Cyclic voltammetry and Langmuir film isotherms of mixed monolayers of N-docosyl-N′-methyl viologen with arachidic acid

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Surface pressure–molecular area isotherms of mixed Langmuir monolayer films of N-docosyl-N′-methyl viologen ($C_{22}MV^{2+}$) with arachidic acid were measured at the air/water interface and the electrochemical behavior of the films were investigated after transfer to an indium tin oxide electrode in aqueous sodium perchlorate solution. The average molecular area in the mixed monolayer films negatively deviates from ideal additivity. Double voltammetric peaks for the first reduction wave of pure $C_{22}MV^{2+}$ converge with addition of arachidic acid and show a single peak at the mole ratio of viologen : arachidic acid = 1:3.

1. Introduction

In a previous electrochemical study of an organized monolayer film of N-hexadecyl-N′-methyl viologen ($C_{16}MV^{2+}$), we reported that $C_{16}MV^{2+}$ formed not only an irreversibly adsorbed film on glassy carbon surfaces but also a Langmuir–Blodgett (LB) film on indium tin oxide electrode surfaces due to the hydrophobicity introduced intentionally to viologen moiety [1]. Although the film adsorbed on a glassy carbon surface by immersion of the electrode into a solution of $C_{16}MV^{2+}$ showed a single cathodic and anodic peak for the first reduction, the LB film at indium tin oxide (ITO) electrode surfaces showed two resolved peaks for the single-electron transfer process. This unusual electrochemical behavior of the LB film was attributed to the regular arrangement of the redox components and the stronger interaction between $C_{16}MV^{2+}$ and $C_{16}MV^{+}$

than between $+2/+2$ or $+/+$ pairs [1,2]. To better understand this electrochemical behavior we carried out an investigation of LB films with an irregular arrangement or weakly interacting redox components, namely, mixed LB films. In doing so, we prepared the new asymmetric viologen with a longer alkyl chain, N-docosyl-N′-methyl viologen ($C_{22}MV^{2+}$), because the LB film of $C_{16}MV^{2+}$ slowly degraded [1]. Because of the stronger hydrophobic attraction, $C_{22}MV^{2+}$ formed a much denser Langmuir monolayer at the air/water interface than $C_{16}MV^{2+}$, and the LB film of $C_{22}MV^{2+}$ on ITO showed more stable double peaks for the single-electron transfer process than that of $C_{16}MV^{2+}$. In this work, we describe the effect of mixing $C_{22}MV^{2+}$ with arachidic acid (AA) to form a monolayer film at the air/water interface and the electrochemical behavior of the mixed LB films transferred to ITO electrode surfaces.

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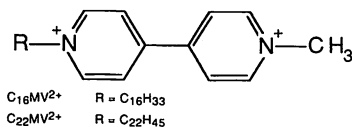
2. Experimental

The $C_{22}MVBr_2$ was prepared by the same method as previously described for $C_{16}MVBr_2$ [1]. Analytical, calculated for $C_{22}MVBr_2$ (MW 639.8): C, 61.89; H, 8.75; N, 4.38; found: C, 61.86; H, 8.74; N, 4.26.

$C_{16}MV^{2+}$ R = $C_{16}H_{33}$
$C_{22}MV^{2+}$ R = $C_{22}H_{45}$

Other reagents were of the best commercial quality available. Solutions were prepared from laboratory-deionized water that was passed through a purification train (Millipore Continental Water System). Rainin Nylon-66 filters (0.2 μm) 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, $23 \pm 2\,°C$. Delta indium tin oxide electrodes from Delta Technologies (Stillwater, MN) were cleaned with soap, potassium hydroxide/alcohol solutions, and distilled water and dried in an oven at $120\,°C$ before each trial. A Lauda film balance system (Brinkman, Westbury, NY) was used throughout for monolayer formation and transfer experiments. A minimal amount of methanol to dissolve the compound(s) was mixed with chloroform and the final solution was used as a stock solution for sample spreading. The indium tin oxide electrode was immersed into the subphase solution, then a small amount of sample solution was added and a monolayer formed; this was then compressed. Monolayer transfer to the electrode surface was made by lifting the electrode at 0.5–2 cm/min at constant surface pressure ($30\ \mathrm{mN\ m^{-1}}$). Conventional commercial electrochemical instrumentation and cells were employed for cyclic voltammetric measurements. Quoted potentials are given with respect to a saturated sodium chloride calomel electrode (SSCE).

3. Results and discussion

Although a moderately concentrated (≈ 0.1 M) $NaClO_4$ solution was required to form stable monolayer films of $C_{16}MV^{2+}$ [1], only a small amount (10 mM) of $NaClO_4$ in the water subphase was required to obtain stable LB films of $C_{22}MV^{2+}$ at the air/water interface. The surface pressure–molecular area isotherm was also much steeper with $C_{22}MV^{2+}$ than with $C_{16}MV^{2+}$. This indicates a stronger intermolecular attraction for the C_{22} species because of larger chain–chain interactions upon increasing the chain length by six carbons. A similar effect was seen with N-methyl-N'-octadecyl viologen [3]. However, the stronger hydrophobic character did not change significantly the electrochemical behavior of an LB

film of $C_{22}MV^{2+}$ on an ITO surface, as discusseed below.

Fig. 1 shows surface pressure–molecular area isotherms for surface films of pure $C_{22}MV^{2+}$ and pure arachidic acid on aqueous solutions of 10 mM $NaClO_4$ and for the mixtures of $C_{22}MV^{2+}$ and AA at the molar ratios of $C_{22}MV^{2+}$: AA $= 2$: 1 and 1 : 1. Pure AA forms almost as dense a monolayer on the $NaClO_4$ solution subphase as it does on a $CdCl_2$ solution subphase [4,5]. Fig. 2 shows the average molecular area of the mixed monolayers of three dif-
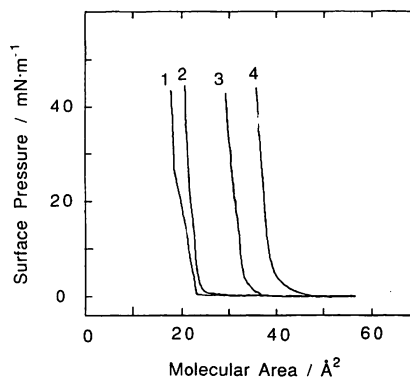

Fig. 1. Surface pressure–molecular area curves at air/10 mM $NaClO_4$ aqueous solution interface. The ratio of arachidic acid : $C_{22}MV^{2+}$, (1) 1 : 0, (2) 1 : 1, (3) 1 : 2, (4) 0 : 1. The 3 : 1 isotherm, which is not shown, was almost identical to the 1 : 0 isotherm (1).
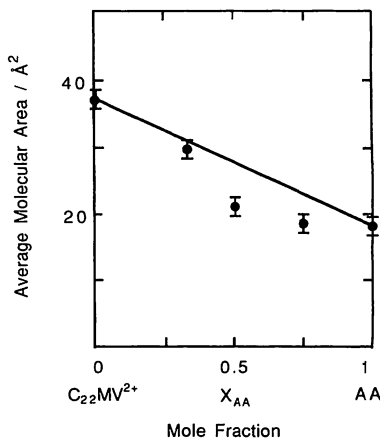

Fig. 2. Average molecular area of the mixed monolayers obtained from isotherms versus mole fraction of arachidic acid.

ferent mole fractions at a surface pressure of 30 mN m^{-1}. The solid line was calculated based on the ideal mixture equation,

$$A_{12} = x_1 A_1 + x_2 A_2,$$

where A_{12} is the average molecular area at a given surface pressure in the two-component film, x_1 and x_2 are the mole fractions of $C_{22}MV^{2+}$ and arachidic acid in the mixture, and A_1 and A_2 are the molecular areas of pure $C_{22}MV^{2+}$ and AA at the same surface pressure [6]. The observed negative deviations from ideal mixing indicate strong molecular interaction between $C_{22}MV^{2+}$ and arachidic acid, possibly due to electrostatic interaction between the positive viologen head groups and the carboxyl groups. The AA may fill gaps present in the hydrocarbon portion of the viologen monolayer and replace the perchlorate anion, thereby promoting a stable arrangement with high molecular packing when the monolayer is slowly compressed.

Fig. 3 shows cyclic voltammetric (CV) measurements at different scan rates in pure electrolyte solutions for LB films of $C_{22}MV^{2+}$ alone and of the mixture of $C_{22}MV^{2+}$: AA = 1 : 3 on ITO electrode surfaces transferred at 30 mN m^{-1}. With the LB film of pure $C_{22}MV^{2+}$, two peaks are observed for the first reduction process which were better resolved than those with $C_{16}MV^{2+}$ [#1]. This may be the result of an even better ordered arrangement of the C_{22} species caused by the stronger hydrophobic intermolecular interactions. Integration of the CV waves gave a surface coverage of $(3.5 \pm 0.4) \times 10^{-10}$ mol/cm^2 (compared to a theoretical value of 4.3×10^{-10} mol/cm^2 based on the molecular area from the surface pressure isotherm). We should note that the reproducibility of transfer of the films to the ITO substrate was poor, so that films showing this coverage were only obtained about 10% of the time. The double peaks are still discernable in a mixture of $C_{22}MV^{2+}$ with an insufficient amount of AA ($\approx$ 1 : 2). At the mole ratio of $C_{22}MV^{2+}$: AA = 1 : 3, however, the voltammetric double peaks coverge to a single cath-
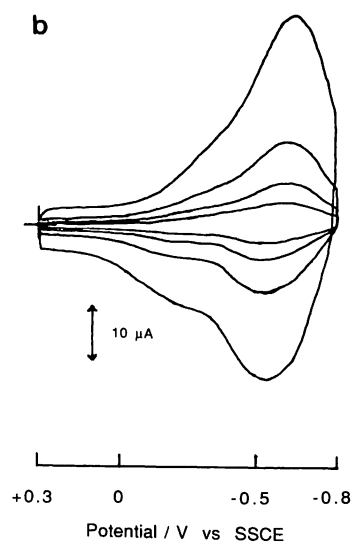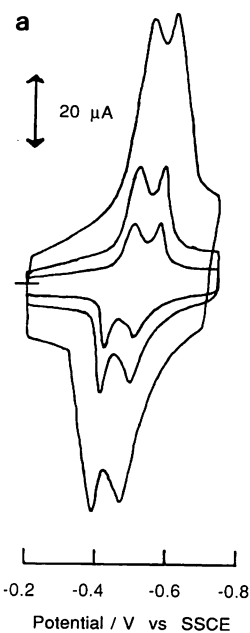

[#1] Potentials were not scanned beyond -0.7 V versus SSCE. Note that multiple voltammetric peaks were observed with adsorbed films of similar viologens when potentials were scanned sufficiently negative to generate neutral viologen from the viologen radical cation. See, for example, ref. [7].

Fig. 3. Cyclic voltammograms of the LB films of (a) pure $C_{22}MV^{2+}$; (b) mixture of $C_{22}MV^{2+}$: arachidic acid = 1 : 3 at indium tin oxide/0.1 M NaClO$_4$ aqueous solution interface. Scan rates 500, 200, and 100 mV/s.

odic and anodic peak (fig. 2b), indicating significant structural changes occurring with the LB film of $C_{22}MV^{2+}$, when $C_{22}MV^{2+}$ is mixed with a sufficient amount of AA. The single cathodic and anodic peak is also similar to the one observed with $C_{16}MV^{2+}$ on

glassy carbon electrode surfaces, where $C_{16}MV^{2+}$ is randomly distributed [1]. These results can be explained by assuming that the mixing between $C_{22}MV^{2+}$ and AA is not random [8] so that at lower mole ratios of arachidic acid/$C_{22}MV^{2+}$ large segregated domains of regularly arranged $C_{22}MV^{2+}$ moieties still exist. However, at sufficiently large ratios, large domains of $C_{22}MV^{2+}$ no longer survive, although smaller clusters may still be present.

An alternative explanation of the double peaks found with $C_{22}MV^{2+}$ would be that the surface species exists in two different conformations, A and A', which are reproducibly reduced to two conformations, B and B'. The effect of addition of AA would then be interpreted as causing a transition of the $C_{22}MV^{2+}$ to a single conformation. Based on the results so far, however, we feel this alternative is less likely.

In summary, $C_{22}MV^{2+}$ forms a tight monolayer film at the air/water interface and is miscible with arachidic acid to form a mixed monolayer. The LB film of $C_{22}MV^{2+}$ on an ITO electrode shows two well-resolved peaks for $C_{22}MV^{2+} + e = C_{22}MV^{+}$. The double peaks converge to one single peak when the LB film of mixtures are diluted sufficiently with ar-

achidic acid. Further studies of the characterization and electron transfer kinetics of the LB film are in progress.

Acknowledgement

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