



UNIVERSITY OF PANNONIA

CHEMICAL ENGINEERING AND MATERIAL SCIENCES DOCTORAL SCHOOL

**Formation of self-assembled molecular layers from amphiphilic molecules;
Investigation of the effects of layer formation conditions by surface analytical methods**

Ph.D. THESIS

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Introduction and Aim of Research

Stainless steels are generally resistant to corrosion; however, under specific conditions, particularly in the presence of chlorides, they are prone to pitting corrosion. There are several methods to enhance the surface corrosion resistance properties. In my research, I employed a special technique involving surface modification with self-assembled layers. For this, I chose a phosphonic acid, undecenylphosphonic acid. In our previous work, we have already demonstrated that amphiphilic molecules containing a phosphono head group are suitable for creating nanolayers (Langmuir-Blodgett: LB, or self-assembled monolayers: SAM) on the surface of iron-based alloys; this results in an orderly structured surface layer that protects the base metal from further corrosion.

In my PhD work, I investigated a molecule containing a special phosphono head group, which has a shorter carbon chain and a double bond at the end of the chain. The significance of this is that it allows for the compression of the layer and the modification of the double bonds through special post-treatments. During my work, I aimed to demonstrate the applicability of this amphiphilic molecule for creating a self-assembled layer that adequately isolates the metal surface from the aggressive environment. Additionally, I examined the effect of post-treatment of the nanolayer (temperature increase and irradiation) on the density and orderly structure of the self-assembled monolayer, always considering that the phosphono group only binds to oxidized surfaces.

I conducted the experiments with the post-treatment of the layer in mind, as described in the literature.

During my experiments, I investigated the effect of the layer formation time and temperature on the properties of the resulting nanofilm (wettability, material composition, anticorrosive behavior); I sought answers to the role of alloying components in layer formation. I provided numerical results demonstrating the dependence of the anticorrosive effect of the nanolayers on the experimental conditions of layer formation (layer formation time and temperature, the effect of post-treatment, alloying elements of stainless steels) and experimentally demonstrated the dependence of the PREN value, which expresses the susceptibility to pitting corrosion, and the metal dissolution caused by NaCl solution, which causes pitting corrosion, on the metal composition and the different SAM nanolayers.

New scientific results: thesis statements of the doctoral dissertation

1. In my work, I demonstrated that undecenyl phosphonic acid forms a self-assembled layer on the surface of the examined 1.0330, 1.4541, 1.4571, and 1.4841 steels (their composition is shown in the table below).

Metal	Fe%	C%	Si%	Mn%	P%	S%	Cr%	Ni%	Mo%	Ti%	N%
1.0330	balance	0.42	0.4	0.8	0.045	-	0.04	-	0.1	-	-
1.4541	balance	0.08	1.00	2.00	0.045	0.015	18.5	12.00	-	0.7	-
1.4571	balance	0.029	0.44	0.89	0.034	<.001	16.9	10.50	2.04	0.31	0.012
1.4841	balance	0.048	1.63	1.45	0.025	0.0010	24.1	19.09	0.37	0.022	0.022

The formation of the layer and the properties of the metals coated with the nanofilm (hydrophobicity, surface visualization with AFM) can be influenced by increasing the duration (4h, 12h, 48h) and temperature (25°C, 35°C) of layer formation: a well-covering, insulating layer forms over a more extended period (24h); increasing the temperature of layer formation allows for reducing the formation time of a better insulating nanolayer. The coverage, hydrophobicity, and density of the nanolayer can be significantly increased by post-treatment with heat or radiation [É.K. Pfeifer, J. Telegdi, Improved hydrophobicity for better corrosion control by special self-assembled molecular coatings, *Int. J. Corros. Scale Inhib.*, 2022, 11(3) 1041–1062; DOI: 10.17675/2305-6894-2022-11-3-9; É.K. Pfeifer, J. Mink, I.G. Gyurika, and J. Telegdi, Effect of heat treatment on the structure of self-assembled undecenyl phosphonic acid layers developed on different stainless steel surfaces, *Hungarian Journal of Industry and Chemistry* 51(2), 7-14 (2023); DOI: [10.33927/hjic-2023-12](https://doi.org/10.33927/hjic-2023-12)].

2. Using various measurement techniques (contact angle measurement, ellipsometry, corrosion experiments in NaCl solution, surface morphology measurement with AFM, roughness parameters), I demonstrated that the composition of the metals used (1.0330, 1.4541, 1.4571, and 1.4841 steels) and their surface properties significantly influence layer formation and the properties of the formed layer: on the almost alloy-free 1.0330 sample, the self-assembled layer is unable to completely protect the metal from the deteriorating effects of the aggressive medium (in our case, sodium chloride solution causing pitting corrosion); the presence of alloying metals (Cr, Ni, Mo, Mn) in different concentrations in stainless steels (primarily chromium oxide) helps improve the quality

of self-assembled layers. I demonstrated this not only with contact angle values characteristic of water-repellent properties but also with ex-situ ellipsometric measurements that allowed the determination of the thickness of the nanolayer. [É.K. Pfeifer, L. Trif, P. Petrik, J. Mink, I.G. Gyurika, J. Telegdi, Influence of gamma radiation on self-assembled molecular layers developed on different metals; Surface & Coatings Technology 489 (2024) 131092; <https://doi.org/10.1016/j.surfcoat.2024.131092>]

3. The molecular structure of crystalline and self-assembled undecenyl phosphonic acid layers was examined using Fourier-transform infrared spectroscopy, and I found that spectra differ between crystalline form and self-assembled layers formed on different compositions (1.0330, 1.4541, 1.4571, and 1.4841) steel surfaces within 24 hours. This demonstrated that the head group and hydrophobic side chain change undecenyl phosphonic acid molecule binding. The binding through metal oxide became clear at head group binding. I demonstrated that gamma irradiation causes structural changes in already formed self-assembled layers, confirming that double bonds at the amphiphilic molecule hydrophobic chain end polymerize. This assumption was confirmed with additional experiments (contact angle measurement, corrosion resistance examination of irradiated layer, surface morphology visualization with AFM) [É.K. Pfeifer, L. Trif, P. Petrik, J. Mink, I.G. Gyurika, J. Telegdi, Influence of gamma radiation on self-assembled molecular layers developed on different metals; Surface & Coatings Technology 489 (2024) 131092; <https://doi.org/10.1016/j.surfcoat.2024.131092>]
4. I showed the corrosion-inhibiting effect determined by the production conditions of self-assembled undecenyl phosphonic acid nanolayers: a homogeneous, well-organized layer does not form within a shorter time (4h) compared to a longer time (24h), showing surface homogeneity that significantly inhibits corrosion. I could increase the anticorrosion efficiency of self-assembled layers formed within 24 hours by post-treatments: heating at 50°C for 5 hours (this facilitates the removal of water molecules formed during head group binding as well as residual solvent molecules, thus increasing layer compactness); ultraviolet irradiation ($\lambda = 254\text{nm}$ for 60 minutes; this post-treatment facilitates the polymerization of unsaturated bonds, making the nanolayer denser); gamma irradiation (in inert and oxygen-containing atmosphere, using Co60 gamma source, absorbed dose: 20kGy): infrared spectra confirmed the absence of previously existing double bonds in the layer and concurrent polymerization, resulting in an additional protective layer function on the metal surface, multiplying the

anticorrosion effect. [Éva Kocsisné Pfeifer, Judit Telegdi, István Gábor Gyurika; The Effect of Heating on the Anticorrosive Self Assembled Phosphonic Acid Nanolayers; Proceedings of the 6th World Congress on Mechanical, Chemical, and Material Engineering (MCM'20) Prague, Czech Republic Virtual Conference – August, 2020 Paper No. MMME 123 [DOI:10.11159/mmme20.123](https://doi.org/10.11159/mmme20.123)]

5 a) Using atomic force microscopy examination, I confirmed the active participation of layers in corrosion inhibition by examining the surface morphology formed due to corrosion on four examined metal surfaces (1.0330, 1.4541, 1.4571, and 1.4841 stainless steels). I showed anticorrosion behavior depending on metal composition and layer formation time (4h, 24h) in both 3D and cross-sectional images. I showed extremely serious corrosion dissolution in alloy-free steel without a layer in 3% NaCl solution, which was slightly reduced by the self-assembled layer formed within a shorter time (4h) but significantly reduced by the nanofilm formed within a longer time (24h). The presence of alloying metals in base metals showed much less metal dissolution due to corrosion, which was significantly improved by the presence of nanofilms. These findings were supported by contact angle measurements and surface roughness factors provided by AFM technique, which supported reduced corrosion processes in the presence of nanolayers, significantly reducing roughness values of metal surfaces. [É.K. Pfeifer, J. Telegdi, Improved hydrophobicity for better corrosion control by special self-assembled molecular coatings, *Int. J. Corros. Scale Inhib.*, 2022, 11(3) 1041–1062; doi:10.17675/2305-6894-2022-11-3-9; É.K. Pfeifer, I.G. Gyurika and J. Telegdi, Anticorrosion activity of phosphonic acid amphiphile in self-assembled molecular layer, *Int. J. Corros. Scale Inhib.*, 2023, 12, no. 3, 1261–1274; [doi: 10.17675/2305-6894-2023-12-3-25](https://doi.org/10.17675/2305-6894-2023-12-3-25)]

b) Using a highly sensitive analytical method, inductively coupled plasma optical emission spectrometry, I quantified and confirmed the effective corrosion-inhibiting effect of nanolayers by measuring the concentration of metal ions (primarily iron) dissolved in the corrosive 3% NaCl solution. This technique allowed for the numerical characterization of the effectiveness of layers in corrosion inhibition, demonstrating the significance of post-treatment: both the nanolayers themselves and post-treatment

significantly reduced the dissolution of metal ions (primarily iron). I characterized the susceptibility of steels to pitting corrosion using the previously introduced PREN (Pitting Resistance Equivalent Number) values, comparing the behavior of base metals and metals with nanolayers in terms of PREN. The numerical values clearly showed that the isolating effect of layers is greater for base metals with higher PREN values, significantly more effectively reducing the pitting corrosion of alloys with higher alloying element content. Additionally, I demonstrated the metal dissolution-reducing effect explained by the presence of a denser nanolayer achieved through gamma irradiation post-treatment of the self-assembled layer. [É.K. Pfeifer, L. Trif, P. Petrik, J. Mink, I.G. Gyurika, J. Telegdi, Influence of gamma radiation on self-assembled molecular layers developed on different metals; *Surface & Coatings Technology* 489 (2024) 131092; pp. 1-9., <https://doi.org/10.1016/j.surfcoat.2024.131092>; Pfeifer, É.K.; May, Z.; Mohai, M.P.; Mink, J.; Gyurika, I.G.; Telegdi, J. Increasing the Resistance of Steel and Austenitic Stainless Steels Against Pitting Corrosion by a γ -Irradiated Self-Assembled Amphiphilic Molecular Layer. *Coatings* 2024, 14, 1601. <https://doi.org/10.3390/coatings14121601>]

Core publications from the PhD thesis work

É.K. Pfeifer, J. Telegdi, Improved hydrophobicity for better corrosion control by special self-assembled molecular coatings, *Int. J. Corros. Scale Inhib.*, **2022**, 11(3) 1041–1062; [doi: 10.17675/2305-6894-2022-11-3-9](https://doi.org/10.17675/2305-6894-2022-11-3-9);

É.K. Pfeifer, J. Mink, I.G. Gyurika, and J. Telegdi, Effect of heat treatment on the structure of self-assembled undecenyl phosphonic acid layers developed on different stainless steel surfaces, *Hungarian Journal of Industry and Chemistry* 51(2), 7-14 (**2023**); [doi: 10.33927/hjic-2023-12](https://doi.org/10.33927/hjic-2023-12);

É.K. Pfeifer, L. Trif, P. Petrik, J. Mink, I.G. Gyurika, J. Telegdi, Influence of gamma radiation on self-assembled molecular layers developed on different metals; *Surface & Coatings Technology* 489 (**2024**) 131092; <https://doi.org/10.1016/j.surfcoat.2024.131092>;

Éva Kocsisné Pfeifer, Judit Telegdi, István Gábor Gyurika; The Effect of Heating on the Anticorrosive Self Assembled Phosphonic Acid Nanolayers; *Proceedings of the 6th World Congress on Mechanical, Chemical, and Material Engineering (MCM'20) Prague, Czech Republic Virtual Conference – August, 2020 Paper No. MMME 123*
[DOI:10.11159/mmme20.123](https://doi.org/10.11159/mmme20.123)

É.K. Pfeifer, I.G. Gyurika and J. Telegdi, Anticorrosion activity of phosphonic acid amphiphile in self-assembled molecular layer, *Int. J. Corros. Scale Inhib.*, **2023**, 12, no. 3, 1261–1274; [doi:10.17675/2305-6894-2023-12-3-25](https://doi.org/10.17675/2305-6894-2023-12-3-25)

Pfeifer, É.K.; May, Z.; Mohai, M.P.; Mink, J.; Gyurika, I.G.; Telegdi, J. Increasing the Resistance of Steel and Austenitic Stainless Steels Against Pitting Corrosion by a γ -Irradiated Self-Assembled Amphiphilic Molecular Layer. *Coatings* 2024, 14, 1601.
<https://doi.org/10.3390/coatings14121601>