Thermochimica Acta, 191 (1991) 241-247
Elsevier Science Publishers B.V., Amsterdam

Phase states of tellurites in the three-component system $Cu(NO_3)_2$–Na_2TeO_3–H_2O at 25 and 100 °C

G.G. Gospodinov

Department of Inorganic Chemistry, Higher Institute of Chemical Technology, Bourgas (Bulgaria)

Received 21 December 1990

Abstract

The solubility isotherms of the system $Cu(NO_3)_2$–Na_2TeO_3–H_2O at 25 and 100 °C were studied and drawn by the method of residual concentration. The phase composition of the compounds obtained was determined. The thermolysis of copper tellurites was studied and the scheme of thermal decomposition was suggested.

INTRODUCTION

The data concerning the interaction of Cu^{2+} ions with alkaline tellurites are confined to two works on the synthesis of $CuTeO_3 \cdot xH_2O$: Berchenko and Beliaev report the synthesis of amorphous $CuTeO_3 \cdot 2H_2O$ [1] and Iakovleva and Ganelina [2] describe the synthesis of $CuTeO_3 \cdot H_2O$ and the phases of varying composition $xCuTeO_3 \cdot yCuSO_4$ and $xCuTeO_3 \cdot yCu(OH)_2$. However, the reaction mechanism of the synthesis and the conditions of existence of copper tellurites, as well as the possibility of obtaining tellurites with different compositions, have not yet been investigated.

The system $Cu(NO_3)_2$–Na_2TeO_3–H_2O was studied at 25 and 100 °C by "the solubility method" and the method of hydrogen ion concentration. The properties of the compounds obtained were determined.

EXPERIMENTAL

Analytically pure $Cu(NO_3)_2 \cdot 3H_2O$ and $Na_2TeO_3 \cdot 5H_2O$ were used as the starting materials. A constant volume of a solution of Na_2TeO_3 (50 ml) was placed in "razotherm" glass ampoules; the same volume (50 ml) of a solution of $Cu(NO_3)_2$ was then added, the concentration of $Cu(NO_3)_2$ decreasing with each experiment such that the mole ratio $TeO_3^{2-} : Cu^{2+}$ should be a whole number corresponding to the stoichiometry of the possible compounds. The ampoules were sealed and then placed in an air thermostat maintained at a temperature of 100 ± 0.5 °C where they were tempered. After reaching equilibrium the ampoules were opened, and the liquid and solid phases were separated by filtration at 100 °C through a G-4 filter. The filtrates were used to determine the concentration of Cu^{2+} and TeO_3^{2-}, and the pH. After removing the filtrate, the precipitate was analysed by the preparative methods described in ref. 3. The composition of the compounds in the systems was determined by the solubility isotherm and the dependence of pH on the mole ratio of the components, by chemical-preparative analysis of the solid phases and by chemical analysis of the thoroughly washed and dried solid phases. X-ray phase analyses and crystalo-optical analyses were made to determine the concentration interval of the phases. The chemical analysis for Cu^{2+} in both the liquid and solid phases was carried out by inverse complexometry at pH 9 with Eriochrome black T indicator [4]. TeO_3^{2-} ions were determined by the bichromate method and also gravimetrically as elementary tellurium after combining the Cu^{2+} ions with complexon [5]. Crystalo-optical analyses were made with a Dokuval-type optical microscope (GDR). X-ray phase analysis was carried out by the Debye and Sherer method on a DRON-2 apparatus with a Cu anode, Kα emission and a nickel filter for β emission. The pH was measured with an LP-17-type laboratory numerical pH-meter, measuring pH values of solutions from 0 to 14 pH. Before using, the device was calibrated by three buffers: a biphthalate solution of pH 4.00, a phosphatic solution of pH 6.88 and a borax solution of pH 9.22.

RESULTS AND DISCUSSION

The solubility isotherm of the system $Cu(NO_3)_2$–Na_2TeO_3–H_2O at 25 °C shows that only one compound, $CuTeO_3 \cdot 2H_2O$, was synthesised at $n = 0$–3. This tellurite is a flaky precipitate having great occluding ability. The sorbed substances are very difficult to separate from the precipitated tellurite.

Our experiments showed that mere washing by repeated boiling with distilled water does not lead to complete removal of the adsorbed ions. Comparing the adsorption ability of copper tellurites with the metal tellurites of the elements in groups IIB, IIIA, IVA and VA of the Periodic Table at 25 °C reveals a pronounced regularity: the adsorption ability of the tellurites increases depending on the position of the metal ions in the Periodic Table, downwards and from left to right. This tendency is particularly true of the tellurites of metals in the second group.

The results obtained by studying the solubility isotherm of the system $Cu(NO_3)_2$–Na_2TeO_3–H_2O at 100 °C are presented in Fig. 1. The initial concentration of Na_2TeO_3 was 0.0125 mol l^{-1} and the concentration of $Cu(NO_3)_2$ was 0.0500 mol l^{-1}. As Fig. 1. shows, there are two minima on the solubility curve, at $n = 1$ and 2. The first minimum corresponds to

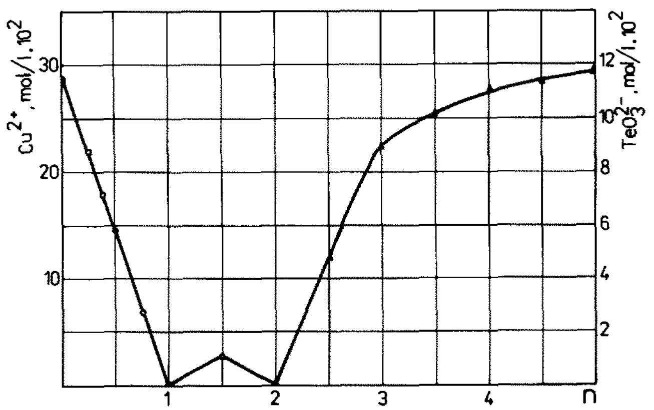

Fig. 1. Solubility for the $Cu(NO_3)_2$–Na_2TeO_3–H_2O system at 100 °C.

$CuTeO_3$ and the second to $CuTe_2O_5$. Chemical analysis shows that when the mole ratio of $TeO_3^{2-}:Cu^{2+}$ is from $n = 0.2$ to $n = 1.5$, the solid phases formed are $CuTeO_3 \cdot H_2O$. The results of the chemical analyses of this compound were: CuO; 30.79, 30.89 and 31.06%, and TeO_2; 82.13% (theoretical calculations for $CuTeO_3 \cdot H_2O$: Cu, 30.90% and TeO_2, 62.06%). From $n = 2$–4, $CuTe_2O_5$ is obtained in the solid phase. The data from the chemical analyses are: CuO; 19.91, 19.75 and 20.51% and TeO_2; 80.07, 80.26 and 79.49% (theoretical calculations for $CuTe_2O_5$: CuO, 19.95% and TeO_2, 80.85%). At $n = 5$, a product having an increased concentration of TeO_3^{2-} is obtained in the solid phase. The synthesis of these two compounds which is shown by the solubility curve, is also demonstrated by the dependence of pH on the mole ratio $TeO_3^{2-}:Cu^{2+}$ (Fig. 2) which has a minimum at $n = 1$ and a maximum at $n = 2$, and by the hatched X-ray pattern (Fig. 3). Preliminary studies showed that copper tellurite is obtained from aqueous solutions in the form of an amorphous product. Therefore, the crystallisation of the final product synthesised at 100 °C was

Fig. 2. The pH dependence of the molar ratio $Na_2TeO_3:Cu(NO_3)_2$.

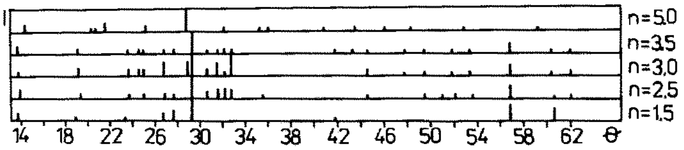

Fig. 3. X-ray pattern of solid phases of the system $Cu(NO_3)_2$–Na_2TeO_3–H_2O at 100 °C ($n = TeO_3^{2-} : Cu^{2+}$).

studied as a function of time. X-ray analysis showed that the compositions with n from 0.2 to 1, tempered at 100 °C for 1 year and corresponding to the synthesised copper tellurite $CuTeO_3 \cdot H_2O$, remain almost amorphous. Hence, they are not visible on the hatched X-ray pattern. Only at $n = 1.5$ is $CuTe_2O_5$ obtained and it has very good crystallinity. Our studies showed that this phase crystallises in the monoclinic system with parameters: $a = 6.870$, $b = 9.322$, $c = 7.604$ Å and $\beta = 109°\ 10' \pm 0.03$. The accuracy of a, b and c was ± 0.003 Å. No lines corresponding to the initial compounds were visible. By addition first of stoichiometric amounts of NaOH and then of $Cu(NO_3)_2$ to sodium tellurite, with preliminary temperature treatment of the solutions at 100 °C and tempering by the above method, $CuO \cdot$

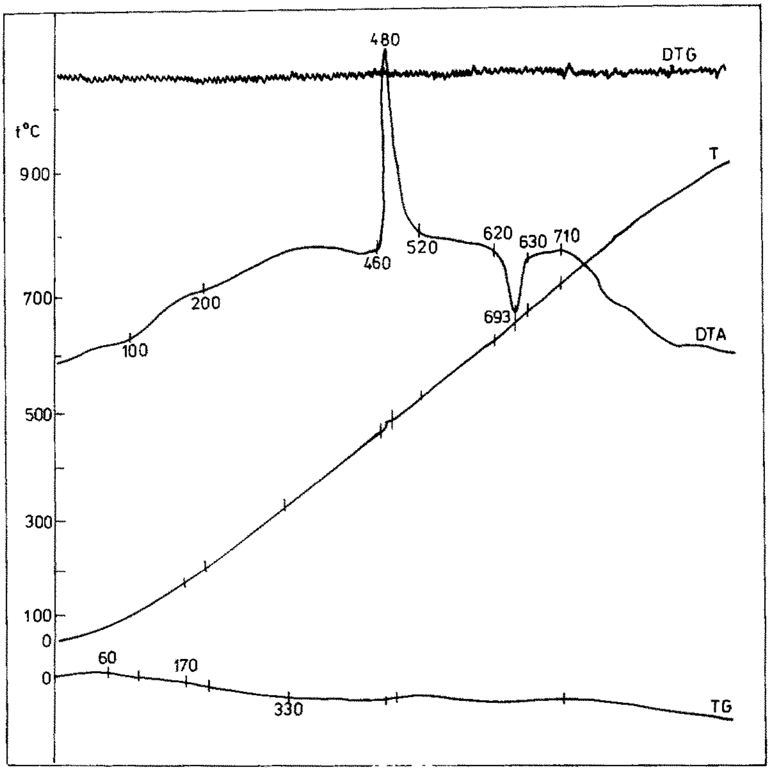

Fig. 4. Derivatogram of $CuTeO_3 \cdot H_2O$.

$CuTeO_3$ was obtained. X-ray phase analysis of this compound showed peaks which, according to their interplanar distance and intensity, correspond to the compound $CuO \cdot CuTeO_3$ obtained here by ampoule synthesis of CuO and TeO_2.

Oxotellurite $CuO \cdot CuTeO_3$ crystallises in an orthorhombic system: $a = 7.264$, $b = 16.027$, $c = 6.357$ Å (accuracy ± 0.002 Å). The number of formula units is $z = 8$ and the space group is D_{2h}^{16}. The experimental density $d_{exp.}$ is 5.77 and $d_{X\text{-ray}}$ is 5.68 g cm^{-3}. Insignificant endothermal peaks are visible at 100 and 200 °C on the derivatogram of $CuTeO_3 \cdot H_2O$ (Fig. 4) which correspond to dehydration of the tellurite. Furthermore, the weight loss is 3.5% which corresponds exactly to the transition $CuTeO_3 \cdot H_2O \rightarrow CuTeO_3$. This is also confirmed by chemical analysis data corresponding to the formula of the compound before heating, $CuTeO_3 \cdot H_2O$, (CuO, 30.90% and TeO_2, 62.09%) and the formula of the anhydrous product obtained by dehydration at 200 °C (CuO, 33.24% and TeO_2, 66.78%). X-ray phase analysis of $CuTeO_3$ shows that its structure is amorphous. The exothermal peak at 480 °C corresponds to crystallisation of anhydrous amorphous $CuTeO_3$. This peak is not accompanied by any mass change in the compounds. The peaks on the X-ray pattern of $CuTeO_3$ heated at that temperature have interplanar distances and intensities which correspond to

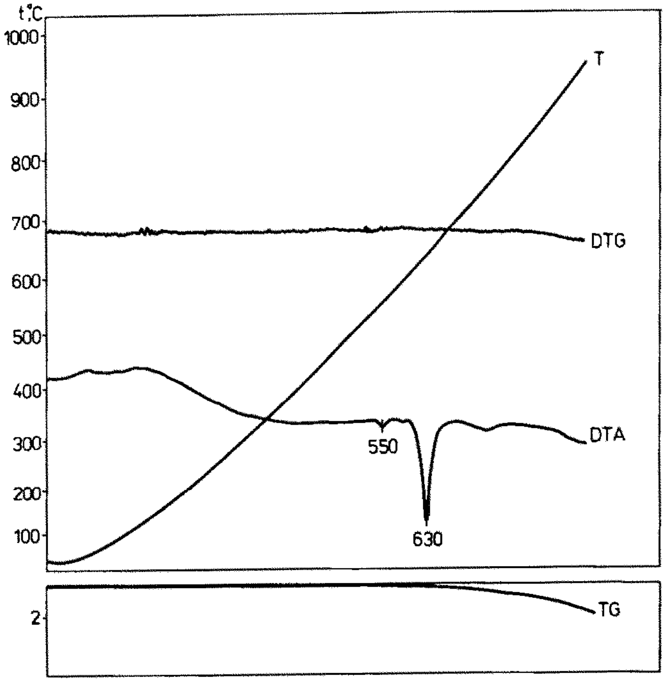

Fig. 5. Derivatogram of $CuTe_2O_5$.

crystalline $CuTeO_3$ synthesised by the author from CuO and TeO_2 using vacuum technology.

Copper tellurite, crystallising in an orthorhombic system, has the elementary cell parameters: $a = 7.607$, $b = 12.704$ and $c = 5.838$ Å (error allowed ± 0.005 Å), $d_{exp.} = 5.618$ and $d_{X\text{-ray}} = 5.634$ g cm^{-3}. The number of formula units is $z = 8$. The X-ray data obtained are in good agreement with those in ref. 6.

Two endothermal peaks are visible on the derivatogram of $CuTe_2O_5$ (Fig. 5). The first, small endothermal peak at 550 °C is not associated with a mass change in the tellurite. X-ray analysis shows that it is due to the enantiotropic polymorphous transition of α-$CuTe_2O_5$ into β-$CuTe_2O_5$. The large endothermal peak at 630 °C is due to melting of $CuTe_2O_5$ (this peak is reversible and melting was also determined visually). From 600 to 720 °C, there is an insignificant increase in the mass of the sample on the TG curve which is due to oxidation of pyrotellurite $CuTe_2O_5$ to Cu_3TeO_6. The endothermal peak at 758 °C is assigned to dissociation of the partially oxidised product to $CuTe_2O_5$. Dissociation of $CuTe_2O_5$ is insignificant. At 950 °C, to which the $CuTe_2O_5$ was heated, the weight loss is as little as 2%.

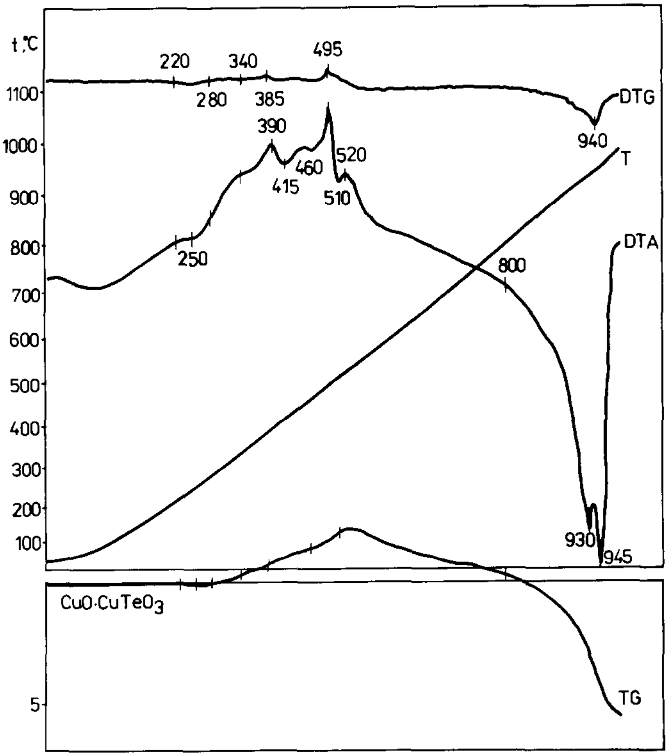

Fig. 6. Derivatogram of $CuO \cdot CuTeO_3$.

On the derivatogram of the oxotellurite, $CuO \cdot CuTeO_3$, recorded in air, a number of exothermal peaks are visible at 220–520 °C which are connected with an increase in the sample weight (Fig. 6). Chemical and X-ray phase analyses show that they are due to oxidation of $CuO \cdot CuTeO_3$ according to the scheme

$$3CuO \cdot CuTeO_3 + O_2 = 2Cu_3TeO_6 + TeO_2$$

The thermogram shows endothermal peaks at 930 and 945 °C which are assigned to melting and dissociation of the newly formed $CuO \cdot CuTeO_3$.

REFERENCES

1 M.A. Berchenko and A.I. Beliaev, J. Neorgan. Chim., 12 (1967) 1774.
2 V.S. Iakovleva and E.Ch. Ganelina, J. Neorgan. Chim., 4 (1959) 513.
3 E.V. Margulis, E.D. Meletina and L.I. Beisekeeva, Zh. Neorgan. Khim., IO (1965) 1481.
4 G. Chvarzenbach and G. Fliachka, Kompleksonometritcheskoe titrovanie, Chimia, Moscow, 1970.
5 S.Iu. Fainberg and N.A. Filipova, Analiz rud zvetnich metalov, Metalurgizdat, Moscow, 1963.
6 J. Moret, E. Filippot and M. Maurin, C.R. Acad. Sci. Paris, 269 (1969) C-123.