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Long Optical Path Length Thin-Layer Spectrochemistry Potential Dependence and Quantitation of 1H-Purine-6-amine Adsorbed on Gold

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The potential dependence of 1H-Purine-6-amine(=adenine) adsorption on a Au electrode in phosphate buffer(pH 7) and the surface excess were studied using a long optical path length thin-layer cell. The maximum adsorption of adenine occurred at 0.3 V vs. Ag/AgCl. In order to determine surface excess, a single filling experiment was advantageous compared to the conventional multiple-filling procedure.

Recently, a long optical path length thin-layer cell (LOPTLC) has been developed, which allows the study of the adsorption of various electrochemically active and inactive species.[1-3] To determine surface excess of adsorbed molecules on an electrode surface experimentally, a vacuum degas/filling prodcedure with multiple fillings of electrolyte solution containing a test compound into LOPTLC, i.e.,conventional multiple filling procedure, was needed.[2,3] This procedure could cause orientational change of adsorbed molecules and/or desorption of the molecules from the surface since the circuit was open-circuited before filling. The desorption would be a serious problem of determination of surface excess for a reversible adsorption system. A single filling of the working solution during an experiment is preferable to preserve the integrity of the adsorbed species. This paper aims to show the advantage of the single filling experiment and reports the extent and potential dependence of 1H-Purine-6-amine (=adenine) adsorption on a Au electrode using the LOPTLC.

The spectroelectrochemical system, which consisted of a Kel-F LOPTLC and a solution filling apparatus, was similar to that described by Gui and Kuwana.[2] The cell was placed in a box having two optical windows. It was kept under N_2 atmosphere and placed in the sample compartment of a Perkin Elmer λ4B spectrophotometer. A piece of 0.1 mm-thick polycrystalline Au foil(Tanaka Kikinzoku Kogyo K.K., 99.99 %) bonded with epoxy to a piece of acryl plexiglas was used as the working electrode. The light travelled through the electrolyte solution in the cell and in parallel to the working electrode surface. The Au surface was polished with 0.3 μm α-alumina slurry on a polishing cloth and cleaned in an ultrasonic bath with Nanopure water. The auxiliary and reference electrodes were a Pt wire and a Ag/AgCl electrode, respectively. The geometric surface area of the Au foil was 0.9 cm^2. The LOPTLC volume(v),determined from the voltammogram of $K_3Fe(CN)_6$ in 0.5 mol dm^{-3}

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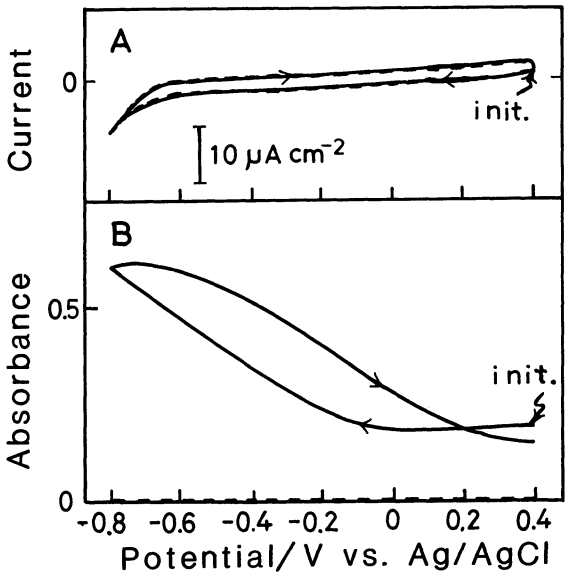

Fig. 1.

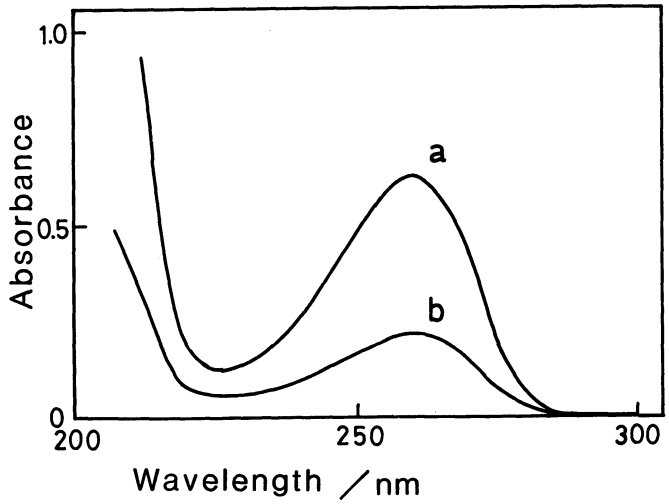

Fig. 2.

Fig. 1. A) Current-potential and B) absorbance-potential curves for (---) 0 and (——) 5.3×10^{-5} mol dm^{-3} adenine in 0.1 mol dm^{-3} phosphate buffer (pH 7) at a Au electrode. Monitoring wavelength: 260 nm. Scan rate: 2 mV s^{-1}.

Fig. 2. Absorbance spectra of 5.3×10^{-5} mol dm^{-3} adenine in 0.1 mol dm^{-3} phosphate buffer (pH7). Applied potential: (a) -0.7 V, (b) 0.4 V vs. Ag/AgCl. Wavelength scan rate: 120 nm min^{-1}.

KCl, was 30.8 μl. The supproting electrolyte solution was 0.1 mol dm^{-3} phosphate buffer (pH 7) prepared with Na_2HPO_4 and NaH_2PO_4 (MCB Manufacturing Chemists Inc.). Adenine obtained from Sigma Chemicals was used without further purification.

Prior to the first injection of the working solution, i.e., 5.3×10^{-5} mol dm^{-3} adenine in 0.1 mol dm^{-3}, in the LOPTLC, the cell was filled with the supporting electrolyte solution and then emptied by evacuation. Current-potential and absorbance-potential curves of adenine were measured simultaneously, as the electrode potential was swept from 0.4 to -0.8 V and then returned to the initial potential at a scan rate of 2 mV s^{-1}. The curves are shown in Fig. 1. No redox peak of adenine suggests that adenine is electroinactive at these potentials. When the potential was scanned negatively, the absorbance as monitored at 260 nm, the maximum absorbance of adenine, increased. On the other hand, the absorbance decreased when the potential was increased. The decrease in absorbance indicates a loss of the solution adenine due to its adsorption onto the Au surface. The hysteresis, observed on the absorbance-potential curve (Fig. 1 B solid line), suggests adenine adsorption controlled by slow diffusion of adenine.

Figure 2 shows the absorbance versus wavelength curves at the applied potentials of -0.7 and 0.4 V. The spectra were measured after waiting for 2.5 min from the time the potential was applied. The absorbance difference at 260 nm between -0.7 and 0.4 V corresponds to the amount of adenine adsorbed at 0.4 V.

When step forms(Fig. 3 B) were applied in potential step experiments, absorbance versus time response were monitored at 260 nm (Fig. 3 A). The absorbance at the positive potentials, such as 0.3 and 0.5 V, is markedly lower than the absorb-

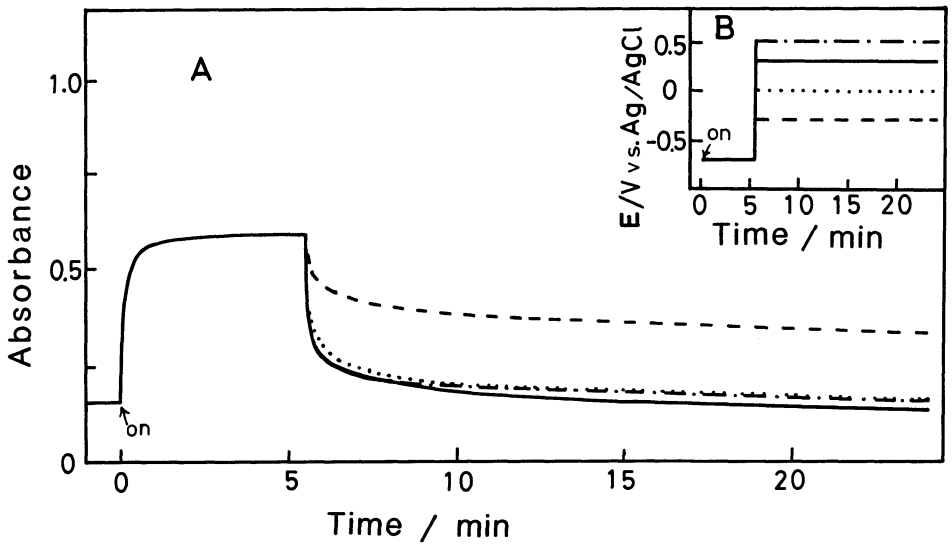

Fig. 3. A. Absorbance versus time responce monitored at 260 nm for 5.3×10^{-5} mol dm^{-3} adenine in 0.1 mol dm^{-3} phosphate buffer (pH 7) during electrolysis of which potential step waveforms are shown in B.

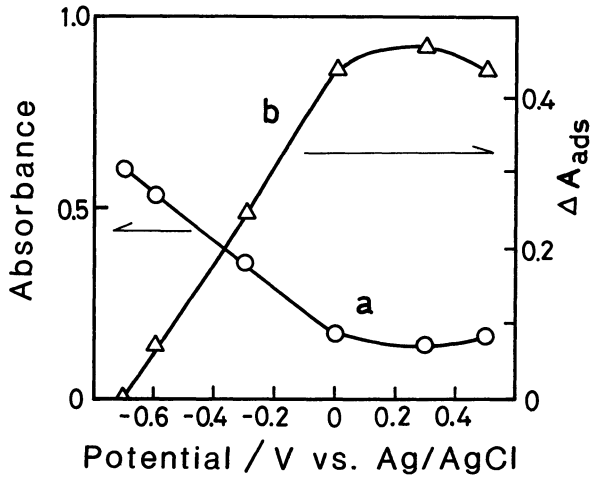

Fig. 4. Potential dependence of (a) absorbance at steady state of adsorption and (b) change in absorbance due to adenine adsorption.

ance at -0.7 V. The steady state value of adsorption, obtained from the data shown in Fig. 3 A, was plotted against the electrode potential in Fig. 4. It appears from the data that the maximum adsorption of adenine occurs at about 0.2 to 0.3 V.

Assuming that adsorption is absent or minimal at -0.7 V, the change in optical absorbance, due to adenine adsorption, is shown in Fig. 4, curve b. The LOPTLC data for adenine adsorption on a Au electrode show similar potential dependence of absorbance change to a previous one by specular reflection (Fig. 2 in Ref. 4). However, the initial potential as well as the potentials where maxima occur are slightly different. Such differences probably reflect differing experimental condition, such as supporting electrolytes and the thin layer and bulk cells. Further experiments are underway to clearify such differences.

In order to determine monolayer amounts of adenine adsorbed on the Au elec-

trode, the absorbance change due to saturated adsorption, ΔA_{ads}, of adenine on the Au electrode was obtained from the data in Fig.4 curve b at 0.3 V. The value of ΔA_{ads} was 0.44. The experimental surface excess, Γ_{expt} for adenine on Au can be determined quantitatively from Eq. 1.

$$\Gamma_{expt} = v \Delta A_{ads} / \varepsilon b S r \quad (1)$$

where ε is the molar absorptivity of adenine, b the apprent optical path length, S the apparent electrode surface area and r roughness factor of Au electrode surface. b is given by Eq. 2.

$$b = A_{des} / \varepsilon C \quad (2)$$

where A_{des} is absorbance of the adenine solution without adsorption, and C, the adenine concentration. Using Eq. 1, Γ_{expt} and σ, the surface area occupied by one adsorbed adenine molecule, were calculated to be approximately 4.5×10^{-10} mol cm^{-2} and 37 $\mathring{A}^2$,respectively, assuming an r value of 3.[5] The σ value suggests that adenine is adsorbed in a flat orientation.

After a single filling, the results for a second filling of the working solution was also evaluated. A potential of -0.7 V was applied to the electrode after which the LOPTLC was evacuated and the curcuit opened. The cell was then throughly washed with supporting electrolyte solution and refilled with the working solution. Absorbance-potential curves and absorbance spectra for the second filling were measured. The absorbance difference between the first and second filling was evaluated according to the procedure reported in Ref. 3. The difference in the absorbance between the single filling and any successive filling experiment was negligibly small. The reason for the absorbance being nearly identical was due to the desorption of adenine from the surface of Au during the washing of the cell. The ΔA_{ads} value for the second filling which was obtained in the same way described above for the first filling was 0.45, which was in agreement with the ΔA_{ads} for the single filling experiment. The results indicate that the single filling experiment suffices and that the conventional successive filling experiment is not applicable to determine surface excess, especially for cases of reversible adsorption such as found for adenine.

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4) K. Takamura, A. Mori, and F. Watanabe, J. Electroanal. Chem., 102, 109 (1979).
5) The roughness factor was calculated using the geometric and the real surface areas. The latter was obtained by measuring the charge corresponding to the formation of chemisorbed oxygen on the Au surface during anodization in 0.1 mol dm^{-3} $HClO_4$.

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