

The Structure of Vanadium(III) Hydroxo complexes*

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The absorption spectrum of vanadium(III) slightly acid solutions ($\text{pH} > 2$) exhibits a strong band with maximum at 436 nm, which so far was ascribed to the VOH^{2+} ion. The average molar absorptivity considerably increases with the increase of metal concentration as well as with the increase of pH up to the value pH 3.2—3.5. At higher pH the absorbance decreases.

Our studies show that the visible absorption spectrum of vanadium(III) in the range pH 2 ÷ 3.5 is a charge-transfer spectrum of the binuclear hydroxo complex.

The weak bands of the VOH^{2+} ion are isolated out of the spectrum graphically and by calculations.

Vanishing absorption in 436 nm band at higher values of pH and normal magnetic behaviour of the binuclear complex may be explained as due to a change of strongly absorbing binuclear complex into a new polynuclear (D_{4h}) complex with higher ratio of OH groups per vanadium atom.

Numerous papers on the hydrolysis of vanadium(III) ion in aqueous solution are reported [1—7] as yet. All investigators claimed the existence of only two mononuclear products of hydrolysis: VOH^{2+} and $\text{V}(\text{OH})_2^+$.

Our potentiometric investigations published last year [8] differ from other works because besides VOH^{2+} and $\text{V}(\text{OH})_2^+$ ions also the evidence of binuclear complex in hydrolysis products is found. Values of hydrolysis constants obtained were in good agreement with the experimental data only at pH values < 3.2 and at higher pH the components of solution were not quite precisely determined (the equilibrium is being established very slowly).

The EMF measurements alone cannot decide about the symmetry of complexes and about their detailed composition. E. g. a binuclear complex-ion of di-ol type $[\text{V}(\text{OH})_2\text{V}]^{4+}$ and that of the oxo-type $[\text{V}—\text{O}—\text{V}]^{4+}$ are likewise possible.

Further conclusions concerning the structure of these complexes were drawn on the basis of our spectroscopic investigations [9].

The unhydrolysed, hydrated V^{3+} ion gives two weak bands at 400 nm ($\epsilon_{\text{max}} = 8.5$) and 580 nm ($\epsilon_{\text{max}} = 5.6$). This spectrum undergoes a fundamental change due to hydrolysis. At $\text{pH} > 2$ there appear a new strong band at 436 nm and two weak bands in region about 340 nm and 670 nm respectively (Fig. 1a and 1b). With increasing pH the absorption increases, but it decreases

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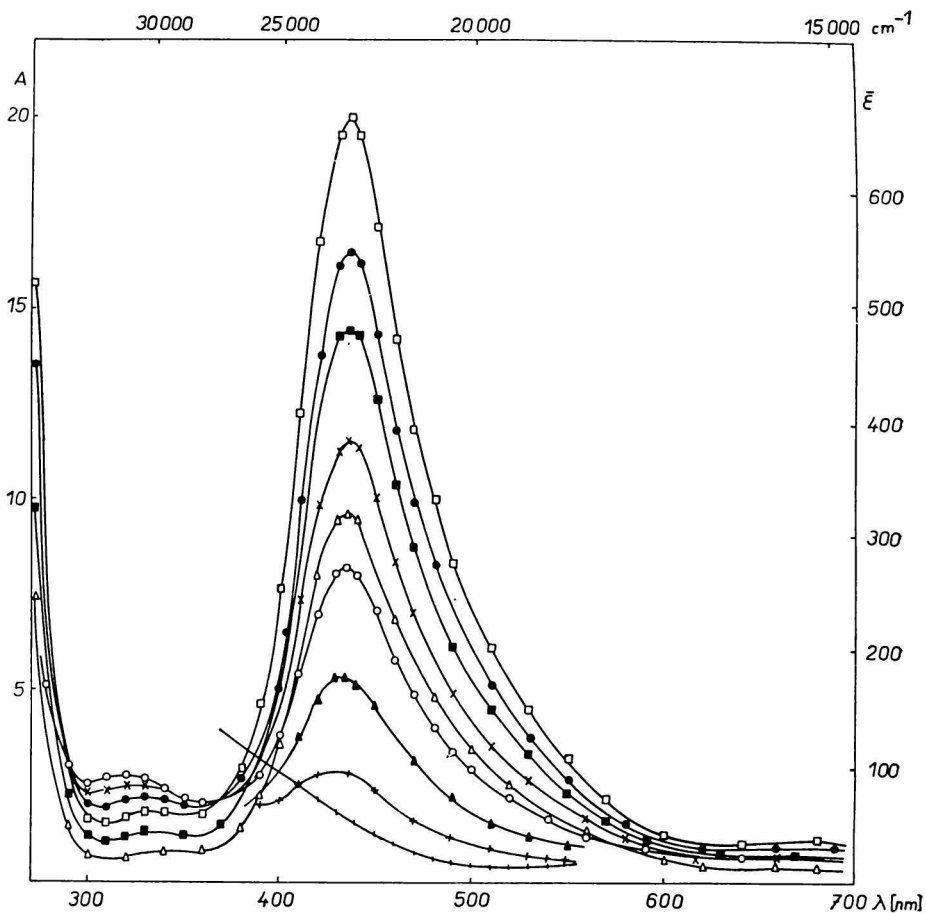


Fig. 1a. Absorption spectra of $2.92 \cdot 10^{-2}$ M-V(III) in 1 M-(Na)Cl.

$\bar{\epsilon}$ is the average molar absorptivity.

pH: \triangle 2.46; \blacksquare 2.77; \square 3.18; \bullet 3.37; \times 3.46; \circ 3.55; \blacktriangle 3.68; $+$ 3.9; $|$ 4.12.

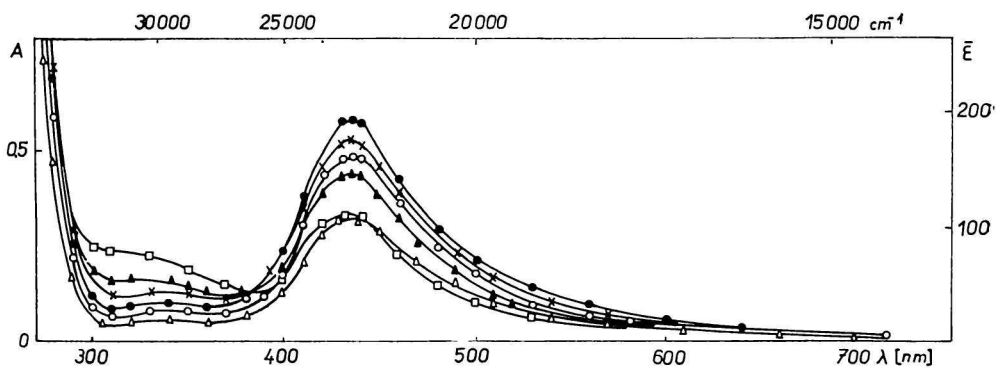


Fig. 1b. Absorption spectra of $2.92 \cdot 10^{-3}$ M-V(III) in 1 M-(Na)Cl.

pH: \triangle 2.72; \circ 3.14; \bullet 3.50; \times 3.90; \blacktriangle 4.06; \square 4.20.

again after the critical points: pH 3.2 [0.03 M-V(III)] and pH 3.5 [0.003 M-V(III)] have been reached (Fig. 2).

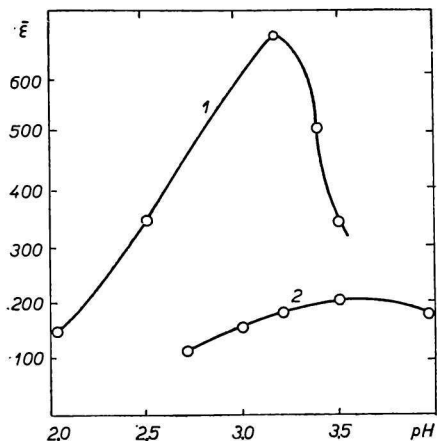
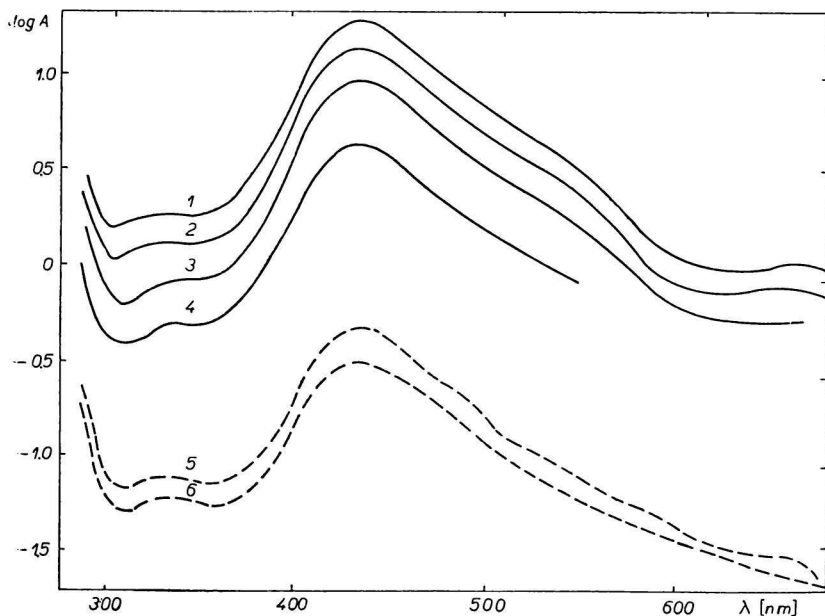
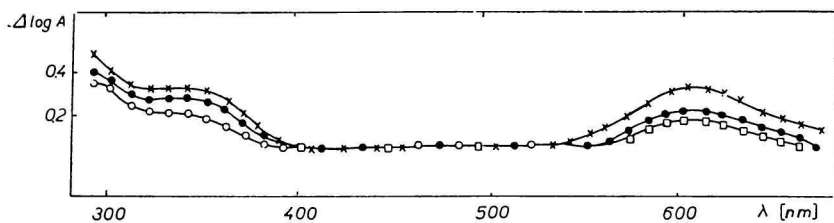


Fig. 2. Effects of changing pH on absorbance of V(III) at 436 nm. Concentrations of V(III) are 29.2 mM (curve — 1) and 2.92 mM (curve — 2).

Fig. 3. Absorption spectra of 29.2 mM (full curves) and 2.92 mM (dashed curves) vanadium(III) for different pH. The upper part of graph represents the results of superimposition of curves $\log A(\lambda)$ with vanadium(III) concentration $c = 2.92$ mM on curves $c = 29.2$ mM in the band of a maximal absorption.

pH: 1. 3.18; 2. 2.77; 3. 2.46; 4. 2.14; 5. 3.14; 6. 2.72.

$l = 1$ cm.



Furman and Garner [7], Lybing [10], Beerl and Ehrenburg [11] (1954) ascribed the strong band (at 436 nm) to VOH^{2+} ion. Since the average extinction coefficient in the whole investigated range to a high degree depends on the change of the total metal concentration (Fig. 2), it is evident that the whole obtained spectrum is the spectrum of one or several polynuclear complexes of vanadium(III).

As the shapes of the curves $\bar{\epsilon}(\lambda)$ are not characteristic because of their dependence on metal concentration, — we chose the following coordinates: $\log A$ as a function of λ (Fig. 3).

The curves in the range 400—560 nm are parallelly shifted only along the ordinate. The superimposition of curves $\log A - (\lambda)$ with different metal concentration demonstrated (upper part of Fig. 3), that in that range we deal practically with spectrum of one polynuclear complex and the particular curves $A(\lambda)$ differ only in the value of molar fraction (α_{22}) of polynuclear ion. Outside that range the influence of mononuclear complex is evident.

Fig. 4a and 4b illustrate the values of the molar fraction (α) of individual ions in solution at a given metal concentration for different pH values. Calculations were based on the hydrolysis constants obtained in our earlier potentiometric work in the same medium [8]:

$$K_1 = 1.4 \cdot 10^{-3}; \quad K_2 = 1.4 \cdot 10^{-4}; \quad \beta_{22} = 1.26 \cdot 10^{-4}.$$

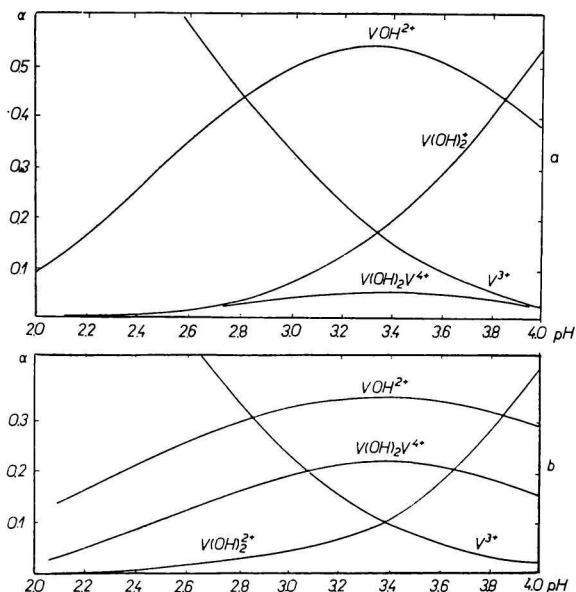


Fig. 4. Distribution of complexes for total vanadium(III) concentration $c = 2.92 \text{ mM}$ (Fig. a) and $c = 29.2 \text{ mM}$ (Fig. b). The ordinate is the degree of complex formation.

It is evident that the binuclear complex is the only ion, whose concentration increases with increase of concentration of the metal (at pH = const).

Now we can check the correlation between the potentiometric and optical results. As we mentioned above we assumed the absorption in 400—560 nm range to be the absorption of the binuclear ion only. Thus we can write:

$$A = c_{22}\epsilon_{22}l = C^0\alpha_{22}\epsilon_{22}l; \quad \epsilon_{22} = A/C^0\alpha_{22}l.$$

Hence, if all α_{22} values are determined correctly, all $\epsilon_{22} = f(\lambda)$ curves ought to give a single absorption curve independently of metal concentration and pH of solution. The result is represented in Fig. 5.

The independently obtained results of optical investigations are in full agreement with potentiometric data. Actually, in the range 400—560 nm we obtain a single curve. Beyond this range there is a marked influence of mononuclear ions.

Fig. 6 shows separate approximate spectra of both: of the binuclear and the mononuclear ion, obtained by solutions of the set of equations of type:

$$A = C^0(\epsilon_{11}\alpha_{11} + \epsilon_{22}\alpha_{22}).$$

According to Schäffer and Jorgensen [12] spectra of complexes with the nuclei coupled by means of two hydroxyl bridges ought not exhibit any considerable changes in comparison with the spectra of mononuclear com-

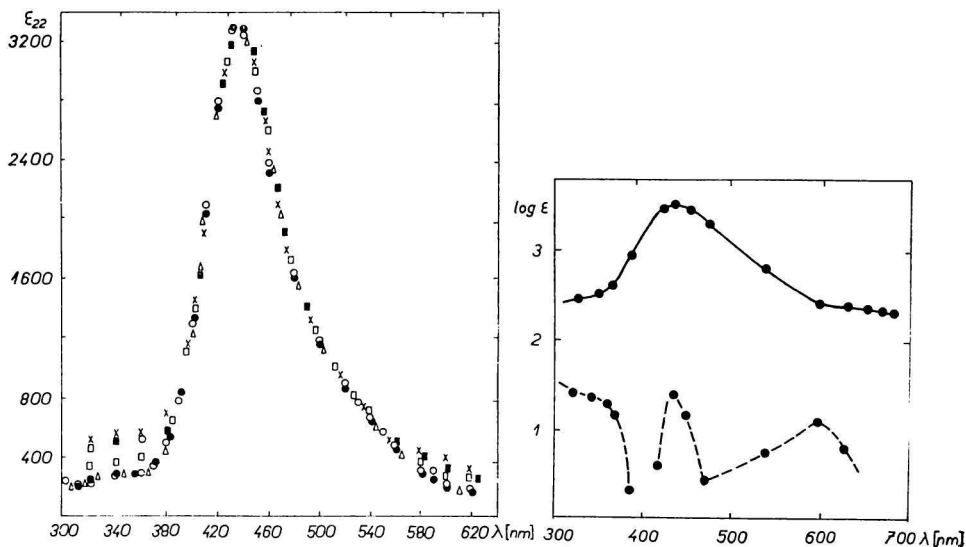


Fig. 5. The curves represent the result of the introduction of α_{22} values from Fig. 5 into equation $\epsilon_{22} = A/C^0\alpha_{22}l$ and the measured absorption values at different pH and metal concentrations.

Fig. 6. Calculated approximate absorption spectra for the dimer (full curve), and monomer VOH^{2+} (dashed curve).

plexes. The presence of oxygen bridges, however, ought to influence the spectrum a great deal. From this point of view — in binuclear products of vanadium(III) hydrolysis — the presence of oxygen bridge should be accepted. High values of binuclear ion absorptivity in 436 nm band, of the order of 10^3 , show that it would be a „charge transfer“ process between ligand groups and metal ions.

As it was mentioned above while discussing the potentiometric data, — identical situation occurs in the course of optical investigations. The interpretation, which is correct at $\text{pH} < 3.2$ does not apply to higher pH values. Processes occurring in solutions of higher pH values need a separate discussion.

The limit value of ligand number $\bar{n} = 2$ obtained by potentiometric investigations shows that a formation of oxyanion $\text{VO}_2^- \cdot x\text{H}_2\text{O}$ of the type is rather improbable.

The comparison of Fig. 2 and 4 shows that likewise a change of binuclear complex into a mononuclear $\text{V}(\text{OH})_2^+$ ion is out of question. The decrease of absorption after maximum has been reached is rapid in contradiction to comparatively much smaller changes of dimer concentration with increase of pH values:

$$\left(\frac{\partial \bar{\epsilon}}{\partial \text{pH}} > \frac{\partial \alpha_{ij}}{\partial \text{pH}} \right)_c.$$

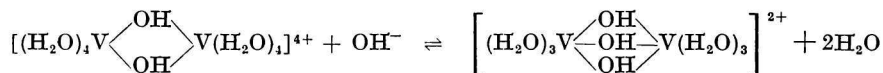
The hydrolysis process of a number of transition metal compounds leads to changes in electronic configuration of metal atoms. This phenomenon was found as yet in binuclear compounds of iron(III) [13], chromium(III) [14], molybdenum(V) [15], ruthenium(IV) [16] and rhenium(IV) [17], which contain the oxygen bridges. These changes of electronic configuration are easily discovered in paramagnetic ions, since the formation of Me—O—Me bonding is accompanied by disappearance of metal paramagnetism. According to Jeżowska-Trzebiatowska and coworkers this may be explained by the aptitude of oxygen to form π -bonds resulting in strong coupling of the bridge system Me—O—Me leading to the formation of common molecular orbitals. The sequence of molecular orbitals as calculated by Jeżowska-Trzebiatowska and Wojciechowski [18]:

$$E_g^b E_u A_{1g} A_{2u} E_g^a$$

may be applied to all complexes of symmetry D_{4h} and hence to vanadium(III) oxygen bridge. The electrons of the V—O—V nucleus should be placed in the $E_g^b E_u$ orbitals causing diamagnetism. As this is not the case, the binuclear octahedral oxo complex is not formed in solution. Even in concentrated, 0.5 molar solutions where more than 80 per cent of vanadium(III) exist in form of binuclear ion a normal paramagnetism of two free electrons is observed [19].

Vanishing absorption in 436 nm band at higher values of pH and normal magnetic behaviour of the binuclear complex may be explained as due to a change of strongly absorbing binuclear hydroxyl complex into a new polynuclear D_{4h} probably threenuclear complex with higher ratio of OH groups per vanadium atom.

Nevertheless the formation of a binuclear complex with three hydroxyl bridges:



cannot be ruled out.

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Symbols used

| | |
|--------------------------------|---|
| A | optical absorbance |
| C^0 | total concentration of metal (M/l) |
| c | total concentration of metal (mM/l) |
| l | thickness of the absorption layer (in cm) |
| $\epsilon_0, \epsilon_{11},$ | molar absorptivities of $\text{V}(\text{H}_2\text{O})_6^{3+}, \text{VOH}^{2+}, \text{V}(\text{OH})_2^{+}$ |
| $\epsilon_{12}, \epsilon_{22}$ | and $\text{V}_2(\text{OH})_2^{4+}$ ions |
| $\bar{\epsilon}$ | average molar absorptivity |
| α_{ij} | fraction of C in form of i -th complex: $\alpha_{ij} = [\text{V}_i(\text{OH})_j]C^{0-1}$ |

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