

Metal tellurites in the three-component systems $\text{Hg}(\text{NO}_3)_2\text{-Na}_2\text{TeO}_3\text{-H}_2\text{O}$ at 25 and 100 °C

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(Received 20 March 1991)

Abstract

The system $\text{Hg}(\text{NO}_3)_2\text{-Na}_2\text{TeO}_3\text{-H}_2\text{O}$ was studied at 25 and 100 °C using crystallo-optical analyses, X-ray phase analysis, solubility isotherms, chemical analysis, and thermal analysis.

INTRODUCTION

The data concerning the synthesis of mercuric tellurites are rather scarce. Last century, mercuric tellurite was obtained from aqueous medium by Berzelius [1]. In more recent years, mercuric tellurite was synthesised by an interaction between a 0.5 N solution of $\text{Hg}(\text{CH}_3\text{COO})_2$ and sodium tellurite [2]. In these cases, the compound was obtained from fixed concentrations of the starting materials. Systematic data for the synthesis of mercuric tellurites and their properties are not available.

EXPERIMENTAL

Pure-for-analysis $\text{Hg}(\text{NO}_3)_2$ and $\text{Na}_2\text{TeO}_3 \cdot 5\text{H}_2\text{O}$ were used to study the system.

The preparation of the samples, the kinetics of reaching equilibrium, and the drawing of the solubility isotherm have been described in detail by the present authors in ref. 3. Chemical analysis of the equilibrium liquid and solid phases was made complexometrically for mercury [4,5], and by the bichromatic method [6] or gravimetrically as elementary tellurium [7], for tellurite ions.

The compounds in the system were identified by the solubility isotherm by plotting the pH against the mole ratio $\text{TeO}_3^{2-} : \text{H}^{2+}$, by the chemical preparative method [8] and, after obtaining them in the pure state, by chemical analysis. In addition, the compounds were identified by a

crystallo-optical method and by X-ray phase analysis. Crystallo-optical analyses were carried out using a Dokuval microscope (Karl Zeiss, Jena, Germany). X-ray phase analysis was made on a DRON-2 apparatus with Cu $K\alpha$ radiation and a nickel filter for β -emission. Thermographic studies were performed using an apparatus constructed by the authors of ref. 9.

RESULTS AND DISCUSSION

The study of the system $\text{Hg}(\text{NO}_3)_2\text{-Na}_2\text{TeO}_3\text{-H}_2\text{O}$ at 25°C showed that only one compound, HgTeO_3 , is obtained over the concentration range under study. Unlike zinc tellurites and cadmium tellurites, which are amorphous at 25°C , HgTeO_3 is in the crystalline state.

The interaction between the components in the system $\text{Hg}(\text{NO}_3)_2\text{-Na}_2\text{TeO}_3\text{-H}_2\text{O}$ at 100°C (Fig. 1) is very complicated. At a ratio between the components of up to $n = 1$, HgTeO_3 is obtained in the solid phase (exp.: HgO , 57.38%; TeO_2 , 42.58%; theor.: HgO , 57.58%; TeO_2 , 42.42%).

The isotherm shows that, at a mole ratio between the components of $n = 2$ and 3, the initial ions precipitate completely, owing to the synthesis of HgTe_2O_5 and HgTe_3O_7 in the solid phase. The composition of pyrotellurite, HgTe_2O_5 , determined by chemical analysis is HgO , 40.39%; TeO_2 , 59.69% (theoretical: HgO , 40.43%; TeO_2 , 59.57%). Chemical analysis indicated that the composition of HgTe_3O_7 is HgO , 30.39%; TeO_2 , 68.90% (theor.: HgO ,

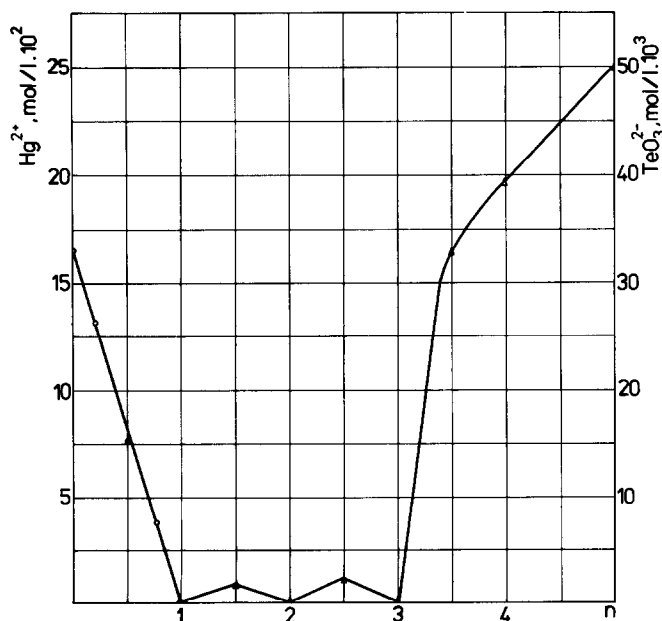


Fig. 1. Solubility for the $\text{Hg}(\text{NO}_3)_2\text{-Na}_2\text{TeO}_3\text{-H}_2\text{O}$ system at 100°C .



Fig. 2. The pH dependence on the molar ratio $\text{Na}_2\text{TeO}_3 \cdot \text{Hg}(\text{NO}_3)_2$.

31.15%; TeO_2 , 68.85%). The synthesis of HgTe_3O_7 is also confirmed by the maximum on the pH curve as a function of the mole ratio of the initial components (Fig. 2).

The hatched X-ray pattern (Fig. 3) shows that HgTeO_3 is obtained as an equilibrium solid phase at $n = 0.5-1$. In addition, HgTe_2O_5 and HgTe_3O_7 are also indicated as definite solid phases. With considerable excess of $\text{Hg}(\text{NO}_3)_2$, a phase with composition varying between $\text{Hg}(\text{NO}_3)_2$ and HgTeO_3 was obtained at $n = 0.2-0.5$. The X-ray pattern of HgTeO_3 is identical with that given in ref. 2 by Markovskii and Pron for the interplanar distances and the relative intensities of the lines. Mercuric tellurites are white crystalline substances, slightly soluble in water and fairly soluble in aqueous solutions of concentrated acids.

The thermogram of mercuric tellurite has three endothermic peaks (Fig. 4). The first endothermic peak at 247°C is assigned to the removal of residual adsorbed moisture. X-ray phase analysis does not indicate any phase change. Chemical analysis of a sample heated to 247°C showed that the phase obtained is HgTeO_3 (HgO , 57.53%; Te_2O_2 , 42.44%). The second endothermic peak at 445°C is not due to any weight loss in the sample; the HgO and TeO_2 contents in the sample correspond to stoichiometric calcula-

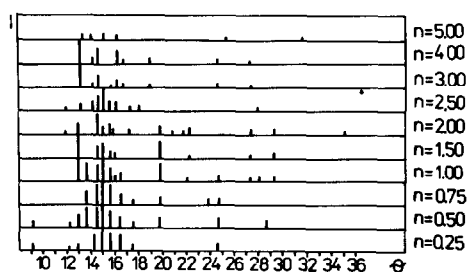


Fig. 3. X-ray pattern of the solid phases of the system $\text{Hg}(\text{NO}_3)_2 - \text{Na}_2\text{TeO}_3 - \text{H}_2\text{O}$ at 100°C ($n = \text{TeO}_3^{2-} : \text{Hg}^{2+}$)

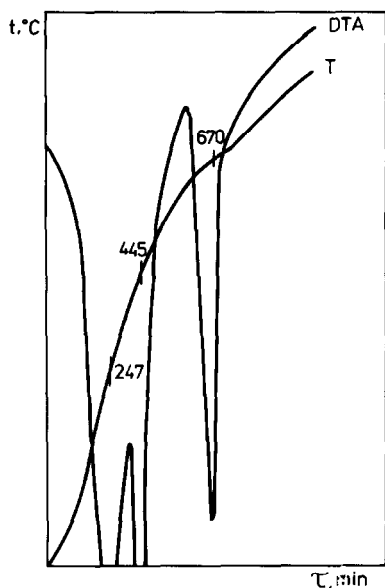


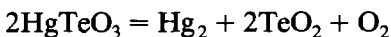
Fig. 4. Derivatogram of HgTeO_3 .

tions. According to X-ray phase analysis data, that peak can be assigned to the polymorphous transition of $\alpha\text{-HgTeO}_3$ to $\beta\text{-HgTeO}_3$. The last endothermic peak at 670°C is due to incongruent melting of the compound and its decomposition, which can be observed visually.

The thermal decomposition of mercuric tellurite at a fixed temperature is accompanied by liberation of mercury and oxygen as a gaseous phase and further addition of TeO_2 to the products left after decomposition.

In ref. 3, tellurium dioxide is reported to begin to evaporate only above its melting temperature, 730°C . In ref. 2, the assertion that tellurite decomposes at 510°C and that the decomposition product HgO evaporates (at 545°C) is not correct: the decomposition temperature of HgO is 440°C .

On the basis of these explanations, the following scheme for the thermal decomposition can be suggested:



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