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Compounds in the three-component systems $Pb(NO_3)_2$–Na_2TeO_3–H_2O at 25 °C and $Pb(CH_3COO)_2$–Na_2TeO_3–H_2O at 100 °C and their physicochemical properties

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Abstract

The possible phases in the three-component systems were determined by drawing the solubility isotherms using the method of residual concentrations. The composition of a crystal hydrate of lead tellurite was more precisely determined than in the literature. The thermolysis of the compound obtained was studied, and the scheme of thermal decomposition was suggested.

INTRODUCTION

Data concerning lead tellurites are rather scarce and contradictory [1–4]. According to some authors [1,2] the compound $PbTeO_3$ does not exist. Other authors [3,4] report the synthesis of $PbTeO_3$ in the two-component system $PbO–TeO_2$. It is reported that the compound $3PbTeO_3 \cdot H_2O$ crystallises from an aqueous medium [3] or that the composition of the crystal hydrate obtained is $PbTeO_3 \cdot \frac{1}{3}H_2O$ [4].

While the composition of the oxotellurite is accepted as $2PbO \cdot PbTeO_3$ by all authors, they do not agree on the composition of the second tellurite. According to some [3] the composition of the oxotellurite is $4PbO \cdot PbTeO_3$, and according to others [2] its composition is $5PbO \cdot PbTeO_3$.

In order to determine the possible tellurites, these systems were studied by the solubility method and by pH measurements of the equilibrium liquid solutions. Analyses of the solid phases were also carried out by using two of the variants of the preparative analytical method.

EXPERIMENTAL

Pure-for-analysis $Pb(NO_3)_2$, $Pb(CH_3COO)_2$ and $Na_2TeO_3 \cdot 5H_2O$ were used to prepare the initial solutions. The titre of the solution of Na_2TeO_3 was determined by the bichromate method. In both cases, 50 ml of

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solutions of $Pb(NO_3)_2$ and $Pb(CH_3COO)_2$, respectively, with decreasing concentrations, were added to 50 ml of a solution of sodium tellurite with constant concentration, so that the mole ratio of the two components (precipitating agent and precipitating solution) was a whole number, $n =$ 0–5. In order to study the system at 25 °C, the samples were placed in thermostating glass vessels where constant temperature was maintained by continuously circulating water of constant temperature from an ultrathermostat. The samples were stirred continuously with a magnetic stirrer. To study the samples at 100 °C, they were placed in glass ampoules, then sealed and put in an air thermostat at 100 ± 0.5 °C. They were shaken periodically.

The time necessary for reaching equilibrium and separating the solid and the liquid phases at the experimental temperature was determined following the method in ref. 5.

Chemical analysis of Pb^{2+} ions was by inverse complexometric titration using an Eriochrome black T indicator at pH 9 [6]. TeO_3^{2+} ions were determined by the bichromate method, as well as gravimetrically as elementary tellurium [7]. Crystallo-optical analyses were made using a Dokuval 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, $K\alpha$ emission and a nickel filter for β-emission. The pH was measured with an LP-17 laboratory numerical pH-meter, used for solutions with pH from 0 to 14 (calibrated with standard buffer solutions).

RESULTS AND DISCUSSION

The analysis of the system $Pb(NO_3)_2$–Na_2TeO_3–H_2O at 25 °C shows that the phase $PbTeO_3 \cdot \frac{1}{3}H_2O$ is obtained in the concentration interval $n = 0.2$–1.0. According to chemical analysis data, it contains PbO, 57.4%, TeO_2, 41.05% and H_2O, 1.54%. These results are in good agreement with theoretical calculations. At $n = 1.5$–3 (which is the experimental concentration), the solid phase $Pb_2Te_3O_8$ is obtained containing PbO, 48.13% and TeO_2, 51.82% (theoretical calculations are: Pb, 48.25% and TeO_2, 51.75%).

The solubility isotherm of the system $Pb(CH_3COO)_2$–Na_2TeO_3–H_2O at 100 °C (Fig. 1) and the dependence of the pH of the equilibrium liquid solutions on the mole ratio between the ions of the precipitating solution and the precipitating agent (Fig. 2), show that an $n = 0.20$–0.75, phases with varying composition are obtained $x Pb(CH_3COO)_2 \cdot y PbTeO_3$. A double salt of similar composition (lead nitrate–lead selenite) has been described earlier in ref. 8. At $n = 1$–5, normal lead tellurite is obtained. The hatched X-ray pattern (Fig. 3) shows that all phases in the system are in the crystal state. Therefore, the high temperature favours dehydration of the

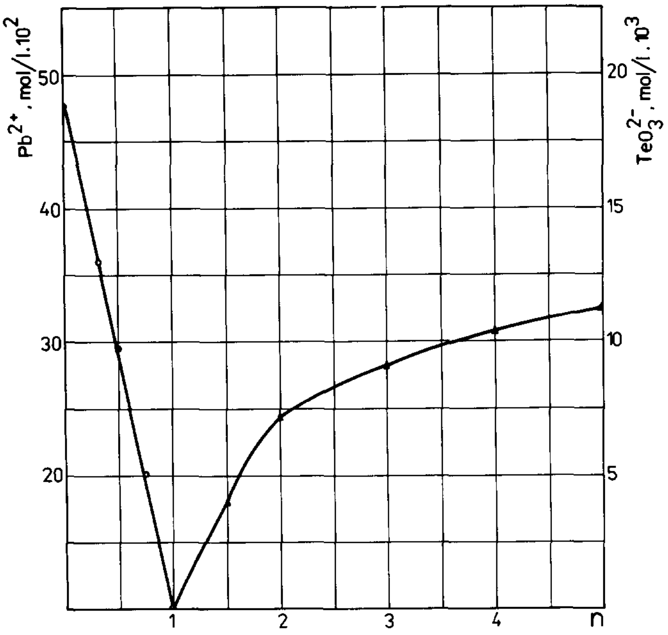

Fig. 1. Solubility for the $Pb(CH_3COO)_2$–Na_2TeO_3–H_2O system at 100 °C.

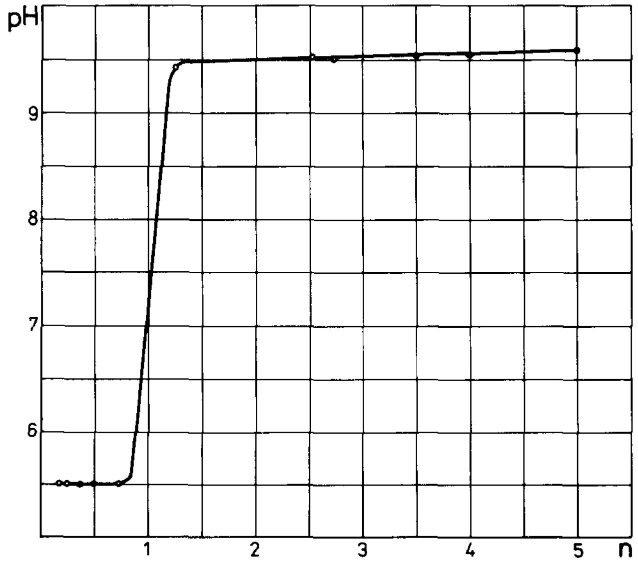

Fig. 2. pH dependence of the molar ratio Na_2TeO_3 : $Pb(CH_3COO)_2$.

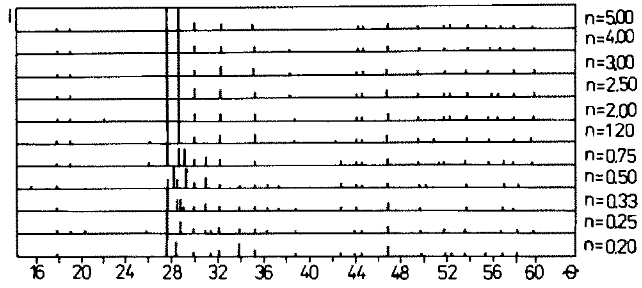

Fig. 3. X-ray pattern of the solid phases of the system $Pb(CH_3COO)_2$–Na_2TeO_3–H_2O at 100 °C ($n = TeO_3^{2+} : Pb^{2+}$).

crystal hydrate $PbTeO_3 \cdot \frac{1}{3}H_2O$ and crystallisation of an amorphous product. Comparison of the available X-ray data shows that the compound obtained is a low temperature α-$PbTeO_3$. According to the main lines of the X-ray pattern, α lead tellurite crystallises in a rhombic system with parameters: $a = 4.110 \pm 0.005$ Å, $b = 4.905 \pm 0.008$ Å and $c = 4.759 \pm 0.00$ Å. All the lines on the X-ray pattern are clearly identified if the parameters of the sub-lattice a and c are doubled and those of the sub-lattice b are increased three times. All lines of β lead tellurite are indicated as belonging to a tetragonal system with doubled parameters of the sub-lattice, $a = 5.321 \pm 0.005$ Å and $b = 5.951 \pm 0.005$ Å.

In order to study the possible oxosellenites in the three-component system Me–Te–O, the system $PbTeO_3$–$NaOH$–H_2O was studied at 100 °C. For that purpose, lead tellurite was added to aqueous solutions of NaOH with concentrations of 0–7 moles NaOH per mole of $PbTeO_3$ and a constant volume of 100 ml. The samples were put into flat-bottomed flasks which were sealed. They were thermostated at 100 °C for 10 days and were stirred continuously. The composition of the equilibrium and solid phases was determined both by the amount of NaOH present (or by its absence) in the mother solution and by preparative analysis of the solid phase.

Furthermore, the composition of the solid phases was determined after they were thoroughly washed and dried. Chemical analysis shows that at mole ratio $NaOH : PbTeO_3 = 2:3$, a solid phase is obtained which is oxotellurite with composition $2PbO \cdot PbTeO_3$ (PbO, 80.81% and TeO_2, 19.28%). At mole ratio $NaOH : PbTeO_3 = 4:5$, the solid phase obtained is oxotellurite $4PbO \cdot PbTeO_3$ (PbO, 87.43% and TeO_2, 12.60%). At intermediate and higher concentrations, a mixture of oxotellurites or a mixture of $4PbO \cdot PbTeO_3$ and PbO was obtained. The composition of these compounds was also determined by X-ray phase analysis. The interplanar distances and intensities of all the lines on the X-ray patterns correspond to these compounds, i.e. no lines belonging to $PbTeO_3$ or PbO were visible.

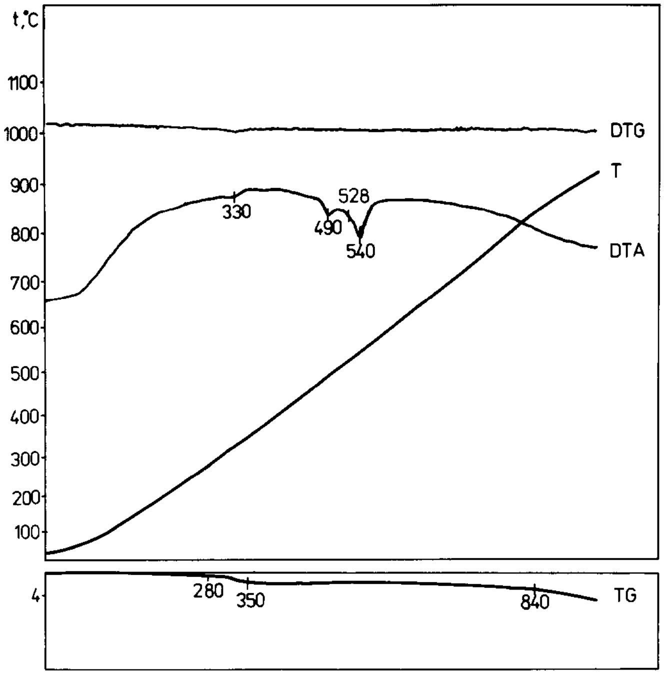

Fig. 4. Derivatogram of $PbTeO_3 \cdot 1/3H_2O$.

The derivatogram in Fig. 4 shows that the lead tellurite obtained is a crystal hydrate. The literature data are contradictory concerning the number of molecules of crystallisation water present. According to Tananaeva and Novoselova [3], the molar ratio between crystallisation water and tellurite is 2:3, and according to Young [4] it is 1:3. Under our experimental conditions, namely, prolonged crystallisation and drying of the product at 100 °C, the number of molecules of crystallisation water is $\frac{1}{3}$ mole per mole of tellurite. This is confirmed by the thermogravimetric curve (the weight loss is 1.5%) as well as by the gravimetric and chemical analysis of samples heated at 400 °C. Water loss begins at 280 °C but complete dehydration takes place at 350 °C. The second endothermal peak on the derivatogram corresponds to the transition of anhydrous lead tellurite from a tetragonal to monoclinic system. This is demonstrated by X-ray analysis.

The phase transition temperature is in good agreement with Young's data [4] (485 °C) but it differs substantially from the temperature reported by Tananaeva and Novoselova [3]. This difference is perhaps due to the unsatisfactory quality of their thermogram for $PbTeO_3$. Moreover, a double endothermal peak is visible on our thermogram due to overlapping of the endothermal peaks at 528 and 555 °C corresponding to the melting of $PbTeO_3$ and its decomposition. From 400 °C to the melting temperature of

$PbTeO_3$, an increase in sample weight is observed on the thermogravimetric curve which is accounted for by the interaction of tellurite with atmospheric oxygen and the synthesis of lead orthotellurite. The thermogravimetric curve also indicates the decomposition temperature of the partially obtained orthotellurite and the synthesis of tellurite at high temperatures. $PbTeO_3$ is thermostable up to 840 °C. At higher temperatures, it decomposes, TeO_2 is obtained and normal tellurite becomes oxotellurite $2PbO \cdot PbTeO_3$. Upon further elevation of temperature and formation of TeO_2, $2PbO \cdot PbTeO_3$ becomes $4PbO \cdot PbTeO_3$. After the final TeO_2 is formed, $4PbO \cdot PbTeO_3$ is converted into high-temperature lead oxide, PbO.

On the basis of the dehydration and dissociation of lead tellurite described above, the following scheme for these processes may be suggested:

$$PbTeO_3 \cdot \tfrac{1}{3}H_2O \xrightarrow{350\,^\circ C} PbTeO_3(\text{tetragon.}) \xrightarrow{490\,^\circ C} PbTeO_3(\text{monocl.}) \xrightarrow{\text{oxid.}}$$

$$Pb_3TeO_6 \xrightarrow{555\,^\circ C} PbTeO_3\,(\text{melting}) \xrightarrow{840\,^\circ C} 2PbO \cdot PbTeO_3 \xrightarrow{875\,^\circ C}$$

$$4PbO \cdot PbTeO_3 \xrightarrow{900\,^\circ C} PbO\,(\text{yellow})$$

On the derivatogram of oxotellurite $2PbO \cdot PbTeO_3$ at 670–800 °C, an increase in its weight and its transition Pb_3TeO_6 can be observed. The reduction and transition of oxotellurate to oxotellurite is observed upon further heating, the dissociation rate increasing after melting at 882 °C. The derivatogram of oxotellurite $4PbO \cdot PbTeO_3$ shows an increase in sample weight at 670–835 °C which is due to oxidation and transition of oxotellurite $4PbO \cdot PbTeO_3$ into oxotellurate $2PbO \cdot Pb_3TeO_6$. At temperatures above 950 °C, both compounds are unstable. This leads to reduction of oxotellurate to oxotellurite and further dissociation of the latter, TeO_2 being formed as a gas phase.

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