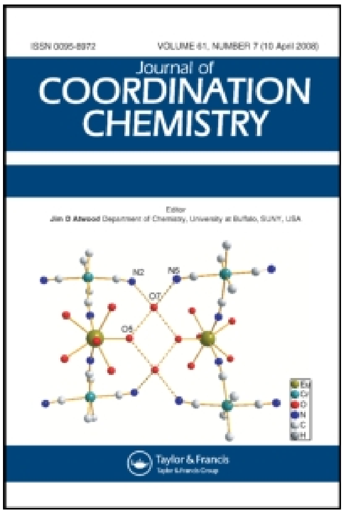

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Synthesis, Spectroscopic and Voltammetric Studies of a Novel Dioxovanadate(V) 8-Hydroxyquinoline Complex

Semiha Çakir[a]; Ender BiÇer[a]; PanČe Naumov[b]; Osman Çakir[a]
[a] Department of Chemistry, Faculty of Arts and Sciences, Ondokus Mayis University, Kurupelit-Samsun, Turkey [b] Institute of Chemistry, Faculty of Sciences, Sv. Kiril i Metodij University, Skopje, Macedonia

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SYNTHESIS, SPECTROSCOPIC AND VOLTAMMETRIC STUDIES OF A NOVEL DIOXOVANADATE(V) 8-HYDROXYQUINOLINE COMPLEX

SEMIHA ÇAKIR[a,*], ENDER BIÇER[a], PANČE NAUMOV[b] and OSMAN ÇAKIR[a]

[a] *Department of Chemistry, Faculty of Arts and Sciences, Ondokus Mayis University, 55139 Kurupelit–Samsun, Turkey;* [b] *Institute of Chemistry, Faculty of Sciences, "Sv. Kiril i Metodij" University, PO Box 162, MK-91001 Skopje, Macedonia*

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A novel solid oxovanadium(V) complex, monoaqua(8-hydroxyquinolinato)dioxovanadium(V), $VO_2(H_2O)(Q)$ ($Q = $ 8-hydroxyquinolinate ion) was synthesized and characterized by FTIR and UV/Vis spectroscopy, voltammetric measurements and Hartree–Fock *ab initio* calculations on the models of the ligand Q and the respective phenol QH. Electrochemical measurements in solution clearly showed complex formation between NH_4VO_3 and 8-hydroxyquinoline, revealing an electrode reaction of the intermediate $NH_4[VO_2(Q)OH]$ species on the mercury electrode in 0.1 M NH_3/NH_4Cl buffer (pH 9.85) as a reversible process at -0.700 V (*vs.* Ag | AgCl | KCl_{sat} reference electrode). The square-wave voltammogram of an aqueous solution of the $VO_2(H_2O)(Q)$ complex obtained with thermal deamination of $NH_4[VO_2(Q)OH]$ presented a new reversible peak at -0.720 V.

Keywords: Ammonium trioxovanadate(V); 8-Hydroxyquinoline; Oxine; FTIR spectra; *ab initio* Calculations; Electronic spectra; Voltammetry

INTRODUCTION

Vanadium is a transition metal with relevant biological properties [1]. Evidence on the biological relevance of vanadium has been continuously accumulated during recent years [2–7], especially regarding the essentiality, distribution and toxicity of this element. Although a number of biochemical and physiological functions have been suggested and despite the magnitude of the accumulated knowledge, vanadium still does not have a clearly defined role in higher organisms [2,3,8]. Its biological and pharmacological activities still constitute an area of growing interest.

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*Corresponding author. Tel.: +90-362-4576020, Int. 5097. Fax: +90-362-4576081.
E-mail: scakir@omu.edu.tr

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8-Hydroxyquinoline (also known as "oxine", QH) is a well-known analytical reagent for metal ion chelation; the resulting metal complexes present remarkable antimicrobial and fungicidal activity [9,10]. Although the reaction mechanisms of these activities on a molecular level are not yet clear, it is generally accepted that the crucial role of the biological function is played by their coordination geometry [11]. Deprotonated ligand appears particularly interesting for model studies related to vanadium biochemistry, as it normally produces bis or tris chelated complexes of types VQ_2 or VQ_3, generating VN_2O_2 or VN_3O_3 environments.

The analytical results showed that our attempted synthesis of oxovanadium mixed-ligand complexes resulted in $NH_4[VO_2(Q)OH]$, a compound for which we were not able to trace any references in the chemical literature. There exist, however, number of articles dealing with the synthesis and characterization of vanadium(V) species containing QH and some of its halogenated derivatives [12–16]. Also, a literature survey revealed that due to the oxidation properties of the metal, voltammetric techniques are particularly convenient for characterization of V(V) complexes [17,18]. Herewith, we report the synthesis and the combined physicochemical characterization by spectroscopic (FTIR, UV/Vis), voltammetric and theoretical methods of the novel adduct of NH_4VO_3 with QH.

EXPERIMENTAL

Synthesis of Monoaqua(8-hydroxyquinolinato)dioxovanadium(V)

All chemicals were supplied from commercial sources. To a solution of 0.585 g (5×10^{-3} mol) NH_4VO_3 slowly dissolved in 50 mL of water, 0.726 g (5×10^{-3} mol) QH was added under continuous stirring at 60°C. The mixture was stirred for 30 min at 60°C. Dark green needle-like crystalline precipitate of $VO_2(H_2O)(Q)$ was obtained upon cooling the solution. The product was filtered, washed several times with small portions of EtOH and dried over calcium chloride. Anal. Calcd. for $VO_2(H_2O)(Q)$%: C, 44.10; H, 3.29; N, 5.71, Found: C, 44.37; H, 3.83; N, 6.38.

Vibrational Spectra

The FTIR spectra in the 4000–400 cm^{-1} region were recorded from KBr pellets with a Jasco FTIR 350 interferometer at a resolution of 4 cm^{-1}, based on averaging 32 sample and 16 background scans.

Electronic Spectra

The electronic absorption spectra in the 800–200 nm range were recorded on Unicam V2–100 UV/Vis spectrophotometer, using 1 cm quartz cells.

Theoretical Calculations

To obtain information on the structural changes that proceed upon the complexation of QH and the structural parameters of the adduct, as well as to interpret the IR features, *ab initio* calculations were carried out on both the QH molecule and its oxoanion.

Models of the isolated gas-phase QH and Q in their groundstates built with *Chem*3D [19] were initially optimized with the MM2 procedure and the default parameters implemented in the program. Resulting structures were then subjected to unrestricted Hartree–Fock SCF geometry optimization by analytical computation of the energy derivatives (Berny's algorithm) [20]. For comparison purposes, a computationally feasible basis set 6-311++G(d,p) was used in both cases, with polarization functions supplied to describe the negatively charged ion and the diffuse functions to account for eventual hydrogen bonding. It is known that when employed for small neutral organic molecules, basis sets of this size can still give a good description of the electronic structure [21–23] and there are a number of occasions where correlated methods fit worse to the experiment. Found stationary points (Fig. 1) were subjected to single-point runs and subsequent harmonic vibrational analyses at the same level, calculating the eigenvalues of the potential energy second-derivative matrix with respect

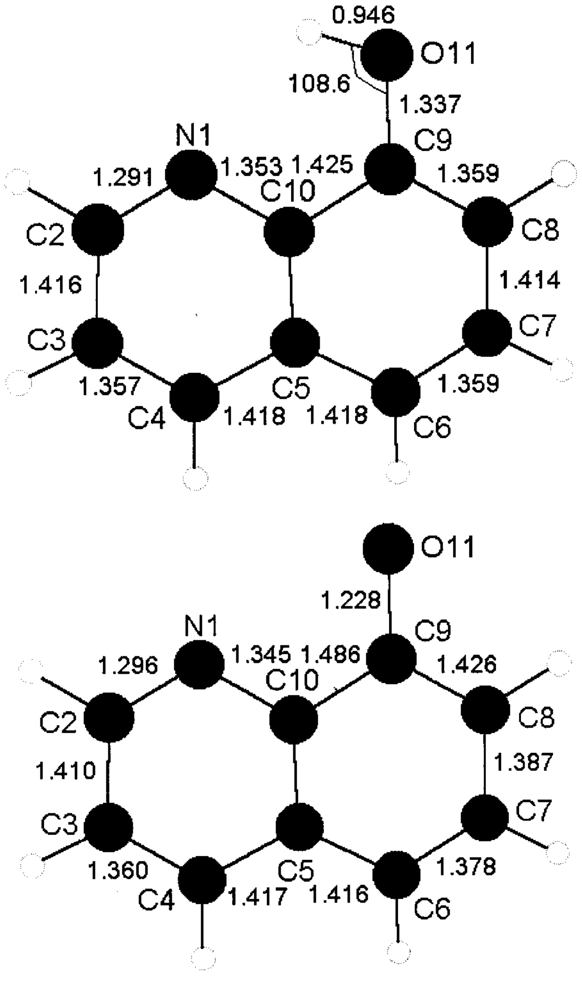


FIGURE 1 The theoretical (HF/6-311++G(d,p)) structures of the 8-hydroxyquinoline molecule (upper part) and its oxoanion (lower part) with relevant distance (Å) and angle values.

to the Cartesian nuclear coordinates. The native wavenumbers were uniformly and linearly scaled with 0.8992 [24] to account for the basis set truncation, correlation effects and vibrational anharmonicity. The *ab initio* calculations were carried out with the *Gaussian*98 program suite [25] operating on the SGI *Origin*2000 supercomputer at the Tokyo Institute of Technology. The vibrational line spectra were reconstructed with the program *Molda*643 [26].

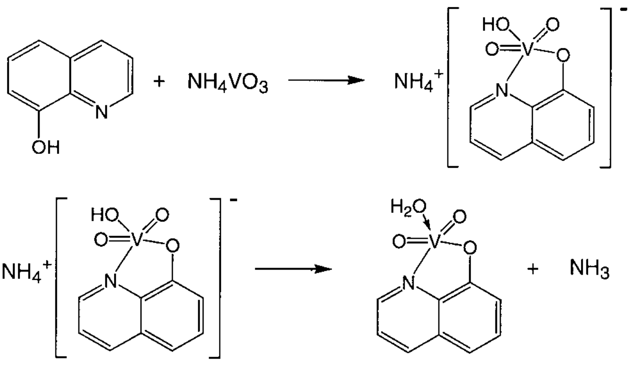
Electrochemical Measurements

Voltammetric experiments were performed with an EG&G PAR Model 384B polarographic analyzer. A standard three-electrode cell (EG&G PARC Model 303A polarographic stand (Princeton, NJ, USA) was used with a Hg working electrode, a Pt counter electrode and a Ag | AgCl | KCl_{sat} reference electrode. All solutions were prepared in deionized and triply-distilled H_2O. Also, the experiments were performed in 0.1 M NH_3/NH_4Cl buffer (pH 9.85) as supporting electrolyte.

Prior to each experiment, a voltammogram of the solution containing only the supporting electrolyte was measured. Solutions of NH_4VO_3 and QH, and the $VO_2(H_2O)(Q)$ complex in water were separately added to the cell containing the supporting electrolyte and their voltammograms were recorded. The solutions were deoxygenated by purging with pure nitrogen (a continuous gas stream was blanketed over the solutions during the measurements).

RESULTS AND DISCUSSION

The analytical data characterized the resulting green solid product as monoaqua (8-hydroxyquinolinato)dioxovanadium(V). Under mild anaerobic conditions in the voltammetric measurements, ammonium hydroxo(8-hydroxyquiniolinato)dioxovanadate(V) is preferably formed (see the discussion below), but the results showed that deamination took place upon prolonged heating during the solution synthesis of the solid, according to the reactions displayed in Scheme 1.



SCHEME 1.

Equilibrium Structures

The optimized gas-phase structures of QH and the corresponding oxoanion, the ligand of interest in this study, are presented in Fig. 1, Table I lists the respective Cartesian coordinates. Both isolated models feature no unusual structural properties. The phenol molecule and the anion are completely planar. In an HF/6-31G(d,p) optimization, the geometry of QH featured hydrogen away from the pyridyl nitrogen atom, contrary to what would be expected from an eventual intramolecular O–H···N interaction; the vibrational analysis yielded all-real frequencies, confirming that the conformation represents a true minimum. With the HF/6-311++G(d,p) method, however, regardless of the intramolecular bond added in the input, the models converged to the same hydrogen bonded minimum, a clear consequence of the diffuse functions supplement. The predicted hydrogen bond geometry is O–H = 0.946 Å, N···H = 2.167 Å, N···O = 2.697 Å, N···H–O = 114.2°. The charge flow within the

TABLE I Cartesian coordinates (x, y, z) of the HF/6-311++G(d,p) optimized structures of an isolated 8-hydroxyquinoline molecule and the corresponding anion (labels refer to Fig. 1)

Atom	*x*	*y*	*z*
8-Hydroxyquinoline molecule			
N1	−0.987359	−1.377373	−0.000008
C3	−2.668408	0.313076	0.000076
C2	−2.232343	−1.034617	−0.000057
C4	−1.736709	1.299825	−0.000041
C5	−0.359601	0.963224	−0.000068
C6	0.686169	1.920520	0.000000
C7	1.977614	1.497036	0.000000
C8	2.303565	0.120895	0.000101
C9	1.316142	−0.813595	0.000045
C10	−0.048835	−0.403128	−0.000037
O17	1.605535	−2.119131	−0.000103
H (on O11)	0.795649	−2.608464	0.000194
H (on C2)	−2.958615	−1.830130	0.000370
H (on C3)	−3.720101	0.532040	0.000159
H (on C4)	−2.028295	2.335588	−0.000097
H (on C6)	0.446107	2.968468	−0.000089
H (on C7)	2.777565	2.215755	0.000034
H (on C8)	3.329351	−0.198012	0.000199
8-Hydroxyquinolinate anion			
N1	−1.019122	−1.395699	0.000034
C2	−2.262872	−1.032780	0.000030
C3	−2.671811	0.316417	−0.000023
C4	−1.711715	1.279322	−0.000021
C5	−0.340800	0.919760	−0.000009
C6	0.692339	1.888342	−0.000020
C7	1.994856	1.439629	0.000002
C8	2.334352	0.094602	0.000065
C9	1.360174	−0.947519	0.000048
C10	−0.046288	−0.466808	0.000022
O11	1.641234	−2.143229	−0.000099
H (on C2)	−3.002945	−1.819111	0.000076
H (on C3)	−3.719734	0.565456	−0.000032
H (on C4)	−1.977528	2.324102	−0.000026
H (on C6)	0.452418	2.937432	−0.000072
H (on C7)	2.793895	2.167156	0.000002
H (on C8)	3.368466	−0.205105	0.000052

conjugated system triggered by deprotonation of QH leads to shortening of the C15–O17 bond by about 0.109 Å and notable lengthening of the second nearest bonds, C8–C15 and C14–C15. The joining bond C5–C10 is also lengthened from 1.401 (QH) to 1.41 (Q). For the other bonds, significant shortening of C7–C8 and stretching of C6–C7 is observed while (aside from C5–C10) the pyridyl bonds remain practically constant.

Infrared Spectra

Theoretical spectra of QH and Q are shown in Fig. 2 together with the experimental spectrum of the title compound. The assignments were supported by inspection of the atomic displacements in the simulated vibrations. Expectedly, the deprotonation of the parent phenol accounts for the pronounced spectral changes.

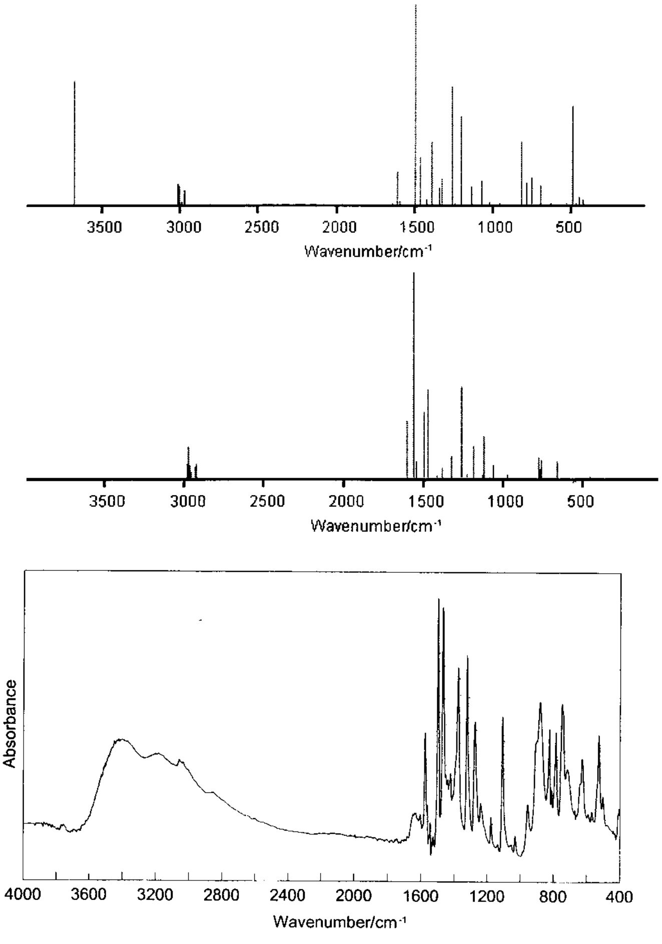


FIGURE 2 Harmonic *ab initio* IR spectra at the HF/6-311++G(d,p) level of 8-hydroxyquinoline molecule (upper line spectrum) and its oxoanion (lower line spectrum). The lowest curve represents the experimental FTIR spectrum of the complex.

Incorporation of medium to strongly hydrogen-bonded crystal water in the title complex is apparent from the broad complex absorption extending from 3600 to below $2600\,\mathrm{cm}^{-1}$ with two maxima (3400 and $3190\,\mathrm{cm}^{-1}$) overlapped by nonfundamentals around $3060\,\mathrm{cm}^{-1}$ and CH stretches. The water bending mode appears as a weak broadened band complex at *ca.* $1633\,\mathrm{cm}^{-1}$. The VO stretching vibration usually observed for similar vanadium complexes between 881 and $892\,\mathrm{cm}^{-1}$, is present as an overlapped doublet at 904 and $876\,\mathrm{cm}^{-1}$, but the former unseparated band could also originate from some of the internal 8-hydroxyquinolinate modes expected from the calculated spectrum (e.g., the bands expected around 945, 908 or $864\,\mathrm{cm}^{-1}$). Otherwise, the higher-frequency, less strong band and the lower-frequency one can be empirically assigned to the symmetric and antisymmetric VO_2 stretching modes, respectively. An inverted frequency order is well known for heavy-metal XO_2 group stretches.

As noted by comparing the $1600–400\,\mathrm{cm}^{-1}$ regions in Fig. 2, satisfactory agreement exists between the experimental and theoretical HF/6-311++G(d,p) spectra of the 8-hydroxyquinolinate ligand (Table I). Notable is the systematic over-estimation of the experimental wavenumbers after scaling with 0.8992, besides the generally conforming trend of relative intensities. In addition to the usual solid state effects on the spectrum, this might be due to greater conjugation of the internal vibrations from bidentate chelation. Almost all Q bands could be assigned from the theoretical spectrum. Most of the mid-IR bands are sharp, energetically well-separated, but inherently heavily coupled ring stretches. In the lower IR region, CH bending and ring bending modes are also present. As our aim in the present study is identification rather than detailed vibrational analysis, we refrain here from detailed discussion of the normal modes.

Electronic Spectra

Electronic spectra of the ligand and the complex were measured in water between 200 and 800 nm. The exact band positions are listed in Table II. The free ligand was yellow in solution; it presented four absorption maxima, in agreement with literature data [15,27], which were assigned as follows: $\pi \rightarrow \pi^*(\lambda_{\max} = 249, 302, 315\,\mathrm{nm})$; $n \rightarrow \pi^*(\lambda_{\max} = 428\,\mathrm{nm})$. The 428 nm band is most affected by coordination, since it is related to the N atom [15].

For $VO_2(H_2O)(Q)$ in solution, the three absorptions at higher energies (206, 227, 261 nm) are assigned to intraligand transitions, probably superimposed with the O→V charge transfer involving the double bonded oxo group [27,28]. The other two

TABLE II Electronic spectra of the ligand (QH) and its complex ($VO_2(H_2O)(Q)$) in aqueous solution (absorption maxima in nm)

QH	*$VO_2(H_2O)(Q)$*
249	206
302	227
315	261
428	363
	385

bands are related to ligand-to-metal charge transfer transitions involving the organic ligand. The higher energy band (363 nm) essentially involves the oxygen atom, whereas the other one (385 nm) may be related to the nitrogen atom [28].

Electrochemical Measurements

For final clarification of the complexation of QH with NH_4VO_3, voltammetric measurements were conducted. A square-wave voltammogram of QH solution in the absence of NH_4VO_3 produces an irreversible peak ($E_p = -1.446$ V) in 0.1 M NH_3/NH_4Cl buffer (pH 9.85) (Fig. 3). The polarographic curves of QH are complicated by the catalytic evolution of hydrogen [29]. On the other hand, NH_4VO_3 in the absence of QH gave an irreversible peak ($E_p = -1.550$ V) in 0.1 M NH_3/NH_4Cl buffer (pH 9.85) (Fig. 4). The peak at −1.550 V is attributed to the reduction of V(V) to V(IV) [18]. Also, it is clear that its peak potential depends on the pH of supporting electrolyte. Addition of NH_4VO_3 solution to a cell containing QH solution, resulted in a new peak at −0.700 V, more positive than those of both free NH_4VO_3 and QH (Fig. 5). This reversible peak can be attributed to the $NH_4[VO_2(Q)OH]$ complex in solution. Under the same experimental conditions, similar results have been also obtained by the aqueous solution of the solid $VO_2(H_2O)(Q)$ complex. The square-wave voltammogram of

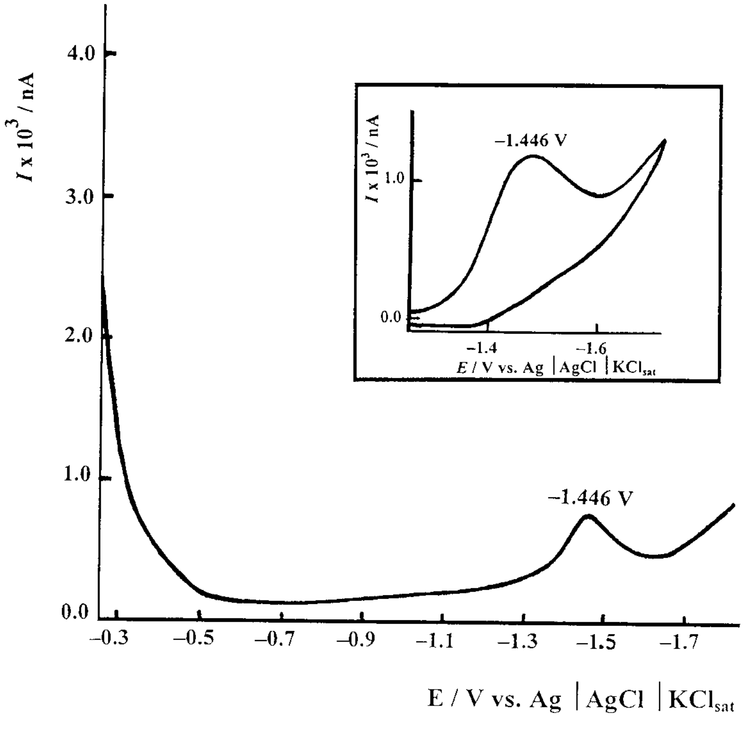


FIGURE 3 Square-wave voltammogram of 8-hydroxyquinoline (QH) solution. Inset: Cyclic voltammogram of QH solution. Experimental conditions: scan rate, 200 mV s^{-1} for square-wave voltammetry (500 mV s^{-1} for cyclic voltammetry); pulse height, 20 mV; scan increment, 2 mV; equilibrium time, 5 s; frequency, 100 Hz; drop size, medium.

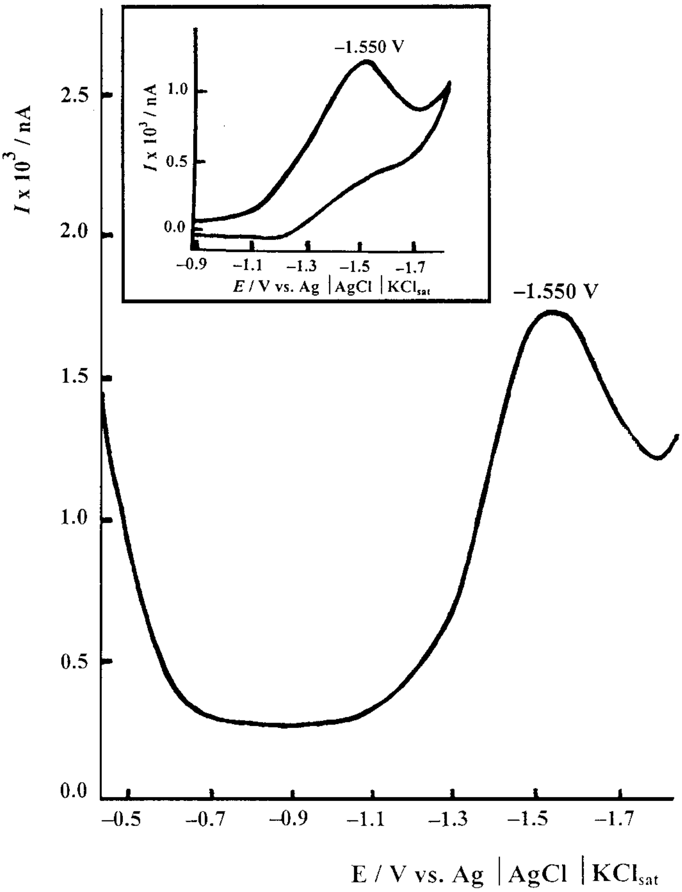


FIGURE 4 Square-wave voltammogram of NH_4VO_3 solution. Inset: Cyclic voltammogram of NH_4VO_3 solution. Other conditions as in Fig. 3.

dissolved $VO_2(H_2O)(Q)$ complex shows a new peak at −0.720 V (Fig. 5) while the peaks of the HVO_3 and QH (−1.386 and −1.526 V) appear on the voltammogram due to dissociation in water, showing only slightly different peak potential values. The peak at −0.720 V can be assigned to the $VO_2(H_2O)(Q)$ complex. Finally, it was observed that the peak potential of $VO_2(H_2O)(Q)$ complex is close to that of $NH_4[VO_2(Q)OH]$. It should be noted here that the reduction potentials of vanadium(V) complexes with QH or imidazole [18] exist at more positive potentials than free NH_4VO_3.

CONCLUSIONS

The experimental evidence for NH_4VO_3/QH allows the following conclusions:

1. Solid oxovanadium(V) complex monoaqua(8-hydroxyquinolinato)dioxovanadium(V), $VO_2(H_2O)(Q)$ ($Q = $ 8-hydroxyquinolinate) was prepared and characterized.

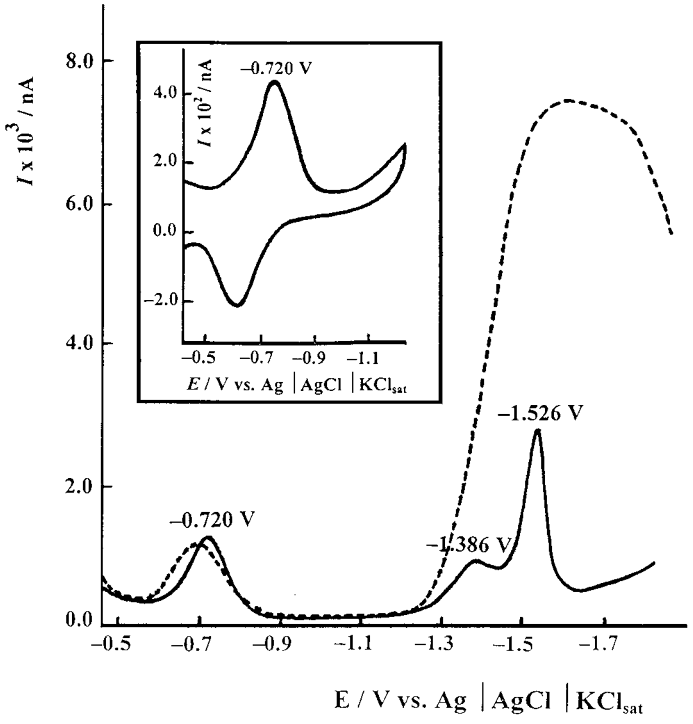


FIGURE 5 Square-wave voltammograms of NH_4VO_3 solution in the presence of 8-hydroxyquinoline (- - -); $VO_2(H_2O)(Q)$ complex solution (——). Inset: Cyclic voltammogram of $VO_2(H_2O)(Q)$ complex solution. −0.720 V, the reduction of $VO_2(H_2O)(Q)$ complex (——); −0.700 V, the reduction of $NH_4[VO_2(Q)OH]$ complex (- - -). Other conditions as in Fig. 3.

2. Oxygen and nitrogen atoms participate in bonding. The intramolecular structural changes expected from the deprotonation and coordination on the infrared spectrum are theoretically simulated.
3. A better understanding of vanadium metabolism in the higher forms of life requires better comprehension of vanadium transport in complex forms. The understanding of the complex formation between NH_4VO_3 and QH is another relevant aspect that is important for model studies related to vanadium biochemistry.

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