solution of tartaric acid into bismuth (III) tartratahydrotartrate trihydrate.

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