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Note

Physico-chemical study of the three-component system $Cd(NO_3)_2$–Na_2TeO_3–H_2O at 25 and 100 °C

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INTRODUCTION

The literature data concerning the chemistry of the tellurites of cadmium are rather scarce. A method of obtaining cadmium tellurite in an amorphous state with composition $3CdTeO_3 \cdot 2H_2O$, by an interaction of solutions of sodium tellurite and cadmium chloride, was described by Lenher and Wolesensky [1]. The synthesis of an anhydrous product was reported in ref. 2. In this case, cadmium tellurite was a white amorphous precipitate obtained by mixing 0.5 N solutions of cadmium sulphate and sodium tellurite. According to ref. 3, cadmium tellurite can be obtained by a solid-phase reaction of a mixture of CdO and TeO_2 in stoichiometric ratio. Synthesis of $CdTe_2O_5$ from CdO and TeO_2 was also reported. The authors cited above synthesised cadmium tellurite from solutions at fixed volume concentrations of the initial solutions. No data are given as to the possibility of obtaining tellurites with different compositions, nor have any systematic studies of cadmium tellurites been carried out.

This work presents the results of a study of the interaction between $Cd(NO_3)_2$ and Na_2TeO_3 in aqueous solutions. The influence of pH on the reaction and the composition of the compounds obtained was studied. The system $Cd(NO_3)_2$–Na_2TeO_3–H_2O was studied at 25 and 100 °C by the Tananaev residue concentration method, by pH measurements and by analysis of the solid phases.

EXPERIMENTAL

The initial reagents were pure-for-analysis $Cd(NO_3)_2$ and $Na_2TeO_3 \cdot 5H_2O$. Samples with mole ratios of the components $n = 0.2$, 0.25, 0.50, 0.75, 1, 2 and 3 were used to study the system $Cd(NO_3)_2$–Na_2TeO_3–H_2O at 25 °C. They were thermostated in thermostatting glass vessels, the circulating water coming from a U-10 ultra-thermostat.

To study the system at 100 °C, 13 ampoules were prepared containing 50 ml of 0.0125 M $Na_2TeO_3 \cdot 5H_2O$. A 50 ml solution of $Cd(NO_3)_2$ was added

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to it in different concentrations, so that the mole ratio n (Na_2TeO_3: $Cd(NO_3)_2$) was from 0.2 to 5. The ampoules were sealed and then placed in an air thermostat at 100 ± 0.5 °C. They were periodically stirred. To study the kinetics of equilibrium, a series of ampoules was filled with the same components. They were thermostatted under the same conditions. Every 10 days an ampoule was opened, the liquid phase was analysed for Cd^{2+} and TeO_3^{2-} and the solid phase was subjected to chemical and X-ray analyses. Equilibrium was considered to be reached if the composition of the liquid and the solid phases remained the same. By X-ray analyses, equilibrium was said to be established if no change in the peak intensities and the interplanar distances of the phases was observed. The system was heated for three months. Then the ampoules were opened, the liquid phase was separated and removed, and the solid phase was chemically analysed.

Cadmium was analysed by inverse complexometric titration, following the technique described in ref. 4. Tellurium was analysed by the bichromatic method and gravimetrically as elemental tellurium [5]. The pH of the equilibrium solutions was determined with an LP-17 laboratory numerical pH-meter. Crystallo-optical analyses were made using a "Dokuval"-type microscope (Germany).

X-ray phase analyses were carried out on a TURM-61 M apparatus using Cu Kα emission and a nickel filter for β-emission.

An OD-102 derivatograph (MOM, Hungary) was used for the derivatographic analysis.

RESULTS AND DISCUSSION

The solubility isotherm of the system $Cd(NO_3)_2$–Na_2TeO_3–H_2O at 25 °C shows that the composition of the compound obtained is $CdTeO_3$. According to pH and chemical analysis data, all the solid phases have that composition. The separated solid phases were highly solvated, which made it difficult to separate them in the pure state. X-ray phase analysis shows that these phases are amorphous. Our results confirm the data obtained by Smirnova et al. [3], namely that the composition of the solid phase is $CdTeO_3$, not $3CdTeO_3 \cdot 2H_2O$.

According to the solubility isotherm of the system $Cd(NO_3)_2$–Na_2TeO_3–H_2O at 100 °C (Fig. 1), two compounds were formed: $CdTeO_3$ and $CdTe_2O_5$. Furthermore, as chemical and X-ray phase analyses show, a phase of varying composition was obtained at $n = 0.25$. The synthesis of these three compounds can be confirmed by the dependence of pH on the mole ratio of the equilibrium liquid solutions (Fig. 2) and the hatched X-ray pattern (Fig. 3). The differences in the composition and form of the crystals obtained point to the fact that amorphous $CdTeO_3$ crystallises at 100 °C. The high temperature favours hydrolysis of Na_2TeO_3, the reaction between H_2TeO_3 and the

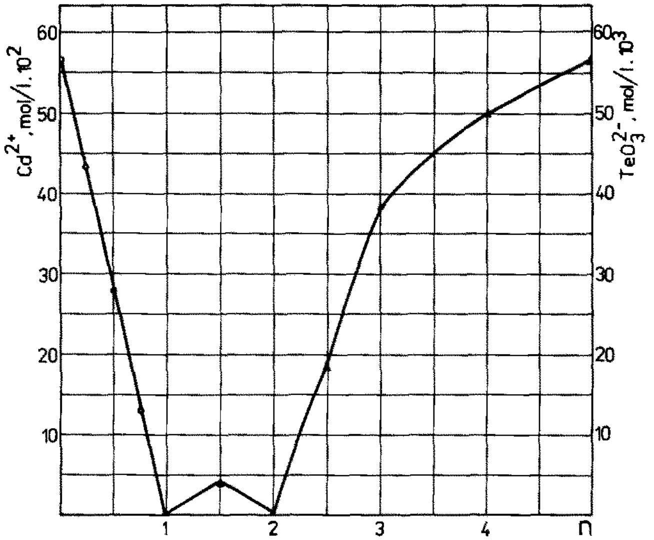

Fig. 1. Solubility for the $Cd(NO_3)_2$–Na_2TeO_3–H_2O system at 100 °C.

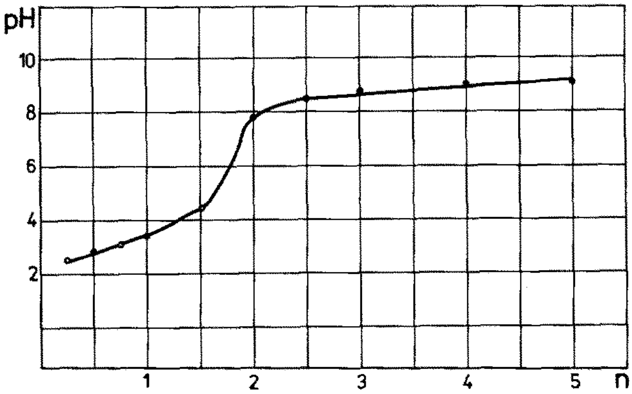

Fig. 2. pH of the equilibrium liquid phases.

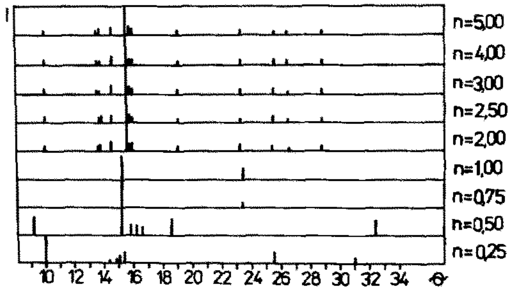

Fig. 3. X-ray pattern of the solid phases of the system $Cd(NO_3)_2$–Na_2TeO_3–H_2O at 100 °C ($n = TeO_3^{2-}: Cd^{2+}$).

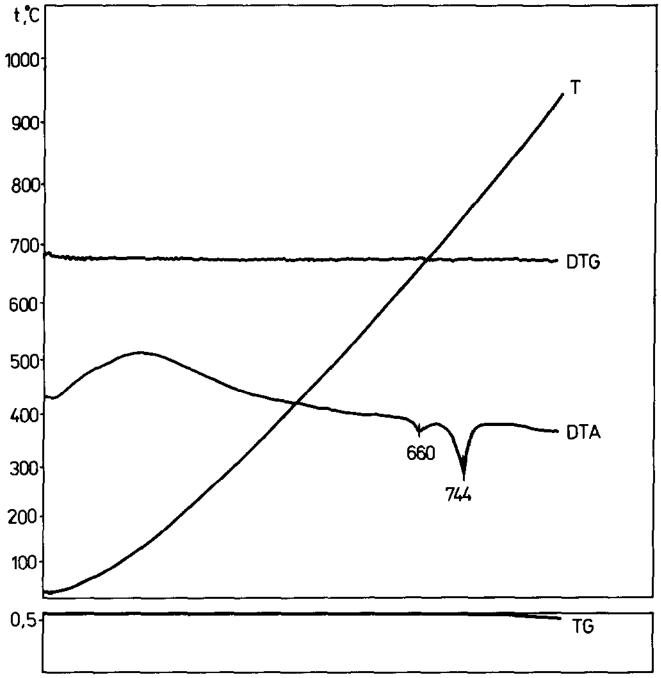

Fig. 4. Derivatogram of $CdTeO_3$.

newly formed amorphous $CdTeO_3$, and the synthesis of $CdTeO_3 \cdot H_2TeO_3$. A subsequent dehydration results in crystalline $CdTe_2O_5$.

The X-ray patterns of $CdTeO_3$ (after additional heating in the solid phase at 500 °C) and $CdTe_2O_5$ were studied. Cadmium tellurite crystallises in a cubic crystal lattice with $a = 5.345$ Å. The error allowed was ± 0.003 Å. $CdTe_2O_5$ crystallises in the monoclinic system with the parameters of the elementary cell being $a = 9.323 \pm 0.001$ Å, $b = 3.851 \pm 0.001$ Å, $c = 3.862 \pm 0.001$ Å and $\beta = 106°$.

Two endothermal peaks are visible on the derivatogram of $CdTeO_3$ (Fig. 4) at 660 and 744 °C. The first is not accompanied by any change in the sample weight. According to X-ray analysis, the peak at 660 °C corresponds to the enantiotropic polymorphic transition of cubic $CdTeO_3$ into hexagonal $CdTeO_3$. The peak at 744 °C is due to melting of the tellurite (the peak is reversible and melting can also be observed visually). The TG curve on the derivatogram shows that the tellurite is thermostable up to 950 °C. Further thermogravimetric studies up to 1200 °C show that $CdTeO_3$ is thermostable up to 1000 °C. At a higher temperature it begins to decompose, TeO_2 becoming a gas phase. The sample heated at 1200 °C decomposes 4.9%.

On the derivatogram of $CdTe_2O_5$ (Fig. 5), only the endothermal peak of melting at 665 °C is visible. The thermogravimetric curve demonstrates the insignificant but uniform weight change due to the dissociation of the compound, and the subsequent evaporation of TeO_2 on heating. The weight

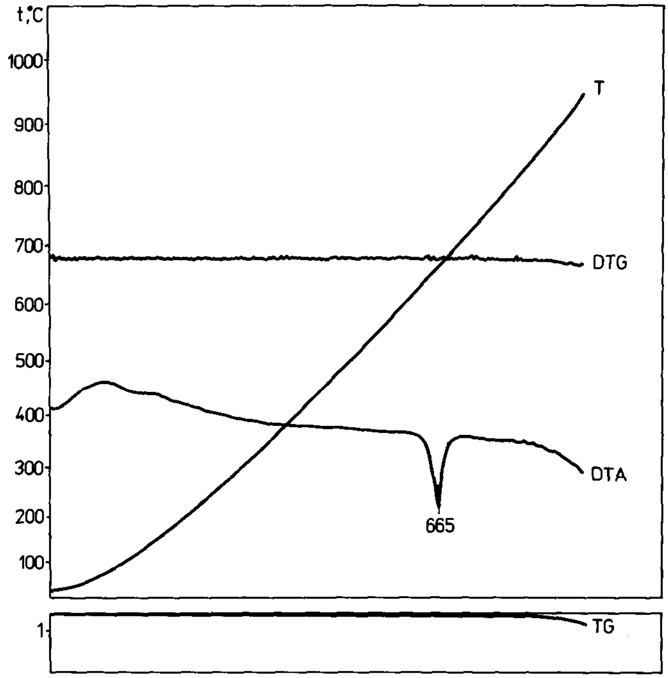

Fig. 5. Derivatogram of $CdTe_2O_5$.

change at 1000 °C is less than 1%. Oxidation of Te^{4+} to Te^{6+} is not observed, unlike as has been reported in the literature for other tellurites.

Chemical analysis of the samples heated at 950 °C shows that the concentration of the elements in the samples is nearly stoichiometric.

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