

Synthesis and Properties of Ethanolammonium Decavanadates

E. RAKOVSKÝ and L. ŽÚRKOVÁ

*Department of Inorganic Chemistry, Faculty of Natural Sciences,
Comenius University, SK-842 15 Bratislava*

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(EAH)₄H₂V₁₀O₂₈ · 2H₂O (A), (EAH)₆V₁₀O₂₈ · 2H₂O (B), (DEAH)₄H₂V₁₀O₂₈ (C), (DEAH)₄H₂V₁₀O₂₈ · 2H₂O (D), and (TEAH)₄H₂V₁₀O₂₈ (E) were prepared by dissolving V₂O₅ in an aqueous solution of ethanolamine (EA), diethanolamine (DEA) or triethanolamine (TEA). The compounds prepared were characterized by IR spectroscopy, and their thermal properties were studied.

A relatively large number of decavanadates with inorganic and organic cations was characterized so far. While the crystal structures of decavanadates with inorganic cations all contain crystal water molecules, the decavanadates with organic cations can also occur as anhydrous salts.

The structure of the bulky V₁₀O₂₈⁶⁻ anion consist of an arrangement of ten edge-shared VO₆ octahedra. The decavanadate anion can be found in different protonation states. The double- and triple-linked oxygen atoms are most susceptible of protonation [1]. The crystal water has a stabilizing role in the crystal structure of decavanadates with inorganic cations. The cations are usually coordinated by water molecules and, due to the hydrogen bonds to the oxygens of decavanadate ion, they strengthen the bonding interactions between the structural units. On dehydration, the crystal structure of such decavanadates is decomposed [2]. The existence of anhydrous decavanadates with organic cations is obviously based also on a strong hydrogen bond formation.

The anhydrous protonated decavanadates are used as precursors for preparation of a new class of highly condensed vanadium compounds with unusual properties.

The aim of this work was the synthesis and characterization of ethanolammonium, diethanolammonium, and triethanolammonium hydrogenecavanadates.

EXPERIMENTAL

V₂O₅ was prepared by thermal decomposition of a previously purified NH₄VO₃. All other chemicals used were of anal. grade.

The elemental analysis was performed on a CHN analyzer 1106 (Erba, Milan). Vanadium was estimated by titration with FeSO₄ using diphenylamine as indicator. pH was measured on a TTT-2 pH-meter (Radiometer, Copenhagen) using a GK 2401C electrode.

The IR spectra in Nujol mulls or KBr pellets were measured on a Specord M 80 spectrophotometer (Zeiss, Jena).

The thermal analysis was performed on a Derivatograph Q-1500 (MOM, Budapest) under following conditions: air atmosphere, sample mass 200 mg, heating rate 5°C min⁻¹, Pt-crucible, Al₂O₃ as internal standard, and temperature interval 20–800°C.

Syntheses

Ethanolammonium decavanadates were prepared by dissolving V₂O₅ in an aqueous solution of ethanolamine. The reaction mixture was kept at room temperature in dark and stirred for 24 h. After being filtered off, the pH of solution was adjusted by hydrochloric acid (*c* = 4 mol dm⁻³) to the value required.

In syntheses of (EAH)₄H₂V₁₀O₂₈ · 2H₂O (A) and (EAH)₆V₁₀O₂₈ · 2H₂O (B), V₂O₅ (1.14 g; 6.25 mmol), EA (0.45 cm³; 7.5 mmol), and H₂O (50 cm³) were used. The EA to vanadium mole ratio, *n*(EA) *n*(V), was 0.6. After dissolving of V₂O₅, the pH of solution was adjusted to 2.2 for A and to 6.6 for B. To the orange solution, ethanol was added until formation of a weak turbidity. The orange crystalline products were formed within 8–10 d from solutions kept in refrigerator. The pH values of mother solutions were in the range 3.5–3.6 for A and 7.5–8.0 for B. The crystals were washed with ethanol and air-dried in dark.

In synthesis of (DEAH)₄H₂V₁₀O₂₈ (C), V₂O₅ (1.36 g; 7.5 mmol), DEA (2.15 cm³; 22.5 mmol), and H₂O (50 cm³) were used. The DEA to vanadium mole ratio, *n*(DEA) *n*(V), was 1.5. After dissolving of V₂O₅, the pH of solution was adjusted to 2.0, one and half volume of ethanol was then added, and the mixture was left to stand in refrigerator. An oil-like layer was formed within few hours. After its separation, the turbid orange solution was placed in a refrigerator. In

an interval of 5–10 d, the orange crystals formed were isolated, washed with ethanol and air-dried in dark.

In synthesis of $(\text{DEAH})_4\text{H}_2\text{V}_{10}\text{O}_{28} \cdot 2\text{H}_2\text{O}$ (D), V_2O_5 (1.82 g; 10 mmol), DEA (2.90 cm³; 30 mmol), and H_2O (100 cm³) were used. The $n(\text{DEA})/n(\text{V})$ mole ratio was 1.5. The pH of solution was adjusted to 2.0. Big orange crystals were formed within 4 d from the solution kept in refrigerator. The pH of mother solution was in the range 2.0–2.3. The crystals were washed with cold water and air-dried in dark.

In synthesis of $(\text{TEAH})_4\text{H}_2\text{V}_{10}\text{O}_{28}$ (E), V_2O_5 (1.36 g; 7.5 mmol), TEA (2.40 cm³; 18 mmol), and H_2O (50 cm³) were used. The $n(\text{TEA})/n(\text{V})$ mole ratio was 1.2. The pH of solution was adjusted to 2.5. The formation and isolation of orange crystalline product were identical as for $(\text{DEAH})_4\text{H}_2\text{V}_{10}\text{O}_{28}$.

For $(\text{EAH})_4\text{H}_2\text{V}_{10}\text{O}_{28} \cdot 2\text{H}_2\text{O}$ $w_1(\text{calc.})$: 40.96 % V, 3.08 % H, 7.73 % C, 4.50 % N; $w_1(\text{found})$: 40.93 % V, 3.05 % H, 7.71 % C, 4.44 % N. For $(\text{EAH})_6\text{V}_{10}\text{O}_{28} \cdot 2\text{H}_2\text{O}$ $w_1(\text{calc.})$: 37.29 % V, 3.83 % H, 10.55 % C, 6.15 % N; $w_1(\text{found})$: 37.05 % V, 3.70 % H, 10.41 % C, 6.01 % N. For $(\text{DEAH})_4\text{H}_2\text{V}_{10}\text{O}_{28}$ $w_1(\text{calc.})$: 36.81 % V, 3.64 % H, 13.89 % C, 4.05 % N; $w_1(\text{found})$: 36.75 % V, 3.59 % H, 13.95 % C, 4.03 % N. For $(\text{DEAH})_4\text{H}_2\text{V}_{10}\text{O}_{28} \cdot 2\text{H}_2\text{O}$ $w_1(\text{calc.})$: 35.87 % V, 3.83 % H, 13.53 % C, 3.95 % N; $w_1(\text{found})$: 35.64 % V, 3.85 % H, 13.36 % C, 3.92 % N. For $(\text{TEAH})_4\text{H}_2\text{V}_{10}\text{O}_{28}$ $w_1(\text{calc.})$: 32.65 % V, 4.26 % H, 18.48 % C, 3.59 % N; $w_1(\text{found})$: 32.43 % V, 4.27 % H, 18.18 % C, 3.56 % N.

RESULTS AND DISCUSSION

From the viewpoint of the polyanion composition, two types of compounds were prepared: 1. decavanadate $(\text{EAH})_6\text{V}_{10}\text{O}_{28} \cdot 2\text{H}_2\text{O}$; 2. dihydrogendecavanadates with general formula $(\text{AH})_4\text{H}_2\text{V}_{10}\text{O}_{28}$, prepared as anhydrous salts ($A = \text{DEA}, \text{TEA}$) or crystallohydrates ($A = \text{EA}, \text{DEA}$).

Which of the two types of decavanadates can be prepared, depends on the cation properties (size, structure, polarizing effect, and considering the organic cations also the ability to form hydrogen bonds) and on the reaction conditions (pH, vanadium concentration in solution, temperature, and solvent used). The stability of the structure of decavanadates with organic cations is influenced by hydrogen bonds between cation and anion, too. In the decavanadates with inorganic cation this is the role of crystal water molecules. This is why decavanadates with inorganic cation are known only as crystallohydrates, while organic cations can form also anhydrous decavanadates. As in the aqueous solution there is an equilibrium between decavanadates with different protonation degree $\text{H}_n\text{V}_{10}\text{O}_{28}^{(6-n)-}$ ($n = 0-4$), the reaction conditions for preparation of different types of decavanadates with the same cation depend also on their solubilities.

The majority of decavanadates prepared so far is of composition $(\text{AH})_4\text{H}_2\text{V}_{10}\text{O}_{28}$. Such decavanadates

were obtained with almost all organic cations used in syntheses, even with cations of macrocyclic tetramines [3]. Only a relatively small number of decavanadates of the composition $(\text{AH})_6\text{V}_{10}\text{O}_{28}$ are known. This fact can be explained by stoichiometry and crystallochemical factors. Though, the $\text{V}_{10}\text{O}_{28}^{6-}$ anion is voluminous, the requirements on cation properties, in case of the cation to anion stoichiometry 6 : 1, increase. That is why the decavanadate of composition $(\text{EAH})_6\text{V}_{10}\text{O}_{28} \cdot 2\text{H}_2\text{O}$ can be prepared only with the smallest cation used. Another factor which allows to prepare both types of ethanolammonium decavanadates as pure substances is the sufficiently great difference in the solubilities of the decavanadates and their dihydrogen derivatives.

The role of crystal water molecules in structures of decavanadates with organic cations being able to form hydrogen bonds is not as important as in those with inorganic cations. At a convenient ionic radii ratio, r_C/r_A , there are the reaction conditions which determine whether a crystallohydrate or anhydrous compound is formed. As the alcoholammonium-cations are able to form hydrogen bonds with $\text{H}_n\text{V}_{10}\text{O}_{28}^{(6-n)-}$ anions ($n = 0, 2$) via OH and $[\text{NH}_x]^+$ ($x = 1-3$) groups as well, anhydrous decavanadates can also be obtained.

The structure of the $\text{V}_{10}\text{O}_{28}^{6-}$ anion is relatively rigid. It is only slightly influenced by the nature of cation and by the hydrogen bonds between cation and

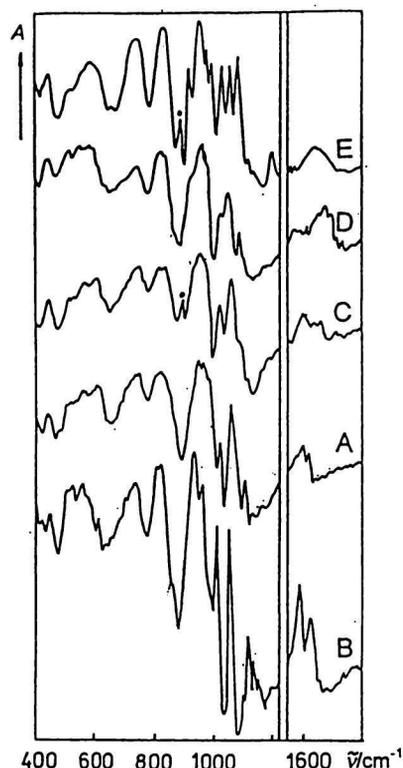


Fig. 1. IR spectra of the prepared compounds.

Table 1. Observed Wavenumbers and Intensities (I) in IR Spectra of Decavanadates in the Regions of 400–1000 cm⁻¹ and 1500–1650 cm⁻¹

(EAH) ₆ V ₁₀ O ₂₈ · 2H ₂ O		(EAH) ₄ H ₂ V ₁₀ O ₂₈ · 2H ₂ O		(DEAH) ₄ H ₂ V ₁₀ O ₂₈		(DEAH) ₄ H ₂ V ₁₀ O ₂₈ · 2H ₂ O		(TEAH) ₄ H ₂ V ₁₀ O ₂₈		Assignment
$\tilde{\nu}/\text{cm}^{-1}$	I	$\tilde{\nu}/\text{cm}^{-1}$	I	$\tilde{\nu}/\text{cm}^{-1}$	I	$\tilde{\nu}/\text{cm}^{-1}$	I	$\tilde{\nu}/\text{cm}^{-1}$	I	
990	sh	988	sh	977	sh	975	sh	999	s	$\nu(\text{V—O}_T)$
971	vs	968	vs	957	vs	967	vs	983	s	
940	vs	949	vs	940	sh	934	s	960	vs	
				903	w	888	sh	920	s	$\delta(\text{V—O—H})$
								893	m	
873	m									$\nu_{\text{as}}(\text{V—O}_B)$
832	vs			844	s	845	vs	834	vs	
822	vs	824	vs	820	s	827	vs			
		810	vs							
				773	sh					
747	s	751	vs							
730	sh	738	vs	740	s	740	s	745	vs	
		724	s	737	sh	720	m			
714	m									
700	m	704	m	704	w	705	w			
		687	m							
671	w	668	sh					662	vw	
652	vw									
		642	sh	646	w					
		621	sh			623	sh			
628	m	609	m	614	m	605	m			
592	s	595	sh			594	m	590	s	$\nu_s(\text{V—O}_B)$
571	s	576	m	572	m	588	m			
		562	m			571	m	565	sh	
538	s	534	m	534	w	558	m			
520	s	520	m			518	m	525	m	
		511	m	513	w					
		480	w							
458	m	450	sh							
434	w	440	m	445	m	445	m	446	m	$\delta(\text{V—O}_B)$
413	m							432	sh	
1665	w	1669	vw			1670	vw			$\delta(\text{H}_2\text{O})$
				1650	m	1648	m	1646	m	
1630	m	1627	m	1625	m	1624	m			
1594	s	1607	m	1595	m	1600	sh	1577	vw	$\delta(\text{NH}_3^+)$ $\delta(\text{NH}_3^+)$ $\delta(\text{C—N}^+—\text{H})$
		1579	m			1575	vw	1561	vw	
1564	sh	1566	w			1572	vw	1545	vw	
		1537	vw							
1514	s					1518	w			

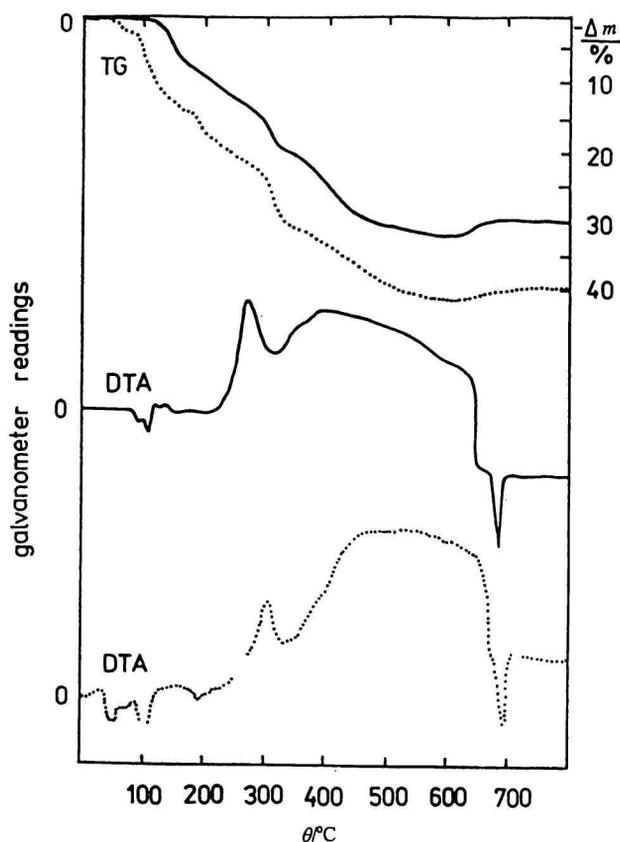


Fig. 2. Thermoanalytical curves of $(\text{DEAH})_4\text{H}_2\text{V}_{10}\text{O}_{28}$ (—) and $(\text{DEAH})_4\text{H}_2\text{V}_{10}\text{O}_{28} \cdot 2\text{H}_2\text{O}$ (...).

anion, and between crystal water and anion, respectively. Therefore, the compounds prepared could be identified based on their IR spectra (Fig. 1, Table 1) in the $\nu(\text{V—O})$ region ($400\text{—}1000\text{ cm}^{-1}$). Some authors believe that the IR spectra allow to distinguish the protonated and nonprotonated decavanadates. According to [4], the IR spectra of compounds with $\text{H}_n\text{V}_{10}\text{O}_{28}^{(6-n)-}$ anion exhibit two characteristic bands at 995 cm^{-1} $\nu(\text{V—O}_T)$ and 630 cm^{-1} $\delta(\text{V—OH})$. Obviously, the protonation of $\text{V}_{10}\text{O}_{28}^{6-}$ anion causes a change in the skeleton with V—O bonds, however, according to our knowledge, the polyvanadate cannot be identified as protonated decavanadate by presence of two bands mentioned above. Some of the dihydrogendecavanadates prepared in our laboratory exhibit these bands [5], but the others do not [3, 6, 7]. The IR spectra of ethanolammonium decavanadates are not in agreement with this hypothesis. The IR spectra of the anhydrous dihydrogendecavanadates C and E exhibit weak absorption bands at 903 and 893 cm^{-1} assigned to $\delta(\text{V—OH})$ [5]. In the IR spectra of the product of recrystallization of D from D_2O , the shoulder at 888 cm^{-1} disappeared and a new shoul-

der at 644 cm^{-1} appeared. The observed shift allows to assign these bands to $\delta(\text{V—OH})$ and $\delta(\text{V—OD})$, respectively.

The IR spectra in the $\delta(\text{N—H})$ and $\delta(\text{O—H})$ region ($1500\text{—}1600\text{ cm}^{-1}$) are, due to hydrogen bonds, very complicated. The exact assignment of the individual bands is thus not possible.

The thermoanalytical curves of C and D (Fig. 2) represent thermal decomposition of ethanolammonium decavanadates with following common features.

The thermal decomposition consists of simultaneous redox processes, dehydration, structure decomposition, and of crystallization of vanadium oxides. Under conditions used, it was not possible to separate the individual processes and to obtain well defined intermediates.

The mass loss starts at about 40°C in the crystallohydrates, or at about 100°C in the anhydrous compounds. Vanadium is reduced just in course of the crystal water release, therefore, corresponding anhydrous decavanadates could not be prepared.

The decavanadate structure is completely decomposed at about 200°C , and an X-ray amorphous product is so formed. The endothermic peaks on the DTA curves up to this temperature are connected with dehydration, corresponding redox reactions, and structure decomposition.

The maximum mass loss is reached in the temperature interval $560\text{—}600^\circ\text{C}$. The intermediates isolated at these temperatures are mixtures of V_2O_5 , V_2O_4 , and of at least one substance, maybe vanadium-oxide bronze, still containing residues of the organic component. In the temperature interval $200\text{—}600^\circ\text{C}$, the DTA curves are dominated by the exothermic effects corresponding to the crystallization of given compounds and redox process in which the gaseous products are released.

At still higher temperatures, due to the oxidation of vanadium(IV) to vanadium(V), a mass increase was observed. The rests of organic components are oxidized, too. The vanadium is quantitatively oxidized only if the thermal decomposition of the compounds with a high content of organic component (B) is performed at a lower heating rate, or in course of a repeated thermal analysis started from 500°C .

The end product of the decomposition is V_2O_5 . Its melting is manifested on the DTA curve by the last endothermic peak. The observed and the calculated total mass losses for all decavanadates are in good agreement.

The compound $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{VO}$ was isolated from the reaction system $\text{TEA—V}_2\text{O}_5\text{—H}_2\text{O}$ at $\text{pH} > 7$ by precipitation with ethanol. The characterization and crystal structure of this compound were published earlier [8, 9].

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