

# Benzylammonium, Imidazolium and Pyridinium Polyvanadates – Synthesis and Characterization

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**Summary.** From the reaction systems,  $B-V_2O_5-HClO_4-H_2O$  and  $B-V_2O_5-H_2O$ , where  $B$  is benzylamine ( $Bz$ ), imidazole ( $Im$ ) or pyridine ( $Py$ ), eight new compounds were synthesized: at 20 °C, the metavanadate and decavanadates of composition  $(BzH)VO_3$ ,  $(BzH)_6V_{10}O_{28} \cdot 3H_2O$ ,  $(ImH)_6V_{10}O_{28} \cdot 2H_2O$ ,  $(PyH)_6V_{10}O_{28} \cdot 2H_2O$ ,  $(ImH)_4H_2V_{10}O_{28} \cdot 2H_2O$  and  $(PyH)_4H_2V_{10}O_{28} \cdot 3H_2O$ , and at 60 °C, the hexavanadates of composition  $(ImH)_2V_6O_{16} \cdot H_2O$  and  $(PyH)_2V_6O_{16} \cdot H_2O$ . The  $pH$  ranges of solutions the polyvanadates can be isolated from, were estimated. The compounds prepared were characterized by chemical analysis and IR spectroscopy. The synthesis of deuterated analogues allowed to assign the IR bands corresponding to vibrations of water in the spectra of deca- and dihydrogendecavanadates and to V–OH vibrations in the spectra of dihydrogendecavanadates.

**Keywords.** Benzylammonium polyvanadates; Imidazolium polyvanadates; Pyridinium polyvanadates.

## Benzylammonium-, Imidazolium- und Pyridinium-Polyvanadate. Synthese und Charakterisierung

**Zusammenfassung.** Aus dem Reaktionssystem  $B-V_2O_5-HClO_4-H_2O$  und  $B-V_2O_5-H_2O$  [ $B$  = Benzylamin ( $Bz$ ), Imidazol ( $Im$ ) oder Pyridin ( $Py$ )] wurden acht neue Verbindungen synthetisiert: bei 20 °C entstanden die Metavanadate und Decavanadate der Zusammensetzung  $(BzH)VO_3$ ,  $(BzH)_6V_{10}O_{28} \cdot 3H_2O$ ,  $(ImH)_6V_{10}O_{28} \cdot 2H_2O$ ,  $(PyH)_6V_{10}O_{28} \cdot 2H_2O$ ,  $(ImH)_4H_2V_{10}O_{28} \cdot 2H_2O$  und  $(PyH)_4H_2V_{10}O_{28} \cdot 3H_2O$ , bei 60 °C entstanden die Hexavanadate  $(ImH)_2V_6O_{16} \cdot H_2O$  und  $(PyH)_2V_6O_{16} \cdot H_2O$ . Die  $pH$ -Bereiche, innerhalb derer Polyvanadate isoliert werden können, wurden abgeschätzt. Die Verbindungen wurden mittels chemischer Analyse und IR-Spektroskopie charakterisiert, wobei die Synthese deuterierter Analoga die Zuordnung von Banden unterstützte.

## Introduction

Due to their specific properties some organic cations can give rise to new types of polyvanadates, e.g. dodecavanadates [1] or pentavanadates containing the isolated  $V_5O_{14}^{3-}$  anion with cage structure [2], which have not been prepared with inorganic cations [3]. In decavanadates, the structure of the isolated  $V_{10}O_{28}^{6-}$  polyanion is built up from ten  $VO_6$  octahedra and it seems not to be influenced by the cation present – both inorganic or organic [4]. Nevertheless, the protonation degree in hydrogendecavanadates with organic cations can be higher than in those with an inorganic cation [5]. In the majority of metavanadates with inorganic

cations, a chain structure built up from  $\text{VO}_4$  or  $\text{VO}_5$  polyhedra was found [6, 7]. However, in tetrabutylammonium metavanadate [8], the polyanion has a tetrameric cyclic structure formed by joined  $\text{VO}_4$  tetrahedra.

We report here the synthesis and properties of vanadates with the organic bases benzylamine, imidazole, and pyridine, with  $pK_B$  values in the range 4.62–8.66, formed in dependence on  $pH$  and temperature, i.e. the main factors determining the composition and the structure of the polyvanadates formed [9, 10].

## Experimental Part

$\text{V}_2\text{O}_5$  was prepared by thermal decomposition of  $\text{NH}_4\text{VO}_3$  being previously purified. All other chemicals used were of analytical grade.

$pH$  values were measured on a PHM-22  $pH$ -meter (Radiometer) with a GK 2401c electrode. The IR spectra in Nujol mulls were registered on a Specord M 80 spectrophotometer (Zeiss). The powder diffraction patterns were obtained on a Philips diffractograph equipped with a PW 1050 goniometer,  $\text{CuK}_\alpha$  radiation was used.

Vanadium(V) was determined by titration with  $\text{FeSO}_4$  ( $c = 0.1 \text{ mol dm}^{-3}$ ) or gravimetrically as  $\text{V}_2\text{O}_5$  after the sample was annealed to constant weight at  $450^\circ\text{C}$ . Carbon, hydrogen and nitrogen were determined on a Hewlett Packard CHN-analyzer.

The meta- and decavanadates were isolated from the  $B\text{-H}_2\text{O-V}_2\text{O}_5$  or  $B\text{-H}_2\text{O-V}_2\text{O}_5\text{-HClO}_4$  reaction solutions obtained by dissolving  $\text{V}_2\text{O}_5$  in aqueous solution of the organic base at  $60^\circ\text{C}$ . The base:vanadium molar ratio was 1:1 for *Bz* and *Im*, and 3:1 for *Py* due to its lower basicity. The initial  $pH$ s of starting solutions with vanadium (V) concentrations of 0.1 and  $0.05 \text{ mol dm}^{-3}$  were: 7.0 and 7.2 for *Bz*, 6.3 and 6.5 for *Im*, and 6.0 and 6.1 for *Py*. The  $pH$  of the individual reaction solutions was then adjusted using perchloric acid ( $c = 1.0 \text{ mol dm}^{-3}$ ) or by an excess of the organic base so that the  $pH$  values differed by 0.5 in the following  $pH$  ranges: 2.5–11.0 for *Bz*, and 2.5–8.0 for *Im* and *Py*.

Except of *PyH* polyvanadates which were precipitated with acetone, all other compounds were formed on slow crystallization at  $20^\circ\text{C}$ .

The products formed were filtered off, washed with ethanol or acetone and dried at room temperature.

The deuterated *ImH* and *pyH* polyvanadates were prepared from  $\text{D}_2\text{O}$  at  $pH$  3.2, resp. 6.0, using the same procedure as for  $\text{H}_2\text{O}$  solutions.

The *ImH* and *PyH* hexavanadates were prepared from the same reaction systems, however, at  $60^\circ\text{C}$ . The solutions with vanadium concentrations  $0.1 \text{ mol dm}^{-3}$  for *Im* and  $0.3 \text{ mol dm}^{-3}$  for *Py* were kept in closed vessels and stirred. The reaction times were: 8 days for *ImH* and 30 hours for *pyH* hexavanadate.

## Results and Discussion

As follows from the chemical analysis and IR spectra, a gray-white metavanadate and orange dihydrogendeca- or decavanadates crystallize out at  $20^\circ\text{C}$ , and red-brown hexavanadates are formed at  $60^\circ\text{C}$ . Their chemical compositions are based on results of chemical analysis and the  $pH$  ranges of solutions suitable for isolation of the compounds are shown in Table 1. A metavanadate was prepared with the strongest base, *Bz*, while the less basic *Im* and *Py* form only decavanadates. The basicity of *Im* and *Py* is obviously lower than needed for reaching an optimum  $pH$  necessary for the metavanadate formation. Our attempts to increase the  $pH$  to 8.0 by addition of sodium hydroxide resulted in formation of sodium vanadate. Another factor which may influence the formation of solid metavanadates or shift the  $pH$  range of their formation is the solubility.

**Table 1.** Composition of *BzH*, *ImH* and *PyH* polyvanadates, *pH* ranges of their preparation and chemical analysis

Compound	<i>pH</i> range	% V	% C	% N	% H	
1	$(BzH)_6V_{10}O_{28} \cdot 3H_2O$	2.7–5.3	calc. 30.68	30.54	5.06	4.00
			found 30.78	30.50	5.08	3.95
2	$(ImH)_6V_{10}O_{28} \cdot 2H_2O$	5.5–7.1	calc. 36.18	15.35	11.93	2.43
			found 36.10	15.30	11.97	2.34
3	$(ImH)_4H_2V_{10}O_{28} \cdot 2H_2O$	2.5–4.0	calc. 40.06	11.33	8.81	2.06
			found 39.95	11.35	8.80	1.98
4	$(PyH)_6V_{10}O_{28} \cdot 2H_2O$	5.0–8.0	calc. 34.55	24.44	5.70	2.73
			found 34.50	24.30	5.60	2.75
5	$(PyH)_4H_2V_{10}O_{28} \cdot 3H_2O$	2.5–4.5	calc. 38.19	18.00	4.20	2.42
			found 37.95	17.80	4.05	2.30
6	$(BzH)VO_3$	7.0–10.5	calc. 24.60	40.59	6.76	4.86
			found 24.65	40.70	6.80	4.88
7	$(ImH)_2V_6O_{16} \cdot H_2O$	4.0	calc. 42.58	10.04	7.80	1.67
			found 42.50	10.10	7.90	1.57
8	$(PyH)_2V_6O_{16} \cdot H_2O$	4.5	calc. 41.32	16.23	3.78	1.95
			found 41.40	16.03	3.80	1.64

**Table 2.** Interplanar distances in nm and relative intensities ( $I_{rel}$ ) for ten most intensive diffractions

Compound	nm ( $I_{rel}$ )
1 <sup>a</sup>	0.807 (100), 0.945 (70), 0.854 (42), 0.3099 (26), 0.4529 (24), 0.4062 (24), 0.5875 (22), 0.679 (21), 0.4739 (18), 0.3149 (16)
2	0.931 (100), 0.3723 (90), 0.2659 (83), 0.961 (80), 0.2321 (55), 0.2062 (40), 0.1854 (23), 0.6281 (19), 0.851 (15), 0.2959 (14)
3	0.982 (100), 0.7196 (81), 1.009 (75), 0.3607 (65), 0.3422 (23), 0.5985 (21), 0.4917 (18), 0.2894 (18), 0.3278 (15), 0.3757 (12)
5	1.105 (100), 0.945 (95), 0.736 (80), 0.906 (50), 0.2872 (41), 0.3149 (40), 0.591 (39), 0.5836 (37), 0.3201 (9), 0.3708 (10)
6	0.3633 (100), 0.4874 (92), 0.5132 (88), 0.4387 (77), 0.731 (70), 0.3414 (68), 0.4051 (38), 0.2659 (35), 0.3732 (33), 0.3038 (30)
7	1.005 (100), 0.5067 (95), 0.3288 (40), 0.3801 (33), 0.2886 (23), 0.3883 (20), 0.2694 (20), 0.5418 (18), 0.3453 (17), 0.2356 (17)
8	1.065 (100), 0.543 (40), 0.3112 (25), 0.3290 (18), 0.1795 (14), 0.2701 (11), 0.3386 (7), 0.4022 (6), 0.2323 (5), 0.2978 (5)

<sup>a</sup> Numbering according to Table 1

The difference in solubilities of unprotonated and protonated decavanadates seems to determine whether both types of polyvanadates can be isolated. Obviously, it is the greater solubility of the hydrogenodecavanadate why *BzH* hydrogenodecavanadate could not be prepared.

In presence of inorganic cations, penta- and hexavanadates are generally formed in reaction solutions at higher temperature. The same effect was observed in the

present systems. At highest *pH* values of ranges given in Table 1, 4.5 for *Py* and 4.0 for *Im*, the *ImH* and *PyH* hexavanadates were isolated at 60 °C while at 20 °C the corresponding dihydrogendecavanadates were formed.

For characterization we have also measured the X-ray diffraction patterns. Except of data for  $(PyH)_6V_{10}O_{28} \cdot 2H_2O$  exhibiting a strong orientation effect and decomposing on grinding before measurement, the interplanar distances and relative intensities for the most intensive diffractions of the other polyvanadates are given in Table 2.

In the region 400–1000  $cm^{-1}$ , the IR spectra of deca- and dihydrogendecavanadates (Table 3) exhibit bands corresponding to vanadium-terminal oxygen

**Table 3.** IR bands of the  $V_{10}O_{28}^{6-}$  anion

1 <sup>c</sup>	2	3	4	5	Assignment
975 m <sup>a</sup>	980 s	990 s	987 sh	990 sh	} $\nu(V-O_t)$
950 vs	962 vs	965 vs	970 vs	970 vs	
			945 sh	945 sh	
920 s <sup>a</sup>		920 sh <sup>a</sup>			
835 vs	840 s		845 s		
	820 vs <sup>a</sup>	825 vs <sup>a</sup>	820 s	827 s	} $\nu(V-O_b)$
740 m		735 sh	765 m	762 m	
	725 s	717 vs <sup>b</sup>			
615 sh	600 sh	605 s		605 s <sup>a</sup>	
575 m <sup>a</sup>		585 s	595 s <sup>a</sup>		
	565 m		565 s	562 m	
		550 m		542 s	
530 m	518 m	518 m	515 m	507 sh	
		500 sh			
453 m	445 m	445 s	440 s	440 m	
410 m	410 s				

<sup>a</sup> Overlapping bands corresponding to  $\nu(V-O)$  and vibrations of the cation

<sup>b</sup> Overlapping bands corresponding to  $\nu(V-O_b)$  and  $\delta(V-OH)$  (or to librations of  $H_2O$ )

<sup>c</sup> Numbering according to Table 1

**Table 4.** Bands in the IR spectra of decavanadates effected by deuteration

$(ImA)_4A_2V_{10}O_{28} \cdot xA_2O$		$(ImA)_6V_{10}O_{28}O_{28} \cdot xA_2O$		$(PyA)_4A_2V_{10}O_{28} \cdot xA_2O$		$(PyA)_6V_{10}O_{28} \cdot xA_2O$		Assignment
A=H	A=D	A=H	A=D	A=H	A=D	A=H	A=D	
1025 m	775 w			1025 m	765 sh			$\delta(V-OA)$ $\delta(V-OA)$ or l.m. <sup>b</sup>
717 s <sup>a</sup>	535 m			890 w	645 w			
585 m	430 m	540 m	?	625 sh	465 m	640 m	?	l.m.

<sup>a</sup> Combined with  $\nu(V-O_b)$

<sup>b</sup> l.m. = libration mode

(V–O<sub>t</sub>) stretchings at 900–1000 cm<sup>-1</sup>, and to vanadium-bridging oxygen (V–O<sub>b</sub>) stretchings at 400–900 cm<sup>-1</sup>, all of them with positions characteristic for decavanadates [11]. Due to the same structure of the polyanion, the band positions in the individual decavanadates are not markedly influenced by the cation present. A certain deformation of the VO<sub>6</sub> octahedra, and thus changes in IR spectra, can occur in protonated decavanadates with hydrogen atoms bonded to the bridging oxygens [4, 5]. Based on the comparison of the IR spectra of the polyvanadates with the IR data for *ImH* and *PyH* cations [12–15] and for their deuterated forms we could assign the bands corresponding to δ(V–OH) vibrations and librations of water molecules (Table 4). On deuteration, all these bands exhibit the expected shifts (wavenumber ratio 1.32–1.37). Besides these bands, some of the ν(V–O<sub>b</sub>) bands in the region 500–550 cm<sup>-1</sup> are slightly shifted on deuteration (up to approx. 15 cm<sup>-1</sup>). This phenomenon can be explained by the coupling of ν(V–O<sub>b</sub>) and δ(V–OD–V) vibrations.

In accordance with the IR spectrum of ethylenediamine metavanadate [16], the bands in the spectrum of (BzH)VO<sub>3</sub> in the 400–1050 cm<sup>-1</sup> region (Fig. 1) we assign as follows: at 945 and 910 cm<sup>-1</sup> to symmetric vibrations of V–O<sub>t</sub> bonds, at 875 and 816 cm<sup>-1</sup> to asymmetric vibrations of V–O<sub>t</sub> bonds, the former being, however, combined with a band of BzH, and at 650 and 530 cm<sup>-1</sup> to vibrations of V–O<sub>b</sub> bonds. The positions of these bands are similar as observed in the spectra of anhydrous alkali metal metavanadates which all have, like pyroxenes, a chain structure built up from VO<sub>4</sub> tetrahedra [17]. This similarity between the spectra of (BzH)VO<sub>3</sub> and other metavanadates allows to propose the same chain structure for (BzH)VO<sub>3</sub>.

The crystallohydrates of *PyH* and *ImH* hexavanadates, (ImH)<sub>2</sub>V<sub>6</sub>O<sub>16</sub>·H<sub>2</sub>O and (PyH)<sub>2</sub>V<sub>6</sub>O<sub>16</sub>·H<sub>2</sub>O, are so far the first hexavanadates with organic cation. In contrary to other types of polyvanadates, the structure of the polyanion in hydrated hexavanadates is unknown. In the 400–1100 cm<sup>-1</sup> region, the profound resemblance between the spectra of *PyH* and *ImH* hexavanadates and the spectrum of sodium

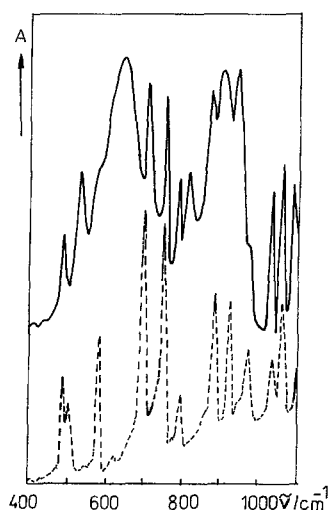
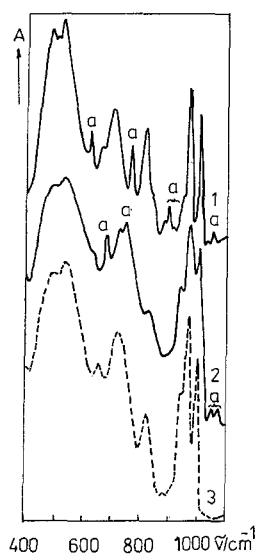


Fig. 1. IR spectra of (BzH)VO<sub>3</sub> (—) and BzHCl (---)



**Fig. 2.** IR spectra of imidazolium (1), pyridinium (2) and sodium (3) hexavanadates; a – overlap of V–O stretchings with vibrations in cation

hexavanadate (Fig. 2) we have previously prepared [18, 19] indicates that all of them will probably have the same polyanion structure.

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