

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

VII. Products of the reactions taking place in acidified solutions of ammonium metavanadate

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Received 22 October 1981

Accepted for publication 7 April 1982

The influence of the degree of solution acidification, temperature, vanadium concentration, and reaction time on composition of the solid substances arising in the system $\text{NH}_4\text{VO}_3\text{—H}_2\text{SO}_4\text{—H}_2\text{O}$ was studied. It has been found that all the studied factors influence composition of the arising ammonium polyvanadates. The orange substance $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$, red-brown hydrogen hexavanadates of the formula $(\text{NH}_4)_{2-x}\text{H}_x\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ ($x \leq 1$), and mixtures of these substances were obtained from the system.

Изучалось влияние кислотности раствора, температуры, концентрации ванадия и времени протекания реакции на состав твердых продуктов, возникающих в системе $\text{NH}_4\text{VO}_3\text{—H}_2\text{SO}_4\text{—H}_2\text{O}$. Оказалось, что все перечисленные факторы влияют на состав образующихся поливанадатов аммония. Из системы был выделен оранжевый $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$, красно-коричневые кислые гексаванадаты состава $(\text{NH}_4)_{2-x}\text{H}_x\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ ($x \leq 1$), или смеси этих соединений.

It results from the papers of several authors that the pH value of medium, concentration of reactants in solution, temperature, and reaction time have influence on composition of the solid vanadates arising in aqueous solutions [1—10]. But we cannot at present draw general conclusions concerning the influence of individual factors because the specific properties of polyvanadates of various metals play a very important role in these reactions. The most important properties of this kind are solubility and stability in a given medium.

This paper deals with the results obtained by investigating the system $\text{NH}_4\text{VO}_3\text{—H}_2\text{SO}_4\text{—H}_2\text{O}$. The aim of this study was to find out how the composition of ammonium polyvanadates crystallizing from a certain system is affected by the changes of given factors in their mutual connection.

Experimental

Ammonium metavanadate of anal. grade (Loba-Chemie, Wien) was purified according to [11]. Its composition corresponded to the formula NH_4VO_3 . Other chemicals were anal. grade reagents of Czechoslovak production.

Vanadium(V) and vanadium(IV) was determined volumetrically by means of a solution of FeSO_4 (0.1 mol dm^{-3}) or KMnO_4 (0.01 mol dm^{-3}) while ammonia was estimated by the distillation method according to Parnas—Wagner.

The pH measurements were carried out with a pH-meter OP 201/1 (Radelkis, Budapest) equipped with a combined electrode OP-807-1/A.

The infrared spectra were taken in Nujol suspension in the region of $400\text{--}1800 \text{ cm}^{-1}$ with a spectrophotometer Spectromaster Grubb Parsons.

The powder diffraction patterns were obtained by means of a diffractograph Philips equipped with a goniometer PW 1058 by using the CuK_α radiation in the range Θ $5\text{--}30^\circ$.

Syntheses

The concentration of the starting solutions of NH_4VO_3 was 0.1 mol dm^{-3} (series I) and 0.2 mol dm^{-3} (series II). The syntheses were carried out at 40, 60, 80, and 95°C in both series.

The solutions used in each series at a given temperature differed from each other by the degree of acidification Z ($Z = n_{\text{H}_2\text{SO}_4} / n_{\text{NH}_4\text{VO}_3}$, n = amount of substance). The value of Z was adjusted with H_2SO_4 (0.5 mol dm^{-3}). The value of Z varied in the range $0.2\text{--}2.0$, the step being 0.1 or 0.5.

The reactions proceeded under constant stirring at constant volume of the reaction solutions (100 ml).

During synthesis, the pH value was measured in regular time intervals. The first pH value was obtained after heating and thermostating the solutions at a required temperature and the last one before isolation of the solid substance.

The solid substances were isolated from the reaction medium at 40°C after 24 h. The reaction proceeded much more rapidly at 60, 80, and 95°C and the solid substances were isolated 15 min after the beginning of the solid substance formation in the first series and 60 min after the beginning of the solid substance formation in the second series. These time intervals were ascertained experimentally and found to be the optimum ones.

After separation, the solid substances were washed with water to negative reaction with respect to SO_4^{2-} and dried freely at laboratory temperature. They were identified on the basis of the results of chemical analysis, infrared spectra, and X-ray diffraction patterns.

Results and discussion

The orange ammonium hexavanadate $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ was formed in the investigated systems and its formation was dependent on conditions of the synthesis. For $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ calculated: 6.03% NH_4^+ , 51.14% V; found: 6.04% NH_4^+ , 50.93% V,

the ratio $n_{\text{NH}_4^+} : n_{\text{V}} = 1 : 3$. Besides, the red-brown ammonium hydrogen hexavanadates with variable composition which could be described by the stoichiometrical formula $(\text{NH}_4)_{2-x}\text{H}_x\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ ($x \leq 1$) or mixtures of these both compounds came into existence.

Ammonium hexavanadate is a known substance which was prepared by Kelmers. It belongs among polyvanadates with layer structure and is isostructural with the hexavanadates of alkali metals [12]. The doublet of intensive absorption bands $\nu(\text{V}-\text{O}_T)$ at about 970 and 1010 cm^{-1} [13] (Fig. 1a) is characteristic in the infrared spectra of these substances.

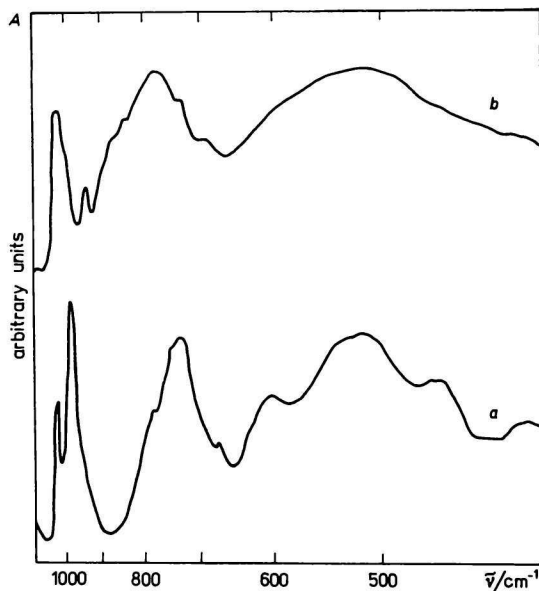


Fig. 1. Infrared spectra of the prepared substances:
a) $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$; b) $\text{NH}_4\text{HV}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$.

The red-brown hydrogen salts of the composition $(\text{NH}_4)_{2-x}\text{H}_x\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ ($x \leq 1$) have not been described in literature up to now. The compound of the composition $\text{NH}_4\text{HV}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$ ($x = 1$) was also prepared. For $\text{NH}_4\text{HV}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$ calculated: 2.92% NH_4^+ , 49.56% V; found: 2.94% NH_4^+ , 49.34% V, $n_{\text{NH}_4^+} : n_{\text{V}} = 1 : 6$. The very intensive absorption band at 1010 cm^{-1} $\nu(\text{V}-\text{O}_T)$ and the band at 922 cm^{-1} which has been assigned to $\delta(\text{V}-\text{OH})$ [14] are characteristic in the infrared spectra of hydrogen hexavanadates (Fig. 1b). The powder diffraction patterns of these substances contain a small number of unsharp diffractions, which indicates a poorly ordered structure.

Table 1. Composition of ammonium polyvanadates in the system $\text{NH}_4\text{VO}_3\text{—H}_2\text{SO}_4\text{—H}_2\text{O}$

Z	40°C				60°C				80°C				95°C			
	t/h	c/mol dm ⁻³		min	c/mol dm ⁻³		min	c/mol dm ⁻³		min	c/mol dm ⁻³		min	c/mol dm ⁻³		
		0.1	0.2		0.1	0.2		0.1	0.2		0.1	0.2				
0.2	24	Δ	Δ	15	A*	A*	15	A	A*	15	A*	A*	60	A*	A*	
				60	A*	A*	60	A	A	60	A*	A*	60	A*	A*	
0.3	24	Δ	Δ	15	A	A+B	15	A*	A	15	A	A*	60	A	A*	
				60	A	A*	60	A	A	60	A	A*	60	A	A*	
0.4	24	A*	A*	15	A	B+A	15	A	A	15	A	A*	60	A	A*	
				60	A	A+B	60	A	A	60	A	A*	60	A	A*	
0.5	24	A*	A+B	15	A+B	B+A	15	A*	A+B	15	A	A	60	A	A	
				60	A+B	A+B	60	A	A	60	A	A	60	A	A	
0.6	24	A+B	A+B	15	A+B	B+A	15	A+B	A+B	15	A	A+B	60	A	A+B	
				60	A+B	A+B	60	A+B	A+B	60	A+B	A+B	60	A	A+B	
0.7	24	A+B	A+B	15	A+B	B+A	15	A+B	B+A	15	A+B	A+B	60	A+B	A+B	
				60	A+B	A+B	60	A+B	A+B	60	A+B	A+B	60	A+B	A+B	
0.8	24	A+B	B+A	15	A+B	B+A	15	A+B	B+A	15	A+B	B+A	60	A+B	B+A	
				60	A+B	B+A	60	A+B	B+A	60	A+B	B+A	60	A+B	A+B	
0.9	24	A+B	B+A	15	A+B	B+A	15	A+B	B+A	15	A+B	B+A	60	A+B	B	
				60	A+B	B+A	60	A+B	B+A	60	A+B	B+A	60	A+B	B+A	
1.0	24	A+B	B+A	15	B+A	B	15	B+A	B+A	15	B+A	B	60	B+A	B	
				60	B+A	B	60	A+B	B+A	60	A+B	B+A	60	B	B	
1.5	24	A+B	B+A	15	B	B	15	A+B	B	15	B+A	B	60	B	B	
				60	A+B	B+A	60	B	B	60	B	B	60	B	B	
2.0	24	A+B	B+A	15	Δ	B	15	B	B	15	B	B	60	B	B	
				60	A+B	B+A	60	B	B	60	B	B	60	B	B	

A — $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$; B — $(\text{NH}_4)_{2-x}\text{H}_x\text{V}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ ($x \leq 1$); * — traces of NH_4VO_3 or $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28} \cdot x\text{H}_2\text{O}$; Δ — solid substance does not arise in the stated time interval.

A great number of reaction products had the content of NH_4^+ varying in the range 3—6%. The X-ray phase analysis unambiguously confirmed only the presence of $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$. The analysis of the infrared spectra has led to the conclusion that these substances are mixtures of orange ammonium hexavanadate and red-brown ammonium hydrogen hexavanadate. The composition of the obtained substances determined on the basis of X-ray phase analysis, infrared spectra, and chemical analysis is presented in Table 1.

By estimating the influence of individual investigated factors influencing the composition of the arising ammonium polyvanadates in acid medium the following facts were observed.

The compound $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ is formed at the lowest investigated values of Z independently of temperature in the reaction medium (in the temperature interval 40—95°C) as well as of vanadium concentration. In some cases, it contains an admixture of NH_4VO_3 and the presence of $(\text{NH}_4)_6\text{V}_{10}\text{O}_{18} \cdot x\text{H}_2\text{O}$ cannot be also excluded at temperature 40°C. An increase in Z (decrease in pH) optimizes the conditions of formation of ammonium hydrogen hexavanadates.

The influence of concentration of the starting solution on composition of ammonium polyvanadates manifests itself mainly at 40 and 60°C in that sense that the increasing concentration of solution supports the formation of hydrogen hexavanadates. This effect is not so conspicuous at 80 and 95°C.

The increase in temperature positively affects the rate of formation of both types of hexavanadates and also has influence on their composition. Hydrogen hexavanadates arose only at temperatures 60, 80, and 95°C.

The time of isolation of the solid substance from reaction medium is also an important factor. In most cases, we may observe that hydrogen hexavanadates in contact with reaction solution are transformed into more stable $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$. However, this transformation was not observed at certain values of Z . The mechanism of this reaction is not for the time being known.

By comparing the pH values of reaction medium at the start of each reaction and at withdrawing of the solid substance, it has been found that the pH value increases in most cases. That means that the reactions involving consumption of the H_3O^+ ions take place in the solution.

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Translated by R. Domanský