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Phase diagrams of the system $Bi(NO_3)_3$–Na_2TeO_3–H_2O at 25 and 100 °C

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Abstract

The solubility iostherms of the $Bi(NO_3)_3$–Na_2TeO_3–H_2O system at 25 and 100 °C have been studied. The phase states of bismuth tellurites in aqueous medium, as well as under the conditions of their thermolysis, have been established.

INTRODUCTION

A few data concerning the phase states of bismuth tellurites in aqueous medium have been reported so far [1,2]. According to some authors [1], when aqueous solutions of $BiCl_3$ and sodium tellurite were mixed stoichiometrically, $Bi_2(TeO_3)_3 \cdot 3H_2O$ precipitated. Other authors [2] reported that $Bi_2(TeO_3)_3$ and $(BiO)_2TeO_3$ were obtained as a result of mixing $Bi(NO)_3$ and Na_2TeO_3 at 298 K. $Bi_2(TeO_3)_3$ was also prepared by fusing Bi_2O_3 and TeO_2 [3]. The existence of $Bi_2(TeO_3)_3$ has, however, been doubted by some [4].

The aim of the present work was to study the phase composition of the compounds in the $Bi(NO_3)_3$–Na_2TeO_3–H_2O ternary system at 25 and 100 °C. The solubility isotherm was obtained in accordance with I.V. Tananaev's method of residual concentrations. The compounds in the system studied were partly identified by their solubility isotherm and by the pH dependence of the mole ratio of the precipitator with respect to the ion precipitated. Other means of identification involved both crystallo-optical and preparative methods, the latter concerning all solid phases present in the system. After thorough washing and drying of the solid phases, chemical and X-ray diffraction analyses were also employed.

EXPERIMENTAL

$Bi(NO_3)_3 \cdot 5H_2O$ and $Na_2TeO_3 \cdot 5H_2O$ (p.a.) were used as starting materials. Volumetric (100 cm^3) mixtures with constant $Na_2TeO_3 \cdot 5H_2O$ initial concentration (0.025 mol l^{-1}) and gradually decreasing $Bi(NO_3)_3 \cdot 5H_2O$ contents were prepared, in order to study the whole system at both 25 and 100 °C. The experiments at 25 °C were carried out with the mixtures of the $Bi(NO_3)_3$–Na_2TeO_3–H_2O system in thermostated glass vessels, the temperature being maintained at 25 ± 0.1 °C by constant-temperature water circulation. The study of the corresponding system at 100 °C proceeded by placing the mixtures in 13 glass ampoules, which were sealed and heated at 100 ± 0.5 °C, using an air thermostat. The $TeO_3^{2-} : Bi^{3+}$ ratio in these ampoules was kept within the range 0–5. Kinetic curves were obtained in order to determine the time necessary to reach equilibrium. After the equilibrium state had been established, the liquid phases were separated from the corresponding solids by filtration at the experimental temperature. The solid phases were analysed using both the preparative and crystallo-optical methods. After thorough washing and drying, the solid phases were also subjected to chemical analysis and X-ray diffractometry.

The chemical analysis was by a complexometric technique at pH 9 using Eriochrom Black T as an indicator [5]. TeO_3^{2-} anions were analysed either by the bichromate method or gravimetrically as elementary tellurium [6]. An optical microscope, Type Dokuval (Germany), was employed for the crystallo-optical studies. X-ray phase analysis was carried out according to the Debay–Sherer method using a Dron-2 apparatus with a Cu anode, $K\alpha$ emission and a nickel filter for β-emission. A laboratory pH meter, LP-17 (pH range 0–14), was used for measuring pH values. The thermal properties were studied on a derivatograph OD-102 (MOM, Hungary).

Two phases were found to be present in the $Bi(NO_3)_3$–Na_2TeO_3–H_2O system at 25 °C. A double salt, $Bi_2(NO_3)_3 \cdot Bi_2(TeO_3)_3$, was formed when the ratio of the components, n, was in the range 0.20–0.75. Oxytellurite $2Bi_2O_3 \cdot Bi_2(TeO_3)_3$ or $(BiO)_2TeO_3$, was formed when the component ratio increased to $n = 1$–3, and, in particular, in the presence of an excess of hydroxyl anions with respect to the stoichiometric quantity.

The double salt $Bi(NO_3)_3 \cdot Bi_2(TeO_3)_3$ was the only compound found in the $Bi(NO_3)_3$–Na_2TeO_3–H_2O system at 100 °C, when the mole ratio $Na_2TeO_3 : Bi(NO_3)_3$ was 1 (Fig. 1). Phases of variable composition, $xBi(NO_3)_3 \cdot yBi_2(TeO_3)_3$, were, however, formed in the system with $n =$ 0.20–0.25. The conclusions of some authors [4] concerning the non-existence of $Bi_2(TeO_3)_3$ following study of the Bi_2O_3–TeO_2 diagrams and their T–X projections, have been confirmed by the present investigations. The presence of the double salt $Bi(NO_3)_3 \cdot Bi_2(TeO_3)_3$ as the only compound in the $Bi(NO_3)_3$–Na_2TeO_3–H_2O system at 100 °C, was confirmed by the solubility isotherm, the chemical preparative method, the crystallo-optical studies., the chemical analysis and the IR spectra of the solid phases. Additional evidence was also provided by the pH value as a function of the TeO_3^{2-}/Bi^{3+} mole ratio (Fig. 2), and from the X-ray diffractograms of the solid phases in the system (Fig. 3).

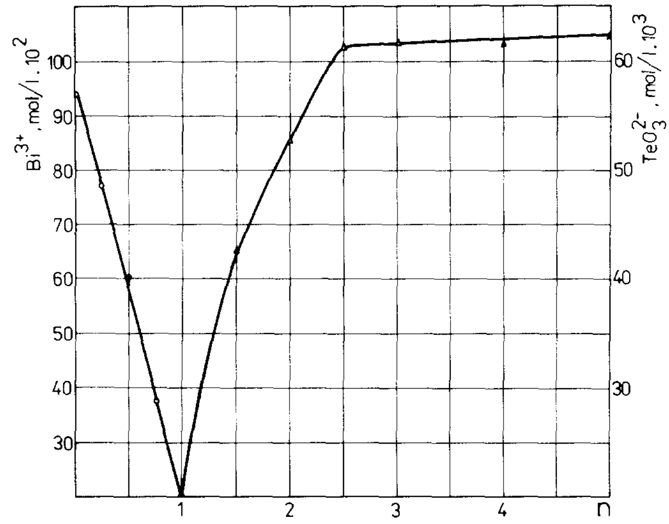

Fig. 1. Solubility of the $Bi(NO_3)_3$–Na_2TeO_3–H_2O system at 100 °C.

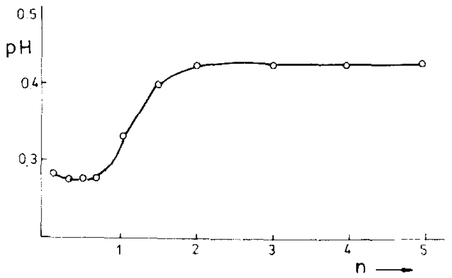

Fig. 2. The pH dependence of the molar ratio $Na_2TeO_3 : Bi(NO_3)_3$.

Thus, all our attempts to prepare $Bi_2(TeO_3)_3$, either at 25 or at 100 °C, were unsuccessful. It is our definite conclusion that $Bi_2(TeO_3)_3$ is unlikely to exist, either as $Bi_2(TeO_3)_3$ alone or as a crystallohydrate. The authors of references 1 and 2 were obviously wrong to state that they had obtained

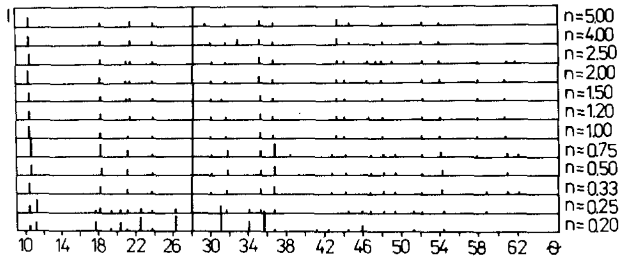

Fig. 3. X-ray pattern of the solid phases of the system $Bi(NO_3)_3$–Na_2TeO_3–H_2O at 100 °C ($n = TeO_3^{2-} : Bi^{3+}$).

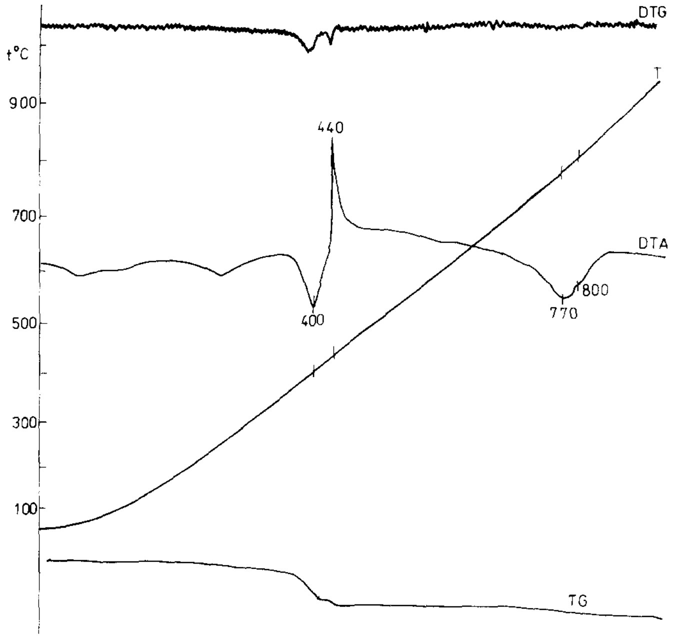

Fig. 4. Derivatogram of $Bi(NO_3)_3 \cdot Bi_2(TeO_3)_3$.

either $Bi_2(TeO_3)_3 \cdot 3H_2O$ or $Bi_2(TeO_3)_3$ in aqueous medium. Our close review of these works has shown that they conducted chemical and derivatographic analyses of the compounds alone, without determining the composition of the volatile products formed during the thermal dissociation. It is probable that no water was obtained under the conditions of thermal dissociation and the composition of the products remained unknown [2].

Several effects were observed on the derivatogram of the double salt (Fig. 4). The endothermal peak at 400 °C corresponds to a decomposition accompanied by elimination of 3 moles of NO_2 per mole of double salt. This was confirmed thermogravimetrically (a weight loss of about 10%) and visually, by the dark colour of the NO_2 liberated. In addition, elemental analysis indicated 3.15 % N (by mass) in the corresponding sample.

The exothermal effect at 440 °C is not accompanied by any mass change and corresponds to a crystallisation of the amorphous oxosalt $Bi_2O_3 \cdot 2Bi_2(TeO_3)_3$ formed initially. This was confirmed by the X-ray diffraction pattern of a $Bi(NO_3)_3 \cdot Bi_2(TeO_3)_3$ sample heated for a prolonged time at 400 and 500 °C, respectively. The endothermal effect of 770–800 °C corresponds to incongruent melting of the bismuth oxotellurite obtained. A change in mass is also observed at this temperature. The thermal destruction of bismuth oxotellurite accompanied by formation of TeO_2 at 920 °C is negligible, amounting to 3.2% of the total $Bi_2O_3 \cdot 2Bi_2(TeO_3)_3$ mass.

The derivatogram of bismuth oxotellurite, $2Bi_2O_3 \cdot Bi_2(TeO_3)_3$ or Bi_2TeO_5, (Fig. 5) shows a mass increase starting from 630 °C, indicated by an

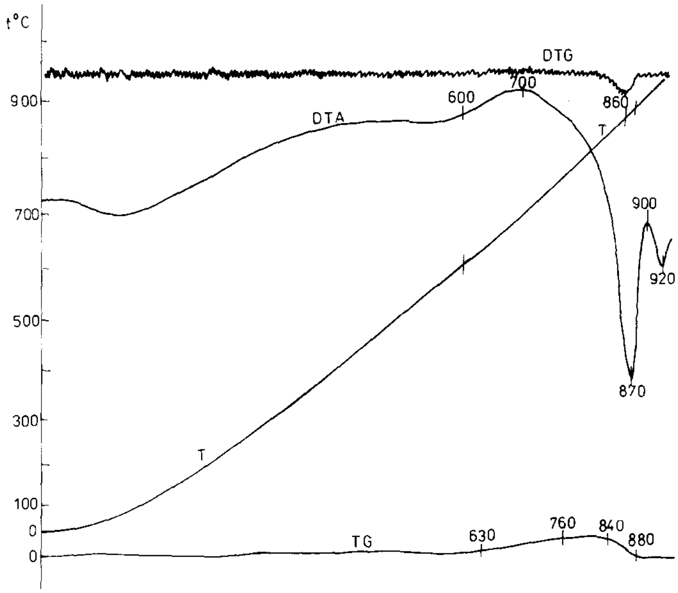

Fig. 5. Derivatogram of Bi_2TeO_5.

exothermic effect at 700 °C. The partly formed bismuth orthotellurate begins its thermal decomposition at 870 °C, leading to a reduction of the initially oxidised sample, so that Bi_2TeO_5 is formed again. This was concluded after modelling the conditions of heating, as well as the chemical and X-ray phase analyses, of samples heated at temperatures lower than 630 °C, and at 840 °C. X-ray analysis of samples heated at 840 °C showed that all the X-ray diffraction patterns indicated interplanar distances and intensities in close accordance with those of the bismuth orthotellurate phase previously described by the author [7]. The melting temperature of Bi_2TeO_5, determined as 920 °C, is in good agreement with the literature data [4].

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