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Organic Corrosion Inhibitors

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Additional information is available at the end of the chapter

Abstract

Organic corrosion inhibitors are one of the five ways, besides material selection, design, cathodic protection and coatings, to protect materials against corrosion. Corrosion is an ubiquitous phenomena that deteriorates all materials, metals, plastics, glass and concrete. The costs of corrosion are tremendous and amounts to 4.0% of gross domestic product (GDP) in USA. The similar losses of GDP are noted in all countries around the world. At this point of time, there is no way to completely stop the corrosion processes. Some new solutions can only slow this process. Organic corrosion inhibitors are widely used in industry because of their effectiveness at wide range of temperatures, compatibility with protected materials, good solubility in water, low costs and relatively low toxicity. Organic corrosion inhibitors adsorb on the surface to form protective film which displace water and protect it against deteriorating. Effective organic corrosion inhibitors contain nitrogen, oxygen, sulfur and phosphorus with lone electron pairs as well can contain structural moieties with π-electrons that interact with metal favoring the adsorption process. This review presents mechanisms and monitoring of corrosion, laboratory methods for corrosion study, relationship between structure and efficacy of corrosion inhibitions, theoretical approach to design new inhibitors and some aspects of biocorrosion.

Keywords: organic corrosion inhibitors, biocorrosion, sulfate-reducing bacteria gemini surfactants, corrosion tests

1. Introduction

The world we live in is chemical. Everything what surrounds us is composed of natural or synthetic chemical compounds. Some of them are very durable, some of them are less stable. But all of them are subjected to interactions with the environment what adversely affects the

structural performance, including reliability over time. The deterioration process concerns all materials, not only metals but also plastics, glass, concrete, wood, leather and paper. The cracking, swelling, crazing, discoloration, phase separation or delimitation of plastics is caused by UV-light, heat, moisture or biological activity, that is, by physical, chemical or biological reactions [1, 2]. Corrosion of glass is due to reactions with atmospheric pollutants such as SO_2 or CO_2 as well as hydroxyl ions attack on siloxane bonds what leads to extraction of silica [3, 4]. Corrosion of concrete materials is also a very important economic problem. The maintenance costs of concrete microbial corrosion (CMC) of sewer pipelines in Hamburg (Germany) in 1970s reached up to €25 million whereas in Los Angeles (USA), the sewer pipe of 208 km in a total length of 1900 km had been damaged by CMC, and the rehabilitation costs were as high as $400 million [5]. Wood may also cleave or decompose what is related to its chemical structure based on cellulose, lignin and hemicelluloses. In natural environment, wood is rapidly colonized by microorganism and insects and the process of decomposition begins [6–8]. Deterioration of wood materials is a serious problem especially for historic wood pieces and monuments [9–11].

The deterioration of different kind of materials is defined as corrosion by American Society for Testing and Materials (ASTM International), that is, *"the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties"* [12]. However, the most undesirable and noticeable is corrosion of metals which is defined by ISO (International Organization for Standardization) as *"physicochemical interaction between a metal and its environment that results in changes in the properties of the metal, and which may lead to significant impairment of the function of the metal, the environment, or the technical system, of which these form a part"* [13]. Total costs of corrosion include *"the design and construction or manufacturing, the cost of corrosion-related maintenance, repair and rehabilitation, and the cost of depreciation or replacement of structures that have become unusable as a result of corrosion"* [14] and is estimated to be US$2.5 trillion what corresponds to 3.4% of the global GDP (2013). The use of current corrosion control practice and procedures, including organic corrosion inhibitors, would allow to save 15–35% costs of corrosion [14]. The cost of corrosion varies depending on branch of industry and usually it is the highest in transportation and chemical industry. In China in 2014, direct corrosion cost in transportation was 268.72 billion RMB that constitutes 23.97% of total corrosion costs [15].

Corrosion is an ubiquitous phenomena and there is no way to completely stop it. Some new solutions can only slow this process. However, the environmental pollution, global warming and climate change are the direct cause for increasing corrosion costs. Only the increase of global temperature by 2°C causes an increase of corrosion rates by up to 15% [16].

2. Mechanism of corrosion

Corrosion is mainly induced by chemical and electrochemical processes. Chemical corrosion takes place in dry gases and nonconductive liquids where there is no current/electron flow. The

main effect of chemical corrosion is an oxide layer as a result of oxidation in the air [17]. Electrochemical corrosion takes place in solution, between metallic materials and electrolytes due to different potentials on the surface of the corroded metal and due to redox reactions. One part of the metal is anode where metal oxidizes and becomes ion.

$$M \rightarrow M^{n+} + n\,e \tag{1}$$

The another part is cathode, where depolarization takes place, mainly reduction of oxygen and hydrogen cation [15, 16].

$$O_2 + 4\,H^+ + 4\,e \rightarrow 2\,H_2O \tag{2}$$

$$2\,H^+ + 2\,e \rightarrow H_2\uparrow \tag{3}$$

A scheme of electrochemical corrosion is shown in **Figure 1**.

Another type of corrosion is biocorrosion, commonly called microbial-induced corrosion (MIC) and is defined as deterioration of metallic material caused by consortia of microorganisms [20]. Microbes form a biofilm on the metal surface which is very good environment for their growth [21]. Biofilms are multicellular communities of bacteria encased in an extracellular matrix of exopolysaccharide, protein and sometime extracellular nucleic acids [22]. Biofilms are very hard to eradicated from any environment. They are resistant to most antimicrobial agents [23]. Sulfate-reducing bacteria (SRB) and sulfur-oxidizing bacteria which form biofilm to large extend are the main reason of the biocorrosion [21].

Another term associated with material's degradation is erosion which means "*a progressive loss of original material from a solid surface due to mechanical interaction between the surface and a fluid, a multicomponent fluid or impinging liquid or solid particles*" [24]. A process involving conjoint corrosion and erosion is named corrosion-erosion [24].
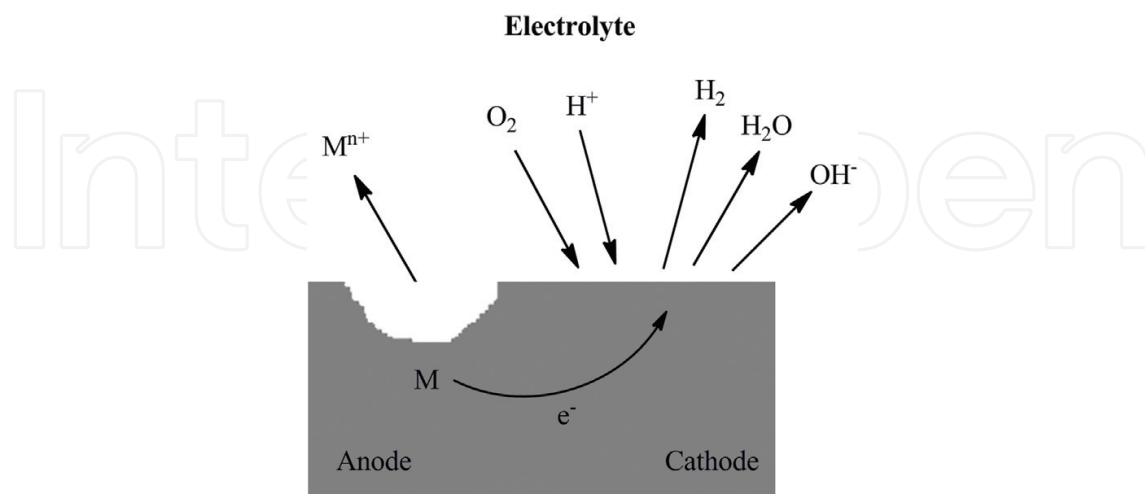
Figure 1. Scheme of electrochemical corrosion.

3. Monitoring of corrosion

To estimate real corrosion damage, many direct and indirect physicochemical analytical methods are used [25]. The most basic method is visual inspection [15, 23]. However, many non-intrusive methods are commonly applied, like ultrasonic [27], potential measurements, radiography, eddy current, magnetic particle inspection [28] and acoustic emission [29]. Ultrasonic allows to control thickness by using sonic waves with high frequency (1–6 MHz). The method can be used for liquids and solids but not for gases [28]. The equipment is calibrated on two thicknesses and by collecting data of material sound velocity, the thickness is calculated. The method can be used in-service and also allows to measure pipe with high temperature and over coatings [27]. The advantage of this method is a possibility to access the material only from one side. The surface of material has to be prepared carefully to have a good contact with the equipment [18, 19]. Acoustic emission measures acoustic sound waves which are emitted due to deformation in the monitored material. The sensors are very sensitive microphones. The sound waves are produced from mechanical stress (pressure or temperature changes) so the technique does not need excitation or human intervention [30]. This technique is a source of large amount of data which requires elaborate filtering and analysis [29]. Potential measurements to control corrosion can be done with a voltmeter with high internal resistance. To get results, the equipment has to be connected to a reference electrode (usually Ag/AgCl electrode). Another method, radiography, uses ability of gamma radiation to penetrate the investigated material. When the beam passes through the material, some energy is absorbed in the material. The thicker the material, the larger amount of the absorbed energy. As a result, a photographic film is obtained where dark color is associated with high intensity of the transmitted beam and light is associated to low intensity. The gamma radiation can penetrate up to 5 cm of the metal with acceptable signal of attenuation [29]. The method is commonly used to control of the permanence of the weld [28]. Radiography is also used for corrosion pits monitoring. Limitation of the methods is a fact that the material has to be available from both sides [18]. Eddy current is a technique used for monitoring of cracking and pitting corrosion of metallic materials. The method depends on the eddy current produced in the surface of the metallic material. The method is restricted to a small layer in the surface of the metal [28]. Magnetic particle inspection method is applied only to ferromagnetic materials and is based on the fact that the surface distortion imparts to a magnetic field. The tested material can be magnetized by several methods like flow an electrical current through material or using electromagnets [28]. Another possibility to control corrosion is to measure indirect changes such as hydrogen evolution which is a product of cathodic reaction. Hydrogen monitoring is applicable to oil and petrochemical industries. The monitoring is based on techniques such as hydrogen pressure or vacuum probe, electrochemical hydrogen patch probe and hydrogen fuel cell probe [29]. Water chemistry analyses can provide interesting information to corrosion monitoring program such as measurement of pH, conductivity or dissolved oxygen [29].

Corrosion monitoring methods like weight loss measurements, linear polarization measurements or electrical sensor utilizing electrical resistance are also used in the field. However, the measurements are indirect which make it difficult to estimate real corrosion damage [25]. All used methods have to be standardized. Examples of extensive collections are the NACE (*National Association of Corrosion Engineers*) standards and the ASTM (*American Society for Testing and Materials*) standards [18].

4. Laboratory methods for corrosion study

The most widespread methods for laboratory corrosion study as well to calculate a corrosion rate (CR) are gravimetric and electrochemical (potentiometry and impedance spectroscopy) techniques, whereas scanning electron microscope (SEM), atomic force microscope (AFM) and transmission electron microscope (TEM) are used to show morphology of surface. The gravimetric method, that is, the weight loss measurements, is one of the simplest methods to carry out. A sample of tested metal, previously carefully degreased and polished is weighed and immersed in an electrolyte solution for specified time (t). After that time, the sample is taken out, sluiced, degreased and weighted. The average weight loss (ΔW) is calculated by following equation:

$$\Delta W = W_1 - W_2 \tag{4}$$

where W_1 and W_2 is samples weight before and after immersion in electrolyte solution for t time, respectively [31]. ΔW is represented in grams. Based on obtained results, corrosion rate can be estimated as

$$CR = (K^* \Delta W)/(A^* t^* d) \tag{5}$$

where K is a constant (8.76×10^4) which allows to represent CR in mm/year; A is the surface of the metal sample (cm^2); t is the immersion time (hours); d is the density of the metal (g/cm^3) [31].

On the other hand, open circuit potential (OCP), named also corrosion potential (E_{corr}), linear polarization resistance (LPR) and potentiodynamic measurements (Tafel slopes) are included in potentiometric methods [32]. The measurements are conducted in standard, three electrode system such as reference (saturated calomel electrode), auxiliary (platinum electrode) and working (sample of the tested metal).

Electrodes are immersed in the electrolyte solution. After reaching an equilibrium, OCP (E_{corr}), which is a difference in potential of microcells of the metal, is registered. At that potential, oxidation and reduction reactions occur which allows to estimate if the metal is resistant to corrosion in tested environment. The higher value of E_{corr}, the higher corrosion resistance of the metal [33]. Graphical representation of results of the potentiodynamic measurements are Tafel slopes: graphs of applied potential (E, V) versus registered current density (i, A/cm^2) (**Figure 2**) [34].

The graph of applied potential versus registered current density is a straight line but that behavior is not observed for measured current (black lines). Due to that, corrosion current density (i_{corr}) is estimated by extrapolation of straight part of the measured current (green lines). The value of corrosion current density is equal for anodic and cathodic reactions, that is, the parameter has a direct influence on the corrosion rate [34].

The value of i_{corr} can also be estimated by measuring linear polarization resistance which is a quick testing technique for this method the material is polarized. The material's resistance (R_p) is found by taking the slope of the potential versus current and the corrosion current density is calculated by using Stern-Geary Equation [35]:
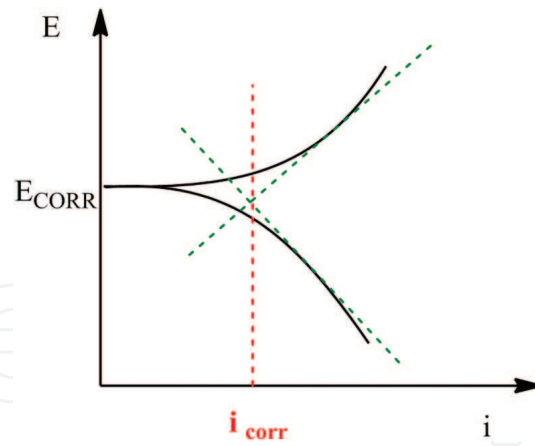
Figure 2. Tafel slopes.

$$i_{corr} = \left(\beta_a\beta_c/2.303\left(\beta_a + \beta_c\right)\right)/R_p \tag{6}$$

where β_a, β_c are slopes of anodic and cathodic of Tafel slopes, respectively [34].

Knowing the i_{corr} value, corrosion rate can be estimated:

$$CR = i_{corr}{}^*\ E_q{}^*\ 10^*\ 3.15^*10^7/F^*\ d \tag{7}$$

where E_q is the equivalent mass of metal exposed to corrosion (g); F is the Faraday constant (96,500 C); d is the density of metal (g/cm^3) and $10\times3.15\times10^7$ is the conversion factor used to obtain the result in mm/year [36].

Electrochemical impedance spectroscopy is also carried out in the standard three electrode system. After reaching equilibrium, impulse with known potential and frequency is applied. It disturbs balance of the electrochemical system. A measured quantity is impedance of the working electrode, Z (Ω), which is described by two types of impedance: real, Re(Z) and imaginary, Im(Z). The results are presented as Nyquist diagrams: a curve in Re(Z)-Im(Z) system [34]. Analysis of obtained data consists in describing the studied system with an equivalent electrical circuit. When the processes are related to charge transfer between metal and electrolyte, then the equivalent circuit consists in: solution resistance (R_s), charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) formed at the metal:solution interface. An example of the Nyquist diagram and the equivalent circuit is presented in **Figure 3**.

In practice, instead of double layer capacitance, constant phase element (CPE) is used. Thanks to that, a fact that the system is not ideal capacitor to be considered. CPE is converted to C_{dl} by following equation [37]:

$$C_{dl} = \left[\left(CPE^*R_{ct}\right)^{1/n}\right]/R_{ct} \tag{8}$$

Where n is a chase shift which represents degree of imperfection [38].
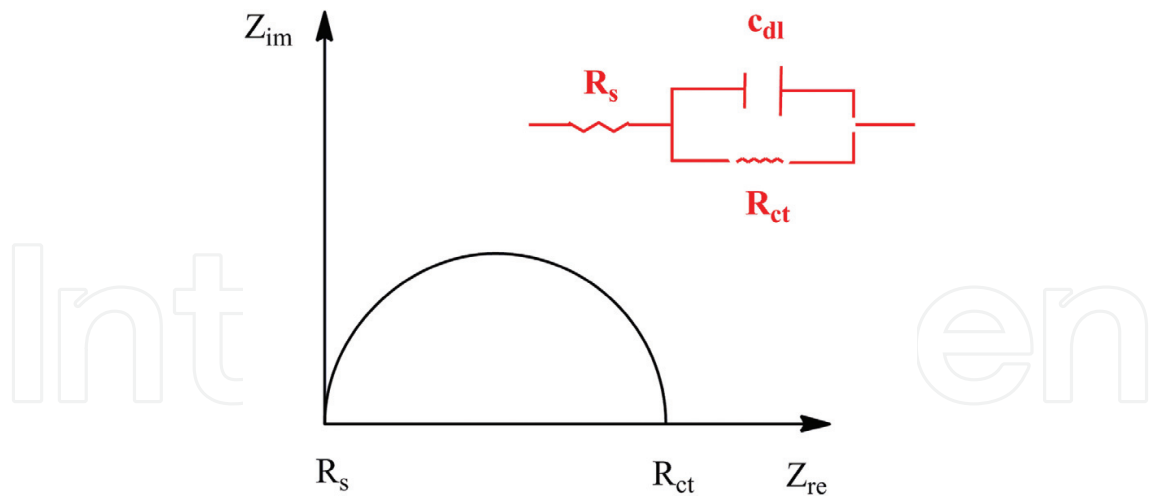
Figure 3. Nyquist diagram and equivalent circuit.

Corrosion rate is calculated from the equation:

$$CR = i_{corr}{}^* \, E_q{}^* \, 10^* \, 3.15^*10^7/F^* \, d \tag{9}$$

Corrosion current density is calculated from Stern-Geary equation [36].

Surface morphology of the metal is examined by using microscope techniques, SEM, AFM or TEM. It allows to observe all surface defects/damage done by corrosion [39]. Very often confocal laser scanning microscope (CLSM) is used to choose the right area of the surface for further SEM/AFM/TEM examinations [37]. The mentioned methods are the most popular but there are also other possibilities to estimate corrosive damage such as analytical methods, volumetric, radiography or magnetic-powder testing. Analytical methods are based on the determination of the metal ions content in environment and qualitative and quantitative analysis of corrosion products by using mass spectrometry, absorption atomic spectrometry or spectrophotometry [31, 37]. Volumetric method measures volume of evolving gas in the corrosive reaction. Radiography is based on phenomenon of radiation absorption by materials. Radiographic images are compared with the image of undamaged sample [41]. Magnetic-powder testing consists in irregularity of distribution of the magnetic field in material's defects. Tested sample has to be magnetized and then magnetic particles are applied and assemble in damage. Magnetic-powder testing is applied only for ferromagnetic materials [34].

5. Corrosion protection methods

There are five primary methods of corrosion control: (I) material selection, (II) design, (III) cathodic protection, (IV) coatings and (V) inhibitors. The simplest method for controlling the corrosion is the selection of the structural materials that change composition, change micro-structure stress and eliminate tensile stress [39, 40]**.** Another method is an application of rational design principles which can eliminate many corrosion problems and reduce the time and costs associated with corrosion maintenance and repair [39, 40]. Cathodic protection is an

electrical method to reduce corrosion rate of metallic structures in electrolytes such as soil or water [42]. To achieve the protection, the impressed current cathodic protection (ICCP) system and the sacrificial anodes cathodic protection (SACP) system are used [44]. Corrosion control by anodic protection is known from the literature [43] but currently it is rarely used due to high restrictions.

Coatings, that is, the isolation of the metal from the corrosive environment is one of the most significant method of protection against corrosion. Coatings could be metallic (tin-plated steel and galvanized steel) or non-metallic (organic or inorganic). The most important are organic coatings, polymers made from epoxides, polyurethanes, polyesters, melamine formaldehyde resins, polyacrylates and phenolic polymers [42, 43].

Recently, many new protective coatings have been developed; they could be based on graphene [47], hybrid based on graphene oxide (GO) and reduced graphene oxide [22, 45, 46], polypyrrole [50], polyaniline/polyvinyl chloride blended [51], nano-hybrid epoxy coatings [52], bio-based polymers [53] or inorganic: siloxane based sol-gel coatings [54], silica-titaniahybrid [55] and iron aluminide coating [56]. Some of them can be used to form the superhydrophobicity surface [48, 49, 54–59, 61]. The coatings can also contain anticorrosive pigments, for example, lanthanum molybdate [62] or sodium phosphomolybdate [63], or anticorrosive coating additives like multiwalled carbon nanotubes [64]. To get the best protection against corrosion as well the optimal economy coatings and cathodic protection can be complementary used [44]. Corrosion inhibitors are special group of substances or their mixtures that prevent or minimize the corrosion. Inhibitors are adsorbed on the surface of the metal and form a protective thin film [39, 62].

The consumption of corrosion inhibitors reached nearly $1.1 billion in USA in 1998 and is forecasted to increase to $2.5 billion in 2017 [66].

Inorganic corrosion inhibitors, besides the oldest one, that is, molybdate anion, belong to calcium nitrite, rare earth metals salts, zinc phosphate, chromates and lanthanide compounds. However, the most numerous class of corrosion inhibitors are organic once [67]. Many of them are surfactants with hydrophilic and hydrophobic molecular moieties [68]. The corrosion inhibitors can be introduced as protective coating [69], bio-based lubricants [67, 68] and smart coatings that are released by the action of specific stimulus (e.g. change of pH, ionic strength or the change of electrode potential) [42, 60, 69–72].

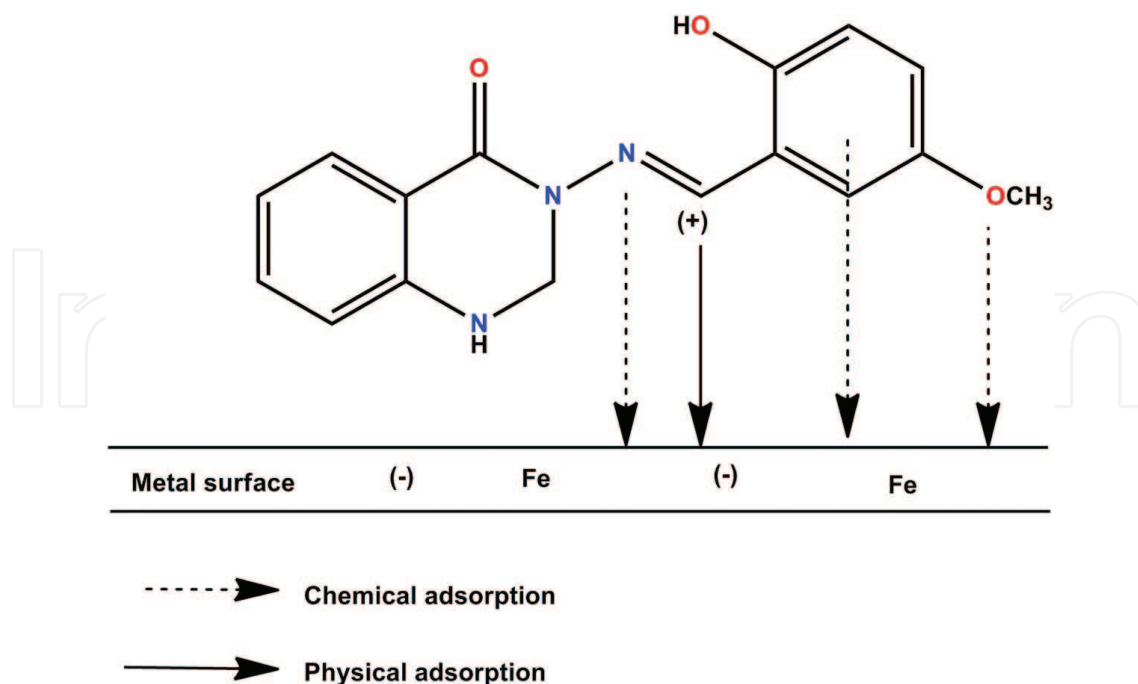## 6. Organic corrosion inhibitors

Organic corrosion inhibitors are widely used in industry because of their effectiveness at wide range of temperatures, compatibility with protected materials, good solubility and relatively low toxicity [78, 79] This is a very important issue for researchers which is confirmed by an increasing number of papers **(Figure 4)**. These compounds act as cathodic and anodic inhibitors. Cathodic corrosion inhibitors move the corrosion potential toward lower values and inhibit or delay the reactions occurring at the cathode (oxygen reduction and hydrogen evolution).
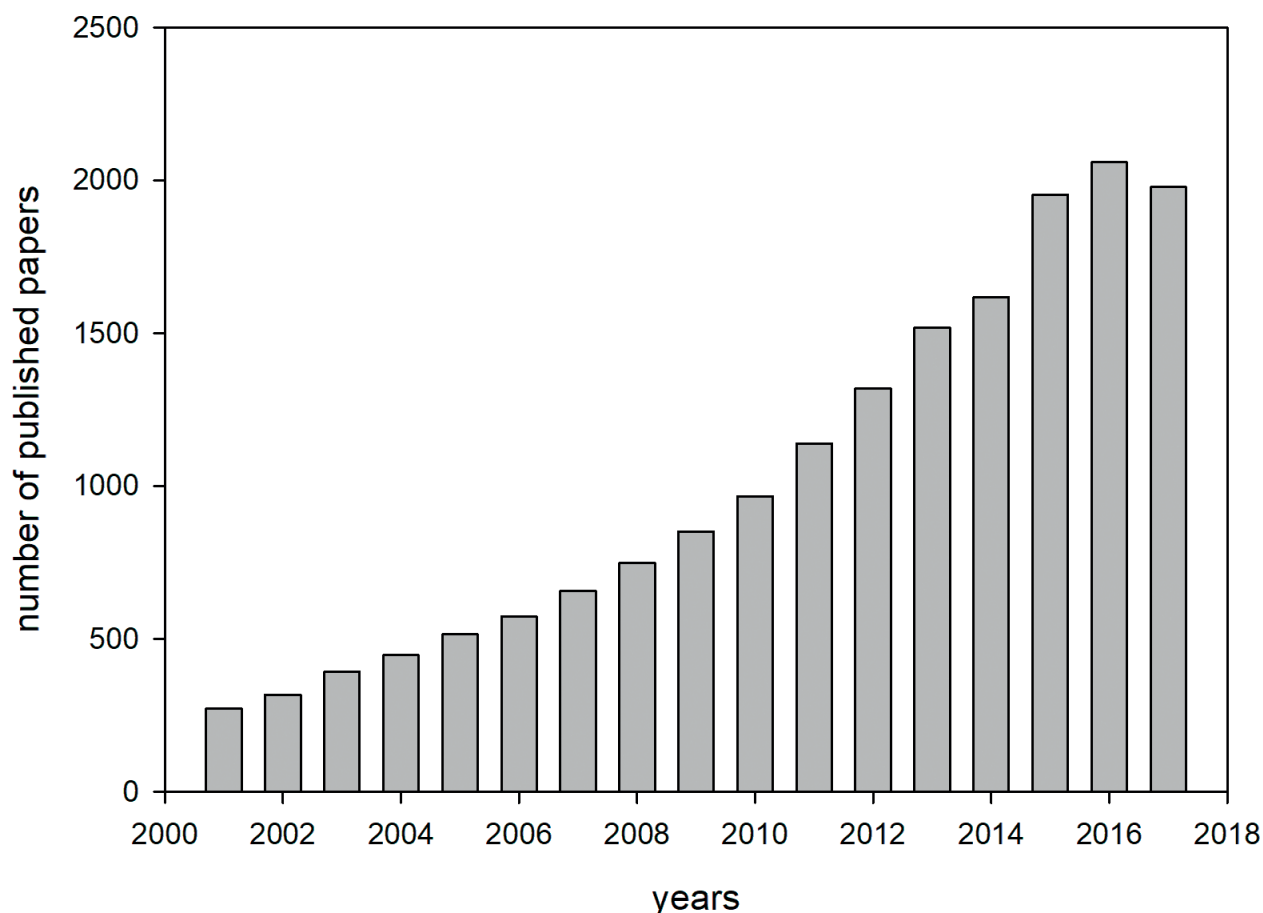
Figure 4. Number of published papers about organic corrosion inhibitors versus year of publication.

In contrast, anode corrosion inhibitors react with the metal cation to form an insoluble hydroxide, block the active sites on the metal surface and move the corrosion potential in the direction of positive values, which prevents further oxidation (dissolution) of the metal thus reducing the rate of corrosion. It is very important to use the right amount of an anode inhibitor, because insufficient concentration to cover all the active sites can lead to localized corrosion which is difficult to detect. Mixed inhibitors provide the highest protection because they affect both cathodic and anodic reactions.

The mechanism of action of organic corrosion inhibitors is based on the adsorption on the surface to form protective film which displace water from the metal surface and protect it against deteriorating. This process is not either purely physical or purely chemical adsorption. Adsorption is influenced by the chemical structure of organic inhibitors, nature and surface charge, the distribution of charge in the molecule and type of aggressive media (pH and/or electrode potential). The physical adsorption is based on electrostatic interaction between the charged metal surface and charged inhibitor molecule. Chemical adsorption is connected with the donor-acceptor interactions between free electron pairs and vacant, low energy d-orbital of metal **(Figure 5)**.

Figure 5. Schematic diagram representing the adsorption mechanism of Shiff bases on mild steel surface [82].

Effective organic corrosion inhibitors should contain heteroatoms (nitrogen, oxygen, sulfur and phosphorus) with lone electron pairs and moiety with π-electrons (aromatic rings and multiple bonds) that can interact with free orbital d metal, favoring the adsorption process [73].

The standard adsorption free energy ($\Delta G°_{ads}$) gives information about type of adsorption. Values up to −20 kJ/mol are connected with the electrostatic interaction (physical adsorption). More negative values, below −40 kJ/mol, correspond to chemisorption process. Negative values mean that both processes are spontaneous. Also the standard enthalpy of adsorption provides valuable information about the mechanism of corrosion inhibition. An endothermic adsorption process ($\Delta H°_{ads} > 0$) is attributed to chemisorptions, whereas an exothermic adsorption ($\Delta H°_{ads} < 0$) is connected to physical or physical/chemical adsorption process [26]. Presence of the heteroatoms with lone pair of electrons like nitrogen, oxygen, sulfur or phosphor as well π-electrons of multiple bonds or aromatic rings enhance adsorption phenomena [74]. Chemisorption involves transfer or sharing of unbounded electrons between the inhibitor molecule and the metal surface [75]. The order of corrosion inhibition is the reverse order of the electronegativity of these atoms

$$P > S > N > O \tag{10}$$

In acid environment, heteroatoms are protonated that additionally promotes the interactions between the inhibitor and the surface. The adsorption of organic corrosion inhibitors onto the surface of a corroding metal may be regarded as a substitution process between the organic compound, especially aliphatic chain in aqueous phase and water molecules adsorbed on the metal surface:

$$Org_{(sol)} + xH_2O_{(ads)} \leftrightarrow Org_{(ads)} + xH_2O_{(sol)} \qquad (11)$$
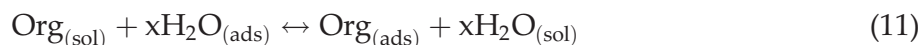
where Org (sol) and Org (ads) are, respectively, the organic species dissolved in the aqueous solution and adsorbed onto the metallic surface; H_2O (ads) and H_2O (sol) is the water molecule adsorbed onto the metallic surface and that in the bulk solution; x is the size ratio representing the number of water molecules replaced by one organic adsorbate.

The aliphatic chain has an influence on the corrosion protection due to the repulsion of nonpolar hydrophobic part of inhibitor and polar medium. The hydrophobic chains form a protective layer at the metal/water interface. The size and molecular weight of organic inhibitor also have an impact on the efficiency of inhibition [76]. Larger the molecule, greater is the inhibition efficiency:

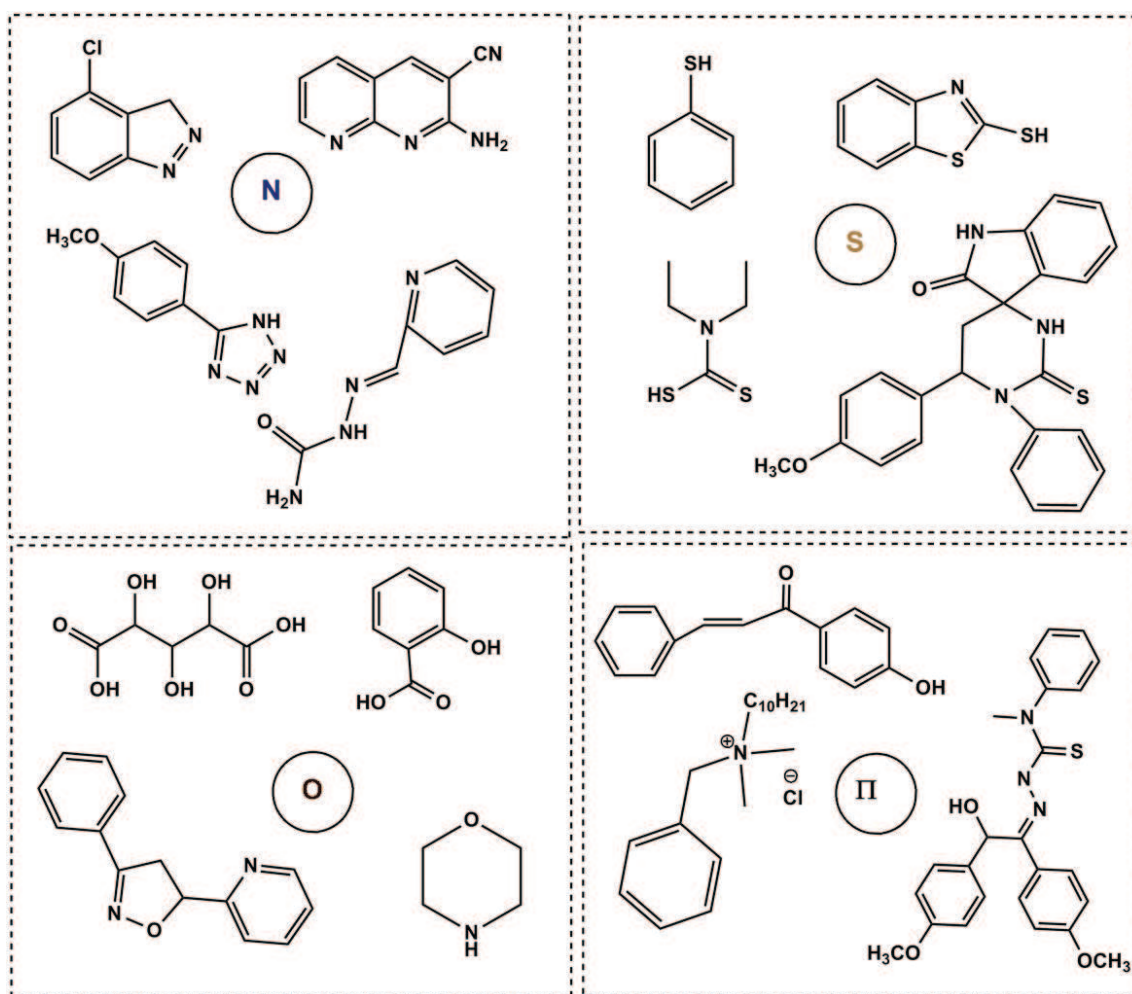$$R_3N > R_2NH > RNH_2 \qquad (12)$$

where R is a hydrocarbon chain.

Figure 6. Nitrogen, sulfur, oxygen and π clusters of organic corrosion inhibitors.

Concentration of corrosion inhibitors has an important impact on the inhibitor efficiency. The corrosion rate decreases with increasing concentration of inhibitors because the adsorption of the inhibitor also increases.

6.1. Structures of organic corrosion inhibitors

The large number of organic corrosion inhibitors can be divided for some clusters with specific elements, like **(Figure 6)**:

- *compounds containing nitrogen:* amines [77], pyridine derivatives [74, 75], quaternary ammonium salts [80], triazole derivatives [81], Schiff base [82], amino acids [64] and indazole [83],

- *compounds containing nitrogen and sulfur:* imidazole derivatives [84], thiadiazole derivatives and thiazole derivatives [85],

- *compounds containing sulfur:* thiourea derivatives [86] ans sulfonates,

- *compounds containing nitrogen and oxygen:* oxazol derivatives [87], phtalimides [88] and plant extracts/natural [89].

Data about material, kind of inhibitor and inhibition efficiency are summarized in **Table 1**.

Polymers have also a high anti-corrosion efficacy. This involves the ability to interact with many, so that surface adsorption is stronger in comparison with monomers. Polymers can be a protective coating, but they can also be used as corrosion inhibitors. For example, deoxyribonucleic acid is a biopolymer with high inhibition efficiency against steel reinforcement [94]. Similarly, natural polymer, chitosan, is used as corrosion inhibitor of copper in hydrochloric acid [95].

| Material	Medium	Corrosion inhibitors	Conc. of inhibitor	Inhbition efficiency (%)	Reference
Mild steel	1 M HCl	2-(4 -nitrophenyl) benzimidazole	1 mM	93.7	[90]
Mild steel	1 M HCl	(6-methyl-3-oxopyridazine-2-yl) acetate	10^{-1} mM	66.7	[91]
Mild steel	1 M HCl	Shiff base	1 mM	92.0	[82]
Low-alloy steel specimen	1% NaCl	L-cysteine	400 ppm	65.7	[64]
Carbon steel (API N80)	1.65 wt%NaCl con. 1 g/L acetic acid	Imidazoline	0.1 g/L	99.3	[84]
Copper	3% NaCl	N-decyl-3-amino-1,2,4-triazole	10^{-3} M	99.2	[92]
Tin	0.5 M HCl	Adenosine	10^{-3} M	73.0	[93]
Indium	0.5 M HCl	Adenosine	10^{-3} M	72.0	[93]
Tin-Indium Alloy (5%Indium)	0.5 M HCl	Adenosine	10^{-3} M	73.0	[93]

Table 1. Data about material, kind of inhibitor and inhibition efficiency.

7. Quaternary ammonium salts as corrosion inhibitors

Due to the presence of positively charged nitrogen atom and the amphiphilic structure, quaternary ammonium salts are the center of interest for using them as highly effective corrosion inhibitors [96–100]. A special attention is devoted to new generation of quaternary ammonium salts—gemini surfactants. These compounds contain two hydrophilic head groups and two hydrophobic tails connected by a spacer at the head groups or closed to them. The spacer can have different structure; it can be rigid or flexible. It can also be hydrophobic or hydrophilic. The neutral charge of the molecule is retained by the presence of organic or inorganic anions. The gemini alkylammonium salts possess a very low critical micelle concentrations (cmc), which is up to hundred times lower than cmc's of corresponding monomeric surfactants. Gemini surfactants also have a larger molecular area in comparison to monomeric analogs which cause them to act more efficiently as corrosion inhibitors [80, 101–110]. Dimeric surfactant 1,4-tetramethylene-bis(*N*-dodecyl-*N,N*-dimethylammonium bromide) (12-4-12) is more efficient in decreasing corrosion rate of carbon steel in 1 M HCl than its monomeric analogue *N*-dodecyl-*N,N,N*-trimethylammonium bromide (DTAB). The relationships of concentration and corrosion rate for both surfactants are presented in **Figure 7.**

Resistance of the carbon steel in a system-containing dimeric surfactant is much higher in comparison to blank solution (1 M HCl) or to solution-containing monomeric surfactant (**Table 2**). It means that metal is less susceptible to corrosion [111].

Inhibition efficiency (IE%) is affected not only by number of positively charged nitrogen atoms but also depends on the length of alkyl chain. Longer the alkyl chain higher is the inhibition efficiency [97, 105] (**Table 3**).
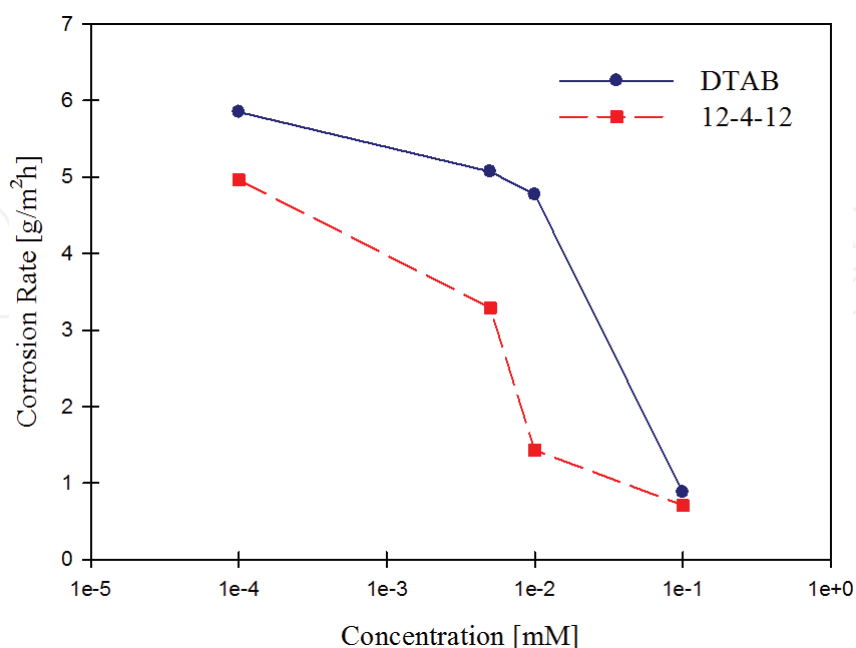
Figure 7. Relationship between corrosion rate of carbon steel and concentrations of surfactants.

	Concentration of surfactant (mM)	R (Ωcm^2)
Blank	—	43
DTAB	0.05	159
12-4-12	0.001	364

Table 2. Resistance of the carbon steel immersed in solution without and with cationic inhibitors.
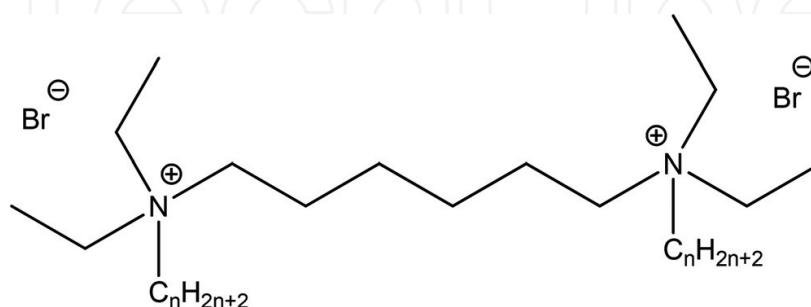
| n	IE (%)
10	93.7
12	95.3
14	96.5
16	98.2

Table 3. Inhibition efficiency of dimeric surfactants for aluminum in 1 M HCl; concentration of surfactants: 1 mM [112].

The same correlation is observed in the spacer length. Longer the spacer, higher is the inhibition efficacy. For gemini surfactant $((C_{12}H_{25})_3N^+\text{-s-}N^+(C_{12}H_{25})_3)$ with two methylene groups as spacer (s) inhibition efficiency is 89% whereas IE is 93% for six methylene units at concentration 5 mM [109].

Additional heteroatoms or π electrons also favor adsorption onto the metal surface [113]. The order of the effective action increases with decreasing the electronegativity of the heteroatom: O < N < S < P [114]. Replacement of isopropyl group to hydroxyethyl or benzyl group leads to the increase of the inhibition efficiency from 95 to 96 or 97%, respectively (**Table 4**) [115]. Oxygen is a source of two unbonded electron pairs whereas benzene ring is a source of three pairs of π electrons, which can interact with free d orbitals of the metal.

Increasing the number of heteroatoms also affects the inhibition efficiency (**Figure 8**) where 12–6-12 is 1,6-hexamethylene-bis(*N*-dodecyl-*N*,*N*-dimethylammonium) dibromide; G6-MOH-12 is (1,6-hexamethylene-bis(*N*-dodecyl-*N*-hydroxyethyl-*N*-methylammonium) dibromide; 12-MOH-O-MOH-12 is 3-oxa-1,5-pentamethylene-bis(*N*-dodecyl-*N*-hydroxy-ethyl-*N*-methyl-ammonium) dichloride [116].

The plots in **Figure 8** present a semicircular shape with a diameter corresponding to the corrosion resistance (large diameter and higher resistance). The stainless steel impedance response in
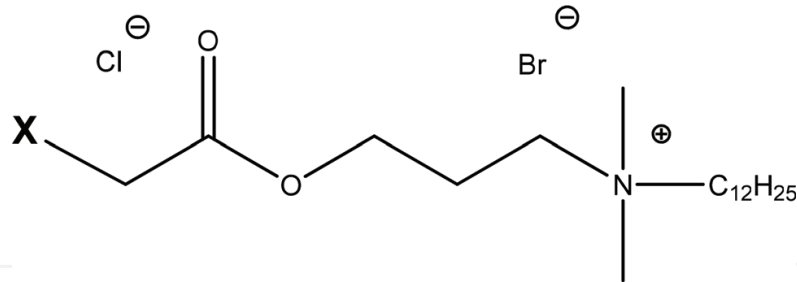
| X	Inhibition efficiency (%)
$(CH_3)_2CHN^+(CH_3)_2$	95.43
$OHCH_2CH_2N^+(CH_3)_2$	96.24
$PhN^+(CH_2CH_3)_2$	97.19

Table 4. Influence of the presence of heteroatoms and π electrons on inhibition efficiency of steel in 1 M HCl.
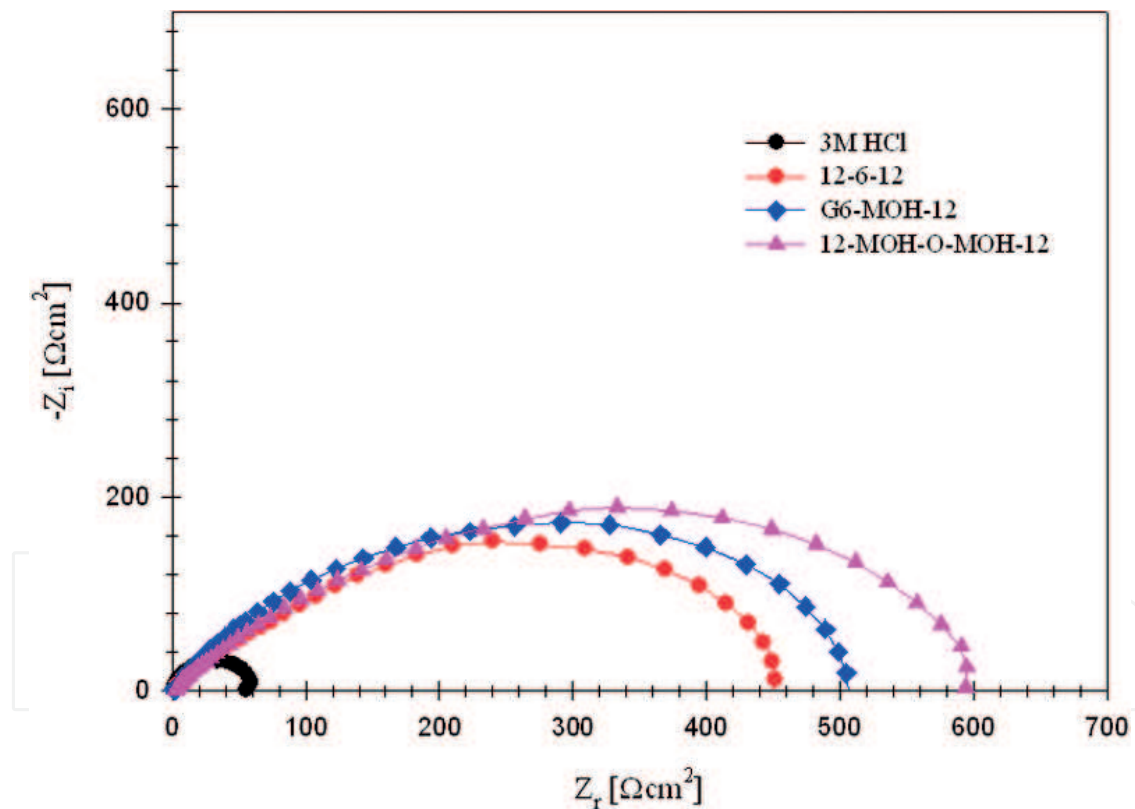
Figure 8. Structure of the gemini surfactants and Nyquist plots for stainless steel in 3 M HCl in the presence and absence of the synthesized inhibitors (naturally aerated, 7 days of immersion).

the blank solution (black) shows a smaller diameter compared to the diameters of the plots for both gemini surfactants, the latter indicating higher resistance, that is, lower corrosion rate. The diameter is the biggest for surfactants functionalized with three oxygen atoms (12-MOH-O-MOH-12) [116]. Some of gemini surfactants, which are already commercially used, are a part of
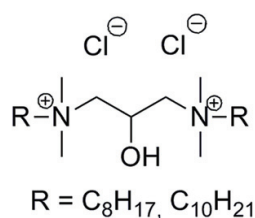
Figure 9. Structure of one commercially used inhibitor.

special compositions which are based on synergistic effect in order to lower the concentrations used [30, 110–112]. Some gemini surfactants are a part of patent about multifunctional corrosion inhibitors for iron alloys (tanks transporting oil and liquid fuel) which are subjected to acidic pollution, sulfur compounds, water, oxygen as well as calcium and magnesium cations [120]. Another patent is about using gemini surfactants as corrosion inhibitors of metallic materials which are used for gas and oil extraction [121]. The inhibitors contain heteroatoms and π electrons, their efficiency is higher than 90%. One inhibitor's structure is presented in **Figure 9** [120].

One of the interesting organic corrosion inhibitors are ionic liquids (ILs) as potentially green chemicals. Amidation of chitosan subsequently quaternized with oleic acid and p-toluene sulfonic acid gave new ionic liquid. The corrosion inhibition of the prepared polymeric ionic liquid on steel in acidic medium was investigated by using different electrochemical techniques [122].

8. Biocorrosion

Microbially induced corrosion (MIC) is one of the fundamental problems in marine industry, pulp and paper industry, natural gas transmission, industrial water transmission, metalworking and chemical process industries. This kind of corrosion is also called as biocorrosion, bacterial corrosion, microbial corrosion is deterioration of metal or non-metal materials as a result of the metabolic activity of microorganisms [116, 117]. Biocorosion is mostly a result of the interaction of mechanical, physical, chemical and/or biological factors. Wind, water, particles of dust, pollution atmosphere and water, and, in the case of stone materials, action light and temperature changes cause damage to materials, allowing penetration moisture and colonization of microorganisms on their surface. This leads to the uprising biofilm, a biologically active layer of various types of microorganisms as well as mucus being the product of their metabolic activity. Biofilm creates very good environment for growing microorganism, and increase rate of corrosion even to 10,000 times. The key to avoid this problem is understanding the dynamics of microbes [118, 119].

8.1. Microorganism and environment

Prerequisites for microbial-induced corrosion are the presence of microorganisms. If the corrosion is influenced by their activity, further requirements are (a) an energy source, (b) a carbon

source, (c) an electron donor and (d) water. The kinetics of biocorrosion is strongly influenced by the concentration of oxygen, presence of salts, pH value, redox potential and conductivity. The living bacteria produce extracellular polymeric substances (EPS) and form biofilms on the metal surface. Biofilms are characterized by strong heterogeneity [120, 121]. Biofilm consists of bacterial cells and extracellular polymeric substances (mixture of polysaccharides, proteins, nucleic acids and fats) which facilitate the attachment of bacterial cells to the surface. The biofilm also includes inorganic sludge from water and/or corrosion products [122, 123]. The most common methods to observe biocorrosion effects are scanning electron microscope (SEM) and confocal laser scanning microscope (CLSM) [128] as well as X-ray photoelectron spectroscopy [124–126] and time of flight-secondary ion mass spectroscopy (ToF-SIMS) [129].

Bacteria involved in corrosion can be divided into following groups:

Sulfate-reducing bacteria (SRB) are anaerobic microorganisms that can obtain energy by oxidizing organic compounds or molecular hydrogen (H_2) while reducing sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S). In a sense, these organisms "breathe" sulfate rather than oxygen in a form of anaerobic respiration [20, 21]. Sea water is a primary source of sulfate-reducing bacteria (SRB) (**Figure 10**).

Metal-reducing bacteria (MRB) affects the corrosion of iron and its alloys by dissolving the passive film on the surface of the metal or by transformation of the sediment to a less stable reduced form that does not inhibit corrosion process. Included in this group are the bacteria of *Pseudomonas* and *Shewanella* have the ability to reduce iron oxide and manganese oxides whereby the speed reduction depends on the type of sediment [130, 133].
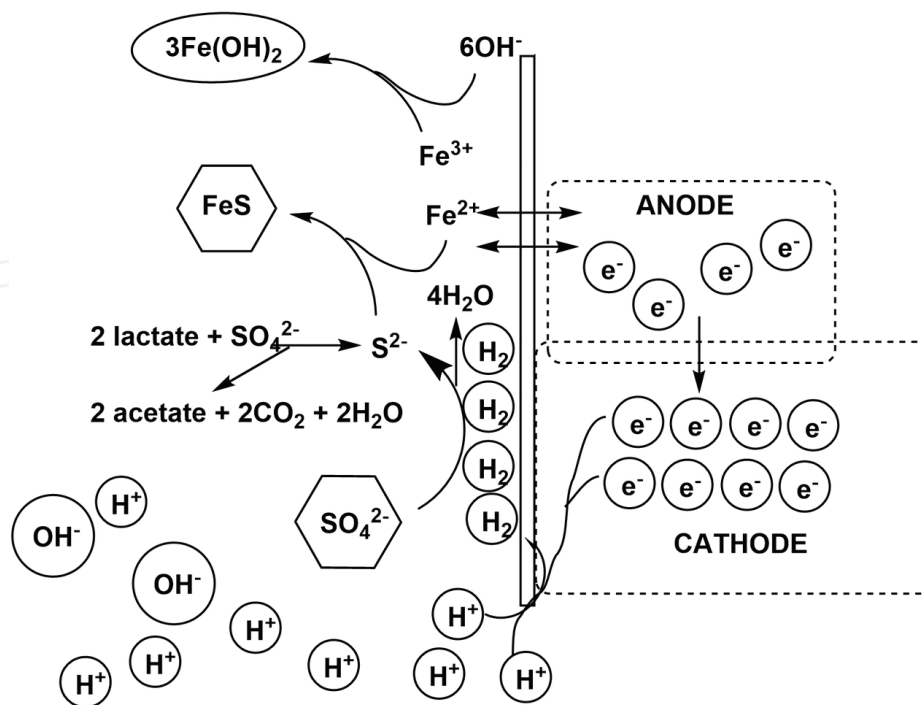

Figure 10. Mechanism of action SRB.

Metal-depositing bacteria (MDB)—*Siderocapsa*, *Gallionella*, *Leptothrix*, *Sphaerotilus*, *Crenothrix* and *Clonothrix* are involved in the biotransformation of iron oxide and manganese. Iron-depositing bacteria (e.g. *Gallionella* and *Leptothrix*) gain energy by oxidizing Fe (II) ions (dissolved or bound in sediments) to Fe (III). All these types of bacteria have the ability to oxidize Mn (II) to Mn (IV) with the precipitation of manganese dioxide that occurs in the rapid filter beds. *Filamentous bacteria* are associated with the formation of pitting corrosion [21].

Hydrogen sulfide-producing bacteria (SPB) are bacteria producing a large amount of extracellular polymeric substances (EPS) during the development of biofilm (e.g. *Clostridium*, *Flavobacterium* and *Desulfovibrio*) their role in the corrosion process consists in covering the metal surface with a EPS layer facilitating the attachment and multiplication of others bacteria [21].

Acid-producing bacteria (APB) are bacteria that secrete inorganic and organic acids as products by-pass metabolism while simple organic acids (acetic, formic and lactic) are metabolites of bacteria heterotrophic [21].

8.2. Biocorrosion inhibitors

Methods to significantly slow have concern on inhibition of the growth of microorganisms and modification of the environment in which the corrosion process takes place. The basic steps to prevent and control biocorrosion are (i) cleaning procedures; (ii) microbiocides; (iii) coatings and (iv) cathodic protection [65].

Obviously it is not easy to stop process of growing bacteria with one compounds. Because these kind of species should have antimicrobial activity and also should be corrosion inhibitors. Example of that kind of multifunctional compounds are gemini surfactants [127, 128]. Biocidal activities of the synthesized surfactants were achieved by dropping the redox potential and confirmed preventing sulfide production in the reactor's bulk phase. This means that all sulfidogenic bacteria are active in the reactor's bulk phase and on the metal surface. Labena et al. describe potential biocorrosion inhibitors that contain quaternary ammonium atom (**Figure 11**) [135].

Quite new approach is using surface modification technologies such as short anti-biofilm peptides applying by immobilization method [136] also using small lipopeptides [137]. Using of coatings based on on silicone and epoxy resins are also method to protection against biocorrosion.
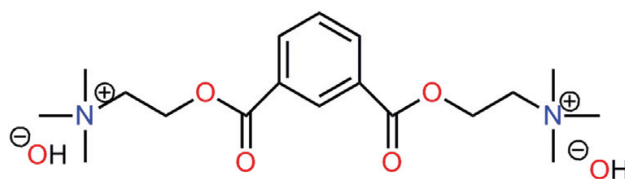
Figure 11. Structure of potential biocorrosion inhibitors.

9. Designing organic corrosion inhibitors

Quantum chemical methods are useful for designing new, effective organic corrosion inhibitors as they relate electron structure of the compounds to their reactivity. Every year density functional theory (DFT) is more often applied for predicting a theoretical ability to inhibit corrosion process according to some quantum chemical parameters: energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), gap energy (ΔE), chemical hardness (η), softness (σ), ionization potential (I_P) and electron affinity (E_A), electronegativity (χ) and fraction of electron transferred (ΔN) [94, 99, 131, 138]. The energy of the highest occupied molecular orbital (HOMO) is associated with the ability of a molecule to donate electrons to the free d orbital of a metal. Compounds with higher E_{HOMO} are more capable of donating electrons. The energy of the lowest unoccupied molecular orbital (LUMO) is related to the ability to accept electrons from the metal. Lower values indicate higher tendency of accepting electrons. Moreover, positive values are connected with chemisorption, whereas negative values with physisorption [94, 132]. Another important parameter is energy gap:

$$\Delta E = E_{LUMO} - E_{HOMO} \tag{13}$$

The lower ΔE, the more reactive molecule, is related to better adsorption of inhibitor's molecules onto the metal surface [133, 134]. The dipole moment (μ) is also an important parameter which gives information about polarity in a bond. Corrosion inhibition efficiency increases with increasing the value of μ, due to the stronger dipole-dipole interactions with the metal surface which results in stronger adsorption and efficient corrosion inhibition [140]. Chemical hardness (η) and softness (σ) provide information about the resistance of a molecule to charge transfer and about the capacity of a molecule to receive electrons. They are calculated according to the equations:

$$\eta = -1/2 \left(E_{HOMO} - E_{LUMO} \right) \tag{14}$$

$$\sigma = 1/\eta \tag{15}$$

The higher σ value suggests softer nature of the molecule and greater tendency to donate electrons to the metal [101]. Energy of HOMO and LUMO orbitals can be used for calculating ionization potential (I_P) and electron affinity (E_A) by the following equations:

$$I_P = -E_{HOMO} \tag{16}$$

$$E_A = -E_{LUMO} \tag{17}$$

The calculated values are used for estimating the electronegativity (χ) [141]:

$$\chi = (I_P + E_A)/2 \tag{18}$$
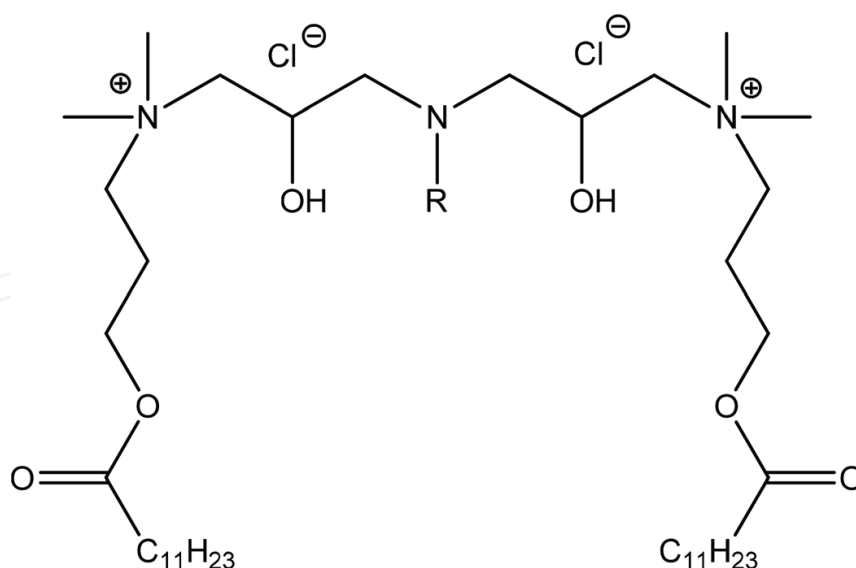
R	IE (%)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (De)	ΔN
C_4H_9	79.86	−4.03	0.86	4.89	2.16	1.11
C_6H_{13}	79.49	−2.10	0.83	2.93	5.45	2.17
C_8H_{17}	81.32	−1.43	0.73	2.16	6.42	3.08

Table 5. Electron parameters and IE% for the gemini surfactants.

High value of χ suggests strong ability to attract electrons from the metal which leads to greater interactions and higher corrosion protection. The last parameter which is calculated is the fraction of electron transferred (ΔN):

$$\Delta N = \chi_{Fe} - \chi_{inh}/2\left(\eta_{Fe} - \eta_{inh}\right) \qquad (19)$$

where χ_{Fe} equals 7 eV and $\eta_{Fe} = 0$ [101]. If $\Delta N > 0$, electrons are transferred from the molecule to the metal and if $\Delta N < 0$, from the metal to the molecule. For all tested gemini surfactants, the values of the fraction of electron transferred are negative indicating transfer from the metal to the molecules. Some quantum parameters for gemini surfactants and corrosion inhibition efficiency (IE%) of carbon steel are presented in **Table 5** [139].

According to the presented results, elongating the alkyl chain (R) leads to increasing corrosion inhibition efficiency from 79.86 to 81.32%. Based on the electron parameters, all values of E_{LUMO} are negative, which are associated with physisorption. The lowest value of E_{LUMO} and the highest value of E_{HOMO} were noticed for a surfactant with octyl group, as well as the lowest ΔE and the highest dipole moment. The electron parameters suggest the compound with octyl group should be the most efficient inhibitor of the tested group. This observation is in agreement with experimental results (IE%). The values of ΔN which are higher than 0 indicate that electrons are transferred from inhibitor to free d orbital of the metal.

10. Summary

Organic corrosion inhibitors with heteroatoms and π-electron moieties are very efficient compounds to fight corrosion. The reviewed literature data clearly indicate that a new way to inhibit deterioration processes can be multifunctional gemini surfactants. Gemini alkylammonium surfactants with the highest corrosion inhibition efficacy can be synthesized according to prediction by theoretical calculations structures. These organic corrosion inhibitors can be also immobilized and used as biocorrosion inhibitors.

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