The effect of Cl⁻ ions for the adsorption process of heptyl viologen cation radicals on ITO electrodes

Yusuke Ayato[a], Takashi Itahashi[b], Akiko Takatsu[c], Kenji Kato[c] and Naoki Matsuda[a]*

[a]* On-site Sensing and Diagnosis Research Laboratory, AIST (807-1, Shuku, Tosu, Saga 841-0052, Japan)
[b] Mechanical and Electrical Systems Engineering Advanced Course, Kurume National College of Technology (1-1-1, Komorino, Kurume, Fukuoka 830-8555, Japan)
[c] National Metrology Institute of Japan, AIST (Central 3, 1-1-1, Umezono, Tsukuba, 305-8563, Japan)
Fax: 81-942-81-3690, e-mail: naoki.matsuda@aist.go.jp

In situ observation of absorption spectra of heptil viologen cation radical ($HV^{+\cdot}$) was performed by slab optical waveguide (SOWG) spectroscopy utilizing indium-tin-oxide (ITO) electrodes. Synchronizing with electrochemical techniques, we observed the adsorption process of $HV^{+\cdot}$ on the ITO electrode. In this study, we carried out the ITO-SOWG observations using KCl as a supporting electrolyte instead of KBr to investigate the effect of counter anions. A few specific absorption bands, which indicated $HV^{+\cdot}$ existed as both monomer and dimer on ITO electrode surface within a monolayer deposition, were observed in UV-visible region. The change in the intensity and the peak position of the absorption spectra from adsorption species of $HV^{+\cdot}$ were correlated with the electrode potential.
Key words: slab optical waveguide (SOWG) spectroscopy, heptil viologen, indium-tin-oxide (ITO) electrode, in situ, absorption phenomena,

1. INTRODUCTION

We have been studying the adsorption process and adsorbed states of various molecules on solid/liquid interfaces by slab optical waveguide (SOWG) spectroscopy [1-7]. Our recent improvement of the SOWG instrument based on the light incidence method utilizing a glycerol drop has enabled us to observe time dependent adsorption behavior [8-11], and to obtain the standard Gibbs free energy (Δ G) value due to adsorption process of proteins on solid/liquid interfaces. The development of an indium-tin-oxide (ITO) coated SOWG (ITO-SOWG) has also allowed us to carry out the spectroelectrochemical observation of adsorbed molecules accompanied by redox reaction at electrochemical interfaces [12-14].

N,N'-Disubstituted-4,4'-bipyridinium salts (viologens) were first studied for electrochromic devices (ECDs) in 1970s and have been attracted much attention for the application owing to their high transmittance changes and fast responses [15-17]. Recent studies have been performed for applications of viologens to herbicides, electron mediators and catalysts [18-20]. 1,1'-Diheptyl-4,4'-bipyridinium (heptylviologen ; HV) is usually studied for electrochromic applications because its one-electron reduction of the dication HV^{2+} to the mono-cation radical salt $HV^{+\cdot}$ in aqueous solutions can form a precipitate with violet color on electrode surfaces [21-30].

HV^{2+} has been known to receive two-step one-electron reactions resulting in the formation of $HV^{+\cdot}$ and HV as follows [29, 33-38].

$$HV^{2+} + e^- \rightarrow HV^{+\cdot} \quad (1)$$
$$HV^{+\cdot} + e^- \rightarrow HV \quad (2)$$
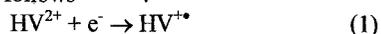
The first reduction step is reversible reaction and immediately follows chemical reaction with proper counter anions (X⁻), which produced a cation radical salt film on electrodes with strong violet color. The second reduction step is less reversible reaction and forms a solid deposit with yellow color on the electrode surface. In the first reduction step, Jasinski reported that the precipitates film of $HV^{+\cdot}X^-$ has amorphous structure in the primary stage of the film formation process, then, the phase gently and unsteadily changes in successive reactions, and the aging process follows [32]. Kawata and co-workers demonstrated the spectroscopic characterization of viologen derivatives with different counter anions [33].

Although a number of researchers have demonstrated for the reduction process of the first reduction step of HV^{2+}, they mainly observed the adsorption states of $HV^{+\cdot}$ in multilayer deposition on the electrode surface. In addition, they usually discussed the behavior of the absorption bands at around 550 nm, so little reports included the results of the absorption bands at around 400 nm. The information of the absorption band only at around 550 nm is insufficient to comprehend the potential dependent adsorption process of $HV^{+\cdot}$ on the electrode surface, because the absorption bands of $HV^{+\cdot}$ monomer and dimer are observed in one broad band consisting of a few absorption bands, which have been difficult to give an accurate assignment or/and to investigate the relationship with the absorption bands at around 400 nm. On the other hand, the absorption bands of the monomer and dimer have been sharply and separately observed at 400 and 375 nm[34]. Thus, the peak position changes, as well as the intensity changes, of the absorption bands of monomer and dimer can be discussed separately by employing the absorption bands at around 400 nm.

We have been investigated the initial adsorption

process of HV$^{+\bullet}$ molecules on the ITO electrodes by employing the absorption bands at around 400 nm in KBr aqueous solution[34]. However it has not been investigated about the effects of anion species. The main aim of present study is to discuss the absorption behavior of HV$^{+\bullet}$ monomer and dimer, especially in a monolayer deposition, separately by employing the absorption bands at around 400 nm. And we will note and investigate the potential dependent adsorption behavior of HV$^{+\bullet}$ molecules by the spectroelectrochemical SOWG using KCl as the supporting electrolyte instead of KBr.

2. EXPERIMENTS

2.1 Materials

Heptylviologen dibromide (HVBr$_2$) purchased from Tokyo Kasei Industry Co., Ltd. was used as received without further purification. Potassium chloride (KCl) used as the supporting electrolyte was guaranteed grade and purchased from Kanto Chemical Co., Inc. The sample solutions were prepared using Milli-Q water (resistivity > 18 MΩcm). The concentrations of HVBr$_2$ were adjusted to 50 μM and that of KCl was 0.3 M.

2.2 Spectroelectrochemical SOWG systems

The experimental details of SOWG have been given elsewhere [11, 13, 31]. A 150-W xenon lamp (System Instruments Co., Ltd., Japan) was used as the light source, and the light was guided by an optical fiber. The SOWG spectra were detected using a CCD detector with monochrometer (PMA-11, Hamamatsu Photonics, Japan). The minimum time resolution of the CCD detector is 20 ms. The ITO film was formed by vapor deposition on a glass plate (0.05 mm × 20 mm × 50 mm, Matsunami Glass Industry, Ltd., Japan) giving a thickness of approximately 20 nm. ITO-SOWG plates were cleaned by soaking in ethanol for 1 h and then rinsed extensively with Milli-Q water. The spectroelectrochemical surface area of ITO-SOWG working electrode covered with sample solution was approximately 1.3 cm^2. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All the potentials in this paper are quoted against Ag/AgCl. The electrode potential was controlled with a potentiostat (EG&G Princeton Applied Research, Model 273) synchronizing with the spectrometer.

2.3 Measurements

The resulting SOWG spectra are shown in terms of absorbance units defined as follows:

$$A = -\log(I_S/I_R) \qquad (1)$$

Where I_S/I_R represent the relative change in the intensity and I_S and I_R are the sample and reference intensities, respectively. All reference spectra on the SOWG analysis was observed at -200 mV in this study.

In situ spectroelectrochemical SOWG observations were carried out with synchronized with cyclic voltammetric measurements. The electrode potential was swept to the cathodic direction from -200 to -600 mV, and back to -200 mV at a sweep rate of 20 mV s^{-1}. The time width of each spectrum was 300 ms and SOWG spectra were obtained continuously.

A potential step method was also applied to in situ SOWG measurements. Before the sample measurements, the electrode potential was held at -200 mV for 30 s and the reference spectrum was measured with the exposure time of 300 ms. The resulting spectra were measured at -600 mV for 60 s with the exposure time of 300 ms.

3. RESULTS AND DISCUSSION

3.1 In situ spectroelectrochemical observations by SOWG spectroscopy synchronizing with cyclic voltammogram measurements

The first one-electron reduction of HV^{2+} giving the radical salt is known to a simple, soluble and reversible reaction. Since the electron transfer reaction is fast, it is effectively diffusion controlled at enough large current densities [39]. The surface coverage of the electrode can be estimated from the oxidation current of the cyclic voltammograms. The charge density of 10 μC cm^{-2} was obtained from the first cycle of the cyclic voltammograms measured from initial potential of -600 mV with sweep rate of 100 mV s^{-1} after the electrode potential was held at -600 mV for 60 s in 50 μM HV containing solution. The charge density for the reduction of HV$^{+\bullet}$ of monolayer coverage, assuming one molecule occupies 0.5 or 1 nm^2 [12], is about 32 or 16 μCcm^{-2}. The electrode surface should be covered within monolayer coverage in all spectroelectrochemical SOWG observations.

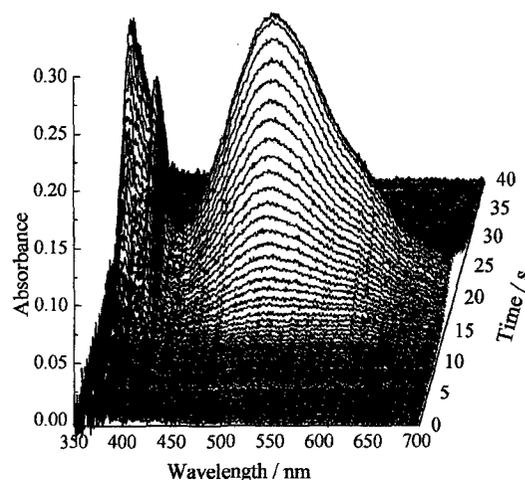Fig. 1 Time-resolved SOWG spectra synchronized with cyclic voltammetric measurements in 0.3 M KCl solution containing 50 mM HV. Sweep rate: 20 mV s^{-1}.

Fig. 1 shows SOWG absorption spectra obtained by synchronizing with cyclic voltammetric measurements using 0.3 M KCl aqueous solution containing 50 μM HV^{2+}. It has been known that several absorption bands assigned to HV$^{+\bullet}$ species are observed in UV-visible region by using a supporting electrolyte of 0.3 M KBr [34]. As shown in the Fig. 1, three positive-going bands were observed at around 380, 400 and 530 nm. The absorption band at around 380 nm, which was assigned to the dimer of HV$^{+\bullet}$ [34], appeared in UV-visible region below about -450 mV and another absorption at around

400 nm, which was assigned to a monomer of $HV^{+\bullet}$ [34], seems to arise from more positive electrode potential. The absorption band at around 530 nm appeared as a broad-band below about -400 mV, which was assigned to dimer of $HV^{+\bullet}$ [40]. The spectrum at 20 s was very similar to that observed by Kawata and co-workers[33].
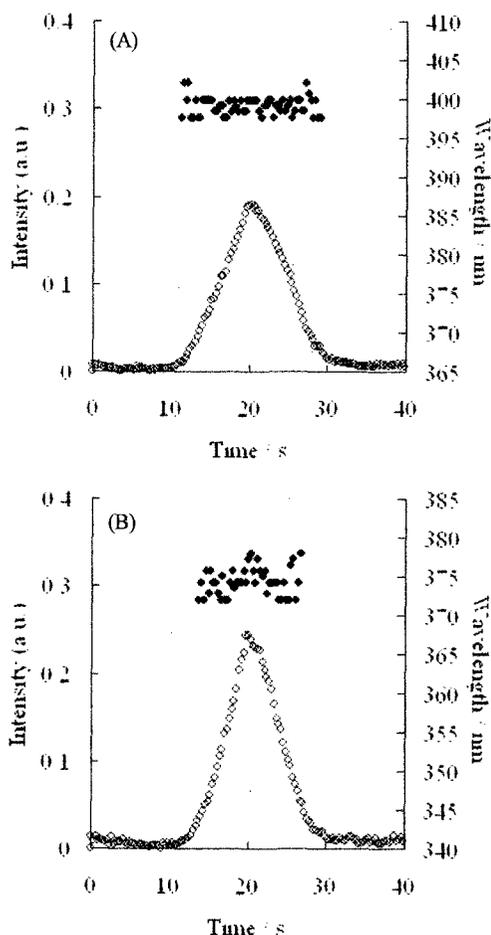

Fig. 2 Change in the intensity (o) and peak position (●) at around 400 (A) and 380 (B) nm obtained from time-resolved SOWG analysis synchronized with cyclic voltammetric measurements in 0.3 M KCl solution containing 50 μM HV. Sweep rate: 20 mV s^{-1}.

Fig. 2 shows the potential dependent change in the intensity and peak position of the absorption bands at around 380 and 400 nm obtained by SOWG data synchronizing with cyclic voltammetric measurements. The intensities of adsorption bands at around 380 and 400 nm started to increase monotonically with decreasing the electrode potential at around 11 and 14 s passed (at -420 and -480 mV). Contrary to the results for the cathodic polarization, the intensities of them decreased with increasing the electrode potential and disappeared completely at around 30 and 27 s (- 400 and -460 mV) in the anodic polarization. Thus, it was confirmed that the dimer of $HV^{+\bullet}$ adsorbed at lower electrode potential region than the monomer of $HV^{+\bullet}$ on the electrode surface.

In the potential dependent peak position change, the band at around 400 nm showed no peak shift of absorption band under this experimental condition, as

shown in Fig. 2(A). This result was very similar to that observed in our former study [34]. On the other hand, the peak position at around 380 nm has been known to show the peak shifts depended on the electrode potential [34]. A clear peak shift of the absorption band at around 380 nm was not observed.

3.2 In situ SOWG measurements using potential step methods

To investigate whether the absorption band at around 380 nm shows the peak shift or not in 0.3 M KCl aqueous solution containing 50 μM HV^{2+}, we carried out time-resolved SOWG observations by synchronizing with potential step measurements. Fig. 3 shows the change in the intensity and peak position of absorption band at around 380 nm obtained by SOWG analysis synchronizing with potential step measurements from −0.2 to −0.6 V for 60 s. The intensity of the absorption band at around 380 nm dynamically increased from 0.3 to 10 s and monotonically increased after 10 s with the passage of time. In potential step measurements, the peak position of the absorption band at around 380 nm exhibited a red shift from around 375 to 385 nm from 0.3 to 60 s. These results good correspond to those obtained in our former study [34], which using 0.3 M KBr aqueous solution containing 100 μM HV^{2+}. Further investigation was needed, however, the change in the peak position of the absorption band at around 380 nm probably depended on the concentration of HV or/and proper counter anions as well as the electrode potential.
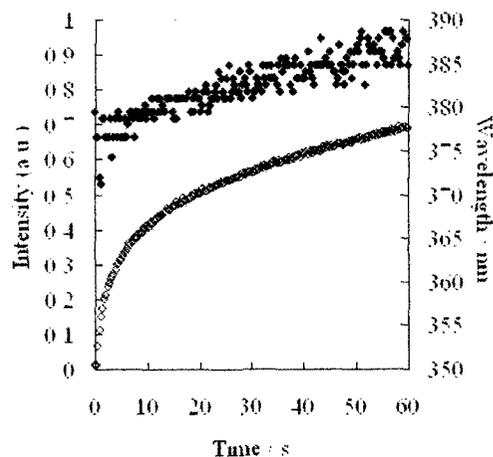
Consequently, very successful observation was made

Fig. 3 Change in the intensity (o) and peak position (●) at around 380 nm obtained from time-resolved SOWG analysis synchronized with potential step measurements in 0.3 M KCl solution containing 50 μM HV.

for the heptilviologen cation radicals on the electrode surface by using spectroelectrochemical SOWG. The adsorption behavior of $HV^{+\bullet}$ could be clearly characterized and distinguished both monomer and dimer by investigating the absorption bands at around 400 nm.

This technique we have presented allowed the very successful observation of both the spectroscopic and electrochemical properties of molecules on surface. Highly sensitive in situ absorption spectra yield essential

molecular information for coverage of monolayer or a few layers.

4. CONCLUSION

The potential dependent structural change was successfully observed by the time-resolved SOWG spectra. It was found from SOWG studies that at least two different species of $HV^{+\bullet}$ due to monomer and dimer adsorbed on the electrode surface. The dimer of $HV^{+\bullet}$ was adsorbed more negative electrode potential than the monomer of $HV^{+\bullet}$ on the ITO electrode surfaces. These monomeric and dimeric $HV^{+\bullet}$ molecules co-adsorbed on the ITO electrode surface in all applied negative electrode potential region.

We presented an application of the SOWG spectroscopy which can easily and directly yield in situ molecular information on solid/liquid interfaces. This powerful technique will disclose the configurations of many other molecules adsorbed on the electrochemical interfaces.

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