Preparation, Investigation and Application of Self-Assembling, Langmuir–Blodgett, and Dip-Coated Nanolayers

PhD thesis booklet

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Introduction and goals

In the thesis, three types of wet nanolayer fabrication techniques are presented: self-assembly, Langmuir–Blodgett, and dip-coating. In all three methods, the building blocks of the prepared layers are organic molecules.

In 2006, I joined a research group having long tradition and remarkable results in the field of wet nanolayer fabrication, study, and application in corrosion inhibition and against microbial attachment. During this time, I participated in two international research projects working on nanolayers. The basic research character of the first project allowed the clarification of some theoretical questions of the nanolayer fabrication. The goal was to study and to compare Langmuir films of several long alkyl chained carboxylic, hydroxamic, phosphonic and chiral amino acid derivatives, to review the factors influencing the formation of the films, and to sort out the optimal compounds and experimental conditions for the preparation of Langmuir–Blodgett (LB) layers. The second project dealt with various aspects of the microbiological corrosion, and was driven by a strong industrial interest. During this project, besides the copper used as model metal, I worked out layer preparation methods for the surface protection of the industrially more important and special two copper alloys (aluminium brass and copper–nickel), as well as stainless steel 304. The literature of self-assembled and LB layers prepared on the two copper alloys is rather scarce, therefore one of the main questions to answer in this project was whether our layers, layer preparation techniques already functioning on the pure metals (copper, iron) are suitable for the protection of these alloys, too? With regard to the possibility of the industrial application, an important question was whether these layers are stable in aqueous environment? Besides the self-assembled monolayers and LB layers, the preparation, characterization and application of more resistant, more robust polymer nanolayers was also a goal. For this purpose, polystyrene was chosen as a model compound, but I also participated in the preparation of PEO–PPO–PEO block-copolymer coating.

In both the corrosion and the microbiological experiments, simplified model systems, which allow the formulation of exact conclusions, and more complex systems, better approaching the industrial circumstances, have been applied. Therefore corrosion experiments were carried out in both 0.5 M NaCl solution and in artificial seawater, and with respect to the microbiological experiments, I worked with both the monoculture of a microbiological corrosion representative species of the sulfate-reducer bacteria, Desulfovibrio alaskensis, and with microorganisms of mixed population of real industrial cooling water.
Experimental and calculation methods

The self-assembled monolayers (SAM) and LB layers were prepared of different long alkyl chained compounds (carboxylic, hydroxamic and phosphonic acids). Langmuir films of $N$-alkanoyl amino acids and $\alpha$-alkyl amino acid derivatives were also studied. The dip-coated layers were prepared of polystyrene (PS) solutions.

The substrates for SAM layers were copper, aluminium brass, copper–nickel 70/30, and stainless steel 304. The LB layers were prepared on copper, mica, and glass substrates. The dip-coated PS layers were prepared on all metal/alloy substrates, and also on silicon wafer with a native oxide layer.

The chemical composition of the substrate surfaces has been determined by X-ray photoelectron spectroscopy (XPS), the surface roughness by atomic force microscope (AFM), and the wettability by contact angle measurements. The changes of these parameters occurring as a result of the different surface treatment steps have also been followed.

The Langmuir films of the different amphiphilic compounds formed on identical or different subphases were studied in a Langmuir–Blodgett trough equipped with a Wilhelmy-type surface pressure sensor and a Brewster angle microscope (BAM). Langmuir films were compared based on their $A_c$ és $A_0$ molecular areas, $\Pi_c$ collapse pressures and $C_s^{-1}$ compression moduli. The effect of the following factors on the formation/structure/properties of Langmuir films has been studied: 1) functional group; 2) alkyl chain length; 3) presence of double bond; 4) composition of the subphase; 5) temperature.

The presence of SAM and PS layers has been confirmed by contact angle measurements and reflection-absorption infrared spectroscopy (RAIRS). The stability of the different SAM layers in aqueous environment has been studied and compared by contact angle measurements, RAIRS, and sum frequency generation spectroscopy (SFG). The degree of order in the alkyl chains of the LB films has also been studied by SFG. The effect of the octadecyl phosphonic acid (OPA) SAM layer on the protein adsorption inhibitor efficiency of a PEO–PPO–PEO layer has been studied by quartz crystal microbalance (QCM), XPS, and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

The thickness of the PS coatings has been estimated from the Landau–Levich–Derjaguin equation, but also determined by both ellipsometer and AFM. The equilibrium contact angles of the layers have been calculated from the measured advancing and receding contact angles by applying Tadmor’s equation. The surface free energies have been calculated from the obtained equilibrium contact angles by applying Neumann’s equation of state. The surface coverage of the PS-chains was calculated from the equilibrium contact angles using the Cassie–Baxter equation.
The anticorrosion efficiency of the layers has been studied in 0.5 M NaCl solution as well as in artificial seawater. The extent of corrosion has been quantified by AFM analysis of the formed pits and by ICP-OES measurements of the metal ion dissolution.

The inhibition effect of the layers against bacterial adhesion has been studied by AFM and EFM, in both mixed population microorganisms of real industrial cooling water, and *D. alaskensis* monoculture. Acridine orange and 4',6-diamidino-2-phenylindole (DAPI) have been used as fluorescent dyes. The work with *D. alaskensis* has been carried out in an oxygen-free environment in a microbiological laboratory.

**Results**

First, the factors influencing the efficiency of layer fabrication have been studied, ones being related to the surface of the solid substrates, while others to the film-forming compounds.

The existing protocol of copper substrate polishing/buffing has been modified, so that about 50% time saving was achieved by the same final result (surface roughness).

Based on a literature reference, a nitric acid–hydrogen peroxide pre-treatment of the copper–nickel and aluminium brass substrates has been introduced, which allowed the regeneration of the oxide layer with unknown history in controlled circumstances. As a result of the pre-treatment, the surface roughness of the samples decreased. In addition, the advancing, receding and equilibrium contact angles, as well as the contact angle hysteresis decreased, that is more wettable, more hydrophilic, and energetically more uniform surfaces have been obtained. Such pre-treatment is important, because it enhances the bonding ability of the functional groups of the film-forming compounds to the substrate.

Langmuir films of carboxylic and hydroxamic acids, *N*-alkanoyl amino acids and *α*-alkyl amino acid derivatives have been compared based on several aspects, such as: functional group, alkyl chain length, presence of double bond, composition of subphase, temperature.

The collapse pressure of the Langmuir-films of compounds with the same functional group, but longer chain length, was higher. The characteristic molecular areas of the hydroxamic acid Langmuir films were larger than those of the corresponding carboxylic acid films, which fact can be explained by the size and geometry differences between the two functional groups, and the resulting orientation differences of the respective alkyl chains. The presence of double bond(s) in the molecular structure of the film-forming compound gave the Langmuir films a less or-
ganized, fluid-like character along with quasi-collapse (gradual crinkling instead of sudden collapse) occurring at small surface pressure values, and large molecular areas. The effect of temperature on the isotherms of oleic and elaidic acid Langmuir films was smaller than on the isotherms of the corresponding hydroxamic acids’ films. In the case of hydroxamic acids, at higher temperatures the curves shifted towards larger molecular areas and larger surface pressures.

Among the studied N-palmitoyl amino acid Langmuir films, the ones of the Ala and Ser derivatives showed nearly identical molecular area and collapse pressure values, presumably due to the similarities of the molecular structures. The Langmuir film of the Glu derivative exhibited larger characteristic molecular area and lower collapse pressure. The largest molecular area and smallest collapse pressure was measured in the case of the Phe derivative. The above established order correlates unequivocally with the size of the base amino acid (Ala ≈ Ser < Glu < Phe) and indicates that with increasing size, due to the increasing space requirement of the molecules, the degree of order of the Langmuir film becomes smaller and smaller. Therefore, good quality (compact, ordered structure) LB films become increasingly harder to prepare.

Among the Langmuir films of the α-alkyl amino acid derivatives, the behaviour of the ones with free carboxylic functional group was closer to ideal than the behaviour of the ones with esterified carboxylic functional group (more mobile, uniformly spreading film, higher collapse pressures, higher compression moduli, and smaller molecular areas measured on identical subphases), the former ones thus being more suitable for the preparation of LB coatings than the latter ones. The presence of Cu(II) ions in the subphase resulted in more compact and rigid Langmuir films in the case of both compounds, presumably due to the formation of ionic or coordinative bonds. Among the several different amino acids dissolved into the subphase, some of these compacted, while others expanded the Langmuir films.

By studying, by SFG, the degree of order in the one and five-layered LB films of carboxylic and hydroxamic acids deposited onto mica and glass, it has been proven that in the case of saturated compounds the alkyl chains in the top layer are ordered, densely packed, and thus more suitable for the protection of the solid substrates’ surface. Contrarily, the top layer of LB films in the analogue compounds of identical chain length, but bearing a double bond in the middle of their molecular structure proved to be less ordered, and thus less suitable for the protection. This lower degree of order can be attributed to the larger space requirement of the double bond and, consequently, the restricted van der Waals-interaction between the hydrophobic chains of the molecules.

Eighteen carbon atoms long, saturated carboxylic, hydroxamic, and phosphonic acid SAM layers have been prepared on the surface of copper, two types of copper
alloys (aluminium brass and copper–nickel 70/30), as well as stainless steel 304. The presence of the formed layers has been confirmed by contact angle measurements. By RAIRS and SFG, it has been proven that these layers are stable in aqueous environment, and that the stability of the layers is enhanced by prolonging the duration of preparation. It has been shown that the octadecylphosphonic acid SAM can be used as an adhesion layer to anchor a PEO–PPO–PEO triblock copolymer onto the surface of titanium and stainless steel, and that the application of such an adhesion layer significantly increases the efficiency of the polymer coating of inhibiting the adsorption of different proteins.

The thickness of the dip-coated PS layers was 50–700 nm. The thickness values measured by two independent methods and also calculated showed very good agreement. The film thickness could be controlled by the adjustment of the PS concentration. With increasing concentration, not only the layer thickness, but also the advancing, receding, and equilibrium contact angles increased, the contact angle hysteresis decreased, the surface free energy decreased, and the calculated surface coverage increased. All these observations indicate that by increasing the PS concentration not only thicker, but also denser films can be prepared, which are more suitable for the protection of the metal/alloy samples.

A possible dual practical application of the prepared SAM, LB, and dip-coated nanolayers against electrochemical and microbiological corrosion has been demonstrated. It has been shown, by AFM and ICP-OES results, that these nanolayers inhibit the corrosion of copper, and the copper alloys in 0.5 M NaCl solution and artificial seawater. The SAM and LB layers most effective against corrosion were the layers of those saturated compounds, for which 1) small molecular areas, high collapse pressures and high compression moduli have been measured in the corresponding Langmuir film; 2) the degree of order of the alkyl chains was high; 3) the measured water contact angles were high. The corrosion inhibition efficiency of the dip-coated PS layers increased with increasing layer thickness and surface coverage. The nanolayers inhibited the adhesion of microorganisms and the biofilm formation, as confirmed by AFM and EFM studies in experiments involving both a monoculture of *D. alaskensis*, as well as mixed population of microorganisms from industrial cooling water.
Thesis points

1. As a result of the microbiological experiments it has been found that the SAM and LB layers of the studied carboxylic and hydroxamic acids, as well as the dip-coated PS layers efficiently inhibited the microbial attachment and the biofilm formation on copper, aluminium brass, copper–nickel 70/30, and stainless steel 304. The inhibitor effect is explained in terms of decreasing surface free energy of the metals/alloys [1, 5].

2. Two wetting measurement methods, sessile drop and Wilhelmy-type, have been compared on three alloy types undergoing a multistep surface modification process, and it has been found that the two methods are equally suitable for following up the individual stages of surface modification [2].

3. The SAM layer of octadecylphosphonic acid (OPA) increases the efficiency of a PEO–PPO–PEO protective layer of inhibiting protein adsorption. The role of OPA SAM layer can be explained by the fact that the middle, hydrophobic PPO block of the PEO–PPO–PEO triblock copolymer can form stronger interaction with the likewise hydrophobic alkyl chains of the OPA SAM layer than with the surface of the bare metal/alloy. Through the PPO blocks, the polymer molecules can thus be anchored more firmly to an OPA SAM layer than to the metal/alloy surface itself, while the hydrophilic PEO blocks, far from the surface, conformationally-entropically inhibit more efficiently the adsorption of different model proteins [3].

4. A method has been worked out for the preparation of protective nanolayers, resistant in aqueous environment, on the surface of aluminium brass, copper–nickel 70/30 and stainless steel 304 [4].

5. Comparing the Langmuir films and Langmuir–Blodgett layers of saturated and unsaturated carboxylic and hydroxamic acids, it has been proved that the degree of order in the Langmuir film, set by the molecular structure of the film forming amphiphilic compounds, is conserved in the Langmuir–Blodgett layers obtained by transferring these Langmuir films onto solid substrates. Furthermore, the protective efficiency of these Langmuir–Blodgett layers against corrosion and microbial adhesion increases with increasing degree of order of the Langmuir–Blodgett layers, and that of the starting Langmuir films [5].
6. A relation has been demonstrated between the changes of contact angles of the protective nanolayers, measured by the Wilhelmy method, and the stability of these nanolayers in aqueous environment. Based on this relation, the stability of a nanolayer exposed to an aqueous environment can be studied and quantified by Wilhelmy-type contact angle measurements, both in situ and ex situ [6].

7. It has been shown that, by the addition of different compounds into the sub-phase, the packing of molecules in the Langmuir films of α-alkyl amino acids can be made closer. By the addition of copper(II) ions, the molecular areas in the Langmuir films become smaller, which fact indicates closer packing. The explanation of closer packing is that the metal ions in the subphase are able to form coordinative bounds with the heteroatoms of the functional head groups. By the addition of certain amino acids, the molecular areas of the Langmuir films also decrease, the collapse pressures increase, and the compression moduli increase, all these facts indicating that the added compound induces closer packing. This closer packing can be explained in terms of the ability of head groups of the film-forming molecules to form hydrogen bridges and/or dipole–dipole interactions with the dissolved amino acid molecules.
Application possibilities

The copper–nickel 70/30 and aluminium brass samples used in the experiments came from cooling circuits’ condenser tubes of power plants operating with seawater. Although these two special alloys have been developed not only for their high heat transfer coefficient, but also for their good corrosion resistance against dissolved ions, as well as good antifouling properties against microorganisms occurring in seawater, the microbiological corrosion of these tubes is still a problem. The biofouling reduces the heat transfer capacity of the tubes, in extreme cases these being clogged up so heavily that the whole system must be shut down and the tubes manually cleaned. The localized corrosion processes starting up under the deposit can result in the pitting of the tubes. Similarly, the stainless steel samples used came from freshwater conduits. Although in freshwater the corrosion of the stainless steel is almost negligible, its biofouling becomes important. Namely, among the three alloys, the stainless steel is the most susceptible to biofouling (as it contains the least copper, toxic for the microorganisms). At present, the only cost-effective solution to the problem is the chlorination of the water. The effect of chlorine (more precisely, chlorine dioxide), as well as the hypobromite generated from the seawater, is dual: on the one hand, it kills the microbes; on the other hand, it passivates the inner surface of the tubes. However, chlorine is highly toxic to the aquatic world, and the amount of chlorine in seawater is controlled by strict regulations.

The nanolayers presented in the thesis proved to be efficient against corrosion of important industrial alloys in artificial seawater. Furthermore, these nanolayers efficiently inhibit the attachment of microbes found in real industrial cooling water, as well as that of the sulfate-reducing, microbiological corrosion-causing bacteria \textit{D. alaskensis}. The presented work is a contribution to the field of more cost-effective and environmentally friendly protection against the microbiological corrosion, inasmuch as both SAM and dip-coated nanolayers can be realized in industrial scale.
Publications

The thesis is based on the following journal articles and conference proceeding paper

   Links: DOI, WoS, Scopus, REAL

   Links: DOI, WoS, Scopus, Full text

   Links: DOI, WoS, Scopus, Full text, REAL

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Other journal article

   Links: DOI, WoS, Scopus
Link: DOI
Links to the book: Other URL, Amazon, Google books

Other conference proceeding papers

Link: Scopus

Link to the proceedings: OSZK


Oral presentations


32. Románszki L, Nitrogén-halogenidek, Báthory Napok, Cluj-Napoca, Romania, 17 Apr. 1998
Poster presentations


