

## Adsorption of Pyridin-carboxylic Acids and Thiourea on Gold Electrodes

M. F. Mora, R. C. Arrúa, G. García and G. I. Lacconi

INFIQC, Depto. Fisicoquímica, Facultad de Ciencias Químicas. Universidad Nacional de Córdoba.  
Pab. Argentina, Cdad. Universitaria. (5000) Córdoba, Argentina.

Pyridin-carboxylic acids (nicotinic, NA, picolinic, PA, and isonicotinic, IA) as well as thiourea (TU) are used as addition agents in metal plating baths [1, 2] and may thus modify the electrodeposition processes. Since these molecules are usually strongly adsorbed on many metal surfaces and they are able to form complex species it is interesting to obtain detailed information on the adsorption processes.

The structure of adsorbate layers during silver or copper electrodeposition in the presence of thiourea and pyridin-carboxylic acids has been studied by means of vibrational spectroscopy [3, 4]. In these studies the activation of the surface for SERS-measurements was the metal electrodeposition process itself in the presence of these molecules. The in-situ surface spectra show that the adsorption of TU occurs via the sulfur atom while in the adsorption of NA or PA both functional groups (pyridine and carboxylic) are coordinated to the metal surface.

In this communication we present a comprehensive quantitative analysis of the adsorption of TU, NA and PA onto polycrystalline gold electrodes through differential capacity measurements and chronocoulometry. The thermodynamic data for the adsorption of these additives lead to a better understanding of the mechanism of the metal electrodeposition process.

The differential capacity measurements were carried out on polycrystalline gold electrodes in 0.1M KClO<sub>4</sub> solutions in the presence of TU, NA or PA in the 1x10<sup>-5</sup> to 1x10<sup>-3</sup> M concentration range. The solutions were carefully deoxygenated with purified nitrogen. The working electrode was a polycrystalline gold disc mechanically polished with a slurry of alumina. All potentials are referred to a saturated calomel electrode (SCE).

Before recording the capacity curves and chronocoulometric pulses, cyclic voltammetry was performed with the purpose of purity control and qualitative characterization of the surface processes. The presence of the organic molecules influence the anodic gold behaviour, i.e. an anodic current caused by the oxidative decomposition of TU at electrode potentials significantly below the anodic gold oxide formation is noticed.

The C-E curves obtained in presence of TU show a minimum shifted to negative potentials relative to the base solutions. The potential range applicable during the chronocoulometric measurements is limited by the oxidation of TU and the hydrogen evolution. In the case of pyridin-carboxylic acids the potential of zero charge determined from the position of the diffuse layer minimum on the C-E curve in 0.1M KClO<sub>4</sub> is 0.1V. The differential capacity measurements allow us to determine

the potential and concentration range in which NA is adsorbed on the gold surface. At a potential of -0.8 V NA (1x10<sup>-3</sup>M) is totally desorbed. The NA adsorption studies were restricted to the -0.8 V to +0.7V potential region.

The sequence of the different steps involved in the data acquisition and processing for the desorption step experiments is based on the Lipkowsky's studies of pyridine adsorption on gold electrodes [5].

The corresponding current-time transients were integrated digitally to obtain the charge-time transients. For the base electrolyte and for solutions containing either TU or NA (PA), the  $\Delta\sigma$ -t curves display a well defined plateau where the charge is virtually independent of time over the whole potential range investigated. The absolute charge densities  $\sigma$  were obtained from  $\Delta\sigma$  values.

The dependence of the interfacial tension with potential determined from the integration of the  $\sigma$ -E curves, show the characteristic parabolic shape and is strongly dependent on the bulk NA concentration. The film pressure calculated do not show the typical bell shape usually observed for the adsorption of neutral organic molecules. The fairly large values of  $\pi$  obtained indicate a large Gibbs energy of adsorption.

Finally, the values of the relative Gibbs surface excess as a function of the electrode potential for the various NA concentrations investigated were calculated and used to find the nature of the adsorption isotherms.

### REFERENCES

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