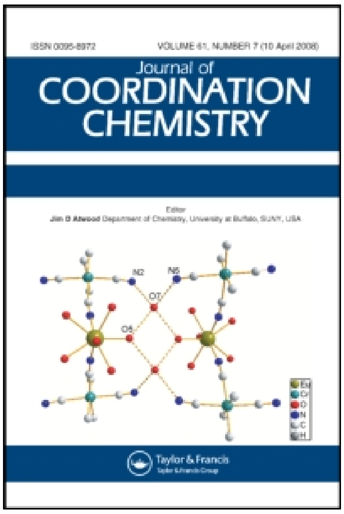

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ELECTROCHEMICAL BEHAVIOR OF SOME INORGANIC ESTERS OF OXOVANADIUM(V)

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The electrochemical behavior of ethylic esters of the type $Q_2VO(OEt)$, derived from the oxovanadium(V) complex $Q_2VO(OH)$ ($Q = $ 8-hydroxyquinoline, 5-chloro and 5,7-dichloro-8-hydroxyquinoline or 2-methyl-8-hydroxyquinoline), was investigated by cyclic voltamperometry in organic solvents. The detailed analysis of the results confirmed the generation of different complex species in solution. The presence of water in the solvents modifies the electrochemical behavior, as a consequence of the formation of a mixed valence dimer of the type $[Q_2VO{-}O{-}OVQ_2]^-$. The somewhat different behavior of the 2-methyl-8-hydroxyquinoline derivative could also be explained. The analysis of the electronic spectra of the investigated solutions, after and during the electrochemical measurements, gave additional support to some of the proposed reactions, steps and mechanisms.

Keywords: Oxovanadium(V)/"oxines"; esters; cyclic voltammetry; electronic spectra

INTRODUCTION

Some oxovanadium(V) complexes of general formula $L_2VO(OH)$, L being a bidentate ligand, show interesting analogies to carboxylic acids.[1] The 8-hydroxyquinoline ("oxine", QH, Figure 1) and some of its derivatives, a well known group of important analytical reagents[2–4] are included in the series of L ligands that stabilize such complex compounds.

The $L_2VO(OH)$ "acids" react with alcohols generating the corresponding esters.[1] This reaction has been employed in the detection and photometric

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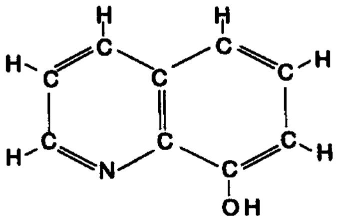

FIGURE 1 Schematic representation of the structure of 8-hydroxyquinoline (QH).

determination of alcohols; its kinetics strongly depend on the nature of the involved alcohol and on the characteristics of the ligand **L**.[5]

As part of our systematic studies of vanadium/"oxine" complexes in solution[6-10] we have analyzed the electrochemical behavior of some ethyl esters of the type $Q_2VO(OEt)$ by means of cyclic voltamperometric measurements. The ligands which were used include "oxine" itself as well as its derivatives 5-chloro-8-hydroxyquinoline (ClQH), 5,7-dichloro-8-hydroxyquinoline (Cl_2QH) and 2-methyl-8-hydroxyquinoline ("quinaldine", QUINH).

As $Q_2VO(OEt)$[11] and $(Cl_2Q)_2VO(OEt)$[12] have equivalent structures, the same can be assumed for $(ClQ)_2VO(OEt)$ whereas the general characteristics of the quinaldine complex, $(QUIN)_2VO(OEt)$,[6] suggest a different structure.

During the voltamperometric measurements, as well as by aging, changes in the colors of the investigated solutions were observed, suggesting chemical transformations of the starting species. In order to clarify the nature and characteristics of these transformations, electronic spectra of the solutions were also recorded. The results gave additional support to the proposed electrochemical mechanisms.

EXPERIMENTAL

Synthesis of the Complexes

The investigated esters were prepared by refluxing the respective "acids"[1,6] with ethanol, according to the general procedure reported for the synthesis of $Q_2VO(OEt)$.[13] They were characterized by chemical analysis and IR spectroscopy.

Electrochemical Measurements

Cyclic voltammetric experiments were performed with a Bioanalytical System Inc. CV-1B assembly. A standard three-electrode cell was used with a Pt working electrode, a Pt counterelectrode and a Ag/(0.01 M) $AgNO_3$ in CH_3CN reference electrode. The potential of this electrode was calibrated *vs.* NHE using the $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$ redox couple as an internal standard, for which a potential of +0.4 V was assumed.[14,15] A small amount of ferrocene was added at the end of each experiment. Potential values are reported in V *vs.* NHE.

All the experiments were performed in high purity CH_3CN (Mallinckrodt) and in absolute ethanol (Merck) solutions with 0.1 M $LiClO_4$ as supporting electrolyte. The CH_3CN solvent was dried over 4 Å molecular sieves (Fluka) and used without further purification. The supporting electrolyte, $LiClO_4$, was purchased from Fluka and used as received.

Prior to each experiment a cyclic voltammogram (CV) of the solution containing only the supporting electrolyte was measured. Solid samples were added to the solution and dissolved with stirring. The concentration of the complexes was approximately 0.1 mM due to the low solubility of the compounds.

Oxygen was removed by purging the solutions with pure nitrogen (a continuous gas stream was passed over the solutions during the measurements).

Electronic Spectra

The electronic absorption spectra were recorded in a Hewlett-Packard 8452-A diode array spectrophotometer, using 10 mm quartz cells.

RESULTS AND DISCUSSION

Electrochemistry

(1) $Q_2VO(OEt)$ in CH_3CN

The CV obtained at a scan rate (ν) of 0.1 V/s in the +1.10 to −0.90 V potential range is shown in Figure 2. On the forward scan two reduction peaks are observed at −0.04 V (A) and at −0.46 V (B), while a single oxidation peak (A′) at +0.025 V, related with the A process, is evident on the reverse anodic scan.

During the measuring time, changes in the reduction currents were observed. Simultaneously, the red-wine colored solution turned gradually to black. In the initial voltammogram the current contribution of peak B was higher than that of peak A (Figure 2, – – –), showing a progressive inversion with time (Figure 2, –· · ·–).

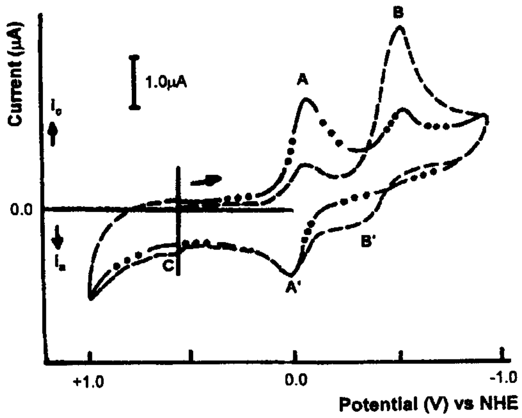

FIGURE 2 CV of $Q_2VO(OEt)$ in CH_3CN. $\nu = 0.1$ V/s. Effect of time (– – –) fresh solution; the same solution after 2 h (–····–).

Other experiments were performed in order to determine the nature of the reactions involved in the A/A′ couple. Voltammograms at different scan rates (0.02 to 0.8 V/s) were recorded over a reduced range potential (+0.85 to −0.25 V) where the second process cannot take place. (Data not shown.)

The analysis of the results shows that the $\Delta Ep = Epa - Epc$ values change with increasing scan rate, from 0.065 to 0.12 V and suggests that the species undergoes a quasi-reversible process in this potential range.

On the other hand the i_{pa}/i_{pc} ratio was smaller than 1. Taking into account that it was difficult to define proper current base-lines from the experimental data, the variation of i_{pa}/i_{pc} as a function of the scan rate was calculated using Nicholson's empirical relation.[16] This ratio changed from 0.56 to 0.72 when the scan rate was increased from 0.02 to 0.8 V/s.

The loss of the anodic current indicates that a chemical reaction coupled with the charge transfer process may be operative. The product of such a reaction should lead to an electrochemical active species responsible for the small anodic current peak that appears, only when $\nu > 0.06$ V/s, at approximately 0.5 V.

In accordance with our previous result[9] the current peak A reveals the presence of a fraction of the dimer $VOQ_2{-}O{-}VOQ_2$ in solution. Thus, for the A/A′ couple the following reaction takes place on the electrode:

$$[Q_2VO{-}O{-}VOQ_2] + e^- \underset{A'}{\overset{A}{\rightleftarrows}} [Q_2VO{-}O{-}VOQ_2]^- \qquad (1)$$

The dimer could be generated in solution as a consequence of the partial hydrolysis of the ester, caused by small amounts of water in the solvent, according to the reaction:

$$2Q_2VO(OEt) + H_2O \rightarrow [Q_2VO{-}O{-}VOQ_2] + 2EtOH \tag{2}$$

Moreover, this process could also explain the color changes in the solutions.

The loss of the oxidation current (A′) arises from decomposition of a small fraction of mixed-valence dimer:

$$[Q_2VO{-}O{-}VOQ_2]^- \rightarrow Q_2VO_2^- + Q_2VO \tag{3}$$

The Q_2VO can be responsible for a very small oxidation wave (C) at +0.50 V, which can only be seen when $\nu > 0.06$ V/s. Thus, after the decomposition, the products diffuse rapidly to the bulk solution. If the scan rate is not fast enough, the corresponding oxidation wave is absent in the voltammogram.

The second electrode process which appears when the potential range is extended to −0.9 V (Figure 2) can be ascribed to reduction of the ester:

$$Q_2VO(OEt) + e^- \rightleftharpoons [Q_2VO(OEt)]^- \tag{4}$$

It comprises the B current peak, which shifts to more negative potential values when the scan rate increases. The absence of the respective oxidation component for all employed scan rates may indicate an irreversible behavior of this process, but a very fast chemical reaction coupled to a reversible charge transfer process should lead to an analogous response.[17]

Moreover, we have observed, during the reverse scan, that the current associated with A′ is higher than obtained in the reduced potential range, where reaction 4 does not take place. This current increment indicates that the concentration of the mixed valence dimer in the interface increases with respect to that obtained in the reduced potential range.

On the other hand, the electrochemical behavior of the complex appears to be water dependent and the results indicate that the following reaction can be operative:

$$[Q_2VO(OEt)]^- + [Q_2VO(OEt)] + H_2O \rightarrow [Q_2VO{-}O{-}VOQ_2]^- + 2EtOH \tag{5}$$

As a consequence of this reaction concentration of the mixed valence dimer increases, and it is oxidized at +0.025 V, during the reverse scan, giving the current peak A′ (equation (1)).

It can be concluded that the irreversibility of the electrode reaction is only apparent, and that the global process can be depicted by both equations (4) and (5).

Another possible reaction of the mixed-valence dimer with the water present in the solvent, described by the following reaction, can be neglected:

$$[Q_2VO{-}O{-}VOQ_2]^- + H_2O \rightarrow Q_2VO(OH) + Q_2VO + OH^- \qquad (6)$$

If this process takes place, an additional wave, at +0.70 V should appear due to oxidation of the reduced species $[VOQ_2(OH)]^-$[9] arising from the reaction:

$$Q_2VO + OH^- \rightleftharpoons [Q_2VO(OH)]^- \qquad (7)$$

Besides, it is valid to suppose that the small amount of water present in the solvent was already consumed in reactions (2) and (5).

Other authors have described reversible behavior of the $[Q_2VO(OCH_3)]/[Q_2VO(OCH_3)]^-$ couple which is modified with time, finally giving a voltammogram of similar characteristics to the one presented in this work.[18] They suggest a reaction analogous to (5) to explain the observed changes but propose generation of the monomer $Q_2VO(OH)$ as the hydrolysis product when the ester reacts with the residual water in the solvent. The results shown in this work and in our previous study of the monomer–dimer species[9] do not agree with this proposal but support equation (2) as the real hydrolysis reaction. If the monomer were present in solution, its reduction peak at +0.5 V should appear in the voltammogram, but that was never the case.

Complementary experiments were performed on CH_3CN solutions with variable contents of water (up to 0.5% in volume), and the results were in accord with the proposed reaction. In this case the initial voltammograms showed a current peak A higher than B, and the solutions also turned to black during the measurement time. Thus, the experimental results indicate that the dimer and not the monomer is the hydrolysis product of the ester (equation (2)).

(2) $Q_2VO(OEt)$ in Absolute Ethanol

Due to the extremely low solubility of the compound in this solvent, the measurements were directly performed on dilutions of the solutions remaining after precipitation of the solid ester from the reaction mixtures:

$$Q_2VO(OH) + EtOH \rightarrow Q_2VO(OEt) + H_2O \qquad (8)$$

The CV obtained in the +0.90 to −0.62 V range, at $\nu = 0.1$ V/s is shown in Figure 3A. Two reduction peaks at +0.22 V (A) and −0.22 V (B) and two oxidation processes at −0.025 V (B′) and +0.37 V (A′) can be seen. The potential of the reduction peaks A and B were shifted to more negative values when ν increases, while the A′ and B′ oxidation peaks slightly moved to more positive potentials.

The electrochemical behavior of the A/A′ couple was also analyzed in a restricted potential range at different scan rates. The experimental evidence shows that the oxidation peak A′ corresponds to the species that is reduced at +0.22 V (peak A) and is independent of the B/B′ couple.

Moreover, and although potential values are not comparable when obtained in different solvents, the potential difference between peaks A and B is the same as that determined working in CH_3CN solutions.

According to the present results and to those obtained in the previous study[9] peak A can be assigned to the presence of a small amount of dimer. This compound arises in solution as a subproduct or as a reactant's impurity, during the synthesis of the ester (equation (8)).

The process related to the A/A′ couple can be described by equation (1), while that corresponding to the B/B′ couple should be the oxidation–reduction of the ester (equation (4)). In contrast with the results obtained in the

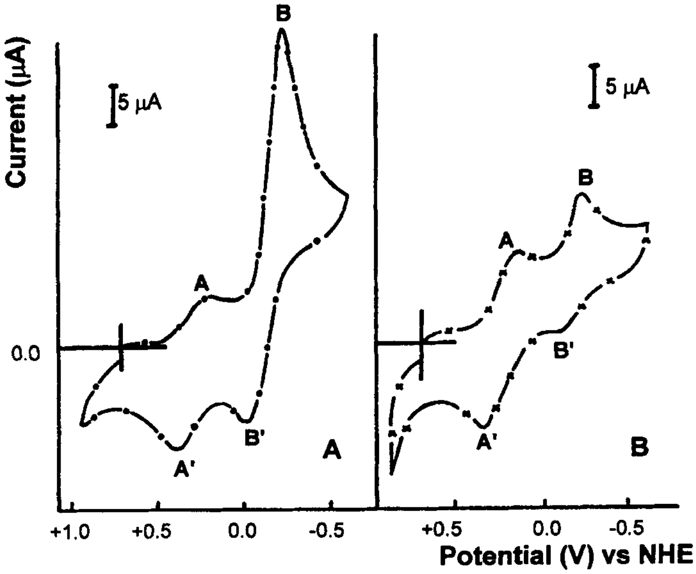

FIGURE 3 CV of $Q_2VO(OEt)$ in ethanol. $\nu = 0.1$ V/s. Effect of water addition (A) in absolute ethanol; (B) in ethanol after addition of water.

CH_3CN solutions, the ester oxidation component is present for all scan rates analyzed. Nevertheless, the i_{pa}/i_{pc} ratio is always less than one, suggesting that part of the reduced species is consumed in another process. Simultaneously, the oxidation peak A′ experienced a current increment in comparison with that obtained in the restricted potential range experiments. This behavior is related to the conversion of a small fraction of the reduced ester into a mixed-valence dimer (equation (5)), due to water present in the solvent as a consequence of reaction (8).

In order to analyze the influence of higher contents of water in the solvent on the electrochemical behavior of the different electrode processes, small amounts of water were added successively to the solution (up to 0.5% in volume). The observed changes can be summarized as follows (Figure 3B):

(a) The current of the reduction peak A increases and its potential shifts to more negative values.
(b) The current of peak A′, corresponding to oxidation of the mixed-valence dimer, also increases.
(c) The current of peak B, related to the reduction of the ester, diminishes and its potential remains constant. The oxidation component B′ gradually disappears.

From these observations, the following processes may be proposed: (1) The ester hydrolyzes, as a consequence of the addition of water, according to equation (2). (2) This reaction is responsible for the decrease in the ester reduction current (B), and the increment in the dimer reduction current (A). (3) The gradual diminution of the current peak related to the ester oxidation (B′) is due to formation of the mixed-valence dimer from the reduced ester, according to equation (5). This process is also in agreement with the increment of the current peak A′, associated with the mixed-valence dimer oxidation (equation (1)). (4) The addition of water to the solution modifies the electrochemical response of the system, turning it similar to that observed in CH_3CN solutions. Thus, these results corroborate the influence of water in the solvent on the electrode processes and the generation of new species in solution.

(3) $(ClQ)_2VO(OEt)$ and $(Cl_2Q)_2VO(OEt)$ in Absolute Ethanol

The electrochemical behavior of these solutions was analyzed in the same conditions as those described in the previous section for $Q_2VO(OEt)$. The responses were very similar for both compounds, only showing slight differences in the peak potential values.

Figure 4 shows the CV of $(ClQ)_2VO(OEt)$ at $\nu = 0.1$ V/s, in the +0.90 V at −0.40 V potential range. On the first scan, a reduction peak at −0.11 V (B) and an oxidation peak, located at +0.41 V (A′) were observed. On subsequent scans a second reduction peak at +0.25 V (A) appeared, and its current enhanced with the number of applied cycles. Simultaneously, the current of the reduction peak B diminished, while that of the oxidation peak A′ gradually increased. Furthermore, shifts of peak B to more negative values and of peak A′ to the positive side, were observed with increasing values of ν.

According to the experimental evidence and by analogy with the results obtained for the $Q_2VO(OEt)$ in the same solvent, the following processes can be proposed:

Initially, the unique electrochemically active species present in solution was the ester. It is reduced at −0.11 V producing the current peak B, according to the equation:

$$(ClQ)_2VO(OEt) + e^- \rightleftharpoons [(ClQ)_2VO(OEt)]^- \qquad (9)$$

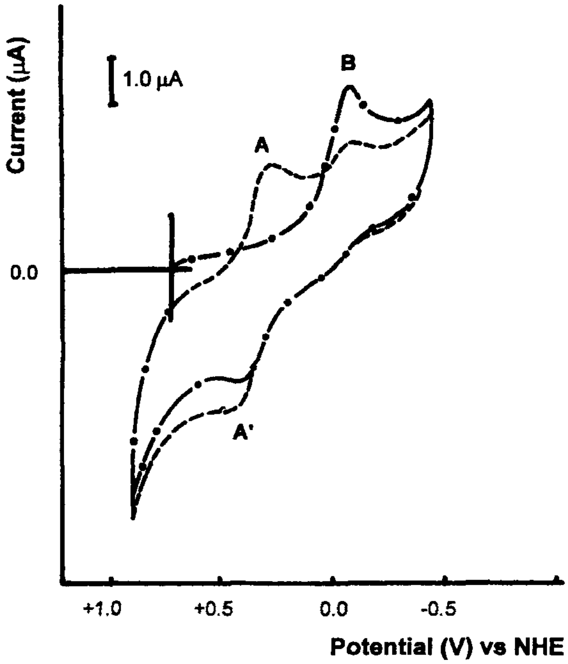

FIGURE 4 CV of $(ClQ)_2VO(OEt)$ in absolute ethanol. $\nu = 0.1$ V/s. First scan (– · – · –); fifth scan (– – –).

The experimental evidence indicates that the oxidation component B′ was absent in the whole scan rate range analyzed. On the other hand, the oxidation peak A′ was always present and the peak A appears from and after the second scan. According to these observations, a chemical reaction coupled with the reversible charge transfer process can be postulated. Thus, the reduced species reacts with the ester and with the water present in the solvent, arising from the synthesis reaction, giving rise to the mixed valence dimer, according to reaction:

$$(\mathrm{ClQ})_2\mathrm{VO(OEt)} + [(\mathrm{ClQ})_2\mathrm{VO(OEt)}]^- + \mathrm{H_2O} \rightarrow [(\mathrm{ClQ})_2\mathrm{VO{-}O{-}VO(ClQ)_2}]^- + 2\mathrm{EtOH} \qquad (10)$$

This equation could explain the absence of the oxidation component (B′) in the whole scan rate range analyzed. On these bases, the current peak A′ would be related to the mixed valence dimer oxidation, in accordance with the presence of the reduction peak A, at +0.25 V, from and after the second scan. The behavior of the redox couple A/A′ can be described by the equation:

$$[(\mathrm{ClQ})_2\mathrm{VO{-}O{-}VO(ClQ)_2}]^- \rightleftharpoons [(\mathrm{ClQ})_2\mathrm{VO{-}O{-}VO(ClQ)_2}] + e^- \qquad (11)$$

Equations (10) and (11) could also explain the progressive changes in the peak currents when successive cycles were applied to the electrode.

Due to the similarity in the responses of $(\mathrm{ClQ})_2\mathrm{VO(OEt)}$ and $(\mathrm{Cl_2Q})_2\mathrm{VO(OEt)}$, the electrode processes may be described by the mentioned equations for both cases. Nevertheless, small differences in the peak potentials were observed. The $(\mathrm{Cl_2Q})_2\mathrm{VO(OEt)}$ is reduced at −0.09 V (peak B), the mixed valence dimer oxidation (A′) occurs at the same potential as for the ClQH compound and the corresponding reduction (A) appears at +0.23 V.

(4) (QUIN)$_2$VO(OEt) · 2H$_2$O in Absolute Ethanol

This complex is an example in which the ligand is monodentate, coordinating the metal only by its oxygen atom. The nitrogen is unable to interact with the vanadium due to the presence of a methyl group bonded to C–2. The coordination sphere is completed with the two water molecules.[19,20]

The solution was prepared in the same way as for the previously discussed compounds. This complex was measured in the +0.80 V to −1.25 V potential range at different scan rates. The voltammograms showed only one irreversible reduction peak and did not show any change in response with the application of successive cycles.

Measurements within a restricted potential range (+0.54 to −0.77 V) with scan rates from 0.02 to 0.8 V/s, were also performed. The voltammogram obtained at $\nu = 0.1$ V/s, showing the reduction peak at −0.31 V, is depicted in Figure 5. This peak is shifted towards lower potential values with increasing scan rates and the process related to it is the irreversible reduction of the ester:

$$(\mathrm{QUIN})_2\mathrm{VO(OEt)} \cdot 2\mathrm{H_2O} + \mathrm{e}^- \rightarrow [(\mathrm{QUIN})_2\mathrm{VO(OEt)} \cdot 2\mathrm{H_2O}]^- \qquad (12)$$

In contrast with the results obtained for the other compounds, there was no evidence for formation of new species from the reduced ester in this case. This behavior is in agreement with the well-known poor tendency of quinaldine complexes to form dimer species, as a consequence of the steric hindrance imposed by the methyl group.

As complementary measurements, the voltammograms of the respective 'acid' $(\mathrm{QUIN})_2\mathrm{VO(OH)} \cdot 2\mathrm{H_2O}$ in absolute ethanol were obtained. They

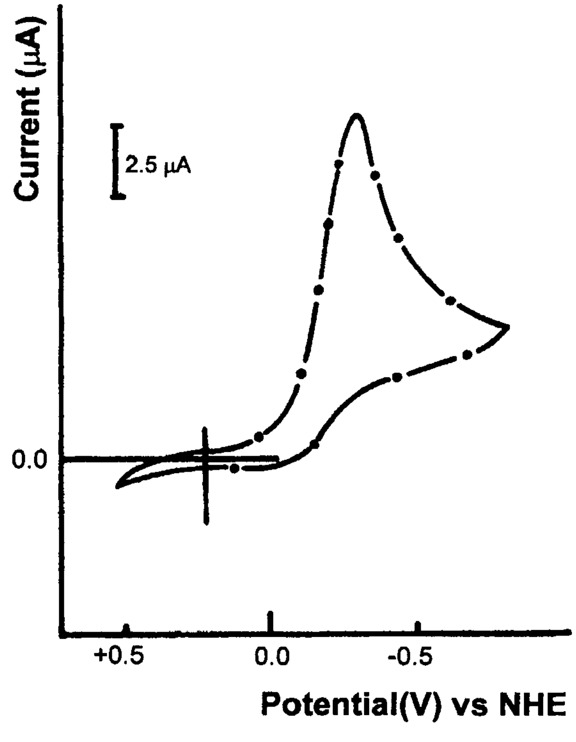

FIGURE 5 CV of $(\mathrm{QUIN})_2\mathrm{VO(OEt)}$ in absolute ethanol. $\nu = 0.1$ V/s.

showed a composite reduction peak, suggesting the presence of two electrochemically active species that are reduced at similar potential values.

The first process appears as a shoulder at approximately −0.24 V, and can be assigned to the reduction of a fraction of acid present in solution, according to equation (13):

$$(\mathrm{QUIN})_2\mathrm{VO(OH)} \cdot 2\mathrm{H_2O} + \mathrm{e}^- \rightarrow [(\mathrm{QUIN})_2\mathrm{VO(OH)} \cdot 2\mathrm{H_2O}]^- \qquad (13)$$

The second process is responsible for the current peak located at −0.40 V, related to the ester reduction described by equation (12). The shift of this peak with respect to the one obtained for the ester solution is due to the presence of acid, and both are reduced at similar potentials. Both species should exist together under the present conditions:

$$(\mathrm{QUIN})_2\mathrm{VO(OH)} \cdot 2\mathrm{H_2O} + \mathrm{EtOH} \rightleftharpoons (\mathrm{QUIN})_2\mathrm{VO(OEt)} \cdot 2\mathrm{H_2O} + \mathrm{H_2O} \qquad (14)$$

To conclude this section it is interesting to comment that there exists a correlation between the reduction potential and the basicity of the ligands, QUINH, QH, ClQH and $\mathrm{Cl_2QH}$. The values are more positive when the ligands are less basic. In other words, the higher the electronegativity of the substituent in the ligand ring, the more stable the respective reduced ester.

Electronic Spectroscopy

It was already mentioned that the solution of the complex esters experienced changes in their color, during the electrochemical measurements. In order to clarify the nature of the transformations, the electronic spectra of these solutions were also investigated.

The originally red-wine colored solutions of $\mathrm{Q_2VO(OEt)}$ in $\mathrm{CH_3CN}$, fade gradually to black during the measurement period, suggesting formation of the monomeric "acid" or the dimeric $\mathrm{Q_2VO{-}O{-}OVQ_2}$ species. The electronic spectra of the solutions were recorded, at different times, simultaneously with the electrochemical measurements. The results obtained by both techniques were in excellent agreement.

Table I compares the absorption maxima of a freshly prepared ester solution in $\mathrm{CH_3CN}$ with those obtained after the voltammetric experiment, confirming generation of the dimer by decomposition of the ester. The spectrum of the last solution, after the addition of water, was also recorded and some shifts in the band positions were observed.

TABLE I Electronic spectra of vanadium(V) species with 8-hydroxyquinoline as ligand (solvent: CH_3CN)*

$Q_2VO(OEt)$ (1)	$Q_2VO(OEt)$ (2)	$Q_2VO(OEt)$ (3)	$Q_2VO{-}O{-}VOQ_2$	$Q_2VO(OH)$
208	208	202	202	208
244	242	242	242	242
330	332	318	330	332
388	390	376	382	380
490	536	580	550	572

*Absorbance maxima in nm; (1): freshly prepared solution; (2): the same solution after 90 min; (3): solution (2) after addition of water.

TABLE II Electronic spectra of vanadium(V) species with the halogen derivatives of 8-hydroxyquinoline as ligands (solvent: CH_3CN)*

$(ClQ)_2VO(OEt)$		$(ClQ)_2VO(OH)$	$(Cl_2Q)_2VO(OEt)$		$(Cl_2Q)_2VO(OH)$
$t=0$	$t=24$ h		$t=0$	$t=24$ h	
198	200	200	204	204	204
246	244	244	250	250	248
	330	330	322[†]	330	318
394	392	394	400	394	400
488	384	596	500	582	600[‡]

*Absorbance maxima in nm; [†]weak intensity band; [‡]very broad bands, undefined maximum.

The spectra of the monomer and of the dimer differ only in the position of the lowest energy band, where maximum is difficult to determine with precision, due to its broadness. However the spectrum of the solution obtained after the electrochemical experiments resembles that of the dimer, while that obtained after addition of water to that solution is coincident with that of the monomer. These results are in agreement with the fact that a large amount of water is needed to obtain the monomer as the final hydrolysis product of the ester.

Acetonitrile solutions of the two esters containing the monochloro and dichloro "oxine" as ligand also changed their color with time. The initially pink solutions turned to green after 24 h, suggesting chemical transformations. The electronic spectra of these green solutions are very similar to those obtained for the respective "acid" monomers, as can be seen from the detailed data presented in Table II.

One may accept that the little amount of water present in the solvent, together with that incorporated to the system from the atmospheric humidity, is reponsible for the ester's hydrolysis. The product of this reaction may be the "acid" or the dimer, depending on the water content of the solution. Addition of water to the pink solutions did not introduce changes in the spectra at short times, suggesting that the hydrolysis of these compounds is slower than that of the corresponding "oxine" ester, $Q_2VO(OEt)$.

The solution behavior of the ester derived from "quinaldine" as a ligand is more complex. The initially yellow solution obtained by dissolution of the solid "acid" $(QUIN)_2VO(OH) \cdot 2H_2O$ in CH_3CN turned rapidly to violet. On the other hand, and as the ester $(QUIN)_2VO(OEt)$ is very unstable against hydrolysis,[6] we prepared its acetonitrile solution directly by dilution of the ethanolic solution, remaining from the synthesis of the ester, in CH_3CN. The resulting amber colored solution changed rapidly to a permanganate-like violet; both violet solutions present similar electronic spectra.

The violet solution of the "acid" changed back to yellow, with time and the same effect is observed when water is added to the solution. This behavior suggests some kind of reversible interaction with the solvent, by substitution of the coordinated water molecules, at least in a partial way.

Due to the strong hydrolysis tendency of the ester, the effects of time and water addition could not be analyzed in this case. However, the analogous spectral behavior of its CH_3CN solution with that of the "acid" can be considered as evidence that the two coordinated water molecules present in the "acid" remain attached to the metal after the esterification reaction.

This implies that in the ester the ligand is coordinated only through its oxygen atom, a conclusion which is in agreement with the absence of dimeric species during the electrochemical experiments, because formation of the dimer requires that "quinaldine" act as a bidentate ligand.[6]

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