

Synthesis of Bismuth (III) Oxohydroxolaurate

YURY M. YUKHIN, KONSTANTIN YU. MIKHAILOV, BORIS B. BOKHONOV and IRINA A. VORSINA

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

E-mail: yukhin@solid.nsk.su

Abstract

Synthesis of bismuth (III) oxohydroxolaurate by the reaction of lauric acid with bismuth-containing perchlorate or nitrate solutions has been studied by X-ray phase analysis, thermogravimetric analysis, electron microscopy, IR spectroscopy, and chemical analysis. Conditions of the reaction forming bismuth laurate $\text{Bi}_6\text{O}_4(\text{OH})_4\text{R}_6$, where R is the lauric acid anion, have been determined, and the solubility of the anion in organic solvents has been investigated. It is recommended that highly pure bismuth laurate should be synthesized from metallic bismuth by preliminary oxidation of the latter with atmospheric oxygen, dissolving the resulting Bi_2O_3 in nitric acid (1 : 1), and purifying bismuth from impurity metals by its precipitation in the form of oxohydroxolaurate by adding a solution of sodium laurate to the solution of bismuth nitrate at $(60 \pm 10)^\circ\text{C}$ (molar ratio HR : Bi = 1.0–1.1, concentration of free nitric acid in solution 0.1 mol/l).

INTRODUCTION

Bismuth carboxylates are currently employed in syntheses of bismuth-containing oxide materials: superconductors, ferroelectrics, piezoelectrics, catalysts, *etc.* and also in syntheses of bismuth-containing medical compositions [1–3]. Metal carboxylates of higher carboxylic acids were shown [4] to be one of the most promising classes of compounds serving for synthesis of nanosized particles in the course of thermal decomposition of these compounds. Developing simple synthetic procedures leading to these compounds, therefore, has recently become an important problem.

Bismuth carboxylates are generally synthesized from bismuth compounds of reagent grade; for example, they are prepared by reactions of bismuth oxide with appropriate monocarboxylic acids, or by substitution of acetate ions by other carboxylate groups in bismuth acetate, or by bismuth precipitation from bismuth nitrate solutions by adding an alkaline carboxylate solution in the presence of glycerol [1]. It was noted that hydrolysis makes it impossible to obtain neutral bismuth (III) carboxylates from solutions. Thus M. Picon [5] reported that interaction of the sodium salts of fatty acids with aqueous bismuth nitrate in glyc-

erol forms basic salts $(\text{RCOO})\text{BiO}$ or $(\text{RCOO})\text{Bi}(\text{OH})_2$. However, studies on syntheses of bismuth salts of oleic, palmitic, and stearic acids [6] showed that Picon's method gave neutral salts with minor impurities of basic salts, but not basic salts themselves, as indicated by M. Picon.

Bismuth (III) compounds are generally obtained from Bi1 grade metal (at least 97.7% Bi) by dissolving it in nitric acid and subsequently purifying bismuth from impurity metals by hydrolysis [7]. Liberation of toxic nitrogen oxides as gases during preparation of bismuth nitrate solutions and the low degree of purification from impurity metals (lead, iron, and silver) are the major disadvantages of this method. It was shown [8] that preliminary oxidation of the metal with atmospheric oxygen permits one to reduce the consumption of nitric acid by a factor of two at the stage of preparation of bismuth nitrate solutions and to avoid release of nitrogen oxides in the gas phase. This opens up an opportunity to prepare nitrate-, perchlorate-, and halide-containing solutions from metallic bismuth.

Extraction of 28 metals with aliphatic monocarboxylic acids ($\text{R}-\text{COOH}$) of the C_7 – C_9 fraction is reported in [9]. From the data obtained it follows that these organic acids are

the best extractants of bismuth. We used bismuth extraction with caprylic acid $C_7H_{15}COOH$ for bismuth purification from the major impurity metals [10]. Thus bismuth purification from impurity metals is possible at the stage of monocarboxylate synthesis, which permits the preparation of high purity compounds directly from the industrial nitrate solutions employed in the production of bismuth compounds. To study the composition of bismuth products obtained in synthesis of monocarboxylates, for the carboxylic acid we took lauric acid $C_{11}H_{23}COOH$, which occupies an intermediate place in the series of monocarboxylic acids and has a relatively low melting point (44.5 °C).

The objective of this work is to investigate the composition of the products of bismuth precipitation with lauric acid from perchlorate and nitrate solutions and to examine the possibility of purification from impurity metals at the stage of precipitation in laurate form.

EXPERIMENTAL

The starting bismuth perchlorate solutions (Bi content 1120 g/l) were prepared by dissolving an oxide of ultrapure grade (13-3; for single crystals, Specs 6-09-02-298-90) in chloric acid with a concentration of 6.0 mol/l. To prepare solutions with lower bismuth concentrations, the starting solutions were diluted with distilled water. Bismuth(III) oxohydroxolaurate $Bi_6O_4(OH)_4R_6$ and a solid solution $Bi_6O_4(OH)_4R_6 \cdot nHR$ of bismuth oxohydroxolaurate and lauric acid were synthesized as follows. A lauric acid sample was added with stirring to distilled water (1.0 l) heated to ~60 °C. Aqueous bismuth perchlorate (1.0 l) with a bismuth content of 12.5 g/l was gradually added with stirring to the resulting mixture. Synthesis was accomplished in Teflon vessels equipped with stirrers. The mixture was stirred for 1 h. After 1 h, the precipitate was filtered off on a vacuum filter, washed with distilled water, and dried in air. To remove unchanged lauric acid from bismuth oxohydroxolaurate, the product was washed, if necessary, with ethanol.

X-ray phase analysis (XRPA) of the products was performed on a DRON-3 diffractometer (CoK_α

radiation, counter velocity 0.5 deg/min⁻¹, $I = 1000$). The differential thermal analysis (DTA) and thermogravimetric (TG) curves of the samples were recorded with a MOM derivatograph (Hungary) at a heating rate of 10 °C/min⁻¹. IR absorption spectra were measured on a Specord 75 IR spectrophotometer (400–4000 cm⁻¹). The samples were prepared as calcined KBr pellets. Electron micrographs were obtained with a JEM-2000FXII transmission electron microscope (accelerating voltage 200 kV). Metal (Bi, Pb, Ag, Fe, Cu, Zn) contents in the liquid and solid phases were determined on a Saturn 2M spectrophotometer by the atomic absorption method. The products were preliminarily processed with a (1 : 1) nitric acid solution.

RESULTS AND DISCUSSION

Our experiments on bismuth precipitation from perchlorate solutions indicated that at pH 2 and lauric acid to bismuth molar ratio of 1.0, 2.0, and 4.0 residual concentration of bismuth in the solution is 0.39, 0.052, and less than 0.001 g/l, respectively; the degree of precipitation is 93.8, 99.2, and more than 99.98 %, respectively. Taking into account that in perchlorate solutions bismuth is in the form of Bi^{3+} aqua ions or $Bi_6O_4(OH)_4^{6+}$ hexanuclear complexes [11, 12], which depends on the concentration, the lauric acid to bismuth molar ratio was taken to be 3 : 1.

XRPA, IR, thermal, and chemical analysis data showed the following. When bismuth is precipitated from perchlorate solutions with additions of lauric acid solutions (or when the order of addition of reagents is reversed) at (60 ± 10) °C, pH 1, and lauric acid to bismuth molar ratio of 1, the product is bismuth oxohydroxolaurate $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6$; at a molar ratio of 3 the product is a solid solution $Bi_6O_4(OH)_4(C_{11}H_{23}COO)_6 \cdot nHR$ ($n=12$) of bismuth oxohydroxolaurate and lauric acid. The chemical analysis indicated that the concentration of perchlorate ions in the precipitation products is up to 0.01 %, and the molar ratio of laurate ions to bismuth is 1.01 in the former case and 2.98 in the latter.

Our X-ray structural study of bismuth laurates indicated that (Fig. 1) these products do not show the characteristic diffraction maxima

inherent in free lauric acid and that the two compounds have some characteristics in common and a number of significant differences. Thus the region of low angles on the X-ray diffraction patterns of the compounds contains reflections identified as Bragg reflections from the (001) basal planes. This diffraction pattern is typical for all known metal carboxylates and reveals layered ordering of metal ions (bismuth cations in this case) and carboxyl group anions. The interlayer distances d_{001} calculated from X-ray diffraction patterns are rather similar for $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$ and for the solid solution of bismuth oxohydroxolaurate with lauric acid (37.5 and 35.79 Å, respectively). However, apart from this similarity of layered ordering in the crystal structures of $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$ and $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6 \cdot n\text{HR}$, X-ray patterns have revealed significant differences. First, the layer reflections of $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$ (see Fig. 1, a) are considerably broadened compared

to those of $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6 \cdot n\text{HR}$ (see Fig. 1, b). Second, there is a wide amorphous halo in the region of large angles on the X-ray patterns of $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$, while for $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6 \cdot n\text{HR}$ this region distinctly shows reflections from the planes with the indices (hkl) where h or k is not zero. In our opinion, this difference between the X-ray diffraction patterns of $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$ and $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6 \cdot n\text{HR}$ indicates that the long aliphatic chains are disordered in the structure of $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$, but ordered in the structure of $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6 \cdot n\text{HR}$. The coexistence of layer reflections and amorphous halo on the X-ray diffraction patterns is indicative of the liquid state of the substance. This is often observed on passing from crystalline to mesomorphic state in smectic crystals [13]. Thus the compound $\text{Bi}_6\text{O}_4(\text{OH})_4(\text{C}_{11}\text{H}_{23}\text{COO})_6$ is initially in the liquid crystal state.

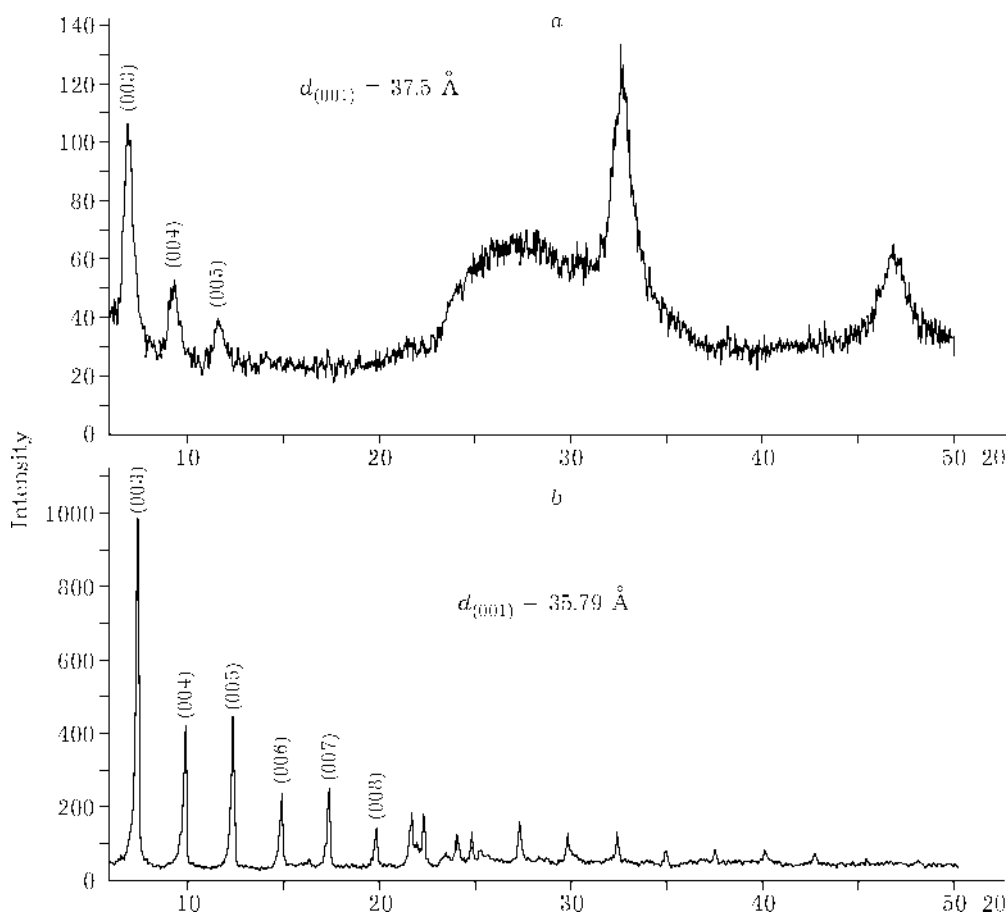


Fig. 1. X-ray diffraction patterns of bismuth oxohydroxolaurate (a) and its solid solution with lauric acid (b).

From thermal analysis data it follows that the TG curve of bismuth oxohydroxolaurate (Fig. 2, *a*) reflects the decomposition of the compound; the DTA curve shows three exo effects: at 180, 320, and 500 °C, eventually leading to the formation of bismuth oxide. The DTA curve of the solid solution of bismuth oxohydroxolaurate with lauric acid (see Fig. 2, *b*) has an endothermal effect at 60 °C. At elevated temperatures, bismuth oxohydroxolaurate decomposes into bismuth oxide (sharp exothermal peaks at 300, 340, 400, and 500 °C). The endothermal effect at 729 °C is due to the polymorphic transformation of the monoclinic α modification of Bi_2O_3 into the high-temperature face-centered cubic δ modification; the endothermal effect at 820 °C is caused by the melting of bismuth (III) oxide [14]. The DSC curve (Fig. 3) recorded at a heating rate of 2 °C/min shows that in the case of bismuth oxohydroxolaurate, thermal effects are absent below 150 °C; in the case of the solid solution, there are two endothermal effects: at 44 and 62 °C. The first effect seems to be due to the melting of lauric acid, and the second is caused by the melting of bismuth oxohydroxolaurate in the presence of a lauric acid melt.

The IR absorption spectrum of bismuth oxohydroxolaurate was compared with the spectrum of pure lauric acid (Fig. 4, curves 1 and 2). The changes in the former spectrum were attributed to substitution of hydroxyl hydrogen by the $\text{Bi}_6\text{O}_4(\text{OH})_4^{6+}$ cation. Indeed, the spectrum of the salt has no vibration bands of the carboxyl group: ν_{OH} 3400–2500 cm^{-1} , δ_{OH} 940 cm^{-1} , and $\nu_{\text{C=O}}$ 1705 cm^{-1} , but contains the vibration bands of the carboxylate ion: ν_{asCOO^-} 1540 cm^{-1} and $\nu_{\text{sCOO}^-} + \delta_{\text{CH}_2}$ 1415 cm^{-1} [15, 16]. Moreover, the intensity ratio between the maxima of the band of CH_3 deformation vibrations (1500–1450 cm^{-1}) also changes, and the intensity of the band with a maximum at 1300 cm^{-1} , which is due to the combination vibrations $\delta_{\text{OH}} + \nu_{\text{C=O}}$ of the acid dimer, decreases drastically. The series of bands in the region 1350–1150 cm^{-1} belonging to the CH_3 wagging vibrations and defining the length of the hydrocarbon chain [15] indicates that the groups are *trans* positioned. The deformation (torsion) vibration band of the methyl group (540 cm^{-1}) is shifted with respect to its

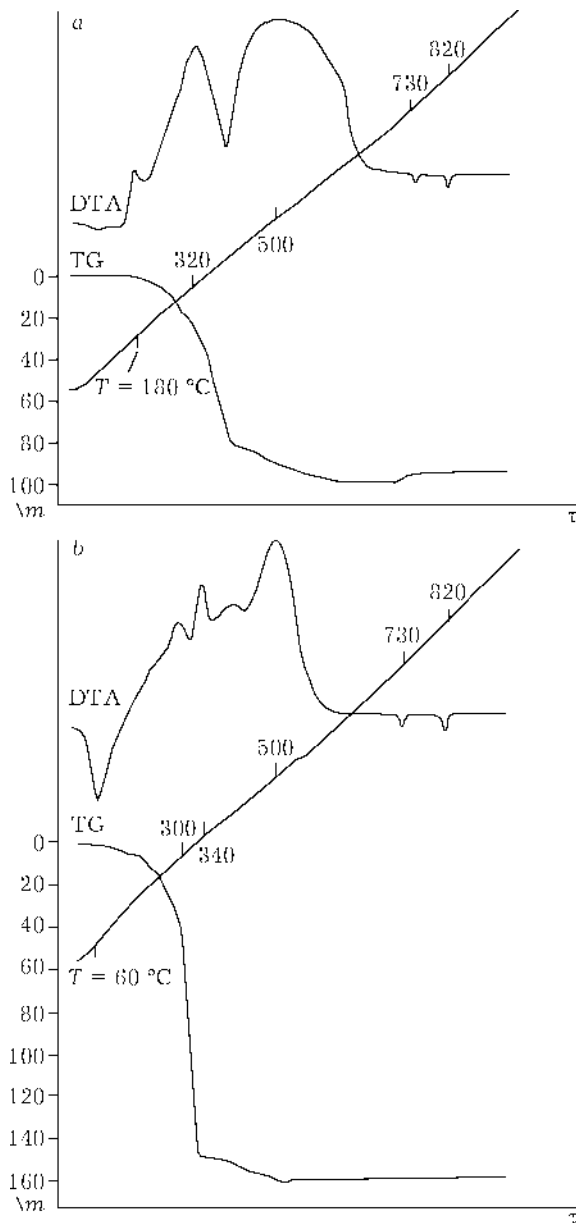


Fig. 2. Thermal analysis curves for bismuth oxohydroxolaurate samples (*a*) and its solid solution with lauric acid (*b*).

position in the spectrum of the acid (550 cm^{-1}) [15]. The presence of the $\text{Bi}_6\text{O}_4(\text{OH})_4^{6+}$ cation in the product may be inferred from the presence of a band with a maximum at 3550 cm^{-1} corresponding to the ν_{OH} vibrations [15, 17]. The broadening of the δ_{CH_3} band (540 cm^{-1}) and the appearance of a shoulder at ~570 cm^{-1} also seem to be due to the vibrations of this cation.

The IR absorption spectrum of the solid solution of bismuth oxohydroxolaurate and lauric acid differs markedly from the spectrum of bis-

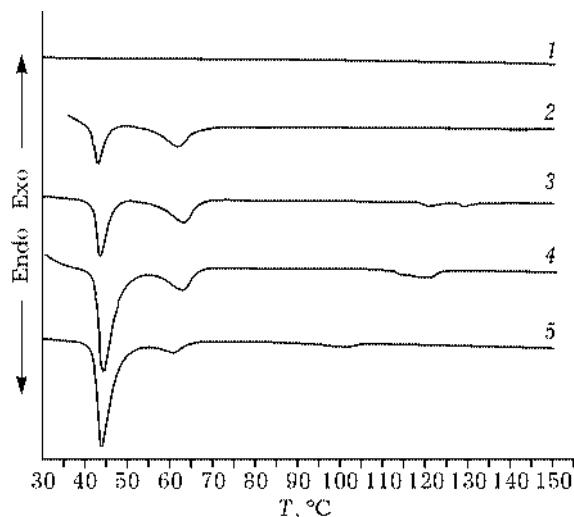


Fig. 3. DSC curves for bismuth oxohydroxolaurate with lauric acid. Laurate ion to bismuth molar ratio is 1 (1), 2 (2), 3 (3), 4 (4), and 6 (5). Heating rate 2 °C/min.

muth oxohydroxolaurate (see Fig. 4, curves 2 and 3). Thus along with the bands of the carboxylate ion $\nu_{as}COO^-$ 1570 cm^{-1} and $\nu_sCOO^- + \delta CH_2$ 1430 cm^{-1} , the spectrum of the product contains the vibration bands of the carboxyl group νOH 3400–2500 cm^{-1} and $\nu C=O$ 1715 cm^{-1} . The shift of the maximum of the latter in the spectrum of the product relative to the position of this band in the spectrum of pure lauric acid (1705 cm^{-1}) is evidence in favor of the formation of a compound of bismuth oxohydroxolaurate with the acid. This also accounts for the displacement of the bands of the carboxylate ion ν_{as} , ν_sCOO^- , and νOH of the $Bi_6O_4(OH)_4^{6+}$ complex ion (1540 \rightarrow 1570, 1415 \rightarrow 1430 and 3550 \rightarrow 3430 cm^{-1} , respectively). The discrepancy between the spectrum of the bismuth oxohydroxolaurate/lauric acid solid solution and the spectrum of bismuth oxohydroxolaurate in the region below 1500 cm^{-1} is also due to the presence of lauric acid in the product. Washing with ethanol removes lauric acid, and the product becomes bismuth oxohydroxolaurate.

According to electron microscopy data, the crystals of bismuth oxohydroxolaurate and of the bismuth oxohydroxolaurate/lauric acid solid solution are platelets generally having no strict faceting. The crystals are 50–100 nm thick, the plate length reaching 1 μm .

We investigated the solubility of bismuth oxohydroxolaurate in a number of solvents. When the temperature is raised from 20 to

60 °C, the solubility increases (g/l) from <0.003 to 0.055 in water, from <0.003 to 1.65 in ethanol, from 0.076 to 10.3 in benzene, and from 2.77 to 30.6 in carbon tetrachloride.

Bismuth compounds are generally synthesized by hydrolytic treatment of bismuth-containing nitrate solutions prepared by dissolving the Bi 1 grade metal in nitric acid [7]. Our studies on bismuth precipitation from nitrate solutions indicated that the product is bismuth oxohydroxolaurate, as in the case of precipitation from perchlorate solutions. Formation of bismuth oxohydroxo compounds with a polynuclear cation and an organic ligand is of interest because it becomes possible to effectively separate bismuth from impurity metals, to drastically reduce the consumption of an organic acid during synthesis of bismuth-containing oxide materials, and to expand the scope of organic precursors for the preparation of metal particles or bismuth oxide with varying morphology. To prepare high purity bismuth oxohydroxolaurate, we examined the

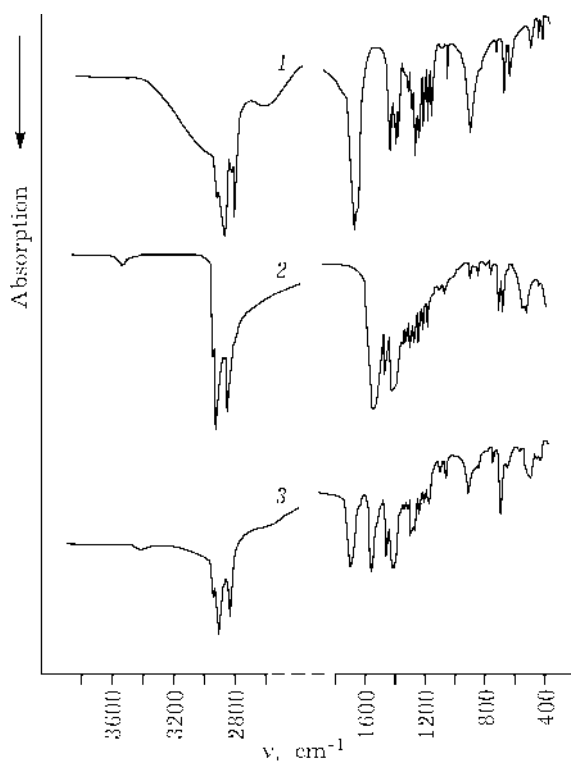


Fig. 4. IR spectra of lauric acid (1), bismuth oxohydroxolaurate (2), and its solid solution with lauric acid (3).

possibility of synthesizing this compound from the industrial solutions of bismuth compounds production. For this purpose we used Bi 1 grade metal with mass fractions, %: 98.5 Bi, 0.88 Pb, $6.4 \cdot 10^{-4}$ Zn, $6.2 \cdot 10^{-3}$ Fe, $1.0 \cdot 10^{-3}$ Sb, $9.5 \cdot 10^{-3}$ Cu, $5.6 \cdot 10^{-2}$ Ag, $1.3 \cdot 10^{-4}$ As, $8.2 \cdot 10^{-5}$ Te. Before synthesis, the metal was oxidized in a stainless steel reactor equipped with a screw for stirring the melt; for oxidation, 20 % bismuth oxide was introduced while stirring in the reactor at 350 °C, and the temperature was raised to 600 °C [8]. The resulting industrial oxide was dissolved in nitric acid of pure grade at a concentration of 6 mol/l. The solution contained 420 g/l bismuth and 80 g/l free HNO₃; its composition was comparable to that of solutions generally employed in the production of bismuth compounds.

Bismuth (III) oxohydroxolaurate was synthesized by adding a solution of sodium laurate obtained by neutralization of lauric acid with a sodium hydroxide solution to a solution of bismuth nitrate (lauric acid to bismuth molar ratio 1.05, temperature 60 °C, and pH 1). The precipitate was washed once with a nitric acid solution to pH 1 and two times with distilled water at 60 °C; then it was dried at 100 °C. The resulting oxohydroxolaurate contained (mass %): 48.2 Bi, $1 \cdot 10^{-5}$ Pb, $1 \cdot 10^{-5}$ Zn, $6 \cdot 10^{-6}$ Fe, $2 \cdot 10^{-6}$ Sb, $7 \cdot 10^{-7}$ Cu, $3 \cdot 10^{-7}$ Ag, $<1 \cdot 10^{-5}$ As, $<1 \cdot 10^{-5}$ Te.

CONCLUSIONS

Thus high purity bismuth (III) laurate may be synthesized by the following procedure for processing bismuth-containing nitrate solutions (industrial solutions of bismuth compounds production): preliminary oxidation of a metal melt

with atmospheric oxygen to the oxide, permitting one to reduce the consumption of nitric acid by a factor of two and to avoid atmospheric release of toxic nitrogen oxides at the stage of the preparation of bismuth nitrate solutions; hydrolytic purification by bismuth precipitation in oxohydroxolaurate form by adding a sodium laurate solution to the bismuth nitrate solution while stirring (laurate ion to bismuth ratio of 1.0–1.1, 60 °C, free acid content in the solution 0.1 mol/l).

REFERENCES

- 1 A. P. Pisarevskiy and L. I. Martynenko, *Koordinats. Khimiya*, 20 (1994) 324.
- 2 G. Briand, N. Burford, *Chem. Rev.*, 99 (1999) 2601.
- 3 Yu. M. Yukhin and Yu. I. Mikhailov, *Khimiya vismutovykh soyedineniy i metallov*, Izd-vo SO RAN, Novosibirsk, 2001.
- 4 A. I. Pomogailo, A. S. Rozenberg and I. E. Uflyand, *Nanochastitsy metallov v polimerakh*, Khimiya, Moscow, 2000.
- 5 M. Picon, *Bull. Soc. Chim. France*, 45 (1929) 1056.
- 6 E. A. Nikitina and S. N. Maksimova, *Zhurn. obshch. khimii*, 19 (1949) 1108.
- 7 Yu. V. Karyakin and I. I. Angelov, *Chistye khimicheskiye veshchestva*, Khimiya, Moscow, 1974.
- 8 Yu. M. Yukhin, T. D. Daminova and V. I. Smirnov, *Khimiya v interesakh ustoychivogo razvitiya*, 7 (1999) 745.
- 9 L. M. Gindin, *Ekstraktsionnye protsessy i ikh primeneniye*, Nauka, Moscow, 1984.
- 10 T. A. Udalova, Yu. M. Yukhin and I. A. Vorsina, *Zhurn. neorgan. khimii*, 40 (1995) 2072.
- 11 C. F. Baes, R. E. Mesmer, *The Hydrolysis of Cations*, J. Wiley, New York, 1976.
- 12 B. Sundwall, *Acta Chem. Scand.*, A34 (1980) 93.
- 13 T. Takahashi, T. Kimura, K. Sakurai, *Polymer*, 40 (1999) 5939.
- 14 G. Gattow, D. Schutze, *Z. anorg. allgem. Chem.*, 328, H 1–2 (1964) 44.
- 15 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1961.
- 16 G. Socrates, *Infrared Characteristic Group Frequencies*, New York, 1980.
- 17 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1970.