

**Influence of temperature, vanadium concentration,
and degree of solution acidification
on composition of the solid products**
**V. System sodium metavanadate—thallium(I)
acetate—acetic acid (nitric acid)—water**

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The influence of concentration of starting solutions, acidification degree, temperature, properties of the acid used, and length of the reaction time on composition of the solid products arising in the systems $\text{NaVO}_3\text{—CH}_3\text{COOTl—CH}_3\text{COOH—H}_2\text{O}$ and $\text{NaVO}_3\text{—CH}_3\text{COOTl—HNO}_3\text{—H}_2\text{O}$ was investigated. The optimum conditions of the preparation of TlVO_3 and $\text{Tl}_3\text{V}_5\text{O}_{14}$, as well as the relations affecting the composition of the solid substances arising in the investigated systems were ascertained.

Исследовано влияние концентрации исходных растворов, степени окисления, температуры, свойств примененной кислоты и продолжительности реакции на состав твердых продуктов, образующихся в системах $\text{NaVO}_3\text{—CH}_3\text{COOTl—CH}_3\text{COOH—H}_2\text{O}$ и $\text{NaVO}_3\text{—CH}_3\text{COOTl—HNO}_3\text{—H}_2\text{O}$. Определены оптимальные условия получения TlVO_3 и $\text{Tl}_3\text{V}_5\text{O}_{14}$, а также зависимости, оказывающие влияние на состав твердых веществ, образующихся в изучаемых системах.

It follows from investigations carried out by several authors [1—6] that the composition of the solid vanadates crystallizing from aqueous solutions is dependent on a great deal of factors. Till the present time, the influence of pH and concentration of the solutions of reactants has been investigated best.

There are two ways of preparation of anhydrous thallium(I) polyvanadates, i.e. reactions between vanadium pentoxide and convenient thallium(I) salts in the solid phase [7—10] or thermal dehydrations of crystallohydrates of thallium(I) vanadates [11, 12] and preparations from aqueous medium. The preparations from aqueous medium appear to be more convenient because a reduction of vanadium(V) to vanadium(IV) may take place in reactions in the solid phase.

Though the preparations of some types of thallium(I) vanadates from solutions are described in literature [13, 14], a complex research comprising the influence of

several factors on the composition of these substances has not been carried out up to this time. This problem is the topic of the present paper.

Experimental

The chemicals used were anal. grade reagents of the Czechoslovak production. Sodium metavanadate was prepared according to [15] and its composition corresponded to $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$.

Vanadium(V) and thallium(I) were determined volumetrically by the use of a solution of FeSO_4 or KBrO_3 . The amount of water was calculated according to the formula: $\% \text{H}_2\text{O} = 100 - (\% \text{V}_2\text{O}_5 + \% \text{Tl}_2\text{O})$.

The concentration of the hydrogen ions was measured with a pH-meter, type OP 201/1 (Radelkis, Budapest) using an electrode of the type 807 — 1/A (Radelkis, Budapest).

The infrared spectra were measured in the range $400\text{--}2000 \text{ cm}^{-1}$ in nujol suspension with a spectrophotometer Spectromaster Grubb Parsons.

The powder diffraction patterns were obtained with an X-ray-diffractograph Phillips equipped with a goniometer PW 1058 by the use of the CuK_α radiation.

Syntheses

The syntheses in both investigated systems $\text{NaVO}_3\text{--CH}_3\text{COOTl--CH}_3\text{COOH--H}_2\text{O}$ and $\text{NaVO}_3\text{--CH}_3\text{COOTl--HNO}_3\text{--H}_2\text{O}$ were performed in an equal way. Two different concentrations of the starting solutions were used, i.e. the aqueous solutions of NaVO_3 and CH_3COOTl of the concentration of 0.1 and 0.05 mol dm^{-3} . CH_3COOH or HNO_3 of concentration 1 mol dm^{-3} was added to the solution of NaVO_3 in varying amounts so that the value of the degree of acidification Z rose in the range 0.1—0.8 Z by step of 0.1 Z . (Z gives the mole ratio of used acid to sodium metavanadate.) The pH of the solutions of NaVO_3 was in the range 4.3—6.7 for acetic acid and 2.7—6.4 for nitric acid. The syntheses were carried out at three different temperatures, i.e. 20, 40, and 60°C . The acidified solutions of NaVO_3 were made up with water to a constant volume and warmed to the required temperature. When the pH value of these solutions did not more change, the solutions of CH_3COOTl of equal concentration as solutions of NaVO_3 were added in such amounts that the ratio $n_n:n_v$ in the reaction system was 6:10. During all syntheses, the volume of the reaction mixture was kept constant by means of refluxes and the reaction mixture was stirred.

As thallium(I) vanadates are slightly soluble in water, the solid products were formed immediately after adding the solution of CH_3COOTl . In order to find out, how the contact time of the solid substance with the mother liquor affects its composition, the reaction products were isolated from the reaction system either after 2 min or after 24 h. The isolation time of 24 h was determined experimentally by analyzing the solid products taken from the reaction systems in certain time intervals. The results of analyses, i.r. spectra, and the diffraction patterns of the solid substances showed that their composition did not change in the time interval 24—96 h.

Results and discussion

The aim of the study of the above systems was to find out the influence of concentration of the starting solutions, acidification degree, temperature, properties of the acid used, and isolation time of the solid product obtained from the reaction medium on the composition of the solid thallium(I) polyvanadates which arise. Furthermore, the aim was to determine the optimum conditions of preparation of certain types of thallium(I) polyvanadates as well as other relations which will be of good use for optimization of the methods of synthesis of those thallium(I) polyvanadates which arose in the reaction mixtures.

TlVO_3 and $\text{Tl}_3\text{V}_5\text{O}_{14}$ were prepared in pure states from the systems.

TlVO_3 was formed in the system containing HNO_3 at $Z=0.1$, 40°C , and 0.1 mol dm^{-3} concentration of the starting solutions and in the system containing CH_3COOH at $Z=0.3$, 20°C , and 0.05 mol dm^{-3} concentration of the starting solutions. In both cases, the syntheses took 24 h.

$\text{Tl}_3\text{V}_5\text{O}_{14}$ was formed after 24 h in the system containing CH_3COOH at $Z=0.4\text{--}0.5$, 40°C , and 0.05 mol dm^{-3} concentration of the starting solutions.

In all other cases, mixtures of thallium(I) polyvanadates were formed. In these mixtures, TlVO_3 , $\text{Tl}_3\text{V}_5\text{O}_{14}$, $\text{Tl}_2\text{V}_6\text{O}_{16}$, $\text{Tl}_6\text{V}_{10}\text{O}_{28}\cdot 4\text{H}_2\text{O}$ and, in some cases, small amounts of a substance denoted X (Tables 1 and 2) were identified. On the basis of chemical analysis, we may assume that the substance X is thallium(I) polyvanadate with the ratio $n_{\text{Tl}}:n_{\text{V}} < 1:1$. The nature of substance X was unambiguously confirmed neither by X-ray phase analysis nor infrared spectroscopy because it was evidently present in the amounts which were under limits of the resolution power of these methods.

It follows from Tables 1 and 2 that the syntheses in the whole designed region could be performed only in the medium of acetic acid. When nitric acid was used, fine crystalline nonfilterable precipitates were formed after 2 min and at higher values of Z , the precipitates appeared immediately after adding the acid into the solution of NaVO_3 .

Even these data demonstrate the influence of the acid used in these syntheses. Although nitric acid enables us to investigate a broader pH region than acetic acid, it is not important from the view-point of preparation of thallium(I) vanadates of a defined composition. On the contrary, acetic acid makes possible a finer division of the pH interval, which is important for preparing thallium(I) polyvanadates that are very little soluble and differ slightly from each other by solubility. For this reason, it is preferable to use starting solutions of low concentration for their preparation.

Among the investigated factors, the degree of acidification Z affects the composition of thallium(I) polyvanadates most. Our results show that the portion of thallium(I) polyvanadates with higher contents of vanadium increases in the

Table 1

Composition of the substances arising in the system $\text{NaVO}_3\text{—CH}_3\text{COOTl—CH}_3\text{COOH—H}_2\text{O}$

| Concentration of solutions | | 0.1 mol dm ⁻³ | | | | | | 0.05 mol dm ⁻³ | | |
|----------------------------|-----|--------------------------|------------------------------|-------------|------|------------------------------|-------------|---------------------------|------------------------------|-------------|
| Duration of synthesis | | 2 min | | | 24 h | | | 24 h | | |
| Temperature | Z | pH | $n_{\text{Tl}}:n_{\text{V}}$ | Composition | pH | $n_{\text{Tl}}:n_{\text{V}}$ | Composition | pH | $n_{\text{Tl}}:n_{\text{V}}$ | Composition |
| 20°C | 0.1 | 6.55 | 1:0.99 | M, X | 6.30 | 1:1.05 | M, D | 6.75 | 1:0.84 | M, X |
| | 0.2 | 6.25 | 1:1.04 | M, D | 6.00 | 1:1.08 | M, D | 6.10 | 1:0.95 | M, X |
| | 0.3 | 6.00 | 1:1.19 | D, M, P | 5.80 | 1:1.22 | M, D, H, P | 5.90 | 1:1.02 | M |
| | 0.4 | 5.85 | 1:1.26 | D, M, P | 5.70 | 1:1.42 | D, M, H, P | 5.70 | 1:1.14 | M, D, H |
| | 0.5 | 5.60 | 1:1.55 | D, M, P | 5.60 | 1:1.58 | D, P, H, M | 5.80 | 1:1.48 | D, M, H |
| | 0.6 | 5.60 | 1:1.65 | D, P, H, M | 5.50 | 1:1.62 | D, P, H, M | 5.90 | 1:1.55 | D, P, H, M |
| | 0.7 | 5.40 | 1:1.65 | D, P, H, M | 5.40 | 1:1.65 | D, P, H, M | 5.70 | 1:1.57 | D, P, H, M |
| | 0.8 | 5.25 | 1:1.64 | D, P, M | 5.20 | 1:1.64 | D, P, H, M | 5.60 | 1:1.65 | D, H, P |
| 40°C | 0.1 | 6.40 | 1:0.97 | M, X | 6.00 | 1:0.99 | M, X | 6.30 | 1:1.06 | H, P |
| | 0.2 | 6.20 | 1:1.17 | M, P, H, D | 6.30 | 1:1.31 | M, P | 6.25 | 1:1.18 | P, H |
| | 0.3 | 6.05 | 1:1.24 | M, P, D | 6.10 | 1:1.49 | P, M | 6.35 | 1:1.56 | P, M |
| | 0.4 | 5.75 | 1:1.50 | D, M, P | 6.00 | 1:1.45 | P, M | 5.95 | 1:1.64 | P |
| | 0.5 | 5.70 | 1:1.52 | D, M, P | 5.50 | 1:1.61 | P, D, H, M | 5.85 | 1:1.65 | P |
| | 0.6 | 5.60 | 1:1.62 | D, P, M | 5.40 | 1:1.63 | D, P, H, M | 5.50 | 1:1.63 | D, H, P, M |
| | 0.7 | 5.40 | 1:1.64 | D, P, M | 5.20 | 1:1.64 | D, H, P, M | 5.15 | 1:1.65 | D, P, M, H |
| | 0.8 | 5.30 | 1:1.64 | D, P, M | 5.00 | 1:1.63 | D, P, M | 5.45 | 1:1.65 | D, P, M, H |

Table 1 (Continued)

| Concentration of solutions | | 0.1 mol dm ⁻³ | | | | | | 0.05 mol dm ⁻³ | | |
|----------------------------|-----|--------------------------|--|-------------|------|--|-------------|---------------------------|--|-------------|
| Duration of synthesis | | 2 min | | | 24 h | | | 24 h | | |
| Temperature | Z | pH | <i>n</i> _{Tl} : <i>n</i> _V | Composition | pH | <i>n</i> _{Tl} : <i>n</i> _V | Composition | pH | <i>n</i> _{Tl} : <i>n</i> _V | Composition |
| 60°C | 0.1 | 6.20 | 1:0.94 | M, X | 6.20 | 1:1.05 | M, P | 6.30 | 1:1.02 | M, P |
| | 0.2 | 5.90 | 1:0.93 | M, X | 6.00 | 1:1.21 | P, M | 6.20 | 1:1.10 | P, M |
| | 0.3 | 5.80 | 1:1.10 | M, P | 5.90 | 1:1.30 | P, M | 6.00 | 1:1.15 | P, M |
| | 0.4 | 5.60 | 1:1.32 | M, P, D | 5.80 | 1:1.42 | P, M, D | 5.50 | 1:1.27 | M, P, H |
| | 0.5 | 5.40 | 1:1.48 | M, P, D, H | 6.90 | 1:1.53 | P, D, M | 5.60 | 1:1.54 | M, P, D, H |
| | 0.6 | 5.30 | 1:1.51 | D, P, H, M | 6.60 | 1:1.59 | D, P, H, M | 5.60 | 1:1.55 | P, D, M, H |
| | 0.7 | 5.20 | 1:1.63 | D, H, P, M | 6.70 | 1:1.52 | D, P, H, M | 5.10 | 1:1.65 | P, D, M, H |
| | 0.8 | 5.10 | 1:1.66 | D, H, P, M | 7.30 | 1:1.65 | D, P, H, M | 5.00 | 1:1.65 | P, M, D |

pH — pH of the reaction system before isolation of the solid substance.

M — TlVO₃; P — Tl₃V₅O₁₄; H — Tl₂V₆O₁₆; D — Tl₆V₁₀O₂₈·4H₂O; X — nonidentified thallium(I) polyvanadate.

Table 2. Composition of the substances arising in the system $\text{NaVO}_3\text{—CH}_3\text{COOTl—HNO}_3\text{—H}_2\text{O}$

| Concentration of solutions | | 0.1 mol dm ⁻³ | | | | | | 0.05 mol dm ⁻³ | | |
|----------------------------|-----|--------------------------|------------------------------|-------------|------|------------------------------|-------------|---------------------------|------------------------------|-------------|
| Duration of synthesis | | 2 min | | | 24 h | | | 24 h | | |
| Temperature | Z | pH | $n_{\text{Tl}}:n_{\text{V}}$ | Composition | pH | $n_{\text{Tl}}:n_{\text{V}}$ | Composition | pH | $n_{\text{Tl}}:n_{\text{V}}$ | Composition |
| 20°C | 0.1 | | | | 6.35 | 1:1.05 | M, D | 6.25 | 1:0.98 | M, D |
| | 0.2 | | | | 6.10 | 1:1.13 | M, D | 6.00 | 1:1.13 | M, H, D |
| | 0.3 | | | | 5.90 | 1:1.16 | M, H, D | 5.75 | 1:1.33 | M, H, D |
| | 0.4 | | | | 5.80 | 1:1.44 | M, H, D | 5.60 | 1:1.63 | D, M, H |
| | 0.5 | | | | 5.05 | 1:1.56 | D, H, M | 5.30 | 1:1.64 | D, M, H |
| | 0.6 | | | | 4.80 | 1:1.55 | D, H, M | 5.00 | 1:1.66 | D, M |
| | 0.7 | | | | 4.55 | 1:1.64 | D, H, M | 4.75 | 1:1.65 | D, M |
| | 0.8 | | | | 4.25 | 1:1.65 | D, H, M | 4.50 | 1:1.66 | D, M |
| 40°C | 0.1 | | | | 6.10 | 1:1 | M | 6.20 | 1:1.17 | M, H, D |
| | 0.2 | | | | 6.00 | 1:1.18 | M, H, D | 6.15 | 1:1.28 | M, H, P, D |
| | 0.3 | | | | 6.30 | 1:1.41 | P, H, M, D | 5.95 | 1:1.36 | P, H, M |
| | 0.4 | | | | 5.40 | 1:1.49 | D, H, M, P | 5.30 | 1:1.44 | P, M, H, D |
| | 0.5 | | | | 5.30 | 1:1.65 | D, H, P, M | 5.40 | 1:1.62 | D, M, P, H |
| | 0.6 | | | | 5.00 | 1:1.65 | D, H, P, M | 5.15 | 1:1.64 | D, M, P, H |
| | 0.7 | | | | | | | 5.00 | 1:1.63 | D, M, P, H |
| | 0.8 | | | | | | | 4.70 | 1:1.65 | D, H, M |
| 60°C | 0.1 | 6.10 | 1:0.98 | M, X | 6.00 | 1:1.19 | M, H, D | 6.25 | 1:1.29 | M, H |
| | 0.2 | 5.90 | 1:1.08 | M, P, H | 6.00 | 1:1.29 | M, H, D | 6.05 | 1:1.22 | M, H |
| | 0.3 | 5.80 | 1:1.31 | M, H, D, P | 5.05 | 1:1.53 | P, M, D | 5.90 | 1:1.47 | M, P, H, D |
| | 0.4 | 5.65 | 1:1.34 | M, D, H | 6.20 | 1:1.55 | P, M, D | 6.00 | 1:1.59 | P, M, D |
| | 0.5 | | | | 5.10 | 1:1.57 | D, H, M | 5.35 | 1:1.64 | P, D, H, M |
| | 0.6 | | | | | | | 5.25 | 1:1.62 | P, D, H, M |
| | 0.7 | | | | | | | 5.00 | 1:1.59 | H, M, D |

mixtures with the value of Z . Lower values of Z are optimum for the formation of TlVO_3 , medium values of Z for the formation of $\text{Tl}_3\text{V}_5\text{O}_{14}$, and medium or higher values of Z for the formation of $\text{Tl}_2\text{V}_6\text{O}_{16}$ and $\text{Tl}_6\text{V}_{10}\text{O}_{28} \cdot 4\text{H}_2\text{O}$.

The influence of temperature on the composition of thallium(I) polyvanadates is significant. Lower temperatures are favourable for the formation of $\text{Tl}_6\text{V}_{10}\text{O}_{28} \cdot 4\text{H}_2\text{O}$, low and medium temperatures are more favourable for TlVO_3 , the temperature of 40°C for $\text{Tl}_3\text{V}_5\text{O}_{14}$, and higher temperatures are favourable for $\text{Tl}_2\text{V}_6\text{O}_{16}$.

The time of synthesis, especially at lower values of Z and higher temperatures, influences the composition of thallium(I) polyvanadates. The primarily TlVO_3 changes into $\text{Tl}_3\text{V}_5\text{O}_{14}$.

From the relationships thus obtained, the following conclusions may be drawn:

1. As to the syntheses of thallium(I) polyvanadates, the starting solutions with lower concentration and the use of CH_3COOH are more suitable for achievement of a required value of Z .

2. The conditions of preparation of TlVO_3 and $\text{Tl}_3\text{V}_5\text{O}_{14}$ are given in Tables 1 and 2.

3. Since $\text{Tl}_6\text{V}_{10}\text{O}_{28} \cdot 4\text{H}_2\text{O}$ as the prevailing substance in the two-component mixture appears only at 20°C , 0.05 mol dm^{-3} concentration of the solution, and higher degrees of Z (0.6—0.8), we may assume that the optimum conditions for its formation are lower temperatures, less concentrated starting solutions and degree of acidification Z near to 0.6. At higher values of Z thallium(I) hydrogenecavanadates may also arise. A strong acid appears to be more suited for the preparation of thallium(I) decavanadate.

4. For the preparation of $\text{Tl}_2\text{V}_6\text{O}_{16}$, it is necessary to find out the optimum conditions by studying the system in which the ratio of substance quantities will be $n_{\text{Tl}} : n_{\text{V}} = 1 : 3$.

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