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Role of Bismuth Polynuclear Oxohydroxocomplexes in the Synthesis of Its Compounds

YU. M. YUKHIN, E. S. KOLEDOVA

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

E-mail: yukhin@solid.nsc.ru

Abstract

The literature data and experimental results of the authors on the state of bismuth in the solutions of perchloric and nitric acids, as well as on the synthesis of various bismuth compounds with the participation of polynuclear complexes, are systematized and summarized. It is shown that hydrolytic processing of bismuth-containing nitric solutions through bismuth precipitation at the process temperature of 65±5 °C and pH 0.7–1.0 in the form of compound $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$, followed by its transformation by means of washing with water into the compound $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ allows efficient separation of bismuth from impurity metals, which leads to a high-purity product with lead, silver and copper content less than $1 \cdot 10^{-5}$ %. It is established that these compounds may be used as precursors to obtain high-purity compounds: basic bismuth carbonate, gallate, succinate, as well as medium bismuth nitrate, citrate, ditartrate trihydrate. It is stated that the complex $[Bi_6O_4(OH)_4]^{6+}$ is the initial cationic form for hydrolytic precipitation of bismuth from solutions; only the ratio of bridging oxo and hydroxo groups changes during hydrolysis, with the conservation of the $Bi_6O_8^{2+}$ core, which serves as the central structural unit. It is shown that the addition of sodium tribromophenolate to the bismuth-containing nitric solution results in the formation of bismuth oxohydroxotribromophenolate $[Bi_6O_6(OH)_2](C_6H_2Br_3O)_4$. It is determined that bismuth precipitates from perchloric and nitric solutions after the addition of even oxohydroxocarboxylates in the form of the compounds with the composition $Bi_6O_4(OH)_4(C_nH_{2n+1}COOO)_6$ (n = 2–22), where $(C_nH_{2n+1}COOO)^-$ is the carboxylic acid anion. Bismuth precipitation from nitric solutions in the form of laurate and stearate allows efficient purification of bismuth from impurity metals. A comparison of bismuth extraction with di-2-ethylhexylphosphoric acid from nitric solutions in the form of solvated complex $Bi(C_{16}H_{34}O_2POO)_3 \cdot 2C_{16}H_{34}O_2POOH$ and oxohydroxodialkylphosphate $Bi_6O_4(OH)_4(C_{16}H_{34}O_2POO)_6$ is carried out. In the latter case, extracts concentrated with respect to bismuth can be obtained, which provides substantial broadening of the possibilities to use extraction-based processes in the technology of obtaining bismuth compounds.

Keywords: perchloric and nitric acid solutions, polynuclear complexes, bismuth compounds, basic carbonate, oxohydroxonitrates, oxohydroxocarboxylates, oxohydroxotribromophenolate, oxohydroxodialkylphosphate

INTRODUCTION

Bismuth consumption in the world accounts for 15–16 thousand tons per year, and about 57.2 % of this amount is used in the form of compounds [1]. Among the compounds consumed in technologies, the most widely used ones are oxide, medium and basic nitrates, and hydroxochromate for obtaining catalysts, pigments, optical glass, ferroelectrics, acousto-optical, superconducting and other materials. Bismuth salts (basic nitrate, basic gallate, basic salicylate, as well as tribromophenolate), bismuth-potassium-ammonium citrate are widely used in medicine for making medicines to treat socially significant diseases [2–4].

Bismuth compounds are highly prone to hydrolysis with the formation of poorly soluble basic salts. The latter fact is widely employed in the analytical chemistry of bismuth [5] and the technol-

ogy of high-purity bismuth compounds [3, 6]. Bismuth exists in the diluted solutions of perchloric acid in the concentration less than $1 \cdot 10^{-5}$ mol/L as mononuclear forms $Bi(OH)_x^{3-x}$, where x takes the values from 0 to 4. In the solutions of perchloric acid with hydrogen ion concentration 1.5 mol/L, bismuth is present in the form of aqua complexes $Bi(H_2O)_8^{3+}$ [7]. It follows from the data reported in [8] that about 4 % of bismuth in the solutions of perchloric acid with hydrogen ion concentration 1 mol/L occur in the form of the first hydroxo complex $Bi(OH)^{2+}$; at pH 4–12 the entire amount of bismuth occurs in the form of $Bi(OH)_3^0$, while at pH 14 – in the form of anion hydroxo complex $Bi(OH)_4^-$. In the case of concentration above $5 \cdot 10^{-4}$ mol/L, bismuth exists in the diluted solutions of acids in the form of polynuclear hydroxo complexes. It was established in numerous studies generalized by Baes and Mesmer in [9] that bismuth exists in moderately acidic solutions in the form of a six-nuclear complex $[Bi_6(OH)_{12}]^{6+}$. In that monograph, the distribution of hydroxo complexes for bismuth concentrations 0.1 and $1 \cdot 10^{-5}$ mol/L is presented, suggesting that an increase in bismuth concentration in solution causes a sharp shift of the equilibrium towards the formation of polynuclear hydroxo complexes. So, in the concentrated bismuth-containing solutions obtained through the dissolution of bismuth oxide or metal bismuth in oxygenated acids within pH 0–1, bismuth is present mainly as the hexanuclear hydroxo complex. In subsequent works, it was established by means of X-ray diffraction studies [10] and EXAFS [11] that the composition of this complex was $Bi_6O_4(OH)_4^{6+}$. This was also confirmed by NMR studies carried out by Grenthe and Toth [12]. The composition of polycation in the solutions in the form of $[Bi_6O_4(OH)_4]^{6+}$ rather than $[Bi_6(OH)_{12}]^{6+}$ is also confirmed by the NMR ^{17}O spectra of water-acetone solutions of basic bismuth perchlorate recorded by Fedotov with co-authors [13]. Two lines 222 and 87 ppm with intensity ratio ≅1 : 1 corresponding to two types of oxygen atoms bound with bismuth were detected. The line at 87 ppm was attributed to OH^--groups. It has been assumed in [14] on the basis of non-linear dependence of the intensity of the band at 177 cm^{-1} in the Raman spectrum after the addition of perchloric acid to the bismuth-containing solution that the transformation of a six-nuclear complex into aqua ions proceeds through the formation of intermediate forms of hydroxo complexes. It is stressed that extremely severe conditions necessary for the destruction of the complex provide evidence of its stability, which is due to the structure of the complex.

The studies of hydrolysis of bismuth-containing perchloric and nitric acid solutions revealed that the structure of hydrolysis products is composed of cage-type polycations $Bi_6O_4(OH)_4^{6+}$, nitrate and perchlorate ions, as well as water molecules [15, 16]. Lazarini [17] determined that eight different bismuth compounds involving polynuclear bismuth complexes were formed during precipitation from nitric solutions. It should be stressed that the complex $[Bi_6O_4(OH)_4]^{6+}$ is the initial cation form during the hydrolytic precipitation of bismuth from solutions, only the ratio of bridging oxo and hydroxo groups changes during hydrolysis, while the $Bi_6O_8^{2+}$ core is conserved, being the central structural unit.

In the present work, the data on obtaining bismuth through precipitation from perchloric and nitric acid solutions involving polynuclear bismuth complexes are generalized.

SYNTHESIS OF BISMUTH COMPOUNDS BY PRECIPITATION FROM SOLUTIONS AND ACCORDING TO THE REACTION SOLID – SOLUTION

Bismuth oxide is well soluble in perchloric acid, so dissolution in the acid with the concentration 6 mol/L leads to the solutions with bismuth concentration 5.1 mol/L. It is reasonable to use these solutions for precipitating various bismuth compounds because in this case there is no danger of product contamination with perchlorate ions as a consequence of the formation of basic salts.

A method has been proposed to synthesize bismuth citrate in a 90 % yield into the final product by adding a solution of citric acid into the bismuth-containing—perchloric solution at 60 °C, with subsequent separation of the precipitate by filtering, its washing and drying [18]. The synthesis procedure is based on the dissolution of 100 g of bismuth oxide at 60 °C in 100 mL of water containing 49 mL of perchloric acid with the density of 1.539 g/cm^3, the addition of 85 g of citric acid dissolved in 1.5 L of water, the addition of water to reach the total volume of 3 L, sequential washing of the precipitate with water, and then with a 1.5 % solution of citric acid, and drying at 50 °C.

Bismuth citrate precipitation from bismuth-containing perchloric solutions was studied in [19]. It follows from the reported results that the addition of the solutions of citric acid at process temperature (20±2) and (60±2) °C at the molar ratio of citrate ions to bismuth (n) within the

studied range 0.28–0.7 causes destruction of the complex $Bi_6O_4(OH)_4^{6+}$, and bismuth precipitates in the form of X-ray amorphous citrate $Bi_6(OH)_6(C_6H_5O_7)_4 \cdot 6H_2O$. The degree of bismuth precipitation for $n = 0.7$ is ~96 %.

The compound with the composition $[Bi_6(OH)_6(C_6H_5O_7)_4]_n$ is registered in Russia by the Yamanouchi Europe company (the Netherlands) as a pharmaceutical substance used to obtain anti-ulcer preparation De-Nol [20]. According to the data of Polfa company (Poland), according to the standard document ND 42-3250-94, Ventrisol substance has the composition $Bi_6(OH)_6C_6H_5O_7 \cdot K_3C_6H_5O_7 \cdot NH_4OH_n$ [21]. As a result of our studies in collaboration with the employees of the State Institute of Drugs and Good Practices (Moscow) [22], the composition of the substances was presented in the following form: $[Bi_6(OH)_6(C_6H_5O_7)_4][K_3C_6H_5O_7]_x[(NH_4)_3C_6H_5O_7)]_y$, where $x = 3.2–4.2$; $y = 0.8–1.8$ with the active component content 38.5–42.0 %, calculated for bismuth oxide.

At present, the process of obtaining bismuth compounds is connected with the treatment of nitric acid solutions. For bismuth precipitation from these solutions by adding alkaline reagents, the degree of bismuth recovery into the precipitate (R) is essentially dependent on the acidity of the medium (pH) and process temperature (Fig. 1). With an increase in pH, the degree of bismuth recovery into the precipitate increases. So that for pH 0.8–1 and process temperature 20±2 °C, it becomes equal to 93–97 % (the residual bismuth concentration in solution is 10–5 g/L). An increase in process temperature promotes the quantitative precipitation of bismuth at lower pH and 60 °C; within pH range 0.8–1.0, R is 97–99 % (the residual concentration of bismuth in solution is 5–2 g/L). An increase in solution pH to 3 allows one to achieve almost complete (R = 99.99 %) bismuth precipitation (the residual concentration of bismuth in solution is 0.030–0.015 g/L).

In the case of bismuth precipitation from nitric acid solutions during their dilution with water, the degree of recovery into precipitate passes through a maximum (see Fig. 1), but complete precipitation of bismuth cannot be achieved even in the case of 200-fold (pH 1.7) or higher dilution of the solutions. At the process temperature of 20 °C within pH 1.2–1.6, the degree of bismuth precipitation is maximal and is within the range of 90–92 % (the residual concentration of bismuth in solution is 10–7 g/L). The presence of the maxima on the R–pH curve may be explained as follows. Along with the formation of hexanuclear complex $[Bi_6O_4(OH)_4]^{6+}$, which is responsible for the formation of basic nitrate precipitating from solution [10], at pH ≥ 1.7 the formation of polynuclear complexes $Bi_9(OH)_{20}^{7+}$, $Bi_9(OH)_{21}^{6+}$, $Bi_9(OH)_{22}^{5+}$ is observed [9]. The concentration of complexes increases with a further increase in pH, which is the reason for a decrease in the degree of bismuth precipitation in the form of oxohydroxonitrate.

The absence of a descending region on the R–pH dependence in the case of bismuth precipitation as a result of the addition of basic reagents is explained by the fact that precipitation is carried out from the solutions with nitrate ion concentration 2–3 mol/L. This promotes the formation of a complex of bismuth with nitrate ions, likely $[Bi_6O_4(OH)_4NO_3]^{5+}$, which takes part in the precipitation of oxohydroxobismuth and prevents the formation of complexes of the type of $Bi_n(OH)_m^{3n-m}$.

With an increase in the process temperature, bismuth precipitation as a result of the dilution of solutions with water, similarly to the addition of alkaline reagents, starts at lower pH. This is caused by the mainly exothermal nature of the reactions of bismuth complexation with nitrate ions [23].

In this situation, the composition of hydrolysis products depends on the pH of the medium, process temperature, and concentration of nitrate

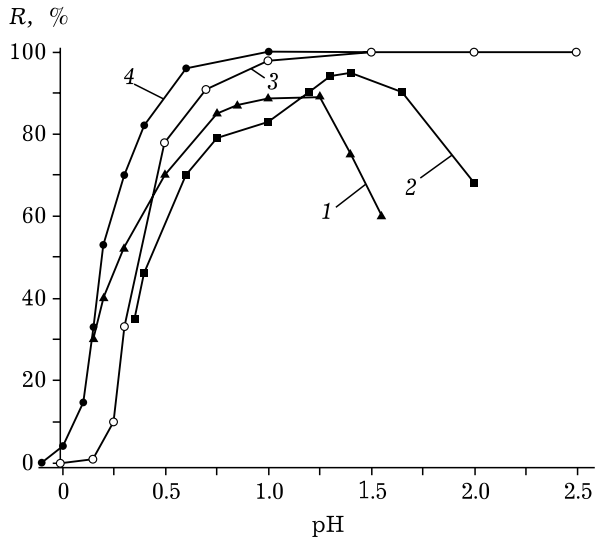

Fig. 1. Dependence of bismuth precipitation degree (R) on pH of the medium for the addition of water (*1, 2*) or sodium hydroxide solution (*3, 4*) to the bismuth-containing solution. Process temperature: 60 (*1, 4*), 20 °C (*2, 3*). The initial composition of the solutions: Bi 220 g/L, HNO_3 40 g/L.

ions in the solution. Depending on precipitation conditions within the region of pH ≤ 3, the existence of four different crystalline forms was established. On the basis of literature data [15, 24–27], these forms were assigned to the compounds of the following compositions: $[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4H_2O$ – I, $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ – II, $[Bi_6(H_2O)(NO_3)O_4(OH)_4](NO_3)_5 \cdot H_2O$ – III and $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ – IV.

It was demonstrated in [24] that compound I containing, %: bismuth 68.66; NO_3^- 19.89; H_2O 4.0, may be obtained at pH 0.7, nitrate ion concentration 0.35 mol/L and temperature 22 °C, while oxohydroxonitrate II containing, %: bismuth 70.28; NO_3^- 20.42; H_2O 1.0, may be obtained at pH 0.7, nitrate ion concentration in solution 0.35 mol/L and process temperature 60 °C. Compound III containing, %: bismuth 69.01; NO_3^- 21.65; H_2O 2.1, may be obtained at pH 0.7, nitrate ion concentration 4.0 mol/L and process temperature 22 °C, while bismuth oxohydroxonitrate IV containing, %: bismuth 72.28; NO_3^- 17.38; H_2O 3.1, may be obtained at pH 1.3, nitrate ion concentration 0.07 mol/L and process temperature 22 °C.

The conditions for processing metal bismuth of Vi1 grade into high-purity bismuth oxohydroxonitrate with the composition (IV) were studied in [28]. Bismuth of Vi1 grade contains not less than 98 % bismuth and is usually used as the initial raw material to obtain bismuth compounds. The main impurity metals in it are lead (not more than 1.8 %), silver (not more than 0.12 %) and copper (not more than 0.10 %). It is demonstrated that bismuth precipitates from nitric acid solutions at the process temperature 65±5 °C and pH 0.7–1.0 in the form of oxohydroxonitrate with the composition $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$, and washing with water is accompanied by hydrolysis with the formation of a high-purity compound having the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ according to the reaction:

$$[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O + 2H_2O \rightarrow [Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O + HNO_3 \quad (1)$$

The product contains lead, silver and copper less than $1 \cdot 10^{-5}$ % and may be used as a precursor to obtain other high-purity bismuth compounds.

The possibility to obtain high-purity bismuth compounds from their oxohydroxonitrates was demonstrated in [29]. For instance, the treatment of the compound $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ with the solution of nitric acid resulted in the formation of bismuth nitrate pentahydrate with the composition $Bi(NO_3)_3 \cdot 5H_2O$, treatment with ammonium carbonate at pH 8 and temperature 22 °C led to the formation of basic carbonate with the composition $(BiO)_2CO_3$, treatment with the solution of citric acid at the liquid to solid ratio equal to 2.3 and process temperature 22 °C resulted in the formation of bismuth citrate with the composition $BiC_6H_5O_7$. Starting from the compound with the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$, its treatment with the aqueous solutions of gallic acid resulted in the formation of basic bismuth gallate $C_6H_2(OH)_3COOBiO \cdot 3H_2O$, treatment with tartaric acid led to ditartrate trihydrate with the composition $[Bi(C_4H_4O_6)(C_4H_5O_6)] \cdot 3H_2O$, interaction with salicylic acid resulted in the formation of basic salicylate with the composition $Bi(C_7H_5O_3)O$ [29], treatment with succinic acid produced basic succinate with the composition $C_2H_4(COOBiO)_2$ [30]. It should also be stressed that the treatment of oxohydroxonitrate having the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ with the aqueous solutions of sodium hydroxide within pH 6.8–7.5 leads to the formation of the compound with the composition $[Bi_6O_6(OH)_3](NO_3)_3$, while within pH 9.7–10.3 – $[Bi_6O_7(OH)_2](NO_3)_2 \cdot 2H_2O$ with the molar ratio of bismuth to nitrate ions equal to 3 [31].

Bismuth 2,4,6-tribromophenolate is widely used in medicine as the drug xeroformium causing local binding and antiseptic action (due to bismuth and phenol). Investigations described in [32] provide evidence that bismuth oxohydroxotribromophenolate $[Bi_6O_6(OH)_2](C_6H_2Br_3O)_4$ can be obtained through precipitation from nitric acid solutions after the addition of the aqueous solution of sodium tribromophenolate at the reaction medium pH 6.5–7.5 and temperature 95 °C.

Bismuth carboxylates are rather widely used in the synthesis of bismuth-containing oxide materials (superconducting, ferroelectric, piezoelectric, catalytic, *etc.*), and in the synthesis of bismuth-containing medicines [33, 34]. The synthesis and structure in the even bismuth oxohydroxocarboxylates with the composition $Bi_6O_4(OH)_4(C_nH_{2n+1}COOO)_6$ (n = 2–22), where $(C_nH_{2n+1}COOO)^-$ is the carboxylate anion, are considered in [35]. It is established that bismuth oxohydroxocarboxylates with the number of carbon atoms $C_n \geq 6$ have a similar layered structure and belong to the same homologous series. The conditions of the formation of bismuth laurate and stearate with the composition $[Bi_6O_4(OH)_4]R_6$, where R is the anion of laurinic or stearinic acids, are described in [36, 37]. It is

demonstrated that it is reasonable to obtain high-purity bismuth laurate and stearate from metal bismuth through precipitation in the form of oxohydroxocarboxylates by adding the solution of bismuth nitrate into the solution of sodium laurate or stearate at a temperature of 60±5 °C, with the molar ratio of laurinic or stearinic acid to bismuth equal to 1.0–1.1, and the concentration of free nitric acid in solution 0.1 mol/L.

The possibility to extract bismuth with di-2-ethylhexyl phosphoric acid (D2EHPA) from the solutions of perchloric and nitric acids was demonstrated, depending on pH and bismuth concentration in the organic phase either in the form of acid solvated complex $BiR_3 \cdot 2HR$, where R is $C_{16}H_{34}O_2POO^-$, or as oxohydroxodialkyl phosphate $Bi_6O_4(OH)_4(C_{16}H_{34}O_2POO)_6$ [38]. The high solubility of bismuth oxohydroxodialkyl phosphate in organic diluents allows one to obtain extracts concentrated with respect to bismuth. For instance, bismuth extraction with D2EHPA in the concentration of 1 mol/L from solutions with pH 0.3 in the form of the compound with the composition $BiR_3 \cdot 2HR$, for bismuth concentration in the organic phase 36 g/L, bismuth dialkyl phosphate forms a precipitate at the interface, while the extraction in the form of oxohydroxodialkyl phosphate from solutions with pH 1.5 may produce the organic phase containing bismuth 180 g/L. The latter fact provides a substantial expansion of the possibility to use extraction in the technology of obtaining bismuth compounds.

CONCLUSION

It is shown that bismuth in the solutions of perchloric and nitric acids in the concentration of more than $5 \cdot 10^{-4}$ mol/L within pH 0–1 exists in the form of a hexanuclear hydroxo complex with the composition $[Bi_6O_4(OH)_4]^{6+}$. This complex plays a decisive part in bismuth precipitation from perchloric and nitric acid solutions and takes an active role in bismuth precipitation or extraction from solutions in the form of compounds of different compositions. Only the ratios of bridging oxo and hydroxo groups changes during hydrolysis, with the conservation of the $Bi_6O_8^{2+}$ core, which is the central structural fragment.

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