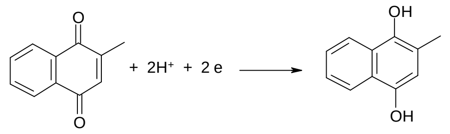
Cyclic Voltammetry and Scanning Electrochemical Microscopic Study of Menadione Permeability through Self-Assembled Monolayer on a Gold Electrode

Céline Cannes, Frédéric Kanoufi and Allen J. Bard
Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78312, USA and Laboratoire Environnement et Chimie Analytique, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

As menadione is a quinone involved in biological and physiological system, its redox behavior (eq 1) at monolayer modified gold electrodes was investigated by cyclic voltammetry (CV) and scanning electrochemical microscopy (SECM) for a better understanding of its behavior in biological environments.



menadione menadiol (1)

The monolayer was prepared by chemical adsorption of octadecanethiol ($C_{18}SH$) on a gold electrode surface. Cyclic voltammogram simulation, using a CEC mechanism, has shown that the monolayer was not free from pinholes and that the electron transfer for ferrocyanide, a hydrophilic compound, corresponds to oxidation at defect sites. However, the menadione cyclic voltammogram at the modified electrode could not be simulated by the same model, i.e. by using a CE_1E_2C mechanism (fig. 1). This difference was attributed to permeation of the menadione into the hydrophobic monolayer.

A simple one-electron transfer coupled to possible partitioning of the reactants between two phases can be described by the equations depicted in the figure 2. We have then applied this simple model, consisting of using a CE_1E_2C' mechanism, to explain menadione reduction at the $C_{18}SH$/Au electrode and to extract the rate constant of the kinetically limiting permeation step (fig. 1). As the menadione redox behavior is quite complex, this approach is simple and rough, but it is useful to obtain a qualitative analysis of the menadione reduction at the $C_{18}SH$/Au electrode. Thus, this technique allowed us to elucidate the mechanism of the menadione redox process at a gold electrode modified by a monolayer. It suggests loss of reduced species formed upon reduction of the menadione in the monolayer with increasing pH. This loss could be related to better affinity of this species for the aqueous phase (i.e. its rapid extraction out of the monolayer) or to its chemical decomposition in the monolayer.

A better estimate of the transport properties was obtained by SECM. Under the SECM conditions used, the redox process at the modified electrodes should be limited by mass transport through the monolayer rather than by the electron transfer. The apparent limiting heterogeneous rate constant obtained by simulation of the approach curves (fig. 3) should then correspond to the rate-limiting mass transport. Despite the crudeness of the CV simulation, the trends observed by both techniques are alike (fig. 4). The permeability is quite constant until pH 7 and decreases for pH values higher than 7. This could be attributed, as discussed earlier, to a smaller permeability of a quinonoid species or of a proton into the monolayer.

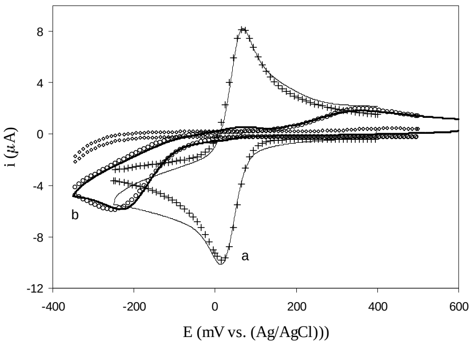


Figure 1 : Cyclic voltammograms (a) and (b) of menadione (0.2 mM) in phosphate buffer (pH = 2.9 ; = 0.2 M) at $v = 0.1$ V s^{-1} respectively at Au electrode (0.07 cm^2) and $C_{18}SH$/Au electrode. (+) : curve simulated with a E_1E_2 mechanism; (◊) curve simulating the pore effect, CE_1E_2C mechanism (O): curve simulating permeability with a CE_1E_2C' mechanism.

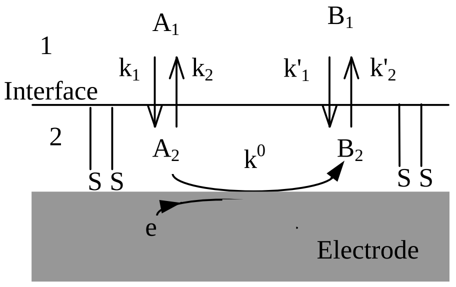


Figure 2 : Schematic representation of the partitioning of reactant A and B between phase 1 and 2.

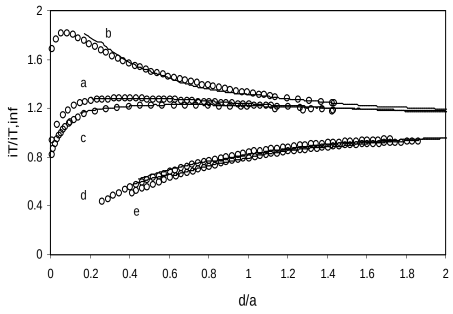


Figure 3 : Current-distance curves for a C tip (r = 7 μm) approaching a $C_{18}SH$/Au substrate in phosphate buffer solution (0.2 M) containing 0.2 mM menadione at pH = (a) 2.9 ; (b) 4.3 ; (c) 7 ; (d) 8 ; (e) 9.3. The tip scan rate was 1 μm s^{-1}. The solid lines correspond to the experimental curves and the dashed lines to SECM theory.

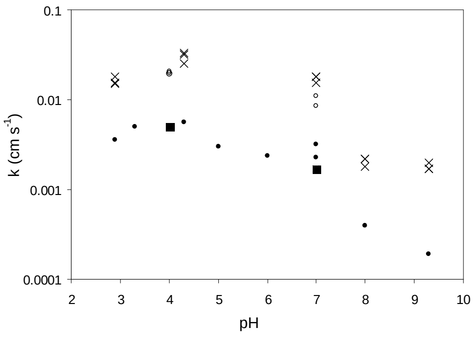


Figure 4 : Variation of the permeability with pH estimated by cyclic voltammetry ((•) and (■)) and by SECM ((×) and (O)) for a phosphate buffer solution containing menadione (0.2 mM ((•) and (×)) or menadiol 0.27 mM ((O) and (■))