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PHASE STATE OF TELLURITES IN THE $In(NO_3)_3$–$Na_2TeO_3(K_2TeO_3)_2$–H_2O SYSTEM

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ABSTRACT

The solubility isotherms of the $In(NO_3)_3$–Na_2TeO_3–H_2O system at 25 °C and in the $In(NO_3)_3$–K_2TeO_3–H_2O system at 100 °C have been constructed and studied. The compounds have been identified according to Cameron's method, and, after their isolation in a pure state, they have undergone chemical and X-ray phase analysis. The thermal dissociation of the compounds obtained has been also studied.

INTRODUCTION

The aim of this study is to investigate the formation, composition and some properties of compounds obtained as a result of the interaction of indium and tellurite ions in aqueous solution. The study was undertaken to augment the comparatively sparse data on this problem [1].

EXPERIMENTAL AND RESULTS

The three-component system was studied by physical and chemical analysis.

To draw the solubility isotherm of the two systems, $In(NO_3)_3$–Na_2TeO_3–H_2O at 25 °C and $In(NO_3)_3$–K_2TeO_3–H_2O at 100 °c, Tananaev's method of residual concentrations [2] was used. This method is based on the knowledge that at a solution–precipitate equilibrium the composition of the precipitate formed can be determined by the change in solution composition. In a series of experiments, chemical precipitation was accomplished by adding increasing quantities of a precipitator to a constant quantity of the precipitating solution.

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The diagram of initial composition of the system, or composition of the mother solution, was drawn using the data from the chemical analysis of the solution, showing the remaining unreacted components in the system. This determined the composition of the precipitates formed.

The advantages of this method include simplicity and the possibility of determining phase compositions with constant or varying characteristics. Also, it allows some conclusions on the precipitate composition to be reached, which are of great importance in study of the precipitation process chemistry. A considerable amount of information can be obtained by studying systems of this kind or by achieving a molar component ratio (precipitator–precipitating component) pH.

The pH study of equilibrium solutions (mother solutions) permits the composition of the equilibrium phases obtained to be determined. In many of their studies, Tananaev et al. [3,4] proved the applicability of pH study to this purpose. The chemical analysis of In^{3+} in the liquid and solid phases was carried out through a reverse compleximetric titration with an indicator such as Eriochrom Black T [5]. TeO_3^{2-} in the liquid phase was determined by the bichromatic method, and in the solid phase iodometrically or gravimetrically after its isolation as elementary tellurium [6]. The X-ray phase analysis was carried out by the Dubay and Sherer method using a DROH-3 apparatus with a copper anode, K_α radiation and a nickel β-radiation filter. The pH is measured using a laboratory digital pH-meter (type LP-17) designed for studying solutions in the pH range of 0–14. The apparatus was calibrated using three buffer solutions: biphthalic solution, pH 4.00; phosphate solution, pH 6.88; and borax solution, pH 9.22.

Derivatographic analysis was carried out on MOM type OD-102 apparatus. The crystal-optical properties were analysed on Docuval apparatus (Karl Zeiss–Jena).

The results of the analysis of $In(NO_3)_2$–Na_2TeO_3–H_2O system at 25 °C show that, in the concentration range $n = 0.2$–1.2, some basic indium tellurites can be isolated. They are transformed at $n = 1.5$ into indium tellurite $In_2(TeO_3)_3 \cdot 14H_2O$ (dried at room temperature to a constant weight). The solid phase washed and dried at 100 °C has the composition $In_2(TeO_3)_3 \cdot 3H_2O$ ($In_2O_3 = 27.07\%$ and $TeO_2 = 72.97\%$; theoretical composition is 26.96% In_2O_3 and 73.04% TeO_2). When $n = 2$ is a solid phase, a double salt with the composition $KIn(TeO_3)_2 \cdot 6H_2O$ is isolated. X-Ray structural analysis shows that $In_2(TeO_3)_3 \cdot 14H_2O$ and $In_2(TeO_3)_3 \cdot 3H_2O$ are X-ray amorphous, whereas $KIn(TeO_3)_2 \cdot 6H_2O$ is in crystalline state. From the reflex intensity of the X-ray pattern of $KIn(TeO_3)_2 \cdot 6H_2O$ and from the interspace distances it is found that the present results coincide with the data of Bolshakova and co-workers [1]. Analysis of the $In(NO_3)_3$–K_2TeO_3–H_2O system at 100 °C shows that, over the whole concentration range, only one compound was obtained — the anhydrous indium tellurite (Fig. 1). High temperature is favourable for the dehydration and crystalliza-

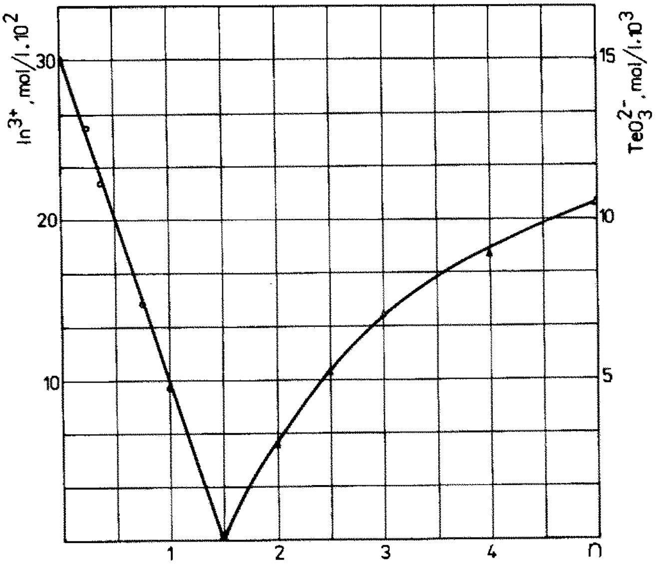

Fig. 1. Solubility isotherm for the $In(NO_3)_3$–K_2TeO_3–H_2O system at 100 ° C.

tion processes. These conclusions can be reached on the basis of the pH dependence in equilibrium solution of the molar ratio $TeO_3^{2-}:In^{3+}$ (Fig. 2). On the basis of the X-ray structural analysis it is found that indium tellurite $In_2(TeO_3)_3$ crystallizes in orthorhombic symmetry with elementary cell parameters $a = 8.074 \pm 0.001$ Å, $b = 9.203 \pm 0.001$ Å and $c = 54.465 \pm 0.001$ Å. The number of structural units in an elementary cell Z is four and the theoretical density is röntgens (R) = 6.27 g cm^{-3}. From the derivatographic analysis data (Fig. 3) and the chemical analysis, $In_2(TeO_3)_3 \cdot 14H_2O$ is stable on heating to 40 ° C, above this temperature a thermal dehydration process starts. This has three stages, which are shown on the derivatogram by three endo-effects, one each at 138, 240 and 302 ° C (Fig. 3). At 138 ° C the crystallo-hydrate isolates 4 mol of water (as a molar product) and is

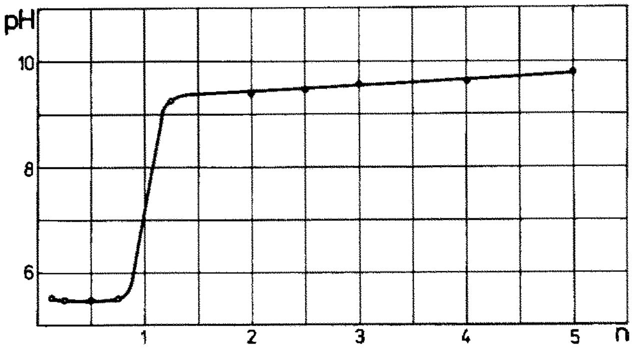

Fig. 2. The pH dependence of the molar ratio $K_2TeO_3:In(NO_3)_3$.

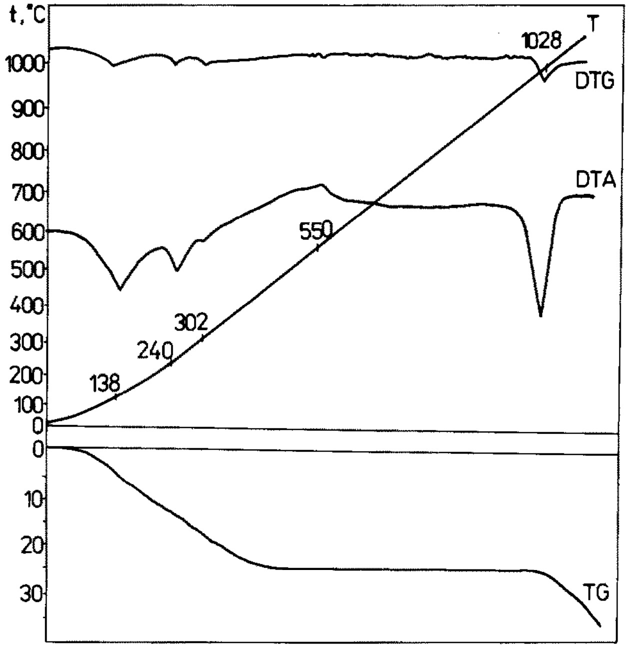

Fig. 3. Derivatogram of $In_2(TeO_3)_3 \cdot 14H_2O$.

transformed into $In_2(TeO_3)_3 \cdot 10H_2O$. At 240 °C, 8 mol are isolated and the product is transformed into $In_2(TeO_3)_3 \cdot 2H_2O$, and at 302 °C anhydrous $In_2(TeO_3)_3$ is obtained. These are in agreement with the following results of the chemical analysis: In_2O_3, 36.58% TeO_2, 63.55%. It should be noted that the initial and the aqueous indium tellurite, obtained on crystallo-hydrate dehydration, are X-ray amorphous (they register on an X-ray pattern). The exo-effect shown on the derivatogram at 550 °C responds to the transformation of the X-ray amorphous $In_2(TeO_3)_3$ to a crystalline form. This conclusion is substantiated by the fact that a sample heated within the temperature interval 302–550 °C is X-ray amorphous, whereas the same sample heated to 550 °C and higher is crystalline. The crystalline indium tellurite thus obtained is stable on heating to 1028 °C. At that temperature it melts and its thermal destruction starts, accompanied by tellurite dioxide isolation, until the In_2O_3 phase is obtained. Up to 1150 °C the weight loss is still negligible, and corresponds to an indium tellurite dissociation of about 10 wt.%. The temperature range thus obtained for $In_2(TeO_3)_3$ melting is in good agreement with the literature values of 1000 ± 30 °C [8] and 1030 °C [7].

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