

KINETICS OF CHEMISORPTION OF EtX^- IONS AND MULTILAYER FILM GROWTH ON Cu, Pb, AND Hg

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Interactions of surface active agents with metals and semiconductors have attracted a considerable interest of researchers in such fields as modified electrodes, photocatalysis, mineral flotation, hydrometallurgy, and corrosion protection [1-4]. In this paper, interactions of xanthates (O-alkyl dithiocarbonates) with different metal surfaces will be discussed.

Self-assembling monolayers of ethyl xanthate ions (EtX^-) on copper, lead, and mercury electrodes were investigated. Although, in general, the adsorption data can be fitted using a Frumkin adsorption isotherm [2], rather considerable deviations are observed in both the low θ and high θ regions. The physically viable Flory-Huggins adsorption model (with 4 water molecules displaced by one EtX^- ion), even with Parsons modifications accounting for lateral interactions, is not suitable for metal-xanthate systems. It is likely that a second monolayer of metal xanthate begins to form before completion of the first monolayer, thus complicating the adsorption isotherm. This is especially well seen for CuEtX films showing a clear asymmetry of the θ - E isotherm. In order to exclude the effect of the second layer formation, the kinetic data for lower coverage range ($\theta < 0.5$) were employed to determine kinetic parameters of EtX^- chemisorption processes.

Kinetics of EtX^- chemisorption on metal electrodes was investigated by following the apparent mass changes of the respective metal piezoelectrodes using the Electrochemical Quartz Crystal Nanobalance (EQCN) technique. We have found that the chemisorption rate increases with metal substrate in the order: Cu < Pb < Hg. The anodic charge-transfer coefficient for the formation of $\text{CuEtX}_{(\text{ad})}$ is: $\alpha_{\text{an}} = 0.18$ and it increases to $\alpha_{\text{an}} = 0.47$, for $\text{Hg}_2(\text{EtX})_{2(\text{ad})}$.

At higher anodic overvoltages, multilayer metal xanthate films can be grown and the growth kinetics can be followed using the EQCN technique. We propose a new molecular model for CuEtX monolayers on Cu substrate, which takes into account recent results of surface Raman

spectroscopy, electroreflectance, and EQCN investigations, as well as the results of wetting angle measurements and flotability.

In the potential-step piezogravimetric experiments, we have found that at each anodic overpotential the film ceases to grow at sufficiently long deposition time t (usually, $t > 200$ s). Also, the final film thickness strongly depends on the applied overpotential. These two observations are characteristic of an electric field-driven film growth process. We have determined the potential drop per monolayer in a multi-layer CuEtX film as equal to $b^* = 27$ mV/ML. The anodic charge-transfer coefficient for the formation of a multi-layer CuEtX film is higher than that for a sub-monolayer adsorption and approaches $\alpha_{\text{an}} = 0.77$. The cathodic overpotential for film stripping depends strongly on the conditions of film deposition and, especially, on the film thickness. The growth rate of multilayer metal xanthate films follows the order: Cu < Pb < Hg.

Further increase of anodic overvoltage results in the formation of dixanthogen [1]. The EQCN resonant frequency shifts become dependent on the actual CuEtX film thickness, electrode potential, and hydrophobic effects which are due to CuEtX clustering and resulting surface inhomogeneity.

References

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