Spectrophotometric study of the formation of oxo-peroxo complexes of vanadium(V) with pyridinecarboxylic acids and ethylenediaminetetraacetic acid in acid medium

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It has resulted from the variations of electronic spectra with pH of the acid aqueous KVO_3—H_2O_2—HL—$HClO_4$ solutions (HL = isonicotinic acid (Hinic), nicotinic acid (Hnic), picolinic acid (Hpic), quinolinic acid (H_2quin), dipicolinic acid (H_2dipic), or ethylenediaminetetraacetic acid (H_4edta)) that the formation of monoperoxo complex involves a coordination only of those carboxylato ligands to vanadium which may be coordinated through nitrogen and oxygen of the carboxyl group to give 5-membered chelates. The coordination of the anions of Hpic, H_2quin, H_2dipic, and H_4edta improves the stability of monoperoxo complex when compared with aqua-monoperoxo complex $[VO(H_2O)_x(O_2)]^+$

Из изменений в электронных спектрах кислых водных ρстворов KVO_3—H_2O_2—HL—$HClO_4$, где HL — изоникотиновая (Hinic), никотиновая (Hnic), пиколиновая (Hpic), хинолиновая (H_2quin), дипиколиновая (H_2dipic) кислота или H_4edta, в зависимости от pH следует, что при образовании монопероксокомплекса на ванадий координируют только те карбоксилатные лиганды, которые способны координировать через атом азота и кислород карбоксильной группы с образованием 5-членных хелатов. Вследствие координации анионов кислот Hpic, H_2quin, H_2dipic и H_4edta повышается устойчивость монопероксокомплекса по сравнения с аква-монопероксокомплексом $[VO(H_2O)_x(O_2)]^+$

In acid aqueous solutions (pH $\approx$ 0—pH $\approx$ 3) vanadium(V) forms with hydrogen peroxide two complex ions, *i.e.* $[VO(H_2O)_x(O_2)]^+$ and $[VO(H_2O)_y(O_2)_2]^-$ The equilibrium of these two species is shifted with decreasing pH value towards monoperoxo ions [1—3]. The presence of the mono- and diperoxovanadate ions manifests itself in electronic spectra by the absorption bands with λ_{max} at about 460 nm and 330 nm, which enables us to investigate spectrophotometrically the substitutions of aqua ligands for other ligands.

The pyridinecarboxylato ligands were chosen as ligands for these substitution reactions because the complexes of some transition elements with these ligands were interesting owing to their catalytic effects in epoxidation and hydroxylation

of hydrocarbons [4—6]. The selection of ligands was completed with H_4edta because it had similar bonding possibilities which could be expected for pyridinecarboxylic acids and the results hitherto obtained by studying this system were fairly extensive [7, 8].

The formation of the complexes of vanadium(V) with Hinic, Hnic, H_2quin, and Hpic in aqueous solutions has not been studied yet. Hpic was used for synthesis of the complexes of the composition $[VO(H_2O)_2(O_2)pic]$ (*I*) and $H[VO(H_2O)(O_2)(pic)_2]$ (*II*) [4], H_4edta for synthesis of the complexes $M[VO(edta)(O_2)] \cdot xH_2O$ (*III*) (M = K^+, Na^+, NH_4^+) [7, 8], and H_2dipic for synthesis of the complexes $M[VO(H_2O)dipic(O_2)] \cdot xH_2O$ (*IV*) (M = H^+, K^+, NH_4^+) [9, 10]. The structures of complexes *I* and *IV* were solved [4, 9].

In this paper, the changes in electronic spectra of the KVO_3—H_2O_2—HL——$HClO_4$ solutions are spectrophotometrically investigated as a function of pH and compared with spectra of the KVO_3—H_2O_2—$HClO_4$ system. The aim of this study has been to find out which of the above acids are able to form the corresponding peroxo complexes and to obtain data about their stability as a function of pH.

Experimental

KVO_3 was prepared by reaction of V_2O_5, anal. grade (Reakhim, Moscow) with KOH, anal. grade in aqueous solution at pH = 8. Isonicotinic, nicotinic (Lachema, Brno), and picolinic (Reakhim, Moscow) acids were purified by recrystallization. Quinolinic acid was synthesized according to [11]. Other chemicals were anal. grade reagents (Lachema, Brno).

The electronic spectra were taken with a spectrophotometer SP 1800 (Pye Unicam), the cell width being $d = 0.1$ cm. The concentrations of the measured solutions were: $c(KVO_3) = 1 \times 10^{-2}$ mol dm^{-3}, $c(H_2O_2) = 6 \times 10^{-2}$ mol dm^{-3}, and $c(HL) = 1 \times 10^{-2}$ mol dm^{-3} The spectra were measured 5 min after the preparation of the solutions from the stock solutions at 22 °C.

The pH values were measured with a pH-meter OP 208 (Radelkis, Budapest) equipped with a combined electrode OP 0808 P. The pH values were varied by adding a certain amount of $HClO_4$ solution ($c = 0.1$—1.0 mol dm^{-3}).

Results and discussion

It results from the spectra of the aqueous KVO_3—H_2O_2—$HClO_4$ solutions exhibiting the pH values in the range 0.1—2.5 that an absorption band at $\lambda = 460$ nm ($\varepsilon(460$ nm$) = 255$ mol^{-1} dm^3 cm^{-1}) appears in the spectra of the solutions containing the $[VO(H_2O)_x(O_2)]^+$ ions (pH ≈ 0.1—1.0) while a band at

$\lambda = 330$ nm ($\varepsilon(330$ nm$) = 660$ mol^{-1}dm^{3}cm^{-1}) is present in the spectra of the solutions containing the $[VO(H_2O)_y(O_2)_2]^-$ ions (pH ≈ 1.0—2.5).

A shift in absorption maximum towards lower wavelengths and a change in value of ε_{max} [12] in comparison with the values found for aqua-peroxo complexes were most frequently observed as a consequence of the change in structure of the complex ion due to the formation of peroxo complexes containing some O—O, O—N or N—N donor ligands which may be regarded as a substitution reaction between the aqua ligand in the above aqua complexes and other ligand.

The changes in spectra of the aqueous KVO_3—H_2O_2—Hnic—$HClO_4$ and KVO_3—H_2O_2—Hinic—$HClO_4$ solutions as a function of pH are identical (positions of maxima and values of ε do not change) with the changes in spectra of the KVO_3—H_2O_2—$HClO_4$ solutions (Fig. 1). Thus we may assume for the investigated pH range 0.1—4.0 that no complexes are formed owing to substitution of aqua ligands for the nicotinato $(1-)$-N,O or isonicotinato $(1-)$-N,O ligands the complexes of which with some transition elements are known, e.g. Cr(III) [13], Mn(II) [14], and Cu(II) [15].
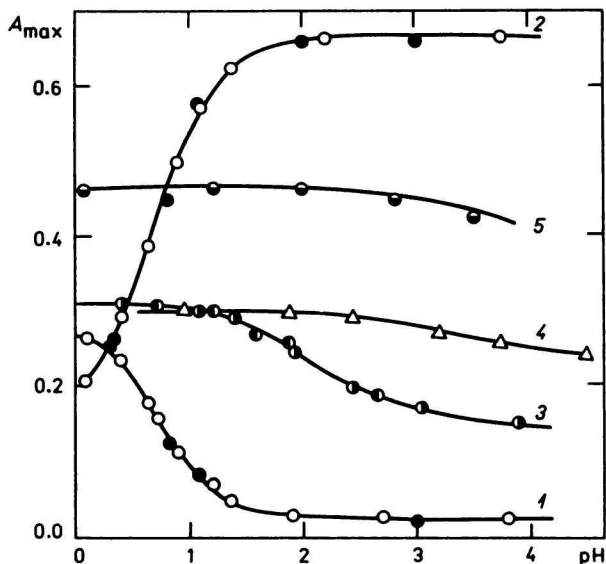

Fig. 1. Variation of A_{max} with pH of the solutions.
1. $\lambda = 460$ nm, ● KVO_3—H_2O_2—$HClO_4$, ○ KVO_3—H_2O_2—Hinic (Hnic)—$HClO_4$; 2. $\lambda = 330$ nm, equal systems as stated under 1; 3. $\lambda = 446$ nm, ◑ KVO_3—H_2O_2—Hpic—$HClO_4$, ◐ KVO_3—H_2O_2—H_2quin—$HClO_4$; 4. $\lambda = 430$ nm, △ KVO_3—H_2O_2—H_4edta—$HClO_4$; 5. $\lambda = 436$ nm, ◖ KVO_3—H_2O_2—H_2dipic—$HClO_4$.

In the spectra of the aqueous KVO_3—H_2O_2—Hpic—$HClO_4$ solutions, the substitution of aqua ligand for picolinato ligand giving rise to the monoperoxo-picolinato complex $[VO(H_2O)_{x-2}(O_2)pic]$ manifests itself by the shift in absorption maximum of the monoperoxovanadate group from $\lambda = 460$ nm corresponding to $[VO(H_2O)_x(O_2)]^+$ to $\lambda = 466$ nm corresponding to the arising peroxopicolinato complex as well as by the increase in value of ε_{max} to $310 \, mol^{-1} dm^3 cm^{-1}$ These values are identical with the values which were obtained from the spectra of the aqueous solution made by dissolving the solid complex $[VO(H_2O)_2(O_2)pic]$ prepared according to [16]. This fact enables us to assume that the equilibrium

$$[VO(H_2O)_x(O_2)]^+ + pic^- \; \rightleftharpoons \; [VO(H_2O)_{x-2}(O_2)pic] + 2H_2O$$

in very acid solutions (pH = 0.1—1.0) is fully shifted in the sense of formation of the picolinato complex (Fig. 1) and the aqua-peroxopicolinato complex might have equal structure in solution as well as in solid state.
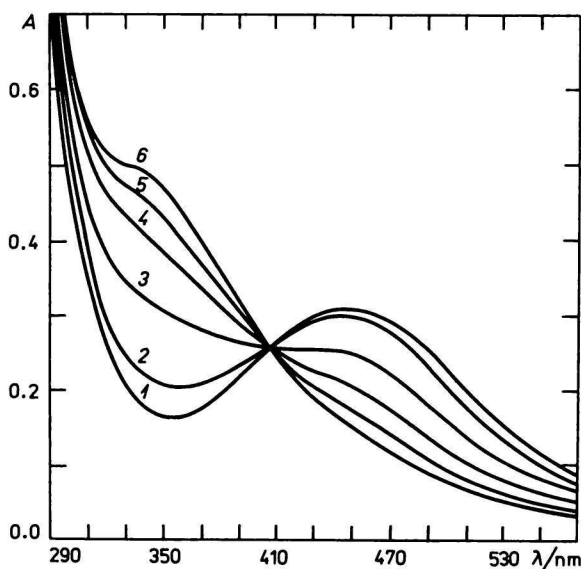

Fig. 2. Electronic spectra of the aqueous KVO_3—H_2O_2—Hpic—$HClO_4$ solutions as a function of pH. pH = 0.30 (1), pH = 1.10 (2), pH = 1.95 (3), pH = 2.45 (4), pH = 3.05 (5), pH = 3.90 (6).

Moreover, it follows from Fig. 2 that an equilibrium of two ions is established with increasing pH in the investigated pH range 0.1—3.9 because the spectra pass through an isosbestic point at $\lambda = 405$ nm. The concentration of the

[VO(H$_2$O)$_{x-2}$(O$_2$) pic] complex decreases with increasing pH and the amount of the diperoxovanadate ion gradually augments, which manifests itself by an increase in absorption in the range $\lambda = 290$—405 nm and a maximum at $\lambda = 330$ nm. According to [12], the solutions containing the [VO(O$_2$)$_2$pic]$^{2-}$ ions exhibit a maximum at equal wavelength. On the basis of equal values of λ_{max} and ε_{max} we cannot unambiguously decide whether the [VO(H$_2$O)$_x$(O$_2$)$_2$]$^-$ ion or [VO(O$_2$)$_2$pic]$^{2-}$ ion is present in the KVO$_3$—H$_2$O$_2$—Hpic—HClO$_4$ system at higher pH values.

The band of monoperoxo complex exhibiting a maximum at $\lambda = 446$ nm ($\varepsilon(446$ nm$) = 310$ mol^{-1} dm^3 cm^{-1}) appears in the spectra of the aqueous KVO$_3$—H$_2$O$_2$—H$_2$quin—HClO$_4$ solutions the pH values of which vary in the range 0.5—1.5 (Fig. 3). These values are identical with the corresponding values found for monoperoxopicolinato complex. On the basis of the known kind of coordination of the dipicolinato and picolinato ligands in monoperoxo complex of vanadium(V) [4, 9], we may assume that the anion of quinolinic acid is coordinated as a quinolinato $(1-)$-N,O ligand to give a 5-membered chelate. It results from the dependence of A_{max} on pH (Fig. 1) that the noncoordinated carboxyl group in position 3 does not influence the stability of the arising monoperoxo-quinolinato complex when compared with the analogous chelate monoperoxo-picolinato complex.
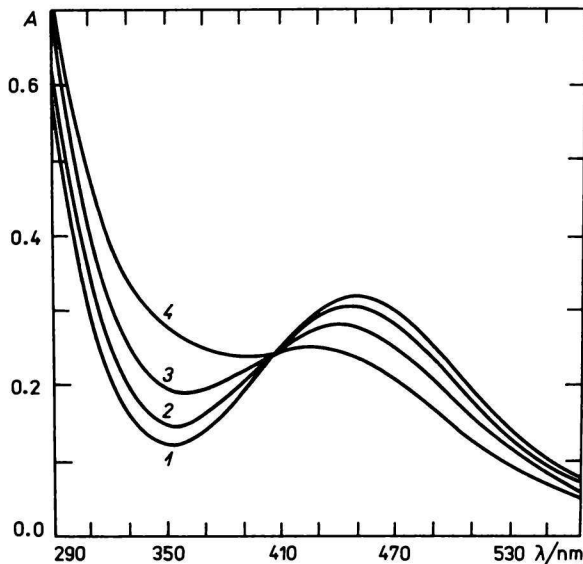

Fig. 3. Electronic spectra of the aqueous KVO$_3$—H$_2$O$_2$—H$_2$quin—HClO$_4$ solutions as a function of pH.
pH = 0.88 (*1*), pH = 1.50 (*2*), pH = 1.82 (*3*), pH = 2.70 (*4*).

The measurements of the spectra of the KVO_3—H_2O_2—H_2dipic—$HClO_4$ solutions (Fig. 4) have shown that only the monoperoxo-dipicolinatovanadate ions are present in the solution in the investigated pH range 0.1—3.5. The position of absorption maximum of the complex with this tridentate ligand is still more shifted into the region of shorter wavelengths ($\lambda_{max} = 436$ nm, $\varepsilon(436\,\text{nm}) = 465\,\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$). These values are identical with the values found for the solution of the concentration $c = 10^{-2}\,\text{mol dm}^{-3}$ obtained by dissolving the solid $H[VO(H_2O)dipic(O_2)]\cdot H_2O$ which was prepared according to [10]. Thus we may assume that the equilibrium

$$[VO(H_2O)_x(O_2)]^+ + dipic^{2-} \rightleftarrows [VO(H_2O) dipic(O_2)]^- + (x-1)H_2O$$

in the measured solutions is shifted quite in favour of the formation of the dipicolinato complex.
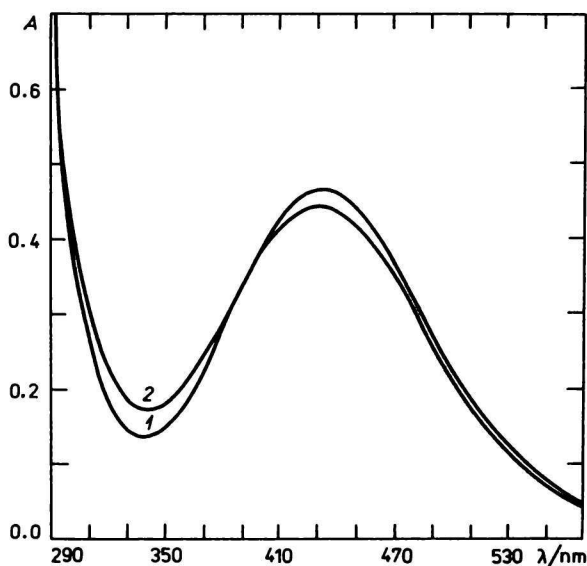
Fig. 4. Electronic spectra of the aqueous KVO_3—H_2O_2—H_2dipic—$HClO_4$ solutions as a function of pH.
pH = 0.15—2.0 (*1*), pH = 3.5 (*2*).

The spectra of the KVO_3—H_2O_2—H_4edta—$HClO_4$ solutions measured in the pH range 1.0—5.4 exhibit similar character as spectra in Fig. 2. They have an absorption maximum at $\lambda = 430$ nm ($\varepsilon(430\,\text{nm}) = 300\,\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$) which corresponds to the formation of the ethylenediaminetetraacetato-monoperoxo complex. The spectra pass through the isosbestic point at $\lambda = 400$ nm. The

concentration of this complex is maximum in the pH region 1.0—1.9 and the absorbance decreases by about 25% provided pH rises to 5.4 which suggests that a very stable monoperoxo complex originates from coordination of the edta ligand and this complex does not appreciably decompose even at those values of pH ($\approx$ 5—6) for which the corresponding aqua complex $[VO(H_2O)_x(O_2)]^+$ is already not present in the solution. The stability of the ethylenediaminetetra-acetato-monoperoxo complex of vanadium(V) (Fig. 1) as a function of pH is similar to the stability of the $[VO(H_2O)dipic(O_2)]^-$ complex. By disclosing how the character of that relationship changes with time, we can determine the pH region where the investigated monoperoxo complex is the most stable (Fig. 5). The monoperoxo complex completely decomposes in the course of 3 days at pH = 1.75, exhibits the highest stability in the pH region 2—3 and is subjected to slow decomposition at pH > 3 (absorbance decreases in the whole investigated range λ = 290—550 nm).
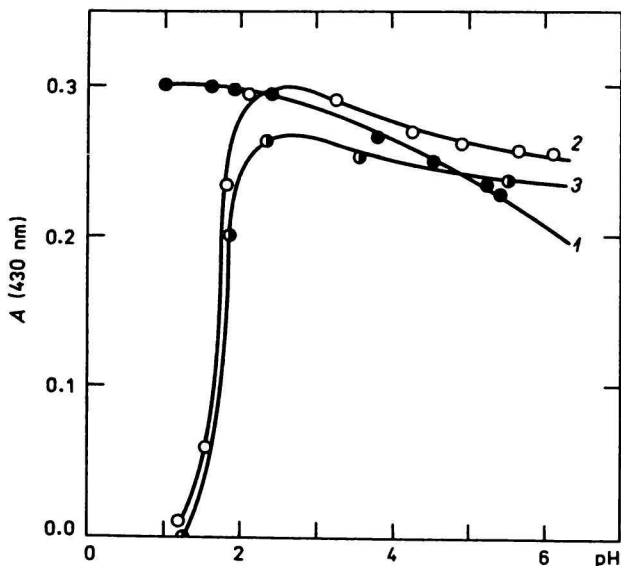

Fig. 5. Variation of A (430 nm) of the KVO_3—H_2O_2—H_4edta—$HClO_4$ solutions with pH and time.
1. After preparation of solutions; *2.* after 3 days; *3.* after 11 days; θ = 20 °C.

The following conclusions may be drawn from the obtained results:

1. The method used appears to be a relatively rapid and reliable method for investigating the formation of the monoperoxo complexes of vanadium(V) due to the substitution reaction

$$[VO(H_2O)_x(O_2)]^+ + L^{n-} \ \rightleftarrows \ [VO(H_2O)_{x-z}(O_2)L]^{(n-1)-} + zH_2O$$

where z is functionality of the ligand. If we determine the dependence of A_{max} on pH in different time moments (Fig. 5), we may ascertain under which conditions the solutions of monoperoxo complexes are the most stable, which represents a valuable information for studying the selected systems from the viewpoint of synthesis because the problem of reproducible synthesis of this type of vanadium(V) compounds continues to be a serious problem.

2. Among the investigated pyridinemono- and dicarboxylic acids, only the anion of picolinic, quinolinic, and dipicolinic acid is coordinated to vanadium(V), *i.e.* only those species which fulfil the conditions for the formation of one or two 5-membered chelate rings of the type
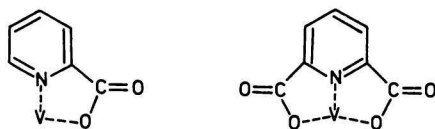
The anions of isonicotinic and nicotinic acids are not coordinated to vanadium(V), not even as bridge ligands in polynuclear complexes that were also observed for V(V), owing to which vanadium(V) differs from some transition elements such as Cr, Cu, and Mn [13—15].

3. The coordinated pyridinecarboxylato ligand stabilizes the pertinent monoperoxo complex. While the $[VO(H_2O)_x(O_2)]^+$ ion is stable merely in very acid solutions (pH < 1), the monoperoxo complexes $[VO(H_2O)_2(O_2)pic]$ and $[VO(H_2O)_x quin(O_2)]$ with one 5-membered chelate are stable up to pH $\approx$ 1.5 and the complexes with several rings, *i.e.* the dipicolinato and ethylenediaminetetraacetato complex, are stable even up to pH $\approx$ 3.5.

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