

***N*-Substituted unusual amino acids as corrosion inhibitors. Part IV: *N*-Acyl derivatives of unnatural amino acids with double bond**

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Abstract

Corrosion inhibition efficiency of unusual phenyl alanine derivatives (substituted in the phenyl ring and double bond in the side chain) were investigated in neutral aqueous solution by weight loss test and by atomic force microscopy. The influence of the substituents in the phenyl ring as well as of the double bond was elucidated and explained. The effect of electrophilic or nucleophilic groups in the phenyl ring was demonstrated by efficacy and roughness parameters.

Key words: *phenylalanine derivatives, corrosion inhibitor, nucleophilic and electrophilic substituents in the phenyl ring, double bond.*

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Introduction

In spite of a lot of achievement in the corrosion science and technology, the undesired deterioration of metals, i.e. corrosion remains a major concern all around the world. The corrosion could be controlled by application of corrosion resistant materials as well as by efficient corrosion inhibitors in different fields (cooling systems, oil and gas industry, paints *etc.*). The inhibitors reduce the corrosion at small concentration acting either as a barrier by forming an adsorbed layer on the metal surface or retarding one of both electrochemical processes (cathodic or anodic inhibitors).

Amino acids, a class of non-toxic organic compounds, which are soluble in aqueous media, can efficiently control the corrosion processes under acidic conditions [1]. These properties justify their use as corrosion inhibitors [2, 3]. Their efficacy depends mainly on the molecular structure [4, 5]. Among the natural amino acids (Ala, Glu, Gln, Asp, Leu, The, Met) the methionine derivative was the most effective in acidic solution [6]. The

substitution of the amino acids and the use of other additives applied together with the inhibitor (*e.g.* cations) affect their applicability.

The phenylalanine and its derivatives were studied mainly under acidic conditions, alone or in combination with other additives. The presence of zinc ion or the ester derivative of the amino acid increased the anticorrosion activity, in some cases synergically [7–9].

In our previous papers different, *N*-substituted derivatives of natural amino acids used as corrosion inhibitors were discussed. The influence of *N*-hydroxymethyl substitution resulted in efficient inhibition in the microbiologically influenced corrosion [10]. In case of *N*-phosphonomethyl and *N*-carboxymethyl groups, the importance of the basic amino acid structure as well as of the number of the substituting groups was demonstrated [11]. In the third part of our publication series we pointed on the fact that not only the amino acid side chain but the structure of the acyl moiety has an important impact on the inhibition [12]. In the present paper unusual amino acids are in focus which have similar structure to the phenylalanine but with some modification in the phenyl ring and, additionally, a double bond in the amino acid is also present. We have chosen quaint structures because we were interested in the influence of the substitution as well as in the effect of the electron withdrawing or electron donating subgroups in the phenyl ring. Additionally, the study of the presence of a double bond in the inhibitor molecule, which could interact with the metal/metal oxide interface, was also in the focus of our research.

2. Experimental

2.1. Materials

Inhibitors: The molecules used as inhibitors in our experiments were the follows:

1. α -acetamido, β -[*p*-(nitro)phenyl]-prop-(2)-ene carboxylic acid,
2. α -acetamido, β -[*o,p*-di(methoxy)phenyl]-prop-(2)-ene carboxylic acid;
3. α -acetamido, β -[*p*-di(methylamino)phenyl]-prop-(2)-ene carboxylic acid,
4. α -benzoylamido, β -[*p*-(amino)phenyl]-prop-(2)-ene carboxylic acid,
5. benzoyl-*p*-amino-phenylalanine,
6. α -benzoylamido, β -[*p*-(dimethylamino)phenyl]-prop-(2)-ene carboxylic acid,
7. benzoyl-*p*-dimethylamino-phenylalanine,
8. α -benzoylamido, β -[*p*-(dimethylamino)phenyl]-prop-(2)-ene carboxamide,
9. α -benzoylamido, β -[*p*-(nitro)phenyl]-prop-(2)-ene carboxylic acid,
10. α -benzoylamido, β -[*p*-(hydroxy,*m*-methoxy)phenyl]-prop-(2)-ene carboxylic acid,
11. acetyl-phenylalanine,
12. benzoyl-phenylalanine,
13. benzoyl-aspartic acid,
14. benzoyl-glutamine,
15. cinnamoyl-glutamic acid

The formulas of all the molecules are demonstrated in Table 1. The synthesis of the inhibitors is not part of this paper.

Table 1. Corrosion efficacy values of phenylalanine analogs with double bond and with different substituents in the phenyl ring.

Number	Inhibitor	Efficiency η [%]
1 S(-I)	$p\text{-O}_2\text{N-C}_6\text{H}_4\text{-CH=C(NH-CO-CH}_3\text{)-COOH}$	38.7
2 S(+I)	$o,p\text{-(CH}_3\text{-O)}_2\text{-C}_6\text{H}_3\text{-CH=C(NH-CO-CH}_3\text{)-COOH}$	92.8
3 S(+I)	$p\text{-(CH}_3\text{)}_2\text{N-C}_6\text{H}_4\text{-CH=C(NH-CO-CH}_3\text{)-COOH}$	6.0
4 S(+I)	$p\text{-H}_2\text{N-C}_6\text{H}_4\text{-CH=C(NH-CO-C}_6\text{H}_5\text{)-COOH}$	12.2
5 S(+I)	$p\text{-H}_2\text{N-C}_6\text{H}_4\text{-CH}_2\text{-CH(NH-CO-C}_6\text{H}_5\text{)-COOH}$	4.1
6 S(+I)	$p\text{-(CH}_3\text{)}_2\text{N-C}_6\text{H}_4\text{-CH=C(NH-CO-C}_6\text{H}_5\text{)-COOH}$	11.1
7 S(+I)	$p\text{-(CH}_3\text{)}_2\text{N-C}_6\text{H}_4\text{-CH}_2\text{-CH(NH-CO-C}_6\text{H}_5\text{)-COOH}$	8.0
8 S(+I) M(+I)	$p\text{-(CH}_3\text{)}_2\text{N-C}_6\text{H}_4\text{-CH=C(NH-CO-C}_6\text{H}_5\text{)-CONH}_2$	27.7
9 S(-I)	$p\text{-O}_2\text{N-C}_6\text{H}_4\text{-CH=C(NH-CO-C}_6\text{H}_5\text{)-COOH}$	28.3
10 $2 \times$ S(+I)	$p\text{-OH,m-OCH}_3\text{C}_6\text{H}_3\text{CH=C(NH-COC}_6\text{H}_5\text{)-COOH}$	68.6
11 M(-I)	$\text{C}_6\text{H}_5\text{-CH}_2\text{-CH(NH-CO-CH}_3\text{)-COOH}$	18.3
12 M(-I)	$\text{C}_6\text{H}_5\text{-CH}_2\text{-CH(NH-CO-C}_6\text{H}_5\text{)-COOH}$	24.3
Comparison of the influence of the acyl part:		
13 $2 \times$ M(-I)	$\text{HOOC-CH}_2\text{-CH(NH-CO-C}_6\text{H}_5\text{)-COOH}$	36
14 $2 \times$ M(-I)	$\text{HOOC-CH}_2\text{-CH}_2\text{-CH(NH-CO-C}_6\text{H}_5\text{)-CONH}_2$	34
15 M(-I) W(+I)	$\text{HOOC-CH}_2\text{-CH}_2\text{-CH(NH-CO-CH=CH-C}_6\text{H}_5\text{)-COOH}$	83

S: strong, M-moderate, W: weak; -I: electron withdrawing group; +I: electron donating group.

Metal under investigation was carbon steel (composition: Fe 99.57%, C 0.05%, Si 0.05%, Mn 0.3%, S 0.01%, P 0.02%).

2.2 Corrosion test

The corrosion rates were determined by gravimetric method. The efficiency (η %) was calculated according to the equation:

$$\eta = (1 - m_i/m_0) \times 100 [\%],$$

where m_0 is the weight loss of metal coupon measured without inhibitor, m_i is the weight loss of the coupon measured in the presence of inhibitor.

The composition of the model solution for the corrosion tests was as follows: 0.47 g $\text{CaSO}_4 \times 2\text{H}_2\text{O}$ + 0.23 g $\text{MgSO}_4 \times \text{H}_2\text{O}$ + 0.11 g NaHCO_3 + 0.13 g $\text{CaCl}_2 \times \text{H}_2\text{O}$] / 1 L distilled water; the pH value was 7.0.

2.3. Atomic force microscopy

Before visualizing the metal surface it was finished with emery paper and polished with diamond past. The mirror-like surface was cleaned with water, degreased with acetone and dried by nitrogen. The imaging by atomic force microscope (Digital Instruments, NanoScope III) took place in contact mode, on air, before and after the corrosive attack. The corrosive solution was the same as used in the gravimetric measurements.

3. Results and discussion

3.1 Results of the weight loss test

All these amino acids are special derivatives of natural phenylalanine. They differ in the substituent in the phenyl ring and have a double bond in the molecule. The results of the corrosion test, the anticorrosion efficiency of these unusual amino acids are listed in Table 1.

The π -electron cloud could be delocalized through a double bond near to the ring and can influence the electron state of the carboxyl group which interacts with the metal/metal oxide surface. This delocalization is influenced by the substituent of the phenyl ring which effect could be electrophilic or nucleophilic. Among these molecules are those which have *ortho*-, *meta*- or *para*-substituent, and, in some cases, *ortho* and *para* as well as *meta* and *para* substitutions. For the sake of comparison the acetyl and benzoyl phenylalanine was also investigated.

Substituent attached to an aromatic ring influences the π electron density in the phenyl ring. Electron donating groups alter the π system to a better nucleophile. On the contrary, the electron withdrawing groups make the π system better electrophile.

There is a difference in activity of inhibitors with nitrogen atoms. A nitro group in the phenyl ring has strong electron withdrawing effect on the electrons of the benzene ring. On the other hand, a free amino group and alkylated amino groups have strong electron donating effect. All molecules with nitrogen-containing substituents in the phenyl ring show weak anticorrosion activity. The presence of these groups both with positive (+I) or negative inductive effect (-I) decreases the effectiveness, with other words, they can't really control the corrosive deterioration of the metal. It seems that the influence of positive and/or negative inductive effects of the substituents in the phenyl ring are far from the amide and carboxylic groups that fix the molecules on the metal surface. The other reason for the difference of the impact between the substituting groups with nitrogen and oxygen atoms is that the nitrogen is less electronegative than the oxygen. When there is a double bond near to the phenyl ring e.g with dimethylamino substituent (molecule 8, compared with molecule 7),

the possibility of the π electron delocalization increases the anticorrosion efficacy (8% \rightarrow 27.7%). The methyl \rightarrow phenyl group replacement in the acyl part (molecules 3 and 8) has not significant effect on the anticorrosion activity. When an acid amide group replaces the carboxyl one (molecule 8 and 6), the inhibitive activity of the molecule increases (11% \rightarrow 27.7%). The double bond near to the phenyl ring makes a decisive difference as the anticorrosion effectiveness data show in cases of molecule 14 \rightarrow molecule 15; the change in the effectiveness is 34% \rightarrow 83%. The difference in the strong electron donating effect of the $-\text{OH}$ and $-\text{OCH}_3$ groups is evident when one compare the activity values of molecule 2 and molecule 10. In the first case the efficiency is 92.85% (substituents are two methoxy groups), in the second case, when one $-\text{OH}$ and one $-\text{OCH}_3$ group are the substituents, the efficacy is 68.8%. The decrease would be much bigger but the difference in the acyl part, *i.e.*, replacement of methyl group with phenyl one in the acyl part of the second molecule additionally supports the anticorrosion activity (see molecules 11 and 12).

3.2 Visualization of the metal surface by atomic force microscope

The surface morphology in the presence of an efficient inhibitor and in the other case of an inefficient inhibitor is demonstrated in Figure 1.

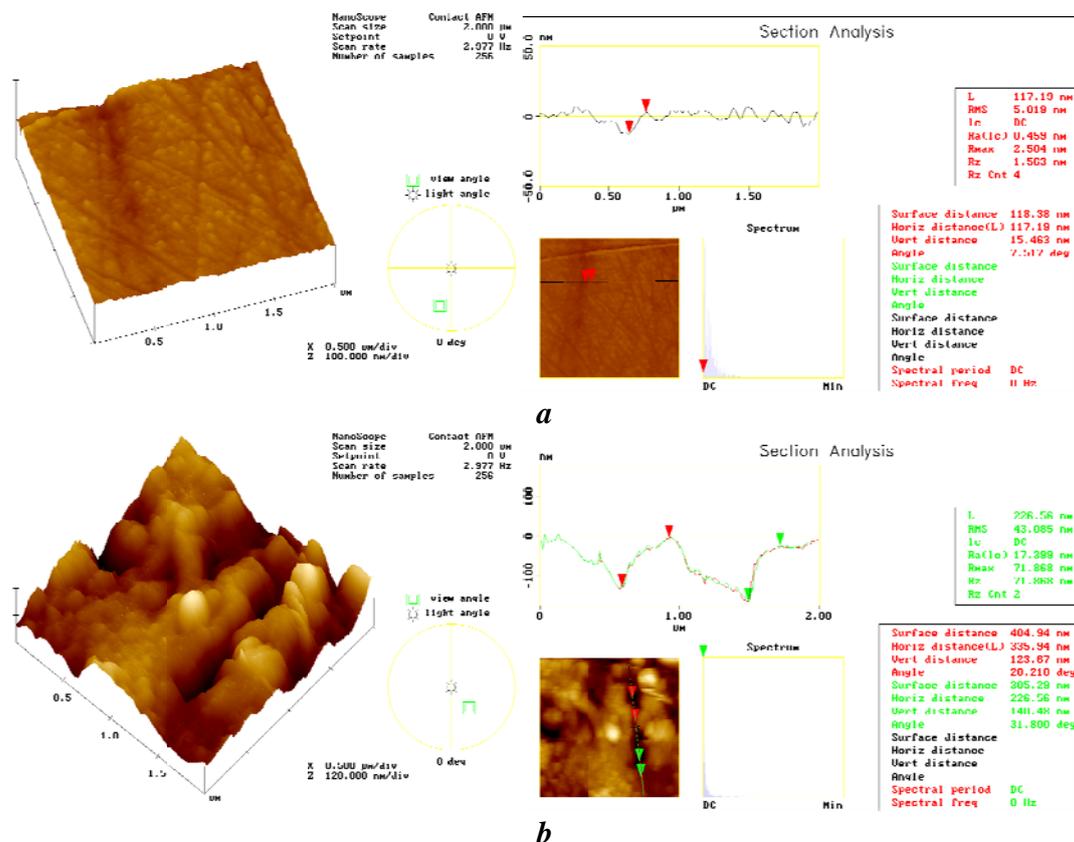


Figure 1. Carbon steel surface after immersion into model solution with: a) Inhibitor 2 and b) Inhibitor 6.

The surface morphologies demonstrate clearly that an efficient inhibitor can reduce the corrosion, inhibit the metal dissolution, the surface remains smooth. But, an ineffective additive used in corrosion test allows the corrosive deterioration and the consequence is a very rough metal surface. The roughness data given by this technique are the follows: in the case of Inhibitor 2 this value is 5.019 nm, and in the solution of the Inhibitor 6 this values increases to 43.085 nm. The section analyses demonstrate unequivocally the significant differences in the anticorrosion effectiveness. The surface evolved in the presence of the effective inhibitor is not only smooth but modified by the presence of the inhibitor. Small physisorbed layer dominates the metal surface.

Conclusion

Corrosion experiments done in the present of unusual, not natural amino acid derivatives showed that a double bond between the phenyl ring and the carboxylic group of the amino acid increases significantly the anticorrosion efficacy. This could be explained by the interaction of the delocalized electron cloud of the phenyl ring with the π electrons of the unsaturated double bond. The electron-delocalization through the double bond alters the charge distribution of the carboxyl group which interacts with the interface on the metal/metal oxide surface and it results in significant increase of the anticorrosion efficiency. According to the most probable conformation got by semi-empirical calculation the free carboxyl and carboxamide groups stand to the interface on the metal surface.

The presence of substituents with oxygen atom (hydroxy, methoxy groups) increases the anticorrosion efficiency to a high degree.

The presence of a nitrogen atom in nitro, amino and dimethylamino groups decreases the inhibition considerably. The primary factor in the layer formation is the physisorption enhanced by the π bond alien to the donor-type interaction at the metal/inhibitor interface.

The results got by weight loss corrosion tests were supported by the surface visualized by atomic force microscopy.

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