ABSTRACT

ELECTROCHEMICAL STUDIES OF ADSORPTION OF INSOLUBLE PYRIDINE SURFACTANTS AND THEIR MIXTURES AT A GOLD(111) ELECTRODE.

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The adsorption of insoluble surfactants, 4-pentadecyl-pyridine (C15-4Py), 10-decyl-9-[2-(4-pyridyl)ethyl]antracene (DPEA), and their mixtures of 10 and 25 mol % DPEA in C15-4Py have been studied using cyclic voltammetry, cyclic ac voltammetry and chronocoulometry.

It was found that a monolayer of surfactants is transferred from the gas-solution (G/S) to the metal-solution (M/S) interface using the single horizontal touching method. This monolayer is unstable and transforms into a bilayer which has properties similar to the bilayer obtained by the double horizontal touching technique. Hence the equilibrium between surfactants at the G/S and at the M/S interfaces is established. Pure DPEA is more stable in the monolayer state suggesting that the transformation of a monolayer into a bilayer requires strong lateral interaction between the adsorbate molecules.

The following aspects of the mechanism of adsorption of insoluble pyridine surfactants were determined:

1. In surfactant bilayers, spontaneous transport of the molecules of the surfactant from the overlayer to the underlayer takes place upon the potential-induced reorientation of

the pyridine heads of the surfactants. The reverse process requires an activation energy and hence is shifted negatively with respect to that observed in the anodic scan. The activation energy and the reorientation rate is a function of the difference in the packing density of the surfactant underlayer before and after the reorientation.

2. Addition of DPEA to C15-4Py decreases the packing density of the adsorbed film resulting in the decrease of the activation energy and an increase in the rate of the reorientation of pyridine heads.

3. When desorbed, surfactants form micelle-like aggregates that can adsorb charged ions and experience electrostatic attraction to the oppositely charged electrode.