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Preliminary note

COMPARATIVE ELECTROCHEMICAL STUDIES OF *N*-METHYL-*N*'-HEXADECYL VILOGEN MONOMOLECULAR FILMS FORMED BY IRREVERSIBLE ADSORPTION AND THE LANGMUIR–BLODGETT METHOD

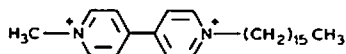
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INTRODUCTION

This study is concerned with the electrochemical behavior of an organized monomolecular film of an electroactive species on an electrode surface prepared by the Langmuir–Blodgett (LB) technique. There has been recent interest in organized assemblies in studies of electron transfer reactions [1–3], in electrode surface modification [4–9], and in the construction of sensors and other devices [10]. Because the LB method utilizes a film balance to deposit a film under pressure [11–15], an organized layer with a specific structure results, and the amount of surface species determined electrochemically (e.g., by a cyclic voltammetric (CV) scan) can be compared to that found from the surface pressure–molecular area isotherm. We report such a comparison here, as well as contrast the electrochemical behavior of the LB film with one produced by adsorption from a solution of the same compound. Finally, we discuss how the CV response is affected by surface intermolecular interactions. For these studies we chose the asymmetric single alkyl chain species, *N*-methyl-*N*'-hexadecyl viologen (C16MV²⁺),



whose electrochemistry has not been studied previously. We also undertook these studies because of our interest in forming films of electroactive materials of precisely defined thickness in connection with electron transfer studies at the ultrathin layer apparatus [16].

EXPERIMENTAL

The C16MV²⁺ was prepared by a literature method [17]. Other reagents were of the best commercial quality available. Solutions were prepared from laboratory-de-

ionized water that was passed through a purification train (Millipore Continental Water System). Rainin Nylon-66 filters ($0.2 \mu\text{m}$) were used to filter the electrolyte solutions for LB experiments. Solutions for electrochemical experiments were deoxygenated with prepurified nitrogen. All experiments were performed at laboratory temperature, $23 \pm 2^\circ\text{C}$. Nesatron indium-tin oxide (ITO) electrodes from PPG (Pittsburgh, PA) were cleaned with soap, potassium hydroxide/alcohol solutions, and distilled water and dried in an oven at 120°C before each trial. The glassy carbon electrode was constructed from a RA 30 S Tokai glassy carbon (International Minerals and Chemicals Co., New York, NY) and its projected area was 0.071 cm^2 . A Lauda film balance system (Brinkmann, Westbury, NY) was used throughout for monolayer formation and transfer experiments. A minimal amount of methanol to dissolve the compound was mixed with chloroform and the final solution was used as a stock solution for sample spreading. The ITO electrode was immersed into the subphase solution, and a small amount of sample solution was added and compressed to form a monolayer. Monolayer transfer to the electrode surface was made by lifting ($0.5\text{--}2 \text{ cm/min}$) the electrode at constant pressure (30 mN m^{-1}). Conventional commercial electrochemical instrumentation and cells were employed for cyclic voltammetric measurements. Voltammograms with LB film were recorded as quickly as possible ($< 5 \text{ min}$) because the film slowly degraded. A Norland Model 3001 (Fort Atkinson, WI) processing digital oscilloscope was used for fast scan voltammetry. Quoted potentials are given with respect to sodium chloride saturated calomel electrode (SSCE).

RESULTS AND DISCUSSION

Adsorbed film

Figure 1a shows the successive cyclic voltammogram recorded after immersing a glassy carbon (GC) electrode into a solution containing $2 \mu\text{M}$ C16MV $^{2+}$ and 50 mM sodium chloride. The magnitude of the CV waves increased with time as C16MV $^{2+}$ diffused to the electrode surface and was adsorbed [18,19]. The voltammogram is characterized by a single broad cathodic and corresponding anodic wave with midpotential of -0.58 V , which is 110 mV more positive than that, -0.69 V , for methyl viologen (MV) [20], indicating stronger adsorption of the reduced radical cation. The total width, 200 mV , at half height ($\Delta E_{p,1/2}$) is greater than 91 mV with small peak splitting of 40 mV , indicating possibly repulsive interaction among adsorbed species [21]. The peak currents (i_{pc} and i_{pa}) attained constant values after about 2 h and at that point, i_{pc} and i_{pa} varied directly with scan rate, ν , over a range of 50 to 500 mV/s with zero intercept, as expected for electrode surface bound redox species [22]. At this solution concentration of C16MV $^{2+}$ the contribution of diffusing species to the peak current is negligible. Thus a MV $^{2+}$ solution at this concentration shows the same current as a blank solution. For the C16MV $^{2+}$ species almost the same voltammetric response as the steady-state voltammogram in the compound solution was observed in a pure supporting electrolyte solution to

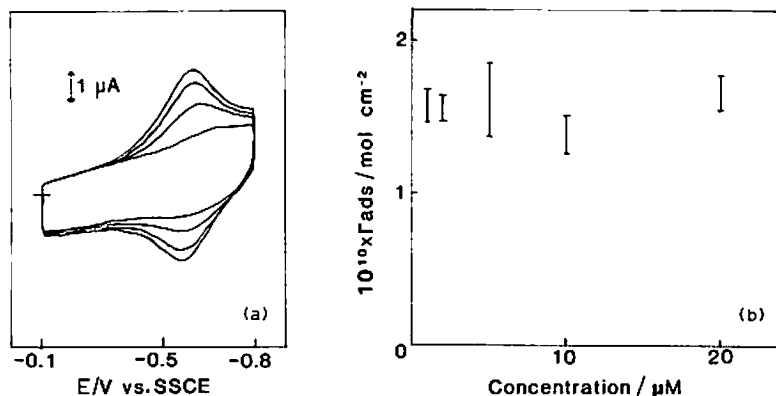


Fig. 1. (a) Cyclic voltammograms as a function of exposure time after immersion of GC electrode into a $2 \mu\text{M}$ C16MV^{2+} aqueous solution of 50 mM sodium chloride. Electrode potential was maintained at -0.2 V between scans. Scan rate: 500 mV/s ; electrode area: 0.071 cm^2 ; time: 0.2, 20, 40, 60 min. (b) Adsorption of C16MV^{2+} at a GC electrode as a function of compound concentration in 50 mM sodium chloride solutions.

which the coated electrode was transferred. The irreversible adsorption observed reflects strong interaction between the GC electrode* and the long alkyl chain introduced to viologen moiety. The extent of adsorption of C16MV^{2+} was estimated by integration of the voltammogram recorded at 10 V/s over the concentration range $1\text{--}20 \mu\text{M}$ (Fig. 1b). The relatively constant adsorption in the five different concentrations studied suggests that full coverage is apparently reached at $1 \mu\text{M}$. The adsorption $1.6 \times 10^{-10} \text{ mol/cm}^2$ corresponds to a monolayer of C16MV^{2+} with a molecular area as 1.40 nm^2 [11–13,25,26] and the microscopic area of the GC electrode as ca. 1.3 times larger than its geometric area.

LB film

Although C16MV^{2+} is soluble in pure water and in sodium chloride electrolyte solutions, it is much less soluble ($< 1 \mu\text{M}$) in moderately concentrated sodium perchlorate solutions (100 mM). In such solutions, stable LB monolayer films can be formed. Above ca. 60 mM NaClO_4 , the surface pressure–molecular area isotherm of C16MV^{2+} did not change significantly under the present experimental conditions, and 0.1 M NaClO_4 solution was used as the subphase for monolayer formation and transfer experiments. A surface pressure–molecular area isotherm is

* The glassy carbon electrode used was not activated. See ref. 23 for hydrophobic characteristics of GC surfaces in electrochemistry. The title compound does adsorb spontaneously at indium–tin oxide electrode surfaces, as was observed with similar surfactant viologen compounds [24], but the voltammetric peak current was much smaller than that at a GC electrode under the experimental conditions of Fig. 1a. A GC electrode was chosen in the adsorption experiments because the present work aimed for comparative studies of the viologen monomolecular films immobilized via hydrophobic interactions.

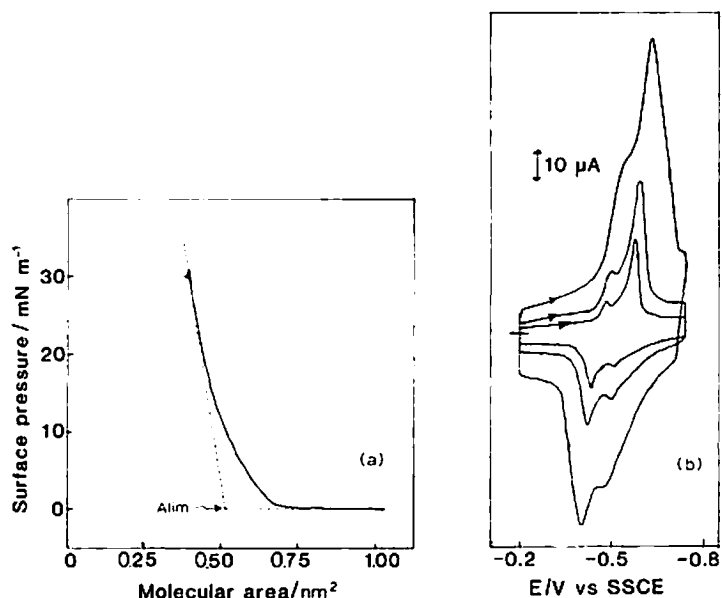


Fig. 2. (a) Surface pressure-molecular area isotherm. Constant pressure segment at 30 mN m^{-1} represents monolayer transfer to an indium-tin oxide electrode. (b) Cyclic voltammograms of C16MV^{2+} LB film on indium-tin oxide electrode in 0.2 M sodium perchlorate solution. Electrode area: 0.52 cm^2 . Scan rate: 500, 200, 100 mV/s .

shown in Fig. 2a. The limiting molecular area (A_{lim}), ca. $0.50 \text{ nm}^2/\text{molecule}$, is much larger than the projected area of an alkyl group [11–13], but accords reasonably with the overall molecular area accounting for the viologen head group [25] and two perchlorate anions [27] in a hypothetical close-packed state at zero surface pressure.

Figure 2b shows CVs recorded at three different scan rates in a pure electrolyte solution for a LB film of C16MV^{2+} on an indium-tin oxide electrode surface transferred at 30 mN m^{-1} , as indicated in Fig. 2a as a constant pressure plateau segment. Integration of the voltammogram shows that the quantity of surface bound electroactive viologen produced by the LB method, $4.0 \times 10^{-10} \text{ mol/cm}^2$, is much larger than that formed by simple adsorption shown in Fig. 1. This suggests that the film formed under pressure by the LB method is more highly organized and compact, with the alkyl chains perpendicular to the surface, than that formed by spontaneous adsorption from solution. In the latter case a less organized monolayer is suggested with the alkyl chains parallel to the surface and perhaps with greater mobility of the surface species. Note that organized films can be formed by spontaneous adsorption from solution (spontaneous assembly) when the head group of the adsorbing molecule interacts strongly with the substrate [28]. The quantity obtained from the integrated charge of the voltammogram corresponds within

experimental error to that calculated, 4.2×10^{-10} mol/cm, based on the molecular area from the LB isotherm, 0.40 nm^2 , at the transfer pressure, 30 mN m^{-1} , implying that each molecule occupies the same area on two different substrate conditions. This fact suggests that LB method offers an alternative way to determine the quantity of immobilized redox species on an electrode surface.

For the LB films the CV peaks are sharp and at low scan rates (100 mV/s) two cathodic and anodic peaks are clearly discernible. The appearance of two peaks in a voltammogram is in agreement with the recent theoretical model of Tokuda and co-workers [9] based on a statistical mechanical description of a surface-bound monomolecular redox film, when the immobilized redox species undergoing electron transfer has a sufficiently negative interaction energy. According to this model, this one-electron transfer peak separation takes place only when surface arrangement is regular, as in the present LB film case; and it does not occur for randomly distributed surface species, even when the redox species are strongly interacting. Our observation of a single cathodic and anodic peak with a more random adsorbed film is also in agreement with this model. To our knowledge, this is the first definitive example of two resolved peaks for a single electron transfer electrode process of an LB film. However, Park et al. [5] also described voltammograms that showed "not always well-defined, but sometimes two peaks".

The interpretation for our observation of double peaks is that interaction between viologen dication and radical monocation is much stronger than that between the dications or the radical monocations within the LB film according to Tokuda and co-workers [9], thus indicating that dimerization of radical monocations is effectively prohibited. We previously observed that methyl viologen radical cations extensively dimerized within a clay structure [29]. The environmental factor is important for dimerization of the radical cations. We believe that hydrophobic environment provided by the long alkyl backbone is a major contributing factor in reversing dimerization of the monocationic radicals in the densely stacked LB film. Although other similar surfactant viologen molecules with long alkyl chains on both N atoms or one N atom of the bipyridine were used in previous electrochemical studies of LB films [6], these did not show the one-electron process double peaks, as found here. In these cases the viologen moieties were probably not as closely packed, because the two long alkyl chains per molecule prevented the formation of compact films and as strong an interaction between neighboring molecules. In the present close-packed film, the viologens appear to have strong intermolecular stacking interactions, as found in the dimerization of radical cations [30] and has been observed with other π -electron containing molecular systems [31].

In conclusion, we have provided an example of a molecule that adsorbs irreversibly on glassy carbon and which forms an LB monomolecular film on the surface of an aqueous sodium perchlorate solution or on an indium-tin oxide electrode. The LB film shows strong intermolecular interaction in the electron transfer process. We also demonstrated that the LB surface pressure isotherm serves as an independent method to determine the immobilized quantity. Further electrochemical and electron transfer studies with ordered films are in progress in our laboratory.

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