Electrochemistry inside a Lipid Film: Fine Tuning of the Redox Potentials of an Amphiphilic Viologen in Phosphatidylcholine Films

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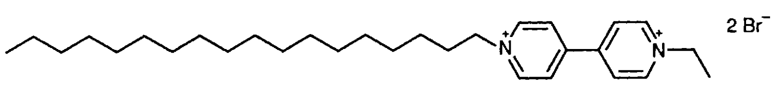
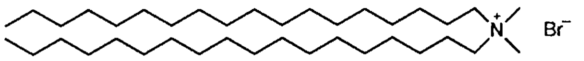
The electrochemistry of a surfactant viologen derivative inside a zwitterionic phospholipid film is strongly affected by the presence of charged surfactants in the film.

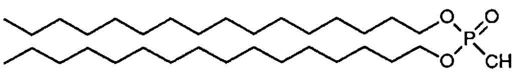
Amphiphilic assemblies are currently attracting considerable attention for the modification of electrode surfaces because they can potentially afford a substantial degree of control on the molecular architecture at the electrode–solution interface. We have recently reported the behaviour of glassy carbon electrodes modified with cast films of egg phosphatidylcholine (PC).[1] These electrodes exhibit permselective properties since redox-active amphiphiles can penetrate the lipid film and undergo electron transfer reactions with the underlying electrode surface while hydrophilic redox-active species are



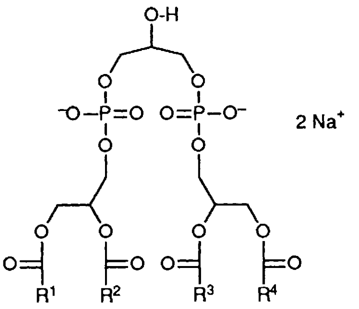
$1{\cdot}Br_2$



DODAB



DCP



CARDI

rejected by the PC film and, therefore, their electrochemistry is essentially blocked.[1] The permselective properties and the relative simplicity of preparation of these electrodes have generated interest in the field of pharmaceutical analysis.[2,3]

We describe here the electrochemical properties of *N*-ethyl-*N*′-octadecyl viologen dibromide, $\mathbf{1}{\cdot}Br_2$, inside PC films cast on glassy carbon (GC) surfaces. The electrodes were simply prepared by deposition of a measured μl volume of a chloroform solution of $\mathbf{1}{\cdot}Br_2$ and PC on the tip of the GC electrode. The chloroform was allowed to evaporate in air while the electrode was rotated (200 rpm) resulting in the formation of a lipid film on the electrode surface. Several authors have shown that cast phospholipid films formed by similar procedures exhibit organized multilayer structures.[4–7] We assume that the presence of the amphiphilic dication $\mathbf{1}^{2+}$ (at a level of 9.1% mol) does not disrupt the multilayer organization of the PC molecules.

The cyclic voltammetric (CV) response of a GC electrode (0.08 cm^2) covered with 4.1×10^{-8} mol cm^{-2} of $\mathbf{1}^{2+}$ and 4.1×10^{-7} mol cm^{-2} of PC is shown in Fig. 1*A*. This level of coverage results in a lipid film having an estimated thickness of 3.7 μm. Two redox processes are clearly visible corresponding to the two consecutive monoelectronic reductions of the viologen nucleus ($\mathbf{1}^{2+}/\mathbf{1}^{+}$ and $\mathbf{1}^{+}/\mathbf{1}$). The approximate constancy of the ratio of the first cathodic peak current to the square root of the scan rate (in the 50–500 mV s^{-1} range) indicates that the currents are controlled by the diffusion of $\mathbf{1}^{2+}$ inside the PC film (the diffusion coefficient was estimated to be around $1\text{–}2 \times 10^{-9}$ cm^2 s^{-1}). The voltammetric behaviour of amphiphilic viologens such as $\mathbf{1}^{2+}$ in aqueous media is usually complicated by the precipitation of the reduced forms $\mathbf{1}^{+}$ and $\mathbf{1}$ on the electrode surface[8,9] as well as by the interfacial self-assembly of the dicationic form $\mathbf{1}^{2+}$.[10,11] The fact that no distortions due to precipitation are detected in the CV of Fig. 1*A* argues strongly in favour of a relatively organized multilayer structure for the cast PC–$\mathbf{1}^{2+}$ film. However, substantial ionic currents can be established through the lipid film, as shown by the observation of diffusion-controlled electrochemistry for $\mathbf{1}^{2+}$

Since these experiments were performed with the lipid film immersed in a pH 7 buffer solution, PC is in its zwitterionic form, and the lipid film has no formal charge. Thus, it becomes possible gradually to modify the nominal charge of the film by introducing varying amounts of anionic or cationic surfactants. We selected dicetyl phosphate (DCP), dioctadecyldimethylammonium bromide (DODAB), and Cardiolipin (CARDI)† as suitable charge modifiers of the lipid film owing to the resemblance of their charged head groups with those of PC.

Fig. 1*B* shows the CV response of a GC electrode covered with 4.1×10^{-8} mol cm^{-2} of $\mathbf{1}^{2+}$, 3.3×10^{-7} mol cm^{-2} of PC, and 0.8×10^{-7} mol cm^{-2} of DODAB.‡ Comparison of the voltammograms in Figs. 1*A* and 1*B* clearly demonstrates that the incorporation of DODAB causes positive shifts in both half-wave potentials for the monoelectronic reductions of $\mathbf{1}^{2+}$. This can be explained by the relative electrostatic destabilization of the unreduced forms ($\mathbf{1}^{2+}$ and $\mathbf{1}^{+}$) relative to the reduced forms ($\mathbf{1}^{+}$ and $\mathbf{1}$, respectively) in both redox couples

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† Cardiolipin was obtained from Sigma (catalogue no. C9138). The distribution of the fatty acid chains (R^1 to R^4) was quoted by the supplier as follows: palmitic, 41%; stearic, 3.2%; oleic, 5.6%; linoleic, 6.4%; others, 43.8%.

‡ All lipid films were cast from chloroform solutions. The films always contained a 10:1 molar ratio of electroinactive (egg PC + charged surfactant) to electroactive ($\mathbf{1}^{2+}$) material. Molar ratios of charged surfactants were calculated without taking into account the electroactive species. The voltammograms shown here were recorded after 10–15 min of cycling the potential of the working electrode at 100 mV s^{-1} between 0.0 and −1.2 V. The error margin of the reported half-wave potentials is about ±0.005 V.

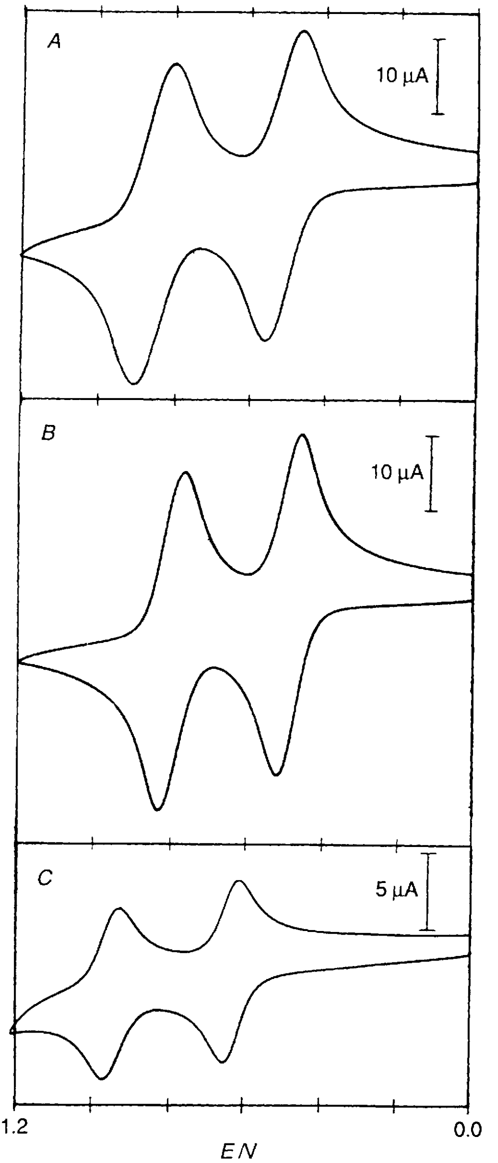

Fig. 1 Cyclic voltammetric response (V *vs.* sodium saturated calomel electrode, SSCE; 50 mV s^{-1}) in 0.100 mol dm^{-3} phosphate buffer (pH 7.0) of a GC electrode (0.080 cm^2) covered with (*A*) 4.1 × 10^{-8} mol cm^{-2} **1**·Br$_2$ + 4.1 × 10^{-7} mol cm^{-2} PC; (*B*) 4.1 × 10^{-8} mol cm^{-2} **1**·Br$_2$ + 3.3 × 10^{-7} mol cm^{-2} PC + 8.2 × 10^{-8} mol cm^{-2} DODAB; (*C*) 2.0 × 10^{-8} mol cm^{-2} **1**·Br$_2$ + 1.2 × 10^{-7} mol cm^{-2} PC + 8.2 × 10^{-8} mol cm^{-2} CARDI

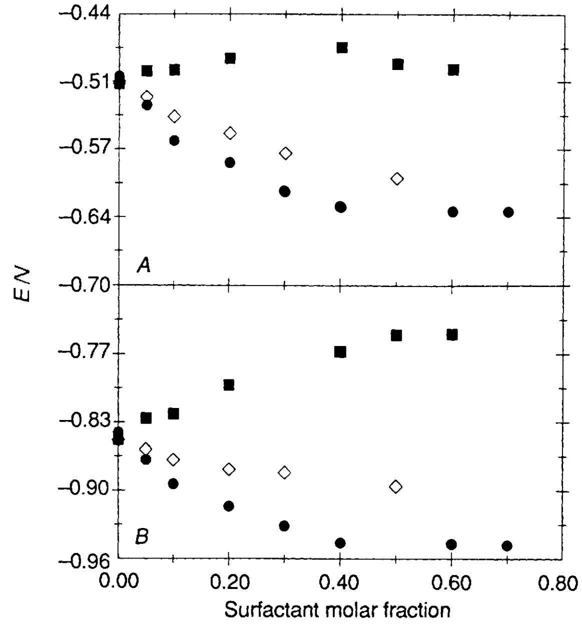

Fig. 2 Dependence of the half-wave potentials (V *vs.* SSCE) for the couples (*A*) $\mathbf{1}^{2+}/\mathbf{1}^{+}$ and (*B*) $\mathbf{1}^{+}/\mathbf{1}$ on the molar fraction of charged surfactant in the lipid film: (■) DODAB, (◊) DCP, (●) CARDI

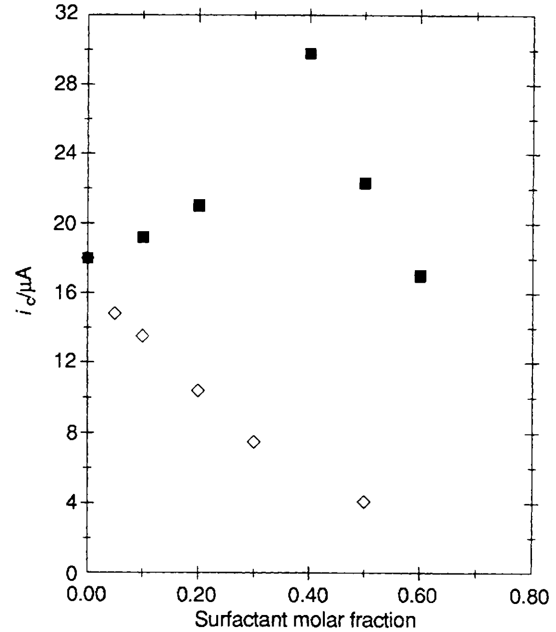

Fig. 3 Dependence of the cathodic peak current (i_c; recorded at 50 mV s^{-1}) of the $\mathbf{1}^{2+}/\mathbf{1}^{+}$ couple on the molar fraction of charged surfactant in the lipid film: (■) DODAB, (◊) DCP; data were obtained with films of 3.7 μm thickness (nominal coverages: 4.1 × 10^{-8} mol cm^{-2} **1**·Br$_2$ and 4.1 × 10^{-7} mol cm^{-2} egg PC + surfactant)

which is brought about by the presence of the cationic surfactant in the lipid film. As expected, the incorporation of the negatively charged amphiphiles CARDI and DCP causes the opposite effect, *i.e.*, negative shifts in both half-wave potentials. Fig. 1*C* shows that a 0.4 molar fraction of CARDI in PC markedly shifts both viologen redox processes to more negative potentials while the diffusion-controlled shape of the voltammogram is maintained. This finding is rationalized by the relative stabilization of the unreduced over the reduced forms in each one of the two viologen redox couples.

The magnitude of these effects can be controlled by changing the molar fraction of charged surfactant in the lipid film. This is demonstrated by the data in Fig. 2 which show the variation of both half-wave potentials for the $\mathbf{1}^{2+}/\mathbf{1}^{+}$ and $\mathbf{1}^{+}/\mathbf{1}$ redox couples with the molar fraction of DODAB, CARDI and DCP, respectively, in the lipid film. CARDI shows a stronger effect in shifting both half-wave potentials than DCP, since CARDI contains two negatively charged phosphate groups while DCP contains only one. Fig. 3 shows the dependence of the first cathodic peak current on the molar fraction of DODAB and DCP. As expected, the presence of the negatively charged DCP slows down the diffusion of the electroactive amphiphile $\mathbf{1}^{2+}$, probably owing to association between both species which is favoured on electrostatic grounds. This results in decreasing values of the peak current as the molar fraction of DCP increases. Conversely, the presence of moderate amounts of the positively charged

DODAB has the opposite effect. However, larger molar fractions of DODAB in the PC film result in diminished currents probably because of the increased structural rigidity that saturated alkyl chains introduce in these multilayer assemblies.[12]

In conclusion, we have shown that the first and second half-wave potentials for the consecutive monoelectronic reductions of an amphiphilic viologen inside a PC film cast on GC electrodes can be adjusted over a range of about 200 mV by incorporating varying amounts of charged surfactants into the cast lipid films. The observed half-wave potentials are controlled by simple electrostatic interactions. This demonstrates the possibility of 'fine tuning' the redox potential of an electroactive compound immobilized in the phospholipid film, a very important goal for applications involving electrocatalysis or mediation of electron transfer reactions by the film.

The authors gratefully acknowledge the partial support of this research by the National Science Foundation (CHE-9000531).

Received, 30th July 1990; Com. 0/03473H

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12 M. Han and A. E. Kaifer, to be submitted. In a parallel study we have investigated the electrochemistry of **1**·Br_2 in lipid films prepared with known ratios of saturated/unsaturated alkyl chains. The results indicate that changes in the fluidity of the film cannot give rise to the large potential shifts observed in this work.