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In Situ Electrochemical Quartz Crystal Microbalance Studies of Self-assembled N-Docosyl-N'-Methyl Viologen Films at Gold Electrodes

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Although we[1] and others[2-4] have investigated the electrochemical behaviors of molecular self-assemblies of asymmetric surfactant viologens, no work has been performed regarding the dynamic movements of ions (and solvents) during the charge transfer process of self-assembled viologen films[5] at electrode surfaces. In this communication, we wish to describe some preliminary results of the first *in situ* electrochemical quartz crystal microbalance (EQCM) studies on the first redox reaction of such films at gold electrode surfaces in aqueous solutions.

The EQCM instrumentation and the experimental procedures were essentially similar to those reported previously[6]. AT cut quartz crystals of 13 mm diameter (Toyo Kurafuto 5 MHz) were coated on both faces with Au (*ca.* 300 nm) by vacuum deposition using a Cr adhesion layer (2 nm). A Pt wire and a sodium chloride saturated silver-silver chloride were used as the counter and reference electrodes, respectively. An asymmetric keyhole electrode arrangement was used, in which the piezoelectrically active area (0.28 cm²) was smaller than the area of the working electrode face (0.64 cm²), to mitigate the effect of compressional stress. The electrochemically active area of the working electrode surface was 0.50 cm². Sufficient time was allowed to elapse for adsorption equilibrium to be achieved prior to EQCM measurements, as judged by absence of further changes in the voltammetric response.

Figure 1 shows the EQCM data for a typical scan across the first redox wave of N-docosyl-N'-methyl viologen ($C_{22}VC_1$) at a solution concentration of 10 μM in the presence of 0.1 M sodium para-toluenesulfonate (TS). The surface cover-
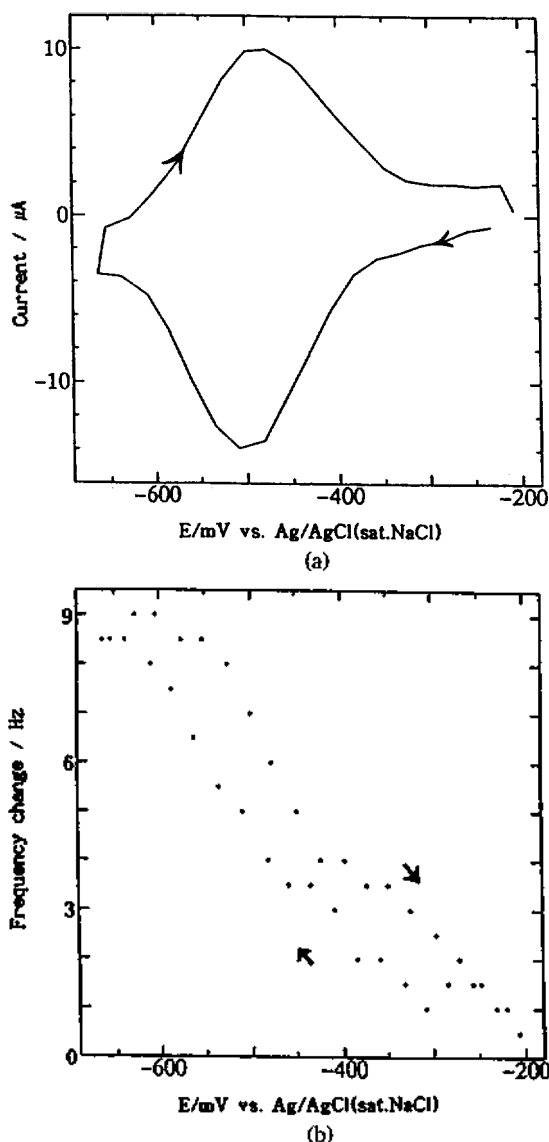

Figure 1. EQCM scan for 10 μM $C_{22}VC_1$ in 0.1 M NaTS. (a) Cyclic voltammogram (100 mV/s) and (b) EQCM frequency response for (a).

age at this concentration of $C_{22}VC_1$, 3.2×10^{-10} mol/cm², obtained from the integration of the voltammogram approximately corresponds to a full monolayer coverage of viologen sites with the anions employed. The resonance frequency of composite resonator increased concomitantly with electroreduction of the viologen dications to monocations at electrode surfaces. From the data in the Figure, a total frequency change of 8.0 (± 0.5) Hz is observed for the redox process, which is equivalent to a reversible mass change at the electrode surface of 441 g/mol of electrons by using the Sauerbrey equation, $\Delta f = -C_f \Delta m$, with a proportionality constant (C_f) of 56.6 Hz·cm²/μg[6,7]. Satisfactory agreement of the half mass change and half charge potentials (-0.5 V *vs* Ag/AgCl) indicates that the mass transport and charge transfer processes are simultaneous. Therefore the data imply that one anion and *ca.* 10 molecules of H_2O simultaneously exit and enter, assuming the unidirectional transport with permselectivity to anions, the viologen monolayer during reduction and

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oxidation, respectively. Experiments in D_2O showed similar results. Movements of a rather large number of solvent molecules with the redox process may indicate the complex nature of monolayer self-assembly/electrolyte interfacial region. More water molecules might be expected to be trapped in the self-assembly/solution interface. Recent EQCM data observed at electrodes modified with osmium polymer complexes also show that a number of water accompany the redox reaction of osmium (III/II) sites.[8] The same type of EQCM experiments with the anions of ClO_4^- and Cl^- were performed to find the variation of the number of solvent molecules moving simultaneously with the first redox process of viologen. Equivalent molar mass (M_{eq}) was determined to be 240 and 598 for perchlorates and chlorides, respectively. Because the molar masses of the anions are 99.5 (ClO_4^-) and 35.5 (Cl^-), M_{eq} determined would imply the simultaneous movements of water molecules (ca. 8 H_2O for ClO_4^- and ca. 31 H_2O for Cl^-) into the self-assembly during oxidation if a unidirectional transport and permselectivity of the film to anions are assumed. The results were again confirmed by separate experiments in D_2O instead of H_2O. Thus the *in situ* mass transport measurements indicate that the self-assembled molecular $C_{22}VC_1$ films formed on gold surfaces contain water molecules and become compact in the order $Cl^- < TS^- < ClO_4^-$. Buttry recently reported that simultaneous incorporation of anions and solvent water into the electroactive self-assembled monolayers of ferrocenes occurs upon electrochemical oxidation of ferrocenes to fericinium ions[9]. Therefore, it appears that self-assembled molecular films on electrode surfaces contain a number of solvent water molecules although they are believed to be firmly organized based on the blocking properties for the reduction of $Ru(NH_3)_6^{3+}$ [2,10] and believed to be hydrophobic because their formation is mainly due to intermolecular hydrophobic interactions. Further EQCM studies are in progress with the self-assembly of asymmetric viologens.

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Asymmetric Borane Reduction of Ketoxime O-Trimethylsilyl Ethers Mediated by a Chiral 1,3, 2-Oxazaborolidine Derived from (−)-Ephedrine

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One of the most convenient methods for the preparation of optically active primary amines is asymmetric reduction of ketoxime derivatives. However such reduction has been sparse and only very limited success has been achieved.[1] Very recently, we undertook the comparison study of asymmetric borane reduction of some representative ketimines and ketoxime ethers possessing $C=N$ bond mediated by various chiral oxazaborolidines.[2] In this study, we found that a chiral oxazaborolidine 1 derived from (−)-ephedrine afforded the best result to give a high optical induction (90% ee) for acetophenone oxime O-trimethylsilyl ether 2d. This result led us to investigate the asymmetric borane reduction of O-trimethylsilyl ethers 2 of other aliphatic and aromatic ketoximes, such as 2-butanone oxime 2a, 4-methyl-2-pentanone oxime 2b, 3-methyl-2-butanone oxime 2c, propiophenone oximes 2e, isobutyrophenone oxime 2f pivalophenone oxime 2g and tetralone oxime 2h, using this reagent. All of the O-trimethylsilyl ethers of ketoximes examined were prepared by treatment of the corresponding ketoximes with chlorotrimethylsilane in the presence of triethylamine in THF.[2]
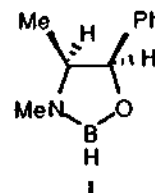
The reductions were carried out with 1 equiv of borane-THF in the presence of 1 equiv of 1 in THF at room temperature. Thus, the reductions of O-trimethylsilyl ethers of unhindered aliphatic ketoxime 2a proceeded smoothly to give the corresponding primary amines 3a in a high chemical yield with 38% ee. However, the reduction of O-trimethylsilyl ethers of relatively hindered aliphatic ketone oximes 2b-2c proceeded at a somewhat slower rate to provide 3b and 3c with optical yields of 44% ee and 66% ee, respectively, showing the increase of optical induction by the variation of the steric size of R in $MeCR=NOTMS$ from Et→i-Bu→i-Pr. The aromatic ketoxime derivatives 2d-2f and 2h