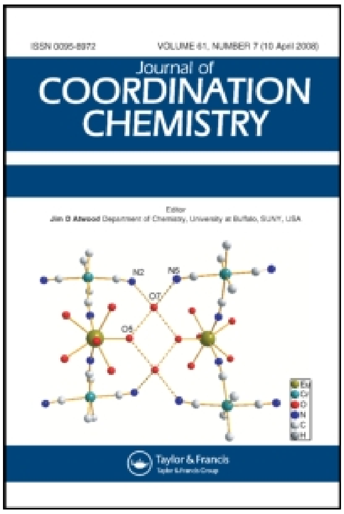

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VOQ_2OH OR $[VOQ_2\text{–}O\text{–}VOQ_2]$ (Q = 8-HYDROXYQUINOLINATE)? A CLASSIC MONOMER–DIMER DILEMMA REVISITED

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The electrochemical behavior of VOQ_2OH or $[VOQ_2\text{–}O\text{–}VOQ_2]$ (Q = 8-hydroxyquinolinate anion) has been investigated by cyclic voltammetry in acetonitrile solutions. Although both species exist simultaneously at every condition analyzed, they can be clearly differentiated by this method. The effect of trace amounts of water on the electrochemical behavior is also discussed.

Keywords: Cyclic voltammetry; V(V)/“oxine”; monomeric and dimeric species; characterization

INTRODUCTION

Complexation of vanadium by 8-hydroxyquinoline (“oxine”) has been frequently investigated, due to the useful characteristics of this ligand as an analytical reagent.[1]

For weakly acidic media, vanadate (V) reacts with “oxine” (QH) to give a 1 : 2 water insoluble black complex. For many years the characterization of this complex was in question because some authors refer to it as the monomeric “acid” VOQ_2OH, while others suggest a dimeric structure $[VOQ_2\text{–}O\text{–}VOQ_2]$ (cf: Refs. 2 and 3, and references therein).

As the spectroscopic differentiation of both compounds is not conclusive,[4] we have tried to reinvestigate the electrochemical behaviour of

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these complexes in acetonitrile solution in order to find a rapid tool for their differentiation, although previous studies indicate that these compounds are indistinguishable electrochemically.[5,6]

The compounds present very low solubility in most of the usual solvents and show also a high reactivity with some of them. Despite the fact that its solubility in acetonitrile is very low, this solvent was chosen because it does not react with the complexes during the time of measurement. On the other hand, we have tried to reinvestigate the electrochemical behavior of these compounds in the same solvent previously used[5,6] in order to compare our results with those previously reported.

EXPERIMENTAL

Synthesis and Characterization of the Compounds

The monomeric acid VOQ_2OH was obtained by reaction of NH_4VO_3 with the ligand in acetic acid, according to reported techniques.[7–9] The dimer $[VOQ_2{-}O{-}VOQ_2]$ was prepared by reaction of the ligand with a suspension of VO(acetylacetonate)$_2$ in acetone, in air.[2]

The IR spectra of the solid complexes in KBr pellets were recorded on a Perkin-Elmer 580 B spectrophotometer. Electronic spectra of CH_3CN solutions of the compounds were obtained with a Hewlett-Packard 845-A, diode array, spectrophotometer. As the differentiation of both complexes by these techniques was not conclusive, the X-ray diffraction powder diagrams were performed on a Rigaku Miniflex CN 2005 diffractometer. Despite the low crystallinity of the samples, the diffractograms showed that the structures of both compounds are different.

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. This electrode was calibrated against the $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$ redox couple, for which a potential of +0.4 V *vs.* NHE was assumed.[10]

All the experiments were performed in CH_3CN solutions with 0.1 M $LiClO_4$ as supporting electrolyte. High purity CH_3CN (Mallinckrodt) was dried over 4 A molecular sieves (Fluka) and used without ulterior purification. The supporting electrolyte, $LiClO_4$, was purchased from Fluka and used as received.

Previous to each experiment a cyclic voltammogram 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).

RESULTS AND DISCUSSION

The electrochemical behavior of the dimeric and monomeric compounds were analyzed at scan rates between 0.05 and 1 V/s. Measurements at higher scan rates on these systems were not possible. Uncompensated resistance and double layer charging effects are both very significant and, in consequence, the voltammograms obtained are distorted.

The voltammograms of $[VOQ_2–O–VOQ_2]$ at two scan rates (ν) are shown in Figure 1. On the first scan this species exhibits one shoulder (A) and one

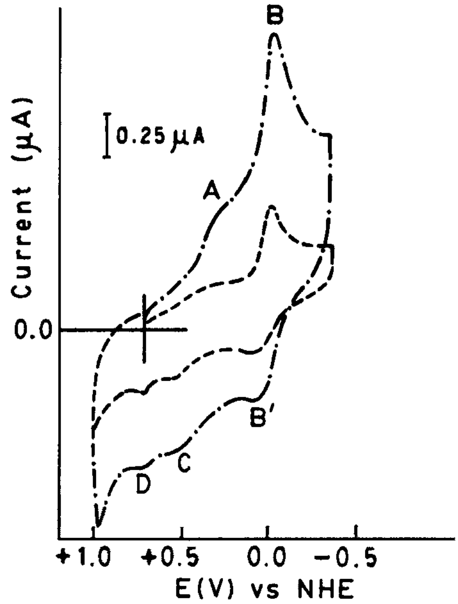

FIGURE 1 Cyclic voltammograms of the dimer $[VOQ_2–O–VOQ_2]$ in CH_3CN solution, at two different scan rates (ν): (----) 0.1 V/s; (- · · · -) 0.8 V/s.

reduction peak at −0.04 V (B). The reverse scan reveals one oxidation peak (B′) at +0.07 V which is coupled to process B, and two small waves at +0.52 V (C) and +0.72 V (D). The presence of these two contributions indicates a rapid appearance of new species in the solution.

The effect of the scan rate (ν) on the mentioned peaks has also been analyzed and the general features of the cyclic voltammogram can be summarized as follows:

(a) Wave A appears at more positive potential with decreasing scan rates.
(b) Couple B/B′ is independent of ν. Moreover the height of the anodic peak is smaller than that of the cathodic peak but the relation i_{pa}/i_{pc} remains constant with a value of 0.6.
(c) The contributions C and D are small and always occur at the same potential.

Reductive cyclic voltammograms of VOQ_2OH at $\nu = 0.8$ V/s is shown in Figure 2. On a forward scan two peaks at +0.5 V (A) and at −0.04 V (B) are observed. On the reverse scan only one broad oxidation wave appears. Nevertheless, the distorted shape of this wave suggests that two processes are involved in this path, which occur at about +0.5 V (shoulder) and at +0.7 V.

The voltammetric changes observed when this compound is measured at different scan rates are as follows:

(a) The reduction peak A is shifted to more negative values when ν decrease.
(b) The position of the reduction peak B is independent of ν and the oxidation component B′ is not observed on the reverse scan, within the analyzed scan rates range.
(c) At low scan rates the current contribution of peak A is smaller than that obtained for peak B. Increasing rates produce an inversion of this ratio.

It was also found that the current for each peak changes as the potential was cycled back and forth, at every scan rate. On continued cycling the relative concentration of the existing species change as evidenced by the relative height of the voltammetric peaks. While peak A increases, peak B decreases and simultaneously the oxidation peak (C, D) grows (cf. Figure 2).

On the basis of the obtained results, the electrochemical behavior of the complexes can be described in the following way:

(a) For the dimer, the reduction wave A, at the first scan, can be ascribed to the presence of a small fraction of monomer generated in solution trough

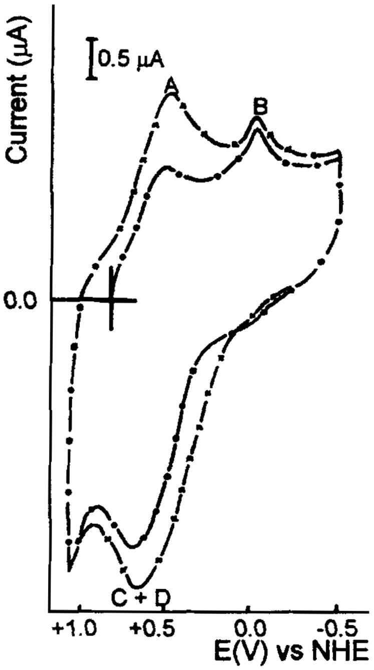

FIGURE 2 Cyclic voltammograms of the monomer VOQ$_2$OH in CH$_3$CN solution, at $\nu = 0.8$ V/s. Effect of successive cycles applied to the electrode: (-····-) 1st cycle; (- × - × - × -) 5th cycle.

the following reaction:

$$[\mathrm{VOQ_2{-}O{-}VOQ_2}] + \mathrm{H_2O} \rightleftarrows 2\mathrm{VOQ_2OH} \tag{1}$$

As the complex concentration is very low, due to its slight solubility, the low water content of the solvent is not "innocent", and is sufficient to produce this reaction.

The monomeric species undergoes an electron charge transfer to:

$$\mathrm{VOQ_2OH} + e^- \longrightarrow [\mathrm{VOQ_2OH}]^- \tag{2}$$

(b) The redox couple B/B′ can be assigned to the oxidation–reduction of the dimer:

$$[\mathrm{VOQ_2{-}O{-}VOQ_2}] + e^- \rightleftarrows [\mathrm{VOQ_2{-}O{-}VOQ_2}]^- \tag{3}$$

(c) The anodic to cathodic current peak ratio, $i_{pa}/i_{pc} < 1$, obtained for this couple indicates that a forward chemical reaction diminishes the concentration of the mixed-valence dimer at the electrode surface from the value it would have for a simple electron transfer reaction. Hence it may be concluded that the decomposition of the mixed valence dimer occurs by one of the following mechanisms:

$$[VOQ_2{-}O{-}VOQ_2]^- + H_2O \longrightarrow VOQ_2OH + VOQ_2 + OH^- \quad (4)$$

$$[VOQ_2{-}O{-}VOQ_2]^- + H_2O \longrightarrow VO_2Q + VOQ_2 + QH + OH^- \quad (5)$$

$$[VOQ_2{-}O{-}VOQ_2]^- \longrightarrow [VO_2Q_2]^- + VOQ_2 \quad (6)$$

Furthermore, the equilibrium between VOQ_2 and OH^-:

$$VOQ_2 + OH^- \rightleftarrows [VOQ_2OH]^- \quad (7)$$

cannot be neglected and the small anodic waves C and D were thought to arise from the oxidation of these two species.

(d) From comparison with the measurements of the dimer species and by analogy with the proposed reactions, it can be inferred that in the solution of the monomer, the reduction of this species occurs at the potential of peak A (equation (2)). As the VOQ_2OH is less soluble than the $[VOQ_2{-}O{-}VOQ_2]$, the concentration of the last species, in a solution of the monomer, is very low. Thus, the second cathodic process (peak B) corresponds to the reduction of a small fraction of dimer (equation (3)) present in this solution as a consequence of the reaction (1). As the content of water in the solvent increases the mixed-valence dimer undergoes a rapid decomposition by water to give the products shown by equations (4) or (5). For this reason the oxidation peak B′ cannot be observed.

(e) Based on the information obtained when successive cycles were applied to the electrode, we conclude that equation (4) is the most appropriate to describe the degradation. The reduction peak A grows with the perturbation and these changes can occur only if the amount of monomer increases in the interface. Moreover, the absence of a peak related to the free ligand reduction (at about −1.62 V) would indicate that the process depicted by equation (5) does not take place.

(f) On the anodic scan, the oxidation peak (C, D) can be explained in terms of the following processes:

$$[VOQ_2OH]^- \longrightarrow VOQ_2OH + e^- \quad (8)$$

$$VOQ_2 \longrightarrow VOQ_2^+ + e^- \quad (9)$$

On the other hand, a reaction between the product of equation (9) and the OH^- species, generated in the degradation of the mixed-valence dimer (equation (4)), can lead to formation of the monomer:

$$VOQ_2^+ + OH^- \longrightarrow VOQ_2OH \qquad (10)$$

(g) The performed measurements indicate that the proportion of the species responsible for peak A is greater than the one that generates peak B when the monomer is the initial compound in solution. In contrast, peak B dominates in the solution of the dimer.

Finally, and with the purpose to confirm the effect of water in the solvent on the voltammetric behavior, small portions of tridistilled water were successively added to the solutions. A progressive increment in the reduction current of the monomer was observed, with a simultaneous decrease in the reduction current of the dimer, in agreement with the reaction proposed by equation (1).

CONCLUSIONS

Based on the differences in voltamperometric responses in CH_3CN, both complexes, the monomer VOQ_2OH and the dimer $[VOQ_2{-}O{-}VOQ_2]$ are perfectly distinguishable under the employed working conditions and can be characterized by their corresponding reduction peaks. This result contradicts that reported by Riechel and Sawyer[5] and Hepler and Riechel,[6] who could find no difference in the electrochemical behavior of these two species.

Moreover, these authors concluded that the monomer is soluble only to the extent that it is transformed into the dimer, so that the later always predominates in solution. We have seen that both complexes exist simultaneously at every condition analyzed, but the compound used to prepare the solution is always the main species present during the time required to perform the experiments. Probably, the water content of the CH_3CN used by these authors was enough to produce the fast interconverssion between the dimer and monomer. As a result, they have the monomer as the main species in both cases, leading to identical voltammograms.

On the other hand, the presence of trace amounts of water in the solvent modifies the electrochemical behavior of both compounds. Water reacts not only with the dimer to give the monomer, but also participates in the degradation of the mixed-valence dimer.

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