

## ABSTRACT

### ELECTROCHEMICAL AND SPECTROSCOPIC STUDIES OF PYRIDINE SURFACTANTS AT THE GOLD-ELECTROLYTE INTERFACE

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Two *in situ* infrared spectroscopic methods have been developed with the purpose of their application for quantitative studies of the potential-induced changes in the orientation and conformation of molecules of ultrathin organic films adsorbed at Au surfaces. Then, (i) subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) was applied to study the dipole-field interactions of pyridine with an electrified Au(110) electrode surface while (ii) polarization modulation Fourier transform reflection absorption spectroscopy (PM FTIR RAS) was utilized to study the monolayers and bilayers of 4-pentadecylpyridine (C15-4Py) obtained at different stages of the transfer of this insoluble surfactant from the surface of the electrochemical cell to the electrode surface (*i.e.*, from the gas-solution (GS) interface to the metal-solution (MS) interface). Neutron reflectometry was utilized to determine the thickness and the structure of C15-4Py monolayers and bilayers while electrochemical methods (alternating current voltammetry and chronocoulometry) were applied to study kinetics of the C15-4Py transfer as well as the mechanism of the potential-induced phase transitions in the films adsorbed at the metal electrode.

SNIFTIRS studies of pyridine at Au(110) demonstrated that the electric field tends to orient pyridine molecules perpendicular to the metal surface while thermal motion prevents ordering. Electrochemical experiments demonstrated that the molecules of C15-4Py can move from the GS interface to the MS interface and spontaneously form a bilayer at the Au electrode surface. The transfer takes place regardless of whether the electrode is initially film-free or covered with a C15-4Py film deposited using the single horizontal touching (Langmuir-Schaefer) method. A nearly identical bilayer can also be deposited onto the electrode surface using the double horizontal touching technique. Studies of the transfer kinetics indicated that the crossing of the triple-phase line (the boundary of the GS, MS and gas-metal interfaces) by C15-4Py molecules is the rate-limiting step. Neutron reflectometry confirmed the monolayer state of the film, deposited using the single touching and the bilayer state of the film, produced by the double touching technique. Structural integrity of the C15-4Py bilayer was also indicated by this technique. PM FTIR RAS studies demonstrated that the bilayer remained in a fluid, liquid crystalline state in the whole range of applied potentials while the monolayer became condensed in a gel state at positive electrode polarizations. The outer leaflet of the bilayer was oriented with its pyridine moieties towards the solution and the inner leaflet was attached to gold *via* a nitrogen heteroatom. Both the monolayer and the bilayer displayed significant changes in orientation when the C15-4Py film was undergoing potential-induced adsorption and desorption. The concerted use of the complementary *in situ* surface analytical techniques demonstrated that C15-4Py is an excellent adhesive material for the fabrication of biomimetic membranes. In addition, this project demonstrated the feasibility of quantitative determination of the orientation of organic molecules in ultrathin films at metal electrodes inside an electrochemical cell.