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B. Łęska [1], A. Tukibayeva [2], N. Kalieva [3]

[1]Adam Mickiewicz University in Poznan, Poland;
[2]M. Auezov South Kazakhstan state university, Shymkent, Kazakhstan;
[3]Kh.A.Yassawi Kazakh-Turkish International University, Kazakhstan
e-mail: ainur_tukibaeva@mail.ru

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].

Silica-based materials are commonly used in the laboratory and frequently synthesized for purposes like separation [9], extraction [10], controlled drug release [11], templating [12], sensing [13], powder-type emulsions stabilization [14], heterogeneous catalysis [15] and many others. Siloxanes, however, are mainly encountered in polymer science, and the usefulness of smaller compounds comprising siloxane bridges remains fairly unexplored, with few notable exceptions in supramolecular chemistry of metal complexes [16-18].

Considerable attention has been drawn during the last few decades to modify noble metal surfaces by forming ordered organic films of few nanometers to several hundred nanometers thickness [19–22]. One of the simplest means of forming these ultrathin films is by the mere immersion of the noble metal surface in a dilute solution (mM) of the organic molecule at ambient conditions and this unimolecular organic film is popularly known as self-assembled monolayers (SAM). Indeed, SAM formation provides one easy route towards surface functionalisation by organic molecules (both aliphatic and aromatic) containing suitable functional groups like –SH, –CN, –COOH, $–NH_2$ and silanes on selected metallic (Au, Cu, Ag, Pd, Pt, Hg and C) as well as semiconducting surfaces (Si, GaAs, indium coated tin oxide etc.) [23]. These type of SAM modified surfaces are highly useful for investigating several fundamental phenomena such as distance dependent electron transfer [24], mechanism of single electron transfer [25], observation of molecular event such as Coulomb staircase [26] etc. on artificially designed nanostructures.

Due to the highlyordered nature and tight packing, these monolayers on metallic surfaces are also important for several practical applications such as chemical sensing, control of surface properties like wettability and friction corrosion protection, patterning, semi-conductor passivation, and optical second harmonic generation [19].

Molecular engineering is an interdisciplinary area where supramolecular systems are designed capable of electronic operations like switching, gating, rectification, amplification etc. The primary objective is to design and synthesize suitable building blocks with novel and potentially useful electronic properties. Aside from organizing interesting molecules in two dimensions, development of nanotechnology also needs suitable size functional building blocks to continue the fabrication of nanoarchitectures. Colloidal particles or clusters of metal and semiconductors are immensely suitable as building blocks to tailor these types of nanodevices due to their unique optical [27] and electronic properties [28]. Flexibility in functionalizing the terminal groups of SAM-modified surfaces allows the build-up of nanoarchitectures with these nanoparticles. If a single molecule can serve as a switch or a logic device its size allows the utilization of about 10^{13} units/cm^2 compared to the presently used level of 10^8 units/cm^2. For memory applications, “one bit per molecule” can give unprecedented storage density along with the other attendant advantages of size reduction. SAM is a simple way to organize 10^{13} molecules/cm^2 and hence is immensely suitable for achieving these objectives [29]. In addition, improved response time and low power, as observed in systems of biological electron transfer, are other benefits.

The word SAM generally denotes a monomolecular thick film of organic compounds on flat (i.e., two-dimensional) metal or semiconductor surfaces. SAM formation providesone of the easiest ways to obtain ordered monolayers through strong chemisorptionsbetween the substrate head group of a desired compound and the metal surface leading tothe preparation of thermodynamically stable monolayers [20-22] as compared to LB(Langmuir–Blodgett) and other techniques, where only physisorbed, thermally unstablemono/multilayer films are obtained. Several studies show that long-chain alkane thiols(containing more than six to seven methylene units) form more well-ordered defect-freemonolayers than short-chain alkane thiols, disulphides or sulphides. Aromatic (pi systemslike benzene, naphthalene or diphenylene systems) or/and hydrogen-bonded moleculeswith multiple contacts, containing functional groups like thiols, amines, sulphides,selenides etc. provide improved stability [19].

One of the important advantages of SAM is that they can be prepared in the laboratoryby simply dipping the desired substrate in the required millimolar solution for a specifiedtime followed by thorough washing with the same solvent and drying, often using a jet ofdry argon. Gas-phase evaporation of the adsorbant can also form good monolayers,although structural control is difficult. Several factors affect the formation and packingdensity of monolayers, like nature and roughness of substrate, solvent used, nature of theadsorbate, temperature, concentration of adsorbate etc. Cleanliness and crystallinity of the substrate also play a crucial role in determining the compactness, often quantitativelyestimated by the pinhole distribution.

Electrochemical techniques like cyclic voltammetry (CV) [30], and impedancemeasurements [31, 32] are easy techniques for monitoring monolayer characteristics. Theseelectrochemical studies also provide useful information about the distribution of defectslike pinholes, redox property of attached groups (ferrocene, ruthenium bipyridine, andsimple bipyridine molecules), kinetics and mechanism of monolayer formation,quantitative estimate of coverage etc.

In this article, we describe the results of a study on the behaviour of compounds of SiCC, SiNN and SiDD and these complexes with lithium cations in solution and after the adsorption process on the silver surface.

Methods

SiCC was synthesized by trans-esterification reaction in benzene of 3-(trimethoxysilyl)-propanethiol with ethanol or ethylene glycol monomethylether and traces of dibuthyltin oxide as a catalyst in benzene as solvent.

The obtained product was purified by vacuum distillation. The purity of the product was controlled by ^{1}H NMR spectroscopy. 3-(trimethoxysilyl)-propanethiol was used as commercial product (Aldrich) after vacuum distillation. The 4,7-diazaheptyl-trimethoxy-silane (SiNN) and vinyl-trialkoxy-silane (SiDD) were commercial products of ABCR Gelest and were used without any purifications. The purity of the products were controlled by ^{1}H NMR spectroscopy.

The electrolyte solutions for electrochemical measurements were made using propylene carbonate (PC) from Merck purified by fractional distillation in dry argon atmosphere and dried over 4 Å molecular lithium sieves. $LiClO_4$ (Aldrich) was dried in a vacuum oven below its melting point.

Adsorption procedure

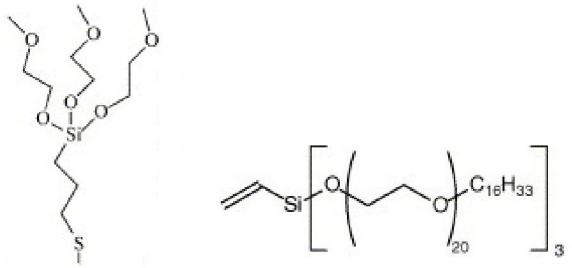
Silver strips (99.999%) were polished with aluminium slurries (Buehler) of successively decreasing final grades (down to 0.05 μm) on polishing cloths (Buehler), rinsed carefully with a dry solvent (acetonitrile or propylene carbonate). The 3-(trimethoxysilyl)-propanethiol, SICC, SINN and SIDDadsorbates were formed on the silver strips both from the liquid thiol compounds and from their acetonitrile or propylene carbonate (PC) solutions (0.2 M). After taking out from the liquid phase, the adsorbates were rinsed with a pure and dried solvent (acetonitrile or propylene carbonate) and allowed to dry 12 h in the water free argon atmosphere. Furthermore, the surface layer was subsequently subjected to hydrolysis and condensation by immersing the SICC modified sample in water for 12 h.

FT-IR spectroscopy

The reflection-absorption spectra for 3-(trimethoxysilyl)-propanethiol, SiCC, SiNN and SiDD adsorbates on smooth silver strips were obtained in an N2 atmosphere on a Brucker 113 V FT-IR spectrometer with an FT-80 grazing angle infrared reflection accessory and a liquid N_2 cooled TGS detector. Typically, 2000 scans with 1 cm^{-1} resolution were performed. Additionally, for comparison, the transmission FT-IR spectra of the thiol substrates were recorded on the same spectrometer.

Results and discussion

The formulae of these molecules are given in Fig 1. [33].

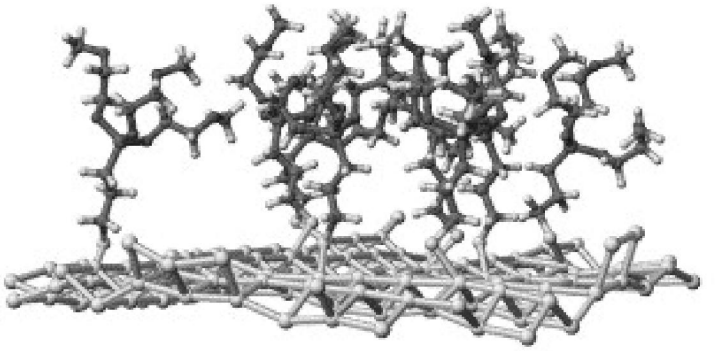


SiCCSiNN

SiDD

Figure 1 - The formulae of 3-[Tris(2-methoxyethoxy)silyl]-propanethiol (SiCC), 4,7-diazaheptyl-trimethoxy-silane (SiNN) and vinyl-trialkoxy-silane (SiDD)

AM1d and PM5 semi-empirical calculations. **Semi-empirical AM1d and PM5 calculations of the structures of non-adsorbed and adsorbed SiCC, SiNN and SiDD molecules as well as their complexes with Li^+ cations and maximum surface packing densitywere made using the WinMopac program (Figs. 2-5).**



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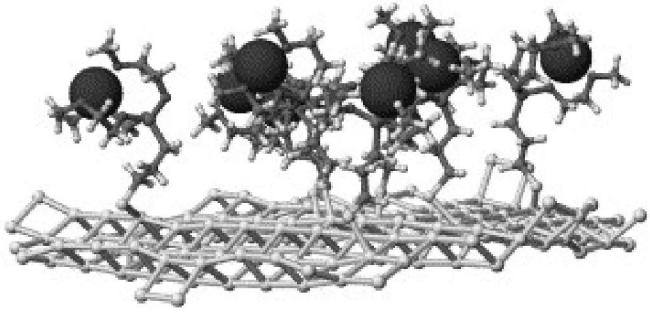
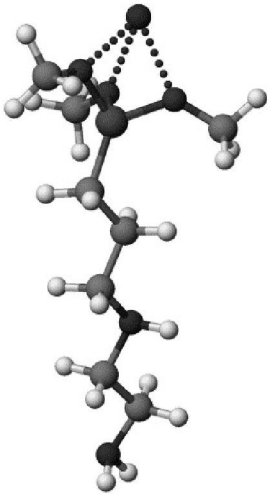


b)

Figure 2 - The structure of the surface layer with 60% of maximum packing density of SiCC molecules on Ag; (a) without Li^+ cations and (b) with Li^+ cations.



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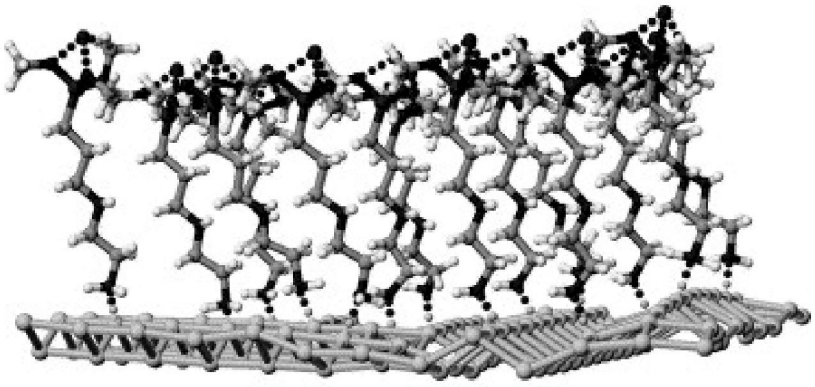

b)

Figure 3 - a) The structure of the complex of SiNN with Li^+ cation; b) The structure of the surface layer of SiNN complexed with Li^+ on Ag with 68.6% of maximum packing

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 results obtained for the SiNN molecule are well comparable with the experimental ΔH data as well as the number of complexed Li^+ cations reported previously [34-35].

The visualization of the representative favourable structures of 1:1 and 1:7 respective complexes are shown in Figs. 3a and 4. The Li^+ cation in the structure of the 1:1 complex of SiDD is coordinated by the oxygen atoms of the methoxy groups. In the structure of SiNNcomplexes the first Li^+ cation is coordinated by the oxygen atoms neighboring the silicon atom and every other cation is localized at a maximal distance from the others. This is visualized in the structure of 1:7 complex of SiNN with Li^+ cations given in Fig. 4.

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.

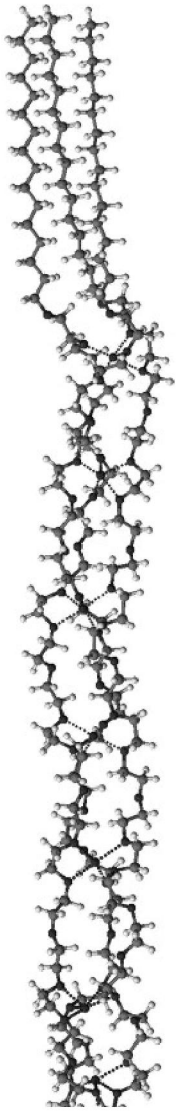

Figure4 - The structure of the 1:7 complex of SiDD with Li^+ cations.

On the basis of the AM1d calculations, the area per one adsorbed molecule in a densely packed layer of SiDD and SiNN with the long oxaalkyl chains in an almost perpendicular orientation with respect to the electrode surface was found to be 0.268 and 0.40 nm^2, respectively. The surface concentration of 3.73×10^{14} molecules per cm^2 for SiDD and 2.50×10^{14} molecules per cm^2 for SiNN at a saturation coverage of the silver surface.

Further calculations were performed for surfaces with about 60% of the maximum packing density. On such assumption, the distribution of SiDD or SiNN molecules on the Ag surface has more or less statistical character. The molecules adsorbed are able to form complexes with Li^+ cations comparable to those discussed above for free molecules. The respective structures of the monolayers on the silver surfaces of non-complexed SiNN molecules and of complexed with Li^+ cations SiDD molecules are shown in Figs. 3 b and 5.

The other calculations were performed for surfaces with 60% of maximum packing density. On this assumption, the distribution of SiCC molecules on the Ag surface has more or less statistical character (Fig. 2a), but the Fig. 2b shows the structure of the same model after complexation of Li^+ cations. The calculations suggest that Li^+ cations are bonded in a favorable way within each molecule between the oxaalkyl chains.

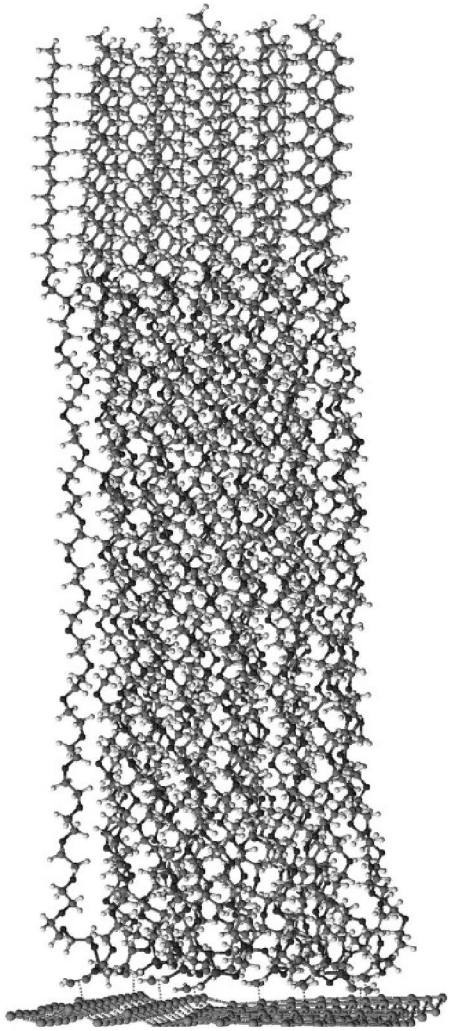

Figure 5 - The structure of the surface layer of SiDD on Ag with 58.0% of maximum packing density.

Conclusions

Silver immersion into SiCC, SiNN and SiDD solutions in PC leads to 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. The SiCC, SiNN and SiDD species alone and after adsorption on the Ag surface form complexes with Li^+ cations, coordinated by oxygen atoms of the oxaalkyl chains.

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Б. Леска [1], А. Тукибаева [2], Н. Калиева [3]

[1]Познаньдағы Адама Мицкевич Университеті, Польша;
[2]М.Ауезов атындағы Оңтүстік Қазақстан Мемлекеттік университеті, Шымкент;
[3]Қ.А.Яссауи атындағы Халықаралық қазақ-түрік университеті, Түркістан

КҮМІСТІҢ БЕТІНДЕ АДСОРБЦИЯЛАНҒАН SI-ОРГАНИКАЛЫҚ ҚОСЫЛЫСТАР МОНОҚАБАТТАРЫНЫҢ ҚҰРЫЛЫМЫ ЖӘНЕ ЭЛЕКТРОХИМИЯЛЫҚ РЕАКЦИЯЛЫҚ ҚАБІЛЕТТЕРІ

Аннотация. Ұсынылып отырған жұмыстакүмістің бетінде адсорбцияланған Si-органикалық қосылыстар моноқабаттарының құрылымы және электрохимиялық реакциялық қабілеттерін зерттеу нәтижелері келтірілген. Пропиленкарбонаттың тотықсыздануына, сондай-ақ, күміс электродының бетіне литийдің тұнуына ингибирлеуші әсер ететін компактылы силоксанды жабындар 3- [Трис (2-метоксиэтокси) силил]-пропантиол (SICC) көмегімен алынды. Сондай-ақ, қазіргі таңда коррозияны алдын алу бойыншша қызы-ғушылық туғызатын 4,7-диазагептил-

триметоксисилан (SINN) және винилтрикоксисилан (SIDD) алынды. Жұмыста осы қосылыстардың күміс бетіндегі электрохмиялық қасиеттері зерттеу нәтижелері келтірілген. SICC, SINNжәне SIDD құрылымдары және күміс бетіндегі катиондармен комплекстері жартылай эмпирикалық тәсілменAM1d есептелді және нақтыланды.SICC, SINNжәне SIDD және олардың комплекстері молекулаларының ерітіндідегі және Ag бетінде адсорбцияланған кейінгі құрылымдары талқыланды.

Комплекстелмеген және комплекстелген түрлері және олардың арасындағы айырымы (ΔHOF) үшін жартылай эмпирикалық есептелген HOF (түзілу жылулары) шамаларының кейбірі PM5 тәсілімен есептелді. Бұл мәндер 1: 1 Li^+катионыменSiDDжәне 1: 7-8 Li^+катиондарымен SiNN комплекстерінің түзілетіндігін көрсетеді. ΔHOF сәйкес есептеулері көрсеткендей, осы молекулалар беткі қабаттағы күміс пен SiDD-дағы ωN атомындағы электрон жұбының арасындағы координациялық байланыспен немесе SiNN-дағы винилді топтың πэлектрондарымен байланысқан, ΔHOF теріс мәндеріне әкелді және осы әрекеттесудің өте ықтимал екендігін көрсетті.Беттік қабаттағы күмісатомы мен сәйкес келетін N атомы немесе SiDD и SiNN молекулаларындағы винильді топтың арасындағы есептелген ара қашықтық сәйкесінше 2,35 және 2,50 Å құрайды. Пропиленкарбонаттағы SiCC, SiNN и SiDD ерітінділеріне күмісті батыру, жақсы реттелген және электрохимиялық активті емес өздігінен ұйымдасатын моноқабаттардың түзілуіне әкеледі. AM1d есептеу-лері, SiCC, SiNN және SiDD молекулалары беттік қабаттағы күміс атомдарымен физикалық адсорбция-ланады.

Түйін сөздер:өздігінен жинақталатын моноқабаттар, кремнийорганикалық қосылыстар, электрохимия-лық белсенділік, күміс электродының беттік қабаты, адсорбция

Б. Леска [1], А. Тукибаева [2], Н.Калиева [3]

[1]Университет Адама Мицкевича в Познани, Польша;
[2]Южно-Казахстанский государственный университет им.М.Ауезова, Шымкент;
[3]Казахско-турецкий международный университет им.Х.а.Ясави, Туркестан

СТРУКТУРА И ЭЛЕКТРОХИМИЧЕСКАЯ РЕАКЦИОННАЯ СПОСОБНОСТЬ МОНОСЛОЕВ SI-ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ, АДСОРБИРОВАННЫХ НА ПОВЕРХНОСТИ СЕРЕБРА

Аннотация. В данной статье даны результаты по исследованию структуры и электрохимической реакционной способности монослоев кремнийорганических соединений, адсорбированных на поверхности серебра. Компактные силоксановые пленки, вызывающие ингибирующее воздействие на электровосстановление пропиленкарбоната, а также осаждение Li на серебряном электроде, были получены с 3- [Трис (2-метоксиэтокси) силил] пропантиолом (SICC). Нами также получены4,7-диазагептил-триметоксисилан (SINN) и винилтрикоксисилана (SIDD), которые могут быть интересны с точки зрения предотвращения коррозии. В работе представлены результаты исследовании электрохимического поведения этих соединений на поверхности серебра. Были рассчитаны и визуализированы структуры SICC, SINN и SIDD и их комплексы с катионами на поверхности серебра полуэмпирическим методом AM1d. Обсуждены структуры молекул SiCC, SINN и SIDD и их комплексов в растворе и после процесса адсорбции на Ag. Некоторые из полуэмпирических вычисленных величин HOF (теплоты образования) для некомплексных и комплексных видов и различий между ними (ΔHOF) расчитаны PM5 методом. Эти значения показывают образования 1: 1 комплексов SiDD с катионом Li^+ и 1: 7-8 SiNN с катионами Li^+.Соответствующие расчеты ΔHOF в предположении, что эти молекулы связаны посредством координационных взаимодействий между поверхностью Ag и электронно-одиночной парой на атоме ωN SiDD или π-электронами виниловой группы SiNN, привели к отрицательным значениям ΔHOF и показали, что этот вид взаимодействия весьма вероятен.Рассчитанные расстояния между атомами Ag с поверхности и соответствующей координирующий N атомом или винильной группой в SiDDи SiNN молекулах составляют 2,35 и 2,50 Å, соответственно. Погружение серебра в растворыSiCC, SiNN и SiDD в пропиленкарбонате приводит к образованию хорошо упорядоченных и электрохимически неактивных самоорганизующихся монослоев. Расчеты AM1d показывают, что молекулы SiCC, SiNN и SiDD физически адсорбируются атомами серебра поверхности.

Ключевые слова:самоорганизующиеся монослои, кремнийорганические соединения, электрохимическая активность, поверхность серебряного электрода, адсорбция

Information about authors:

ŁęskaBogusława – Dc.Sc., professor of department of Chemistry, Adam Mickiewicz University in Poznan (Poland),e-mail: bogunial@amu.edu.pl;

TukibayevaAinur – candidate of Chemistry, associate professor, department of Chemistry, M.Auezov South Kazakhstan State University, e-mail: ainur_tukibaeva@mail.ru;

KalievaNurzia– master of Sc., senior teacherof the Department of Preventative medicine, Kh. A.Yassawi Kazakh-Turkish University, e-mail: nur_2773@mail.ru.