

Influence of temperature, vanadium concentration, and degree of solution acidification on composition of the solid products

VI. Products of the reactions taking place in acidified solutions of strontium metavanadate

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The influence of temperature, vanadium concentration, and degree of acidification of the solution on the composition of strontium polyvanadates arising in the system $\text{Sr}(\text{VO}_3)_2\text{—HClO}_4\text{—H}_2\text{O}$ was investigated. According to variation of these conditions, three types of solid substances come into existence: $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{SrV}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ [$n \in (6\text{—}10)$], and $\text{Sr}_{1-x}\text{H}_{2x}\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ [$x \in (0.3\text{—}0.6)$, $n \in (5\text{—}8)$]. These substances were identified by means of chemical analysis, X-ray diffractography, and infrared spectroscopy. The last method was also used for investigating the shifts in absorption bands of infrared spectra of the deuterated solid substances.

Изучено влияние температуры, концентрации ванадия и кислотности раствора на состав поливанадатов стронция, образующихся в системе $\text{Sr}(\text{VO}_3)_2\text{—HClO}_4\text{—H}_2\text{O}$. В зависимости от вариации этих факторов возникают три типа твердых соединений: $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{SrV}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ [$n \in (6\text{—}10)$] и $\text{Sr}_{1-x}\text{H}_{2x}\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ [$x \in (0,3\text{—}0,6)$, $n \in (5\text{—}8)$]. Эти соединения были идентифицированы на основе результатов элементарного анализа, рентгеноструктурного анализа и ИК-спектроскопии. Последний метод был использован и при изучении сдвигов полос поглощения в ИК-спектрах дейтерированных твердых веществ.

The formation of solid polyvanadates from aqueous solutions is affected by many factors. The most important factors are: vanadium concentration, degree of acidification, and temperature of solution [1—3]. The influence of the present cation also appears to be important [1, 4].

Up to the present, there are no consistent ideas of the essence of the solid polyvanadates arising in strongly acidic solutions. According to [5, 6], hexa- and

dodecavanadates are formed under these conditions. These substances were defined as hexa- and hydrogen hexavanadates by the authors of other papers [2, 3, 7, 8]. These authors direct their attention to characteristic properties and point out the similarity with solid polyvanadic acid [9] and zeolites [10]. Nevertheless, both groups of authors regard the ratio of concentration of the oxonium ions to concentration of the polyvanadate ions in solution as the main factor determining the kind of arising polyvanadate.

This study is concerned with the factors determining the formation of solid strontium polyvanadates in the system $\text{Sr}(\text{VO}_3)_2\text{—HClO}_4\text{—H}_2\text{O}$.

Experimental

The used chemicals were anal. grade reagents of Czechoslovak production. Ammonium metavanadate was purified according to [11]. Strontium metavanadate was prepared according to [12] and its chemical composition, infrared spectrum, and X-ray diffraction pattern corresponded to a substance of the composition $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$.

Vanadium was determined volumetrically (FeSO_4), strontium gravimetrically as SrSO_4 [13], and the content of water was calculated according to the formula $\% \text{H}_2\text{O} = 100 - (\% \text{V}_2\text{O}_5 + \% \text{SrO})$.

The infrared spectra were taken in Nujol suspension in the region of $2000\text{—}500 \text{ cm}^{-1}$ with spectrophotometers Spectromaster (Grubb Parsons) and PE 180 (Perkin—Elmer) (deuterated samples).

The powder diffraction patterns were made with an X-ray diffractograph (Philips) equipped with a goniometer PW 1058 by the use of the CuK_α radiation.

The pH measurements were performed with an instrument TTT-2 (Radiometer) by using a combined electrode GK 2301 C.

Method of experiment

$\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in a solution of H_2O_2 diluted in the ratio 1 : 10. HClO_4 ($10^{-1} \text{ mol dm}^{-3}$) was added into these solutions in quantities corresponding to the subsequent values of the degree of acidification Z : 0.15—0.2—0.25—0.3—0.35—0.4—0.5—1.0—1.5—2.0 ($Z = c_{\text{H}_3\text{O}^+}/c_{\text{V}}$). After the addition of acid, the peroxidic bonds were degraded by boiling and the solutions were filled up to the constant volume (100 cm^3) so that the concentration of vanadium was $2 \times 10^{-2} \text{ mol dm}^{-3}$ or $10^{-2} \text{ mol dm}^{-3}$. These systems were heated and held at temperatures 20, 40, and 60°C under stirring. The pH values of solutions continued to be measured (pH_t^s). If the solid phase did not arise, the thermostating and stirring were finished after 240 h. Provided the solid phase was formed, the thermostating continued till the pH value got settled (pH_s^s). After separation, washing and drying, the solid products were characterized by the use of chemical analysis, infrared spectroscopy, and X-ray diffraction patterns.

Results and discussion

The equilibrium pH values in solutions of the investigated system are given in Table 1. According to temperature, the time necessary for reaching pH_e^I changes as follows: at 20°C and for $Z = 0.15\text{--}0.4$, pH_e^I is established in the course of 120 h, for $Z = 0.5\text{--}2.0$ in the course of 5 h; at 40°C and for $Z = 0.25\text{--}0.4$, pH_e^I is established in the course of 24 h and for $Z = 0.5\text{--}2.0$ in the course of 5 h; at 60°C pH_e^I is established irrespective of Z in the course of 5 h.

From the view-point of formation of the solid phase, one of the following phenomena takes place in the investigated solutions.

1. Immediately after acidification, a light green-yellow crystalline substance (substance *A* in Table 1 and later) comes into existence. The region Z contracts with increasing temperature towards less acid solutions from which this substance crystallizes. At 40°C it arises at both concentrations of vanadium while it is formed only from $2 \times 10^{-2} \text{ mol dm}^{-3}$ solutions at 20 and 60°C.

2. When pH_e^I is established, a red-brown precipitate appears (substance *B* in Table 1 and later). Its formation is accompanied by consumption of the oxonium ions ($\text{pH}_e > \text{pH}_e^I$, Table 1). Another concomitant phenomenon consists in an almost quantitative transition of vanadium into the solid phase. Substance *B* arises at optimum temperatures and degrees of acidification (Table 1).

3. After establishment of pH_e^I , a brown-grey precipitate (substance *C* in Table 1 and later) arises and the pH value does not practically change during its formation. Its formation is conditioned by reaching a state of considerable acidity of the solution and the transition of vanadium into the solid phase is not complete (50–90%).

4. The solid phase does not arise.

Substance *A* is $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($V_{\text{exp}} = 28.70\%$, $V_{\text{theor}} = 28.50\%$, $\text{Sr}_{\text{exp}} = 24.55\%$, $\text{Sr}_{\text{theor}} = 24.50\%$), the infrared spectrum (Fig. 1a) as well as the diffraction pattern is in harmony with the published data [14, 15]. However, $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ does not arise at 20°C in any $10^{-2} \text{ mol dm}^{-3}$ solutions or in $2 \times 10^{-2} \text{ mol dm}^{-3}$ solutions provided $Z > 0.3$ ($\text{pH} < 4.80$). Under these conditions, some polycondensation reactions take place in the solutions [16] and the concentration of the metavanadate ions is lower than the solubility product of $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ does require. The formation of strontium metavanadate is to be observed even in $10^{-2} \text{ mol dm}^{-3}$ solutions at 40°C, which may be due to lower solubility of this substance at 40°C. In contrast to the observation at 20°C, $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ does not arise at 40 and 60°C if $Z = 0.25$ and 0.3. This fact may be explained by changes in solubility of $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ at these temperatures in the reaction medium or by a shift in equilibria in favour of polycondensation reactions at increased temperatures. The second alternative is, however, in contradiction with the observations hitherto obtained in the presence of other cations [4].

Table 1

Conditions of formation of strontium polyvanadates in the investigated system

Z	$c_v/\text{mol dm}^{-3}$	$t/^\circ\text{C}$								
		20			40			60		
		pH_e^1	pH_e^2	s.p.	pH_e^1	pH_e^2	s.p.	pH_e^1	pH_e^2	s.p.
0.15	10^{-2}	5.70	—	2	1	5.10	A	5.00	—	2
	2×10^{-2}	5.80	5.25	A	1	5.10	A	1	4.80	A
0.2	10^{-1}	5.50	—	2	1	5.10	A	4.70	—	2
	2×10^{-2}	1	5.30	A	1	5.00	A	1	4.70	A
0.25	10^{-1}	4.70	—	2	4.90	—	2	4.20	—	2
	2×10^{-1}	1	5.25	A	4.75	—	2	4.60	—	2
0.3	10^{-1}	4.20	—	2	3.80	—	2	3.50	—	2
	2×10^{-2}	1	5.25	A	3.50	—	2	3.55	—	2
0.35	10^{-1}	3.30	—	2	3.20	3.80	B	3.30	—	2
	2×10^{-1}	3.25	—	2	3.00	3.60	B	2.85	3.45	B

Table 1 (Continued)

<i>Z</i>	<i>c_v</i> /mol dm ⁻³	<i>t</i> /°C								
		20			40			60		
		pH _e	pH _s	s.p.	pH _e	pH _s	s.p.	pH _e	pH _s	s.p.
0.4	10 ⁻	2.90	—	2	3.00	3.30	<i>B</i>	3.10	3.40	<i>B</i>
	2 × 10 ⁻²	2.75	—	2	2.75	3.30	<i>B</i>	2.65	3.30	<i>B</i>
0.5	10 ⁻²	2.70	—	2	2.70	2.80	<i>C</i>	2.75	2.95	<i>C</i>
	2 × 10 ⁻²	2.40	2.55	<i>C</i>	2.45	2.55	<i>C</i>	2.60	2.70	<i>C</i>
1.0	10 ⁻	2.20	2.10	<i>C</i>	2.20	2.20	<i>C</i>	2.25	2.25	<i>C</i>
	2 × 10 ⁻²	1.80	1.75	<i>C</i>	1.90	1.90	<i>C</i>	2.00	2.00	<i>C</i>
1.5	10 ⁻²	1.90	1.85	<i>C</i>	2.00	1.95	<i>C</i>	1.95	1.95	<i>C</i>
	2 × 10 ⁻²	1.65	1.55	<i>C</i>	1.70	1.70	<i>C</i>	1.70	1.70	<i>C</i>
2.0	10 ⁻	1.80	—	2	1.80	1.80	<i>C</i>	1.90	1.90	<i>C</i>
	2 × 10 ⁻	1.50	—	2	1.50	1.50	<i>C</i>	1.40	1.35	<i>C</i>

$$Z = \frac{c_{\text{H}_3\text{O}^+}}{c_v}$$

pH_e — equilibrium pH of solution under given conditions; pH_s — equilibrium pH during separation of the solid phase.

1. pH_s could not be determined because the solid phase arises immediately; 2. the solid phase does not arise.

A. Light green-yellow crystals; B. red-brown precipitate; C. brown-grey precipitate.

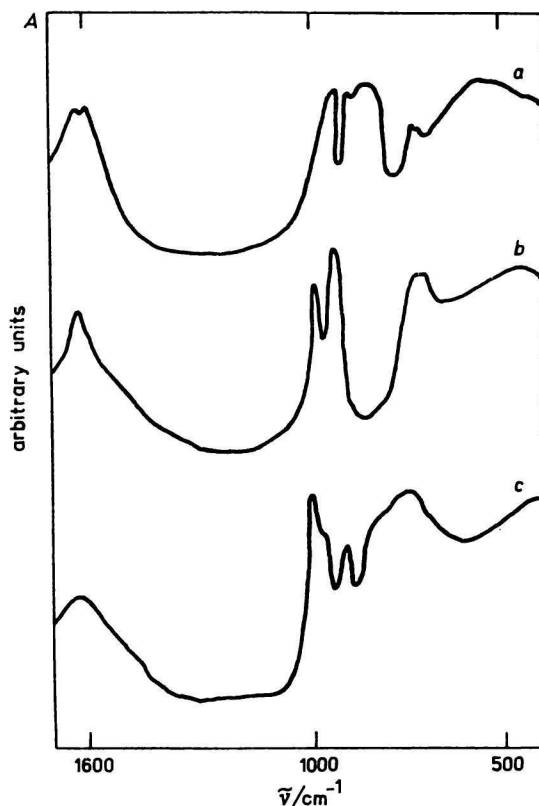


Fig. 1. Infrared spectra of $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ (a), $\text{SrV}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ (b), $\text{Sr}_{1-x}\text{H}_x\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ (c).

Solid substances *B* and *C* were identified by means of chemical analysis (Table 2), infrared spectroscopy (Fig. 1b, c; Table 4), and X-ray diffraction patterns (Table 3).

The ratio of amounts $n\text{Sr} : n\text{V}$ in substance *B* is constant in the scope of experimental error (0.85–0.95): 6 and approximately equal to the ratio in hexavanadates. In substance *C*, the ratio of amounts $n\text{Sr} : n\text{V}$ does not indicate any substance of constant composition and it decreases from 0.75 : 6 to 0.40 : 6 with increasing acidity of the solution from which this substance arises. Like sodium and calcium hexavanadates [1, 7, 8], substances *B* and *C* exhibit in diffraction patterns a small number of diffractions (Table 3).

The infrared spectra of substance *B* (Fig. 1b) are always equal and exhibit absorption bands in the regions of the wavenumbers characteristic of hexavanadates [5, 6, 17]. On the basis of these facts, substance *B* may be regarded as a crystallohydrate of strontium hexavanadate $\text{SrV}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ [$n \in (6-10)$].

Table 2

Chemical analysis of substances *B* and *C*

<i>t</i> /°C	<i>Z</i>	<i>c_v</i> /mol dm ⁻³	% V	% Sr	% H ₂ O	Sr : V	s.p.
20	0.5	2 × 10 ⁻²	42.90	7.40	15.20	0.56 : 6	<i>C</i>
		10 ⁻²	42.15	6.25	17.70	0.49 : 6	<i>C</i>
	1.0	2 × 10 ⁻²	41.10	6.25	19.60	0.50 : 6	<i>C</i>
		10 ⁻²	42.20	7.00	16.85	0.54 : 6	<i>C</i>
	1.5	2 × 10 ⁻²	42.80	6.80	16.00	0.52 : 6	<i>C</i>
		10 ⁻²	37.25	9.55	22.40	0.91 : 6	<i>B</i>
40	0.35	2 × 10 ⁻²	39.40	10.40	17.60	0.95 : 6	<i>B</i>
		10 ⁻²	37.80	10.05	20.90	0.94 : 6	<i>B</i>
	0.4	2 × 10 ⁻²	40.60	10.25	15.60	0.94 : 6	<i>B</i>
		10 ⁻²	39.85	8.70	18.80	0.73 : 6	<i>C</i>
	0.5	2 × 10 ⁻²	43.55	6.75	14.80	0.50 : 6	<i>C</i>
		10 ⁻²	43.15	7.05	15.10	0.53 : 6	<i>C</i>
	1.0	2 × 10 ⁻²	42.60	5.90	17.30	0.50 : 6	<i>C</i>
		10 ⁻²	38.60	6.20	24.20	0.52 : 6	<i>C</i>
	1.5	2 × 10 ⁻²	42.55	5.10	18.40	0.40 : 6	<i>C</i>
		10 ⁻²	37.95	7.80	23.55	0.65 : 6	<i>C</i>
	2.0	2 × 10 ⁻²	38.40	7.40	23.20	0.60 : 6	<i>C</i>
		10 ⁻²	39.95	10.10	17.50	0.95 : 6	<i>B</i>
60	0.35	2 × 10 ⁻²	40.10	10.20	17.40	0.91 : 6	<i>B</i>
		10 ⁻²	40.75	9.95	15.50	0.87 : 6	<i>B</i>
	0.4	2 × 10 ⁻²	42.30	6.10	17.60	0.58 : 6	<i>C</i>
		10 ⁻²	42.65	5.95	17.15	0.55 : 6	<i>C</i>
	0.5	2 × 10 ⁻²	42.05	6.10	17.70	0.52 : 6	<i>C</i>
		10 ⁻²	43.10	5.70	16.70	0.48 : 6	<i>C</i>
	1.0	2 × 10 ⁻²	42.55	5.86	17.04	0.42 : 6	<i>C</i>
		10 ⁻²	43.00	5.55	17.15	0.40 : 6	<i>C</i>
	1.5	2 × 10 ⁻²	37.05	5.60	27.25	0.49 : 6	<i>C</i>
		10 ⁻²	38.00	5.10	26.55	0.43 : 6	<i>C</i>
	2.0	2 × 10 ⁻²	37.05	5.60	27.25	0.49 : 6	<i>C</i>
		10 ⁻²	38.00	5.10	26.55	0.43 : 6	<i>C</i>

The infrared spectra of substance *C* are also always identical (Fig. 1c). Though the composition of this substance rather varies (Table 2), the identity of the infrared spectra as well as X-ray diffraction patterns suggests that the essence of substance *C* is uniform. As for the interpretation of the infrared spectra of this

Table 3

Interplanar distances of substances *B* and *C*

<i>B</i>		<i>C</i>	
<i>d</i> /nm	<i>I</i> / <i>I</i> ₀ (%)	<i>d</i> /nm	<i>I</i> / <i>I</i> ₀ (%)
0.580	30	0.348	90
0.460	40	0.343	100
0.388	25	0.323	40
0.342	80	0.262	65
0.324	70	0.258	70
0.311	100	0.192	50
0.289	20	0.191	50
0.262	30	0.179	75
0.239	20		
0.230	30		
0.221	40		
0.213	35		
0.212	35		
0.196	15		
0.179	50		

substance, there are two mentions in literature. Some authors [5, 6] regard these spectra as characteristic of dodecavanadates whereas they are attributed to hydrogen hexavanadates in review [1] and papers [7, 8]. It has been published [18] that the hydrogen salts exhibit bending vibrations of the functional M—O—H groups in the wavenumber region of 1500—600 cm⁻¹. In order to clear up the composition of substance *C*, we carried out its synthesis in heavy water. Table 4 contains the relative intensities of characteristic absorption bands of deuterated and nondeuterated substance *C*.

Table 4

Relative intensities (%) of the absorption bands $\delta(\text{OH}_2)$ and $\delta(\text{VOH})$ of substance *C* prepared in D₂O (1, 2) and H₂O (3)

Sample	$\delta(\text{OH}_2)/\text{cm}^{-1}$ 1620—1610	$\delta(\text{VOH})/\text{cm}^{-1}$ 920
1	70	70
2	55	40
3	100	100

Intensity of the absorption band $\nu(\text{VO})$ (1010 cm⁻¹) was used as a standard.

It results from this table that D_2O was only partially bonded into the solid phase, which is comprehensible because, except D_2O , all components participating in the synthesis contained light hydrogen. After partial deuteration, the relative intensities of two absorption bands, i.e. $\delta(OH_2)$ at 1620 cm^{-1} and the band at 920 cm^{-1} in the infrared spectra decreased. The assignment of the band at 920 cm^{-1} was up today ambiguous. According to our results, this band may be assigned to bending vibrations $\delta(VOH)$. It is corroborated not only by reduction of the relative intensity of this band after deuteration (Table 4) but also by the fact that shoulders of weak or medium intensity were observed in the calculated region of vibrations $\delta(VOD)$ ($700\text{--}680\text{ cm}^{-1}$). If we take into account all results obtained, we may write the following formula for substance *C*: $Sr_{1-x}H_{2x}V_6O_{16} \cdot nH_2O$ [$x \in (0.3\text{--}0.6)$, $n \in (5\text{--}8)$]. This formula admits variability in composition as well as constancy of physicochemical properties.

On the basis of the results obtained, we may say that substances *B* and *C* are strontium hexavanadates and hydrogen hexavanadates, in accord with papers [1, 7, 8]. A confrontation of infrared spectra and X-ray diffraction patterns with the data published for strontium deca- and metavanadates [14, 15, 19] eliminates the presence of these compounds in substances *B* and *C*. We assume that the protons in hydrogen hexavanadates arising in strongly acidified solutions are bonded to the oxygen atoms of the V—O skeleton. This skeleton gets deprotonated with decreasing acidity of the reaction medium (with increasing ratio $Sr^{2+} : H_3O^+$) and the protons are successively replaced by the strontium cations.

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