# THE INFLUENCE OF SOLVENT ON PROPERTIES OF SELF–ASSEMBLED MONOLAYERS OF STEARIC ACID


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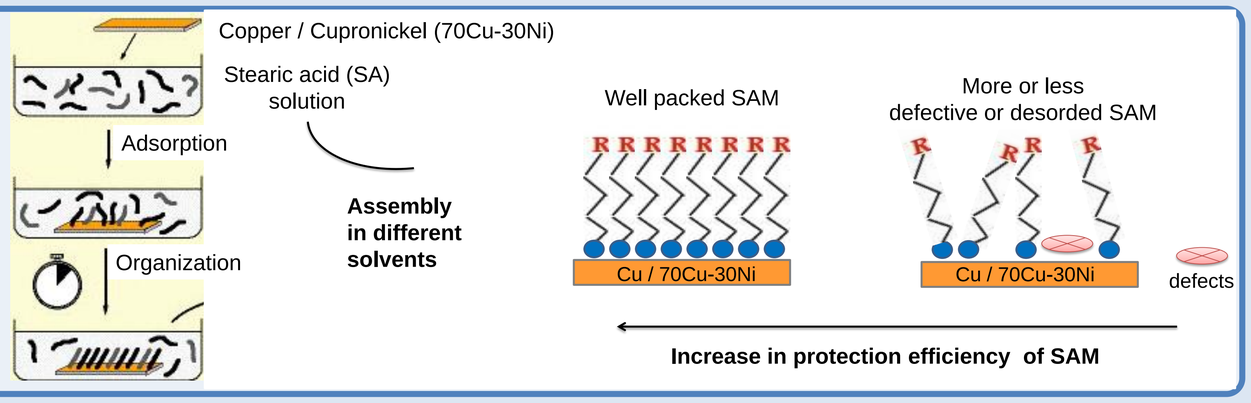
## INTRODUCTION

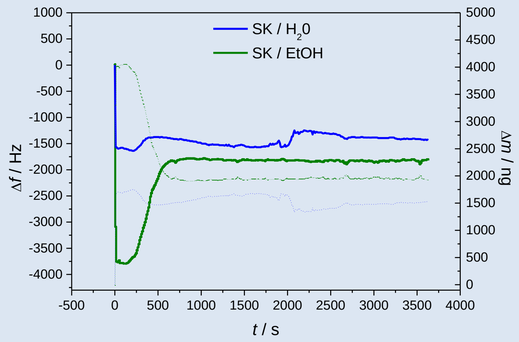
The increase of corrosion resistance can be achieved by modification of metal surface with thin, well-ordered films of long-chain carboxylic acids, so-called self-assembled monolayers, which are environmentally and economically acceptable. In order to achieve efficient corrosion protection, self-assembled monolayer should be **dense, well-ordered and defect free** to act as an efficient barrier against aggressive ion diffusion towards metal surface. Furthermore, they should be **strongly bound** to surface in order to prevent metal dissolution when exposed to aggressive medium.

The structure, stability and number of defects in the final monolayer formed on metal surface strongly depend on **the nature of the solvent** used. The solvent parameters, such as dielectric constant and interaction ability, are important factors that affect the quality of monolayer. The purpose of this study was to examine how solvents with different dielectric constants affect the adsorption and the quality of monolayer assembled on metal surface.




## RESULTS

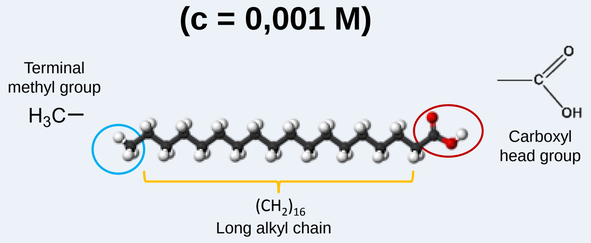
### ADSORPTION OF STEARIC ACID ON COPPER FROM DIFFERENT SOLVENTS



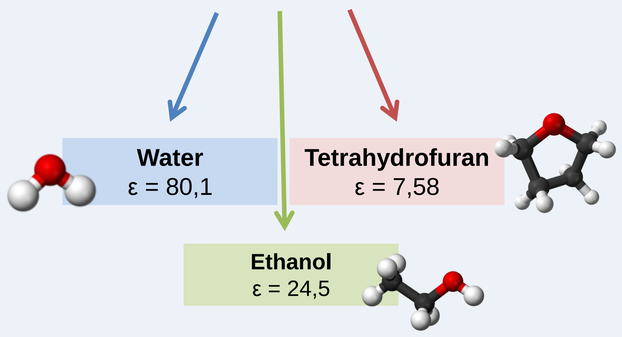

Frequency (solid line) and mass (dot line) changes dependance on time of exposure to stearic acid solution

Quartz Crystal Microbalance (QCM)

### STEARIC ACID (c = 0,001 M)



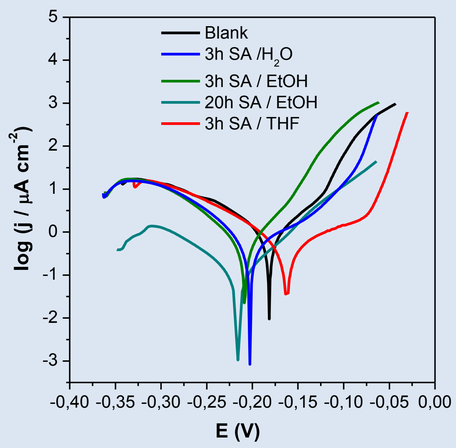

### IN DIFFERENT SOLVENTS



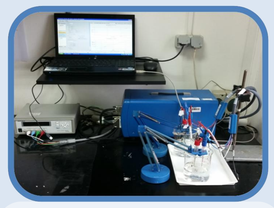

Samples preparation procedure for corrosion and surface analysis measurements.

| SAMPLE | Oxidation | | Adsorption | | Drying | |
|---|---|---|---|---|---|---|
| Blank | 80 °C | 24 h | - | - | - | - |
| 3h SA | 80 °C | 24 h | 40 °C | 3 h | 50 °C | 5 h |
| 20h SA | 80 °C | 24 h | 40 °C | 20 h | 50 °C | 5 h |

### PROTECTIVE PROPERTIES OF ADSORBED LAYERS ON CUPRONICKEL SURFACE IN ARTIFICIAL SEAWATER




Polarization curves for non-treated and SA treated samples obtained in 3% NaCl.

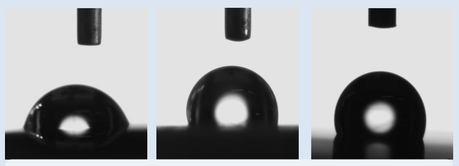


**Electrochemical methods:**
Linear Polarization
Tafel Extrapolation
Electrochemical Impedance Spectroscopy (EIS)

Corrosion parameters determined by Tafel extrapolation method from polarization curves.

| | $E_{corr}$ / mV | $j_{corr.}$ / μA cm$^{-2}$ | $b_a$ / mV dec$^{-1}$ | $-b_c$ / mV dec$^{-1}$ | $IE$ / % |
|---|---|---|---|---|---|
| Blank | -177 | 1.115 | 78 | 95 | - |
| 3h SA / $H_2O$ | -202 | 0.391 | 84 | 49 | 65 |
| 3h SA / EtOH | -212 | 0.372 | 43 | 53 | 67 |
| 20h SA / EtOH | -201 | 0.093 | 50 | 79 | 92 |
| 3h SA / THF | -170 | 0.365 | 55 | 66 | 67 |

### HYDROPHOBICITY OF ADSORBED LAYERS



CA = 60° CA = 103° CA = 112°

Contact angles of a drop of water on: non-treated sample, 3h treated in SA/THF and 20h treated sample in SA/EtOH

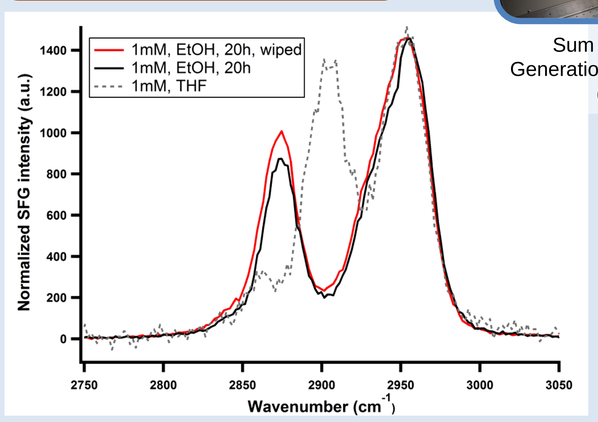
Contact Angle (CA)

The water contact angle for all samples

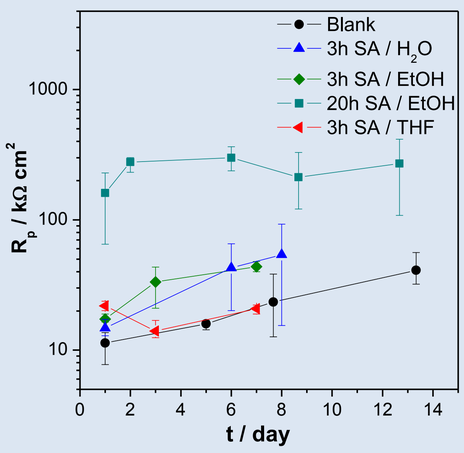
| SAMPLE | CONTACT ANGLE / ° |
|---|---|
| Blank | 60 ± 3 |
| 3h SA / $H_2O$ | 110 ± 6 |
| 3h SA / EtOH | 105 ± 1 |
| 20h SA / EtOH | 112 ± 2 |
| 3h SA / THF | 103 ± 2 |

### SPECTRAL ANALYSIS OF ADSORBED LAYERS

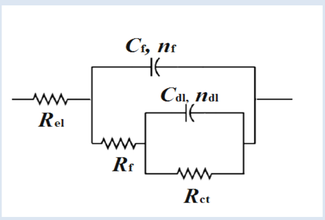
Sum Frequency Generation Spectroscopy (SFG)



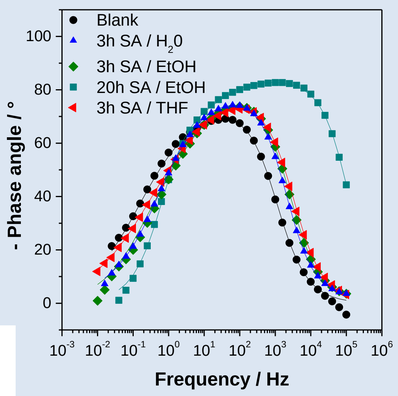

SFG spectra of SA layer deposited on Cu-Ni alloy from ethanol (continues lines) and THF (dotted line) as solvent.

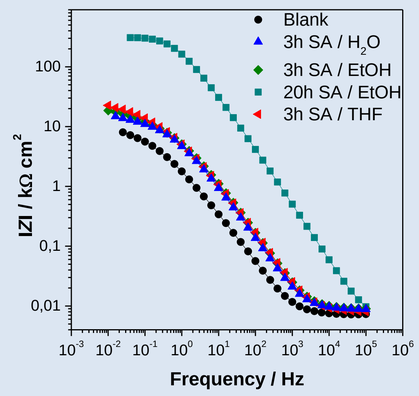



Polarization resistance dependence on time of exposure to chloride medium.




Equivalent electrical circuits used for fitting EIS spectra.




EIS spectra for non-treated and SA treated samples. Dots present experimental data and lines fitted data obtained by fitting the spectra to model given in figure on the left.

Impedance parameters obtained by fitting experimental data to selected equivalent circuits.

| SAMPLE | $C_f$ / μF cm$^{-2}$ | $n_f$ | $R_f$ / kΩ cm$^2$ | $C_{dl}$ / μF cm$^{-2}$ | $n_{dl}$ | $R_{ct}$ / kΩ cm$^2$ |
|---|---|---|---|---|---|---|
| Blank | 36.4 | 0.86 | 0.263 | 134.6 | 0.5 | 12.2 |
| 3h SA / $H_2O$ | 0.007 | 0.50 | 0.005 | 16.4 | 0.91 | 16.3 |
| 3h SA / EtOH | 14.7 | 0.88 | 3.82 | 46.3 | 0.56 | 15.0 |
| 20h SA / EtOH | 0.45 | 0.93 | 58.6 | 0.29 | 0.73 | 259 |
| 3h SA / THF | 14.5 | 0.87 | 2.94 | 68.3 | 0.50 | 24.5 |

## CONCLUSIONS

Quartz crystal microbalance measurements showed that adsorption of stearic acid on copper is a fast process that takes less than 20 minutes in all studied solvents. However, electrochemical and spectroscopic studies show that longer time is necessary to obtain well ordered and compact layer.

SFG measurements indicate that choice of solvent has significant impact on the structure of stearic acid film. The lowest protection was observed when water was used as a solvent. Samples prepared in THF solution showed initially the best protection but it diminishes rapidly in time which can be explained based on SFG results that indicate formation of disordered layer.

## ACKNOWLEDGMENTS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