Abstract of Ph.D. thesis

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MODIFICATION OF SOLID SURFACES WITH LANGMUIR-BLODGETT FILMS: NANOLAYERS IN CORROSION PROTECTION

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INTRODUCTION

A quarter of the world's annual metal production goes to waste due to corrosion. This direct damage is merely to the applied metallic materials. There is far exceeding cost which due to the indirect damages, in production, service delays, manufactured product contamination, accidents, environmental hazards, etc., due to machinery and equipment malfunctions. It is for this reason that corrosion protection is of major importance in the field of industrial research and development.

Metal and non-metal structures can be damaged by the presence of bacterial proliferation on their surfaces. Modest estimates place the microbiological induced corrosion damage at 20% of the total corrosion damage in the world. The development and adoption of various past and present corrosion protection technologies have hindered the corrosion damages, however they are still considerable.

The degree of corrosion can be decreased in various ways, from the adequate planning and construction of equipments, through the proper choice of materials and the use of inhibitors and coatings. One of the main endeavors of the last decade has been to treat the surface of materials in such a way as to modify their surface properties.

The intention was always there increase the life span of metals by avoiding the application of water-soluble additives. This can be achieved by forming novel mono- and multilayer molecular layers on metal surfaces. Protective molecular layers can be deposited on metal surfaces either self-assembling molecules or the Langmuir-Blodgett technique. Self-assembling molecules spontaneously form self-assembled molecular layers (SAMs) while Langmuir-Blodgett technique is a method of forming molecular surface films in highly controllable way. The formation of a stable, packed, continuous mono-molecular layers make it a suitable candidate for corrosion protection application. With well chosen compounds metal surfaces can be coated with stable protecting film. These types of research have considerable environmental importance as well, since it can lead to replacement of traditional techniques and thereby decreasing the synthetic chemical burden on our environment.

AIMS AND SCOPES

The aim of this dissertation is to lay the foundation for the application of the Langmuir-Blodgett (LB) technique in corrosion protection by studying the LB layer's properties of corrosion resistance to chemical and microbiological corrosion.

In my studies I used long-chained hydroxamic acids and phosphonic acid compounds. Previously, at our department corrosion, inhibitor compounds with similar functional groups have been intensively studied, however these were low molecular weight, water-soluble compounds. In my research work, long alkyl chain compounds with the above mentioned functional groups were used in order to study their nanolayer forming capability as Langmuir-Blodgett films and compare their effectiveness and applicability in corrosion inhibition with respect to water soluble corrosion inhibitors.

Throughout the experimental work the optimum parameters for layer formation with the chosen compounds I investigated first, then the properties of the layers on glass and metal (copper and Armco iron) surfaces. The molecular structure, homogeneity, molecular conformation and molecular associations in the layers formed on the solid surfaces were determined using various experimental methods. I studied the surface orientations and the specific surface interactions. Reasons for deviation in properties of the condensed phases were determined when ever observed. These experiments made it possible to highlight new functional groups that can be used in the future for applicable chemical and microbiological corrosion protection uses.

SUMMARY

The modification of metal surfaces using nanolayers besides the traditional inhibition methods provides a corrosion inhibition technique with a decreased environmental burden.

Hydroxamic acid and phosphonic acid layers on solid surfaces formed with the Langmuir-Blodgett (LB) surface modifying technique were investigated. The interaction between the molecules and the solid surface was also determined. The molecular structuring of the layers, their homogeneity were clarified and their anticorrosion effect to both chemical and microbiological corrosion was determined with various methods.

NEW FINDINGS AND RESULTS OF THE DISSERTATION:

1. To form stable Langmuir layers on solid substrate surfaces firstly a dense and well organized LB layer must be prepared on an air/water surface. Langmuir monolayers formed on air/water surfaces of hexadecanoyl- and octadecanoyl hydroxamic acid, octadecyl phosphonic acid compounds I studied at various pH and temperature values, using their isotherms and Brewster angle microscope. The following I determined:

- With both types of compounds both the pH and the temperature effect the stability of the monolayers on ultra pure water sub-phase. At acidic and basic pH values the molecules occupy a larger surface area, which is due to the extent of ionization and in, parallel with this the interaction between the molecular main groups and their alkyl chains.
- The shorter the alkyl chains of the studied compounds the less effect the pH of the sub-phase had on the monolayer structure.
- In the case of octadecyl phosphonic acid at basic pH values the solubility of the molecules increased. Therefore in pH range Lagmuir monolayers could not be formed.
- With the increase of the sub-phase temperature the main groups of the studied compounds required more space and the collapse occurred at a lower pressure. This phenomenon at the air/water interface is determined by the various molecular interaction forces (electrostatic repulsion, H-bonds, van der Waals forces).

2. From the results of the Lagmuir-films studies an optimal pH and temperature (pH=5,6; T=23^{0}C) I determined to prepare LB monolayers and multilayers on solid substrates (glass, copper, Armco iron) using octadecanoyl hydroxamic acid and octadecyl phosphonic acid. Those layers quality were also determined with various measurements. Accordingly the results are:

- XPS measurements showed that before an LB layer is formed on metal substrate surfaces a mixed metal oxide organic impurities cover the metal surface. In the case of the iron substrate the iron oxide composition is Fe_2O_3 (3,3–3,5nm), in the case of copper there is a Cu_2O (3,5–4,0nm) phase with slight quantities of Cu(II) which suggests the presence of hydroxide. Neither the thickness nor the composition of the mixed layer on the surface of the metal substrates changes when immersed in the ultra pure water sub-phase. The LB layers do not, or just negligibly, remove the mixed impurities. The octadecanoyl hydroxamic acid and the octadecyl phosphonic acid molecules bind to the surface of the metal substrates following a condensation reaction with a water molecule resulting, which is proven by the fact that the main groups are deprotonated and in the case of copper the surface hydroxide partly disappear.

- With contact angle measurements I determined that the surface of the solid substrates becomes hydrophobic after the LB layer has been applied.
- Sum frequency vibrational spectroscopy was applied to study the orderliness and homogeneity of the prepared layers. I determined that the alkyl chains of both the detergents used to form the LB monolayers are close to right angles to the – glass, Armco iron and copper substrate - surfaces and all are in *all-trans* conformation.
- With infrared spectroscopic measurements I determined that in the case of 3–11 layers the octadecanoyl hydroxamic acid and the octadecyl phosphonic acid molecules stand at 20^0 angles to the normal of the surface. From the CH3 groups CH binding energies it can be concluded that the monolayers that form the LB film are ordered Y-type.
- The atomic force microscope measurements allowed me to conclude that independent from the substrate material both types of LB monolayers have two dimensional oblique structures.

3. The LB monolayers formed with octadecanoyl hydroxamic acid and the octadecyl phosphonic were tested using electrochemical dc and ac measurements. The following was determined:

- In neutral ClO_4^- containing solution the LB monolayer effectively inhibited the dissolving of Armco iron; the high inhibition efficiency of both type LB layers is due to their blocking effect. By comparing the corrosion inhibition of the two different main group containing LB layers I determined that the detergent with the smaller main group and larger surface density octadecanoyl hydroxamic acid monolayer was a more effective corrosion inhibitor that the octadecyl phosphonic acid monolayer.
- With copper substrates, in sulfate containing acidic solutions the hydroxamic monolayer by increasing the carbon atoms in the alkyl chain the corrosion inhibitive effect was enhanced. It is also determined that from the same alkyl chain with different head groups containing

hydroxamic acid and phosphonic LB monolayers the N-containing octadecanoyl hydroxamic acid LB layers are more effective.

4. Microbiological methods were also applied to test the LB monolayers formed with octadecanoyl hydroxamic acid and the octadecyl phosphonic acid. New results were produced:

- With a mixed population of microorganisms found in cooling water I found that both the octadecanoyl hydroxamic acid and the octadecyl phosphonic acid LB layers inhibited the sticking of these microbes to the substrates.
- In the case of Gram-negative bacteria isolated from cooling water I found that on glass and copper both type of compounds LB layers effectively inhibited the biofilms forming, whereas on Armco iron just octadecyl phosphonic acid LB layers inhibited the microbes sticking.
- In the case of *Acidithiobacillus ferrooxidans* microorganisms the octadecanoyl hydroxamic acid LB layer effectively inhibited the forming of biofilms.

5. During practical applications of octadecyl phosphonic acid and the octadecanoyl hydroxamic acid for LB films, their effectiveness as corrosion and microbiological corrosion inhibitors on Armco iron and copper was shown.

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DISSERTATIONS

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