

Highly Pure Bismuth (III) Oxochloride Synthesis

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Abstract

Bi(III) oxochloride (BiOCl) synthesized from oxohydroxobismuth (III) nitrate trihydrate and NH_4Cl , was characterized by means of X-ray diffraction analysis, chemical and thermogravimetric analyses, electron microscopy and IR spectroscopy. In the work the practical usefulness of the ultra pure bismuth (III) oxochloride synthesis from metallic bismuth was shown. This method is comprised of the following stages: metallic bismuth is oxidized by an air, forming Bi_2O_3 . The latter is dissolved in nitric acid solution (1 : 1). Then an insoluble bismuth (III) oxohydroxonitrate trihydrate is formed and precipitate is treated with NH_4Cl and HCl solutions at $(60 \pm 10)^\circ\text{C}$ with chlorine ions : bismuth = 1 : 1 molar ratio. This set of procedures helps to purify the initial bismuth composition from contaminants.

INTRODUCTION

Bismuth (III) oxochloride is used in medicine (radiopaque medium), in cosmetics (nacre-like substance for use in lipsticks, nail varnish and makeup) and in chemical industry (cracking process catalyst). Some reports [1] suggest BiOCl can be used as a component of light-sensitive silver-free photographic layers. Bismuth (III) oxochloride is usually synthesized according to the following: Bi_2O_3 is dissolved in HCl solution, then the solution is diluted (about 10 times) and the precipitate is formed [2, 3]. The purity of the final substance is of great importance. But an analysis of the products yielded from the technically pure bismuth oxide, had shown a presence of major concomitant elements, such as lead and silver. Therefore, there is a need to develop a method of highly pure bismuth oxochloride synthesis.

Bismuth(III) compounds are usually made by metal (Vil brand, containing at least 97.7 % of Bi) dissolution in 9 M HNO_3 , followed by a bismuth hydrolytic purification from

contaminants at pH 1.5–2.0 [5]. The method has some important drawbacks, in particular: toxic nitrogen oxides emission to the atmosphere during the bismuth reaction with nitric acid and low level of bismuth purification during the process. It was shown [6], that preliminary metallic bismuth oxidation results in a twofold decrease of HNO_3 consumption, making it possible to avoid nitrogen oxides emission at the stage of bismuth nitrate solution synthesis. One effective way for a purification of the initial material is a $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ precipitation from bismuth nitrate solutions [7]. Bismuth (III) oxohydroxonitrate trihydrate (BOHN) was used as a reactant for highly pure bismuth (III) oxocarbonate (reaction with $(\text{NH}_4)_2\text{CO}_3$) and nitrate pentahydrate (reaction with HNO_3) formation [8, 9]. Therefore, it is of great practical interest to investigate the highly pure bismuth oxochloride formation from BOHN and solutions of NH_4Cl and HCl. The presented study is concerned with an investigation into the process of bismuth oxochloride formation due to BOHN reaction with NH_4Cl solutions.

EXPERIMENTAL

Bismuth (III) trihydrate oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (72.28 % of bismuth and 17.38 % of nitrate ions) was generated by means of ammonia carbonate ($C = 2.5 \text{ mol/l}$) adding to the bismuth-containing nitric acid solution (concentrations: Bi 380 g/l, HNO_3 110 g/l), till the pH reached value ~ 0.9 . Then the produced precipitate was filtrated, rinsed with distilled water and dried at air. 10 g specimens of BOHN powder were treated at $(20 \pm 3)^\circ\text{C}$ and $(60 \pm 3)^\circ\text{C}$ with NH_4Cl solutions for 3 h. Precipitates were filtered on the vacuum filtering system, then were rinsed on the filter with distilled water and air dried. X-ray diffraction analysis was made using DRON-3 diffractometer with $\text{CuK}\alpha$ radiation, counter rotation speed was 2 deg/min. Differential thermal analysis (DTA) and thermogravimetric (TG) investigations were made using MOM (Hungary) apparatus at the heating speed $10^\circ\text{C}/\text{min}$. Absorbance IR spectra were made in the $400\text{--}4000 \text{ cm}^{-1}$ range on spectrophotometer Specord 75-IR. Specimens were made in form of a tablets with addition of annealed KBr. Electron microscopy investigations were made on the transmission electron microscope JEM-2000FXII at 200 kV accelerating potential. Bismuth macro quantities in specimens were detected using titrimetry technique with complexon III and xylenol orange as an indicator. Microquantities were detected by means of photolorimetry (in a presence of KI) or atomic absorption spectroscopy, using Saturn 2M spectrophotometer. Prior to analysis, reaction products were dissolved in HNO_3 (1 : 1). Ionic concentrations were measured using voltamperometric techniques with renewing copper electrode for nitrate ions, and silver electrode for chloride ions [11]. The latter ionic solutions were produced after precipitate treatment with 2 M sodium hydroxide solutions at $70\text{--}90^\circ\text{C}$.

RESULTS AND DISCUSSION

Bismuth oxohydroxonitrate trihydrate with stoichiometric formula $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (monoclinic spatial lattice, group $P2_1/c$) consists

of nitrate ions, water molecules and polycationic species, in which two cell-like structures $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$ are bound to the symmetry center through oxygen "bridge" atoms [12].

Experiments involving BOHN reaction with aqueous NH_4Cl solutions (Fig. 1), revealed that the more the concentration of chlorine ions in a system, the more the molar ratio of chlorine ions and bismuth (n) in a precipitate (curves 1, 2), and the less is the ratio of nitrate ions (curves 3, 4). At $n = 1.6$ bismuth (III) and chlorine ions molar fraction in precipitate equals to 1.0. Figure 1 shows that increase of process temperature (60°C) makes it possible to form oxochloride from BOHN, and at $n = 1.1$ conversion reaches almost 100 % value.

According to the X-ray diffraction data (Fig. 2), increase of chloride ions concentration in solution at temperature 23°C resulted in a dramatic decrease of diffraction maxima intensity, which are characteristic for $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (curve 1). These are maxima corresponding to $d = 13.60, 7.50, 6.73, 4.50, 3.83, 3.29, 2.67$ and 2.12 E . New maxima appear on diffractograms at $d = 7.35, 3.68, 3.44, 2.75, 2.67, 2.20, 1.94, 1.69$ and 1.57 E , which correspond to BiOCl [13] (tetragonal spatial lattice, group $P4/nmn$). The compound has a structure of a decahedron, so that every

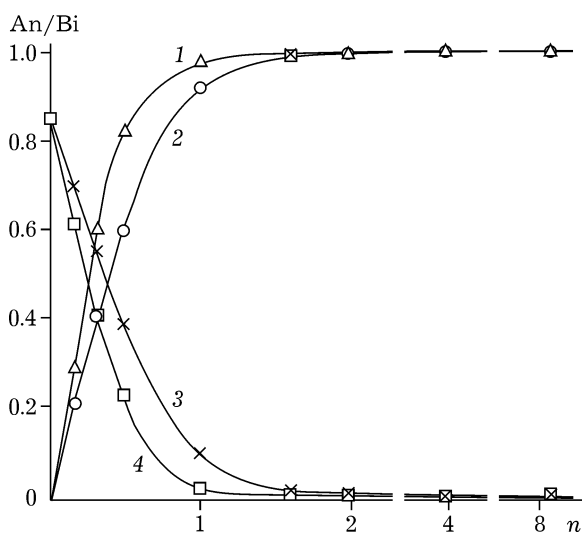


Fig. 1. Dependence of the values of the ratios of chloride ions (1, 2), nitrate ions (3, 4) and bismuth in a precipitate from n , for a system: BOHN- NH_4Cl solution. Temperature, $^\circ\text{C}$: 60 (1, 4), 23 (2, 3).

bismuth atom is coordinated with four oxygen and chlorine atoms, with an atomic spacing equals to 2.316 and 3.059 E [14].

According to the obtained data, the precipitate formed at $n = 0.5$ and temperature 23 °C (see Fig. 2, curve 2) is a mixture of these two substances. At $n = 0.5$ and temperature 60 °C product diffractogram contains maxima corresponding to bismuth oxochloride and additional maxima at $d = 8.62$, 2.85 and 2.57 E (see Fig. 2, curve 3), which were attributed to $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_2(\text{NO}_3)$ [15]. At $n = 1.6$ (see Fig. 2, curves 4, 5) and temperatures 23 and 60 °C complete replacement of nitrate ions takes place, which in turn yields in a bismuth (III) oxochloride formation.

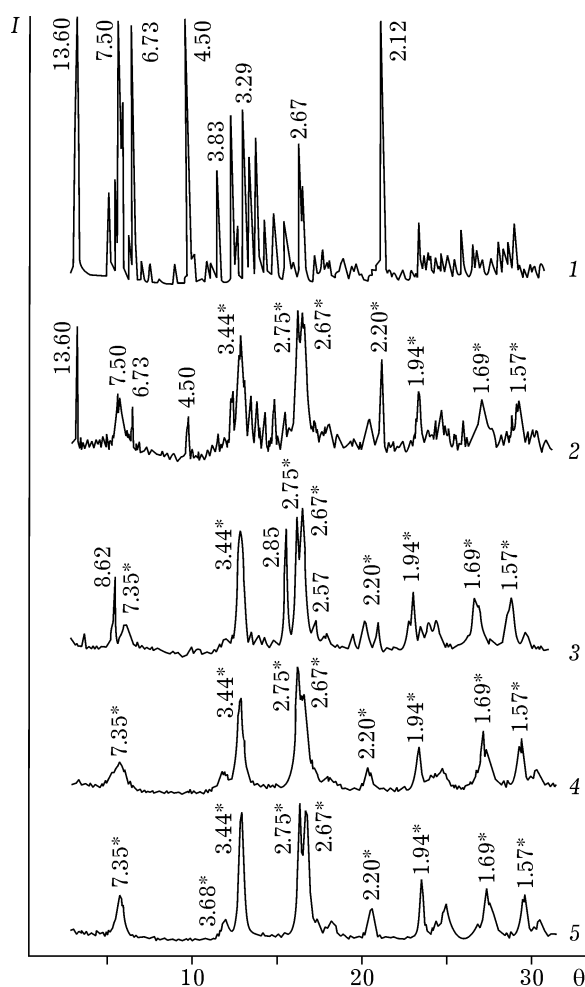


Fig. 2. Diffractograms of bismuth oxohydroxonitrate (1) and products obtained after NH_4Cl solution treatment, at $n = 0.6$ (2, 3) and 1.6 (4, 5). Temperature, °C: 23 (2, 4), 60 (3, 5).

BOHN and bismuth oxochloride at air (formed at temperature 60 °C, $n = 0.6$ and 1.1) thermal (DTA, TGA) behaviour data suggest a series of consequential endothermic stages (Fig. 3). BOHN thermogram (see Fig. 3, a) is very similar to the one presented in the work [16]. Three endothermic effects at 125, 180 and 220 °C were ascribed to three water molecules successive removals. After a water molecule is removed from the inner complex sphere (endothermic effect at 270 °C) dehydroxilation process starts, followed by the next five endothermic effects (temperature 330, 375, 440, 520 and 600 °C) which were ascribed to the dehydroxilation finalization, five nitrate ions destruction and Bi_2O_3 phase formation, respectively. An endothermic effect at 730 °C corresponds to a polymorphic conversion of $\alpha\text{-Bi}_2\text{O}_3$ into a high-temperature $\delta\text{-Bi}_2\text{O}_3$ form, while similar effect at 824 °C was ascribed to the bismuth (III) oxide fusion process [17]. Comparative study of the TG curves for two specimens revealed that bismuth oxochloride, obtained at $n = 1.1$ (see Fig. 3, c), is stable in a wide temperature range. Being heated BiOCl starts to lose its mass only at temperatures as high as 700 °C, which corresponds to decomposition product sublimation in the form of bismuth chloride. As can be derived from Fig. 3, b, this product, yielded at $n = 0.6$, is a mixture of BOHN and oxochloride.

Using IR spectra analysis one can observe the gradual conversion of BOHN to oxochloride as NH_4Cl solution concentration increases. From a $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (Fig. 4, curve 1) spectrum, in 1400–700 cm^{-1} range, one can see characteristic for C_{2v} symmetry nitrate ions absorbance bands [18]: ν_1 (1040 and 1030 cm^{-1}), which are prohibited for a free NO_3^- ion (D_{3h}); ν_2 (810 cm^{-1}); ν_4 (725 cm^{-1}); and very intense band with several minima in a range 1420–1290 cm^{-1} , corresponding to a valent asymmetrical vibration of an unbound nitrate ion ν_3 . One has to ascribe the broad diffuse band at frequencies lower than 3600 cm^{-1} to the valent vibrations of crystallization water and OH^- groups, which form strong hydrogen bonds. Deformation vibrations of crystallization water molecules match with a 1620 cm^{-1} band. An intense band with maxima at 600 and 565 cm^{-1} can be ascribed to the fan-like

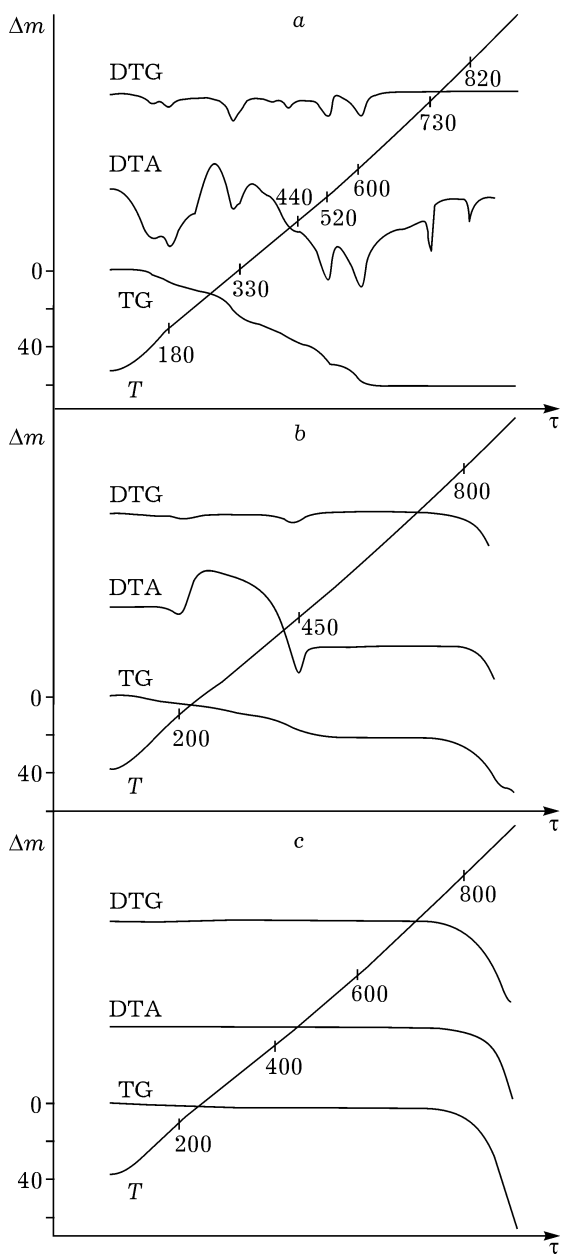


Fig. 3. Thermograms of bismuth oxohydroxonitrate (a) and products obtained after NH_4Cl solution treatment at $n = 0.6$ (b) and 1.1 (c). Temperature: 60°C . Specimen mass: 300 mg.

vibrations of the water molecules [19]. The characteristic feature of the spectra shown in Fig. 4, curves 2 and 3, is a decrease in the intensity of nitrate ions signals. However, at initial stage of the process ($n = 0.25$, see Fig. 4, curve 3) and temperature 60°C , the broadening of the $\nu_3(E)$ in a $1300\text{--}1500\text{ cm}^{-1}$ range (which was also accompanied by a pronounced splitting, $\Delta\nu_3(E) > 100\text{ cm}^{-1}$) occurs. Basing on these facts, one can make a conclusion that nitrate ions are coordinated by a bismuth atom. An increased

intensity of the $\nu_1(A_1)$ band in that compound can be regarded as another corroboration of the nitrate ions coordination in a central atom field. According to [15], this compound, which composition can be described by the formula $[\text{Bi}_6\text{O}_6(\text{OH})_3(\text{NO}_3)_2](\text{NO}_3)$, was made in a triple treatment of BOHN with water at 70°C .

In the IR spectrum of bismuth oxochloride derived from BOHN- NH_4Cl synthesis at $n = 1.1$ (see Fig. 4, curves 4 and 5) was a band corresponding to valent symmetrical, A_{2u} -type vibrations of Bi-O bond (515 cm^{-1}). It is worth mentioning, that IR spectrum of the product made in a BOHN reaction with NH_4Cl solution at 23°C , has some distinctions from the spectrum obtained in similar experiment, but at 60°C . In particular, there was a weak absorbance band located about 1380 cm^{-1} , that can be interpreted as not completed conversion of BOHN into oxochloride.

As can be seen from the electron microscopy pictures (Fig. 5), the initial BOHN consists of relatively big, block-like crystals with basic plane dimensions $30\text{--}60\ \mu\text{m}$ and $\sim 10\ \mu\text{m}$ thickness (see Fig. 5, a). Blocks have the

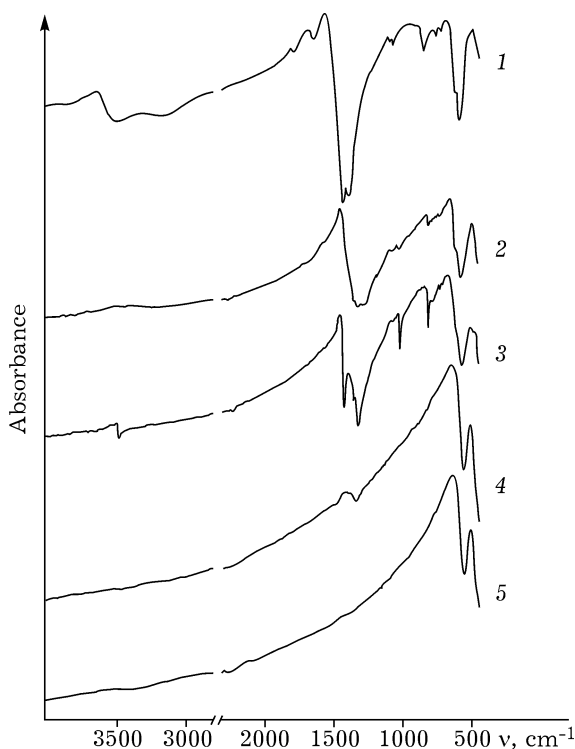


Fig. 4. IR absorbance spectra of bismuth oxohydroxonitrate (1) and products obtained after NH_4Cl solution treatment, at $n = 0.5$ (2, 3) and 1.1 (4, 5). Temperature, $^\circ\text{C}$: 23 (2), 60 (3, 4).

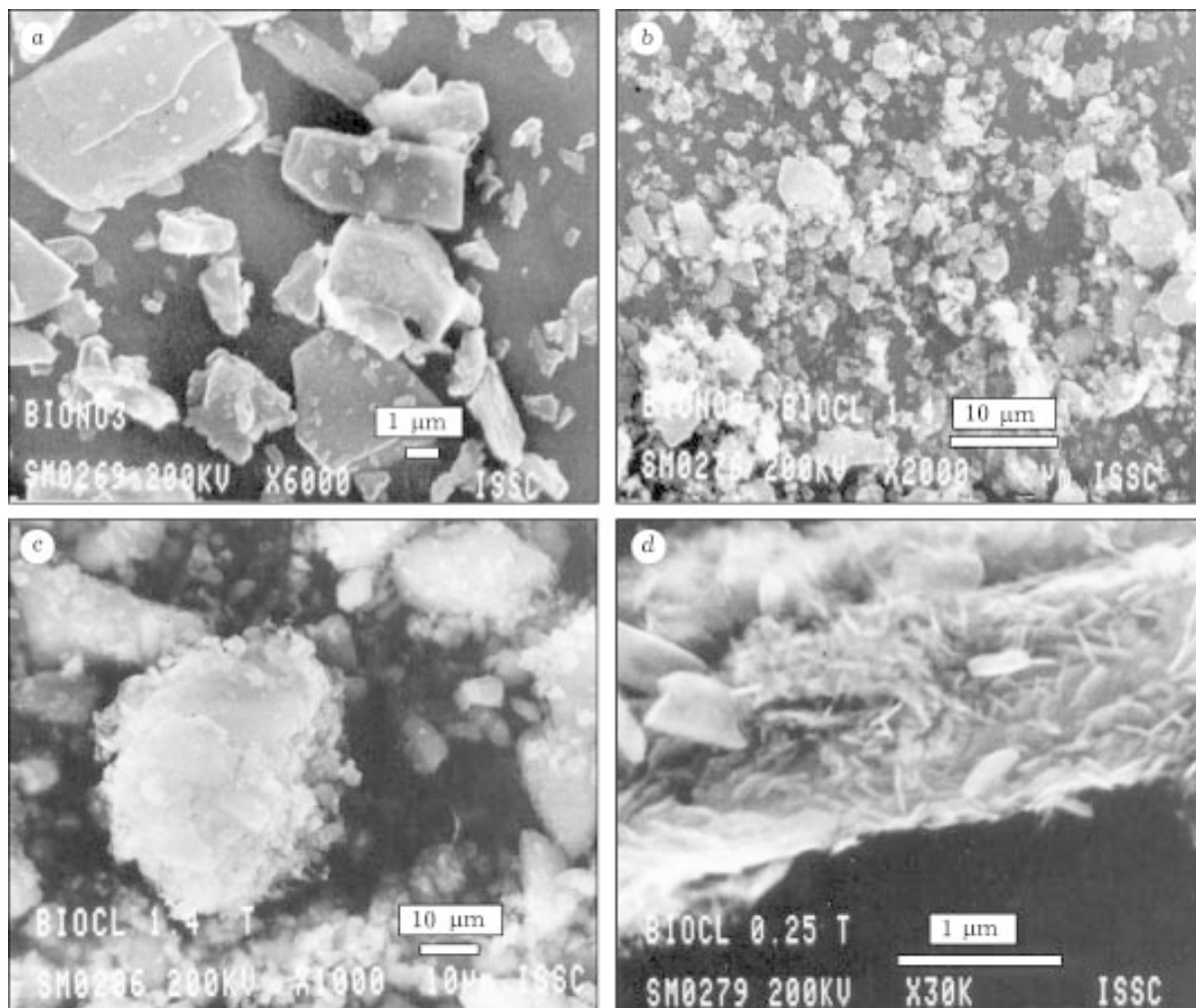


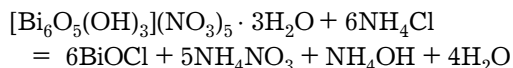
Fig. 5. Microphotographs of bismuth (III) oxohydroxonitrate (a), oxochloride (b, c) and the mixture of them (d) obtained after NH_4Cl solution treatment at $n = 1.4$ (b, c) and 0.25 (d). Temperature, °C: 23 (b), 60 (c, d).

structure of flat prismatic crystals, with basic planes dimensions 3–20 μm , and thickness about 1–3 μm . When BOHN is exposed to NH_4Cl solution, the crystals got split, forming bismuth oxochloride of different structure: minute (with size about a micrometer) lamellar crystal aggregates. Dimensions of these aggregates are dependant on the process temperature: equaling to 1–5 μm at 23 °C and 10–50 μm at 60 °C. It can be inferred from Fig. 5, d, that at the initial stage of BOHN reaction with NH_4Cl ($n = 0.25$) the surface of the former substance is covered with oxochloride lamellar crystals.

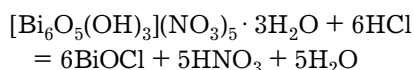
Authors of work [18] studied bismuth oxochloride and oxonitrate solubilities in chloric and nitric acid solutions. It was shown that equilibrium constants of reactions:

$$\text{BiOAn} + 2\text{H}^+ = \text{Bi}^{3+} + \text{An}^- + \text{H}_2\text{O}$$

where $\text{An} = \text{Cl}^-$ and NO_3^- were equal to $1.9 \cdot 10^{-7}$ and $1.2 \cdot 10^{-2}$, respectively. This, in turn, means that bismuth oxonitrate has better solubility bismuth oxochloride. Indeed, when these substances are treated with water, bismuth solution concentration is 1.09 g/l for 23 °C or 0.044 g/l for 60 °C in oxonitrate solutions, while concentration in oxochloride solutions for both temperatures doesn't exceed 0.001 g/l. Hence, BOHN's reaction with chloride-containing solutions can be described in the following way. BOHN, when treated with solutions of NH_4Cl , becomes completely dissolved and dissociated, forming bismuth ions, which combine with chloride ions into an oxochloride precipitate. The exchange process of BOHN decomposition and oxochloride formation can be described by the following formula:



Along with NH_4Cl , in order to form oxochloride BOHN can be treated with HCl solutions. Comparative tests held with these solutions at $n = 1.1$ and temperature 60°C revealed that, degree of bismuth extraction into bismuth oxochloride equals to 99.99 %, when treated with NH_4Cl , and 99.94 %, when treated with HCl. In other words, HCl solutions also can be used for the quantitative BOHN into oxochloride conversion. In that case there would be no need to clean reaction products from ammonia ions. Bismuth concentration in mother waters, depending on the process temperature (23 or 60°C), is either 0.013 or 0.042 g/l, respectively. In that case reaction can be written according to the following:



Basing on the studies of bismuth (III) oxohydroxonitrate trihydrate reaction with NH_4Cl or HCl, previous knowledge of hydrolytic bismuth purification after precipitation from nitric acid solutions, one can propose the following scheme of the highly pure bismuth (III) oxochloride synthesis (using common precursor – Vil brand metal). Metallic bismuth, with composition (%): 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 fused at 350°C . Then to the flux 20 % of bismuth oxide were added (from previous stage of metallic bismuth oxidation). After that temperature was increased to 600°C and powder was stirred during 4 h. Thus obtained bismuth oxide was dissolved in 6 M HNO_3 . Bismuth was precipitated from solution (380 g/l Bi and 110 g/l HNO_3) using 2.5 mol/l $(\text{NH}_4)_2\text{CO}_3$ addition at 60°C and solution agitation. After separation from mother waters by decantation, precipitate was rinsed with distilled water and then treated with HCl at 60°C and $n = 1.1$ for 2 h. The last procedures included solution agitation. Bismuth concentration in mother waters was 0.038 g/l. The precipitate was rinsed with distilled water two times and dried at 100°C . Bismuth oxochloride obtained in an enlarged test conditions had the following composition (%): Bi 37.1, Pb $1.0 \cdot 10^{-4}$, Cu $3 \cdot 10^{-6}$,

Ag $5 \cdot 10^{-6}$, Fe $1 \cdot 10^{-4}$, Zn $1 \cdot 10^{-5}$, Cd $1 \cdot 10^{-5}$, nitrate ions less than $5 \cdot 10^{-3}$.

CONCLUSIONS

Bismuth (III) oxochloride synthesis from metallic bismuth can be done according to the following scheme. First, metallic bismuth is oxidized by an air, then bismuth is purified from metals – contaminants using nitrate solutions precipitation in a form of bismuth (III) oxohydroxonitrate trihydrate. The latter is then treated with an aqueous HCl solution forming bismuth (III) oxochloride.

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