

Thin layer liquid-liquid interface based on self-assembled polyelectrolyte layers –the influence of the growth conditions on the electrochemical performance

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The use of micro-techniques (like droplets, microemulsions and supported thin liquid films) represents one of the recent trends in electrochemistry at the interface of two immiscible electrolyte solutions (ITIES). Supported liquid phase thin films are particularly interesting since they allow to use common three-electrode potentiostats. A convenient method to support ultra-thin hydrophilic films on metal electrodes described by, e.g. Descher et al.¹ or Corn et al.², is based on the self assembly polyelectrolyte multilayers. The polypeptides supported liquid-liquid interface can be additionally used as more realistic model system for the mimicking the processes relevant to biological membranes.

In this paper we focus on the effect of the deposition conditions on the characteristics of the poly-L-lysine/poly-L-glutamic acid multilayer films and their electrochemical performance at the interface with 1,2-dichloroethane (DCE). Polypeptide multilayer films were prepared by two modifications of layer by layer approach, (the substrate is alternately exposed to buffered solution of each polypeptide). In the first case the films were dried after each layer deposition. These films are further denoted as „dry“¹. In the second case we performed the deposition in a flow cell in which the buffered polypeptide solution was periodically exchanged, i.e. the films were not dried during deposition process. These films are further denoted as “wet”.

As show the quartz crystal microbalance (QCM) data, the deposition of the multilayer film results in monotonous increase of the mass with each polypeptide layer (see Fig. 1). The apparent mass of the films grown by “dry“ approach is significantly smaller than that observed for films grown by “wet“ approach. The QCM data, however, ought to be taken with care since the crystal impedance data indicate non-uniform change of the deposited film viscosity (see Fig. 2).

The ability of the ferro/ferricyanate doped films to act as the aqueous phase in the ITIES experiments depends on the ionic strength of the buffers used in deposition process. As can be shown on electron transfer reaction between ferro/ferricyanate incorporated in the polypeptide film and decamethylferrocene in DCE the electrochemical activity of the multilayer films is affected by the film thickness (see Fig. 3). The observed voltammograms indicate a pseudo-steady state character of electron transfer process. The applicability of polypeptide multi-layers to serve as advanced membrane models we examined on adsorption of 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC). The results show, that a bi-layer like systems are formed on the polypeptide film surfaces. According to the fluorescence microscopy data the interactions between adsorbed DOPC layer and polypeptide multilayer system are rather strong, which results in low DOPC molecule mobility.

Acknowledgement: This work was supported by the Grant Agency of the Academy of Sciences of the Czech

Republic under contract No. B4040305.

References

¹ G. Decher, *Science*, **277**, 1232 (1997)

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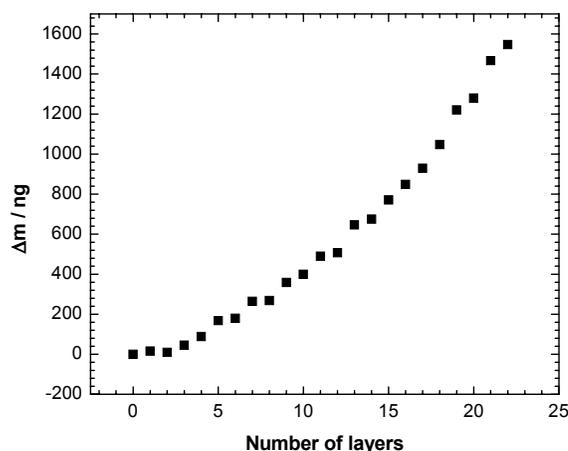


Fig. 1. Dependence of mass changes on number of layers during growth of polypeptide multilayer

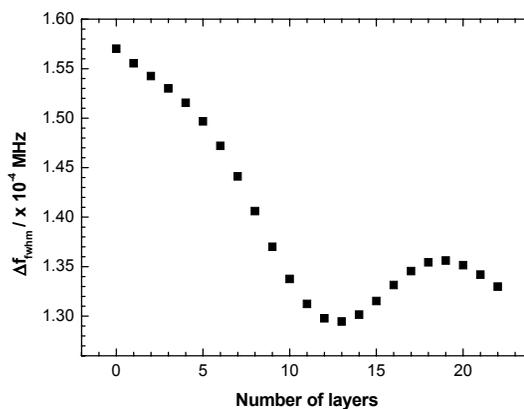


Fig. 2. Full width at half maximum of the crystal admittance peak as a function of number of layers.

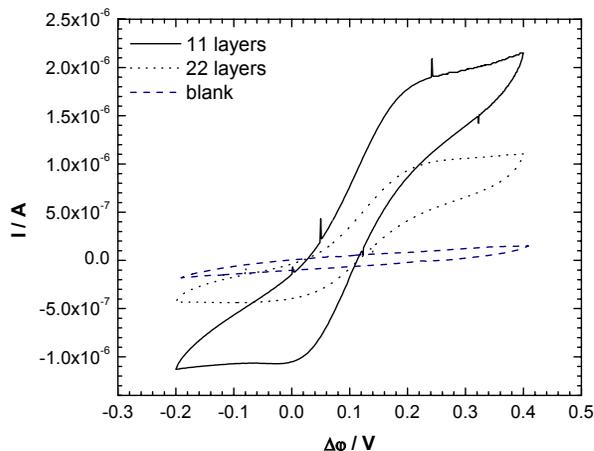


Fig. 3. Cyclic voltammograms of the electron transfer across DCE|polypeptide film for films of 11 (solid line) and 22 (dotted line) layers. Applied scan rate was 10 mV.s⁻¹.