—Communication—

Adsorption of Vitamin K₃ on a Gold Electrode Studied by Specular Reflection and Absorption Spectroscopy

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1 INTRODUCTION

Considerable attention has been directed to the electrochemical behavior of quinone and related compounds¹⁾. Some of these, such as 2-methyl-1,4-naphthoquinone (VK₃), are substances of biological importance and act as mediators on electrodes. For clarification of their adsorption characteristics, especially the orientation of adsorbed species, on solid electrodes, Hubbard and his coworkers studied the adsorption by the thin layer electrochemical cell (TLC) method²⁻⁵⁾, Gui and Kuwana, by the long optical path length thin layer cell (LOPTLC) method^{6,7)} and Krauskopf and Wceckowski, by the radio-active labeling method⁸⁾. However, it is difficult to observe in situ adsorption-desorption behavior accompanying electron transfer reactions by these methods. The specular reflection method, however, is simple, easy to conduct and sensitive for dynamic monitoring an adsorption process onto an electrode surface.

In this study, the adsorption of VK₃ on a gold electrode in acid solution was studied by specular reflection and LOPTLC methods.

2 EXPERIMENTAL

2-methyl-1,4-naphthoquinone (VK₃, reagent grade from Wako Pure Chemical Co.) was used without further purification. The supporting electrolyte solution was 0.1 mol dm⁻³ HClO₄. Water purified to 17

MΩ·cm through NANO pure II (Barnstead Co.) was used for all experiments.

Instrumentation for specular reflection measurement was the same as that used previously^{9,10)}. The light beam with a wavelength of 500 nm and perpendicular polarization was directed to the working electrode surface at an incidence angle of 15°. A gold plate (20 mm × 30 mm, Tanaka Kikinzoku Kogyo Co., 99.99 %) served as the working electrode.

Instrumentation for spectroelectrochemical measurement using LOPTLC was essentially the same as that of Gui and Kuwana⁷⁾. The cell assembly was placed in the sample compartment of the spectrophotometer (UV-265, Shimazu Co.) and kept under a nitrogen atmosphere. A piece of the 1 mm thick polycrystalline gold plate (10 mm × 10 mm, Tanaka Kikinzoku Kogyo Co., 99.99 %) was used as the working electrode. The geometric surface area of the electrode was 0.6 cm². The volume of LOPTLC, as determined from voltammogram of K₃Fe(CN)₆ in 0.4 mol dm⁻³, was 7.6 μl.

The gold surface of the working electrode was polished with 0.6 μm alumina using a polishing cloth (Microcloth, Buehler Ltd.), and cleaned in an ultrasonic bath with water immediately before each measurement. The counter electrode was a Pt wire or gold plate. The reference electrode was an Ag/AgCl electrode in saturated KCl solution. Pure argon gas was bubbled through the electrolyte solution to remove dissolved oxygen before measurement. All measurements were made at 26 ± 1°C.

3 RESULTS AND DISCUSSION

3.1 Voltammetric measurement

Figure 1 shows cyclic voltammograms

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of $0.1 \text{ mol dm}^{-3} \text{ VK}_3$ at a gold electrode obtained after the initial potential, E_i , had been maintained constant for 5 min. One pair of redox peaks at about 0.15 V , corresponding to the quinone/hydroquinone redox reaction of VK_3 in the solution, and two small humps, one above the other, around 0.25 V was seen on the voltammograms. The electroreduction of VK_3 occurs through the $2e, 2\text{H}^+$ reaction to give the hydroquinone (HQ) form.¹⁾ According to the theoretical study of Wopschall and Shain¹¹⁾, if the product is strongly adsorbed, a separate adsorption peak should occur prior to the peak of charge transfer on the voltammogram. In this study, when E_i was 0.3 or 0.2 V , the current of the first anodic scan was the same as that of the second, and reduction and oxidation peak heights were almost identical. The current of the first anodic scan was larger than that of the second when E_i was -0.1 or 0 V . It was considered that HQ would be strongly adsorbed on the gold electrode and accumulate on the gold surface during electrolysis at E_i .

3.2 Specular reflection measurement

Voltammograms and relative reflectivity-potential ($R/\text{Ro}-E$) curves of the gold electrode measured simultaneously in 0.1

Fig.1 Cyclic voltammograms for $0.1 \text{ mmol dm}^{-3} \text{ VK}_3$ at a gold electrode in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$. E_i : initial potential at which the electrolysis was made for 5 min before potential scanning. Potential scan rate: $100 \text{ mV} \cdot \text{s}^{-1}$.

$\text{mol dm}^{-3} \text{ HClO}_4$ containing different concentrations of VK_3 are shown in Fig. 2. Gold oxide formation¹²⁾ started at about 1.1 V on the anodic scan, and correspondingly R/Ro began to decrease steeply. During the reverse scan, R/Ro increased with reduction of the oxide layer. The concentration of VK_3 was too low to detect redox peaks near 0.1 V . Two small humps appeared at about 0.25 V . When no VK_3 was present in the electrolyte solution, no significant change was observed on the $R/\text{Ro}-E$ curve at the negative potential region. When VK_3 was present, R/Ro decreased and hysteresis observed in the potential region became more negative than 0.2 V (curves b-e in Fig. 2). R/Ro at 0 V decreased with increase in the concentration of VK_3 , but became saturated at a concentration exceeding $0.01 \text{ mol dm}^{-3} \text{ VK}_3$. The hysteresis was most evident at an intermediate concentration. Such decrease, which has been found for adsorption of organic compounds¹⁰⁾, indicates that VK_3 and/or HQ is adsorbed on the gold electrode. The effect of the scan rate on the $R/\text{Ro}-E$ curve is shown in Fig. 3. When the potential scan rate was slow, decrease in R/Ro at constant concentration was greater. The rate of adsorption would thus appear to be slow enough to compete with the scan rate, and consequently, adsorption rate may be controlled by the

Fig.2 Current-potential (left) and reflectivity-potential (right) curves of gold in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ containing VK_3 at $30 \text{ mV} \cdot \text{s}^{-1}$. Concentration of VK_3 : (a)0, (b)4.3, (c)8.3, (d)12, (e)15 $\mu\text{mol dm}^{-3}$. E_i : 0.5 V vs. Ag/AgCl .

Fig. 3 Reflectivity-potential curves of Au in 0.1 mol dm^{-3} HClO_4 containing VK_3 at 10, 30 and 100 $\text{mV} \cdot \text{s}^{-1}$. Concentration of VK_3 : (a) 0, (b) 4.3, (c) 8.3, (d) 12, (e) 15 $\mu\text{mol dm}^{-3}$. E_i : 0.5 V vs. Ag/AgCl .

slow diffusion of VK_3 .

The time dependence of R/R_0 was measured by the potential step method using 15 $\mu\text{mol dm}^{-3}$ VK_3 . The potential was first set at 0.7 V where there was no adsorption of VK_3 or oxidation of gold and then stepped to a more negative potential, E_{ad} . R/R_0 vs. time curve was recorded until R/R_0 became constant. The procedure was also applied to the supporting electrolyte solution. The difference in R/R_0 at its equilibrium value with and without VK_3 was determined in terms of change in R/R_0 , $|\Delta R/R_0|$. The $|\Delta R/R_0|$ -E

Fig. 4 (A) Potential dependence of the reflectivity change obtained in 0.1 mol dm^{-3} HClO_4 solution containing 15 $\mu\text{mol dm}^{-3}$ VK_3 , (B) R/R_0 vs. time relation in the potential step method. Concentration of VK_3 : (---) 0, (—) 15 $\mu\text{mol dm}^{-3}$.

curve is shown in Fig. 4. When surface excess of adsorbed species is less than that needed for monolayer coverage and optical property of adsorbed layer is uniform, reflectivity change is proportional to the surface excess¹⁰. VK_3 and/or HQ was adsorbed at negative potentials than 0.3 V, and the adsorption maximum was -0.1 V. The cathodic scan in Fig. 1 shows reduction of VK_3 to have started at about 0.3 V. The adsorbed species on the gold electrode surface was thus possibly HQ.

Fig. 5 Absorption spectra for 20 $\mu\text{mol dm}^{-3}$ VK in 0.1 mol dm^{-3} HClO_4 . Applied potential: (a) 0.40, (b) 0.14, (c) 0.12, (d) 0.10, and (e) 0 V vs. Ag/AgCl .

Fig. 6 Absorption spectra for 20 $\mu\text{mol dm}^{-3}$ VK in 0.1 mol dm^{-3} HClO_4 at 0.1 V and 0.2 V vs. Ag/AgCl . 1st, 2nd and 3rd were obtained for the first, second and third fillings of VK_3 solution in LOPTLC, respectively.

3.3 Spectroelectrochemical measurement using LOPTLC

Figure 5 shows absorption spectra for $20 \mu\text{mol dm}^{-3}$ VK_3 in 0.1 mol dm^{-3} HClO_4 various applied potentials. The absorption maximum of VK_3 was at 250 nm and that of its reduced form, HQ, was 235 nm. Isosbestic points of the spectra of VK_3 and HQ were 246 and 280 nm. From a Nernst plot, a n value of 2 is calculated from the slope and a value of the formal redox potential, taken from the y intercept, is 0.12 V. Figure 6 shows spectra obtained in a multifilling experiment using LOPTLC. The VK_3 solution was injected into LOPTLC, the absorption spectrum at a given potential for the first filling was recorded, and then LOPTLC was evacuated. LOPTLC was refilled with VK_3 solution to obtain the spectrum following the second filling. Spectra for the second and third fillings were the same. Absorbance difference, ΔA , for the first and second fillings corresponded to the adsorption amounts of VK_3 and/or HQ on the gold electrode surface, even during evacuation (less than 30 mTorr). ΔA at 246 nm was plotted against applied potential (Fig. 7). The adsorption of HQ was clearly observed to occur at potentials more negative than 0.3 V, as also indicated by specular reflection measurement.

Using Lambert-Beers' law, surface excess was calculated from ΔA at -0.1 V as approximately $6 \times 10^{-11} \text{ mol cm}^{-2}$, which corresponds to the submonolayer of HQ.

Fig. 7 Potential dependence of change in absorbance due to VK_3 adsorption.

4 CONCLUSIONS

The reduced form VK_3 is adsorbed on a gold electrode at more negative potential than 0.3 V, as determined by voltammetry, and specular reflection, and spectroelectrochemical measurement using LOPTLC. The specular reflection method provides information concerning dynamic adsorption-desorption behavior of VK_3 during potential scanning. This facilitates distinction between faradaic reaction and adsorption of VK_3 on the voltammograms.

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