Precipitation of Bismuth(III) Oxobromide from Bromide Media

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Abstract—Abstract—X-ray phase analysis, thermogravimetry, IR spectroscopy, and chemical analysis were used to study bismuth(III) precipitation from nitrate solutions upon addition of aqueous solutions of hydrobromic acid or ammonium bromide, and from bismuth-containing hydrobromic acid solutions. The conditions in which bismuth(III) oxobromide of BiOBr composition is formed were determined and the possibility of obtaining a high-purity product was assessed.

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Bismuth oxobromide is used in veterinary medicine [1], in technology for manufacture of piezo-, pyro-, and ferroelectric materials, and in physical development of silver-containing photographic materials [2, 3]. This compound is obtained by dissolving bismuth oxide of reagent-grade purity in hydrobromic acid, with the subsequent dilution of the resulting solution with hot water [4, 5]. A method is known for preparation of bismuth oxobromide, in which a mannitol-containing aqueous solution of bismuth nitrate is reacted with an alkali metal bromide at pH 5.0–5.2 in the presence of a buffer mixture based on urotropin and hydrobromic acid [6].

Bismuth compounds are commonly synthesized from a metal of VI1 brand (mass fraction of Bi ≥98%) by dissolution of its grains in 9 M nitric acid, followed by hydrolytic purification of bismuth to remove impurity metals at pH 1.5–2.0 [7]. A disadvantage of this method is in that toxic nitrogen oxides are released into the gas phase in the stage of preparation of bismuth nitrate solutions, because the dissolution process occurs in accordance with the equation

$$\text{Bi}_2\text{O}_3 + 6\text{HNO}_3 = 2\text{Bi(NO}_3)_3 + 3\text{H}_2\text{O}. \hspace{1cm} (2)$$

Hydrobromic acid well dissolves bismuth oxide, as also does nitric acid, and the dissolution reaction has the form

$$\text{Bi}_2\text{O}_3 + 6\text{HBr} = 2\text{BiBr}_3 + 3\text{H}_2\text{O}. \hspace{1cm} (3)$$

It is of practical interest in this context to study synthesis of bismuth(III) oxobromide directly from solutions produced by dissolution of technical-grade bismuth oxide in nitric or hydrobromic acid.

This communication reports on a study of the influence exerted by the concentration of bromide ions and the process temperature on the purity and degree of bismuth(III) oxobromide precipitation from nitrate and bromide solutions. The metal was oxidized in a stainless steel reactor equipped with a screw for melt agitation. A single batch charged into the oxidation reactor was 150–160 kg. The metal was melted at a temperature of 350°C and bismuth oxide from the preceding stage of oxidation of metallic bismuth was introduced in an amount of 20% into the melt under agitation. The temperature was raised to 600°C and the powder was agitated for 6 h. The technical-grade oxide contained 88.4% bismuth.
Hydrolytic processing of technical-grade bismuth oxide I to give oxobromides II–IV

<table>
<thead>
<tr>
<th>Product</th>
<th>Pb</th>
<th>Cu</th>
<th>Ag</th>
<th>Fe</th>
<th>Zn</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.08</td>
<td>8.7 × 10⁻³</td>
<td>5.0 × 10⁻²</td>
<td>5.6 × 10⁻³</td>
<td>5.8 × 10⁻⁴</td>
<td>27 × 10⁻³</td>
</tr>
<tr>
<td>II</td>
<td>6.2 × 10⁻²</td>
<td>7.5 × 10⁻⁴</td>
<td>3.0 × 10⁻³</td>
<td>1.0 × 10⁻⁴</td>
<td>2.0 × 10⁻⁵</td>
<td>5.0 × 10⁻⁵</td>
</tr>
<tr>
<td>III</td>
<td>0.22</td>
<td>7.8 × 10⁻⁴</td>
<td>9.0 × 10⁻³</td>
<td>5.2 × 10⁻⁴</td>
<td>1.2 × 10⁻⁵</td>
<td>3.6 × 10⁻⁵</td>
</tr>
<tr>
<td>IV</td>
<td>4.8 × 10⁻⁵</td>
<td>1.0 × 10⁻⁶</td>
<td>2.0 × 10⁻⁶</td>
<td>&lt;1.0 × 10⁻⁴</td>
<td>1.0 × 10⁻⁵</td>
<td>5.0 × 10⁻⁶</td>
</tr>
</tbody>
</table>

Its composition (I) in terms of impurity metals is presented in the table.

A bismuth(III) nitrate solution containing 380 and 110 g l⁻¹ of Bi(III) and free nitric acid, respectively, was prepared by dissolving technical-grade oxide in 6 M nitric acid. The composition corresponded to that of solutions commonly used in the technology of bismuth compounds. A bismuth(III) bromide solution containing 385 g l⁻¹ of bismuth and 70 g l⁻¹ of free hydrobromic acid was obtained by dissolving technical-grade bismuth(III) oxide in 7 M hydrobromic acid. The volume ratio between the starting and final bismuth-containing solutions was 1 : 10. Upon addition of hydrobromic acid or an ammonium bromide solution to the bismuth nitrate solution, it was adjusted by addition of distilled water.

The bismuth-containing bromide solution was processed by its dilution with distilled water (1 : 9). This was done in glass vessels with the use of stirrers. The mixture was agitated for 20 min. After settling for 0.5 h, the precipitate was filtered off with the use of a vacuum, washed on the filter with distilled water, and dried in air. An X-ray phase analysis (XPA) of the precipitation products was made on a DRON-3 diffractometer with CuKα radiation, counter rotation rate of 0.5 deg min⁻¹, and I = 4000. Curves of differential thermal analysis (DTA) and thermogravimetry (TG) were measured for the samples under study on an MOM derivatograph (Hungary) at a heating rate of 10 deg min⁻¹. Electron microscopic images of the products were obtained using a JSM-20 scanning electron microscope with a resolution of 200 Å. The specific surface area of the samples obtained was measured by the chromatographic method of thermal desorption of argon. Macroscopic amounts of bismuth(III) in the liquid and solid phases were determined by titration with a solution of Complexon III, with Xylenol Orange as indicator, and microscopic amounts, by photocoelometry in the presence of KI. The concentrations of metals (Pb, Ag, Cu, Fe, Zn) were determined by the atomic-absorption method on a Saturn 2M spectrophotometer. The precipitation products were preliminarily dissolved in nitric acid (1 : 1). The concentration of nitrate ions was found by voltammetry on a renewable copper electrode [9], and that of bromide ions, on a silver electrode, after being transferred to solution by preliminary treatment with a sodium hydroxide solution (2 M) at 70–90°C.

The study of the hydrolytic processing of bismuth-containing bromide solutions demonstrated that, upon their dilution with distilled water (1 : 9), the degree of bismuth(III) recovery into oxobromide at 25 and 65°C is 97.9 and 96.5%, respectively. In precipitation of bismuth(III) from nitrate solutions by addition of a hydrobromic acid solution, the dependence of the degree R of metal precipitation on the molar ratio n between bromide ions and bismuth in solution passes through a maximum at 1.0–1.1 (Fig. 1). In this case, the degree of bismuth(III) precipitation is 99.4%. The decrease in the degree of bismuth(III) precipitation at n > 1 is due to the formation of bromide complexes of the type BiBr₃⁻, which hinders bismuth precipitation in the form of oxobromide. It can also be seen in Fig. 1 that raising the process temperature has virtually no effect on

![Fig. 1. Degree R of bismuth(III) precipitation from a nitrate solution vs. the molar ratio n between bromide ions and bismuth(III) in the system. Process temperature (°C): (1) 22 and (2) 90.](image-url)