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Solid-Liquid Reactions in the Synthesis of High-Purity Bismuth Compounds

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Abstract

Processing of the nitric solutions from the production of bismuth compounds by adding water was studied by means of X-ray phase and chemical analyses, and electron microscopy. It is shown that bismuth gets precipitated from solutions at the process temperature of 65 ± 5 °C and pH 0.7–1.0 in the form of oxohydroxonitrate $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$, and washing with water causes hydrolysis with the formation of high-purity $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ compound. These compounds are used as precursors for obtaining high-purity bismuth compounds through a solid–liquid reaction. It is demonstrated that the treatment of bismuth oxohydroxonitrate with the solutions of citric, gallic, tartaric, salicylic, nitric acids and ammonium carbonate may result in obtaining bismuth citrate $\text{BiC}_6\text{H}_5\text{O}_7$, bismuth oxogallate trihydrate $\text{C}_6\text{H}_2(\text{OH})_3\text{COOBiO} \cdot 3\text{H}_2\text{O}$, bismuth ditartrate trihydrate $[\text{Bi}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_4\text{H}_5\text{O}_6)] \cdot 3\text{H}_2\text{O}$, bismuth oxide salicylate $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$, bismuth nitrate pentahydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, bismuth oxocarbonate $(\text{BiO})_2\text{CO}_3$, respectively. The powders of metal bismuth with particle size 1–5 and 10–50 μm were obtained by the reduction of oxohydroxonitrates of the compositions $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ and $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$, respectively, in the solution of benzyl alcohol. The reduction of these oxohydroxonitrates in ethylene glycol solution in the presence of hydrazine hydrate in the case of $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ results in the formation of bismuth glycolate, while in the case of $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ – in the formation of metal bismuth with particle size 10–50 μm . The powders of metal bismuth with particle size 1–5 and 10–50 μm were obtained by means of the reduction of the compounds $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ and $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$, respectively, in the aqueous medium with sodium borohydride as the reducing agent, with the molar ratio of bismuth/sodium borohydride is equal 1, pH 12 and a temperature of 25 °C.

Keywords: metal bismuth, oxide, nitric solutions, hydrolytic purification, bismuth oxohydroxonitrate, treatment with acid solutions, bismuth compounds

INTRODUCTION

Bismuth compounds and materials based on them attract much attention in modern materials science because their properties are multifunctional [1–5]. Bismuth materials are used in medicine, catalysis, electronics, solid fuel elements, etc. The major requirements to the compounds obtained for medicine and technology are high purity and reactivity. In this connection, the development of simple and available methods of the

synthesis of high-purity bismuth compounds, either by precipitation from bismuth-containing solutions or according to the reaction of a solid substance with a solution or through thermal decomposition, becomes highly relevant [6].

At present, bismuth compounds are obtained from metal bismuth of Vi1 grade (bismuth content being not less than 98 %), which is a product of pyrometallurgical processing of bismuth-containing ores and concentrates. The main impurity metals in bismuth are lead, silver, copper, zinc,

antimony, arsenic, iron, and tellurium. The possibility of efficient hydrolytic purification of bismuth from impurity metals by means of its precipitation from nitric solutions in the form of oxohydroxonitrate with the composition $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ was demonstrated in [6].

Herein we present the data on processing metal bismuth leading to oxohydroxonitrate with the composition $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ and on its use as a precursor for obtaining bismuth oxohydroxonitrate trihydrate, oxocarbonate, citrate, nitrate pentahydrate and metal bismuth through the interaction of the solid substance with a solution.

Experimental Nitric acid HNO_3 , ammonium hydroxide NH_4OH , ammonium hydrocarbonate NH_4HCO_3 of Kh. Ch. reagent grade (chemically pure), metal bismuth of Vi1 grade, GOST 10928-90 TOO Kaztsink (Ust-Kamenogorsk, Kazakhstan) were used in the work. Bismuth oxidation was carried out in a reactor made of corrosion-proof steel, equipped with a screw to mix the melt. The single charge of bismuth into the oxidation reactor was 150–160 kg. Bismuth was fused at a temperature of 320 °C, and 20 mass % of technical-grade bismuth oxide from the previous oxidation stage was loaded into the reactor under mixing. Then the temperature of the melt was raised to 600 °C, and bismuth oxidation was carried out for 8 h.

Initial bismuth-containing solutions (bismuth 380 g/L, free nitric acid 110 g/L) were prepared by dissolving 685 kg of technical-grade bismuth oxide in nitric acid with the concentration of 7.0 mol/L during mixing in the reactor made of corrosion-proof steel 2.0 m³ in volume. Hydrolytic purification of bismuth from impurity metals was carried out in a special reactor for hydrolysis, made of corrosion-proof steel, 1.6 m³ in volume, under the following conditions: 900 L of distilled water heated to 70 °C was poured into the reactor, then 90 L of bismuth-containing solution was added under mixing, and the pulp was mixed for 60 min. After settling for 2 h, the mother solution was separated from the precipitate by decanting, the precipitate was washed two times with 1.0 m³ of distilled water at a temperature of 60±3 °C and pH 1. The acidity was created by adding HNO_3 solution. The resulting precipitate of bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ was dried on a tray made of corrosion-proof steel at a temperature of 100 °C for 6 h and then directed to the stage of obtaining compounds or high-purity metal bismuth. Mother and washing

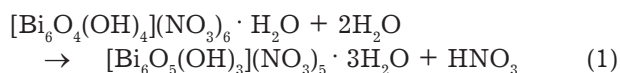
solutions were united in the reactor of additional precipitation 2 m³ in volume, and an additional amount of bismuth was precipitated from these solutions by adding a solution of NH_4OH to pH 1. The precipitate was directed to the stage of obtaining bismuth oxide of reaction-grade purity. Practically complete precipitation of bismuth from solutions (to the residual concentration 0.015–0.030 g/L) was achieved by adding NH_4OH solution to pH 3 in the reactor of bismuth precipitation 2 m³ in volume, and this precipitate was directed to the stage of obtaining the bismuth-containing solution.

X-ray phase analysis (XPA) of the products was carried out with a powder diffractometer D8 Advance (Bruker, Germany) using CuK_α -radiation, with the counter rotation speed equal to 0.5 deg/min. Phases were identified using the powder database PDF2 (2008). The morphological characteristics of the samples were investigated by means of scanning electron microscopy (SEM) using a TM 1000 electron microscope (Hitachi, Japan). To measure the specific surface of the samples, we used the method of the thermal desorption of argon with an internal reference at the liquid nitrogen temperature. Bismuth concentration in solution and its content in the solid reaction products were determined by means of titration of the solution of complexon III using xylenol orange as an indicator. Metal bismuth and its compounds were preliminarily dissolved in HNO_3 with the concentration 7 mol/L. The concentrations of bismuth and impurity metals in the solution were determined by means of atomic absorption with an AA 280FS spectrophotometer (Varian, Australia), and by means of mass spectrometry with inductively coupled plasma. The concentration of free HNO_3 in technological solutions was determined by means of acid-base titration after preliminary masking of bismuth with complexon III.

Results and discussion Investigation of the hydrolytic purification of bismuth-containing nitric solutions by diluting them with water provides evidence of the efficient purification of bismuth from impurity metals. Results of the analysis of the metal of Vi1 grade and oxohydroxonitrate obtained as a result of metal processing $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ are shown in Table 1. The diffraction pattern of this oxohydroxonitrate is shown in Fig. 1, curve 1. According to SEM data (Fig. 2, a), this oxohydroxonitrate is composed of the jams of short prismatic crystals with the larg-

est size in the base plane 1–5 μm and the thickness of 1–3 μm .

As a result of two-fold treatment of this compound with water at the mass ratio of water/precipitate = 5 and temperature 22 $^{\circ}\text{C}$, its hydrolysis proceeds with the formation of bismuth oxohydroxonitrate having the composition $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ according to the reaction



The diffraction pattern of this oxohydroxonitrate is shown in Fig. 1, curve 2. As a result of recrystallization, the product may be additionally purified from lead, the major impurity metal. According to SEM data, the obtained bismuth oxohydroxonitrate is composed of elongated flat prismatic crystals with a size of 10–50 μm in the base plane and about 1–5 μm thick (see Fig. 2, b). The specific surface of this oxohydroxonitrate is 0.45 m^2/g .

Basic bismuth nitrate is widely used in medicine to make anti-ulcer preparations Vikalin and Vikair. The compound used in medicine had been previously considered as having the composition $5\text{Bi}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ [7]. According to USP 40

(USA), European Pharmacopeia 8.0, and the Russian Registry of pharmaceuticals, the composition attributed to this compound is $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$ (CAS 1304-85-4) with an explanation that this is a mixture of BiONO_3 , $\text{Bi}(\text{NO}_3)(\text{OH})_2$, $\text{BiO}(\text{OH})$. Its molecular mass is 1461.99, and the mass fraction of bismuth oxide is not less than 79.0 %. However, X-ray studies provide evidence that the pharmacopeial preparation is an individual compound and appears to be bismuth oxohydroxonitrate having the composition $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ [8, 9]. The molecular mass of the indicated compound is equal to 1748.97, and the mass fraction of bismuth oxide is 79.9 %, which is in agreement with the requirements of the pharmacopeial item USP 40.

Along with bismuth oxohydroxonitrate, bismuth oxocarbonate is also used as a pharmacopeial preparation because it exhibits antibacterial properties with respect to *Helicobacter pylori*, which causes gastropathogenic effect [10]. For the purpose of obtaining bismuth oxocarbonate with high purity and large specific surface, we studied the treatment of bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ with the aqueous solution

TABLE 1

Chemical analysis of metal bismuth, bismuth oxohydroxonitrates and citrate

Impurity	Content, mass %			
	Bi_{met} (LLP Kazzink)	Bismuth oxohydroxonitrate		Bismuth citrate
		$[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$	$[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$	
Be	n/d ($1 \cdot 10^{-6}$)	n/d ($1 \cdot 10^{-6}$)	n/d ($1 \cdot 10^{-6}$)	n/d ($1 \cdot 10^{-6}$)
Na	n/d ($1 \cdot 10^{-2}$)	n/d ($1 \cdot 10^{-2}$)	n/d ($1 \cdot 10^{-2}$)	n/d ($1 \cdot 10^{-2}$)
Mg	$1 \cdot 10^{-4}$	n/d ($5 \cdot 10^{-5}$)	n/d ($5 \cdot 10^{-5}$)	n/d ($5 \cdot 10^{-5}$)
Al	$2 \cdot 10^{-4}$	$4 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$4 \cdot 10^{-5}$
Ti	n/d ($3 \cdot 10^{-5}$)	n/d ($3 \cdot 10^{-5}$)	n/d ($3 \cdot 10^{-5}$)	n/d ($3 \cdot 10^{-5}$)
V	n/d ($1 \cdot 10^{-6}$)	n/d ($1 \cdot 10^{-6}$)	n/d ($1 \cdot 10^{-6}$)	n/d ($1 \cdot 10^{-6}$)
Cr	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)
Mn	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)
Fe	$3 \cdot 10^{-4}$	n/d ($1 \cdot 10^{-4}$)	n/d ($1 \cdot 10^{-4}$)	n/d ($1 \cdot 10^{-4}$)
Ni	$6 \cdot 10^{-3}$	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)
Cu	$3.3 \cdot 10^{-3}$	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)
Zn	$3 \cdot 10^{-3}$	n/d ($4 \cdot 10^{-5}$)	n/d ($4 \cdot 10^{-5}$)	n/d ($4 \cdot 10^{-5}$)
Ga	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)
As	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)
Ag	$1.0 \cdot 10^{-1}$	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)
Cd	n/d ($1 \cdot 10^{-6}$)	n/d ($1 \cdot 10^{-6}$)	n/d ($1 \cdot 10^{-6}$)	n/d ($1 \cdot 10^{-6}$)
Sn	n/d ($5 \cdot 10^{-6}$)	n/d ($5 \cdot 10^{-6}$)	n/d ($5 \cdot 10^{-6}$)	n/d ($5 \cdot 10^{-6}$)
Sb	$1 \cdot 10^{-3}$	n/d ($5 \cdot 10^{-6}$)	n/d ($5 \cdot 10^{-6}$)	n/d ($5 \cdot 10^{-6}$)
Te	$1 \cdot 10^{-4}$	n/d ($5 \cdot 10^{-6}$)	n/d ($5 \cdot 10^{-6}$)	n/d ($5 \cdot 10^{-6}$)
Hg	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)	n/d ($1 \cdot 10^{-5}$)
Pb	$7.1 \cdot 10^{-1}$	$8 \cdot 10^{-5}$	n/d ($1 \cdot 10^{-5}$)	$8 \cdot 10^{-5}$

Note. n/d – not detected.

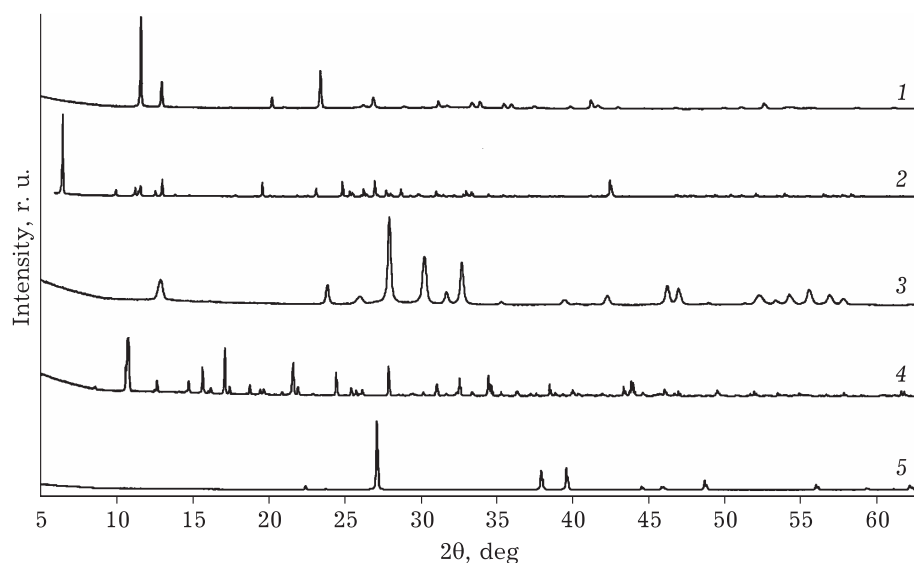
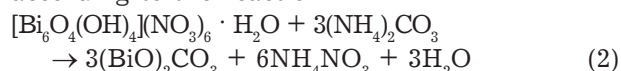


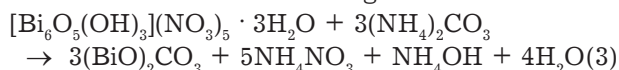
Fig. 1. Diffraction patterns of the samples of bismuth oxohydroxonitrates $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ (1), $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (2), oxocarbonate $(\text{BiO})_2\text{CO}_3$ (3), nitrate pentahydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4) and metal bismuth (5).

of ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$. The formation of bismuth oxocarbonate $(\text{BiO})_2\text{CO}_3$ proceeds according to the reaction



The diffraction pattern of bismuth oxocarbonate is shown in Fig. 1, curve 3. The resulting oxocarbonate is comprised of the aggregates up to 10 μm in size, which are composed of spherical particles about 1–2 μm in size. In turn, these spherical particles are composed of thin plate-like crystals (see Fig. 2, b). Bismuth oxocarbonate was obtained by treating oxohydroxonitrate with the solution of ammonium carbonate at pH 8 and temperature of 22 $^\circ\text{C}$ for 2 h, two-fold washing with distilled water and drying at 70 $^\circ\text{C}$. Bismuth oxocarbonate obtained as a result of enlarged tests contained, mass %: bismuth 81.9, lead $8 \cdot 10^{-5}$, silver $1 \cdot 10^{-5}$, copper $1 \cdot 10^{-5}$, iron $3 \cdot 10^{-5}$, arsenic $<1 \cdot 10^{-5}$, cadmium $<1 \cdot 10^{-5}$, zinc $4 \cdot 10^{-5}$, nitrate ions 0.036, which corresponds to the requirements of USP 40 for pharmacopeial bismuth oxocarbonate. The specific surface of the product is 8.4 m^2/g . Bismuth oxocarbonate obtained under the same conditions from oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ is composed of elongated flat prismatic crystals with a size of 10–50 μm in the base plane and about 1–5 μm thick, built of the particles 1–3 μm in size (see Fig. 2, d). The treatment of oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ with the solution of am-

monium carbonate results in the formation of bismuth oxocarbonate according to the reaction



The reactions of solid bismuth oxohydroxonitrate with a solution of carboxylic acid were used by us previously to obtain bismuth compounds for medicine. Thus, it was proposed to obtain bismuth citrate for use in microbiology to prepare nutrient media and for use in medicine to prepare anti-ulcer preparations by means of the treatment of oxohydroxonitrate with the aqueous solution of citric acid. Bismuth citrate was obtained as a result of the treatment of oxohydroxonitrate $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ with the aqueous solution of citric acid at the liquid to solid mass ratio L/S = 2.3 and at a temperature of 22 ± 2 $^\circ\text{C}$, as well as by the treatment of the compound having the composition $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ with the aqueous solution of citric acid at the L/S = 10.4, pH 0.1–0.3 and process temperature 22 ± 2 $^\circ\text{C}$ [11]. The specific surface of bismuth citrates in the former case is 1.79 m^2/g , and in the second case it is 2.49 m^2/g , and these compounds are comprised by aggregates 10–15 μm in size, composed of flaky particles about 1–3 μm in size (see Fig. 2, e, f, respectively). The data on the concentrations of impurity metals in citrate are listed in Table 1. These concentrations meet the requirements of the pharmacopeial item USP 40.

In [12], the advisability of obtaining high-purity bismuth oxogallate (applied in medicine in

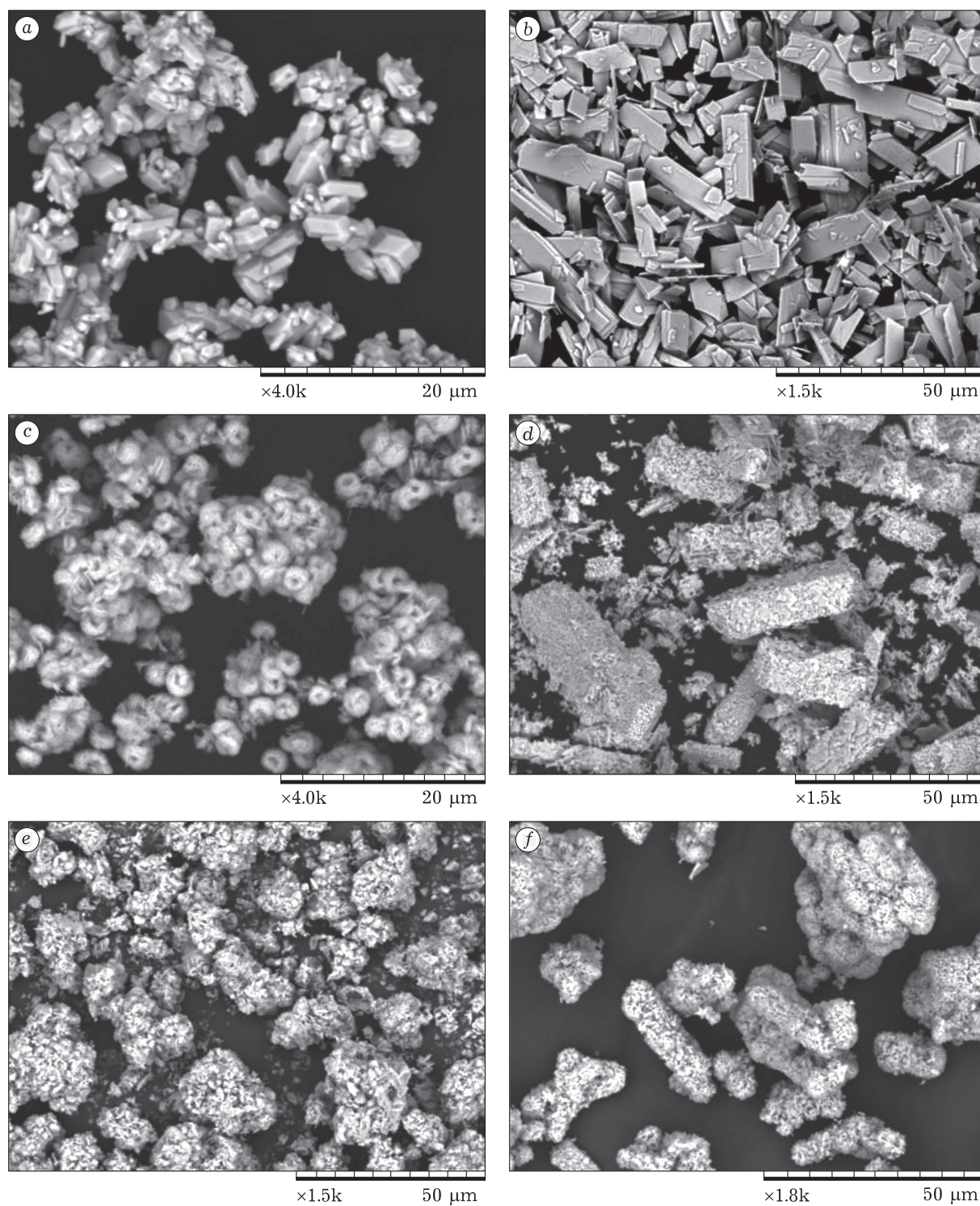


Fig. 2. Electron microphotographs of the samples of oxohydroxobismuth nitrate monohydrate (a), oxohydroxobismuth nitrate trihydrate (b), as well as bismuth oxocarbonates (c, d) and citrates (e, f) obtained from these oxohydroxonitrates, respectively.

the form of Dermatol preparation) through the interaction of the compound with the composition $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ with the aqueous solutions of gallic acid was demonstrated. The synthesis was carried out with the molar ratio of

gallate ions to bismuth equal to 1.0–1.1, HNO_3 concentration in solution equal to 0.5–1.0 mol/L and process temperature 20–70 °C. It was demonstrated [13] that high-purity bismuth ditartrate trihydrate $[\text{Bi}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_4\text{H}_5\text{O}_6)] \cdot 3\text{H}_2\text{O}$ may be ob-

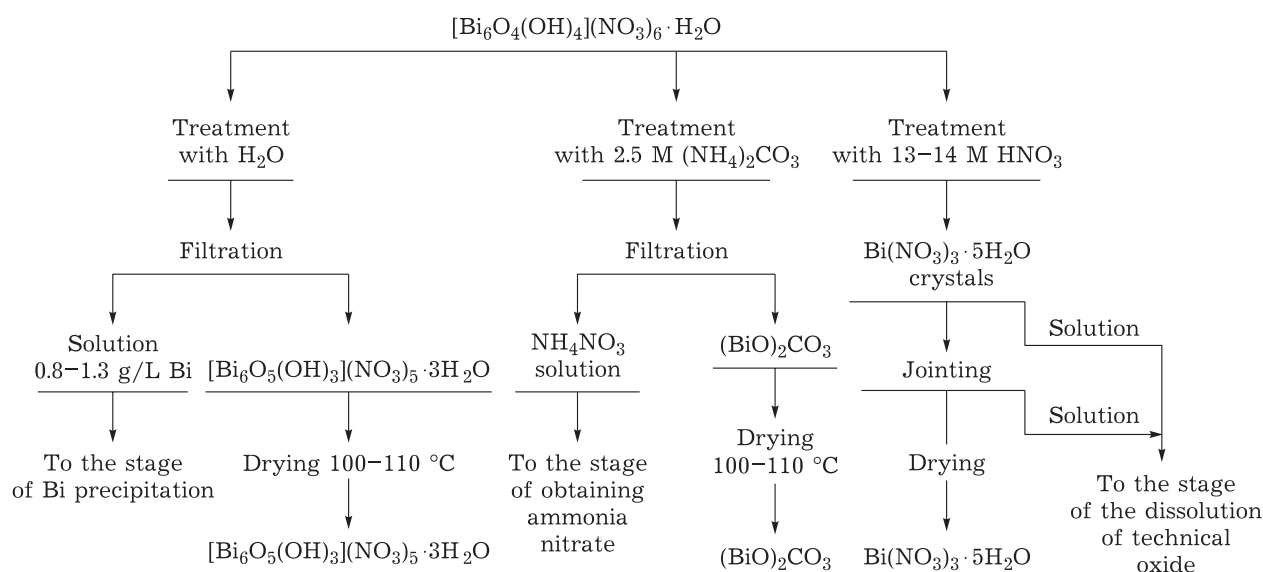


Fig. 3. Technological scheme of obtaining compounds from bismuth oxohydroxonitrate with the composition $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$.

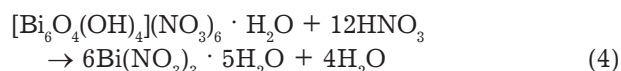
tained as a result of the interaction of bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ with the aqueous solutions of tartaric acid at the molar ratio of tartrate ions to bismuth equal to 2.1, hydrogen ions concentration in solution 0.2–0.6 mol/L and process temperature 20 ± 3 °C.

Bismuth oxide salicylate $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)\text{O}$ is widely used in medicine to make antidiarrheal preparation Desmol (USA). The possibility to synthesize this compound in the highly pure state through the interaction of oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ with the aqueous solution of salicylic acid at the molar ratio of salicylic acid to bismuth equal to 1.0–1.2, pH 0.9–3.0 and process temperature 70 °C was demonstrated.

Bismuth nitrate pentahydrate is widely used in the chemical industry for the synthesis of bismuth-molybdenum and bismuth-antimony catalysts for selective oxidation of hydrocarbons, in technology for manufacturing functional materials, and in medicine for making pharmacopeial preparations. Usually, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ is obtained from metal bismuth as a result of its dissolution in nitric acid with the concentration 7–8 mol/L, subsequent evaporation of the solution to achieve the density 1.9 g/cm³ and cooling [15]. The major disadvantage of this method is the release of toxic nitrogen oxides into the atmosphere at the last stage of solution evaporation.

It is shown that high-purity bismuth nitrate pentahydrate may be obtained avoiding the stage of the

evaporation of bismuth-containing nitric solution by treating oxohydroxonitrate $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ with concentrated solutions of nitric acid. In the interaction with relatively concentrated (4–7 mol/L) solutions of nitric acid, initial oxohydroxonitrate is transformed into the compound with the composition $[\text{Bi}_6(\text{H}_2\text{O})(\text{NO}_3)_4(\text{OH})_4](\text{NO}_3)_5$ [16], and with the further increase in the initial concentration of HNO_3 (9.0 mol/L and more) bismuth nitrate pentahydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ is formed [17]. The diffraction pattern of the compound is shown in Fig. 1 (curve 4). The interaction of bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ with nitric acid leading to the formation of bismuth nitrate pentahydrate may be described by the reaction



The process of obtaining high-purity bismuth nitrate pentahydrate from oxohydroxonitrate was carried out as follows. Nitric acid (100 L) with the concentration 13.9 mol/L was poured into a vessel made of corrosion-proof steel equipped with a mechanical mixer. The treatment was carried out for 1 h. This was accompanied by self-heating of the reaction mixture to a temperature of 40 ± 5 °C, which promoted the complete transformation of initial oxohydroxonitrate into bismuth nitrate pentahydrate. After cooling to 20 °C mother solution was collected with the help of vacuum, and humid crystals

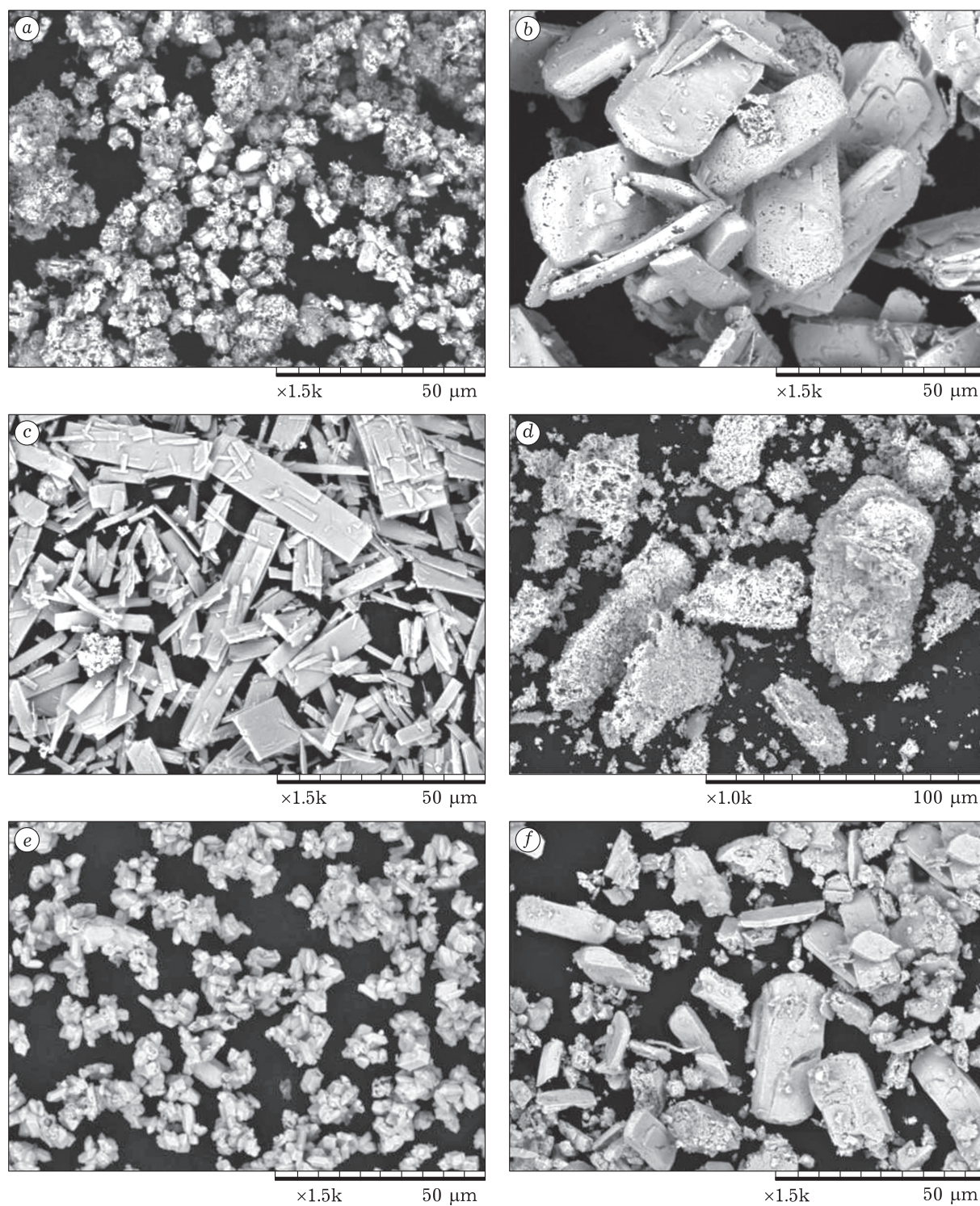


Fig. 4. SEM images of the samples of metallic bismuth obtained by the reduction of oxohydroxonitrates $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ (a, c, e) and $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (b, d, f) in benzyl alcohol (a, b) or ethylene glycol (c, d) with hydrazine hydrate and in water with sodium borohydride (e, f). Temperature, °C: 90 (a, b), 100 (c, d), 25 (e, f).

were transferred into the centrifuge. Crystals squeezed in the centrifuge were dried at a temperature of 55 ± 5 °C. The resulting product with the composition $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ contained, %:

barium $< 1 \cdot 10^{-4}$, vanadium $< 1 \cdot 10^{-6}$, tungsten $< 1 \cdot 10^{-4}$, iron $< 5 \cdot 10^{-5}$, calcium $< 1 \cdot 10^{-4}$, cobalt $< 2 \cdot 10^{-5}$, magnesium $< 5 \cdot 10^{-5}$, manganese $< 5 \cdot 10^{-6}$, copper $< 5 \cdot 10^{-5}$, molybdenum $< 4 \cdot 10^{-5}$, sodium

$<1 \cdot 10^{-4}$, nickel $<4 \cdot 10^{-5}$, lead $<1 \cdot 10^{-4}$, titanium $<3 \cdot 10^{-5}$, chromium $<1 \cdot 10^{-5}$, zinc $<5 \cdot 10^{-5}$. The mother solution with bismuth concentration 162 g/L and free nitric acid 10.8 mol/L was strengthened with concentrated HNO_3 and used in the next treatment of bismuth oxohydroxonitrate. The direct recovery of bismuth into the final product is 85.2 %. The technological scheme of processing bismuth oxohydroxonitrate with the composition $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ to obtain pharmacopeial bismuth oxohydroxonitrate, oxocarbonate and nitrate pentahydrate is shown in Fig. 3.

Intense studies are carried out for the purpose of obtaining bismuth in the form of metal powder. The reduction of bismuth compounds is carried out either in water or in an organic medium using hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) [18, 19] or sodium borohydride (NaBH_4) as a reducing agent [20, 21]. It was demonstrated by us previously that the metal bismuth powders with spherical particles 100–300 μm in size may be obtained as a result of the reduction of bismuth formiate [22] or caprylate [23] in benzyl alcohol for 2 h at a temperature of 200 °C. Modern industry needs also metal bismuth powders with a particle size up to 100 μm . Figure 4, a, b shows the electron microphotographs of metal bismuth powders obtained as a result of the reduction of 5.0 g of bismuth oxohydroxonitrates under investigation in the solution of 90 mL of benzyl alcohol in the presence of 10 mL of hydrazine hydrate (80 %) for 30 min at a temperature of 90 °C. One can see that the appearance of initial compounds is conserved after the reduction of bismuth oxohydroxonitrates to the metal. It should be noted that in the case of the reduction of 5.0 g of bismuth oxohydroxonitrates in ethylene glycol (90 mL) in the presence of 10 mL of hydrazine hydrate for 30 min, metal bismuth is formed if the compound $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ is used (see Fig. 4, d), while the compound $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ is transformed into well crystallized bismuth glycolate (see Fig. 4, c), which is composed of elongated prismatic crystals with the size of 20–50 μm in the basic plane, 0.2–1 μm thick.

The results of investigation provide evidence that the reduction of bismuth oxohydroxonitrates may be carried out in water at usual temperature if sodium borohydride is the reducing agent. For instance, metal bismuth powders were obtained by means of the reduction of 5.0 g of oxohydroxonitrate in 100 mL of water at the molar ratio $\text{Bi}/\text{NaBH}_4 = 1$, pH 12 and temperature 25 °C for

60 min in both cases. The appearance of initial bismuth oxohydroxonitrates is conserved (see Fig. 4, e, f). The diffraction pattern of metal bismuth is shown in Fig. 1 (curve 5).

CONCLUSION

The reasonableness of obtaining high-purity bismuth compounds through the interaction of bismuth oxohydroxonitrates with the solutions of various organic acids or nitric acid is demonstrated. Efficient hydrolytic purification of bismuth-containing nitric solutions should be carried out by means of the aqueous hydrolysis with bismuth precipitation in the form of oxohydroxonitrate $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ followed by its transformation into the compound $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ through treatment with water. It was established that oxohydroxonitrates of this composition may be used as precursors to obtain bismuth citrate, oxogallate, tritartrate trihydrate, oxide-salicylate, nitrate pentahydrate and oxocarbonate as a result of the treatment of bismuth oxohydroxonitrates with the solutions of citric, gallic, tartaric, salicylic, nitric acids or ammonium carbonate, respectively. The possibility to obtain metal bismuth powders with particle size 1–5 or 10–50 μm as a result of the reduction of bismuth oxohydroxonitrates in benzyl alcohol, ethylene glycol or water in the presence of hydrazine hydrate or sodium borohydride was demonstrated.

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