

UDC 542.65:66.093:661.887

Preparation of Bismuth (III) Citrate *via* Precipitation from the Solutions of Mineral Acids

E. S. NAYDENKO, YU. M. YUKHIN and L. I. AFONINA

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

E-mail: vivienne@ngs.ru

(Received June 14, 2011; revised August 2, 2011)

Abstract

Using the methods of XRD phase analysis, Raman and IR spectroscopy, thermogravimetry and chemical analysis the process of bismuth (III) citrate precipitation was investigated concerning the solutions of perchloric acid, nitric acid and hydrochloric acid under adding thereto a solution of citric acid or trisodium citrate. Conditions were determined with respect to the formation of compounds $\text{BiC}_6\text{H}_5\text{O}_7$, $\text{BiOC}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$ and $\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4 \cdot 6\text{H}_2\text{O}$. It was demonstrated that bismuth (III) citrate such as $\text{BiC}_6\text{H}_5\text{O}_7$ used in medicine for the synthesis of pharmaceuticals and in microbiology the production of bacterial preparations are appropriate to obtain *via* the precipitation from nitric acid solutions from manufacturing bismuth compounds with adding citric acid; the molar ratio between citrate ions and bismuth ions in the solution should be equal to 1.1–1.2, the process temperature being of $(60 \pm 5)^\circ\text{C}$.

Key words: bismuth (III) citrate, precipitation, mineral acids

INTRODUCTION

For the last time, pharmaceutical preparations based on bismuth citrate are widely used in medicine for treating the diseases of the gastrointestinal tract [1]. As a pharmacopoeia drug one mainly uses bismuth citrate $\text{BiC}_6\text{H}_5\text{O}_7$, the main component of pharmaceuticals for the treatment of the stomach and duodenum ulcer (De-Nol from Yamanouchi Europe, the Netherlands; Pylorid from GlaxoWellcome Operations, United Kingdom; Tribimol from Torrent, India). Within the acidic environment of the gastrointestinal tract, these preparations use to form a protective film on the surface of ulcers and erosions, which promotes cicatrization and protects against the action of gastric juices. They exert a bactericidal effect on bacteria *Helicobacter pylori*, those in some cases cause the emergence of chronic gastritis and stomach ulcer recurrence. Bismuth (III) citrate is also used for the preparation of nutrient media in

the course of producing a bacterial preparation bismuth sulphite agar that generates a strongly selective medium for the isolation of *Salmonella*.

Citric acid salts alongside with its salts (citrates) is widely used in the pharmaceutical and food industry (E330). Being a tribasic weak organic hydroxy acid, it is capable of forming various complexes with metal ions. The literature describes different designs of bismuth compounds with citric acid. It was demonstrated [2] that bismuth can be precipitated as a compound such as $(\text{BiOH})_3(\text{C}_6\text{H}_5\text{O}_7)_2$ from the solution of lactic and acetic acids solution at a molar ratio between bismuth oxide and citric acid being equal to 1 : 1. Bismuth citrate $\text{BiC}_6\text{H}_5\text{O}_7$ was obtained *via* adding a solution of bismuth nitrate to a solution of ammonium citrate, with further heating the mixture using a steam bath [3], as well as *via* reacting the solid basic bismuth nitrate with a solution of citric acid at the process temperature

(60±10) °C [4]. It was found that bismuth citrate $\text{BiC}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ is produced in the form of a precipitate in the course of adding a solution of citric acid into a bismuth-containing solution prepared *via* dissolving bismuth nitrate in glacial acetic acid as well as *via* the reaction between bismuth oxocarbonate or hydroxide with a solution of citric acid under boiling [5].

The main industrial method for the preparation of bismuth compounds, both with organic and inorganic anions, consists in hydrolytic precipitation. In order to study the compositions of bismuth compounds under precipitation it is appropriate to use perchloric acid solutions wherewith bismuth does not form complexes with perchlorate ions. In the course of diluting such solutions with water, unlike bismuth salts solutions in other of mineral acids (such as sulphuric, nitric, hydrochloric acid), there is no formation observed concerning the precipitates of mixed bismuth hydroxo complexes containing the anions of mineral acids. From a practical standpoint, of interest are nitric acid solutions commonly used in industry for the preparation of bismuth compounds, as well as hydrochloric acid solutions used in the hydrometallurgy of bismuth [6].

This paper presents the results of studying the processes of bismuth (III) citrate precipitation from the solution of perchloric acid, nitric acid and hydrochloric acid, the influence of citrate ion concentration, temperature and pH upon the precipitation level of bismuth (III), as well as upon the composition of the precipitation products.

EXPERIMENTAL

In the experiments we used chemical purity or mineral acids, salts and alkali. The initial solutions of perchloric acid (940 g/L) nitrate (296 g/L) and chloride (230 g/L) were prepared *via* dissolving special purity 13-3 grade bismuth oxide in perchloric acid, nitric acid or hydrochloric acid, respectively, with the concentration of 6 mol/L. Precipitates obtained after adding citric acid or trisodium citrate solution to bismuth-containing solutions, were separated from the mother liquor by filtration, washed with distilled water and dried in air. The bis-

muth content in the solutions and precipitates was determined using a photocolometric technique and in the presence of KI with the help of a KFK-2 spectrophotometer. The product of precipitation was preliminary dissolved in nitric acid (1 : 1). The determination of citric acid and nitric acid anions in the solid reaction products was carried out after preliminary treating the precipitates with 2 M NaOH solution at 70–90 °C.

The concentration of nitrate ions was determined with the use of voltammetric method on a renewable copper electrode [7], the content of citrate ions was determined using a permanganatometric titration technique [8]. The carbon and hydrogen content in the samples synthesized was determined at the Laboratory of Microanalysis of the Multi-access Chemical Service Center of the SB RAS (Novosibirsk) using a modified Pregl method with a gravimetric analysis finishing. The X-ray diffraction phase analysis (XRD) of the reaction products was performed using a DRON-3 diffractometer, CuK_α radiation. The rotation rate of the detector was equal to 0.5 deg/min. The differential thermal analysis (DTA) and thermogravimetric (TG) curves for the samples were registered using a MOM derivatograph (Hungary) in air at a heating rate ranging within 5–10 °C/min. The IR absorption spectra (400–4000 cm^{-1}) were registered using a Specord 75 IR spectrophotometer. The samples were prepared in the form of tablets with calcined KBr. The solution pH values were measured using a OP-264/1 pH meter (Hungary) with a glass electrode or a renewable solid electrode.

RESULTS AND DISCUSSION

Bismuth is present in dilute perchloric acid solutions at the concentrations less than $1 \cdot 10^{-5}$ mol/L in the form of mononuclear $\text{Bi}(\text{OH})_x^{3-x}$, where $x = 0-4$. Increasing the total concentration of bismuth in the solution leads to the formation of polymeric hydroxo complexes. Studying the polynuclear species of bismuth (III) hydroxo complexes [9] demonstrates that at the pH values ranging within 1.0–2.0 commonly used for the hydrolytic processing of bismuth-containing solutions one can observe the formation of hexanuclear complexes such as

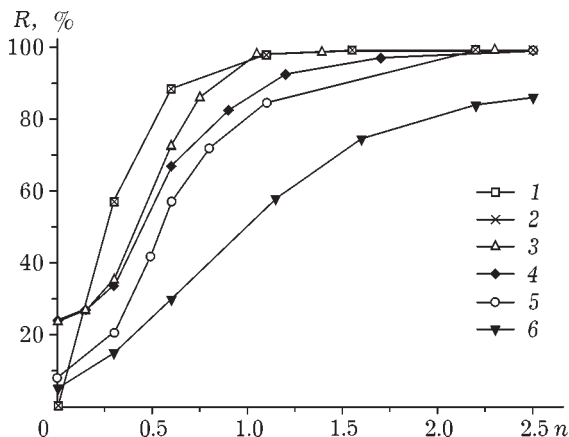


Fig. 1. Level of bismuth precipitation (R) depending on the molar ratio between citrate ions and bismuth (n) in solution: 1, 2 - HClO_4 (H_3Cit); 3, 5 - HNO_3 (Na_3Cit); 4 - HNO_3 (H_3Cit); 6 - HCl (Na_3Cit); temperature ($^\circ\text{C}$): 22 (2, 5) and 60 (1, 3, 4, 6).

$\text{Bi}_6(\text{OH})_{12}^{6+}$. Changing the acidity of the solution up to $\text{pH} > 3.0$ results in the formation of complexes with a high polymerization level such as $\text{Bi}_9(\text{OH})_{22}^{5+}$, $\text{Bi}_9(\text{OH})_{21}^{6+}$, $\text{Bi}_9(\text{OH})_{20}^{7+}$. In the course of more recent studies using X-ray diffraction [10] and NMR investigations [11], it was found that the hexanuclear complex exhibits the composition corresponding $\text{Bi}_6\text{O}_4(\text{OH})_4^{6+}$.

The studies performed concerning the precipitation of bismuth citrate from bismuth-containing perchloric acid solutions (Fig. 1) indicate that the addition of citric acid at the process temperature values equal to 20 and 60 $^\circ\text{C}$ at a molar ratio between citrate ions and bismuth $n = 0.28\text{--}0.7$ results in the complex destruction with bismuth citrate precipitation in the form of X-ray amorphous compound such as $\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4 \cdot 6\text{H}_2\text{O}$ (Fig. 2, curve 1). The precipitation level of bismuth at $n = 0.7$ is equal to approximately 96 %. The precipitate has the following composition (calculated values being presented in parentheses) (%): bismuth 55.70 (56.47), citrate ions 33.57 (34.07), carbon 12.41 (12.98), H 1.70 (1.73); the molar ratio between citrate ions and bismuth in the precipitate $n = (0.67 \pm 0.01)$. The compound with the same value of n was earlier obtained *via* the precipitation of bismuth the from the solutions of acetic and lactic acids, and was assigned with a formula $(\text{BiOH})_3(\text{C}_6\text{H}_5\text{O}_7)_2$ [2], whereas compound $[\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4]_n$ was registered in Russia by

Yamanuchi Europe Company as a drug substance used in the preparation of an antiulcer preparation (De-Nol) [12].

Increasing the concentration of citrate ions in the system results in increasing the level of bismuth precipitation to reach the value equal to 99.8–99.9 % within the range of $n = 1.0\text{--}2.3$. When the process temperature amounts to $(22 \pm 2)^\circ\text{C}$, the bismuth precipitation occurs in the form of compound such as $\text{BiOC}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$ that exhibits diffraction maxima with d/n the values equal to 10.26, 5.63, 4.64, 3.92, 3.37, 2.11 Å (see Fig. 2, curve 2). The precipitate has the following composition (calculated value being presented in parentheses) (%): bismuth 48.38 (48.14), citrate ions 43.82 (44.03), carbon 16.70 (16.60), H 1.88 (2.09); $n = (0.98 \pm 0.03)$. The compounds of similar composition can be precipitated *via* the addition of gallic [13], benzoic acid [14] or salicylic [15] acids to bismuth-containing perchloric acid solutions. In the case of performing the process at a temperature of 60 $^\circ\text{C}$ in the range $n = 1.0\text{--}2.3$ under investigation, one can observe bismuth to precipitate in the form of compound such as $\text{BiC}_6\text{H}_5\text{O}_7$ that

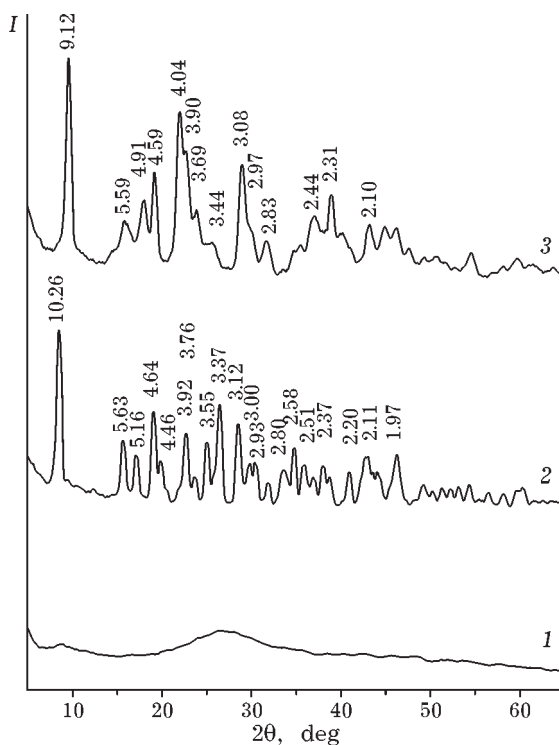


Fig. 2. Diffraction patterns of different bismuth citrate samples: 1 - $\text{BiC}_6\text{H}_5\text{O}_7$, 2 - $\text{BiOC}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$, 3 - $\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4 \cdot 6\text{H}_2\text{O}$.

exhibits diffraction maxima with d/n values equal to 9.12, 4.59, 4.04, 3.08, 2.10 Å (see Fig. 2, curve 3). The precipitate has the following composition (calculated value being presented in parentheses) (%): bismuth 51.62 (52.50), citrate ions 46.24 (47.50), carbon 17.88 (18.10), H 1.20 (1.27); $n = (0.99 \pm 0.02)$. It should be noted that the compound of this composition could also be obtained in the course of carrying out the process at a room temperature with further heating the pulp up to 60 °C.

According to XRD, the precipitation of bismuth from nitric acid solutions without citrate ions at the process temperature equal to 22 °C results in the formation of basic nitrate such as $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$, whereas at 60 °C compound $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ is observed to be formed [16, 17]. At the temperature values of 22 and 60 °C and the molar ratio between citrate ions and bismuth in the system $n < 0.7$, bismuth is precipitated in the form of a compound such as $\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4 \cdot 6\text{H}_2\text{O}$. When the process temperature is equal to 22 °C at $n = 1.0\text{--}2.5$ the precipitate represents of bismuth oxocitrate monohydrate $\text{BiOC}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$, whereas at the temperature of 60 °C bismuth citrate is formed.

From the data presented in Fig. 1 one could see that in the course of the precipitation from nitric acid solutions one can observe the precipitation level of bismuth to increase with increasing the temperature (see Fig. 1, curves 3 and 5). The latter is caused by the fact that the complex formation between bismuth and nitrate ions occurs mainly according to exothermic reactions [18]. As a consequence, in the course of increasing the temperature there occurs decreasing the level of bismuth complexation with nitrate ions and thus there is observed increasing the bismuth recovery into the precipitate in the form of citrate. Furthermore, in the case of bismuth precipitation from nitric acid solutions when sodium citrate is used as a donor of citrate ions instead of citric acid (see Fig. 1, curves 3 and 4) the level of bismuth precipitation demonstrates an increase, which could be caused by decreasing the concentration of hydrogen ions in the solution. It should be noted that in the case of using sodium citrate at $n \geq 1.1$ the precipitation of bismuth citrate begins to occur in the form of

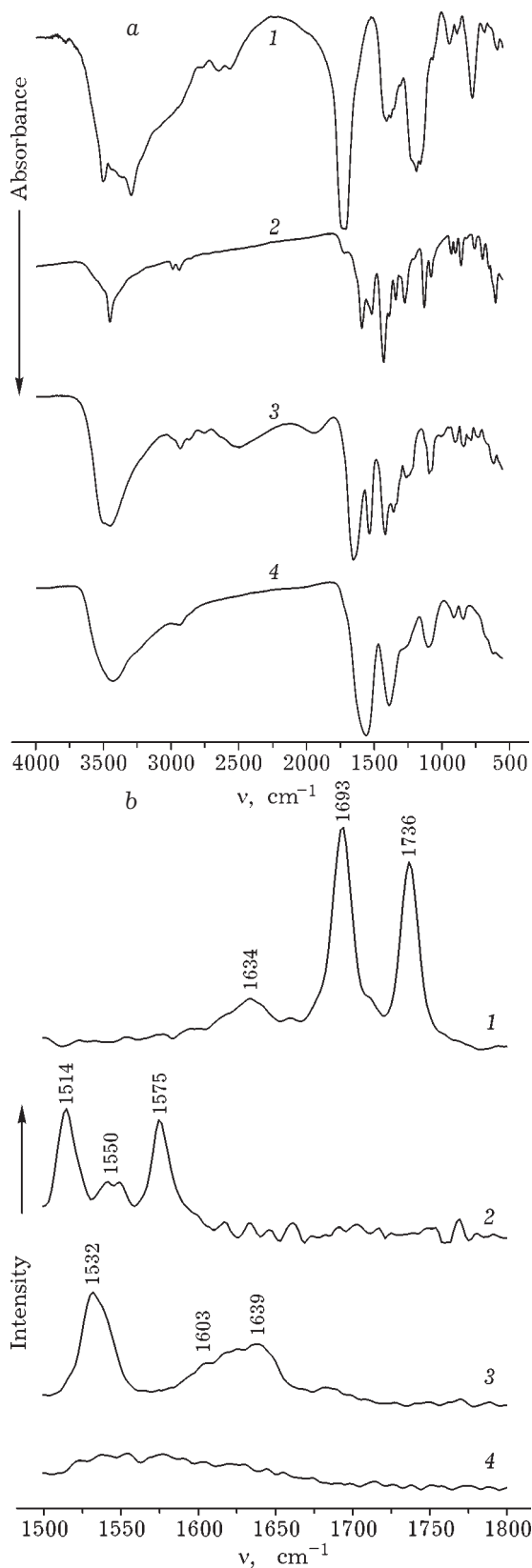


Fig. 3. IR absorption (a) and Raman (b) spectra for citric acid and for products of bismuth precipitation: 1 - $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, 2 - $\text{BiC}_6\text{H}_5\text{O}_7$, 3 - $\text{BiOC}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$, 4 - $\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4 \cdot 6\text{H}_2\text{O}$.

sodium salt, both at a room temperature and at elevated temperature values.

As far as the solutions of hydrochloric acid are concerned, as it is indicated by XRD data, in the case when $n = 0.3\text{--}1.2$ and trisodium citrate is used, the bismuth can be precipitated therein only in the form of oxochloride BiOCl . Increasing the n value up to to 2.3 produced results in the formation bismuth citrate sodium salt.

Thus, in the course of bismuth precipitation from perchloric acid and nitric acid solutions depending on the ratio between citrate ions and bismuth in the system and the process temperature there occurs the formation of three compounds: $\text{BiC}_6\text{H}_5\text{O}_7$ (**I**), $\text{BiOC}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$ (**II**) и $\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4 \cdot 6\text{H}_2\text{O}$ (**III**). We draw the conclusions concerning the composition of the compounds obtained both basing on chemical analysis data, XRD studies, and basing on the results of IR and Raman spectroscopy as well as thermogravimetric analysis.

The features of the structure of bismuth citrates were judged by data resulting from the analysis of IR absorption spectra and Raman spectra (Fig. 3). The assignment of characteristic bands in the spectra was performed *via* comparing with the spectra of citric acid and citrates of other metals [19, 20]. The spectra of bismuth citrate exhibit appearing the bands $\nu_{\text{as}}(\text{COO}^-)$ inherent in the asymmetric stretching vibrations of carboxylate groups at 1592 and 1516 cm^{-1} (IR) (**I**), 1579 and 1516 cm^{-1} (RAMAN) (**I**); 1675 , 1642 and 1533 cm^{-1} (IR) (**II**), 1680 , 1638 and 1532 cm^{-1} (RAMAN) (**II**); 1558 (IR) (**III**) and 1559 cm^{-1} (RAMAN) (**III**), as well as symmetrical vibrations $\nu_{\text{s}}(\text{COO}^-)$ inherent in carboxylate groups at 1424 cm^{-1} (IR, Raman) (**I**, **II**), 1391 cm^{-1} (IR) (**III**) and 1402 cm^{-1} (RAMAN) (**III**). In addition, the carbonyl stretching bands $\nu(\text{C}=\text{O})$ at 1739 cm^{-1} (IR, Raman) present in the spectra of the initial citric acid [21] are observed to disappear, which corresponds to transforming the carboxyl groups into the anionic form. The difference between the symmetric and asymmetric stretching vibrations $\Delta(\nu_{\text{as}} - \nu_{\text{s}})\text{COO}^-$ in the spectra of compounds **I** and **III**, does not exceed 170 cm^{-1} , which indicates that there occurs a predominantly bidentate coordination of the citrate anion, whereas the spectrum of compound **II** exhibits the

maximum value of the mentioned difference equal to 250 cm^{-1} .

This indicates that some of the carboxyl groups of citric acid are either free or coordinated with respect to Bi^{3+} in a monodentate manner. The spectrum of compound **I** exhibits valence vibrations $\nu(\text{OH})$ of free hydroxyl

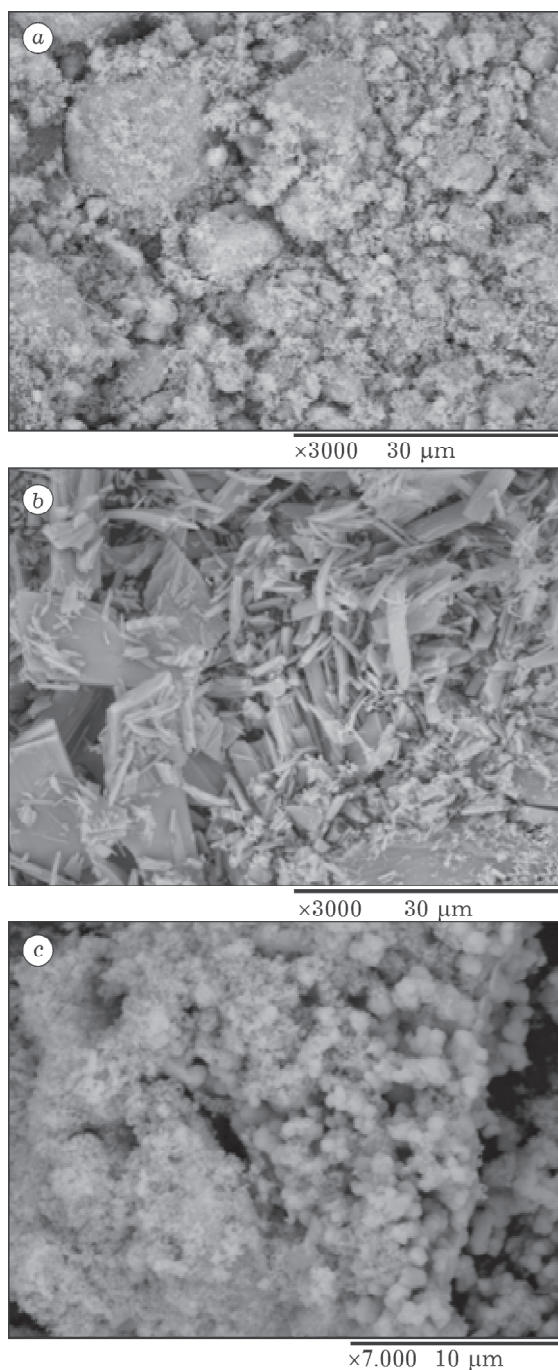


Fig. 4. Micrographs obtained for the samples of bismuth hydroxycitrate hexahydrate (a), oxocitrate monohydrate (b), and citrate (c).

groups inherent in citric acid as a strong narrow band at 3452 cm^{-1} in the IR mode and a very weak band (3455 cm^{-1}) in the Raman mode. There are no vibrations observed corresponding to water molecules. In citrates **II** and **III** within the range below 3500 cm^{-1} exhibit broad absorption bands those are masking $\nu(\text{OH})$ (free hydroxy group) and belong to the stretching vibrations of bound water molecules. Furthermore, a wide absorption band at $2700\text{--}2200\text{ cm}^{-1}$ in the IR spectrum of compound **II** can be caused, to all appearance, by the presence of intermolecular hydrogen bonds [11].

Figure 3, b demonstrates the Raman spectra of citric acid for compounds **I**, **II** and **III** within the wave number range of $1500\text{--}1800\text{ cm}^{-1}$. The spectrum of citric acid distinctly exhibits narrow absorption bands at 1736 and 1693 cm^{-1} , as well as a less intense band at 1634 cm^{-1} . The first two bands correspond to the stretching vibrations $\nu(\text{C}=\text{O})$ of the central and lateral carboxyl groups, respectively. These bands are used to determine the coordination between the citric acid carboxyl groups $-\text{COOH}$ and the metal atom. Curve 2 demonstrates shifting the signal from 1736 to 1575 cm^{-1} , which indicates binding between the $-\text{COOH}$ central group and the bismuth ion. As well, shifting the absorption band from 1693 to 1550 cm^{-1} and its broadening are observed, which, to all appearance, might be explained by coordination between the two lateral carboxyl groups with ion Bi^{3+} ion. Shifting the band from 1634 to 1514 cm^{-1} and increasing its intensity could be connected with increasing the electron density at the complex cation in the system that corresponds to the bismuth atom with a high electron density [22]. Shifting the bands from 1736 to 1639 cm^{-1} ($\Delta\nu_{\text{as}} = 97\text{ cm}^{-1}$) and from 1693 to 1603 cm^{-1} ($\Delta\nu_{\text{s}} = 90\text{ cm}^{-1}$) with a decrease in the intensity values (see Fig. 3, b, curve 3) is, to all appearance, indicative of different coordination between citric acid carboxyl groups and the bismuth atom. As well, shifting the absorption band is observed from 1639 to 1532 cm^{-1} , in a similar manner as the Raman spectrum of compound **I**. In the case of compound **III** (see Fig. 3, b, curve 4) all of the absorption bands are shifted and to a considerable extent broadened, which could be connected with a complex polynuclear structure of the compound.

The electron microscopic studies (Fig. 4) indicate that the normal bismuth citrate represents aggregates up to $10\text{ }\mu\text{m}$ in size composed of fine crystals about $0.1\text{ }\mu\text{m}$ in size. The samples of bismuth oxocitrate monohydrate represent elongated prismatic crystals up to $15\text{ }\mu\text{m}$ in size, being from 0.5 to $3\text{ }\mu\text{m}$ in cross section. Bismuth hydroxocitrate hexahydrate is com-

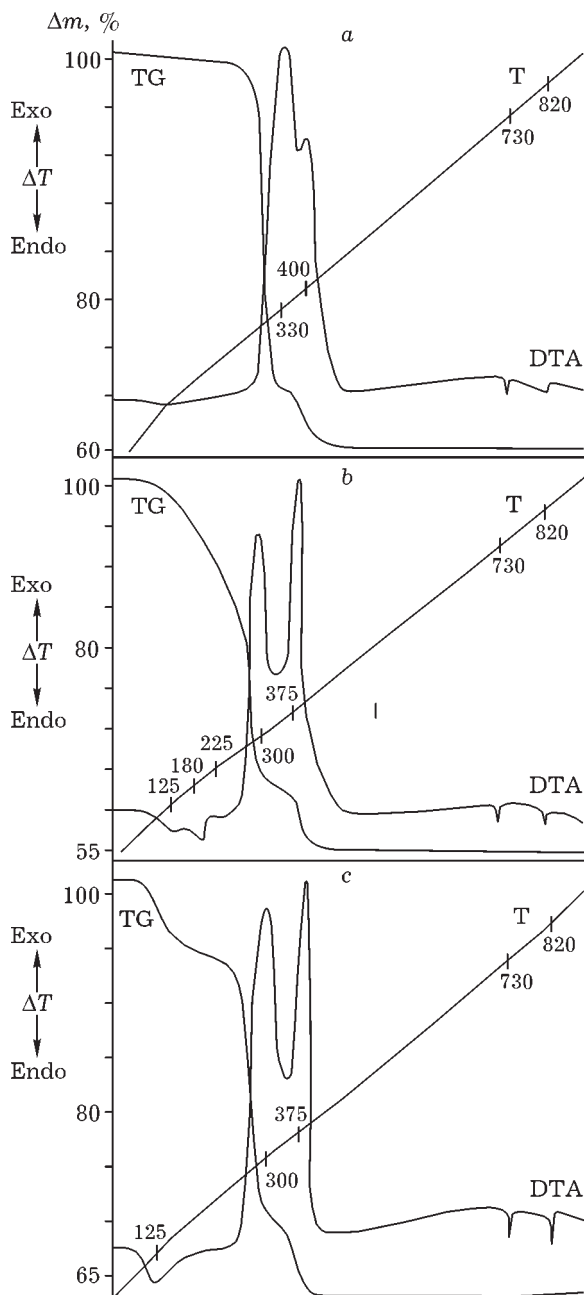


Fig. 5. Thermogravimetric profiles for the samples of $\text{BiC}_6\text{H}_5\text{O}_7$ (a), $\text{BiOC}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$ (b), $\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4 \cdot 6\text{H}_2\text{O}$ (c) in air. Sample weighed portion being equal to 200 mg .

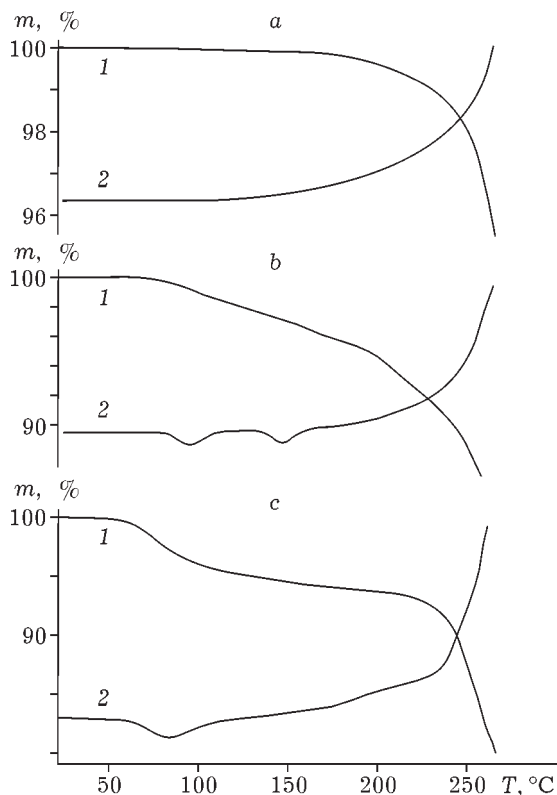


Fig. 6. Heating for compounds **I** (a), **II** (b), **III** (c): 1 – TGA; 2 – DSC at a heating rate of 2.5 °C/min. Sample weighed portion being equal to 1.5 g.

posed of aggregates with the size up to 5 μm consisting of small amorphous particles of 0.1–0.5 μm and individual particles of the mentioned size.

The data obtained from DTA and thermogravimetric (TGA, DTG) analysis (Figs. 5, a and 6, a) indicate that the normal bismuth citrate $\text{BiC}_6\text{H}_5\text{O}_7$ is stable till the temperature amounting to 200 °C, where after the citrate ion begins to decompose (exothermic effects at 330 and 400 °C, accompanied by mass loss) with the further formation of bismuth oxide (III). The endothermic effects at 730 and 820 °C correspond to the polymorphic transformation of monoclinic modification $\alpha\text{-Bi}_2\text{O}_3$ into face-centred cubic high temperature modification $\beta\text{-Bi}_2\text{O}_3$ that is stable up to the melting point of oxide observed at 824 °C (endothermic effect at 810–850 °C) [23]. Calculated values of mass loss (41.47 %), connected with the decomposition of $\text{BiC}_6\text{H}_5\text{O}_7$ with producing Bi_2O_3 , and are in a good agreement with the values found (41.2 %).

The process of compound **II** decomposition (see Fig. 5, b) begins with the removal of one

molecule of water (endothermic effects at 125 and 180 °C), the mass loss in this case is equal to 4.2 %. With increasing the temperature, removing the second molecule of water occurs with the formation of bismuth citrate $\text{BiC}_6\text{H}_5\text{O}_7$, which is indicated by X-ray diffraction data. The exothermic effects at 300 and 375 °C correspond to the destruction of citrate ion, and to the formation of bismuth oxide. The calculated values of the mass loss are equal to 46.33 %, the found values being of 45.9 %. The removal of water molecules from compound **III** is realized *via* one stage at a temperature of 125 °C being accompanied by a mass loss equal to 4.4 %, which corresponds to six molecules of water. The calculated mass loss value for the mentioned compound is equal to 4.87 %, the found value being of 4.6 %. From the data of Fig. 5 one could see that the heating of the samples in all the cases is finished by forming bismuth oxide, *i. e.*, the bismuth oxide could be obtained *via* bismuth citrate thermal decomposition.

CONCLUSION

Thus, bismuth can be precipitated from perchloric acid and nitric acid solutions in the form of three compounds different in composition depending on the concentration of citric acid added to the system and the process temperature. In the course of the precipitation from the bismuth solutions in nitric and perchloric acids with adding thereto the solutions of citric acid or sodium citrate at the temperature values amounting to (22 ± 2) and (60 ± 2) °C at a ratio between citrate ions and bismuth $n \leq 0.7$ the bismuth was precipitated in the form of an X-ray amorphous product $\text{Bi}_6(\text{OH})_6(\text{C}_6\text{H}_5\text{O}_7)_4 \cdot 6\text{H}_2\text{O}$. At the process temperature equal to (22 ± 2) °C and at a molar ratio between citrate ions and bismuth (III) in the solution $n \geq 1.0$ bismuth is precipitated in the form of compound $\text{BiOC}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$, whereas at (60 ± 5) °C the composition the compound precipitated is presented as $\text{BiC}_6\text{H}_5\text{O}_7$. It is demonstrated that the normal bismuth (III) citrate $\text{BiC}_6\text{H}_5\text{O}_7$, used in medicine and microbiology, is appropriate to obtain *via* the precipitation from bismuth-containing solutions through adding citric acid or sodium citrate thereto at a

molar ratio between citrate ions and Bi^{3+} in solution $n = 1.0\text{--}1.2$ and at the process temperature amounting to $(60 \pm 5)^\circ\text{C}$.

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