

# **Influence of temperature, vanadium concentration, and degree of solution acidification on composition of the solid products. III.**

## **Products of the reactions taking place in acidified solutions of sodium metavanadate**

V. SUCHÁ and L. ŽÚRKOVÁ

*Department of Inorganic Chemistry, Faculty of Natural Sciences,  
Komenský University, 816 31 Bratislava*

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The influence of vanadium concentration, pH, and temperature on composition of the solid products arising in the systems  $\text{NaVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  was investigated. The compounds  $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$ ,  $\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$ , and  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  were prepared and the conditions of their preparation in particular systems were optimized. Besides the above compounds, the brown products with varying composition which may be regarded as intermediates in the formation of  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  were also isolated from the given systems.

Было исследовано влияние концентрации ванадия, pH и температуры на состав твердых продуктов, образующихся в системах  $\text{NaVO}_3\text{—HNO}_3\text{—H}_2\text{O}$ . Были приготовлены соединения  $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$ ,  $\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$ ,  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  и оптимизированы условия их приготовления в указанных системах. Кроме указанных соединений из данных систем были изолированы коричневые продукты переменного состава, которые можно считать промежуточными продуктами в ходе образования  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ .

It ensues from the results published by several authors which are synoptically summarized in [1] that different kinds of the vanadate ions are present in aqueous solutions of vanadates and depend on vanadium concentration and pH. The equilibria of these ions are established very slowly in most cases and, besides the above factors, they are also dependent on temperature. Moreover, the influence of the cation used must be also taken into account [2, 3] because the results hitherto obtained are based mainly on the study of sodium and potassium vanadates.

It ensues from these facts that the composition of the solid vanadates crystallizing from these solutions must depend on conditions of the preparation.

The orange salts of the composition  $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$  and  $\text{Na}_4\text{H}_2\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$  were isolated from the saturated aqueous solutions of sodium vanadates in acid region [4]. Under certain conditions, the brown-red compounds were formed in such solutions, too. As to their composition, the views

are not uniform and a survey of the papers dealing with this topic is embodied in publications [5—7].

The influence of temperature in reaction medium on composition of solid vanadates arising in aqueous solutions has not yet been systematically investigated. The present paper deals with this problem. Another purpose of this study is to find out the optimum conditions for preparing the pure compounds arising in the above-mentioned systems.

### Experimental

The chemicals used were anal. grade reagents of the Czechoslovak production. Sodium metavanadate was prepared according to [3] and its composition corresponded to  $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ . The infrared spectra were measured in nujol suspension on a spectrophotometer Spectromaster Grubb Parsons. The powder diffraction patterns were taken on an X-ray diffractograph Philips equipped with a goniometer PW 1058 by using the  $\text{CuK}\alpha$  radiation. The pH was measured on a pH-meter PHM 22, Radiometer, with a combined Ag/AgCl electrode. Sodium was determined with a flame photometer (Zeiss, Jena), equipped with a metal interference filter for Na 591 nm. Vanadium(V) was determined volumetrically with  $\text{FeSO}_4$ , vanadium(IV) with  $\text{KMnO}_4$ , and water was estimated gravimetrically and computed according to the formula  $\% \text{H}_2\text{O} = 100 - (\% \text{V}_2\text{O}_5 + \% \text{Na}_2\text{O})$ .

Different amounts of  $\text{HNO}_3$  ( $1.0 \text{ mol dm}^{-3}$ ) were added to the solutions of  $\text{NaVO}_3$  in such a way that  $Z$  changed in the range 0.4—0.7 by the step 0.05 ( $Z = [\text{H}_3\text{O}^+]/[\text{V}]$ ). The concentration of the acidified solutions of  $\text{NaVO}_3$  was  $0.5 \text{ mol dm}^{-3}$  or  $1.0 \text{ mol dm}^{-3}$  for all values of  $Z$  and the volume was constant. The solutions were thermostatted for 45 and 60 h (the time of thermostating was determined experimentally) at 20, 40, and 60°C. The pH value of solutions should serve as a criterion of the establishment of equilibrium. The solid products formed under given conditions were separated from mother liquor, washed thoroughly with water, and dried at laboratory temperature. If the reaction solutions remained limpid after 60 h thermostating, they were concentrated at a certain temperature for crystallization. In some cases, the filtrate obtained after separation of the first product was concentrated again and other fractions came into existence.

### Results and discussion

Provided the concentration of the initial solutions was  $0.5 \text{ mol dm}^{-3}$  and  $Z = 0.40$  or  $Z = 0.45$  (20°C), no solid substance appeared even after 60 h. A small amount of brown precipitate which did not increase with time appeared at  $Z = 0.50$  or  $Z = 0.55$  (20°C) and  $Z = 0.40$  or  $Z = 0.45$  (40°C). The pH value of these solutions did not practically change with time (Table 1). The pH values indicate that the decavanadate or hydrogendecavanadate ions prevail in these solutions [1]. After separating the brown precipitate and concentrating the solutions, decavanadate and hydrogendecavanadate of the composition  $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$  and  $\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$  (Table 1) crystallized from these solutions.

Table 1. Products obtained from the systems  $\text{NaVO}_3\text{—HNO}_3\text{—H}_2\text{O}$ [V]  $0.5 \text{ mol dm}^{-3}$ 

20°C				40°C				60°C			
Z	pH		Product	Z	pH		Product	Z	pH		Product
	$t_1$	$t_2$			$t_1$	$t_2$			$t_1$	$t_2$	
0.40	6.05	6.05	D	0.40	5.68	5.65	D	0.40	5.58	5.85	X
0.45	5.75	5.70	D	0.45	5.15	5.20	D	0.45	5.42	5.85	HE
0.50	4.70	4.65	HD	0.50	4.20	4.70	HE	0.50	5.10	5.90	HE
0.55	3.50	3.50	HD + X	0.55	2.70	4.60*	HE	0.55	4.70	5.95	HE
0.60	2.60	2.80	X	0.60	2.30	4.03	X	0.60	4.10	5.90	HE
0.65	2.10	3.20	X'	0.65	1.90	4.10	X	0.65	3.38	5.80	HE
0.70	1.90	3.10	X'	0.70	1.90	4.10	X	0.70	3.00	4.68	HE

[V]  $\text{mol dm}^{-3}$ 

20°C		40°C		60°C	
Z	Product	Z	Product	Z	Product
0.40	X	0.40	D	0.40	X
0.45	X	0.45	D	0.45	HE
0.50	X	0.50	HE	0.50	HE
0.55	X	0.55	HE	0.55	HE
0.60	X	0.60	HE	0.60	HE
0.65	X	0.65	HE	0.65	HE
0.70	X	0.70	HE	0.70	X

$t_1$  — pH after preparation of solutions;  $t_2$  — pH after 60 h; D —  $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$ ; HD —  $\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$ ; HE —  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ ; X — brown product (intermediate); X' — brown product with the smallest content of Na and V; \* — pH after 13 days.

For  $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$  calculated: 35.88% V, 9.71% Na, 22.84%  $\text{H}_2\text{O}$ ; found: 35.75% V, 9.50% Na, 22.80%  $\text{H}_2\text{O}$ .

For  $\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$  calculated: 34.66% V, 7.82% Na, 26.96%  $\text{H}_2\text{O}$ ; found: 34.66% V, 7.80% Na, 26.96%  $\text{H}_2\text{O}$ .

$\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$  was also proved indirectly on the basis of different X-ray powder diffraction patterns of this substance and  $\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$  (Table 2). The infrared spectra of these substances do not differ from the infrared spectra of decavanadates in literature [8] except that the spectrum of  $\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$  contains further absorption band at  $1028\text{ cm}^{-1}$  which can correspond to the  $\delta(\text{V—O—H})$  vibrations [9].  $\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$  has not been described in literature up to now.

In other solutions, a greater amount of the brown precipitate arose as early as in the course of acidification or soon after the preparation of these solutions. The amount of the brown product increased with  $Z$ , temperature, and time. The pH value of these solutions increased continuously with time and the equilibrium was not established. It may be stated that the  $\text{H}_3\text{O}^+$  ions are consumed in the formation of this compound (Table 1).

With the aim to find out whether the time of isolation of the solid product from reaction medium affects its composition, we isolated the substance at  $Z = 0.55$  ( $40^\circ\text{C}$ ) only after 13 days. Its composition did not change, the time had influence only on the yield.

The infrared spectra of the brown compounds (Table 3) arisen at  $Z = 0.45\text{—}0.70$  ( $60^\circ\text{C}$ ) and  $Z = 0.50$  or  $Z = 0.55$  ( $40^\circ\text{C}$ ) contain a distinct pair of absorption maxima at  $1008$  and  $969\text{ cm}^{-1}$  as well as an intensive absorption maximum at  $725\text{ cm}^{-1}$  the position and intensity ratio of which correspond to anhydrous potassium, rubidium, and caesium hexavanadate [10]. The infrared spectra of our substances, however, reveal the presence of crystal water ( $1643\text{ cm}^{-1}$   $\delta(\text{H—O—H})$ ). The spectral region  $400\text{—}700\text{ cm}^{-1}$  is, to a certain extent, different, which may be due to different structure of the compared compounds owing to the presence of water in the sodium salt.

On the basis of this similarity in infrared spectra, we consider the brown product to have the formula  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$ . According to chemical analysis, it is a trihydrate.

For  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  calculated: 46.19% V, 6.95% Na, 8.16%  $\text{H}_2\text{O}$ ; found: 46.34% V, 7.10% Na, 8.30%  $\text{H}_2\text{O}$ .

The authors of paper [5] assign the formula  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$  to sodium vanadate the infrared spectrum of which is identical with the infrared spectrum of our salt while the authors of paper [11] put forward the formula  $\text{Na}_2\text{V}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$  for this substance. Anhydrous sodium hexavanadate is not known for the present.

In the brown products prepared at other values of  $Z$  which are denoted  $X$  and  $X'$  the content of sodium varies from 3.32% to 5.70% and the content of vanadium

Table 2

## Interplanar distances

$\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$		$\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$		$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$	
$d/\text{nm}$	$I_{\text{rel}}$	$d/\text{nm}$	$I_{\text{rel}}$	$d/\text{nm}$	$I_{\text{rel}}$
1.072	s	1.042	m	0.786	vs
0.990	vs	0.948	vw	0.362	vw
0.877	vs	0.898	m	0.340	w
0.807	m	0.837	m	0.308	s
0.724	s	0.767	vw	0.288	w
0.608	vw	0.722	vw	0.241	vw
0.587	vw	0.656	s	0.231	vw
0.543	vw	0.604	w	0.225	w
0.501	vw	0.584	vw	0.204	vw
0.444	vw	0.436	vw	0.199	vw
0.383	vw	0.421	vw	0.179	w
0.364	m	0.397	vw	0.175	vw
0.347	m	0.386	vw	0.166	vw
0.344	m	0.373	vw		
0.336	vw	0.356	vw		
0.327	vw	0.352	vw		
0.324	vw	0.331	m		
0.294	vw	0.325	vw		
0.288	w	0.318	vw		
0.286	vw	0.315	vw		
0.277	vw	0.307	w		
0.272	vw	0.299	vw		
0.268	vw	0.295	vw		
0.260	vw	0.287	m		
0.255	w	0.275	vw		
0.245	s	0.271	vw		
0.239	vw	0.268	vw		
0.227	vw	0.257	vw		
0.223	vw	0.250	w		
0.220	vw	0.247	vw		
0.216	w	0.242	vw		
0.213	vw	0.238	vw		
0.204	w	0.229	vw		
0.200	vw	0.214	vw		
0.197	w	0.207	vw		
0.193	vw	0.199	vw		
0.186	vw	0.197	w		
0.179	vw	0.196	vw		
0.177	vw	0.181	vw		
0.174	vw	0.175	vw		
0.172	vw				

Table 2 (Continued)

$\text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}$		$\text{Na}_5\text{HV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$		$\text{Na}_2\text{V}_6\text{O}_{10} \cdot 3\text{H}_2\text{O}$	
$d/\text{nm}$	$I_{\text{rel}}$	$d/\text{nm}$	$I_{\text{rel}}$	$d/\text{nm}$	$I_{\text{rel}}$
0.171	vw				
0.169	vw				
0.161	vw				
0.156	vw				
0.154	vw				

vs — very strong, s — strong, m — medium, w — weak, vw — very weak.

Table 3

## Infrared spectra

$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$		X		X'		Empirical assignment [10]
$\tilde{\nu}/\text{cm}^{-1}$	$I$	$\tilde{\nu}/\text{cm}^{-1}$	$I$	$\tilde{\nu}/\text{cm}^{-1}$	$I$	
1643	m	1642	m	1640	m	$\delta(\text{H}_2\text{O})$
1008	s	1003	vs	1003	s	
969	vs	971	vs	972	m	$\nu(\text{OV})$
951	sh	952	sh	—	—	
—	—	921	vw	922	w	
828	w	822	m	857*		
					s	$\nu(\text{OV}_2)$
725	vs	722	vs	691		
655	vw	—	—	—	—	
534	vs	560*		560*		
			m		w	$\nu(\text{OV}_3)$
484	vs	475		475		
418	vw	—	—	—	—	$\delta(\text{VO}_x)^a$

a) Bending vibrations with contribution of the final OV groups.

\* — Broad absorption maximum; sh — shoulder.

from 43.12% to 45.50%. At  $Z = 0.65$  and  $Z = 0.70$  (20°C), the substance (X') with the smallest content of sodium (3.32%) and 44.91% content of vanadium was prepared. The empirical formula  $\text{NaV}_6\text{O}_{15.5} \cdot 6\text{H}_2\text{O}$  or  $\text{NaHV}_6\text{O}_{16} \cdot 5.5\text{H}_2\text{O}$  may be assigned to this substance [12]. The infrared spectrum of this substance does not, in principle, differ from the infrared spectra of  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  (Table 3). However, it is less resolved and contains another band at  $922 \text{ cm}^{-1}$  and the absorption band at  $972 \text{ cm}^{-1}$  is less intensive. A small number of diffractions in the X-ray powder pattern indicates an insufficiently developed structure.

In the products prepared at  $Z = 0.60$ — $0.70$  ( $40^\circ\text{C}$ ) the content of sodium has increased approximately by 2% and that of vanadium by 1%. In the infrared spectra (Table 3) a decrease in intensity of the absorption band at  $921\text{ cm}^{-1}$  is to be observed and the intensity of the absorption band at  $971\text{ cm}^{-1}$  is substantially increased. All significant diffractions corresponding to  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  are present in the X-ray powder diffraction pattern. On the basis of these facts, we assume that these substances (X) may be intermediates in the formation of  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ .

In order to estimate the influence of vanadium concentration on formation of the solid products in given systems, the solutions of sodium metavanadate of the concentration of  $1.0\text{ mol dm}^{-3}$  were also investigated.

At this concentration, sodium decavanadate may be prepared only for  $Z = 0.40$  or  $Z = 0.45$  ( $40^\circ\text{C}$ ) after preceding separation of small amount of the brown precipitate and concentrating the solutions. By investigating the dependence of pH on time and amount of the formed precipitate, we obtained similar relationships as with the solutions of the concentration of  $0.5\text{ mol dm}^{-3}$  except for  $Z = 0.70$  ( $20$  and  $60^\circ\text{C}$ ) at which the pH values initially increase and afterwards decrease. In solutions with lower values of  $Z$  such a large amount of the voluminous brown precipitate was formed during acidification that the pH measurement was tedious and inaccurate. For this reason, these values are regarded as orienting ones and are not presented.

$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  arises at  $Z = 0.50$ — $0.70$  ( $40^\circ\text{C}$ ) and at  $Z = 0.45$ — $0.65$  ( $60^\circ\text{C}$ ) in 45 h, at  $Z = 0.50$ — $0.55$  ( $40^\circ\text{C}$ ) in 60 h. The content of vanadium and sodium of the compound prepared at  $Z = 0.70$  ( $60^\circ\text{C}$ ) does not correspond to the above formula and the X-ray powder pattern indicates a less developed structure. The results obtained with all values of  $Z$  at  $20^\circ\text{C}$  were analogous to those obtained at  $Z = 0.70$  ( $60^\circ\text{C}$ ).

For completeness, we have to mention that V(IV) was determined in all brown products and its amount was 0.5% approximately. In the effort to remove V(IV), the substances were boiled in distilled water with a small amount of hydrogen peroxide, decanted, and dried at  $25^\circ\text{C}$ . This experiment was not successful.

On the basis of these results it may be stated that the composition of resulting products depends on concentration. In the case of more diluted solutions there is a larger region of the  $Z$  values at which sodium decavanadate or hydrogen-decavanadate may be prepared and the brown products arise slower and in smaller yield.

The rate of formation and yield of the brown product are directly proportional to the value of  $Z$ .

The composition of  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  is likely to depend not only on  $Z$  but also on pH of the reaction medium during isolation. The pH value of this medium is, however, affected by the degree of acidification and amount of the precipitate

formed because the equilibria solid phase—solution must be taken into consideration in these systems. The optimum pH value for isolation of  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  is in the range 4.5—5.9.

Temperature has substantial influence on the rate of formation and yield of the brown substance because decavanadates or hydrogendecavanadates arise at lower temperature under equal other conditions. This conclusion results from the fact that the brown products arise at 60°C in the whole range of  $Z$  (sodium decavanadates cannot be prepared in this case). At 40°C, the brown precipitate also arises primarily in the whole range of  $Z$  (decavanadates may be obtained at  $Z = 0.40$  or  $Z = 0.45$  after separating the precipitate and concentrating the solutions). At 20°C, the brown substance appears in solutions of the concentration of  $0.5 \text{ mol dm}^{-3}$  at  $Z = 0.60$ — $0.70$  (with other values of  $Z$  decavanadates and hydrogendecavanadates can be prepared). Solutions of the concentration of  $1.0 \text{ mol dm}^{-3}$  (20°C) represent an exception. In this case, the brown substance of varying composition ( $X$ ) precipitates at all values of  $Z$ . The temperature increase affects the composition of the brown substances so that a higher temperature favours the formation of  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ .

In conclusion, it may be summarized that the region of  $Z$  where  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  or its intermediate ( $X$ ) with varying content of vanadium and sodium is to be obtained extends with increasing temperature and concentration.

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