Inhibition of Copper Corrosion by self Assembled Amphiphiles

J. Telegdi,[+] H. Otmačić-Ćurković,* K. Marušić, F. Al-Taher, E. Stupnišec-Lisac,* and E. Kálmán

Hungarian Academy of Sciences, Chemical Research Center, Budapest, Hungary
*University of Zagreb, Faculty of Chemical Engineering and Technology,
Zagreb, Croatia

The advantage of nanolayers that can replace the traditional inhibitors of solids is the significant decrease in chemicals. The consequence is a lower environmental pollution.

On a copper surface, special hydroxamic acid amphiphiles ($C_nH_{2n+1}CONHOH$, $n = 9–17$) were used in self-assembled molecular layers (SAM). The impact of time in SAM formation as well as the carbon chain length in the amphiphilic molecules was in the focus of the experiments. The time-dependent layer structure was characterized by sum frequency vibrational spectroscopy. The anti-corrosion efficiency of nanolayers was measured by different electrochemical techniques (electrode impedance spectroscopy, polarization) and by micro-calorimeter. The comparative analysis of data proved that the increase in time of SAM formation up to 1 hour enhances the stability, the ordering as well as the efficiency of nanolayers. The length of the carbon chain in the SAM layer, less significantly increases the anticorrosion efficiency in a corrosive environment than the layer thickness in LB films.

Key words:
Alkyl hydroxamic acid, self assembling molecular layer, inhibition, corrosion, microbial adhesion, electrochemical techniques, microcalorimetry.

Introduction

Extension of a structural material's life in a corroding (chemical, electrochemical and microbiological) environment is important. Corrosion and microbiologically influenced corrosion is a widespread problem in industrial installations, pipelines, etc. The economic significance is expressed in energy and efficiency loss, in undesired accumulation of deposits and in adhesion of microorganisms to solids. The inhibition of corrosion and microbial adhesion is generally achieved either by dissolved chemicals (inhibitors, biocides) or by coatings. Special types of coatings are those, where the films are composed of mono- and multimolecular layers.

Modification of metal surfaces by nanolayer via chemical/physical interaction is an important tool in surface engineering. The replacement of traditional techniques like dissolved chemicals and macro-coatings results in reduced undesired environmental impact of the additives. If metals are covered homogeneously with a nanolayer, the environmental impact of toxic chemicals is significantly decreased and the anticorrosion protection will be less expensive.

The formation of mono- and multimolecular layers needs special conditions, it is not applicable everywhere. For example, the increasingly of computerized world (where tiny panels suffer from chemical, electrochemical and microbiologically induced corrosion) explains the importance of nanolayers used against corrosion. The pre-adsorbed, well-organized nanolayers that form physical barriers between the solid surface and the environment, prevent direct contact between the metal surface and the liquid, decrease the risk of corrosion, and improve the chemical and mechanical properties of the metal surfaces. Of course, the nanocoatings must be homogeneous, compact and stable, i.e. not altered by the environment.

Nanolayers are generally deposited by two techniques. Langmuir-Blodgett (LB) films are prepared in Langmuir filmbalance, the self assembled molecular layers are formed on metallic and non-metallic solids either in aqueous or in organic solvents of amphiphilic molecules.

In the literature there are numerous examples for metal surface modification by self assembled molecular layers where the films are formed from amphiphiles like thiols,[1–6] silans,[7–9] phosphonic acids[10–16] or hydroxamic acids.[17–19] Generally, the layer stability depends on special forces that keep the film together (interactions between head groups, Van der Waals forces, hydrogen bonding, etc.). Under

aggressive conditions the inhibition of metal corrosion with nanolayers depends on the layer thickness. On solid surfaces the inhibition mechanisms are often explained by the blocking effect of active spots. In the case of phosphonic and hydroxamic acids it was proved by photoelectron spectroscopy that they are adsorbed mostly on metal oxides.

Copper corrosion could be inhibited by different types of additives. In most of them a molecules with sulfur and nitrogen atoms are responsible for repressing the deterioration processes.[20–23] Molecules with mercapto groups are generally adsorbed on the metallic copper, with nitrogen atom(s) on the copper oxide surface forming chelates, films or solid deposits that mostly homogeneously cover the surfaces. Some substituents in the basic molecules can enhance the anticorrosion efficiency.[24–27]

In our previous work detailed information was given about anticorrosion and biostatic activity of Langmuir-Blodgett films prepared from amphiphiles with $CONHOH$ and PO_3H_2 head groups.[28,29] The importance of the LB layer thickness in the inhibition process as well as the influence of the layer on the microbial adhesion was demonstrated by different techniques (polarization, contact angle measurement, fluorescence microscopy).

In this paper we shall give an account of the effectiveness of the self organized nanolayer prepared from amphiphilic hydroxamic acids with a systematically changed structure under a corrosive environment with and without microorganisms. The corrosion processes were monitored applying two different techniques. One method was the microcalorimetry which for the first time was applied to monitor the corrosion processes inhibited by nanolayers. The heat evolution caused by copper corrosion was measured by microcalorimetry. The efficiency of the nanocoatings on copper and the mechanisms of the corrosion are demonstrated by electrochemical techniques. The results obtained by different methods will be compared. The repellent activity of nanolayers in the presence of microorganisms will be demonstrated.

Experimental

Materials

The alkyl monohydroxamic acids

$$(C_nH_{2n+1}CONHOH_{2n+1}, n = 9–17)$$

were synthesized from hydroxylamine and the appropriate acyl chlorides in the presence of bicarbonate dissolved in water. The alkyl hydroxamic acids were purified by re-crystallization, analyzed and identified by melting points, elemental analysis, in-frared spectroscopy, and thin layer chromatography. Their purity was $\geq$ 99.5 %.

Metal surface preparation: The copper surface was polished with alumina paste to a finish of 0.3 μm, washed with acetone and water in an ultrasonic bath. The metal surface was exposed to air for one hour to obtain a natural oxide layer on the copper before being used in SAM coating experiments, because the oxide layer facilitates the adsorption of these molecules.[30]

The copper (99.99 %) electrodes (d = 10 mm) were embedded into a two-component epoxy polymer. For microcalorimetric measurements, copper rods – without polishing - were used (diameter, d = 2 mm; length: l = 20 mm) with and without SAM layers.

Layer preparation

The SAM layers of hydroxamic acids were developed by immersion of the copper samples into a dilute ($5 \cdot 10^{-3}$ mol dm^{-3}) solution of the appropriate amphiphilic compound dissolved in tetrahydrofurane (Merck), at room temperature. After removal of the copper samples from the organic solutions they were rinsed with pure solvent and air-dried.

Characterization of nanolayers

The time-dependent development in the ordered structure was monitored by s*um-frequency vibrational spectra*.[31]

The copper samples with and without SAM coatings were immersed into cooling water (cell number concentration: C_c = aerobic $5 \cdot 10^7$ cm^{-3}; anaerobic $C_c = 3 \cdot 10^5$ cm^{-3}. The microbial adhesion was visualized with a *fluorescence microscope* (Zeiss) after acridin orange staining.

Electrochemical measurements were performed in a three-electrode cell, filled with 300 mL of 0.5 mol dm^{-3} sodium sulphate electrolyte (pH 5.0, room temperature), copper with or without coating was the working electrode, saturated calomel electrode the reference, and platinum the counter electrode. The measurements started after half hour stabilization. Polarization curves were registered in a potentiostat (Radiometer PGP-201) with a scan rate 10 mV/min. Electrode impedance spectroscopy technique was used for study of inhibition kinetic caused by nanocoating on metals. The Nyquist diagrams of SAM-coated copper surfaces were fitted to a R(Q(R(QR)) equivalent circuits. As an inductive loop was observed for copper, R(Q(R(QR)RL)) equivalent circuit was used for its fitting.

Microcalorimetric measurements were carried out in a Thermal Activity Monitor 2277. The copper rods (with and without surface layers) were im-

mersed into a nitric acid solution (0.5 mol dm^{-3}) and, after being kept at 20 °C, the heat evolution was recorded.

Results and discussion

The modification of solids via self organization of amphiphiles is a powerful tool in surface engineering. Organic molecular layers can effectively modify the surface properties of metals.

The microcalorimetric on-line measurements allowed testing the efficiency of SAM layers. The results summarized in Table 1 show the influence of the aggressive environment on copper uncoated or coated with amphiphilic layers. The heat evolution was followed in all cases for 20 minutes. As these results present, the barrier properties of SAM layers increase with increasing time of self assembling layer formation. In other words the homogeneity and compactness, the ordering of the layer significantly influences the rate of corrosion. With increasing time the layer structure approaches an ideal order, i.e. the structure which can most effectively decrease the accessibility of the aggressive environment to the metal surface. This observation is supported by the SFG spectra where the intensity of peaks increases in time. If there is not any ordering in the surface layer we do not get any spectrum with this technique only horizontal line. The time-dependent sum-frequency vibrational spectroscopic spectra of SAM layers (Fig. 1) have proved that already in 30 min a compact, well-ordered molecular layer is formed on the copper surface. The compactness which is the consequence of the well ordered structure increases up to 1 h. The decrease
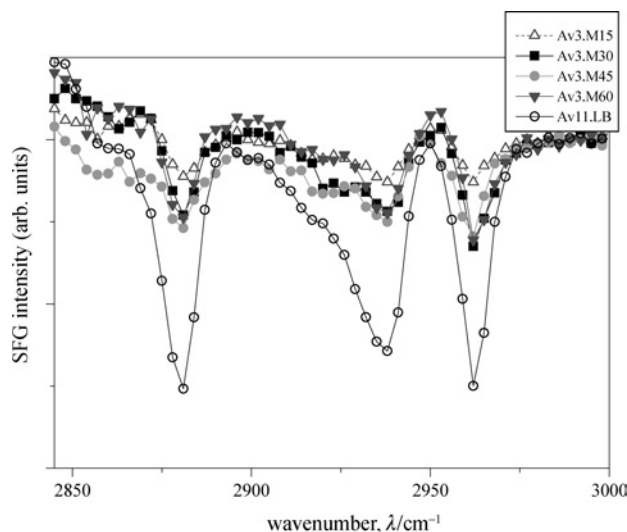

F i g . 1 – *Time-dependent sum frequency vibrational spectra of C$_{17}$CONHOH SAM layers after 15, 30, 45 and 60 min; spectrum of C$_{17}$CONHOH LB monolayer is also shown for comparison*

in the heat evolution in microcalorimetric measurements goes parallel with the increase of ordering and compactness of the nanolayer.

The electrode impedance spectroscopy (EIS) was used to study the inhibition kinetic caused by the nanocoating on copper (Table 2).

On the Nyquist diagrams of copper coated by SAM developed in 15 min an inductive loop was observed which implies corrosion processes and, parallel, some desorption of SAM layer (which is not compact due to the short formation time). Results of the EIS measurements are summarized in Table 2. The R_1 and C_1 data are attributed to the resistance and capacitance of the oxide layer, R_2 to the charge transfer resistance, and C_2 to the double-layer capacitance. When the layer formation time was 1 h, the values of R_1 and R_2 increased significantly in time – which means that the self-assembled molecular film forms a protective layer on the copper oxide surface. The C_1 and C_2 capacitance values are very low, much lower than usually expected for double layer capacitance. These results are in good agreements with those obtained by previous methods. The increase in the ordering and compactness results in much higher resistance and lower capacitance. Even the 15 min long SAM layer formation time resulted in a significant increase in the resistance of the nanolayer, i.e. in increase in anticorrosion efficiency.

The efficacy of the layers was also measured and calculated by polarization measurements. The E_{corr} values of SAM coated coppers (Table 3) are shifted into the cathodic potential range which means that these layers behave like cathodic inhibitors. In the presence of nanocoatings the decrease in

T a b l e 1 – *Heat evolution - measured by microcalorimeter - in the course of corrosion of copper covered by SAM layers. Influence of the layer formation time and alkyl chain length of the amphiphile on the anticorrosion efficiency.*

Time of SAM layer formation amphiphiles	Heat evolution in 20 min $\Phi/\mu J/s^*$				
	5 min	15 min	30 min	60 min	24 h
C$_9$ CONHOH	510	460	200	186	160
C$_{11}$ CONHOH	580	338	190	191	144

*Uncoated copper: $\Phi = 910$ μJ s^{-1}

Amphiphiles	C$_9$ CONHOH*	C$_{11}$ CONHOH*	C$_{15}$ CONHOH*	C$_{17}$ CONHOH*
heat evolution in 20 min $\Phi/\mu J$ s^{-1}	186	191	162	110

*SAM layer formation time: 60min

T a b l e 2 – *Impedance parameters for copper with and without SAM layer; the importance of the layer formation time*

	R_1 kΩ cm^2	C_1 μF cm^{-2}	α_1	R_2 kΩ cm^2	C_2 μF cm^{-2}	α_2
SAM formation:15 min						
Blank after 1h	1.31	12.67	0.92	4.88	41.18	0.50
Blank after 2h	2.80	12.45	0.93	7.24	17.63	0.59
[Cu+C9CONHOH] 1 h in electrolyte	8.44	0.25	0.89	106.14	0.78	0.63
[Cu+C9 CONHOH] 20 h in electrolyte	21.81	0.25	0.92	305.13	0.36	0.36
SAM formation:1h						
[Cu+C9CONHOH] 1 h in electrolyte	117.59	0.011	0.96	2564.6	0.023	0.62
[Cu+C9 CONHOH] 20 h in electrolyte	162.73	0.016	0.94	8595.9	0.37	0.50

T a b l e 3 – *Electrochemical parameters measured on corrosion of copper covered by SAM nanolayers (0.5M Na$_2$SO$_4$, pH=3)*

	E_{corr} mV	j_{corr} μAcm^{-2}	η/%
Copper	–26	0.91	–
[Cu+C$_9$ CONHOH]SAM	–36	0.13	76
[Cu+C$_{11}$CONHOH]SAM	–38	0.17	81
[Cu+C$_{15}$CONHOH]SAM	–39	0.16	82
[Cu+C$_{17}$CONHOH]SAM	–40	0.14	85

the current corrosion values points to the efficiency of the SAM layers which is expressed in efficacy values (η). Longer alkyl chain in the amphiphile enhances the efficiency. The same effect was observed by the microcalorimetric technique.

The influence of nanolayers on microbial adhesion is presented in Fig. 2. The images obtained by fluorescence microscope demonstrate the importance of the SAM layer and the SAM layer formation time on the microbial adhesion, biofilm formation. On the copper surface without any surface layer there are a many large and small colonies and single cells (white spots). A short SAM layer formation time (the surface is not homogeneously covered with a nanolayer and is not sufficiently hydrophobic) does allow the adhesion of microorganisms. In longer time a more compact, more ordered
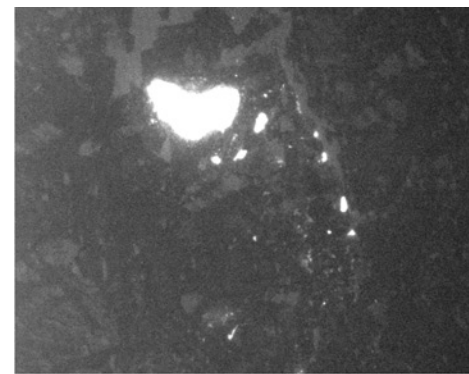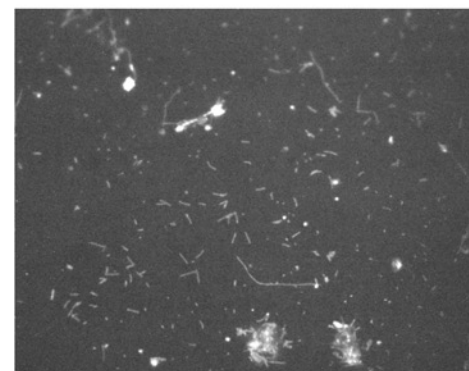
a

b

c

d

F i g . 2 – *Influence of SAM layer formation time on bacterial adhesion; copper with SAM layer of C$_9$CONHOH in cooling water for 5 d. Visualization: after acridin orange staining by fluorescence microscope.* **a**: *copper, copper+SAM after* **b**: *5 min,* **c**: *15 min,* **d**: *60 min*

surface layer is formed (as was already proved by other measuring techniques), and the consequence is that the metal surface is not accessible to microbes and the layers display their repellent activity. In other words, the microorganisms adhere much less to the hydrophobic metal surface.

The complex character of the nanolayers in cooling water is demonstrated in Fig. 3. The influence of the nanolayers on the corrosion rate is shown not only in the case of copper but also of iron. While the iron corrosion rate is not influenced by the $C_9CONHOH$ layer, the copper corrosion was decreased by both films prepared from amphiphils with shorter and longer alkyl chains, but in the presence of the more hydrophobic, the anticorrosion efficiency was significantly enhanced.
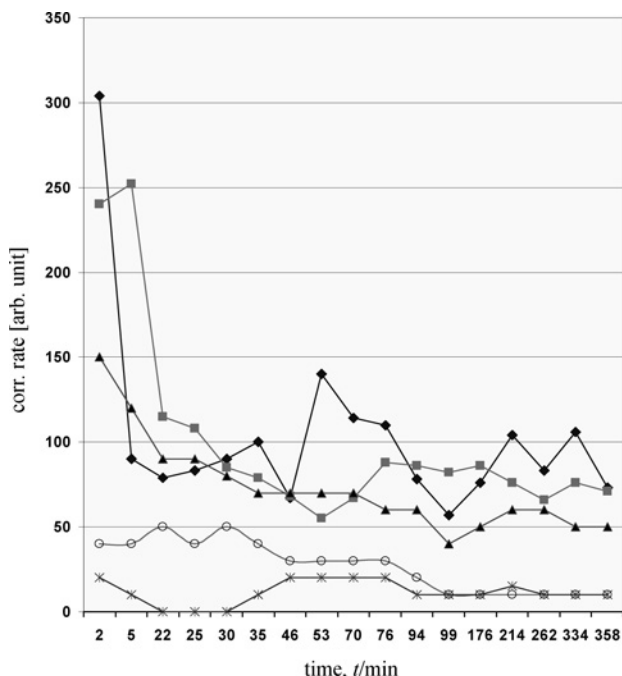

F i g . 3 – *The time dependent inhibition of copper and iron corrosion induced by self assembled amphiphiles in cooling water.* –◆–◆–◆– *iron;* –■–■–■– *iron* + *C₉CONHOH;* –▲–▲–▲– *copper;* –○–○–○– *copper* + *C₉CONHOH;* –✳–✳–✳– *copper* + *C₁₇CONHOH*

Conclusion

Self assembled nanolayers of hydroxamic acid amphiphiles were investigated in corrosive and microbial environment with different techniques. The microcalorimetric measurements – which were first used for evaluation of nanolayer effectiveness in corrosion processes - and the SFG spectra supported the electrochemical results. A compact, homogeneous, well-ordered SAM layer of alkyl hydroxamic acids on copper has been formed in one hour. The effectiveness of the nanolayers and

the mechanisms is explained by the blocking effect of nanofilms. With increasing hydrophobic surface character not only does the anticorrosion efficacy increase but also the inhibition of microbial colony formation and adhesion.

List of symbols

C – capacitance, μF

C_c – cell number concentration, cm^{-3}

c – concentration, $mol\ dm^{-3}$

d – diameter, mm

E – potential, mV

j – current density, $\mu A\ cm^{-2}$

l – lenght, mm

R – resistance, Ω, $k\Omega$

t – time, min, h

η – efficiency, %

λ – wavenumber, cm^{-1}

Φ – heat evolution, μW

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