SYNTHESIS AND PROPERTIES **OF INORGANIC COMPOUNDS**

Precipitation of Bismuth(III) Salicylates from Mineral Acid Solutions

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Abstract—Powder X-ray diffraction, IR spectroscopy, Raman spectroscopy, thermogravimetry, and chemical analysis were used to study the precipitation of bismuth(III) salicylates from perchloric, nitric, and hydrochloric acid solutions as dependent on the salicylate ion concentration, temperature, and pH. Depending on the synthesis parameters, precipitation from perchloric and nitric acid solutions yields monosalicylate BiOC₇H₅O₃ or disalicylate Bi₂O(C₇H₅O₃)₄.

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Bismuth compounds are used in medicine for treatment of various gastrointestinal diseases since the end of the 18th century. The first liquid preparation containing bismuth subsalicylate as the drug substance was developed in 1900 in the United States.

Salicylic acid and many of its derivatives are widely used as drugs [2]. Salicylic acid is bibasic, thus forming diverse complexes with metals. In acid and neutral solutions, salicylic acid exists as C₆H₄OHCOO⁻ (HSal⁻) ions and undissociated molecules. In alkaline solutions, $C_6H_4OCOO^{2-}$ (Sal²⁻) doubly charged ions are formed. Thus, the compounds of salicylic acid with metals are categorized into two groups depending on whether they contain HSal⁻ or Sal²⁻ anions [3].

Various bismuth compounds of salicylic acid are described in the literature. For example, basic bismuth salicylates containing one salicylic acid anion per bismuth(III) cation can form: C₆H₄(OH)COOBiO [4], $C_7H_5BiO_4$ [5], and $C_6H_4(OH)COOBi(OH)_2$ [6]. The composition of basic bismuth salicylate is also represented as a mixture with oxide ($[C_6H_4(OH)COOBi +$ Bi_2O_3 [7]) or as a compound containing one and a half salicylic acid anions ($(C_7H_5O_3)_6Bi_4O_3$ [8]) or two salicylic acid anions [9]. Neutral compounds containing three salicylic acid ions $(C_7H_5O_3)_3Bi$ [10] and $(C_7H_5O_3)_3Bi \cdot 4H_2O$ [8]) and neutral bismuth salicylate $(Bi_2(C_6H_4OHCOO)_3 [11])$ have also been documented.

Basic bismuth salicylate (bismuth subsalicylate) is a widely used antiulcer pharmaceutical [12]. This compound is an odorless and tasteless white powder and is insoluble in water and ethanol. Basic bismuth salicylate is the drug substance of antiulcer and antidiarrhea medications Desmol, Pepto-Bismol, and Bismatrol. These medications are also enveloping and antimicrobial agents. They are active against Helicobacter pylori, which plays the key role in chronic gastritis, ulcer, and stomach cancer.

It is pertinent to study the composition of bismuth compounds with various anions that precipitate from perchloric acid solutions. When bismuth perchlorate solutions are diluted with water, basic bismuth salts do not precipitate, unlike in other solutions of bismuth salts [13]. Therefore, the contamination of precipitates with bismuth compounds of mineral acid anions is avoided here. Inasmuch as bismuth(III) compounds are usually prepared by precipitation from nitric acid solutions, it is of practical interest to study the precipitation of basic bismuth salicylate directly from nitric acid solutions and from hydrochloric acid solutions, which are used in hydrometallurgy of bismuth.

Here, we present the results of our study of the effect of salicylate ion concentration, temperature, and pH on the percentage bismuth precipitation from perchloric, nitric, and hydrochloric acid solutions and on the composition of the products.

EXPERIMENTAL

The mineral acids, salts, and alkalis used in this work were of chemically pure or high purity grade. The initial solutions of bismuth perchlorate (900 g/L), bismuth nitrate (420 g/L), and bismuth chloride (230 g/L) were prepared by dissolving bismuth oxide (os.ch. 13-3 grade) in 6 M perchloric, nitric, and hydrochloric acid, respectively.

Hydrolytic precipitation of bismuth from solutions was carried out in Teflon vessels equipped with stirrers; the vessels were thermostated on WB-2 water baths. To



Fig. 1. Percentage bismuth(III) precipitation R(%) vs. mole ratio of salicylate ions to bismuth(III) n in (1-3) perchloric, (4) nitric, and (5) hydrochloric acid solutions upon addition of (1, 2, 4, 5) sodium salicylate and (3) salicylic acid to the bismuth-containing solution. Temperature, °C: (1) 23 and (2-5) 70.

precipitate basic bismuth salicylate from perchloric, nitric, and hydrochloric acid solutions, the proper bismuth-containing solution was added to an aqueous solution of sodium salicylate or salicylic acid. The ratio of the volumes of the initial and final solutions was 1 : 10; this ratio was adjusted with distilled water. The mixture was stirred for 1 h. The precipitate was filtered off, washed with distilled water, and dried in air.

Powder X-ray diffraction analysis of precipitation products was carried out on a DRON-3 diffractometer (Cu K_{α} radiation; counter speed: 0.5 deg/min). Differential thermal analysis (DTA) and weight loss (TG) curves were recorded on an MOM derivatograph; the heating rate was 10 K/min. Absorption spectra in the IR range (400-4000 cm⁻¹) were recorded as disks with calcined KBr on a Specord IR-75 spectrophotometer. Raman spectra were recorded on a Bruker FT-Raman spectrometer model RFS 100/S equipped with an Nd:YAG laser (maximal power: 5 W; laser wavelength: $1.64 \,\mu\text{m}$). Electron micrographs were obtained using a JEM-2000FXII transmission electron microscope (accelerating voltage: 200 kW). pH was measured on an OP-264/1 pH meter with a glass electrode. Specific surface areas were measured chromatographically as thermal argon desorption.

Bismuth(III) macroconcentrations in solutions were titrated with complexone III with the Xylenol Orange indicator. Bismuth(III) microconcentrations were determined photocolorimetrically with sodium iodide [14]. Precipitation products were dissolved in dilute HNO_3 (1 : 1) under heating. Salicylate anions and

nitrate ions in solid reaction products were determined after they were solubilized by 2 M NaOH at 70–90°C. Salicylate ions and free salicylic acid in precipitates were determined photocolorimetrically [15]. Free salicylic acid was determined after it was solubilized by ethanol. Nitrate ions were determined photometrically with sodium salicylate [16].

RESULTS AND DISCUSSION

Our experiments to precipitate basic bismuth salicylate by sodium salicylate solutions from perchloric acid solutions at 23 and 70°C (Fig. 1; curves 1, 2) or by salicylic acid solutions at 70°C (Fig. 1, curve 3) showed that the percentage bismuth precipitation depends on the amount of salicylate ions and temperature. As the salicylate ion concentration or temperature increases, the percentage bismuth precipitation (R) also increases. When the mole ratio of salicylate ions to bismuth in solution (n) is 1.0, the percentage bismuth precipitation is (1) 83.1, (2) 95.8, and (3) 91.7%. As n increases to 1.1, the percentage bismuth precipitation increases to 94.5, 99.9, and 96.5%, respectively. When bismuth is precipitated from nitric or hydrochloric acid solutions, the percentage precipitation also increases with salicylate ion concentration; it is at least 99.0% for n = 4 in nitric acid solutions (Fig. 1, curve 4) and for n = 6 in hydrochloric acid solutions (Fig. 1, curve 5).

Chemical analyses of the products of bismuth precipitation by sodium salicylate from perchloric acid solutions at 70°C with n varied from 0.25 to 6 (pH increases from 1.4 to 4.4, respectively) indicate that these precipitates are bismuth monosalicylate $BiC_7H_5O_4$. The analyses were as follows (%): bismuth, 57.6 (calcd., 57.7); salicylate ion, 37.6 (calcd., 37.9); free salicylic acid, at most 0.2%; and n = 1.0. The compound has characteristic X-ray diffraction peaks with *d*/*n* of 2.38, 2.78, 2.83, 3.33, 3.46, 3.68, 3.77, 4.16, 4.60, 5.43, 7.42, 8.30, 10.2, 11.0, and 16.4 (Fig. 2 curve a). The precipitates obtained at 23°C are also bismuth monosalicylate as identified by chemical analysis and X-ray powder diffraction; the admixture of free salicylic acid increases with increasing n because of the low water solubility of salicylic acid under ambient temperature and pressure [17].

Inasmuch as salicylic acid is dibasic (in acid and neutral solutions, it dissociates with the elimination of carboxyl proton ($pK_1 = 2.8$), and in alkali solutions, with the elimination of the phenolic hydroxide proton ($pK_2 = 13.4$) [18]), we studied the percentage bismuth precipitation and the composition of precipitates as affected by solution pH in order to substitute bismuth-containing cations for the two protons of salicylic acid. In these experiments, an alkali solution of bis-cylate was added to perchloric acid solutions of bis-

muth with n = 0.5. After the system was alkalinized until its equilibrium pH was 1.4, bismuth monosalicylate precipitated. When equilibrium pH was 3.7 and 8.8, precipitates were X-ray amorphous and the ratio of salicylate ions to bismuth was 0.82 and 0.50, respectively. IR and Raman spectra did not contain characteristic bands of doubly deprotonated salicylate anions. Therefore, the samples synthesized under the specified conditions are likely mixtures of bismuth monosalicylate and oxohydroxoperchlorate.

When salicylic acid was used to precipitate bismuth from perchloric acid solutions at 70°C, the precipitates with n ranging from 0.25 to 1.5 were identified by X-ray diffraction with bismuth monosalicylate. The precipitate prepared with n = 1.0 contained 57.1% bismuth, 37.8% salicylate ions, and 0.13% free salicylic acid. Thus, salicylic acid precipitates bismuth as monosalicylate with n varied from 0.25 to 1.5. As the ratio of salicylate ions to bismuth in solution increased to 2, the precipitate contained 46.6% bismuth and 45.7% salicylate ion; the ratio of salicylate ions to bismuth in the precipitate was 1.5. The X-ray diffraction pattern for the precipitate contained peaks from bismuth monosalicylate and extra peaks with d/n: 1.88, 2.06, 2.26, 2.31, 2.73, 3.15, 3.26, 3.99, 4.31, 4.44, 4.54, 4.99, 6.14, 6.77, 7.48, and 14.9 (Fig. 2, curve b). These peaks are the major ones for compounds prepared with *n* increasing from 3 to 4 (Fig. 2, curve *c*). For example, the precipitates prepared with n = 3 and 4 contained 41.9% bismuth (calcd., 42.5%) and 55.9% salicylate ions (calcd., 55.8%); the stoichiometric ratio of salicylate ions to bismuth was 2.0, corresponding to the formation of bismuth disalicylate. Chemical analysis, IR, and Raman spectra showed that the aqueous ethanol treatment of the precipitates at room temperature did not change the product composition. The X-ray diffraction patterns of the products do not contain peaks from free salicylic acid, d/n: 2.26, 2.37, 2.46, 2.54, 2.58, 2.74, 2.81, 2.93, 3.12, 3.21, 3.56, 5.22, 5.91, and 8.22.

Our experiments also show that, when the mole ratio of salicylate ions to bismuth increases to 5-20, the precipitation products are mixtures of bismuth disalicylate and salicylic acid. This is verified by powder X-ray diffraction, IR spectroscopy, Raman spectroscopy, and chemical analysis. We failed to precipitate bismuth salicylate with the stoichiometry salicylate : bismuth = 3 from perchloric acid solutions.

When bismuth is precipitated by sodium salicylate from nitric acid solutions at 70°C and the mole ratio salicylate : bismuth = 0.5, the free salicylic acid concentration in solution is 0.5 mol/L. The precipitate from such solutions is dark red, apparently because of partial nitration of salicylic acid in solution with the formation of its nitro derivatives [19]. As the mole ratio increases further to 1.1, pH increases to 0.9 and the precipitate is



Fig. 2. X-ray diffraction patterns for (*a*) bismuth(III) monosalicylate, (*c*) bismuth(III) disalicylate, and (*b*) their mixture. θ is Bragg's angle (deg).

bismuth monosalicylate that contains 0.032% nitrate ions. As the ratio increases to 1.5, the precipitate is a mixture of bismuth monosalicylate and disalicylate. When n = 2-6, bismuth precipitates as disalicylate; pH changes from 1.1 to 4.2. When bismuth is precipitated from hydrochloric acid solutions by addition of sodium salicylate until the ratio of salicylate ions to bismuth in solution becomes 6, X-ray diffraction identifies the precipitate as bismuth oxochloride BiOC1 [20]. In this case, the sodium salicylate–induced decrease in hydrogen ion concentration in solution is responsible for the increased bismuth precipitation percentage.



Fig. 3. IR absorption spectra of (*a*) salicylic acid, (*b*) bismuth(III) monosalicylate, and (*c*) bismuth(III) disalicylate.



Thus, bismuth monosalicylate for use as a drug substance can be precipitated from both perchloric and nitric acid solutions (which are usually used to synthesize bismuth compounds) when the mole ratio of salicylate ions to bismuth in solution is 1.0 : 1.2.

We found X-ray diffraction data only for bismuth salicylate $Bi_2(C_6H_4OHCOO)_3$ in Hanawalt et al.' work [11]. Comparing the X-ray diffraction patterns of the precipitation products with various ratios of salicylate ions to bismuth (1, 1.5, and 2) (Fig. 2), we see that only two bismuth compounds (monosalicylate and disalicylate) can be precipitated from perchloric or nitric acid solutions. The product of the 1.5 stoichiometry is a mixture of these two compounds. Our data imply that bismuth salicylate described by Hanawalt et al. [11] as $Bi_2(C_6H_4OHCOO)_3$ with characteristic diffraction peaks (d/n = 2.02, 2.08, 2.26, 2.40, 2.52, 2.75, 3.15, 3.40, 3.98, 4.48, 4.95, 6.20, 6.80, 7.50, 16.0) is actually a mixture of bismuth monosalicylate and disalicylate.

Structural features of bismuth monosalicylate (I) and disalicylate (II) were determined from the analysis of IR absorption and Raman vibration spectra (Figs. 3, 4). Characteristic bands in the spectra were assigned with reference to the spectra of salicylic acid and other metal salicylates [21, 22]. For example, the substitution of a bismuth-containing cation for carboxy protons is proven by the following spectral features: antisymmet-

rical stretching vibrations of carboxylate groups $v_{as}(COO^{-})$ appear in the bismuth salicylate spectra as bands at 1525 and 1545 cm⁻¹ (IR) for I, 1519 and 1540 cm⁻¹ (Raman) for I, 1510 and 1540 cm⁻¹ (IR) for II, and 1504 and 1540 cm⁻¹ (Raman) for II; symmetrical stretching vibrations of carboxylato groups $v_s(COO^-)$ appear as bands at 1390 cm⁻¹ (IR) for I and 1414 cm⁻¹ (Raman) for I, 1365 cm⁻¹ (IR) for II and 1412 cm⁻¹ (Raman) for II; the bands of the stretching vibrations of the carbonyl v(C=O) at 1660 cm⁻¹ (IR) and 1636 cm⁻¹ (Raman), which appear in the spectra of salicylic acid [21], disappear from the spectra. For bismuth salicylates, $\Delta v(COO^{-}) = v_{as}(COO^{-}) - v_{s}(COO^{-})$ in IR spectra is 135 and 160 cm⁻¹ for **I** and 145 and 175 cm⁻¹ for **II**; these values indicate that the salicylate ligand in compound I is mainly bidentate coordinated and in compound II has bidentate and bidentate-bridging coordination [23].

The substitution of a bismuth-containing cation for protons in the carboxylate group of salicylic acid is proven by the following features of the IR spectra of bismuth salicylates: weak broad bands within 2500–3000 cm⁻¹ associated with the stretching mode v(OH)_{COOH}, bands of the out-of-plane bending vibrations δ_s (OH)_{COOH} at 892 cm⁻¹, and those of scissoring vibrations δ (OH)_{COOH} at 1445 cm⁻¹ do not appear; instead, medium-intensity



bands of scissoring vibrations $\delta_s(\text{COO}^-)$ appear at 860 cm⁻¹ in I and a weak band appears at 875 cm⁻¹ in II; bands of stretching vibrations v(Bi–O) appear at 485 cm⁻¹ (IR) for I and II, 365 and 391 cm⁻¹ (Raman) for I, and 353 and 389 cm⁻¹ (Raman) for II [24]; and strong bands of the bending vibrations δ (Bi–O) appear at 163 cm⁻¹ (Raman) for I and 154 cm⁻¹ (Raman) for II [25].

The existence of undissociated phenolic groups in coordinated salicylate anions is proven by the appearance of the stretching vibrations v(C–O) of the phenol group at 1250 cm⁻¹ (IR), 1237 and 1250 cm⁻¹ (Raman) for **I**, 1250 cm⁻¹ (Raman) for **II**; the in-plain bending vibrations δ (CO–H) at 1345 cm⁻¹ (IR), 1389 cm⁻¹ (Raman) for **I** and 1390 cm⁻¹ (Raman) for **II** in the spectra of bismuth salicylates. If the phenol hydroxide group were coordinated to the bismuth-containing cation via the oxygen atom, the stretching vibrations v(C–O) have shifted to lower frequencies [18].

The IR spectra of bismuth salicylates in the region 2950–3350 cm⁻¹ feature broad absorption bands with peaks at 3060 cm⁻¹ (for I and II), which are associated with the in-ring stretching vibrations v(CH), and peaks at 3200 cm⁻¹ (I) and 3180 cm⁻¹ (II) with a shoulder at 3260 cm⁻¹ (II); the last peaks are associated with the stretching vibrations of phenolic groups, which are involved in the system of hydrogen bonds.

From the examination of the IR and Raman spectra of bismuth salicylates and chemical analysis data, we infer that the bismuth-containing cations in our prepared compounds are bound to salicylate ligands through carboxy groups; the bismuth-containing cations are not directly coordinated to phenolic hydroxy groups. Our results imply that bismuth monosalicylate (I) and bismuth disalicylate (II) are formulated as $BiOC_7H_5O_3$ and $Bi_2O(C_7H_5O_3)_4$, respectively.

DTA and thermogravimetry (TG and DTG) for bismuth salicylate samples (Figs. 5a, 5b) in air indicate the occurrence of a series of consecutive endothermic and exothermic stages and the possibility of preparing bismuth oxides by thermolysis of its salicylates. Bismuth monosalicylate thermolysis starts with melting (endotherm at 280°C) and then involves the decomposition of salicylate ions (exotherm at 400°C) and the formation of bismuth oxide. The thermoanalytical curves for bismuth disalicylate have a more complex trend; endotherms appear at 180, 250, and 340°C and an exotherm appears at 400°C. According to X-ray diffraction data [20], bismuth monosalicylate thermolysis for 6 h at 300° C yields bismuth oxide as tetragonal β -Bi₂O₃, which transforms to monoclinic α -Bi₂O₃ at 350°C and above. We have not observed metallic bismuth, although it is usually formed as a result of thermolysis of monocarboxylates. We found metallic bismuth only in the products of monosalicylate thermolysis at 300-400°C in vacuo. However, metallic bismuth powders flash in air at ambient temperature, and their surface is covered by oxide. Noteworthy, the thermal transformations of bismuth monosalicylate and disalicylate are of practical value for preparing various bismuth oxide polymorphs for use in manufacturing bismuth oxide materials, and these transformations need special and comprehensive investigation. The thermoanalytical curves in both cases show that heating ends with bismuth oxide formation. The endotherm at 720°C is due to the polymorphic transformations of monoclinic α -Bi₂O₃ to cubic face-centered high-temperature δ -Bi₂O₃ (730°C) [26]. The latter is stable until the oxide melts (at 825°C) [26]; the relevant endotherm has a peak 810°C. The calculated weight loss for the thermolysis of BiOC₇H₅O₃ and Bi₂O(C₇H₅O₃)₄ to Bi₂O₃ agrees with the found value: 71.3 mg (calcd., 71.6 mg) and 104.4 mg (calcd., 105.1 mg), respectively.

Electron micrographs show that bismuth monosalicylate samples precipitated by salicylic acid from perchloric acid solutions at 70°C (pH 0.9) are needleshaped crystals (Fig. 6a) 10-20 um long and 0.2 um thick. As pH increases to 1.6, the product consists of needle-shaped crystals with sizes up to 1 µm; these crystals are piled into loose agglomerates up to 5 µm in size (Fig. 6b). Precipitation from nitric acid solutions with pH of 0.9-3 at 70°C yields bismuth monosalicylate in the form of needles 1-5 µm long and about 0.2 µm thick (Fig. 6c). The Ural Chemicals Plant produces bismuth monosalicylate as elongated crystals $10-30 \,\mu\text{m}$ long and $0.2-2 \,\mu\text{m}$ thick (Fig. 6d). The bismuth disalicylate samples (70°C, pH 0.9) precipitated from either perchloric or nitric acid solutions are elongated prismatic crystals with basis planes of $10-50 \,\mu\text{m}$ and thicknesses of $3-5 \,\mu\text{m}$ (Figs. 6e, 6f).

Our experiments also show that the specific surface area of bismuth monosalicylate depends on pH and temperature. For example, for bismuth monosalicylate precipitated from perchloric acid solutions at 70°C and pH 0.9 and 1.6, the specific surface area is 6.2 and 20.7 m²/g, respectively; at 25°C and pH 0.9, the specific surface area is 12.8 m²/g. Upon precipitation from nitric acid solutions at pH 2.0 and 50, 70, or 90°C, the specific surface area of bismuth monosalicylate is 9.9, 9.3, or 6.3 m²/g, respectively. Bismuth monosalicylate produced by the Ural Chemicals Plant (Specification TU 6-09-02-55-88) has a specific surface area of 0.80 m²/g. For bismuth disalicylate precipitated at 70°C from perchloric or nitric acid solution, the specific surface area is 0.25 and 0.20 m²/g, respectively.

Thus, bismuth is precipitated by sodium salicylate from perchloric acid solutions as monosalicylate



Fig. 5. Thermoanalytical curves for (a) bismuth(III) monosalicylate and (b) bismuth(III) disalicylate samples in air. Sample size: 200 mg.



Fig. 6. Micrographs of (a–d) bismuth(III) monosalicylate and (e, f) bismuth(III) disalicylate precipitated from (a, b, e) perchloric acid and (c, f) nitric acid solutions at 70° C and pH of (a, b, e, f) 0.9 and (c) 1.6. (d) Micrograph of a commercially available sample.

 $BiOC_7H_5O_3$, and from nitric acid solutions, both as monosalicylate and disalicylate $Bi_2O(C_7H_5O_3)_4$. In cases where salicylic acid is added to perchloric acid solutions, bismuth precipitates as monosalicylate or disalicylate, depending on the salicylate ion concentration. It is pertinent to prepare bismuth(III) monosalicylate from nitric acid solutions with mole ratios of salicylate ions to bismuth of 1.0–1.2, pH of 1–3, and temperature of 50–90°C. When mole ratios of salicylate ions to bismuth exceed 1.5, precipitates contain a bismuth disalicylate impurity; when the mole ratio is 3.0 or higher, bismuth disalicylate precipitates as an individual com-

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pound. We have shown that the synthesis parameters considerably affect the morphology and specific surface area of the products.

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