

Electrochemical characterization of the ultrathin polypeptide film/1,2-dichloroethane liquid | liquid interface[☆]

Yufei Cheng^a, Lasse Murtomäki^b, Robert M. Corn^{a,*}

^a Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706, USA

^b Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, PO Box 6100, FIN-02015 Hut, Finland

Received 22 November 1999; received in revised form 10 January 2000; accepted 11 January 2000

Abstract

A model liquid | liquid interface formed by an ultrathin hydrophilic polypeptide film at a chemically modified gold surface in contact with a 1,2-dichloroethane (DCE) electrolyte solution is characterized with a combination of electrochemical and in situ polarization modulation FTIR (PM-FTIR) measurements. The hydrophilic films are prepared by the sequential layer by layer electrostatic adsorption of the polypeptides poly-L-lysine and poly-L-glutamic acid onto gold thin films that have been derivatized with an ω -carboxylic acid functionalized alkanethiol monolayer. The polypeptide film thickness can be varied from 5 to 30 nm, and ionic electroactive species such as ferri/ferrocyanide can be incorporated into the film. The oxidation–reduction reactions of this electrochemical system are characterized with cyclic voltammetry and potential step measurements, and require both an electron transfer step at the gold | film interface and an ion transfer step at the film | DCE interface. No diffusion processes are observed in these ultrathin film systems, but the voltammetric response is asymmetric and broader than that observed in reversible monolayer systems. Based on digital simulations, the standard rate constant is estimated to be ca. 0.24 s^{-1} , and the standard deviation of the formal potential distribution is found to be approximately 130 mV. When the film is brought in contact with an organic solution containing decamethylferrocene, an electrocatalytic reaction is observed in the cyclic voltammetry corresponding to an electron transfer reaction across the film | DCE interface. In situ PM-FTIR experiments show that the cyclic voltammetry samples only a fraction of the electroactive species in the polypeptide film. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polypeptide multilayers; Liquid | liquid interfaces; Electrostatic adsorption; FTIR

1. Introduction

Quite recently, we reported [1] a study on ultrathin hydrophilic polypeptide films which were deposited by electrostatic adsorption onto alkanethiol derivatized gold slides. These films are able to incorporate ionic species, and can form a novel type of immiscible liquid | liquid (L | L) interface when brought into contact with an organic electrolyte solution. A schematic drawing of this system is depicted in Fig. 1. By applying an external potential difference across the interface, het-

erogeneous L | L charge transfer processes can be studied. There are several advantages of this model system

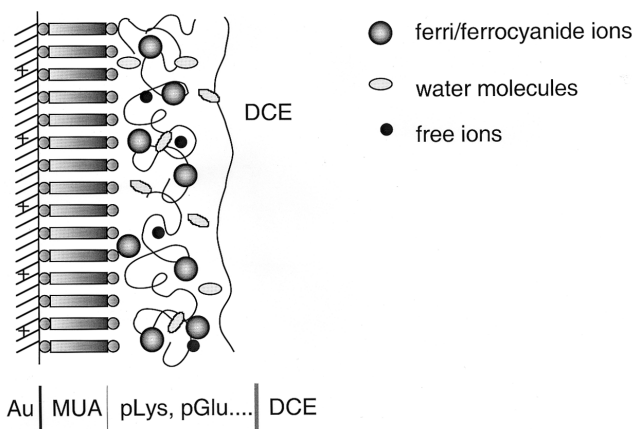


Fig. 1. A schematic drawing of the multilayer polypeptide film in contact with DCE solution.

[☆] Paper presented at the Euroconference on Modern Trends in Electrochemistry, Finland, 28 August–3 September, 1999.

* Corresponding author. Tel.: +1-608-2621562; fax: +1-608-2620453.

E-mail address: corn@chem.wisc.edu (R.M. Corn)

over conventional electrochemical cells that employ two bulk solvent phases [2,3]: (i) the progress of charge transfer reactions can be monitored spectroscopically with polarization modulation FTIR (PM-FTIR) and surface plasmon resonance (SPR) measurements because signals generated from the interface are not attenuated by an aqueous bulk solvent phase; (ii) the analysis of the electrochemical data is simplified greatly since the electroactive species are immobilized within the ultrathin film and there is no need to consider transport processes; and (iii) the thickness of these films and the amount of charge incorporated into the interface can be controlled in a precise manner by varying the number of adsorbed layers [1].

Two electrochemical charge transfer processes are studied in this communication. In the first system, a ferri/ferrocyanide couple immobilized within the film, undergoes a redox reaction at the modified gold electrode. To maintain film electroneutrality, a complementary charge transfer process must occur at the film | organic solution interface: either the uptake of ions from the organic phase into the film or the movement of ions in the opposite direction [4–6]. It is also possible, at least in principle, to drive redox reactions at the gold electrode by ion transfer at the liquid | liquid interface [7]. In the second system studied, the electrode coated with the multilayer film is brought into contact with the organic phase containing decamethylferrocene (DCMFC). An electrocatalytic reaction takes place where the decamethylferrocene is oxidized to decamethylferrocenium by the ferricyanide ions in the film. In this case, the ferri/ferrocyanide couple acts as an electron shuttle between the gold electrode and the organic redox couple.

2. Experimental

Poly-L-lysine (pLys, MW 34 300 Sigma), poly-L-glutamic acid (pGlu, MW 95 000 Sigma), $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, NaH_2PO_4 , Na_2HPO_4 (Fluka), decamethylferrocene (DCMFC, Aldrich) and 11-mercaptoundecanoic acid (MUA, Aldrich) were used as received. Tetrabutyl-ammonium tetraphenyl borate (TBATPB, Fluka) and tetrabutyl chloride (TBACl, Aldrich) were used as the organic supporting electrolyte in the 1,2-dichloroethane (DCE, Aldrich) and in the aqueous reference solution, respectively. Other electrolytes used were of reagent grade purity or higher.

Multilayer films of pLys and pGlu were deposited by sequential electrostatic adsorption onto a 1000 Å gold film that was first chemically derivatized with a self-assembled MUA monolayer. The detailed preparation and characterization of pLys and pGlu multilayer films are described previously [1]. Briefly, the polypeptide multilayer film was prepared by sequential adsorption

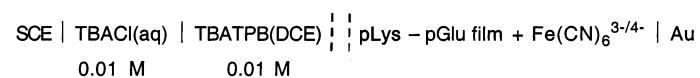
of pLys and pGlu from their buffered aqueous solutions (1 mg ml⁻¹ in 0.1 M phosphate solution, pH 8.0). A washing and N₂-blow drying procedure was applied after each adsorption step and the deposited film was examined by PM-FTIR spectroscopy. The amount of trapped electroactive ions depended on the pH of the assembly solution [1] and also on the pH of the ferri/ferrocyanide bathing solution. For example, a five layer film can incorporate three times more of this redox couple at pH 5.6 as compared to the amount incorporated at pH 10. This is because the amine residues on pLys side chains are protonated ($pK_a = 10.5$) at the lower pH and the number of positive sites available for $Fe(CN)_6^{3-/4-}$ anion binding is increased. Therefore, the incorporation of the ferri/ferrocyanide couple into the films was performed by dipping into a 1.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution of pH 5.6 for 30 min.

Electrochemical measurements were conducted in a standard three-electrode cell configuration as shown in Scheme 1, where Au denotes the gold slide working electrode and a Pt wire was used as the counter electrode. The potential was controlled by an EG&G potentiostat (Model 173, Princeton Applied Research) combined with a Universal Programmer wave generator (Model 175, Princeton Applied Research). In the electrocatalytic experiments, the concentration of decamethylferrocene (DCMFC) in the organic phase was 0.12 mM. All potentials reported here are referenced to the saturated calomel electrode (SCE) after correcting for the liquid junction potential between the DCE and aqueous phase.

3. Results and discussion

3.1. Redox reactions of ferri/ferrocyanide in the polypeptide film

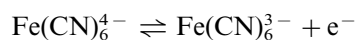
The pLys/pGlu multilayer films that were formed on the MUA derivatized gold substrates consisted of 3–15 layers with thickness ranging from 6 to 30 nm. The adsorption of $Fe(CN)_6^{4-}$ into the films appeared to be very fast: after exposing a film to the 1.0 mM $K_4Fe(CN)_6$ solution for only 1 min, an intense band at 2040 cm⁻¹ corresponding to the CN stretching mode for $Fe(CN)_6^{4-}$ was observed in the PM-FTIR spectrum. To insure that the concentration of the redox couple in the films was saturated, a dipping time of 30 min was typically used.



Scheme 1.

The electrochemical behavior of the multilayer film/DCE system was studied in detail by cyclic voltammetry. Fig. 2 shows typical cyclic voltammograms (CVs) of an 11 layer film in contact with a 0.01 M TBATPB DCE solution obtained at four different scan rates. In the absence of ferri/ferrocyanide ions, only capacitive current could be detected within the potential region of ± 0.6 V versus SCE. Incorporation of the redox couple into the film gave rise to an asymmetric voltammetric wave with a current peak that was much wider than expected for redox polymer films or bound redox monolayers on electrode surfaces [8]. As can be seen in the inset of Fig. 2, the peak current was directly proportional to the scan rate. These cyclic voltammetry results are examined in more detail in Section 3.2 below.

The electrochemical observations demonstrate that (i) the observed current is due to a reaction of the redox couple immobilized within the film; and (ii) the current is not limited by diffusion of ions in the organic phase. If the ferricyanide ions were transferred across the film|DCE interface, then the reverse current peak which corresponds to the return of the ions into the film would have been proportional to the square root of the scan rate [9]. Furthermore, transfer of the highly charged and hydrophilic ferri/ferrocyanide ions into the DCE is unlikely due to the large Gibbs energy of transfer, and should occur only at negative potentials due to the high negative charge of the ferrocyanide ion. Therefore, the only remaining source of the observed Faradaic current is the reaction of ferricyanide at the gold electrode surface:



The large peak separation observed in the experiments is not due to the uncompensated ohmic potential drop in the organic phase, because in separate experiments, in which the organic supporting electrolyte concentration was increased from 10 to 50 mM, only a slight decrease in ΔE_p was observed. Since an electron must traverse the MUA layer during the reduction and oxidation processes, the observed peak potential separation probably reflects the sluggish kinetics of the surface redox reaction. For a seven layer film (thickness ca. 12 nm), the peak separation, ΔE_p , is almost 90 mV at a sweep rate of 5 mV s⁻¹. This agrees with the observations of Finklea et al. [10] in a similar system. As the number of layers increased, the measured ΔE_p was virtually constant within experimental error; for example, at 20 mV s⁻¹ ΔE_p values of 110, 112, 115 and 110 mV were obtained for films with 3, 7, 11 and 15 layers, respectively.

In general, the multilayer polypeptide films were very stable during the electrochemical measurements, i.e. both the reduction and oxidation peak currents and the shape of voltammogram were unchanged during repeated cycling over 30 min. PM-FTIR measurements also showed that the intensities of the ferri/ferrocyanide bands are virtually the same before and after potential scans, suggesting that there is no loss of redox ions to the organic phase. These results are expected due to the strong ionic interaction between $\text{Fe}(\text{CN})_6^{3-/4-}$ and the quaternary ammonium residues of pLys [10,11]. The high stability of the system may also be accounted for by the fact that the hydrophilic pLys/pGlu multilayer film protects the MUA monolayer from the organic solvent. However, when the multilayer film was much

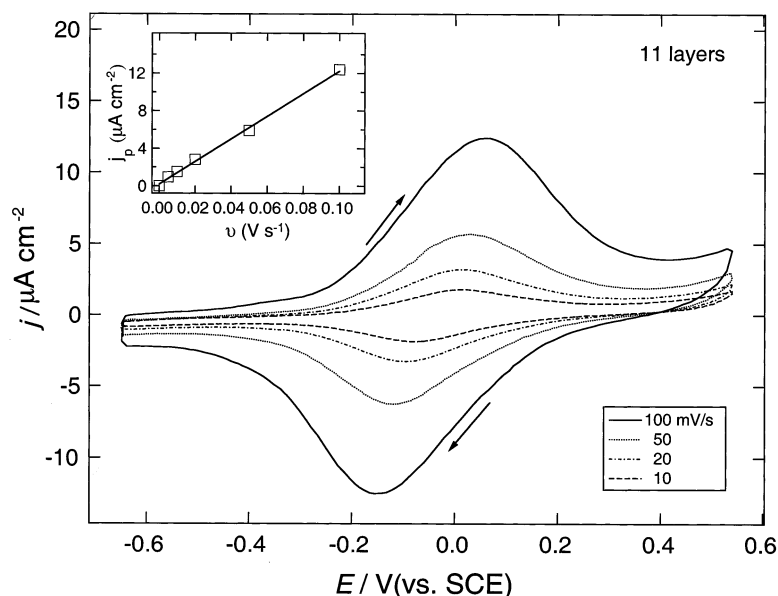


Fig. 2. Cyclic voltammograms of an 11 layer film obtained at scan rates of 10, 20, 50 and 100 mV s⁻¹ in the presence of bound ferri/ferrocyanide. Inset: oxidation peak current density (j_p) as a function of scan rate.

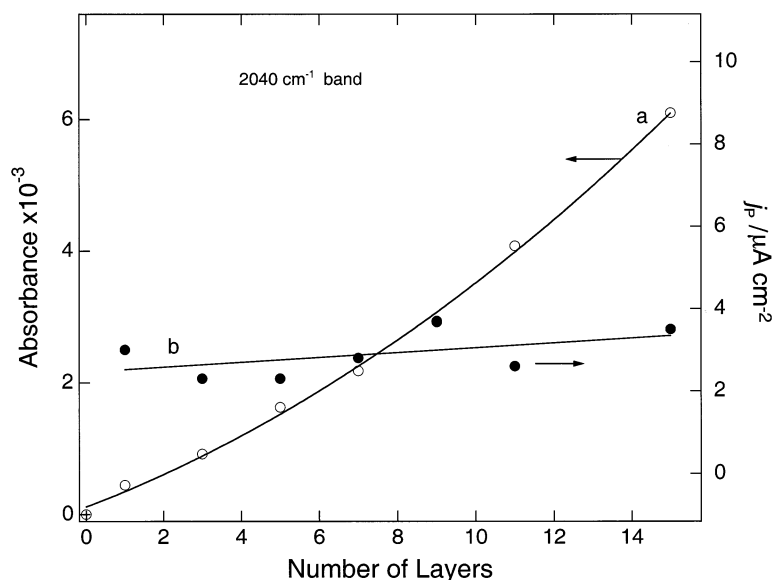


Fig. 3. Intensity (a) of the ferrocyanide band (2040 cm^{-1}) of ex-situ PM-FTIR spectra and (b) the oxidation peak current density (j_p) of ferrocyanide as a function of the number of the layers. The potential sweep rate used was 20 mV s^{-1} .

thinner, for example, with only one or three polypeptide layers, the cyclic voltammograms became unstable. Also, when the scan was extended beyond the potential limits in Fig. 2, the current increased rapidly because the organic electrolyte ions or solvent molecules penetrate the film and reach the electrode surface. These results are consistent with work reported previously in non-aqueous solvents concerning the electrochemistry of organothiol layers on the electrode surfaces. It has been observed that direct contact of alkanethiol monolayers with organic solvents in an electrochemical environment causes loss of thiol to the solution and disintegration of the film on the electrode surface [12,13].

A series of ex-situ and in-situ PM-FTIR experiments were performed in order to complement the electrochemical measurements. In Fig. 3, curve (a) shows a plot of the intensity of the ferrocyanide band at 2040 cm^{-1} (ex-situ measurements) as a function of the number of adsorbed polypeptide layers. As anticipated, the FTIR results show that the amount of adsorbed ferrocyanide increases with the number of layers. In contrast to the spectroscopic results, practically no significant effect on the peak current in cyclic voltammetry was observed with increasing number of polypeptide layers (curve (b) in Fig. 3). Only the half wave potential, $E_{1/2}$, shifted to more positive values with film thickness, indicating that the reaction had become more unfavorable thermodynamically. A set of potential step measurements (not shown) was performed where the potential was stepped from -400 to $+400\text{ mV}$. The resulting current decayed to less than $1\text{ }\mu\text{A}$ in ca. 5 s during which a charge of ca. $25\text{ }\mu\text{C cm}^{-2}$ was transferred, regardless of the thickness of the film. Further-

more, the current transient showed neither exponential nor Cottrell ($1/\sqrt{t}$) behavior. An exponential decay would be expected for the reaction of immobilized redox species, and Cottrell behavior for diffusing species [8,9].

To understand these results, additional experiments were performed on a film in which only one pLys layer was adsorbed on the MUA derivatized gold substrate. Although the film deteriorated rather quickly, the electrochemical response was very similar to the 11 layer film, i.e. the current peak in the two CVs had similar height, width and peak separation. Therefore it can be deduced that the electrochemical response observed in multilayer films during cyclic voltammetry corresponds to the oxidation of a small amount of ions which is approximately equal to that observed in a single pLys monolayer. From the electrochemistry, the concentration of ferrocyanide ions in this film can be estimated as ca. $2.6 \times 10^{-10}\text{ mol cm}^{-2}$, equivalent to ca. 0.13 M bulk concentration. This highlights the great affinity for the incorporation of ferrocyanide ions into the film due to electrostatic binding [11].

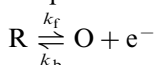
To resolve the contradiction between the electrochemical and spectroscopic responses in Fig. 3, in-situ PM-FTIR spectra were recorded during the oxidation of ferrocyanide in the polypeptide film. As can be seen in Fig. 4, the spectrum measured stepping the potential for 2 min , to the positive limit shows a 50% decrease in intensity of the ferrocyanide band. After about 20 min of electrolysis, the oxidation of ferrocyanide is almost completed. The remaining small band at $2050 \pm 5\text{ cm}^{-1}$ may be due to some different type of residual iron-cyanide complexes [10]. Hence, in our electrochemical experiments, only a small percentage of the ions in the

film are oxidized [14]. The results in Fig. 4 differ from those we reported previously [1], where the 2040 cm^{-1} band disappeared completely upon oxidation. This is due to the extremely long electrolysis times used in the first studies. Improved sensitivity of our PM-FTIR experiments now allow us to take spectra more rapidly.

It must be realized that the potential drop applied across the system is distributed across two interfaces, the electrode|film interface and the film|DCE interface, and the distribution probably evolves with time. This process is very difficult to study, but the linear dependence between the peak currents and the scan rate implies that the complementary process taking place at the film|DCE interface is not limiting the reaction rate of the ferri/ferrocyanide couple. Such a process could be, for example, rapid exchange of protons between the film and the DCE phase. Studies to understand the nature of the complementary reaction are underway.

3.2. Modeling of the cyclic voltammetry

In order to interpret the CV results obtained above, the kinetics for the reaction of an immobilized redox couple are considered. For a reaction given by



the current, I , is given by Eq. (1) as:

$$I = -nFA \frac{d\Gamma_R}{dt} = nFA \frac{d\Gamma_O}{dt} \quad (1)$$

In Eq. (1), F is Faraday's constant, A is the geometrical area of the electrode and Γ_R and Γ_O are the surface concentrations of the reduced and oxidized species, respectively. Since the species are immobilized on the

electrode, it follows that $\Gamma_R + \Gamma_O = \Gamma^0$, where Γ^0 is the total surface concentration of the species. Applying the Butler–Volmer relationship for the reaction kinetics, it follows that

$$I = nFAk^0[\Gamma_R \exp(\alpha n f(E - E^0)) - \Gamma_O \exp((\alpha - 1)n f(E - E^0))] \quad (2)$$

where k^0 is the standard rate constant (s^{-1}), α is the charge transfer coefficient, E is the potential and E^0 is the formal potential of the redox reaction; $f = F/RT$. The potential is swept linearly, i.e. $E = E_i + vt - 2vu(t - t_s)(t - t_s)$ where E_i is the initial potential, v is the sweep rate, t_s is the time at the switching potential, and $u(t - t_s)$ is the unit step function ($u = 0$ for $t \leq t_s$ and $u = 1$ for $t > t_s$). After some rearrangements, a differential equation is obtained by combining Eq. (1) with Eq. (2):

$$-\frac{dy}{dz} = K\theta_i^2[y \exp(\alpha[z - 2u(z - z_s)(z - z_s)]) - \theta_i^{-1}(1 - y) \exp((\alpha - 1)[z - 2u(z - z_s)(z - z_s)])] \quad (3)$$

where the following dimensionless quantities have been used:

$$y = \frac{\Gamma_R}{\Gamma^0}, \quad \theta_i = \exp(nf(E_i - E^0)); \quad z = at = nfv t; \quad K = \frac{k^0}{a} \quad (4)$$

where z_s corresponds to the switching potential of the sweep. Eq. (3) is solved by using the Matlab[®] fourth-order Runge–Kutta subroutine ODE45. Thus, knowing

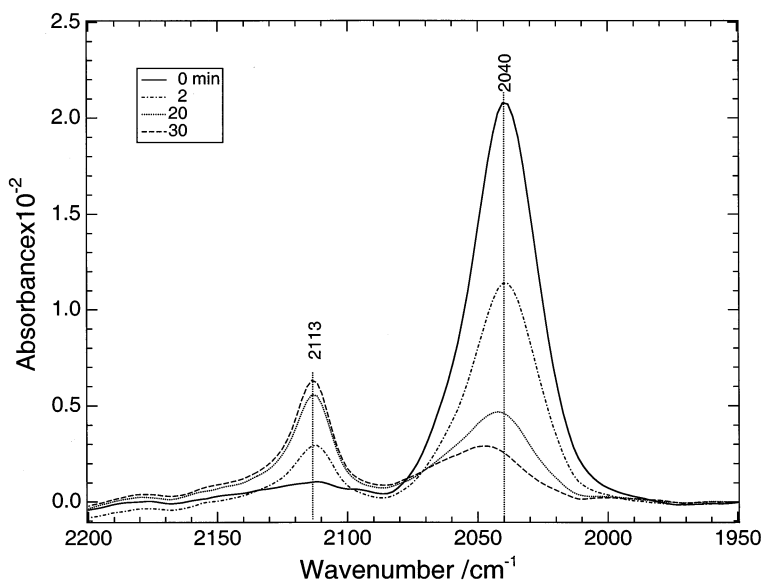


Fig. 4. In-situ PM-FTIR spectra of an 11 layer film showing the progress of the oxidation of bound ferrocyanide as a function of time. The applied potential was first held at -0.48 V and then switched to 0.67 V for different period of time as indicated.

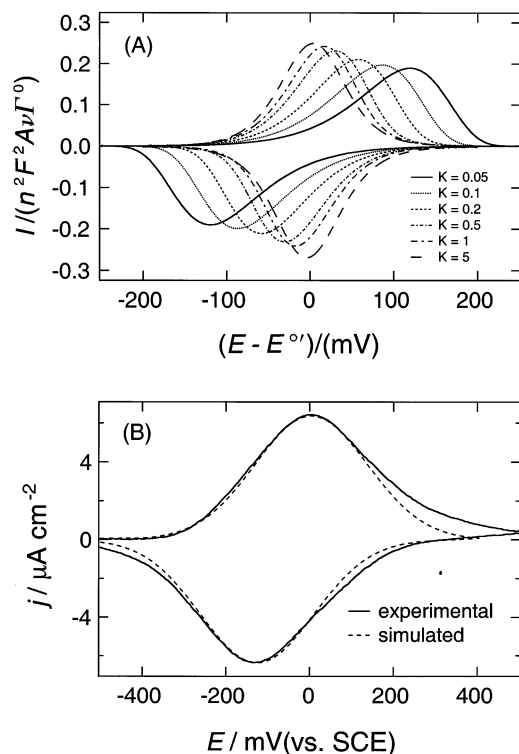


Fig. 5. (A) Simulated voltammograms with $\alpha = 0.5$, $n = 1$ and varying values of K . (B) Comparison of an experimental voltammogram (seven layer film with incorporated ferri/ferrocyanide ions) with a simulated curve considering a Gaussian distribution of the formal potential.

y , the current can also be calculated without numerical derivation from Eq. (3) as:

$$I = -\frac{n^2 F^2 A v \Gamma^0}{RT} \frac{dy}{dz} \quad (5)$$

In Fig. 5 simulated cyclic voltammograms with $\alpha = 0.5$ and $n = 1$ and with varying values of K are presented. By simply adjusting the value of K , it is possible to achieve the experimental peak potential separation (Fig. 5(A)). This gives an estimated $k^0 = 0.24 \text{ s}^{-1}$. The width of the simulated current peak does not correspond to the experimental one.

The current transient due to a reaction of an immobilized redox molecule following a potential step should decay exponentially, $I \sim \exp[-(k_r + k_b)t]$ where k_r and k_b are the electrochemical rate constants [8]. The fact that the observed decay was not exponential in the present system, i.e. not characterized by a single time constant, implies a distribution of time constants. In the literature, it is usually addressed to the distribution of the formal potential of the reaction due to double layer and ion-pairing effects [8,9,15]. Making an assumption that this distribution is a normalized Gaussian function,

$$f(E^o) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\left(\frac{E^o - \hat{E}^o}{\sqrt{2}\sigma}\right)^2\right] \quad (6)$$

the width of the current peak in Eq. (6) can be calculated (Fig. 5(B)). In Eq. (6), E^o is the formal potential of the reaction and \hat{E}^o is its average value, and σ^2 is the variance of the distribution [8]. With trial and error, an estimated $\sigma = 127 \text{ mV}$ was reasonable to fit the CV data. The distribution of the formal potential (σ) of the redox reaction explains the distribution of k_r and k_b but preserves the linear dependence of the peak current on the scan rate.

3.3. Electrocatalysis of decamethylferrocene

In a final set of experiments, the redox species DCMFc is added in the organic phase in order to observe an electrocatalytic reaction at the film | organic phase interface. Fig. 6 shows voltammograms of the DCMFc reaction at an electrode modified with a pLys/pGlu multilayer film. DCMFc does not undergo reaction without $\text{Fe}(\text{CN})_6^{3-/4-}$ in the film (curve (a)). When a film that contains ferri/ferrocyanide is placed in contact with an organic solution containing DCMFc, an irreversible wave (curve (b)) due to the DCMFc oxidation is observed in the CV with a peak potential of ca. -15 mV .

The anodic peak current observed in the CV (curve (b) in Fig. 6) is four to five times that observed in the absence of DCMFc. The anodic peak current from this CV is also linearly proportional to the DCMFc concentration and the square root of the scan rate. These observations suggest a diffusion controlled electrocatalysis of DCMFc by ferricyanide ions in the film. On the negative sweep, two current peaks are observed: a small peak at ca. -80 mV that is attributed to the reduction of $\text{Fe}(\text{III})$, and a broad peak at ca. -430 mV that is attributed to the reduction of DCMFc^+ .

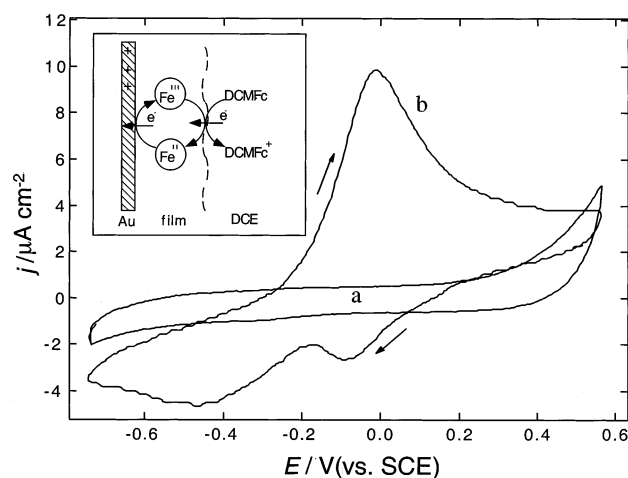


Fig. 6. CV of a 0.12 mM DCMFc + 0.01 M TBATPB DCE solution in contact with an 11 layer pLys/pGlu film that (a) did not contain and (b) contained ferri/ferrocyanide. Sweep rate was 20 mV s^{-1} .

The oxidation of DCMFc by the ferri/ferrocyanide couple confined in the film is highly irreversible. Similar irreversible behavior has been observed in a conventional two-phase electron transfer system involving the DCMFc redox couple [16]. It must be emphasized, however, that only the total potential drop across the electrode–film–organic phase system can be controlled, and the actual potential drop at the film|solution interface remains unknown. Therefore, the comparison of the peak potentials with those obtained in a conventional two phase system is not meaningful. The complete understanding of the various processes taking place at the film|organic solvent interface and their coupling with each other, both in the absence and presence of the redox couple in the organic phase, requires more experiments varying the electrolyte type and concentration.

4. Conclusions

In this paper we have demonstrated how a polypeptide multilayer thin film can be deposited on an alkanethiol derivatized gold electrode, and a novel type of an immiscible liquid|liquid interface (ITIES) can be formed between the film and an organic electrolyte solution (1,2-dichloroethane). Two type of ferri/ferrocyanide populations were observed: (i) a small ferrocyanide subpopulation corresponding to the approximate amount observed in one pLys monolayer that could undergo a rapid reduction and oxidation cycle and was responsible for the observed cyclic voltammetry; and (ii) a larger ferrocyanide population that could be converted to ferricyanide only by a much slower electrochemical process. Digital simulations give an estimate of 0.24 s^{-1} for the standard rate constant of the rapid redox reaction, and a broad Gaussian distribution ($\sigma \approx 130 \text{ mV}$) of the formal potential is needed to interpret the width of the current peaks in cyclic voltammetry.

In a second set of experiments, the ferri/ferrocyanide redox couples immobilized within the film were used as electron shuttles between the gold electrode and redox-active molecules DCMFc in the organic phase. The

anodic catalytic current observed in this system appeared to be controlled by the diffusion of DCMFc in the DCE. However, the highly irreversible nature of this process raises questions about how this electrocatalytic process is coupled with ion transfer across the film|solution interface, and what is the actual potential distribution across the three phase system; also the multilayer structure could lead to further complications. These questions will be addressed in a subsequent paper.

Acknowledgements

Y. Cheng and R. Corn acknowledge the National Science Foundation for financial support. L. Murtomäki acknowledges the Academy of Finland for a research position.

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