



A study of organic substances as inhibitors for chloride-induced corrosion in concrete

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ABSTRACT

Chloride-induced corrosion of carbon steel reinforcement is the most important cause of premature failure on reinforced concrete structures. Among available methods, corrosion inhibitors offer a simple and cost effective prevention technique, primarily to prevent and stop chloride-induced corrosion. Nevertheless, performance of commercial inhibitors is only partially satisfactory. This paper deals with a basic study on the inhibitive action of organic substances toward chloride-induced corrosion on carbon steel rebar in alkaline environment. The effect of aminic and carboxylic groups was investigated through electrochemical potentiodynamic polarisation tests in simulating concrete pore solution in the presence of chlorides, to ascertain inhibitor effectiveness to increase pitting potential. Results are discussed taking into account the most likely mechanism of inhibition, in relation to the functional group of tested organic compounds.

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1. Introduction

Reinforcement corrosion is the most important cause of premature failure of reinforced concrete structures world-wide and became of great interest at the end of 80's and early 90's when its elevated economic and social impact was pointed out. Steel in concrete is protected from corrosion by a passive film promoted by concrete alkalinity. This protective film can be destroyed (i.e., depassivation) by the presence of chlorides (usually from de-icing salts or marine environment) and by pH reduction of concrete pore solution, promoted by the reaction with CO₂ from the atmosphere (i.e., concrete carbonation). In the presence of chlorides, corrosion starts when chloride concentration at rebar level exceeds a critical threshold, typically 0.4–1% by cement weight in the case of atmospherically-exposed concrete structures. Once corrosion has started, three main consequences occur: reduction of reinforcement cross section, concrete cover cracking and spalling in the case of carbonation [1].

The prevention of carbon steel reinforcement corrosion is primarily achieved in the design stage by using high quality concrete (low W/C ratio) and adequate cover, as indicated in the European Standard EN 206. Additional prevention methods are adopted when severe environmental conditions exist or on structures requiring very long service life, as well as in repairing and rehabil-

itation. Among available methods, corrosion inhibitors can offer a simple and cost effective prevention technique, primarily to prevent and stop chloride-induced corrosion. Corrosion inhibitors can work either on initiation period of time (increasing chloride threshold value or reducing chloride penetration rate) or on propagation period, reducing corrosion rate [1,2].

Nowadays, there is a number of admixtures available on the market: inorganic compounds based on nitrites (especially used as additives) [3–9] and sodium mono-fluoro-phosphate (used as surface applied liquid on hardened concrete) [10–12], or organic compounds based on mixtures of alkanolamines and amines (proposed both as additive and migrating compound) and emulsion of unsaturated fatty acid ester of an aliphatic carboxylic acid and a saturated fatty acid (as additive) [13–20]. Early application of nitrites for concrete structures, which are the most studied inhibitors, dates back to the late 50's, while systematic investigations of inhibitors as additive to fresh concrete started later in 70's [2]. However, there are still conflicting opinions about the effectiveness of inhibiting compounds on reinforcement corrosion protection, and there is very few information about the mechanism by which these organic substances show their inhibitive action [2,11–22].

In the last 10 years, there is a lot of interest in studying new compounds able to prevent or stop corrosion, as well as in understanding the inhibition mechanism [2]. Studies were carried out on both inorganic (zinc oxide, molybdates, borates, stannates) and organic compounds (benzoate and its derivatives, carboxylate ions, quaternary ammonium salts, citrate and other compounds) [2,23–28].

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In this paper the inhibition effectiveness in preventing chloride-induced corrosion on carbon steel rebars of 80 organic substances was studied by means of electrochemical potentiodynamic polarisation tests in synthetic alkaline pore solution. The 10 organic compounds that showed the best inhibition efficiency were then exposed to potentiostatic electrochemical tests and to electrochemical impedance spectroscopy in order to study the long-term efficiency and the adsorption of substances on the passive layer; main results are reported in [29,30]. It must be underlined that the inhibition efficiency in solution needs a confirmation in concrete, to take into account chemical or physical interactions with cement paste.

2. Materials and methods

Organic corrosion inhibitors are said to act by adsorption on the metal surface through a polar group, then forming an organic layer, that may slow either anodic or cathodic process: for these reasons they are considered mixed inhibitors. Some organic corrosion inhibitors are also said to be chelating agents, which can form five- or six-membered chelate rings as a results of the bonding between two or more functional groups of the inhibitor (such as $-\text{NH}_2$, $-\text{OH}$, $-\text{SH}$, $-\text{COOH}$ and $-\text{SO}_3\text{H}$) and the metal cation.

About 80 organic substances were tested: primary and tertiary amines and alkanolamines, aminoacids, mono- and poly-carboxylates. Such substances were selected with the purpose to analyse the effect of functional groups (aminic or carboxylic), the position and number of the substituents and to study the influence of either electron-donor (nucleophile groups like oxidrilic, aminic and alkyl groups) or electron-attractor groups (electrophile agents like halogen, carboxylic group and atoms with high electronegativity), as well as the effect of carbon-chain length.

Amines and alkanolamines are largely used as constituents in commercial products, due to their high water solubility and their negligible influence on properties of both fresh and hardened concrete. The functional group responsible for amines and alkanolamines adsorption on metal surface is the lone pair of the nitrogen atom: iron ions on metal surface act as a Lewis acid, because they accept electrons from a donor group. Amines adsorption is influenced by the electronic properties of the functional groups, R, bound to the nitrogen atom (Fig. 1).

Organic carboxylate substances were tested to study the effect of the delocalization of the electrical charge of the carboxylate anion ($-\text{COO}^-$), the functional group responsible for the adsorption on carbon steel surface. Carboxylates adsorption is influenced by the presence of electron-donor or electron-attractor groups, R, bound to the carboxylate anion (Fig. 1).

2.1. Amines and alkanolamines

Amines are organic compounds that contain a nitrogen atom with a lone pair, which is, as said, responsible of the adsorption on metal surface. Amines basicity depends on electronic properties of substituent groups (R) bound to the nitrogen atom. Amines

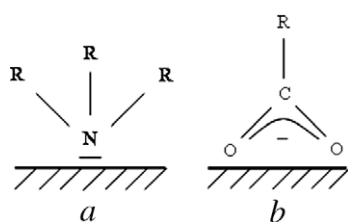


Fig. 1. Functional groups of amines (a) and carboxylates (b).

effectiveness was studied changing the chemical nature and the length of substituent groups: tested amines and alkanolamines are listed in the Table 1.

2.2. Carboxylate substances

Organic carboxylate substances are characterized by the presence of a carboxylic group ($-\text{COOH}$). They are proton donors and are considered Brønsted–Lowry acids. Mono-carboxylates were studied to verify the influence of electron-donor and electron-attractor groups; poly-carboxylates were studied changing either carbon-chain length or, in some cases, some functional groups within the chain. Tested carboxylates are shown in the Table 2. At pH 12.6 all the studied carboxylate compounds are in their ionic form.

2.3. Aminoacids

Aminoacids are molecules containing both aminic and carboxylic functional groups. According to the chain length, the analysed substances are divided in short chain aminoacids, with a single methylenic group bonded to the side group R_3 (Table 3), and long chain aminoacids, with two methylenic groups bonded to the side group R_3 (Table 4).

2.4. Potentiodynamic tests

The influence on chloride-induced corrosion of tested organic substances, was studied through cyclic potentiodynamic test (E -log i curves) to identify pitting potential (E_{pit}), repassivation potential (E_{rep}) and passivity range. Potentiodynamic tests were performed according to the Standard Test Method ASTM G61 for “Conducting cyclic potentiodynamic polarization measurements for localised corrosion susceptibility of iron-, nickel-, or cobalt-based alloys” [31]. This test method covers a procedure for conducting cyclic potentiodynamic polarization measurements to determine relative susceptibility to localised corrosion for iron-based alloys in a chloride rich environment. An indication of the susceptibility to initiation of localised corrosion in this test method is given by the potential at which the anodic current increases rapidly. The more noble this potential, obtained at a fixed scan rate in this test, the less susceptible is the metallic material to initiation of localised corrosion. The results of this test are not intended to correlate in a quantitative manner with the rate of propagation that one might observe in service when localised corrosion occurs; cyclic potentiodynamic tests did not give any reliable indication on corrosion rate, since the kinetic behaviour is influence by the imposed potential scan rate [1,31–34].

Carbon steel specimens, 10 mm in diameter, 40 mm long and 1000 mm² net exposed surface area, were machined from com-

Table 1
Amines and alkanolamines ($\text{N}-\text{R}_3$).

Amines	
Methylamine	CH_3-NH_2
Dimethylamine	$(\text{CH}_3)_2-\text{NH}$
Ethylamine	$\text{CH}_3\text{CH}_2-\text{NH}_2$
Propylamine	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2$
Cyclohexylamine	$\text{C}_6\text{H}_{11}-\text{NH}_2$
Triethylenetetramine (TETA)	$\text{NH}_2-\text{CH}_2\text{CH}_2-(\text{NHCH}_2\text{CH}_2)_2-\text{NH}_2$
Hexamethylenetetramine (EMTA)	$\text{C}_6\text{H}_{12}\text{N}_4$
Alkanolamines	
Monoethanolamine (MEA)	$(\text{OH CH}_2\text{CH}_2)-\text{NH}_2$
Triethanolamine (TEA)	$(\text{OH CH}_2\text{CH}_2)_3-\text{N}$
Dimethylethanolamine (DMEA)	$(\text{CH}_3)_2(\text{OH CH}_2\text{CH}_2)-\text{N}$
Methyldiethanolamine (MDEA)	$(\text{CH}_3)(\text{OH CH}_2\text{CH}_2)_2-\text{N}$

Table 2Mono-carboxylates ($R\text{-COO}^-$) and poly-carboxylates ($^-\text{COO-R-COO}^-$).

Mono-carboxylates	
Acetate	$\text{CH}_3\text{-COOH}$
Trifluoroacetate	$\text{CF}_3\text{-COOH}$
Trichloroacetate	$\text{CCl}_3\text{-COOH}$
Pivalate	$(\text{CH}_3)_3\text{C-COOH}$
Cyclohexanecarboxylate	$\text{C}_6\text{H}_{11}\text{-COOH}$
2-Methylbutyrate	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{-COOH}$
Benzoate	$\text{C}_6\text{H}_5\text{-COOH}$
Poly-carboxylates	
Oxalate	HOOC-COOH
Malonate	$\text{HOOC-CH}_2\text{-COOH}$
Succinate	$\text{HOOC-(CH}_2)_2\text{-COOH}$
Glutarate	$\text{HOOC-(CH}_2)_3\text{-COOH}$
Suberate	$\text{HOOC-(CH}_2)_6\text{-COOH}$
Azelate	$\text{HOOC-(CH}_2)_7\text{-COOH}$
Malate	$\text{HOOC-CH(OH)-CH}_2\text{-COOH}$
Tartrate	$\text{HOOC-(CHOH)}_2\text{-COOH}$
Citrate	$\text{HOOC-COOH-(CH}_2\text{COOH)}_2$
Fumarate	HOOC-CH=CH-COOH
EDTA	$(\text{HOOC})_2\text{-N-CH}_2\text{-N-(COOH)}_2$

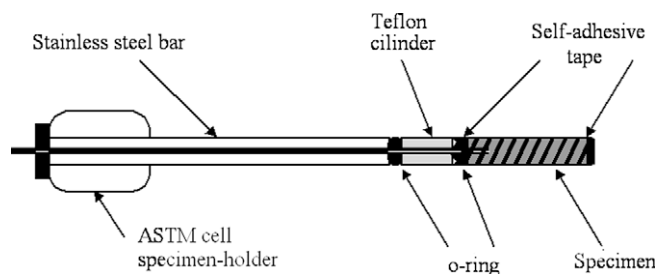
Table 3Short chain aminoacids ($R_1R_2\text{)-CH-CH}_2\text{-R}_3$.

R_1	R_2	R_3	Compounds
-COOH	-NH_2	-CH_3	α -Aminoisobutyrate
		-OH	Serine
		-SH	Cysteine
		-Ph	Phenylalanine
		-COOH	Aspartate
		-CONH_2	Asparagine

Table 4Long chain aminoacids ($R_1R_2\text{)-CH-CH}_2\text{-CH}_2\text{-R}_3$.

R_1	R_2	R_3	Compounds
-COOH	-H	-NH_2	Amino- <i>n</i> -butyrate
	-NH_2	-H	α -Aminoisobutyrate
		-COOH	Glutamic acid
		-CONH_2	Glutamine
		-SCH_3	Methionine

mercial reinforcing steel, then sandblasted and carefully coated with self-adhesive tape on both ends to isolate the transversal sections (Fig. 2). Cyclic potentiodynamic tests were performed at potential scanning rate of 1 V/h, starting from -1.2 V SCE in the anodic direction until 10 mA current was reached (corresponding to about 10 A/m^2), then reversing the potential scanning to the cathodic direction up to -1.2 V SCE. Starting the potential scanning at so negative value allows the passive layer to form on carbon steel, and the formation of the passive layer is influenced by the composition of the alkaline solution, in particular by the presence of organic substances and chlorides. Tests started 1 h after the

**Fig. 2.** Specimen assembly.

immersion of the specimen in the solution, to avoid passivation of steel, which is a spontaneous phenomenon in alkaline solution. In fact, the 1 h lasting time it is not enough to assure the passivation of carbon steel in alkaline solution: in free corrosion conditions more than 2 days are necessary to reach a good passive state [1,35,36]. Test assembly consisted of an ASTM cell, with an EG&G Princeton Applied Research potentiostat/galvanostat, a platinum counter-electrode and a saturated calomel reference electrode SCE, as shown in Fig. 3.

Tests were carried out in a synthetic pore solution: saturated calcium hydroxide solution with NaOH 0.01 mol/L (pH 12.6). This solution is considered as representative of concrete pore solution [1]. pH value was measured before and after the test by a pH-meter. When adding any organic substance we checked the stability of pH value and maintained it fixed at 12.6. Tests were carried out at 20°C ($\pm 2^\circ\text{C}$). Three different chloride concentrations were considered: 0.1, 0.3 and 1 mol/L. This concentration range is representative of practice experience: first and second values are close to the lower and upper chloride critical threshold, respectively, whilst third value exceeds the critical range that means corrosion conditions occurrence.

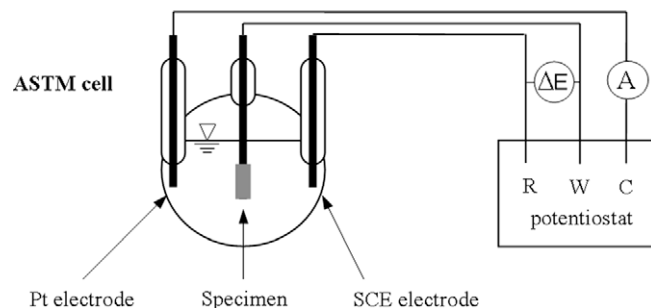
Organic substances were added to the solution in concentration of 0.1 mol/L and 0.3 mol/L. Two reference solution were considered: control alkaline solution (NaOH 0.01 mol/L + Ca(OH)_2 , sat., pH 12.6); control alkaline solution with 0.1 mol/L sodium nitrite, that is an inorganic inhibitor whose effectiveness in alkaline environment, as well as in concrete, is largely reported in literature [2–9].

3. Results

Potentiodynamic tests were performed in non-stationary conditions, with a potential scan rate of 1 V/h. As reported in standard test method ASTM G61 [31], results of these tests are not intended to correlate in a quantitative manner with the rate of propagation that one might observe in service when localised corrosion occurs, so experimental data cannot be considered as absolute values; nevertheless, they can be used as screening-test to rank different substances [32–34]. The real effectiveness of an inhibitor has to be confirmed by long-lasting tests, in solution first, then in concrete slabs, as well as on real structures.

Fig. 4 reported a typical potentiodynamic curve. The curves were interpreted as follow [1,31–34]:

1. From -1.2 V to about -0.95 V SCE: cathodic reaction of hydrogen evolution (-1.0 V SCE is close to the equilibrium potential of iron [34]).
2. From -0.95 V to about -0.85 V SCE: active region and initiation of passive layer formation.
3. Pitting potential, E_{pit} : “the potential at which the anodic current increases rapidly” (according to ASTM G61 [31]). Localised corrosion starts above this potential.

**Fig. 3.** Cell to potentiostat connections.

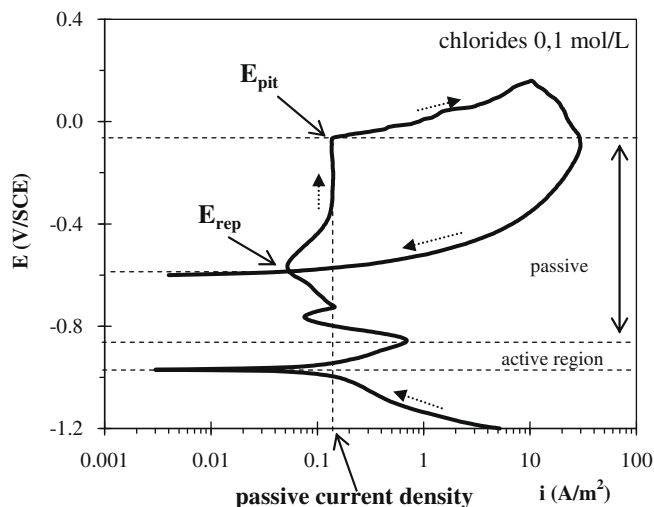


Fig. 4. Electrochemical parameters obtained by a potentiodynamic curves.

- From -0.85 V SCE to pitting potential: passive region. The increase of current density when the pitting potential is reached is related to localised anodic dissolution of carbon steel. Localised attacks were in fact observed on carbon steel specimens at the end of the tests.
- Repassivation potential, E_{rep} : the interception between the backward potential scan and the passive interval: below this value localised corrosion can not start or it stops if initiated. All tested organic substances, regardless their concentration, showed a repassivation potential below -500 – -550 mV SCE, close to the values obtained in the case of test with control solution in the absence of any inhibitors. Then, only the effect of tested organic compounds on pitting potential, E_{pit} , is reported.

The current density associated to the passive potential interval is called “passive current density”.

During potentiodynamic curve, since potential scan started from cathodic conditions (i.e., at potential -1.2 V SCE) all oxygen was first depleted so that only hydrogen evolution took place as occurring cathodic process. For this reason, since oxygen is not present, free corrosion potential was negative as reported (close to -0.95 V SCE, Fig. 4); this value is around the potential for hydrogen evolution. This corrosion potential is not representative of real atmospherically-exposed structures. In fact, in the case of passive carbon steel reinforcements free corrosion potential is in the range of $-0.1/0$ V SCE in passive condition, and about -0.5 – -0.6 V SCE in active conditions [1,35,36]. In the case of structure where concrete cover is water saturated (i.e., concrete structures buried in soil or permanently immersed in water and sea water) oxygen diffusion is stopped and free corrosion potential is much more negative, also for passive steel, as reported in literature, around -0.8 V SCE [1,35,36,38,39].

The inhibition effectiveness is presented and discussed on the basis of Pedeferrri's type diagrams, E -Log $[Cl^-]$, where pitting potential, E_{pit} , was plotted as a function of chlorides concentration [37–40].

Among the tested organic substances a candidate effective inhibitor should show a twofold effect on pitting potential, at fixed chloride content:

- Increase pitting potential to values higher than 50 mV SCE, being the latter the free corrosion potential of steel reinforcement in atmospherically-exposed concrete structures.
- Increase pitting potential of at least 300 mV above the value measured in the control solution.

Results are also compared to those obtained in the presence of sodium nitrite.

3.1. Control solution results

Two control solutions were considered:

- Alkaline solution NaOH 0.01 mol/L + $Ca(OH)_2$, sat. (pH 12.6).
- Alkaline solution NaOH 0.01 mol/L + $Ca(OH)_2$, sat. +0.1 mol/L sodium nitrite.

Pitting potential and repassivation potential at varying chlorides concentration are reported in Table 5. In control solution without organics and nitrite pitting potential decreased from -200 mV SCE to -500 mV SCE as chlorides content increased from 0.1 to 1 mol/L; pitting potential was always below 0 mV SCE. Repassivation potential remained constant, close to -600 mV SCE, regardless the chlorides content. The presence of 0.1 mol/L sodium nitrite produced an increase of pitting potential at least of 400 mV for all tested chlorides concentrations. The value of pitting potential was higher than 50 mV SCE except in the case of 1 mol/L, where pitting potential dropped below 0 mV SCE, in agreement with literature, localised corrosion occurs when chlorides/nitrites molar ratio exceeded a critical threshold varying between 0.6 and 2 [2–9].

3.2. Amines and alkanolamines

Amines are the main constituents of many commercial inhibitors. Primary and tertiary amines and alkanolamines were tested (Table 1). Amines behaviour was studied changing the chemical nature and the length of substituent groups. Fig. 5 reports potentiodynamic curves obtained in solution with 0.1 mol/L chlorides at different content of dimethylethanolamine (DMEA), a tertiary alkanolamine: pitting potential increased with DMEA content, reaching +100 mV SCE in correspondence to the higher content, of about 10% by weight. It is important to notice that such a high inhibitor concentration is not recommended to be used in concrete since it negatively influences workability of fresh concrete, as well as mechanical properties of hardened concrete.

The high volatility of amines with low molecular weight was responsible of poor results reproducibility. For example, Fig. 6 reports potentiodynamic curves obtained in a solution 0.1 mol/L chlorides with 0.1 mol/L of monoethanolamine (MEA), a low molecular weight alkanolamines; it can be noticed that pitting potential ranged from -300 mV SCE to 0 mV SCE. In order to assure a better reproducibility, sealed cells were used in testing such volatile inhibitors.

Pitting potential values in the presence of studied amines, in concentration 0.1 and 0.3 mol/L, at different chlorides content are plotted in Pedeferrri's type diagrams (Figs. 7 and 8, respectively). Dotted lines indicate the free corrosion potential range usually measured on real structures exposed to the atmosphere in alkaline chloride-free concrete. Pitting potential in control solutions at pH

Table 5
Pitting potential and repassivation potential for the reference solutions.

	Chlorides (mol/L)	E_{pit} (mV/SCE)	E_{rep} (mV/SCE)
NaOH + $Ca(OH)_2$ sat	0.1	-200	-580
	0.3	-400	-600
	1	-500	-600
NaOH + $Ca(OH)_2$ sat + Sodium Nitrite 0.1 mol/L	0.1	350	-150
	0.3	100	-230
	1	-100	-320

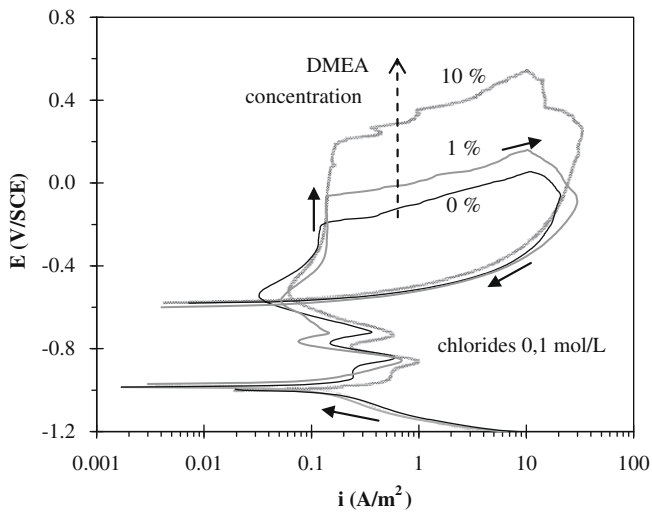


Fig. 5. Potentiodynamic curves with increasing DMEA concentration.

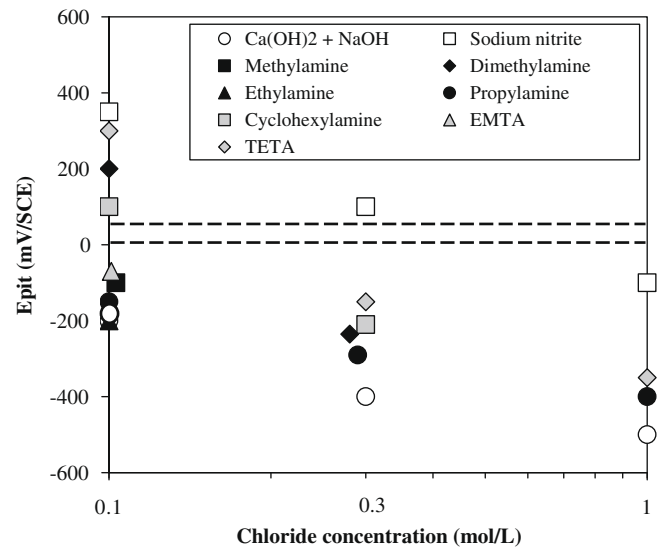


Fig. 8. Pitting potential values in solution with amines (0.3 mol/L).

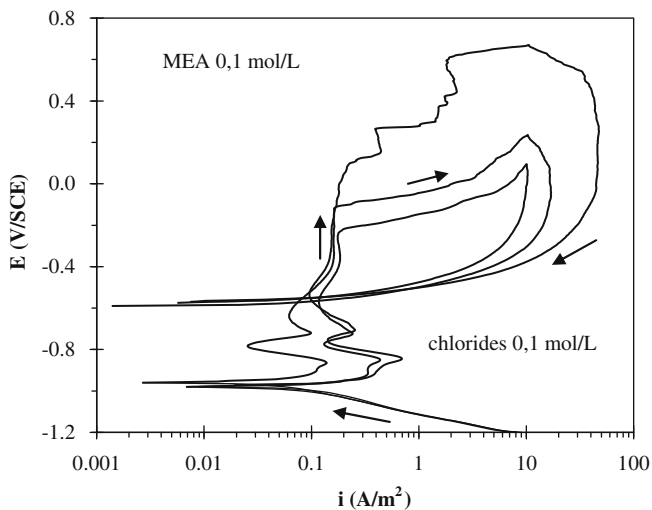


Fig. 6. Irreproducibility in presence of low molecular weight amines (MEA).

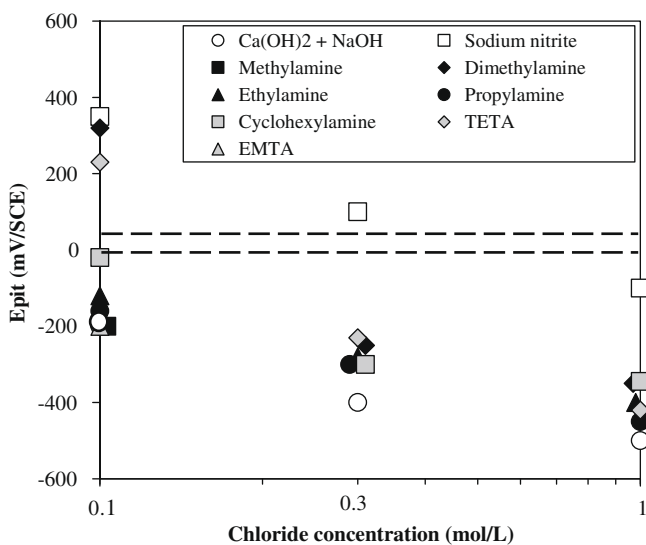


Fig. 7. Pitting potential values in solution with amines (0.1 mol/L).

12.6 decreased linearly in a semilogarithmic plot as chlorides concentration increased from 0.1 to 1 mol/L. In low chlorides containing solution with organic inhibitor 0.1 mol/L, only dimethylamine and triethylenetetramine (TETA) showed pitting potential above 0 mV SCE. With chlorides 0.3 mol/L and amines 0.1 mol/L, pitting potential was below -200 mV SCE for all studied substance; as inhibitor concentration increased to 0.3 mol/L, dimethylamine and cyclohexylamine showed a pitting potential above 0 mV SCE. TETA showed the best increase of pitting potential in all the studied experimental conditions.

Potentiodynamic tests with alkanolamines 0.3 mol/L were performed only in solution with 0.1 and 0.3 mol/L chlorides (Figs. 9 and 10). Only in case of 0.3 mol/L dimethylethanolamine (DMEA), a pitting potential above 0 mV SCE was measured.

Summarising, in the presence of amines and alkanolamines, no significant increase of pitting potential was observed for chlorides concentration equal or higher than 0.3 mol/L. Only in the presence of TETA some interesting results were obtained. Moreover, such substances showed pitting potential below typical free corrosion potential in pristine concrete.

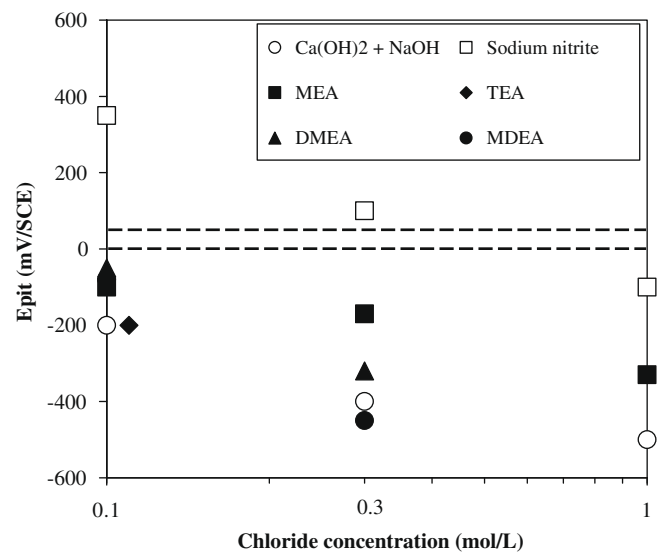


Fig. 9. Pitting potential values in solution with alkanolamines (0.1 mol/L).

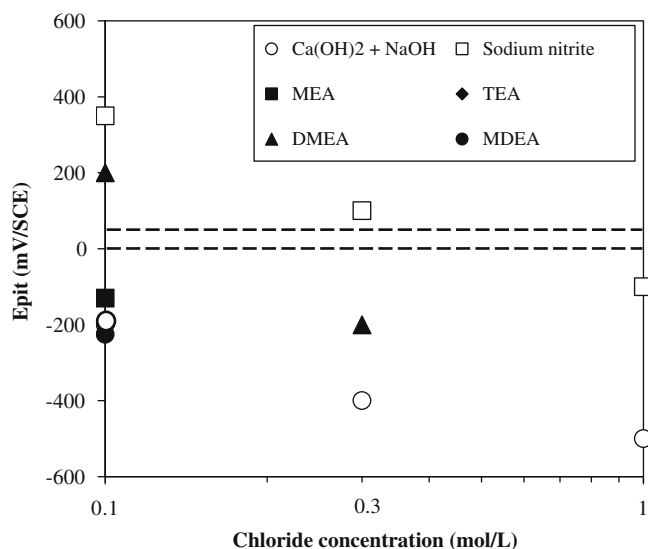


Fig. 10. Pitting potential values in solution with alkanolamines (0.3 mol/L).

3.3. Carboxylate compounds

Mono- and poly-carboxylates were tested to verify the influence of electron-donor and electron-attractor groups, carbon-chain length and functional groups.

Pedferri's type diagrams were reported in Figs. 11–13, in the case of mono- and poly-carboxylate compounds, respectively. Biggest markers refer to high dosage inhibitor (0.3 mol/L). With chlorides 0.1 mol/L, pitting potential values were higher than +400 mV SCE in the presence of many of tested carboxylate substances, indicating a very good inhibitive effectiveness. In solution with 0.1 mol/L chlorides and in the presence of EDTA, succinate, glutarate, tartrate, citrate and fumarate, localised corrosion did not initiate. In solution with tartrate, citrate, fumarate and EDTA, pitting potentials higher than values measured in the presence of sodium nitrite were obtained also in the presence of 0.3 mol/L chlorides. With 1 mol/L chlorides, pitting potential values are generally lower than –300 mV SCE. Nevertheless, in the presence of citrate, tartrate and EDTA 0.3 mol/L a pitting potential 300 mV higher than values measured in solution without any organic substances was measured.

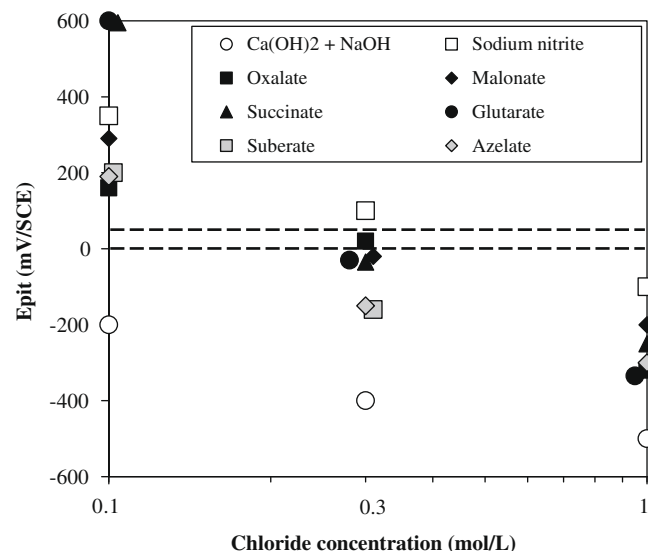


Fig. 12. Pitting potential values in solution with poly-carboxylates.

Carboxylates substances showed very interesting results in term of increase of pitting potential.

3.4. Aminoacids

Tested aminoacids belonged to two categories: short chain aminoacids, with only one methylenic group, and long chain aminoacids, with two methylenic groups. Figs. 14 and 15 show results obtained in solution with short chain and long chain aminoacids, respectively. Biggest markers refer to high dosage inhibitor (0.3 mol/L). In solution with chlorides 0.1 mol/L and short chain aminoacids, pitting potential was higher than +200 mV SCE for phenylalanine, aspartate and asparagine (Fig. 14). In solution with chlorides 0.1 mol/L and long chain aminoacids, pitting potential was higher than +200 mV SCE for glutamate, glutamine and methionine (Fig. 15). Increasing chloride content to 0.3 mol/L only aspartate, asparagine and glutamate showed a significant increase of pitting potential. No significant potential increasing was observed in the presence of chlorides 1 mol/L for all tested aminoacids.

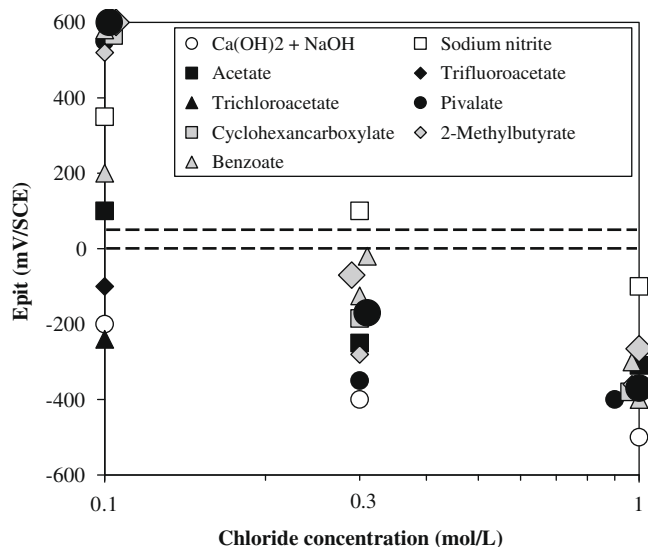


Fig. 11. Pitting potential values in solution with mono-carboxylates (biggest markers refer to 0.3 mol/L inhibitor content).

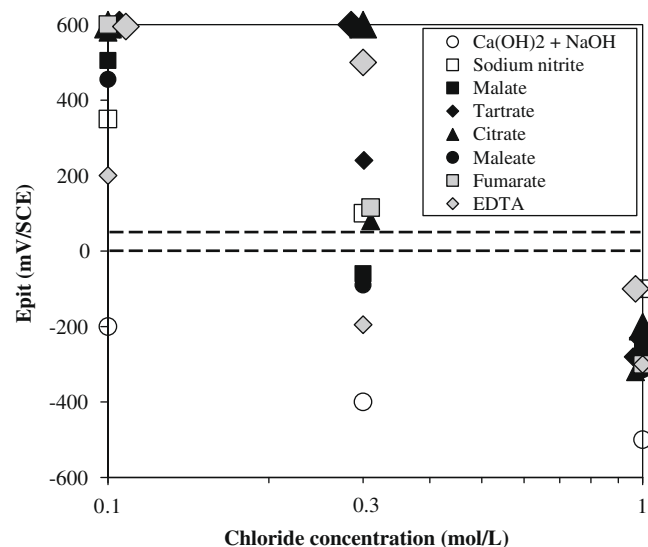


Fig. 13. Pitting potential values in solution with poly-carboxylates (biggest markers refer to 0.3 mol/L inhibitor content).

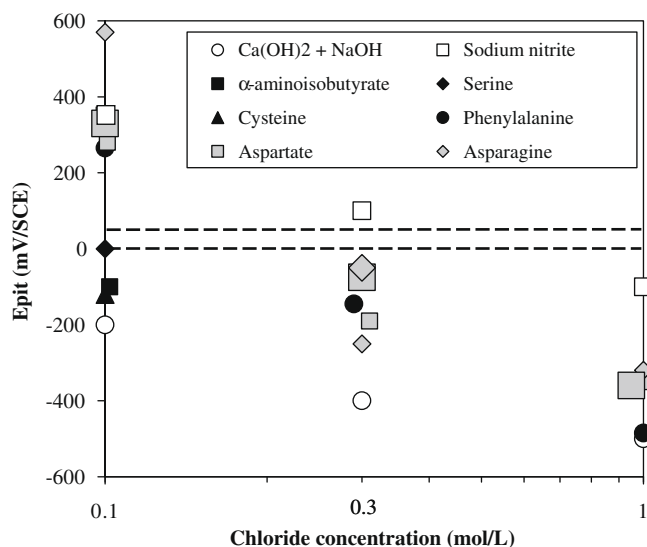


Fig. 14. Pitting potential values in solution with short chain aminoacids (biggest markers refer to 0.3 mol/L inhibitor content).

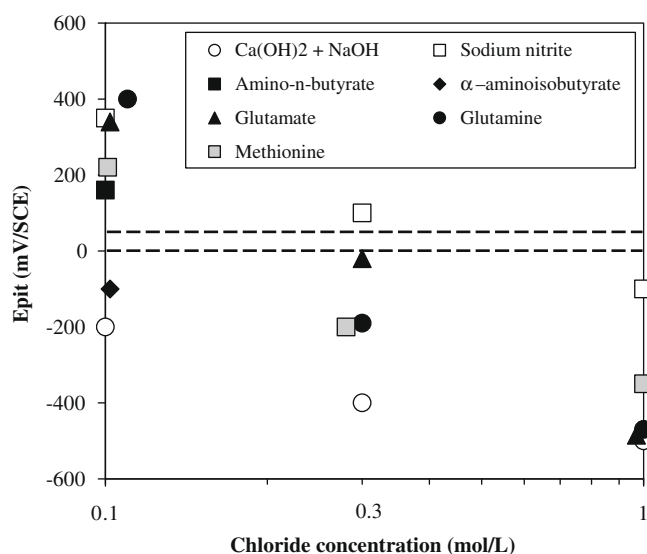


Fig. 15. Pitting potential values in solution with long chain aminoacids.

Aminoacids showed a better inhibition action than amines, as pitting potential increased of 300 mV for $[Cl^-]/[substances]$ molar ratio equal to 1. This effect faded when chlorides concentration was 1 mol/L, not even with higher substances content in the solution.

4. Discussion

To understand the effectiveness of amines, alkanolamines, aminoacids, mono- and poly-carboxylates as candidate for corrosion inhibitors, cyclic potentiodynamic test results were analysed and compared with those obtained in alkaline solution without organic substances ($NaOH$ 0.01 mol/L + $Ca(OH)_2$ sat, pH 12.6) and alkaline solution with 0.1 mol/L sodium nitrite, at the same chlorides content.

4.1. Influence of functional groups and substituents on pitting potential

Fig. 16 illustrates in the Pedferri's type diagram the range of pitting potential as a function of chlorides content and organic substances nature. For comparison purposes results obtained with the

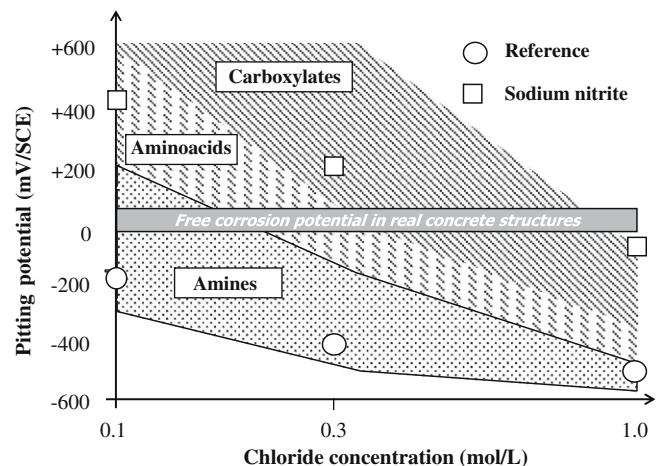


Fig. 16. Pitting potential range obtained for amines, aminoacids and carboxylates with increasing chlorides concentration.

two control solutions are also reported. It was assumed that inhibition effect was acceptable if pitting potential increased of more than 300 mV. Moreover, as free corrosion potential of steel reinforcement in atmospherically-exposed concrete structures usually is below +50 mV SCE, for an inhibiting effect, pitting potential have to exceed it.

In solution without inhibitors, pitting potential decreased from –200 mV to –500 mV SCE as chlorides concentration increased from 0.1 to 1 mol/L. In the presence of sodium nitrite (a worldwide recognised effective inhibitor for concrete [2–9]) pitting potential increase of about 600 mV for each chloride content. Low molecular weight amines showed scattered results due to their high volatility, while other amines and alkanolamines showed pitting potential above 0 mV SCE also in 0.1 mol/L chlorides solution; increasing chlorides content, pitting potential lowered to –200 mV SCE. Based on these results, it can be concluded that amines and alkanolamines showed moderate effectiveness despite their wide use in commercial products, since they have high solubility in water and low influence on fresh and hardened concrete properties. Water solubility strongly decreases with hydrophobic chain length and zeros when exceeds 6–7 carbon atoms, so only amines with short chain length were tested. Moreover, the presence of oxidrilic groups in alkanolamines guarantees stronger hydrogen bonds than those in amines, and this ensures a high solubility.

The inhibition efficiency of aminoacids is in between amines and carboxylates (Fig. 16). Aminoacids are molecules containing both aminic and carboxylic functional groups. Tested aminoacids belonged to two categories: short chain, with only one methylenic group ($R_1-CH_2-R_2$), and long chain, with two methylenic groups ($R_1-CH_2-CH_2-R_2$). Considering long chain aminoacids, by changing the two substitutes R_1 and R_2 in the molecule it was possible to analyse separately their influence on pitting potential. Results lead to the following conclusion: the presence of only the aminic group in the molecule (propylamine, Table 1) did not inhibit pitting initiation ($E_{pit} = -160$ mV SCE), confirming previous data obtained on amines; the presence of both aminic and carboxylic groups (methionine and amino-*n*-butyrate, Table 4) increased the pitting potential ($E_{pit} \approx +400$ mV SCE), even in solution with 0.3 mol/L chloride (this effect was more evident with glutamate and glutamine, long chain aminoacids with a second carboxylic group or its derivative, Table 4); the presence of only the carboxylic group in the molecule (2-methylbutyrate, Table 2) increased significantly the pitting potential ($E_{pit} = +595$ mV SCE).

As far as short chain aminoacids are concerned, results obtained by changing substitutes R_1 and R_2 in a molecule with chemical structure $R_1-CH_2-R_2$ showed that the presence of only the aminic

group in the molecule (ethylamine, Table 1) did not inhibit pit initiation ($E_{\text{pit}} = -180$ mV SCE), the presence of a second carboxylic group (aspartate) or aminic group (asparagine) lead pitting potential to values above +300 mV SCE. Results are in agreement to the ones obtained in case of long chain aminoacids.

Mono- and poly-carboxylates present in the ionic form COO^- showed the best behaviour among studied organic compounds (Fig. 16). Carboxylates adsorption on metal surface occurs through the delocalised electrical charge on the two oxygen atoms of the carboxylic group. In 0.1 mol/L chloride-containing solution, pitting potential exceeded +400 mV SCE in the presence of most of tested carboxylate substances that is even above values measured in sodium nitrite solution, also with 0.3 mol/L chlorides. In 1 mol/L chloride-containing solution, pitting potential was below -300 mV SCE for most substances and about -200 mV SCE for few, that is an increase of 300 mV with respect to control solution.

As carboxylate substances showed the best results, an intensive study regarded the effect of chain length variation and the presence of electron-donor or electron-acceptor substitute types on pitting potential, namely:

1. Presence of more than one carboxylic group in the molecule.
2. Nature and position of substituent groups.
3. Carbon-chain length.

4.2. Mono/poly-carboxylate ion comparison

Poly-carboxylates showed the best inhibitive effectiveness, as pitting potential increased clearly in 0.1 mol/L chlorides solution for acetate ($E_{\text{pit}} = +100$ mV SCE), succinate ($E_{\text{pit}} = +590$ mV SCE), glutarate ($E_{\text{pit}} = +600$ mV SCE) and citrate (pitting did not even started). Fig. 17 shows the molecule structure of these substances. The good behaviour of these compounds could be associated to steric and electrostatic effects, the former linked to carbon-chain length and functional groups not actively involved in the adsorption process, the latter, responsible of electrostatic repulsion towards chlorides, as a result of side interactions given by carboxylic groups, not taking part in adsorption, and the negative charge set up by the polar functional groups adsorbed on steel surface. Carboxylates exhibit a chelate effect to form complexes with calcium and iron ions, however, with respect to those above discussed, this one appears to be secondary.

4.3. Effect of substituent nature

Fig. 18 reports the molecular structure and pitting potential obtained in 0.1 mol/L chlorides solution for carboxylates with differ-

ent substituent groups of $\text{R}_3\text{-C-COO}^-$ molecular structure type. Pitting potential decreased when electron-acceptor substituents were halogens, from +100 mV SCE in 0.1 mol/L acetate solution to -240 mV SCE with trichloroacetate. The presence of electron-donor groups increased pitting potential and accordingly the inhibition effectiveness (2-methylbutyrate $E_{\text{pit}} = +520$ mV SCE, pivalate $E_{\text{pit}} = +550$ mV SCE and cyclohexancarboxylate ($E_{\text{pit}} = +580$ mV SCE). A clearly beneficial steric effect was observed as pitting potential increased in the series: acetate, 2-methylbutyrate, pivalate and cyclohexancarboxylate. Fig. 19 shows pitting potential as a function of substituent group characteristic, i.e., electron-acceptor to electron-donor, for some tested carboxylates. This trend was also obtained with succinate and its derivatives, malate and tartrate, that have one and two oxidrilic groups, respectively, where oxidrilic groups are electron-donors because of electrical charge delocalization of one lone pair on the oxygen atom prevails on oxygen tendency to attract electrons. In this case, the effect on pitting potential is less marked than in the presence of mono-carboxylate ions, probably because oxidrilic groups generates a repulsion effect between two molecules, then reducing the covering efficiency.

Results confirmed that adsorption on metal surface strongly depends on nature of substituent groups. In fact, adsorption process is governed by the combination of an inductive and resonance effects on the electron density of the molecule. The inductive effect depends on the electronegativity of the substituent group and acts through the carbon-chain (Fig. 20). This effect decreases as distance between carboxylic and substituent group increases. The resonance effect depends on electron delocalization on the molecule. This effect does not vary in relation to distance, since depends on the overlapping of atomic orbitals.

4.4. Effect of chain length

The influence of carbon-chain length was studied for poly-carboxylates of the series $\text{OOC}^-(\text{CH}_2)_n\text{-COO}^-$, with n in the range 0–7 (Fig. 21). In these molecules, a carboxylic group, if not directly engaged in the adsorption, should exert a sort of electrostatic repulsion versus chloride ions.

Pitting potential reached a maximum for an intermediate chain length, corresponding to glutarate ($n = 3$), then decreasing as chain length increased to 6 (suberate): this effect could be related to a higher hydrophobicity and lower solubility in water, despite longer chain, as azelate ($n = 7$) would have shown a positive steric effect against chloride migration towards the metal surface, playing a sort of physical barrier. Molecules with more than seven methylen-

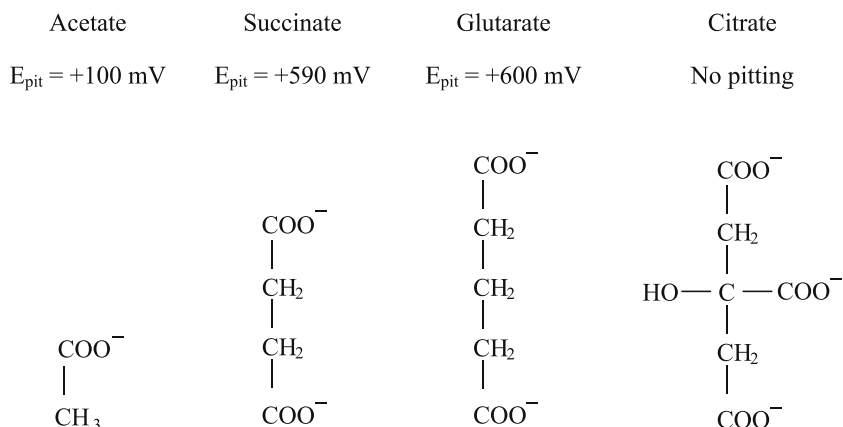


Fig. 17. Chemical structure and pitting potential (vs SCE) for some carboxylates.

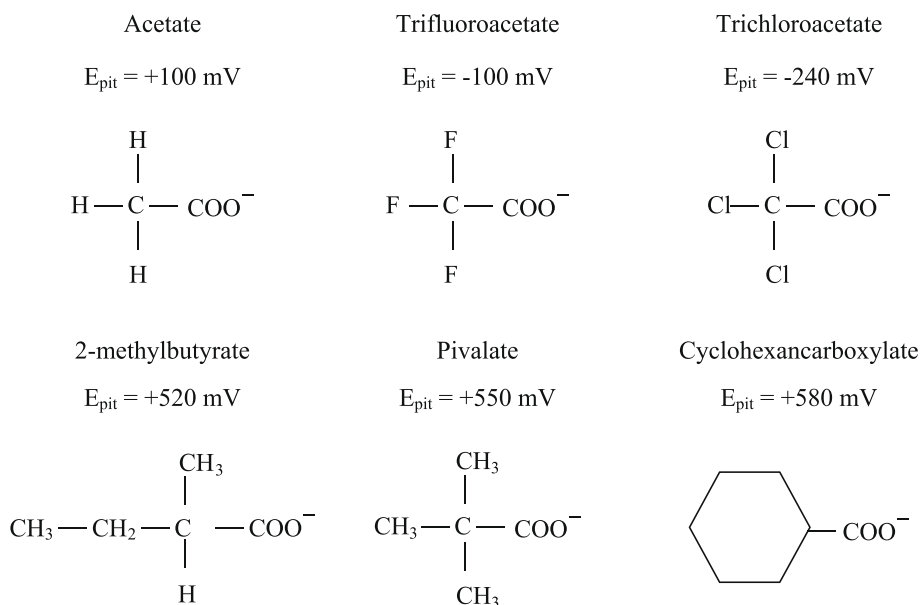


Fig. 18. Chemical structure and pitting potential (vs SCE) for some carboxylates.

ic groups could not be taken into account because of their poor water solubility.

Results are in agreement with previous studies [41] in solution at pH 8.4 that showed the existence of an optimal chain length in order to inhibit corrosion of steel. A clear inhibition increase of inhibitor effectiveness was registered for intermediate chain substance but the presence of a longer chain (and so with bigger hydrophobicity and a lower water solubility) leads to a decrease in the inhibitive effectiveness.

5. Conclusions

More than 80 organic substances were tested as candidate inhibitors for reinforcement corrosion in chlorides containing concrete. Based on potentiodynamic curves obtained in chloride containing alkaline solutions, the following conclusion can be drawn:

1. Amines showed poor inhibition effect, with very scattered result when their volatility increased.
2. Aminoacids showed some inhibition effect, but not sufficient for an industrial applications.
3. Carboxylate substances, especially poly-carboxylates, showed very good inhibition effectiveness, making them the most promising candidates among the tested substances. A confirmation on concrete slab specimens is required to check compatibility with concrete and long-term effectiveness.

As far as carboxylate substances, a strong link was found between inhibiting properties and molecular structure. The inhibition action is influenced by one or more of these factors:

1. *Electron-attractor* or electron-donor effect: Electron-donor substituent, that gives up electrons, promotes the adsorption process through the negative charge localisation on oxygen and

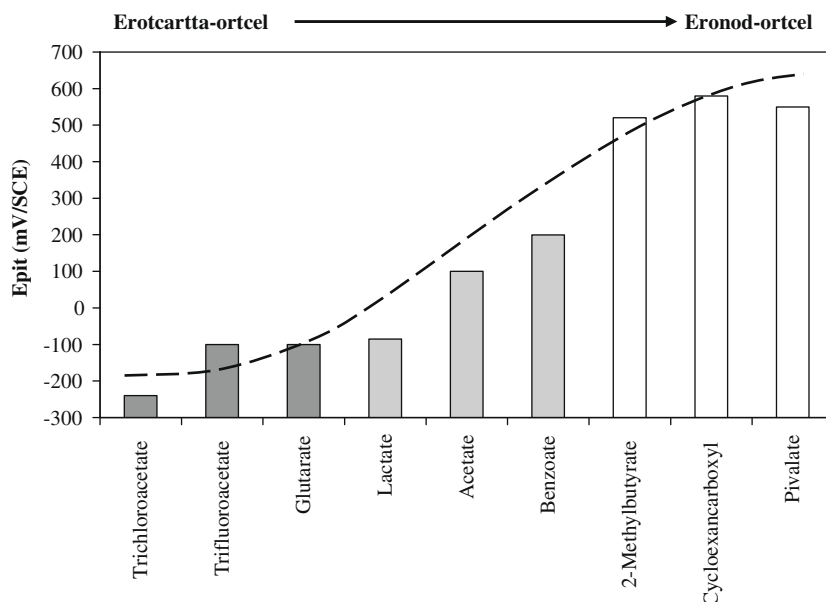


Fig. 19. Pitting potential trend as electro-donor behaviour increases.

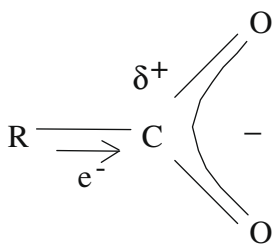


Fig. 20. Inductive effect of a substituent group (R) on the carboxylic group $-\text{COO}^-$.

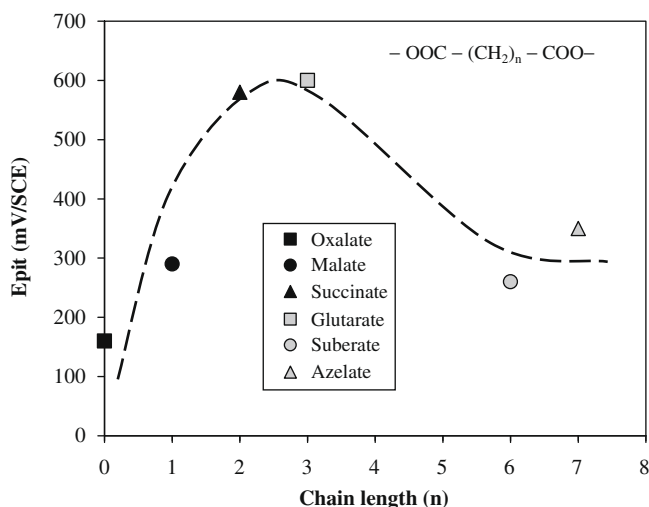


Fig. 21. Pitting potential with respect to chain length for bi-carboxylates.

on carboxylic group (adsorption is a combination of inductive and resonance effect on electron density of the molecule); on the opposite, high electronegative substituent tends to be electron-attractor then weakening adsorption process being electrons not available for it.

2. **Electrostatic effect:** Adsorbed molecules with a negatively charged substituent or a lone pair electrons develop a repulsive action towards chloride ions, avoiding chloride to be in contact with the carbon steel passive layer.
3. **Steric effect:** Alkyl chain or voluminous substituent groups form a sort physical barrier that blocks or delay chloride arrival to the metal surface.
4. **Lateral interaction effect:** Some repulsion effect between adsorbed molecules is possible, because of the presence of highly polar group.

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