

Impedance Studies of Alkanethiol-Coated Gold in Propylene Carbonate

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The preparation and characterization of self-assembled monolayers (SAMs) an important area in the study of well defined modified interfaces.

Despite the tremendous interest in applications using SAMs during the last several decades only scattered reports regarding the electrochemistry of immobilized electroactive adsorbates and electron transfer through the blocking films in nonaqueous solvents have appeared [1]. Attempts to use alkanethiol monolayers as barrier layers in nonaqueous solvents have for most part been unsuccessful, presumably because of low stability of the monolayer. This is unfortunate, since nonaqueous solvents usually allow one to work in a wider range of potentials compared to aqueous media. Many of the most interesting redox-active probe molecules that one might like to investigate at SAM-covered electrodes are incompatible with aqueous media, because of either solubility or chemical stability considerations.

It is known that the blocking of the approach of electroactive solutes forces electron transfer to occur over the relatively long distance across the monolayer; this is of fundamental interest with respect to the mechanism of long range electron transfer. Varying the solvent is an important strategy in this kind of research, since contemporary theory makes specific predictions regarding how such reactions should be affected by changes in solvent properties [2].

In this paper we present results of the studies of alkanethiol based SAMs on gold single crystal electrodes in propylene carbonate (PC) – an interesting and widely used solvent in electrochemistry. Cyclic voltammetry shows that these films are stable in PC with time and over a wide range of potentials (~2.0V). Integrity of the structure maybe still an open question and cannot be completely elucidated by cyclic voltammetry.

Electrochemical impedance spectroscopy (EIS) was chosen as a tool for our studies. EIS previously was shown to be an efficient method for studying blocking properties of SAM toward heterogeneous electron transfer [3].

Our current investigations show that immediate studies of electron-transfer through the SAM without knowledge of film integrity and its structure under particular experimental conditions may be confusing and can lead to misinterpretations of the data. We show how EIS can be used to deduce the properties of the SAM on gold prior to the introduction of the redox active species in the system.

Using the different graphical representations of the data in EIS helps one to see the response of the system in real time coordinates. This helps in constructing an electrical circuit equivalent to the chemical and physical changes and processes taking place in the studied interface.

The impact of different factors like solvent, supporting electrolyte, applied potential, temperature and the nature of the redox active species on the SAM structure are discussed. Behavior of the Au / SAM interface in the PC is demonstrated to be somewhat different from the equivalent aqueous system. Some

relevant examples are shown on Figure 1.

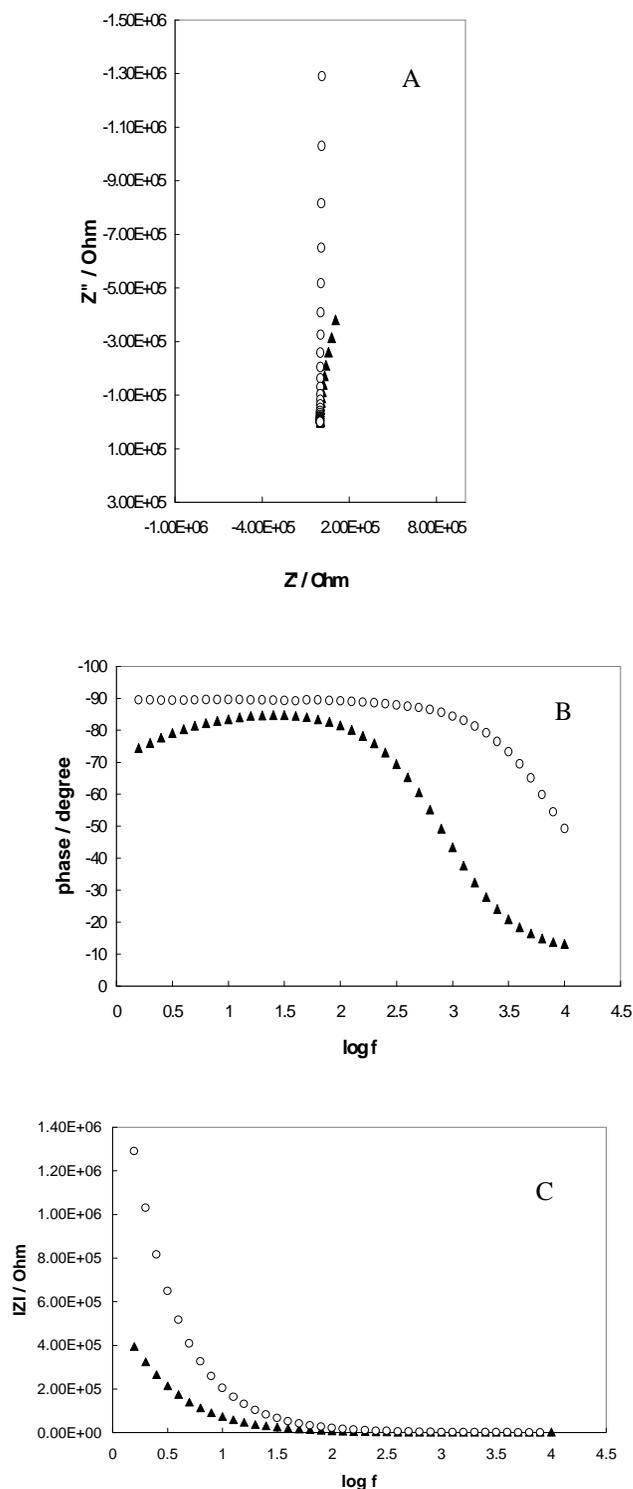


Figure 1. Nyquist (A) and Bode plots (B, C) for two interfaces Au/SAM (C16) in PC (▲) and Au/SAM (C16) in water (○). 0.1M NaClO₄ is used as supporting electrolyte. Spectra were taken at open circuit potential.

References:

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