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STRUCTURE AND ELECTROCHEMICAL REACTIVITY OF Si-ORGANIC COMPOUNDS MONOLAYERS ADSORBED ON SILVER SURFACE

Abstract. In this paper, the results of the research onthe structure and electrochemical reactivity of silicon-organic compounds monolayers adsorbed on the silver surfaceare given. The compact siloxane films, bringing about inhibiting effect on the electroreduction of propylene carbonate as well as Li deposition on the Ag electrode, have been obtained with 3-[Tris(2-methoxyethoxy)silyl]-propanethiol (SiCC). We also obtained 4,7-diazaheptyl-trimethoxy-silane (SiNN) and vinyl-trialkoxy-silane (SiDD), which could be also interesting in view of corrosion prevention. The results of a study on the behaviour of these compounds on the silver surface are presented. The structures of SiCC, SiNN and SiDD and these complexes with cations on the Ag surface were calculated and visualized by the AM1d semi-empirical method. The structures of the SICC, SINN and SIDD molecules and their complexes in solution and after the adsorption process on silver are discussed. Some of semi-empirical calculated HOF (heat of formation) values for uncomplexed and complexed species and the differences between them (ΔHOF) are calculated by PM5 method. These values indicate the formation of 1:1 complexes of SiDD with Li^+ cation and 1:7–8 of SiNN with Li^+ cations. The respective calculations ΔHOF on the assumption that these molecules are bonded by the coordinative interactions between the Ag surface and the electron lone pair at ω N atom of SiDD or the π electrons of the vinyl group of SiNN resulted in the negative ΔHOF values and demonstrating that this kind of interactions is very probable. The calculated distances between the Ag atoms from the surface and the respective coordinating N atom or vinyl group in SiDD and SiNN molecules are 2.35 and 2.50 Å, respectively.Silver immersion into SiCC, SiNN and SiDD solutions in PC leads to the formation of well-ordered and electrochemically inactive self-assembled monolayers. The AM1d calculations suggest that the SiCC, SiNN and SiDD molecules are physically adsorbed with the silver surface atoms.

Keywords: Self-assembled monolayers, silicon-organic compounds,electrochemical activity, silverelectrode surface, adsorption.

Introduction

Organosilicon chemistry is based on the fact that although the energy of Si-O and Si-C bonds is similar to that of their purely organic counterparts, these bonds are longer and more polarized, which makes them more flexible in terms of physical and chemical properties [1-3].

The steric hindrance and, therefore, barrier for rotation is far lower in a siloxane backbone than in a carbon chain, which implies higher gas permeability, lower melting points and glass transition temperatures along with a wider range of solubility observed for siloxanes [4]. At the same time, the electronegativity of silicon atom (1.90, Pauling) is sufficiently low for the siloxane bridge to be cleaved in alkaline and highly acidic conditions [5]. Condensation of resulting silanol moieties, Si-OH, is the basis for obtaining a whole class of siliceous materials, from cost-effective amorphous silica gels, to specifically tailored silica nanoparticles (e.g. Stober silica)[6], to periodic mesoporous organosilicas (PMOs) [7]. All of those can be easily further functionalized. Taking advantage of the aforementioned reactivity of the polarized Si-O bond, one can graft specific organic moieties on the surface of a resilient, non-toxic and well-defined matrix, very often with a large surface area [8].