# Influence of temperature, vanadium concentration, and degree of solution acidification on composition of the solid products. II. Products of the reactions taking place in acidified solutions of calcium metavanadate

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The composition and conditions of formation of the solid product arising in the system $Ca(VO_3)_2$—$HClO_4$—$H_2O$ are studied in this paper. The formula $Ca_{(1-0.5x)}H_xV_6O_{16} \cdot nH_2O$ $(0 < x < 0.5)$ is proposed for the isolated product.

В работе изучались состав и условия образования твердого продукта, образующегося в системе $Ca(VO_3)_2$—$HClO_4$—$H_2O$. Для изолированного продукта была предложена формула $Ca_{(1-0.5x)}H_xV_6O_{16}$ $nH_2O$, где $0 < x < 0,5$.

Different solid polyvanadates· mostly of alkaline metals were obtained by crystallization from aqueous solutions of vanadates in the pH region of 2—5. The processes taking place in such solutions have not been sufficiently investigated so far. The concentrations of the hydroxonium ions and vanadium have significant influence on composition of the vanadium oxoanions in solution. In heterogeneous systems solution—arising solid substance, the equilibria are frequently established very slowly. The composition of the solid vanadates also depends on character of the cation. Identification of the products among which several types of vanadates may occur is relatively difficult.

These phenomena result in the fact that there are mentions in literature of the existence of vanadates of different composition though these substances were prepared by similar methods. This especially refers to dark- or even red-brown substances arising by acidification of solutions of some metavanadates of alkaline metals. Some authors express the composition of these substances as hydrated vanadium(V) oxide $V_2O_5 \cdot nH_2O$ [1, 2] whereas the others suppose hexavanadic acid $H_4V_6O_{17}$ [3]. Sometimes, it is expressed as hexavanadate of the composition $Na_2H_2V_6O_{17} \cdot nH_2O$ [4, 5], another time as $Na_2V_6O_{16} \cdot nH_2O$ [6]. Later, it was

found that the composition of the products depended on the ratio Na/V in solution and varied in the range $NaHV_6O_{16} \cdot yH_2O$—$Na_2V_6O_{16} \cdot yH_2O$ [7]. In papers [8, 9], the authors describe the formation of two types of compounds which mainly differed in infrared spectra. The first type arises at the ratio $H^+/VO_3^-$ 0.9—2.1 and has the structure similar to anhydrous $V_2O_5$ and the authors take it for the hydrated $V_2O_5$ with possible presence of the $VO_2^+$ ions. The second type which is the hydrated hexavanadate according to the authors was formed at the ratio $H^+/VO_3^-$ equal to 0.7. They also stated the possibility of expressing the composition of the investigated substance by the formula $Na_x(VO_2)_{5-x}HV_{10}O_{28} \cdot nH_2O$. This substance is regarded as pentavanadate or decavanadate in [10] where it is expressed by the formula $NaHVO_2V_5O_{14} \cdot 3.5H_2O$ or $K_2(VO_2)_3V_5O_{15}.4H_2O$ for potassium.

These facts demonstrate the diversity in views concerning the composition of the substances discussed.

In literature, there are very few mentions related to compounds of similar type with bivalent cations and the influence of temperature on composition of these substances has not been hitherto investigated. This paper is concerned with the study of the solid products arising in acidified solutions of calcium metavanadate at different temperatures. Another aim was to investigate the possibility of preparing calcium hexavanadate which has not been hitherto prepared in laboratory though the essential component of the mineral hewetite is $CaV_6O_{16} \cdot 9H_2O$ [11].

## Experimental

Calcium metavanadate was prepared according to [12] and purified by crystallization from aqueous solution. Its composition corresponded to the formula $Ca(VO_3)_2 \cdot 4H_2O$ ($V^{IV}$ was not detected). $V^V$ and $V^{IV}$ were determined volumetrically by titrating with 0.1 N-$FeSO_4$ and 0.1 N-$KMnO_4$ while Ca was estimated gravimetrically [13].

The diffraction patterns were taken on an X-ray diffractograph (Philips) with a goniometer PW 1058 by using $CuK_\alpha$ radiation. The thermal analysis was carried out on a derivatograph MOM, Budapest (system F. Paulik, J. Paulik, L. Erdey). The rate of heating was 5°C per minute. The infrared spectra were recorded in the range 400—1800 $cm^{-1}$ on a spectrometer UR-10 (Zeiss, Jena) in nujol suspension. The pH values were measured on a pH-meter Radelkis (type OP 201/1) with a combined electrode.

0.05 M solutions of calcium metavanadate were used. 1 N solution of $HClO_4$ was applied to acidification. The reaction proceeded at temperatures 40, 60, 75, and 85°C. For each temperature, the solutions with $Z = 0.33$, 0.50, 0.66, and 0.73 were prepared, $Z$ being the ratio of substance amounts $[H_3O^+]/[VO_3^-]$. The value $Z = 0.66$ corresponds to the formation of hexavanadate according to the following equation

$$3Ca(VO_3)_2 + 4H_3O^+ = CaV_6O_{16} + 2Ca^{2+} + 6H_2O \qquad (A)$$
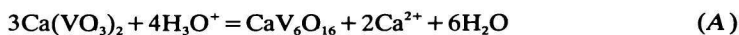
A constant volume and temperature were preserved during the reactions. An air stream was introduced into the solution in order to stir the solution and prevent the reduction of $V^V$ to

750

$V^{IV}$. Before adding the calculated amount of acid, the original solution was heated for 1 h at a given temperature. When the pH value was settled, a solid product was separated from the system.

## Results and discussion

*Kelmers,* who prepared potassium, rubidium, cesium, and ammonium hexavanadates [14] states that the solutions of metavanadates must be heated for about 1 h before their acidification. Therefore this procedure was also applied in this study. But the results obtained showed (the time interval 0—5 h was applied) that this procedure had no observable effect on composition and yield of the solid products. At higher temperatures the colour of the solution of calcium metavanadate changes from bright-yellow to colourless, which may be related to the formation of lower condensed vanadate ions. The arising ions may be suited for the reaction yielding the solid product and thus affect the rate of this reaction.

After acidification the solution immediately changed colour to orange and in most cases, a red-brown precipitate started to form in the course of few minutes or hours. The higher was the temperature of solution and the value of $Z$, the sooner it started to form. After isolation and drying in air, the volume of precipitate decreased several times. The substance obtained was compact and difficult to triturate. The precipitate did not appear at $Z = 0.33$ and 40 or 60°C as well as at $Z = 0.5$ and 40°C.

In systems where the precipitate did not arise the pH value of solution did not practically change for three days. The formation of the solid product is accompanied by an increase in pH, *i.e.* a consumption of $H_3O^+$ which increases with temperature and the value of $Z$. At higher temperatures and $Z$ values, the $H_3O^+$ ions are released after initial consumption until an equilibrium is attained. The equilibrium state of pH was established only at 85°C and $Z = 0.66$ or $Z = 0.73$ (Fig. 1*a—d*). Therefore, all further reactions were performed at 85°C and $Z = 0.66$ and the products were isolated after two days. The rate with which the equilibrium between consumption and liberation of $H_3O^+$ is established increases with $Z$ and, in particular, with temperature.

The yield of reaction undeniably increases with $Z$ and temperature. The highest yield ($Z = 0.73$ and 85°C) is by about 5% greater, than the theoretical one for $CaV_6O_{16} \cdot 9H_2O$ according to eqn (*A*). The content of $V^V$ and Ca in the substances obtained is usually somewhat greater than the theoretical one in $CaV_6O_{16} \cdot 9H_2O$ ($V^V_{theor} = 40.02\%$, $Ca_{theor} = 5.25\%$). The content of $V^V$ in the obtained substances exhibits, even though not quite obviously, a decreasing tendency with increasing temperature (Table 1).

The determinations of $V^V$ in the mother solutions from which the solid product was isolated have shown that the content of $V^V$ decreases with increasing
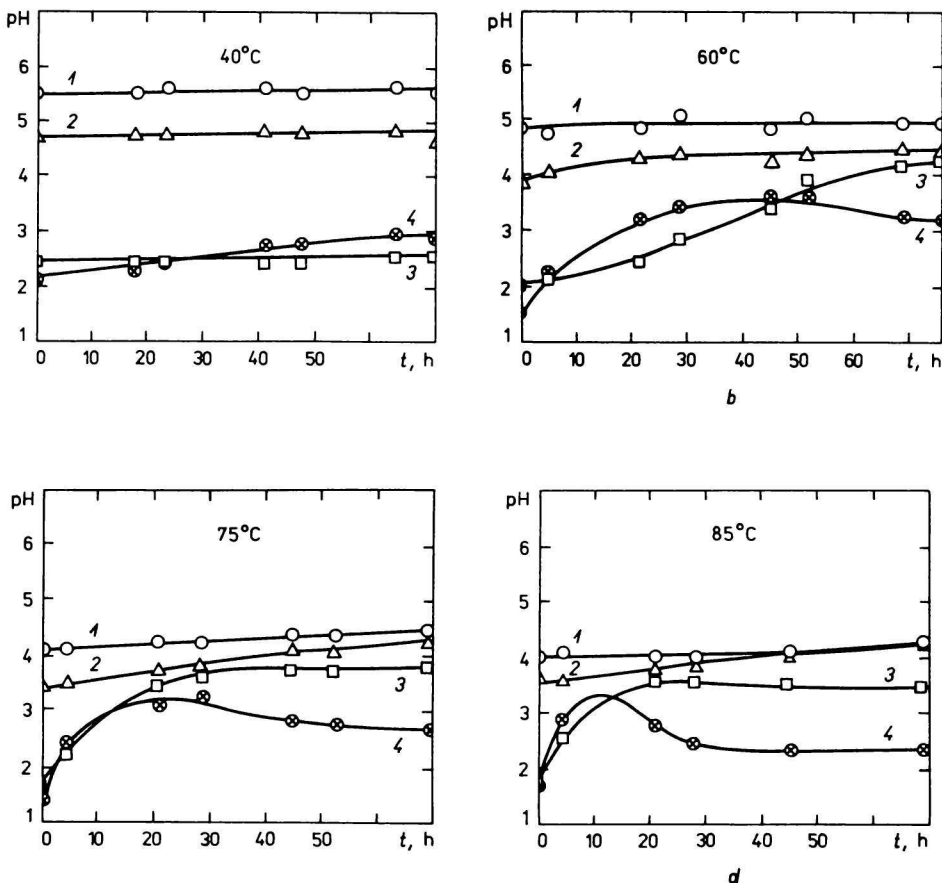
*Fig. 1a—d.* Variation of pH with time at different temperatures and values of $Z$.
*1.* $Z = 0.33$; *2.* $Z = 0.50$; *3.* $Z = 0.66$; *4.* $Z = 0.73$.

temperature and $Z$. At $Z = 0.73$ and temperatures of 60, 75, and 85°C, vanadium was fully consumed in the solution and at $Z = 0.66$ and the above-mentioned temperatures, only a negligible amount of vanadium remained in the solution.

The dependence of pH on $Z$ in final mother solutions (Fig. 2) enables us to observe that pH decreases quite slowly up to the value $Z = 0.66$. A rapid increase in $[H_3O^+]$ concentration appears above this value of $Z$. The hydroxonium ions might be consumed to the formation of the solid product below this value of $Z$ while they remained in solution above this value.

The infrared spectra of the substances prepared did not substantially differ from each other. A conspicuous couple of absorption maxima at 975 and 1010 cm$^{-1}$

*Table 1*

Analyses of the products obtained

| $Z$ | $t$, °C | Yield g | % $V^V$ | % $V^{IV}$ | % Ca | % $H_2O$ |
|------|------|------|------|------|------|------|
| 0.66 | 40 | 0.24 | 42.98 | 0.9 | — | — |
| 0.73 | 40 | 0.69 | 43.75 | 0.4 | 3.5 | 16.3 |
| 0.50 | 60 | 0.18 | 40.18 | 0.3 | — | — |
| 0.66 | 60 | 1.06 | 41.35 | 0.3 | 4.9 | 18.9 |
| 0.73 | 60 | 1.18 | 40.84 | 0.3 | 5.1 | 19.7 |
| 0.33 | 75 | 0.51 | 40.75 | 0.5 | 6.7 | 16.9 |
| 0.50 | 75 | 0.78 | 41.62 | 0.4 | 7.0 | 16.2 |
| 0.66 | 75 | 1.15 | 40.91 | 0.3 | 6.4 | 17.5 |
| 0.73 | 75 | 1.21 | 40.93 | 0.3 | 5.1 | 19.4 |
| 0.33 | 85 | 0.61 | 39.62 | 0.2 | 8.1 | 17.6 |
| 0.50 | 85 | 0.89 | 40.29 | 0.2 | 6.0 | 19.3 |
| 0.66 | 85 | 1.23 | 39.39 | 0.2 | 7.2 | 20.6 |
| 0.73 | 85 | 1.31 | 37.63 | 0.4 | 7.1 | 22.2 |

% $H_2O$ was calculated according to the formula: % $H_2O = 100 - (\% \ CaO + \% \ V_2O_5)$.
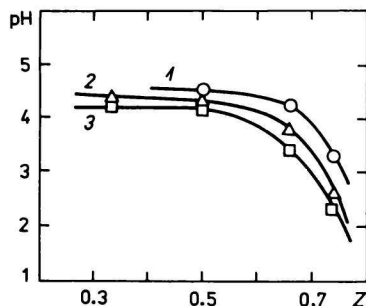


*Fig. 2.* Variation of pH with $Z$ in the final mother solution.
*1.* $t = 60°C$; *2.* $t = 75°C$; *3.* $t = 85°C$.

characteristic of the known hexavanadates appears in these spectra (Fig. 3, curve *a*). The spectral region between 700 and 1100 $cm^{-1}$ corresponds to the infrared spectra of hexavanadates of univalent metals [15] by the number of maxima, their position, and intensity ratios. The region between 400 and 700 $cm^{-1}$ is already less conformable, which may be due to different structures of the hexavanadates compared (the justification of this assumption is also confirmed by the fact that hexavanadates of univalent metals are anhydrous whereas the maximum at 1640 $cm^{-1}$ indicates the presence of water in the compounds investigated in this study) or to an admixture of other compounds. As for the possible compounds, the nonstoichiometric compounds of $V^V$ with $V^{IV}$ come into consideration. The small amounts of $V^{IV}$ (max. 1%) found in the products obtained may correspond to

a certain percentage of the content of these compounds. From this point of view, it is worth noticing that the infrared spectra of some vanadium bronzes are similar to the spectra of the substances prepared by us in the region $700$—$1100 \ cm^{-1}$ [16]. The infrared spectrum in Fig. 3, curve $a$, too, does not rule out the presence of small amounts of decavanadate or perchlorate which are, however, well soluble under the given conditions and have not been detected by the X-ray powder method.

In order to elucidate the character of the investigated substances in more detail, "the hydrated vanadium(V) oxide" was prepared by dissolving anhydrous $V_2O_5$ in boiling 1 N-$HClO_4$ and evaporating the solution at $100°C$. A dark-brown substance was formed. The infrared spectrum of this substance (Fig. 3, curve $b$) resembles the infrared spectrum of the investigated substances (Fig. 3, curve $a$), but the conspicuous maximum at $975 \ cm^{-1}$ is missing. The small maximum at $925 \ cm^{-1}$ could correspond, according to [17], to bending vibrations of the hydroxyl groups.

In further experiment ($Z = 0.66$, $t = 85°C$), the solid product was isolated as early as in an hour. The mother solution was given back into the reaction vessel and allowed to stay at the given temperature for two days. The yield of both portions was somewhat smaller than that obtained in the noninterrupted reaction. The substance isolated after two days did not differ from the investigated substances (contents: $V^V = 39.27\%$, $V^{IV} = 0\%$, Ca = $6.0\%$, $H_2O = 21.5\%$) while the intermediate was darker and after drying more brittle (contents: $V^V = 42.55\%$, $V^{IV} = 0.3\%$, Ca = $3.4\%$, $H_2O = 18.7\%$). It results that the content of $V^V$ in the final product decreased by $3.3\%$ with respect to intermediate while the content of Ca increased by $2.6\%$. There is only a slight indication of the absorption band with maximum at $975 \ cm^{-1}$ in the infrared spectrum of the intermediate (Fig. 3, curve $c$). But this spectrum looks like the spectrum of "the hydrated $V_2O_5$" (Fig. 3, curve $b$). The comparison of these three infrared spectra suggests that the solid "hydrated $V_2O_5$" is formed first in the investigated solution and subsequently it changes its structure to a certain extent.

The concentration of the initial solution of calcium metavanadate (investigated in the range $0.05$—$0.005$ M) influences composition of the products obtained so that their content of vanadium increases with decreasing concentration. The infrared spectra of these substances are similar to the infrared spectrum of the intermediate (Fig. 3, curve $c$).

As the investigated precipitate greatly reduced its volume during drying, one part of the final product was deprived of the mother solution by pressing while the second part was allowed to dry in free. The content of $V^V$ in the pressed product increased by about $2\%$ whereas the content of Ca decreased by about equal value. This observation may explain the fact that we failed in preparing the substances of entirely equal composition under equal conditions. The investigated substance is evidently very porous and able to include a great amount of the mother solution.

*Table 2*

Interplanar distances in $CaV_6O_{16} \cdot 9H_2O$

| $d$, nm | 0.593 | 0.384 | 0.344 | 0.326 | 0.289 | 0.256 | 0.232 | 0.191 | 0.179 | 0.152 |
|---|---|---|---|---|---|---|---|---|---|---|
| $I$ | vw | w | w | vw | w | vw | vw | w | w | vw |

When the substances obtained after drying and pulverizing were subject to boiling in distilled water (0.5—1 h), their analysis ($V^V = 40.02\%$, $V^{IV} = 0\%$, $Ca = 5.40\%$) was in good agreement with the formula $CaV_6O_{16} \cdot 9H_2O$. The diffraction pattern of this substance (Table 2) may be related with an insufficiently developed structure.

When the final product was allowed to boil (approximately 1 h) in water acidified with HCl, the content of $V^V$ in the substance obtained increased and its infrared spectrum became similar to that of the intermediate (Fig. 3, curve $c$). It ensues from these experiments that the $H_3O^+$ ions shift the equilibrium in favour of the product which arises immediately after acidification of the solution of $Ca(VO_3)_2$.

The derivatogram of the substance purified by boiling in water (Fig. 4) indicates a three-step weight loss which corresponds to liberation of differently bonded water. Initially, the sorbed water is likely to be released (weight loss begins at 35°C)
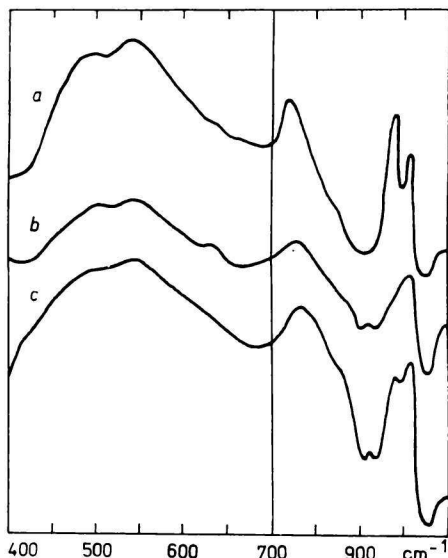


*Fig. 3.* Infrared spectra of the investigated substances.

*a*) Final product; *b*) "pure (without cations) hydrated $V_2O_5$"; *c*) intermediate.
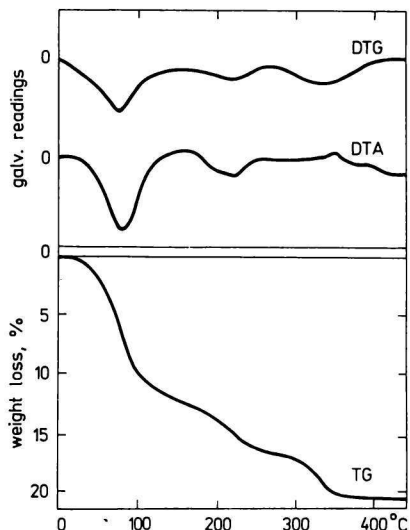


*Fig. 4.* Thermogram of the substance purified by boiling in water.

and subsequently the structural water takes its turn. The weight loss in the interval 255—425°C on the DTA plot corresponds to an exothermic process (maximum at 355°C). This process is a superposition of three effects at least, *i.e.* dehydration, destruction of original structure, and formation of $V_2O_5$ and $Ca(VO_3)_2$. The last two substances were found as products of thermal decomposition of the hydrate of calcium hexavanadate by the method of X-ray phase analysis and infrared spectroscopy according to the procedure and identification material described in [18].

In proposing the composition of the substances isolated from solutions in equilibrium state ($t = 85°C$, $Z = 0.66$) and deprived of admixtures by pressing and boiling in water, we started from these experimental facts:

1. The method of preparation is similar to that used for preparation of the hexavanadates of alkaline metals.

2. The infrared spectra confirm in principle that we are up against hexavanadates.

3. The thermal analysis indicates the presence of strongly bonded water.

4. The degree of acidification $Z$ varies within the range 0.66—0.73. The values $Z = 0.66$ and $Z = 0.83$ are necessary for the formation of $V_6O_{16}^{2-}$ and $HV_6O_{16}^{-}$, respectively. The ion $H_{0.5}V_6O_{16}^{1.5-}$ corresponds to $Z = 0.73$. The above range of $Z$ is not sufficient for other oxovanadium(V) ions known.

For the reaction conditions ascertained, the ion of the composition $H_xV_6O_{16}^{(2-x)}$ is the most probable ($0 < x < 0.5$) and the compounds investigated are expected to have the composition $Ca_{(1-0.5x)}H_xV_6O_{16} \cdot nH_2O$.

Thus it may be assumed that the essence of the solid intermediate initially arising on acidification of the heated solution of calcium metavanadate is hexavanadic acid $H_2V_6O_{16} \cdot nH_2O$ which successively exchanges protons for $Ca^{2+}$ This assumption is also confirmed by the observation that the $H_3O^+$ ions are firstly consumed in the course of the reactions and afterwards liberated (Fig. 1c and 1d) and if the final product is boiled in dilute hydrochloric acid, the equilibrium is shifted in favour of the intermediate formation.

The formation of a small amount of $V^{IV}$ in the investigated substances is evidently significant. The mineral hewetite contains about 0.8% of $V^{IV}$ [11]. It will be still necessary to pay attention to the formation and role of $V^{IV}$ in these compounds.

Some properties of the investigated compounds, especially the ability to sorb water, exchange the cations of metal for $H_3O^+$ and *vice versa,* and the presence of bonded constitution water the liberation of which is accompanied by destruction of the structure, indicate a possible relation to aluminosilicates of the zeolite type [19].

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