



Review

Corrosion inhibition of offshore oil and gas production facilities using organic compound inhibitors - A review



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ABSTRACT

Corrosion is the destructive chemical attack, abrasive action of tidal waves, and microbial attacks upon a metallic structure by its environment, and it is the commonest electrochemical phenomenon that is experienced in day-to-day activities of offshore oil and gas production. Corrosion control of metallic structures is an important activity in technical, economic, environmental and safety terms. The negative impacts of corrosion are so enormous, and it is therefore imperative for oil and gas industry, particularly offshore industry to have corrosion awareness in their daily activities with a view to providing corrosion protection of offshore structures, and ensure safe and productive drilling operations. This review discusses extensively multi-component synthetic organic compounds and phytochemicals of green inhibitors with S, N and O functionalities in their structure, for use as corrosion inhibitors against the corrosion of offshore oil and gas production facilities such as pipelines and storage containers in corrosive media, stressing specifically their synthesis (where applicable), properties and efficiency of inhibitors. Also addressed in this review are the future challenges in flow assurance due to the formation of gas hydrates in flowline, especially for offshore oil and gas production. The corrosion performance tests are extensively discussed.

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1. Introduction

In recent times, there has been rapid progress in the scientific exploration and exploitation of crude oil at the ocean depth which has led to the design of equipment for deep-ocean investigation and underwater activities. Offshore operators have in recent years built offshore facilities such as offshore platforms, pipelines, ships and underwater storage and shore facilities for their exploration and drilling activities. However, structural integrity of these offshore structures has been reported not to be fully understood [1]. These marine and offshore structures are constructed from steel and thus, every parts of these facilities from drilling rigs to production facilities have been reported to be susceptible to both internal and external corrosion due to the harsh environments such as ultra-high temperatures and high-pressure environments to which these facilities interact with [2–4]. Degradation and wear of these structures results in loss of their mechanical properties such as strength, ductility and impact strength and at times to complete failure. Structural degradation of offshore oil and gas facilities can occur due to chemical attack, abrasive action of waves, and microorganism attacks. Corrosion is of major economic significance because corrosion costs of oil and gas facilities, including costs for new construction, maintenance costs on aging/corroding equipment, inspections, structural integrity evaluations, and the correction of corrosion-related failures and wears have been reported to run into billions of dollars per year [5], and as estimated by World Corrosion Organization (WCO), the annual cost of corrosion could be around \$US2.4 trillion [6]. In recent times, offshore facilities operators are focusing on cost savings with continuous search for new innovative technologies and solutions to prolong structural life of existing assets and infrastructure while lowering costs of corrosion on offshore facilities, and reducing environmental impact of their operations. Hence, this review focuses on discussion of various types of organic corrosion inhibitors, including synthetic and natural organic corrosion inhibitors with S, N and O functionalities in their structure, for use as corrosion inhibitors against corrosion of offshore oil and gas production facilities such as pipelines and storage containers, with special emphasis on their synthesis (where applicable), properties and efficiency of inhibitors. Also addressed in this review are some of the severe technical challenges in flow assurance due to the formation of gas hydrates in flowline, especially for ultradeepwater operations.

2. Mechanisms of action of corrosion inhibitors

Corrosion inhibitors are chemical compounds that are added in small concentration to a fluid to minimize or prevent the corrosion-related problems triggered by widely varying processing conditions and concentrations of salts and water at different stages of oil and gas production processes. Corrosion inhibitors can be chemically adsorbed (chemisorptions) on the surface of the metallic substrates and form a protective thin film with inhibiting effect or increase the potential of the metal surface so that the metal enters the passivation region where a natural oxide film forms. The corrosion inhibitors can also react with a potential corrosive components present in aqueous media, thereby preventing the anodic or cathodic process by simply blocking active sites on the metal surface [7,8]. Depending on their mechanism of action and composition, these corrosion inhibitors can be classified into interface (or barrier) inhibitor and environmental conditioners (neutralizing and scavenging). A qualitative classification of inhibitors is presented in Fig. 1.

2.1. Barrier inhibitors

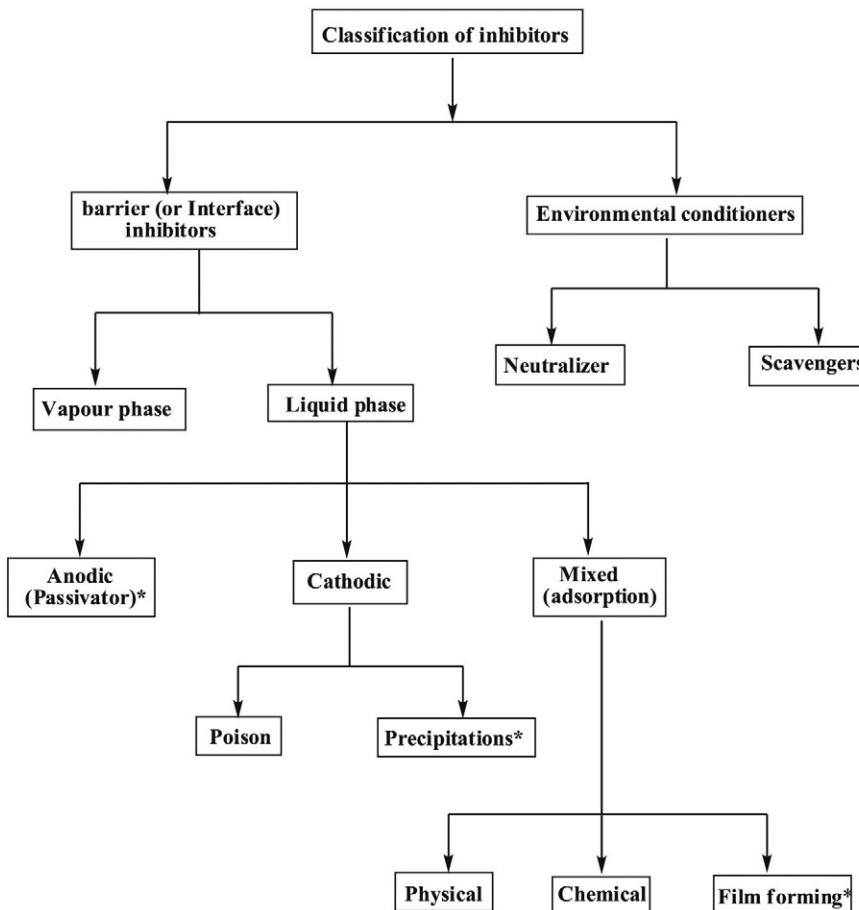
Barrier inhibitors, also known as film forming corrosion inhibitors or interface inhibitors form a protective barrier on the metal surface through strong interactions such as electrostatic adsorption, chemisorptions and π -orbital adsorption, leading to significant reduction in the penetration of corrosive substances [9]. These chemical inhibitors are

composed of polar head which interact with the metal surface and a hydrophobic group that extends away from the surface, and which also provide additional protective layer against aqueous species as it interacts with hydrocarbon molecules of the stream (Fig. 2). They are the largest class of inhibitive substance and they do not need to interact with acids or corrosive elements to be effective [10]. These film-forming or interface inhibitors can be classified into liquid- and vapor-phase inhibitors.

The liquid phase inhibitors can further be classified into anodic, cathodic or mixed-type, depending on the type of electrochemical reaction that is being blocked [11,12]. Since the anodic reaction involves the dissolution of the metal to metal cations, most anodic inhibitors are those materials that can form sparingly soluble deposits such as oxides, hydroxides, or salts in near neutral solutions [11]. They form, or facilitate the formation of passivating films that inhibit the anodic metal dissolution reaction, and are also referred to as passivating inhibitors. Corrosion may be accelerated due to insufficient concentration of an anodic inhibitor, and is therefore imperative to determine the critical inhibitor concentration above which the inhibitors are effective, and this concentration depends on the nature and concentration of corrosive ions. On the other hand, cathodic inhibitors usually control corrosion by either decreasing the reduction rate (cathodic poisons) or by precipitating selectively on the cathodic areas (cathodic precipitators). In cathodic poisons, protective films layers are formed on cathodic areas against hydrogen in acidic conditions or decrease the cathodic reaction rate by limiting the diffusion of oxygen to the metal surface in alkaline solutions. Cathodic poisons can cause hydrogen induced cracking (HIC), hydrogen embrittlement or sulfide-stress cracking [11]. Hence, it is necessary to perform hydrogen permeation studies to determine the effectiveness of cathodic inhibitor [13]. Cathodic precipitators on the other hand, increase the alkalinity at cathodic sites, leading to precipitation of insoluble compounds on the metal surface. The most widely used cathodic precipitators are the carbonates of calcium and magnesium.

The last category is the mixed-type inhibitor, where about 80% of organic compounds fall in this category. Mixed-type inhibitors provide the required protection for metals by physical adsorption (physisorption), chemisorption and film formation. Physical adsorption is due ionic or electrostatic interaction between the inhibitor and the metal surface. Physically adsorbed inhibitors interact rapidly, but increase in temperature facilitates desorption of physically adsorbed inhibitor molecules. The most effective inhibitors are those that chemically adsorb (chemisorb) on metallic substrate, a process that involves charge sharing or charge transfer between the inhibitor molecules and the metal surface. Increasing temperature increases adsorption and inhibition performance of chemisorption process unlike physisorption. Chemisorption is slower than physisorption and is not completely reversible [14]. The adsorbed inhibitor may undergo surface reaction producing polymeric films. Corrosion protection increases significantly as the polymeric films grow from nearly two-dimensional adsorbed layers to three-dimension films up to several hundred angstroms thick. Inhibition is effective only when the films are adherent, non-soluble, and prevent access of the solution to the metal surface. Protective films may be non-conducting or conducting (self-healing films).

Vapor phase inhibitors (VPs) can only achieve temporary protection against atmospheric corrosion, particularly in an enclosed environment [15]. The vapor phase inhibition involves two steps, including transport of inhibitor to the metal surface and interaction of inhibitor on the surface. A VPI may vapourize either in the molecular form or may first dissociate and then vapourize. Amine for example has been reported to vapourize in the undissociated molecular form, while dicyclohexylamine nitrite dissociates to liberate amine and nitrous acid, which are then deposited on the metal surface [16]. VPs in both molecular and dissociated forms adsorb either physically or chemically on metal surface to inhibit corrosion.



* Form three-dimensional layers at the interface, so they are classified collectively as interphase or barrier inhibitors

Fig. 1. Classification based on mode of corrosion inhibitors.

2.2. Neutralizing inhibitors

The corrosive action of acids produced or used during oil well acidization can be managed by adding neutralizing inhibitors to reduce the concentration of the hydrogen ions in the corrosive environment. It has been reported that they are widely used in boiler water treatment and on flow lines [17]. Some common neutralizing inhibitors include ammonia, sodium hydroxide, morpholine and several amines, alkylamines, and polyamines [18]. The physical states of the materials need to be considered in order to maximize their potential as inhibitors, for instance ammonia is an inexpensive neutralizer but its insolubility in the condensates and its quick evaporation compromises its effectiveness as inhibitor [19,20].

2.3. Scavenging inhibitors

Scavenging inhibitors are used in oil and gas production to remove corrosive ions. Hydrazine and sodium sulfite are the well-known scavenging inhibitors [21]. These two inhibitors have been reported to remove dissolved oxygen from treated boiler water [22,23], in accordance with the following equations:

Sodium sulphite reaction;



Hydrazine reaction;

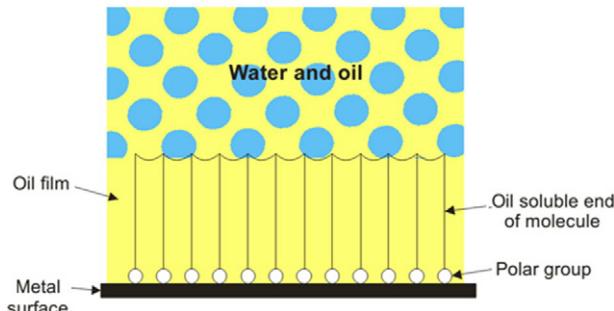
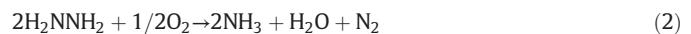


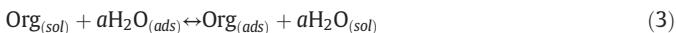
Fig. 2. Protective mechanism of barrier inhibitors.

However, the known toxic effects of hydrazine on human body [24, 25] and non-volatile nature of sodium sulphite, which make them to be unable to provide efficient protection against oxygen based corrosion, necessitate the need for alternative oxygen scavenger. Among the alternative volatile oxygen scavengers is the application of hydrazine derivatives like carbohydrazide, which again form hydrazine under increased temperature conditions, while other alternatives like oximes and hydroxylamine compounds show disadvantages in their thermal stability and reaction speed. Therefore a new type of chemical oxygen scavenger has been developed which was found to show excellent oxygen reduction effect over a wide variety of conditions and was able to replace hydrazine derivatives [26], sodium sulfite, hydroxylamine derivatives [27], ketoxime compounds [28] in anti-corrosion applications without

showing the typical disadvantages of other replacement chemicals. Heterocyclic compounds having N-substituted amino group (Fig. 3) were evaluated and were found to be the most effective replacement for hydrazine in anti-corrosion applications, where 1-amino-4-methylpiperazine was reported to show excellent corrosion inhibition among the N-substituted amino group [29].

3. Organic corrosion inhibitors

The organic compounds that are used as inhibitors may block anodic or cathodic or both sites, thus preventing metallic substrate from undergoing metal dissolution or hydrogen evolution reactions with predominance of film-forming surface adsorption. The inhibitory potential of organic inhibitors has been reported to be exhibited by a strong affinity for metal surfaces' compound, with low impacts on the environment [30]. They build up a protective hydrophobic film molecules adsorbed on the surface of metallic substrate, thus providing a barrier to dissolution of the metal in the electrolyte. Inhibitory action of organic compounds has been explained by well accepted model (Eq. (3)) [31–33], which involves adsorption of organic molecules on the corroding metal surface via displacement of adsorbed water molecules from the metal surface as represented by the following equation:



The four principal modes of adsorption associated with inhibitor organic molecules at the metal surfaces include electrostatic interaction of the corrosion inhibitor (CI) with the metal substrate (physisorption), charge sharing between the metal surface and CI (chemisorption), π -back bonding, and organometallic complex formation [33]. Furthermore, the stability of the adsorbed organic compound films/layer on the metal surface depends on the nature of functional groups, aromaticity, possible steric factors, electronic density of donors, type of corrosive medium and nature of interaction between its p -orbital with the d -orbital of iron. The various types in this category include synthetic organic compounds, green corrosion inhibitors (GCIs), and natural corrosion inhibitors synthesized from petroleum fractions.

3.1. Synthetic organic corrosion inhibitors

This can further be subdivided into liquid phase organic corrosion inhibitors (LPOCIs) and volatile organic corrosion inhibitors (VOCIs).

3.1.1. Liquid phase organic inhibitors

The inhibitory efficiency of these organic compounds is related to the heterocyclic nature of the compounds with N, S, O and P heteroatoms in their molecules, which serve as reaction centers for adsorption on the metal surface [34]. The inhibition efficiency of the heteroatoms in heterocyclic compounds follows the sequence O < N < S < P [7,30]. The electron transfer from these inhibitors to the metal surface is facilitated

by the availability of non-bonded (lone pairs) and π -electrons in the inhibitor molecules, leading to formation of coordinate covalent bond with iron (Fe). The strength of chemisorption bond, and thus the performance of an organic inhibitor depend on the electron density on the donor atom of the functional group, polarizability of the group and the electronic structure of the inhibitor molecules. The inhibition action could be due to adsorption of the molecules or its ions on anodic and/or cathodic sites, increase in cathodic and/or anodic overpotential, and ability to form protective barrier film. Some of the factors that could influence this inhibition action include chain length/molecular size, bond strength, aromaticity/conjugated bonding, type and number of bonding atoms or groups in the molecule (either π or σ), cross-linking ability and solubility in the environment. However, with increasing chain length of the hydrocarbon, there is tendency to observe decrease in corrosion inhibition performance due to the decreasing solubility in aqueous solution. The inhibition performance could be enhanced if the hydrogen atom attached to the carbon in the ring is replaced by electron-donating substituents such as $-\text{NH}_2$, $-\text{NO}_2$, $-\text{CHO}$, or $-\text{CO}_2\text{H}$ [35]. This will lead to changes in electron density in the metal at the point of attachment resulting in retardation of the cathodic or anodic reaction, thereby minimizing corrosion. The following are the various classes of liquid organic corrosion inhibitors that will be discussed under this section.

3.1.1.1. Simple organic molecules. Simple organic compounds such as azoles (imidazole, benzimidazole, benzotriazole, triazole, tetrazole), amines, urea, mercaptobenzothiazole (MBT), aldehydes, heterocyclic nitrogen compounds, sulfur-containing compounds, acetylenic compounds and also ascorbic acid, succinic acid, and tryptamine have been reported to be effective organic corrosion inhibitors [7,30,36,37]. A lot of studies have been carried out on the corrosion inhibition performance of various synthesized simple organic compounds on metallic substrates. Li et al. [32] investigated the adsorption and inhibition effect of 6-benzylaminopurine (BAP) on cold rolled steel (CRS) in 1.0 M HCl at 25–50 °C, using weight loss (WL) and potentiodynamic polarization (PDP) techniques. Their results showed that BAP was a good inhibitor in 0.1 M HCl, and the inhibition efficiency (IE) was reported to increase with increasing BAP concentration. The adsorption of BAP on the surface of CRS was found to obey Langmuir adsorption isotherm model, and the adsorption process was found to be spontaneous and exothermic with an increase in entropy. The BAP was also reported to act as mixed-type inhibitor, based on PDP measurements.

In a related study, the inhibitory performance of 1-butyl-3-methylimidazoliumchloride (BMIC) and 1-butyl-3-methylimidazolium hydrogensulfate ($[\text{BMIM}]HSO_4$) on the corrosion of mild steel in 1 M HCl was investigated by Zhang and Hua [38], using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) and weight loss (WL) measurements. Their PDP studies revealed that the two compounds are mixed-type inhibitors. The inhibition efficiencies of the two compounds were reported to increase with increasing

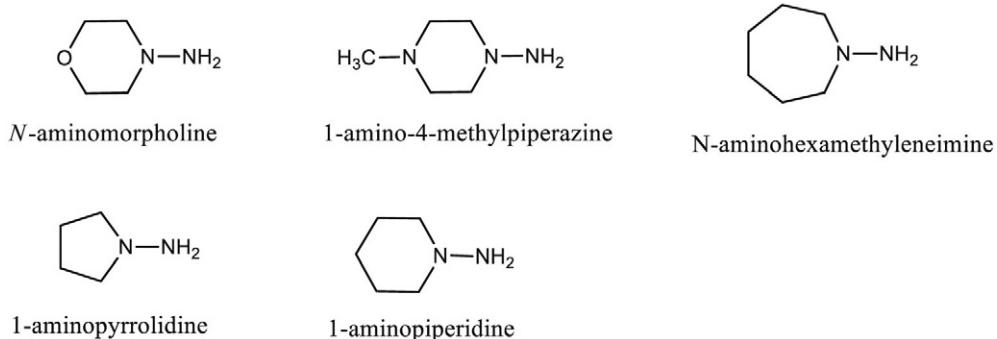


Fig. 3. Chemical structures of the tested N-amino substituted heterocyclic compounds [29].

concentration of the inhibitors, and the efficiency follows the order [BMIM]HSO₄ > BMIC. The adsorption process of the inhibitors was found to obey Langmuir adsorption isotherm. Okafor et al. [39] studied the inhibition and adsorption behavior of 2-undecyl-1 sodium ethanoate-imidazoline salt (2 M2) and thiourea (TU) on N80 mild steel in CO₂-saturated 3 wt% NaCl solutions at 25 °C using electrochemical methods. They found that both 2 M2 and TU are effective inhibitors for the corrosion of N80 mild steel in CO₂-saturated 3% NaCl solutions and the extent of inhibition was found to be dependent on the concentration of the compounds. Yadav et al. [40] carried out corrosion inhibition study of two amino acid compounds; 2-amino-N-decyl-3-phenyl propionamide (Inh 1) and 2-amino-N-decylacetamide (Inh 2) for N80 steel in 15% HCl. They reported that the inhibition efficiencies of inhibitor 1 (Inh 1) is greater than that of inhibitor 2 (Inh 2). Fang et al. [41] synthesized Schiff base compound, 1-phenyl-3-(1-aniline)-1-propene (PAP) by a condensation reaction of aniline with Cinnamaldehyde in ethanol solvents in the molar ratio of 1:1 for 8 h (**Scheme 1**), and its inhibitive effect against the corrosion of N80 steel in 15% HCl solution was investigated by using weight loss (WL) and electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP). The inhibitive performance of PAP was reported to exceed 99%, and the inhibitor was found to act as mixed-type inhibitor based on PDP measurements.

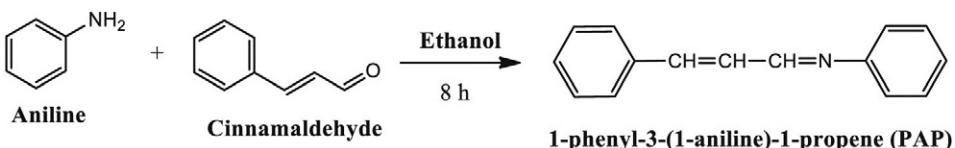
In a related study, Okafor et al. [42] evaluated the inhibition performance of rosin amide imidazoline (RAIM) on N80 and P110 carbon steels (CS) in CO₂-saturated simulated formation water. Their findings indicated that N80 CS performs better than P110 CS with RAIM at lower temperature while P110 CS performs better at higher temperatures. The performance of the selected inhibitors, including thioglycolic acid (TGA), diethylenetriamine (DETA), and naphthalene acid imidazolines (NAIM), on the bare surface of N80 steel and its scaled surface pre-corroded in CO₂-saturated 1%NaCl solution was carried out by Liu et al. [43]. Their results indicated a remarkable difference in inhibition performance of these inhibitors on the N80 steel, which was attributed to the molecular size of the inhibitors and the interaction of the inhibitor with the corrosion scale. López León et al. [44] studied the electrochemical behavior of organic compounds as corrosion inhibitors over a carbon steel AISI 1018 immersed in a corrosive synthetic environment of brine type in the absence and presence of hydrocarbon using potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). Based on the PDP curves, it was found that increasing concentration of the compounds affected both the anodic and cathodic stages of corrosion process while the inhibitory performance decreased in the presence of hydrocarbon of different systems. From the EIS results, the interaction of hydrocarbon with different organic compounds studied was reported to modify the corrosion processes and the arrival of the corrosive agents to the metal surface via generation of corrosion products which are soluble in some cases or insoluble in others.

Three *N*-thiazolyl-2-cyanoacetamide derivatives, i.e., *N*-(4-phenylthiazol-2-yl)-2-phenylazo-2-cyanoacetamide (a), *N*-(4-phenylthiazol-2-yl)-2-(*p*-tolylazo)-2-cyanoacetamide (b), and *N*-(4-phenylthiazol-2-yl)-2-(*p*-methoxyphenylazo)-2-cyano acetamide (c) were tested as corrosion inhibitors for aluminium in 0.01 M NaOH solution at 30 °C using the weight loss (WL) and galvanostatic polarization (GSP) techniques by Abdallah et al. [45]. The inhibition performance of these derivatives was reported to increase with increasing concentration, but decreased with increasing temperature. Their data revealed that the inhibition performance decreased in the order (c) > (b) > (a), which was attributed to the polar effect of the *p*-substituents

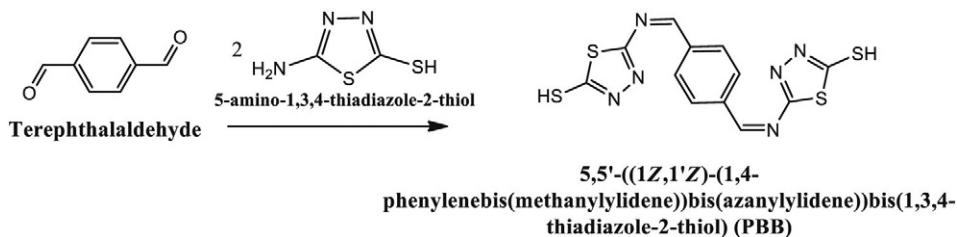
on the phenylazo group, where *N*-(4-phenylthiazol-2-yl)-2-(*p*-methoxy phenylazo)-2-cyanoacetamide has a highly electron donating *p*-OCH₃ group which enhanced the delocalization of *p*-electrons on the molecule. The authors further reported an increase in inhibition effectiveness upon the addition of 1 mM MCl₂ (M = Mg, Ca, Sr, Ba), which also followed the order Ba²⁺ > Sr²⁺ > Ca²⁺ > Mg²⁺. These compounds were reported to act as mixed-type inhibitors based on the polarization measurements. In a related study, Abdallah et al. [46] reported the inhibition performance of three bidentate azo dyes, i.e., 1-(4-(2-hydroxy-3-nitrophenyl)diazaryl)phenyl propan-1-one (a), 1-(4-(3-amino-2-hydroxy phenyl) diazaryl) phenyl propan-1-one (b), and 1-(4-(2,4,6-trihydroxyphenyl)diazaryl)phenyl propan-1-one (c), as corrosion inhibitors for aluminium in 0.1 M NaOH solution, using the weight loss (WL) and galvanostatic polarization (GSP) techniques at 30 °C. Their results revealed that the inhibition performance increased in the order (c) > (b) > (a), which was attributed to the presence of the electron-donating group in the chemical structure of the dyes. These compounds were reported to act as mixed-type inhibitors based on polarization measurements. Their inhibitory performance was attributed to the adsorption of a stable complex formed on the aluminium surface. The addition of 1 mM solutions of chlorides of Mg²⁺, Ca²⁺ and Ba²⁺ was reported to improve the inhibitive action of the bidentate azo dyes, probably due to the chemisorptive ability of the cations on the aluminium surface in alkaline solutions. The inhibition performance of these compounds was reported to follow the order Ba²⁺ > Ca²⁺ > Mg²⁺. Al-Amriy et al. [47] synthesized 5,5'-(1Z,1'Z)-(1,4-phenylenebis(methanlylidene)) bis(azanlylidene)) bis(1,3,4-thiadiazole-2-thiol) (PBB) by refluxing terephthalaldehyde with 2-amino-5-mercaptop-1,3,4-thiadiazole (1:2) in the presence of few drops of hydrochloric acid, (**Scheme 2**), followed by investigation of its corrosion inhibition effects on mild steel in 1.0 M HCl at different temperatures using open circuit potential (OCP), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). Based on their results, PBB was found to exhibit excellent inhibition performance on mild steel corrosion as a mixed-type inhibitor and the inhibitory efficiencies were found to increase with increasing concentration of inhibitor, but proportionally decreased with solution temperature.

Verma et al. [48] synthesized three novel 2-aminobenzene-1,3-dicarbonitrile derivatives namely, 5'-amino-2,4-di-hydroxy-4"-methyl-1,1':3',1"-terphenyl-4',6'-dicarbonitrile (ABDN-1), 5'-amino-2,2",4-trihydroxy-1,1':3',1"-terphenyl-4',6'-dicarbonitrile (ABDN-2) and 5'-amino-2,3",4-trihydroxy-1,3-methoxy,1":3',1"-terphenyl-4',6'-dicarbonitrile (ABDN-3) by microwave irradiation (**Scheme 3**), followed by evaluation of their corrosion inhibition performance on AA1060 aluminium alloy in 0.5 M NaOH.

The inhibition performance was reported to increase with increasing concentration of ABDN. These compounds were reported to act as mixed-type inhibitors based on the potentiodynamic polarization (PDP) measurements. They concluded from their study that these compounds adsorbed on the alloy surface, forming a protective film. Qafsaoui et al. [49] investigated inhibitory role of 1-pyrrolidine dithiocarbamate (PDTC) as a corrosion inhibitor for pure aluminium and AA2024-T3 aluminium alloy in 0.2 g/L NaCl solution, using the weight loss (WL) and electrochemical techniques. They concluded from their investigation that PDTC has only little effect on the corrosion of pure aluminium, but strongly inhibited the alloy corrosion. According to the authors, this was attributed to the presence of copper-rich particles in the alloy. PDTC was reported to increase the galvanic coupling



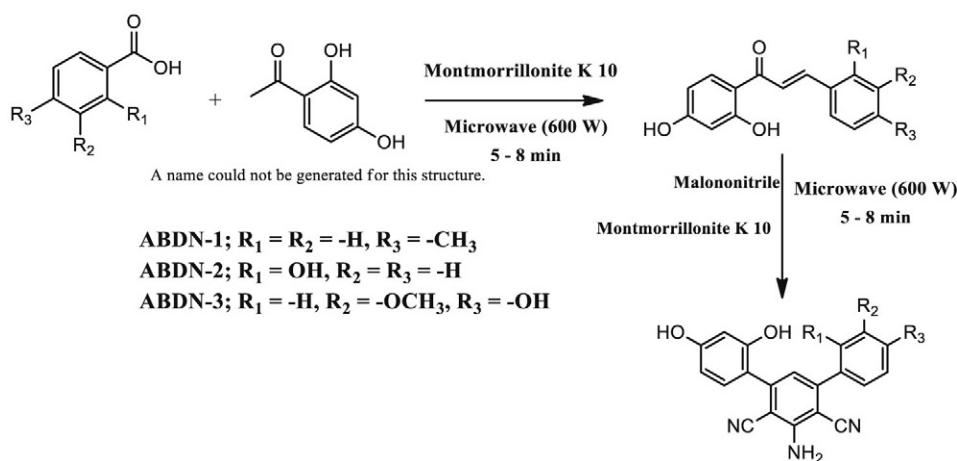
Scheme 1. Synthesis of PAP as corrosion inhibitor in acidic environment [41].



Scheme 2. Synthesis of PBB as corrosion inhibitor in acidic environment [47].

resistance through strong interaction with the Cu-rich cathodic sites associated with the intermetallics through its sulfur atoms. The reduction of the active cathodic surface sites was attributed to a stable and adherent Cu(I)-PDTC complex formed by the interaction between PDTC and these intermetallic particles. The PDTC was also found to be adsorbed preferentially on the Al-Cu-Mg particles based on the SEM-EDX analysis. In a related study, Marcellin and Pebere [50] evaluated the inhibition performance of 8-hydroxyquinoline (8-HQ) and benzotriazole (BTA) on the corrosion of AA2024 aluminium alloy in a mixture of 0.1 M Na₂SO₄ and 0.05 M NaCl. The mixture of these two inhibitors was reported to show a synergistic effect, with BTA acting mainly on the Cu-rich intermetallic particles, while 8-HQ acted on the aluminium matrix due to the chelating properties. The galvanic coupling between the aluminium matrix and the intermetallic particles was found to be strongly limited when the inhibitor mixture was used compared to when they were separately used. Ren et al. [51] reported the inhibitory performance of triisopropanol amine (TIPA) against the corrosion of ADC12 aluminium alloy in 3 wt% NaCl solution, at 25 °C, using the WL, PDP, and EIS techniques. The inhibition performance was found to increase with increasing concentration of TIPA. The TIPA was found to act as a mixed-type inhibitor based on the PDP measurements. The thermodynamic and kinetic data were reported to reveal a mixed-type (both physisorption and chemisorptions) adsorption mechanism of TIPA on the surface of aluminium alloy. The authors concluded that TIPA adsorbed on the aluminium surface through the oxygen atom based on the results of their quantum chemical calculations. Abd El-Rehim et al. [52] evaluated polyoxyethylene(20) sorbitan monooleate (Tween 80) as a corrosion inhibitor for A5754 aluminium alloy in 0.5 M NaOH solution at 25 °C, using the PDP technique. The inhibition performance of this compound was found to increase with increasing concentration of the compound, but decreased with increasing temperature. The Tween 80 was reported to act as mixed-type inhibitor based on the PDP measurements. Their thermodynamic calculations suggested comprehensive adsorption (both physisorption and chemisorptions) of Tween 80 on the alloy surface.

Recently, Qiang et al. [53] evaluated the inhibitive ability of 2,6-diaminopyridine, tartaric acid and their synergistic effect towards mild steel corrosion in 0.5 M HCl solution at various concentrations using potentiodynamic polarization (PDP) measurements, electrochemical impedance spectroscopy (EIS), and weight loss (WL) experiments. Their findings revealed a favorable synergistic effect of 2,6-diaminopyridine with tartaric acid, which was reportedly effective to protect mild steel from corrosion. They used quantum chemical calculations and Monte Carlo simulation to affirm the inhibition mechanism of the synergistic effect. In a related study, Gerengi et al. [54] carried out investigation into the corrosion inhibition of low carbon steel in 0.1 M HCl solution by 1-ethyl-1-methylpyrrolidinium (EMTFB) and the effect of KI addition on the inhibition efficiency using potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDAX) techniques. Based on their results, the EMTFB was found to suppress low carbon steel dissolution in acidic environment, and the inhibition efficiency was reported to increase with increasing EMTFB concentration, with enhanced inhibition performance on addition of iodide ions to EMTFB. The EMTFB was found to affect majorly anodic reactions while EMTFB + KI acted as cathodic-type inhibitor, based on PDP measurements. The adsorption process was found to involve physisorption mechanism, and followed Langmuir adsorption isotherm model. Surface morphology studies with SEM and EDAX confirmed the adsorption of EMTFB and EMTFB + KI onto the steel surface. Wang et al. [55] evaluated the inhibition performance of L-cysteine as a corrosion inhibitor for AA5052 alloy in 4 M NaOH solution at 30 °C, using the hydrogen evolution (HE), Tafel extrapolation, and EIS techniques. The inhibition performance was reported to increase with increasing concentration of the inhibitor. The L-cysteine was found to act as a cathodic-type inhibitor based on the polarization measurements. They concluded that the L-cysteine was adsorbed on the aluminium surface through the carboxyl groups. They also reported that strong hybridization that occurred between the s- and p-orbitals of L-cysteine and the sp-orbital of the aluminium atom might be contributing to the inhibitive performance of the



Scheme 3. Chemical synthesis of ABDN-1, ABDN-2 and ABDN-3 as corrosion inhibitors alkaline environment [48].

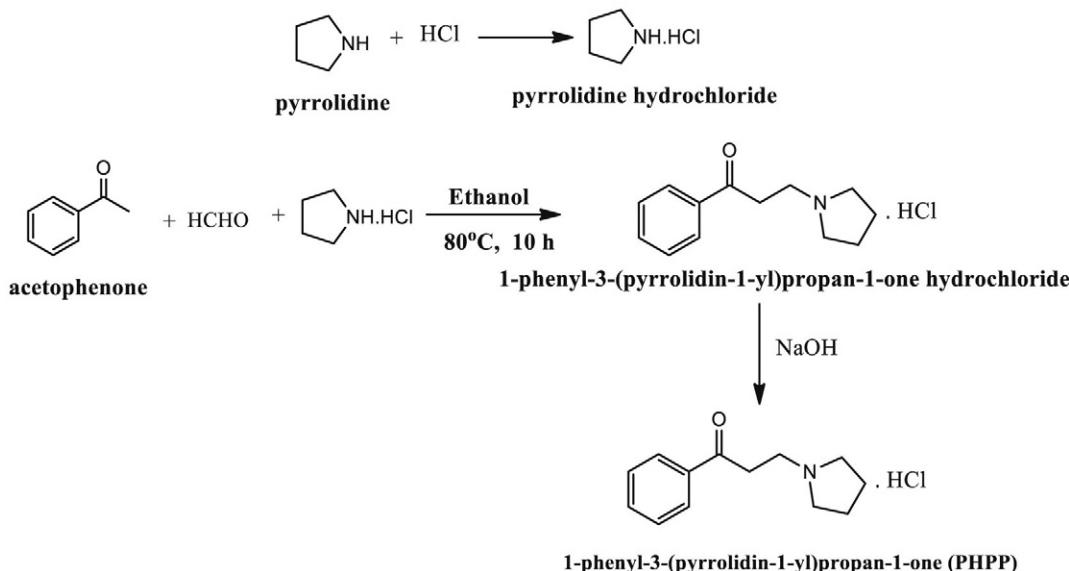
inhibitor. In a similar study, Abdallah et al. [56] investigated the inhibitory performance of gelatin as a corrosion inhibitor for pure aluminium and two aluminium alloys, i.e., AA6063 and AA20556 (92.47% aluminium), in 0.1 M NaOH solution at 30–60 °C, using the PDP, EIS and cyclic voltammetry (CV) techniques. The inhibition performance was reported to increase with increasing concentration of gelatin, but decreased with increasing temperature and increasing Si content of the alloys. The inhibitory performance of gelatin on these materials was reported to decrease in the order: pure aluminium > AA6063 > AA20556, which was attributed to the lower affinity of gelatin to adsorb on silicon than aluminium. The gelatin was reported to provide the corrosion protection to these materials by formation of a barrier on their surface. Aouniti et al. [57] investigated the adsorption and corrosion inhibition behavior of (E)-2-methyl-N-(thiophen-2-ylmethylidene)aniline (T) at steel/1.0 M HCl interface using gravimetric and electrochemical methods at 308 K. The inhibition performance of this thiophene derivative was found to increase with increasing concentration of the inhibitor. The compound was reported to act as mixed-type inhibitor based on the PDP studies. The Langmuir adsorption isotherm model was reported to assume that inhibition occurred via adsorption of the components of the thiophene derivative on the mild steel surface. Zhan et al. [58] synthesized a Mannich base, 1-phenyl-3-(1-pyrrolidinyl) propanone (PHPP), with acetophenone, pyrrolidine and formaldehyde at pH of approximately 2–3 (Scheme 4), followed by investigation of the corrosion inhibition performance of PHPP against corrosion of N80 steel in 15% hydrochloric acid (HCl), using weight loss (WL) method, scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX). Their results revealed that PHPP exhibited excellent corrosion inhibition performance, and has potential to enhance oil production in oilfield development as an oil-well acidizing inhibitor. The SEM and EDAX results confirmed the adsorption of PHPP on the surface of N80 steel, which was found to involve chemisorption mechanism and obeyed Langmuir adsorption isotherm model.

Very recently, Keleş and Keleş [59] synthesized imine compound, (2-methoxyphenyl)-N-(2-(phenylthio)phenyl)methanimine (MPM) (Scheme 5), followed by investigation of its corrosion inhibitory performance against the corrosion of low carbon steel in HCl solution at various concentrations and temperatures using electrochemical and microscopic techniques. Based on their results, MPM was found to reduce the corrosive effect of HCl, and the inhibition performance was found to increase with increasing concentration of MPM. The

potentiodynamic polarization also revealed that MPM acted as a mixed-type inhibitor with predominance of cathodic curve over the anodic side.

The chemical structures of some of these synthetic organic compounds that have been used as corrosion inhibitors in acidic, neutral or alkaline environments are given in Fig. 4.

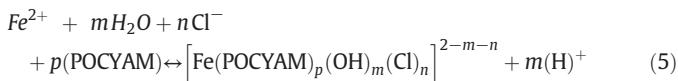
3.1.1.2. Synthetic organic polymers. Organic polymeric materials can also be efficient corrosion inhibitors because they contain potent heteroatom functional groups that form inhibitor (polymer)–metal ions complexes; which can occupy large zone over metallic surface and protect it from the corrosive media. Yurt et al. [60] investigated the inhibition performance of novel synthesized water-soluble triblock copolymers-2-(diethyl amino) ethyl methacrylate-block-2-(dimethyl amino) ethyl methacrylate-block-2-(N-morpholino)ethylmethacrylate[PDEA-PDMA-PMEMA] and 2-(diisopropyl amino) ethylmethacrylate-block-2-(dimethyl amino) ethyl methacrylate-block-2-(N-morpholino) ethyl methacrylate [PDPA-PDMA-PMEMA] of two different molecular weights on the corrosion behavior of mild steel in 0.5 M HCl, using potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and linear polarization (LP) techniques. Their study revealed that all the studied copolymers acted as mixed-type inhibitors based on PDP measurements. The inhibition performances were reported to increase with increasing concentrations of the copolymers. The inhibition action of these copolymers was reported to be due mainly to the adsorption of the copolymers on the steel surface, which followed Langmuir adsorption isotherm. The use of polymers as metal corrosion inhibitors has been extensively reviewed by Umoren [61], where he highlighted that water soluble polymers are effective corrosion inhibitors for aqueous media. He concluded in his review that polymers corrosion protection proceeds through adsorption mechanisms which are dependent on the nature of corrosive environment, nature of the metal surface and chemical/physical properties of the polymers such as hero functional group, steric hindrance, aromaticity nature of donor atoms and electron clouds over molecular skeleton. The inhibition performance of three synthesized nonionic polymers on carbon steel corrosion in 1 M H₂SO₄ was investigated by Negm et al. [62] using gravimetric and electrochemical techniques. The inhibition action of the inhibitors was reported to be attributed to their adsorption on the carbon steel surface and formation of dense protective layer which was found to increase with increasing concentration of the inhibitors. Their study also revealed that the



Scheme 4. Chemical synthesis of PHPP as corrosion acidizing inhibitor [58].

inhibitors acted as mixed-type inhibitor in 1 M H₂SO₄ with dominance of anodic type properties, and their inhibition on carbon steel was reported to proceed by physical adsorption (physisorption) which obeyed Langmuir adsorption isotherm model. Roy et al. [63] evaluated polyacrylamide grafted guar gum (GG-g-PAM) with various grafting levels as potential inhibitor against corrosion of mild steel in 1 M HCl, with special emphasis on the effect of percentage grafting (% G) on the inhibition performance of polyacrylamide grafted guar gum (GG-g-PAM). The grafting copolymer was found to maintain inhibition efficiency of higher than 90% for about 50 h of exposure with up to 86% grafting. The grafted polyacrylamide was found to behave as mixed-type inhibitor with formation of an inhibitive layer on metal surface, which followed Langmuir adsorption isotherm. The synergism that was found to exist in GG and PAM moieties was reported to have great influence on adsorption isotherm. The authors concluded based on their FTIR studies that GG backbone of GG-g-PAM uses the endocyclic and exocyclic O atoms of sugar units to form a chelate with Fe²⁺ during adsorption; while PAM units of grafted GG, on the other hand, interacted with the metal surface through the amide groups. In a related study, Atta et al. [64] used the produced AgNPs to prepare hybrid polymer (AMPS/NIPAm-AgNPs) based on N-isopropylacrylamide (NIPAm), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), N,N-methylenebisacrylamide (MBA) and potassium persulfate (KPS) using a semi-batch solution polymerization method (Scheme 6). They investigated the corrosion inhibition performance of the hybrid copolymer towards steel corrosion in the presence of hydrochloric acid, using polarization and electrochemical impedance spectroscopy (EIS) methods. AMPS/NIPAm-AgNPs was reported to behave as a mixed-type type-inhibitor and the inhibition efficiency was found to increase with increasing inhibitor concentration. AMPS/NIPAm-AgNPs was also reported to show good protection of steel based on the results of polarization and EIS measurements.

Thirumoolan et al. [65] evaluated hyperbranched poly(cyanurateamine) (POCYAM) as a novel corrosion inhibitor for mild steel in 0.5–3 M HCl using chemical and electrochemical techniques at 25–70 °C. Their results showed that the compound has good corrosion inhibiting properties for mild steel in HCl at very low concentration, which also increased with increasing POCYAM concentration. The inhibition mechanism was reported to involve blockage of the active sites on iron surface by the inhibitor molecules via adsorption, which obeyed the Langmuir adsorption isotherm. The specific adsorption of chloride was reported to lead to the formation of low stable iron-chloro complexes [66] at low concentrations of POCYAM, which was found to be modified to higher stable iron inhibitor complex at high concentration of POCYAM. The formed complex (Eq. (5)) was reported to reduce the anodic dissolution via its adsorption on the anodic sites.

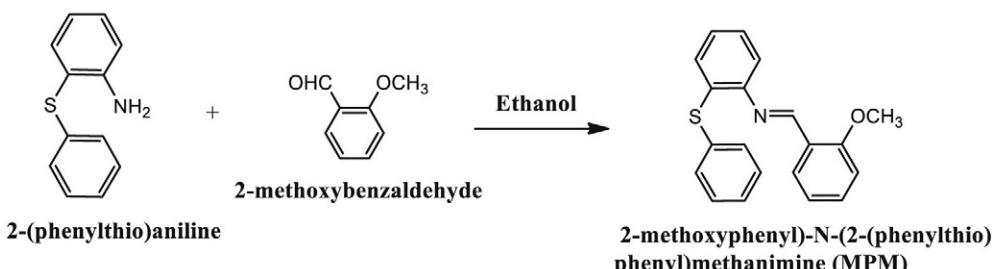


Recently, Dhawan et al. [67] synthesized hydrophobic polyaniline-SiO₂ composite (PANI/SiO₂) by chemical oxidation polymerization of aniline and SiO₂, using ammonium persulfate (APS) as an oxidant in the

presence of perfluoro-octanoic acid (PFOA) medium. The corrosion protection efficiency of mild steel coated PANI/SiO₂ in 3.5% NaCl aqueous solution was evaluated using Tafel Extrapolation method, salt spray test and weight loss methods. The observed excellent corrosion protection performance by HPSC coated mild steel was attributed to the strong adherence of polymer film which uniformly covers the entire electrode surface. The presence of SiO₂ particles entrapped in polymer matrix was found to provide the reinforcement to PANI chain, which reduced the degradation of polymer in corrosive medium. Hydrophobic PANI/SiO₂ coating was reported to protect metal by dual mechanism, including formation of passivating as well as acting as physical barrier which inhibited the entrance of water onto metal surface. Ansari and Quraishi [68] synthesized polymeric Schiff base containing aniline, formaldehyde and piperazine (AFPP) (Scheme 7), and the compound was evaluated for its inhibition performance against corrosion of mild steel in 1 M HCl by weight loss (WL), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization(PDP) techniques. AFPP was reported to be an effective inhibitor for mild steel in 1 M HCl, and inhibiton performance was found to increase with increasing concentration of the inhibitor with attainment of maximum inhibition efficiency of 98%. The AFPP was found to behave as a mixed-type inhibitor with predominance of cathodic type, based on PDP studies. The adsorption of inhibitor on the mild steel surface was found to follow Langmuir adsorption isotherm.

Mansri et al. [69] also recently evaluated the inhibition performance of micro-composite (bleaching clay(BC)/polyacrylamide (PAM)) against the corrosion of mild steel in 1 M HCl, using weight loss and potentiodynamic measurements. The micro-composite was reported to reduce the corrosion rate and the inhibition efficiency was found to increase with increasing concentration of the micro-composite, with attainment of 80% inhibition efficiency at 400 mg/L. The adsorption of BC-PAM micro-composite inhibitor on the steel surface in 1 M HCl was reported to obey Freundlich adsorption isotherm model. In a related study, Kumar et al. [70] synthesized polyurethane based tri-block copolymers namely poly(*N*-vinylpyrrolidone)-*b*-polyurethane-*b*-poly(*N*-vinylpyrrolidone) (PNVP-PU) and poly((dimethylaminoethylmethacrylate)-*b*-polyurethane-*b*-polydimethylaminoethylmethacrylate) (PDMAEMA-PU) through atom transfer radical polymerization (ATRP) mechanism (Scheme 8). The corrosion inhibition performances of these compounds were investigated on mild steel (MS) in 0.5 M H₂SO₄ medium using electrochemical measurements, surface analysis, quantum chemical calculations and molecular dynamic simulations (MDS). The polymers were reported to behave as mixed-type corrosion inhibitors base on potentiodynamic polarization (PDP) measurements, and inhibited the corrosion of mild steel by adsorbing on the steel surface to form pseudo-capacitive interface. The inhibition performance was found to increase with increasing concentration of the inhibitors and decreased with increasing temperature. The adsorption process of the two polymeric materials on mild steel surface was found to obey the Langmuir adsorption isotherm, involving both physisorption and chemisorption mechanisms.

Very recently, Al-Amiry [71] synthesized a novel and stable organic compound, namely 3-((4-nitrobenzylidene) amino) coumarin from 2-



Scheme 5. Chemical synthesis of MPM as corrosion inhibitor in acidic environment [59].

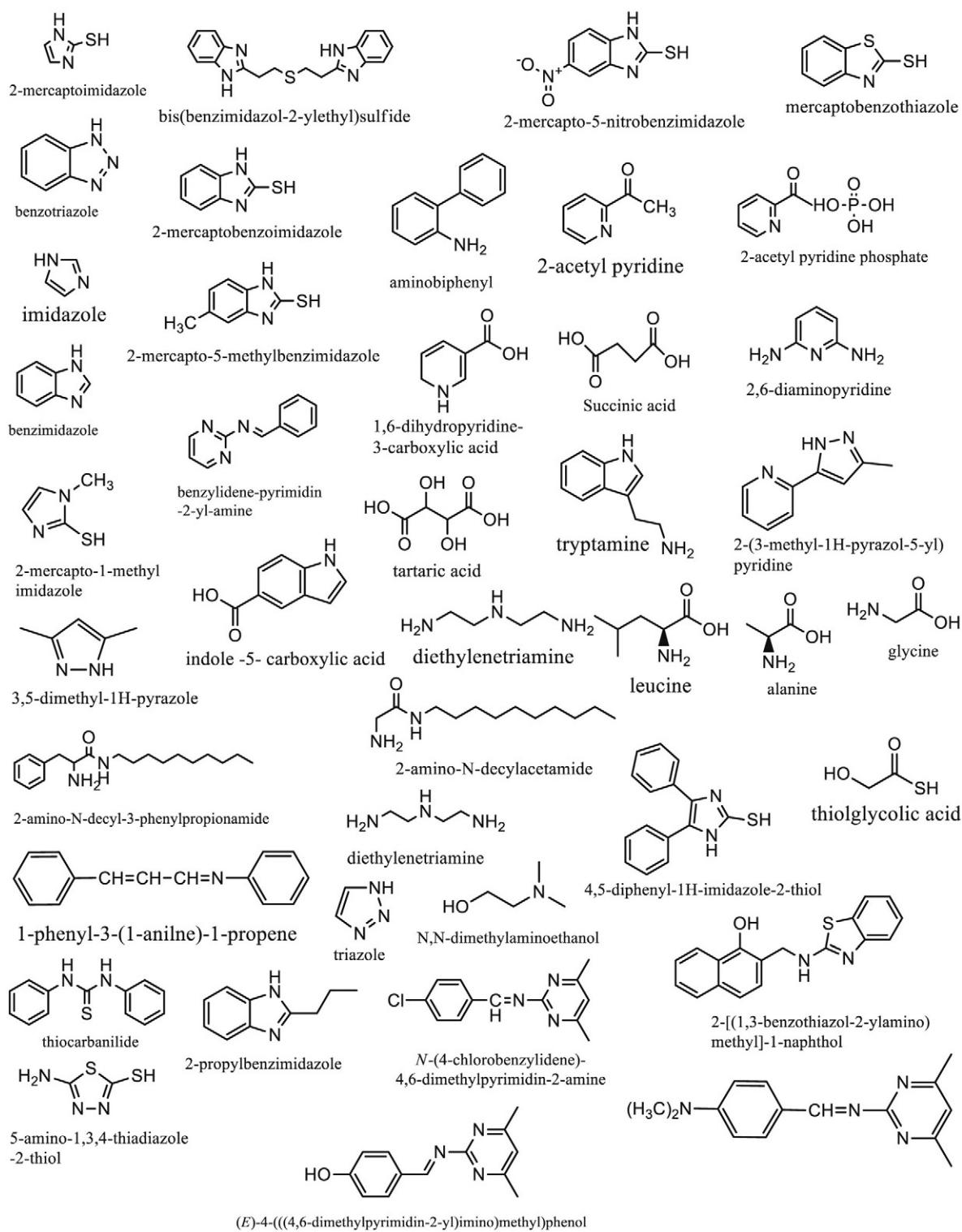
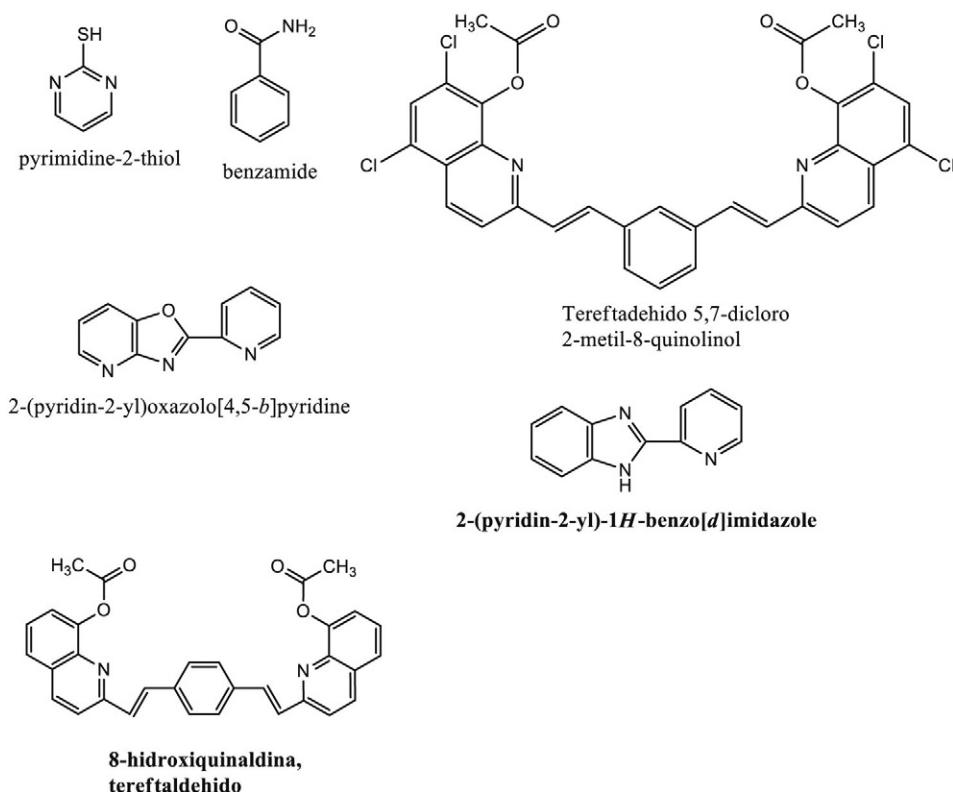


Fig. 4. Chemical structures of synthetic organic compounds used as corrosion inhibitors in corrosive media.

acetamidoacetic acid, 2-hydroxybenzaldehyde and acetic anhydride (**Scheme 9**). The synthesized compound was evaluated as inhibitor against the corrosion of mild steel in solution of 1 M HCl using weight loss (WL) method. 3-((4-nitrobenzylidene)amino) coumarin was reported to demonstrate good inhibition performance, which increased with increasing inhibitor concentration and reached the maximum inhibition efficiency of 71.4% at 0.5 g/L of 3-((4-nitrobenzylidene)amino)coumarin.

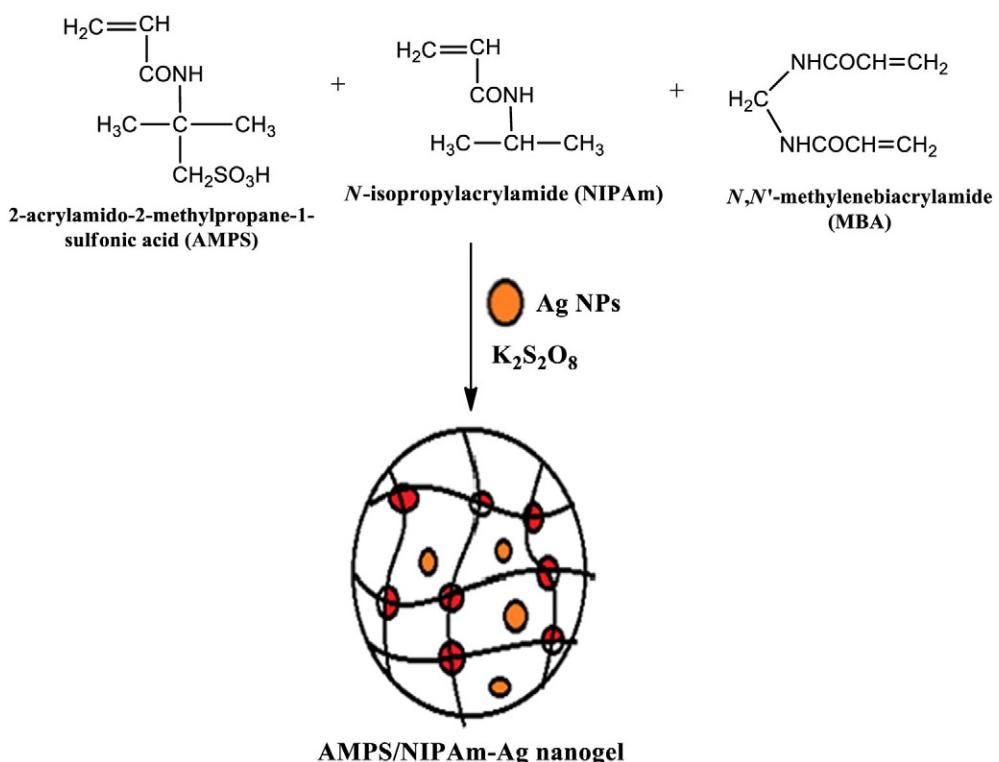
In a related study, Hafeez et al. [72] carried out solvent free synthesis of nanoparticle sized polyaniline (PANI) (46 to 58 nm) by the oxidation of aniline with ammonium persulphate using chemical oxidation method (**Scheme 10**). The polymer was evaluated as inhibitor against corrosion of mild steel in 3.5% NaCl by preparing homogenous dispersion of PANI in flexible epoxy resin. They found that PANI in the epoxy resin showed considerable decrease in the corrosion rate (0.34–0.19 g/m² h) of the coating as compared to neat epoxy

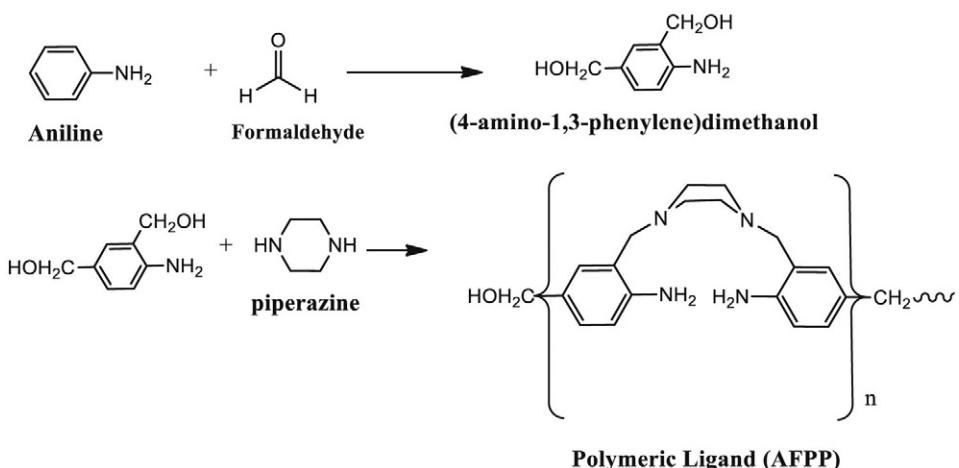
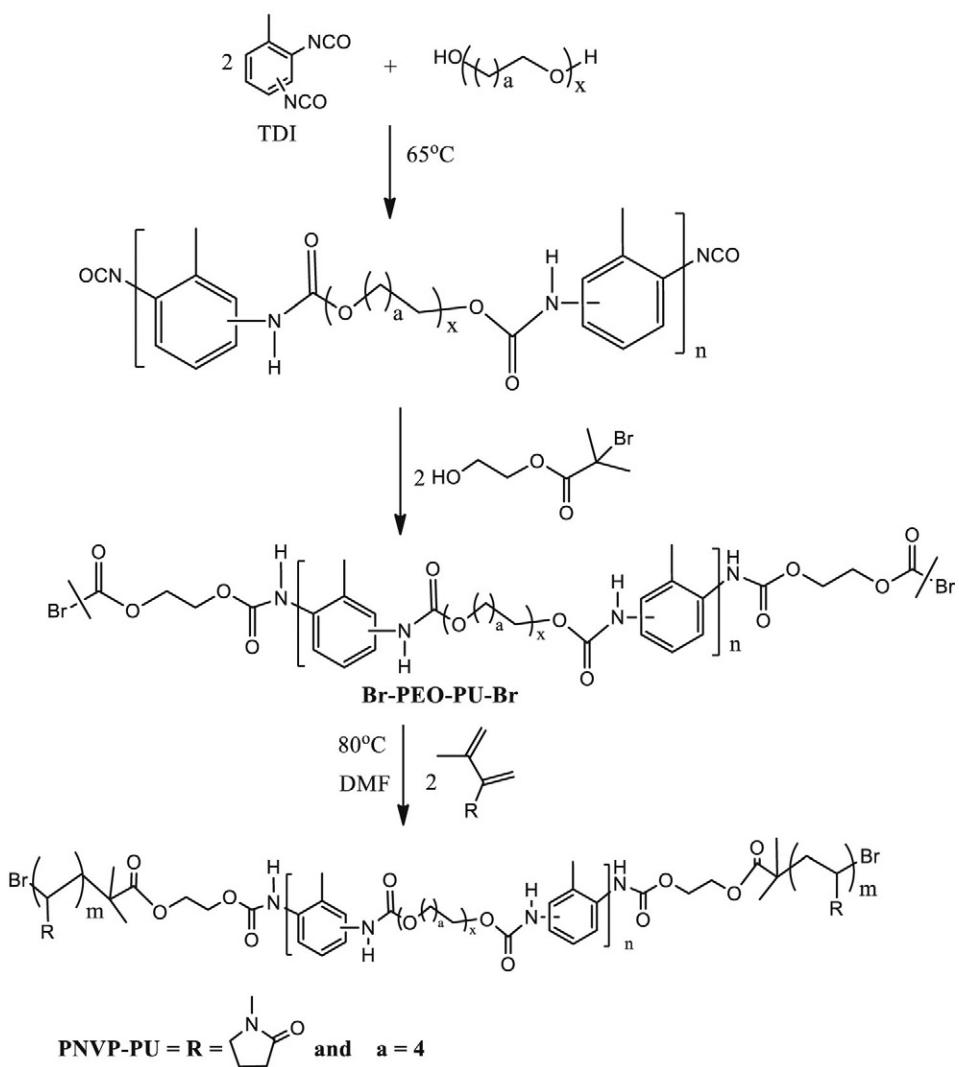
**Fig. 4.** (continued).

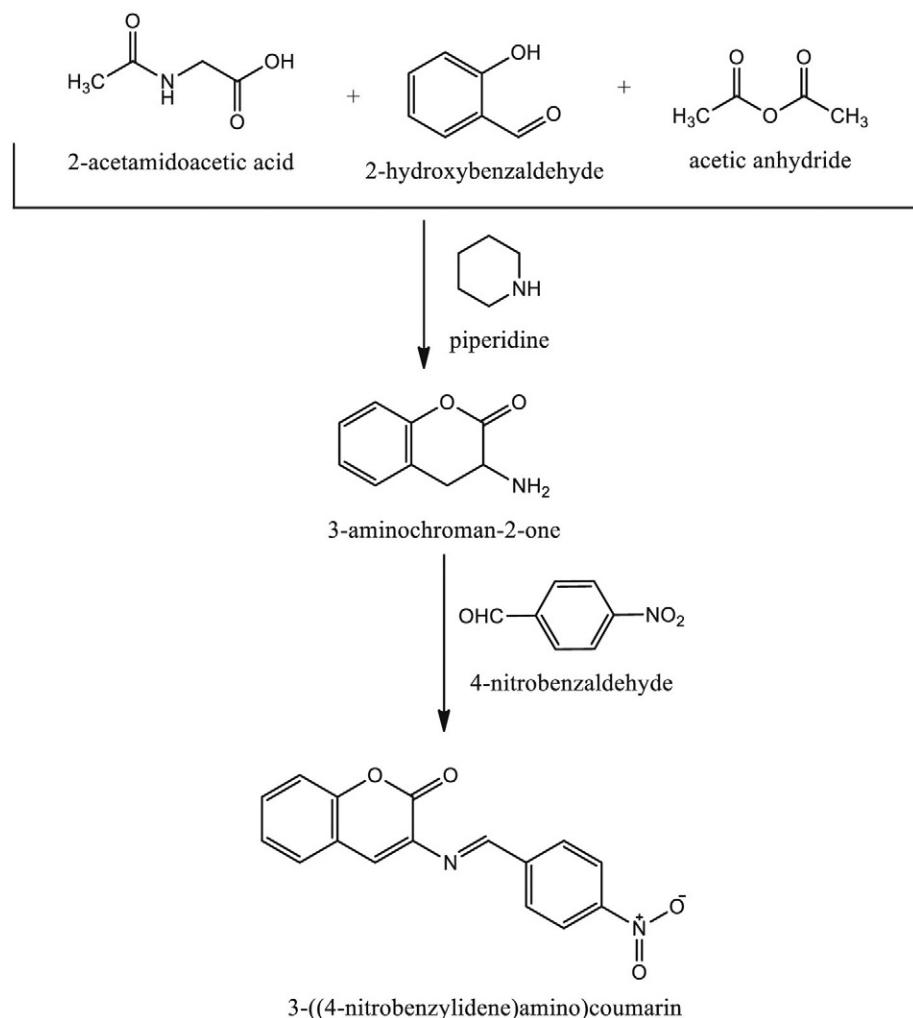
(3.25 g/m² h). The inhibition performance was found to increase with increasing concentration of PANI in epoxy matrix.

Table 1 shows the chemical structures of some synthetic organic polymers that have been used as corrosion inhibitors.

3.1.3. Surfactant molecules. Surfactants (Surface active agents) is another class of synthetic organic inhibitors, which have also been extensively used as commercial corrosion inhibitors and their inhibition efficiency may be attributed to their ability to affect the nature of

**Scheme 6.** Synthesis of silver AMPS/NIPAm hybrid polymer for use as corrosion inhibitor in acidic environment [64].

**Scheme 7.** Synthesis of polymeric ligand (AFPP) for use as corrosion inhibitor in acidic environment [68].**Scheme 8.** Chemical Synthesis of PNVP-PU and PMAEMA-PU as corrosion inhibitors in acidic environment [70].



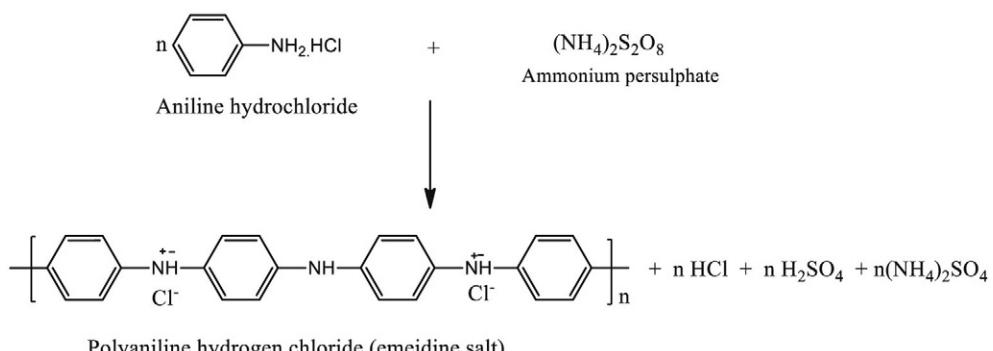
Scheme 9. Chemical synthesis of 3-((4-nitrobenzylidene)amino)coumarin as corrosion inhibitor in acidic environment [71].

metal surfaces and solution interfaces. It is generally assumed that adsorption of the surfactant molecules onto the metal surface is the first stage in the mechanism of surfactants as corrosion inhibitors in aggressive media. The adsorption process is influenced by the nature and the surface charge of the metal, the chemical structure of the surfactant, and the nature of the aggressive electrolyte. Adsorption of the surfactant molecules on the metal surface can be expressed [31] in accordance with the following equation:



Where n is the number of water molecules removed from the metal surface for each molecule of surfactant adsorbed and it depends on the cross-sectional area of the surfactant molecule with respect to that of the water molecule.

Adsorption of the surfactant molecules onto the metal surface has been reported to occur as a result of higher interaction energy between the surfactant molecules/ metal surface than that between water molecules/ metal surface [73]. So the inhibition performance of surfactants was attributed to the adsorption of the surfactant molecules via their functional groups onto the metal surface. The adsorption rate has been reported to be usually very fast, which consequently shielded the



Scheme 10. Chemical synthesis of PANI as corrosion inhibitor in acidic environment [72].

Table 1

Chemical structures of some synthetic polymeric corrosion inhibitors.

Name	Chemical structure	Metal type	Medium	Reference
Polyethylene glycol		Mild steel	HCl	John et al. [188], Mobin and Khan [189].
Polyurea		Aluminium Steel	NaOH HCl	Abdallah et al. [45], Awad et al. [190] Aly and Hussein [191]
Polyvinyl pyrrolidine		Carbon steel Mild steel Stainless steel	NaCl/HCl HCl	Al Fuhaman et al. [192] John et al. [188], Karthikaiselvi et al. [183]. Khaled [193]
Polyvinyl alcohol		Mild steel	HCl	Umoren and Gasem [194], Karthikaiselvi et al. [183], Mobin and Khan [195], Sabirneza et al. [196].
Poly(<i>o</i> -phenylenediamine)		Mild steel	HCl	Abd El Rehim et al. [197]
Polyaniline		Mild steel	NaCl H2SO4	Hou et al. [198], Ashassi-Sorkhabi and Es'haghi [199] El-Deeb et al. [200]
Polypyrrole		Mild steel Aluminium Nickel	H2SO4 NaCl	Hou et al. [198] Zor et al. [201] Flamini et al. [202]
Polyacrylic acid		Aluminium	H2SO4	Umoren et al. [203]
Polyethyleneimine (PEI)		Low carbon steel Stainless steel	H3PO4 NaCl	Jianguo et al. [204] Finsgar et al. [205]
Polyethylene glycol methyl ether (PEGME)		Mild steel	H2SO4	Dubey and Singh [206]
Poly(<i>p</i> -aminobenzoic acid)		Iron	HCl	Manivel and Venkatachari [207]
Poly(diphenylamine)		Iron	H2SO4	Jeyaprabha et al. [208]
Poly(<i>o</i> -aminophenol)		Steel	H2SO4	Abd El-Ghaffar et al. [209]
Poly(<i>o</i> -aminothiophenol)		Steel	H2SO4	Abd El-Ghaffar et al. [209]
Poly(<i>m</i> -anisidine)		Steel	H2SO4	Abd El-Ghaffar et al. [209]

reactive metal from the aggressive environment [74]. Anti-corrosive performance of surfactant depends on the adsorption ability of the surfactant molecules on the corroding surface, which is directly related to the capacity of the surfactant to aggregate to form clusters (micelles). Therefore, critical micelle concentration, CMC, has been reported to be a key determining factor in the effectiveness of surfactant as a corrosion inhibitor [74].

Migahed and Al-Sabagh [75] reviewed the role of surfactants as corrosion inhibitors in the petroleum field. They concluded that corrosion inhibition performance of surfactant is based on the adsorption capacity of surfactant molecules over the reactive sites of the metal surface, which increased along with the number of carbon atoms in the aliphatic hydrocarbon chain and varied with critical micelle concentration (CMC) properties. Malik et al. [76] also reviewed the corrosion inhibition

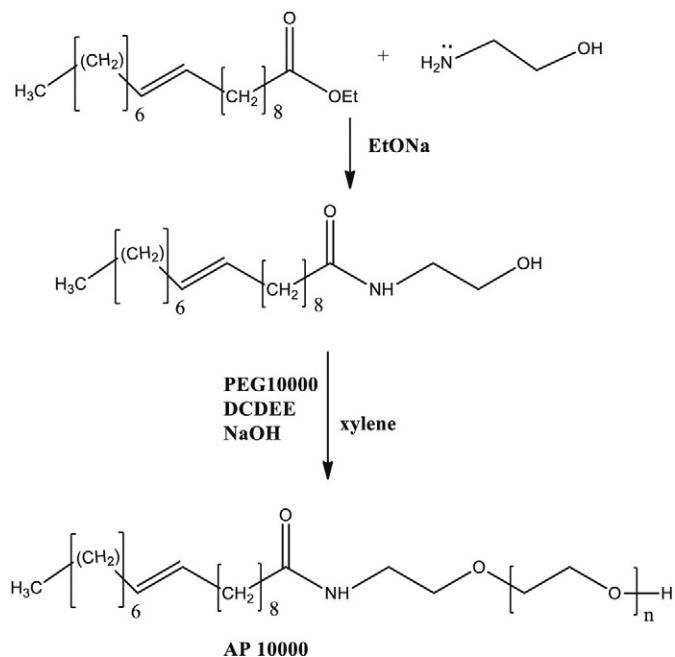
performance of surfactants, where they concluded that surfactant molecules have high affinity to adsorb over the interfaces and forms micelles. This property was reported to make the surfactant to have high potential in resolving corrosion issues over metal surface, and therefore provides protection for metals against corrosion.

The inhibition effect of a cationic surfactant, *N,N,N*-trimethyldodecylammonium bromide (TDAB) on the corrosion of mild steel in 1 M HCl at different temperatures was studied by Prathibha et al. [77] using weight loss, Tafel polarization and electrochemical impedance spectroscopy. TDAB was reported to be a good inhibitor and its inhibition efficiency (IE) was found to increase with increasing inhibitor concentration and increasing temperature. The adsorption process of the inhibitor on the mild steel surface was reported to obey the Langmuir adsorption isotherm model. TDAB was also found to act as a

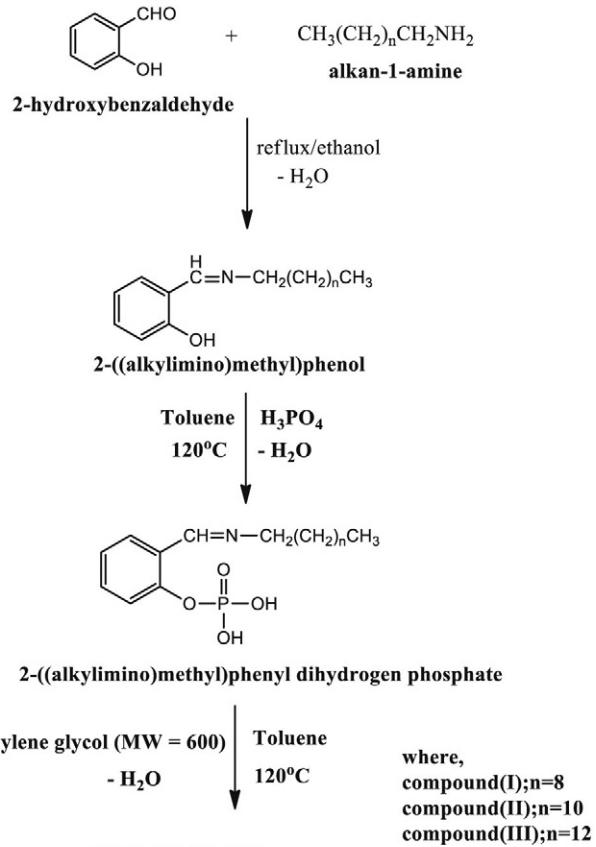
mixed-type inhibitor in hydrochloric acid based on PDP curves. Abdel Hameed et al. [78] synthesized nonionic polymeric surfactant, amido poly ethylene oxide (AP10000) by ethoxylation of *N*-(2-hydroxyethyl) oleiamides, (HA) using polyethylene glycol (PEG) in the presence of bimolar ratio of β , β' -dichlorodiethyl ether (DCDEE), and bimolar ratio of sodium hydroxide (Scheme 11). The inhibition action of AP10000 on the corrosion rate of mild steel in 2 M HCl corrosive media was then evaluated, using weight loss (WL), open circuit potential (OCP) and potentiodynamic polarization (PDP). The inhibition performance was found to increase with increasing concentration of the inhibitor and decreased with increasing temperature. Adsorption process was also found to follow the Langmuir isotherm model, and the polarization curve indicated that the compound acts as mixed-type inhibitors.

Hegazy et al. [79] sequentially synthesized three novel nonionic surfactants, 2-((alkylimino)methyl)phenol, 2-((alkylimino)methyl)phenyl dihydrogen phosphate and 2-((alkylimino)methyl)phenylbis(53-hydroxy 3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48,51-heptadecaoxatripent using Schiff base reaction followed by esterification reaction (Scheme 12). The inhibition effect of these three nonionic surfactants on the corrosion of carbon steel in 0.5 M H₂SO₄ was investigated using polarization, EIS and weight loss measurements. It was found that the three nonionic surfactants were effective inhibitors, and their inhibition performance was significantly increased with increasing concentration and temperature. The polarization curves were reported to reveal that the three nonionic surfactants represent mixed-type inhibitors. The adsorption of used inhibitor was reported to lead to a reduction in the double layer capacitance with an increase in the charge transfer resistance. The adsorption process of fused compounds was found to be chemisorptive and obeyed Langmuir isotherm model.

Kellou-Kerkouche et al. [80] studied the corrosion inhibition performance of sodium dodecylbenzene sulfonate (SDBS) against the corrosion of an elaborated annealed alloy Fe-3Ti-2C in 1 N sulphuric acid solution containing dissolved oxygen, using potentiodynamic polarization (PDP), linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS) techniques. The surfactant was reported to inhibit the alloy dissolution in the sulphuric acid, through its adsorption on the metal surface without modification of the mechanism of corrosion process. The highest inhibition performance was recorded at a concentration above its critical micelle concentration. The adsorption process was reported to obey Langmuir adsorption isotherm model.



Scheme 11. Synthesis of AP10000 as inhibitor in acidic environment [78].



where,
compound(I);n=8
compound(II);n=10
compound(III);n=12

2-((alkylimino)methyl)phenylbis(53-hydroxy 3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48,51-heptadecaoxatripent)phosphate

Scheme 12. Synthesis of the novel nonionic surfactants as corrosion inhibitors in acidic environment [79].

Pandarinathan et al. [81] investigated the adsorption of four CO₂ corrosion inhibitors, namely cetylpyridinium chloride monohydrate (CPC), 1-dodecylpyridinium chloride hydrate (DPC), 2-mercaptopurimidine (MPY) and thiobenzamide (TB) on silica sand and their subsequent inhibition activity at sand-deposited steel. The presence of a sand deposit was reported to affect the inhibition performance of inhibitors at carbon steel due to their competitive adsorption on sand. Sulfur-containing organic compounds was found to show minimal adsorption on sand compared to pyridinium surfactants, which was attributed to charge attraction and alkyl group interactions under CO₂ saturated conditions. The electrochemical studies were used to establish relationship between the degree of adsorption and inhibitor properties. The corrosion rates of carbon steel in inhibited test solutions in the presence of sand deposit was found to increase in the order: CPC > DPC > TB ≈ MPY.

Kadhum et al. [82] synthesized and characterized a new coumarin derivative, *N,N'*-(2E,2'E)-2,2'-(1,4-phenylenebis(methanylidene)) bis(hydrazinecarbothioyl)bis(2-oxo-2H-chromene-3-carboxamide) (PMBH) by refluxing thiosemicarbazide with terephthalaldehyde in the presence of a few drops of hydrochloric acid, followed by reaction with coumarin-3-carboxylic acid (Scheme 13). The corrosion inhibition effect of PMBH on mild steel in 1.0 M HCl was investigated using corrosion potential (E_{corr}), potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) measurements. The compound was reported to exhibit excellent inhibition performance as a mixed-type inhibitor. The

inhibition performance was found to increase with increasing inhibitor concentration but reduced proportionally with temperature.

Hussain [83] synthesized gemini surfactant polyamide, [(2,2'-1,22-diamino-8,15-dioxo-7,10,13,16-tetraazadocosane-10,13-diyl) diacetic acid] from hexamethylenediamine (HMDA) and ethylenediaminetetra-acetic acid (EDTA), followed by evaluation of its inhibition performance against the corrosion of carbon steel in 1 M HCl solution using corrosion potential and corrosion current. The polyamide was reported to offer some degrees of protection in the acidic environment. The adsorption process of the inhibitor was found to obey Langmuir adsorption isotherm model. Zhu and FreeM [84] investigated the corrosion inhibition efficiency of mixtures of three homologous benzalkonium chlorides (BAC) surfactants including benzyl dimethyl dodecyl ammonium chloride (C12Cl), benzyl dimethyl tetradecyl ammonium chloride (C14Cl), and benzyl dimethyl hexadecyl ammonium chloride (C16Cl) with assay value of higher than 99%, using electrochemical measurements and modeling; followed by its evaluation using the surface aggregation concentration (sac) and critical micelle concentration (cmc) of surfactant. The corrosion inhibition of BAC surfactant was reported to increase rapidly with increasing concentration of surfactant to the sac, indicating the formation of a relatively complete surfactant monolayer around the sac that effectively protects the steel electrode from corrosion.

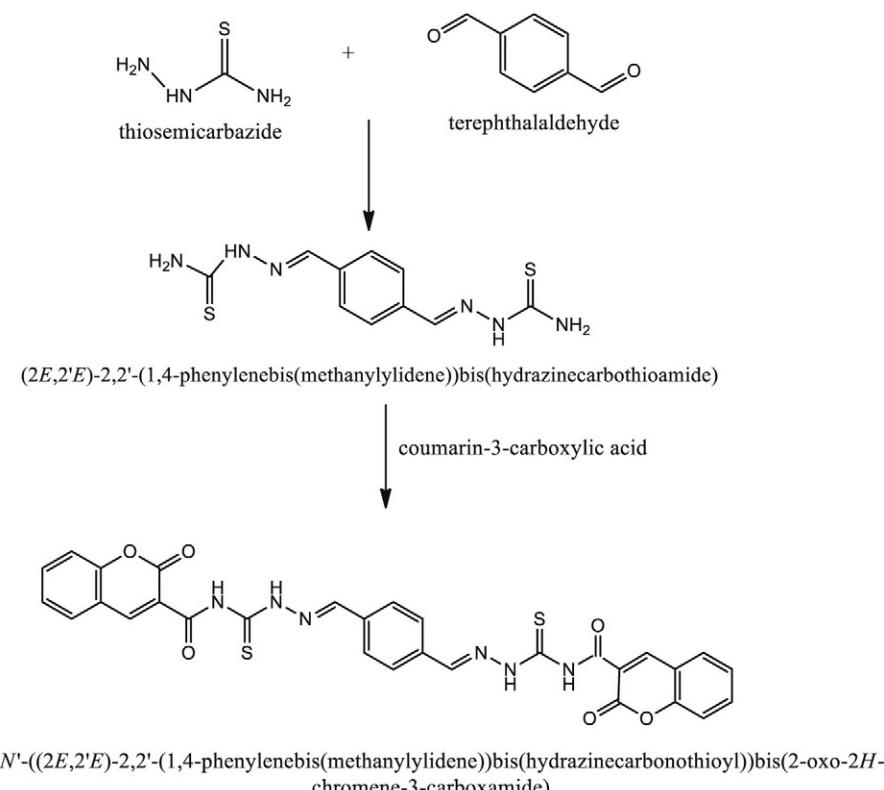
In a related study, Hegazy et al. [85] synthesized and characterized novel cationic and gemini surfactants (Scheme 14), followed by evaluation of inhibition efficiencies of the synthesized compounds against corrosion of carbon steel in 0.5 M H₂SO₄ using weight loss (WL), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). The cationic and gemini surfactants were reported to effectively inhibit the corrosion of carbon steel in 0.5 M H₂SO₄, and were found to act as mixed-type inhibitors based on PDP studies. The adsorption of the inhibitors on carbon steel surface was reported to obey Langmuir isotherm model.

Tawfik [86] synthesized and characterized biopolymer alginate surfactant (AS) and its metal complexes (AS-M, where M = Co, Cu and Zn)

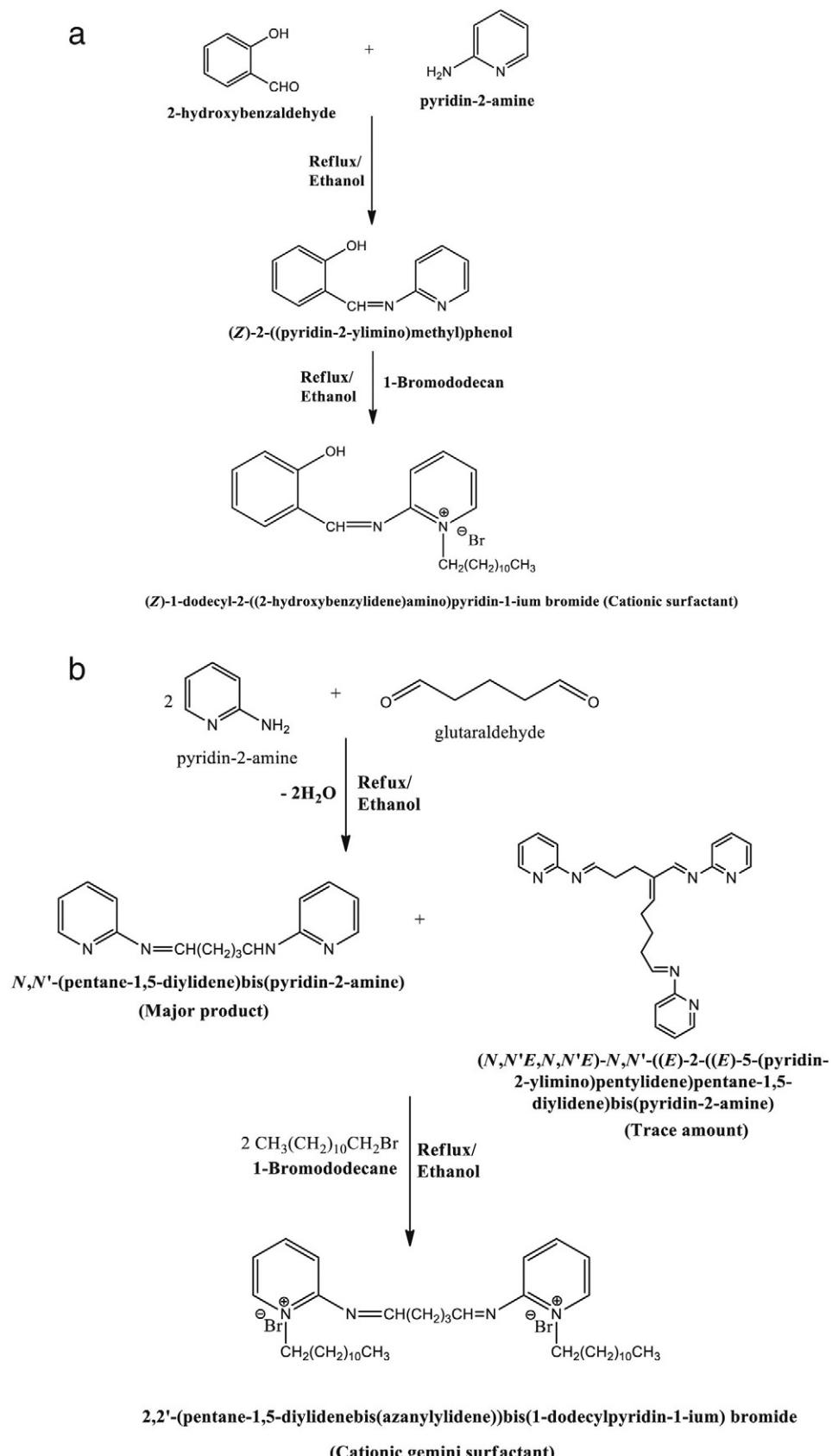
(Scheme 15); followed by investigation of the influences of the metal complexes as novel corrosion inhibitor for carbon steel in 1 M HCl using gravimetric, electrochemical, EDX and SEM techniques. The alginate derivatives were reported to show good inhibition performance for acid induced corrosion of carbon steel, and the inhibition performance were found to increase with increasing alginate derivatives concentration and solution temperature. The alginate derivatives were classified as mixed-type corrosion inhibitors with predominance control of the cathodic reaction based on potentiodynamic polarization measurements. The adsorption process of the inhibitors was found to obey Langmuir isotherm model.

In a related study, Zhang et al. [87] synthesized and characterized a quaternary ammonium gemini surfactant containing an ester spacer, namely (diethylhexanedioate)diyl- α , ω -bis(dimethyl myristyl ammonium bromide) (14-DEHA-14) using a two-step procedure with dimethylhexanedioate, dimethylaminoethanol, and 1-bromotetradecane (Scheme 16). The inhibition efficiency of the synthesized gemini surfactant was evaluated against corrosion of carbon steel in 1.0 M HCl solution by weight loss measurements. The gemini surfactant was reported to be an excellent corrosion inhibitor in 1.0 M HCl solution. The adsorption of gemini surfactant onto the carbon steel surface was found to be chemisorptive, and obeyed Langmuir adsorption isotherm model.

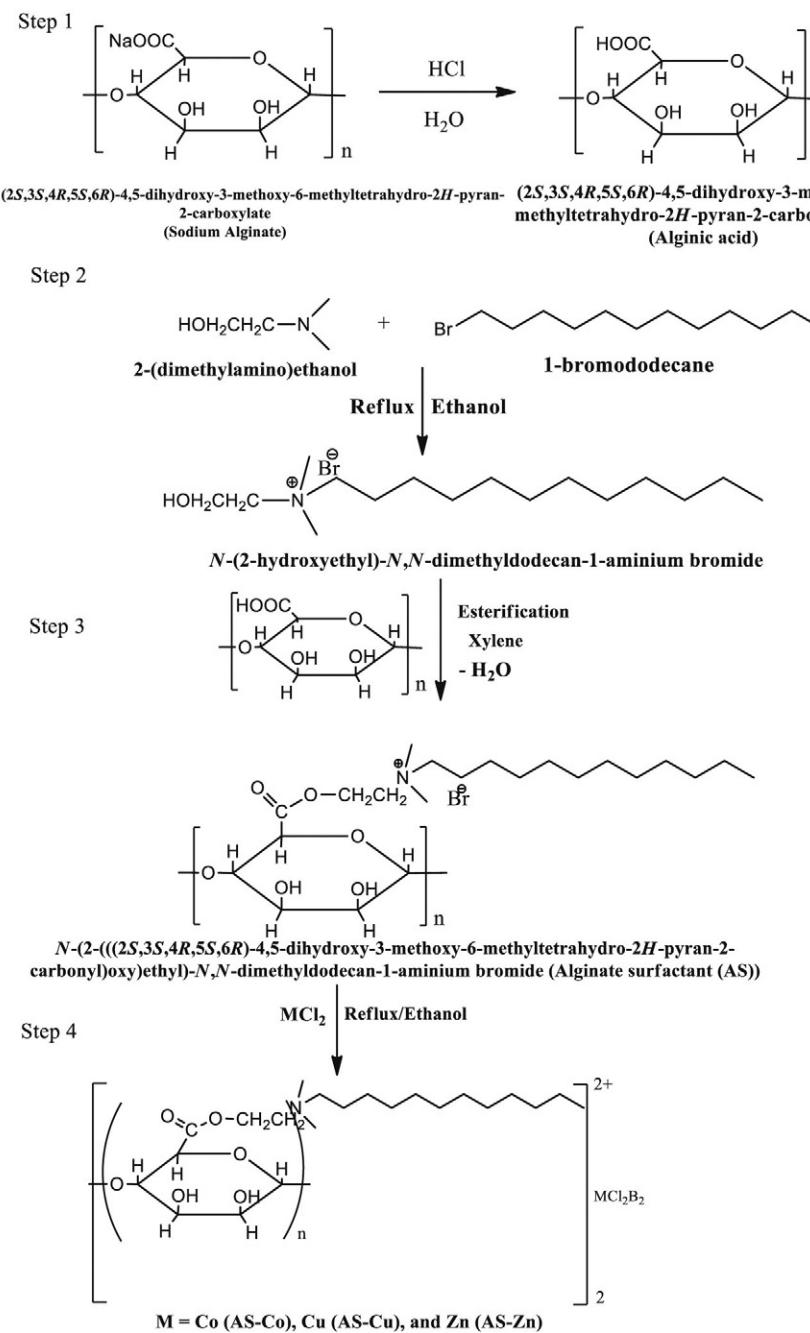
Migahed et al. [88] synthesized ethoxy-(5-methyl-benzotriazol-1-yl) (EMB) (Scheme 17), followed by evaluation of its corrosion inhibition performance against the corrosion of X-65 type carbon steel exposed to CO₂ saturated oil well produced water using potentiodynamic polarization (PDP) and electrochemical impedance (EIS) techniques. The synthesized EMB compound was reported to retard both anodic metal dissolution and cathodic oxygen reduction based on PDP curves, and acted as mixed-type inhibitor. The adsorption of inhibitor molecules on metal surface was found to obey the Langmuir adsorption isotherm. The inhibition mechanism was attributed to the strong adsorption ability of the EMB surfactant on carbon steel surface,



Scheme 13. Synthesis of PMBH as corrosion inhibitor in acidic environment [82].



Scheme 14. a. Synthesis of a novel cationic surfactant as corrosion inhibitor in acidic environment [85]. b. Synthesis of a novel gemini surfactant as corrosion inhibitor in acidic environment [85].



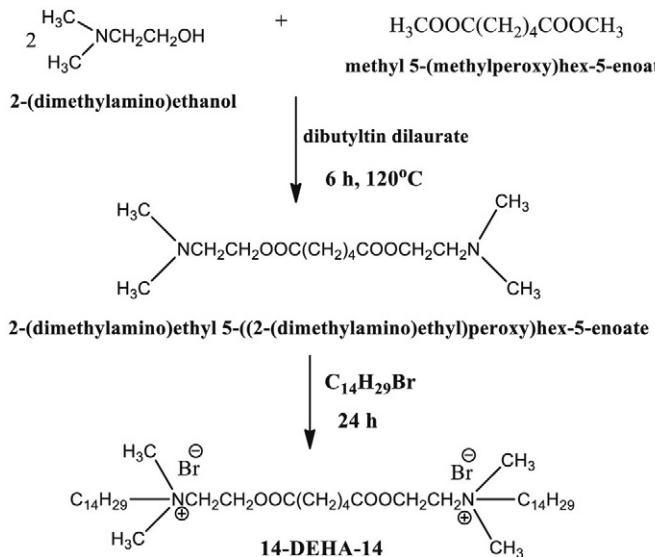
Scheme 15. Chemical synthesis routes for Alginate cationic surfactant and its metal complexes as corrosion inhibitors in acidic environment [86].

forming a good protective layer, thus isolating the surface from the aggressive environment.

Recently, Adawy et al. [89] synthesized two new Schiff base cationic surfactants (**Scheme 18**) and their inhibition performance against carbon steel corrosion in 1 M HCl solution was evaluated using weight loss and electrochemical techniques. The compounds were reported to exhibit excellent corrosion inhibitors, and their inhibition performances were found to increase with increasing inhibitors concentrations. The adsorption process was found to obey Langmuir adsorption isotherm model and they acted as mixed-type inhibitors, affecting both cathodic hydrogen reduction reactions and anodic metal dissolution.

Mobin et al. [90] synthesized and characterized bio-/environment-friendly cationic gemini surfactant, ethane-1,2-diyl bis(*N,N*-dimethyl-N-hexadecylammonium acetoxy) dichloride, referred to as 16-E2-16. The corrosion inhibition performance of 16-E2-16 on mild steel (MS)

surface in 1 M HCl solution at 30, 40, 50 and 60 °C was evaluated using gravimetric analysis (GA), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) measurements. The inhibition efficiency of the studied inhibitor was reported to increase with increasing concentration and solution temperature. The compound was found to behave as a mixed-type inhibitor and acted by blocking the electrode surface by means of adsorption obeying the Langmuir adsorption isotherm. The authors further investigated the surface active properties and corrosion inhibition effects of 16-E2-16 in the presence of inorganic (NaI) and organic (NaSal) salts, and it was found that 16-E2-16/NaSal system showed the lowest CMC value supporting the system as the most effective corrosion inhibitor for MS in HCl solution. In a related study, Mobin and Noor [91] synthesized zwitterionic gemini surfactant, 2-decyldiphosphate-1-(*N,N*-dimethyl, *N*-tetradecyl ammonium) ethane (**Scheme 19**). The adsorption and



Scheme 16. Synthetic route for 14-DEHA-14 as corrosion inhibitor in acidic environment [87].

corrosion inhibition behavior of zwitterionic gemini surfactant on mild steel in 0.5 M HCl in the temperature range of 25–65 °C was investigated using weight loss (WL), potentiodynamic polarization (PDP), electrochemical impedance (EIS) measurements while thermodynamic/kinetic parameters were used to elaborate the adsorption and corrosion inhibition mechanism of the surfactant. The zwitterionic gemini surfactant was reported to act as an excellent inhibitor for mild steel corrosion in 0.5 M HCl and inhibition performance was found to be concentration and temperature dependent. It was also found that zwitterionic gemini surfactant behaved as a mixed-type corrosion inhibitor based on PDP measurements. The adsorption process of the surfactant on mild steel surface was reported to obey Langmuir adsorption isotherm model, and the calculated thermodynamic parameters revealed a strong interaction between the inhibitor and the mild steel surface.

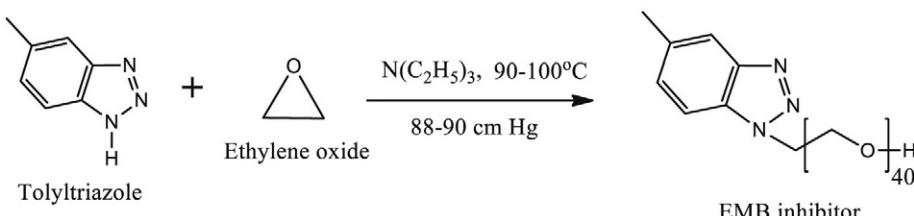
In a related study, El-Dougdoug et al. [92] synthesized a fatty amidationionic surfactant (Scheme 20), followed by evaluation of the inhibition efficiency of the synthesized surfactant against the corrosion of carbon steel in 1 M HCl solution using weight loss and galvanostatic polarization (GSP) methods. The surfactant was reported to be a good corrosion inhibitor for mild steel in 1 M HCl solution; and the inhibition performance was reported to increase with increasing inhibitor concentration and decreased with increasing temperature. The data obtained from weight loss measurements also suggested corrosion inhibition was by adsorption mechanism, which obeyed the Langmuir adsorption isotherm model.

Tammam et al. [93] also studied the inhibition actions of three different classes of surfactants including cationic surfactant: cetylpyridinium bromide (CPBr), non-ionic surfactant: triton (TX-100) and anionic surfactant: dodecyl benzene sulphonate (DBS) for corrosion of mild steel in 1 M H₂SO₄ using electrochemical impedance spectroscopy (EIS), polarization measurements and weight loss (WL). The inhibition

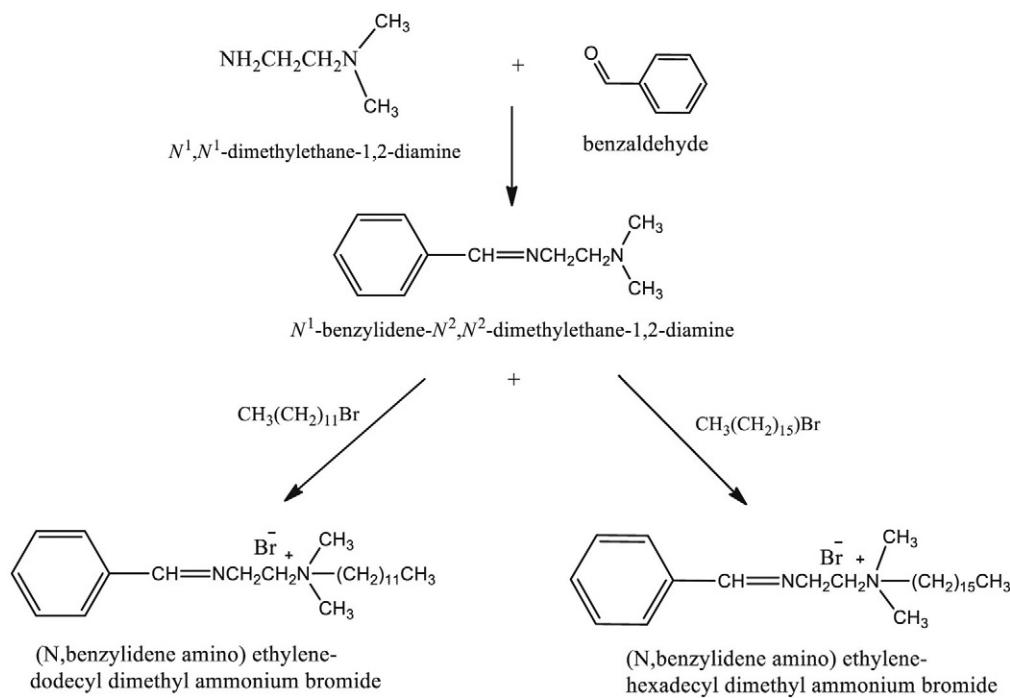
performance was found to follow the order: CPBr > TX-100 > DBS, which was attributed to the difference in the molecular structures of the three surfactants. CPBr was reported to give the best inhibition action, while DBS suffered from the lower polarizability of the $-SO_3^-$ group and TX-100 gave lower inhibition actions due to presence of a bulky group. The three surfactants were reported to act mainly as cathodic inhibitors. In a related study, the inhibition effect of some anionic surfactants such as 1- Dodecane sulfonate sodium (SSD) and Diocetyl sulfosuccinate sodium (AOT) at various combinations of these organic compounds on the corrosion behavior of carbon steel in 0.5 M H₂SO₄ medium at temperature of 25 °C was reported by Branzoi et al. [94], using potentiostatic and potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FT-IR) and metallurgical microscopy techniques. It was found that these organic inhibitors exert a great inhibition effect on carbon steel corrosion, and acted as a mixed-type inhibitor. The inhibition efficiency of these surfactants was reported to follow the order: AOT > AOT/SSD > SSD. The inhibition performance of the organic inhibitor was attributed to either the adsorption of inhibitor molecules building a protective film or the formation of an insoluble complex of the inhibitor adsorption, which obeyed the Langmuir adsorption isotherm model. Ali [95] synthesized four novel aziridinium, pyrrolium and azepanium bis-quaternary ammonium salts joined within similarly aromatic spacer (Scheme 21), and evaluated the inhibition actions of these four novel based surfactants on the corrosion of carbon steel in 1 M HCl using galvanostatic polarization method. The galvanostatic polarization data was reported to indicate that the inhibition efficiency of these compounds increased with increasing concentration of the inhibitor, ($\eta\%$), with attainment of maximum inhibition efficiency of 82% at 500 ppm of the inhibitor. The adsorption of these compounds on the metal surface was found to obey Tafel adsorption isotherm. The inhibitors were suggested to be mixed from physical and chemical adsorption on the steel electrode on the basis of the high values of the adsorption-desorption equilibrium constant, K_{ads} , and the free energy of adsorption, G_{ads} of these compounds.

Kong et al. [96] synthesized a novel Mannich-modified imidazoline (MMI) as cationic emulsifier via three steps - acylation, cyclization, and Mannich reaction using Lauric acid, tetraethylenepentamine, xylene, with final addition of methanal and acetone to the intermediate (Scheme 22). The corrosion inhibition performance of MMI against corrosion of five types of steels in the simulated corrosion solution was investigated by static weight loss (WL) tests. The MMI was reported to effectively inhibit the corrosion of the different steels in HCl solution. The main inhibition mechanism was reported to be most likely due to the organic adsorption film on the steel surface, thus preventing the corrosion medium from the steel surface.

Very recently, Cedeño et al. [97] investigated corrosion inhibition effect of Teen 80 surfactant against corrosion of steel AISI-SAE 1020 in CO₂-brine solution (3% NaCl), using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) techniques. The surfactant was reported to show an excellent corrosion inhibition performance, which increased with increasing fluid velocity. The morphology of the steel surface after exposure to the solution of 3% NaCl with and without surfactant was reported to indicate the inhibition phenomenon, which was attributed to the adsorption of the surfactant



Scheme 17. Chemical synthesis of nonionic surfactant, EMB [88].



Scheme 18. Chemical synthetic route for the two new Schiff base cationic surfactants as corrosion inhibitors in acidic environment [89].

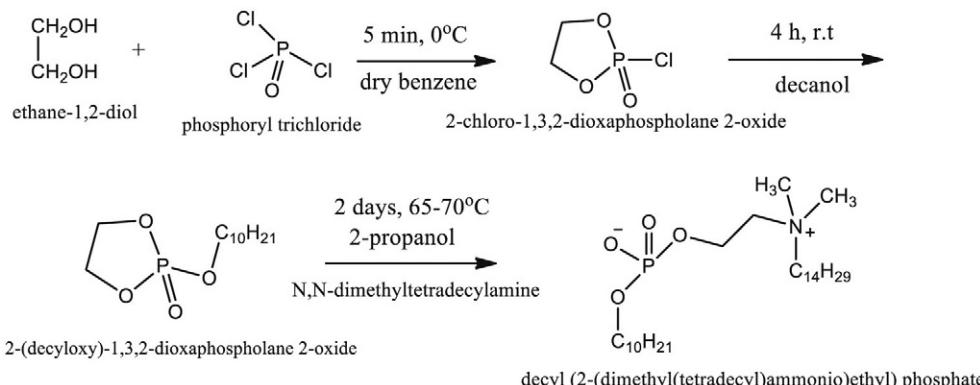
molecules, insulating the surface of the corrosive medium and reduced the surficial attack. Al-Sabagh et al. [98] synthesized new ethoxylated non-ionic surfactants based on 1,4 diaminobutane (DAB); 1,6 diaminohexane(DAH) and 1,8 diaminooctane (DAO), followed by evaluation of their inhibition performance against the corrosion of carbon steel pipelines in deep oil wells formation water using potentiodynamic polarization (PDP) measurements. All the non-ionic surfactants were reported to be effective corrosion inhibitors for carbon steel in oil wells formation water, and the inhibition efficiency (IE%) of the surfactants was found to increase with increasing degree of ethoxylation of inhibitor molecules. The inhibitor molecules were also reported to behave as mixed-type inhibitors, inhibiting both anodic metal dissolution and cathodic oxygen reduction. The inhibition mechanism was attributed to the strong adsorption ability of the surfactants on the surface of carbon steel leading to formation of a good protective layer, thus isolating the surface from aggressive environment. Masroor and Mobin [99] recently carried out extensive review on the application of surfactants as corrosion inhibitors for different metals and alloys. They showed different types of surfactants that are applicable to different metals, where

they emphasized and has rightly observed in this review, that most surfactants are used as corrosion inhibitors for mild steel or carbon steel, and therefore much research is needed for their anti-corrosion performances on other metals. **Table 2** shows chemical structures of surfactants that have been reported as corrosion inhibitors.

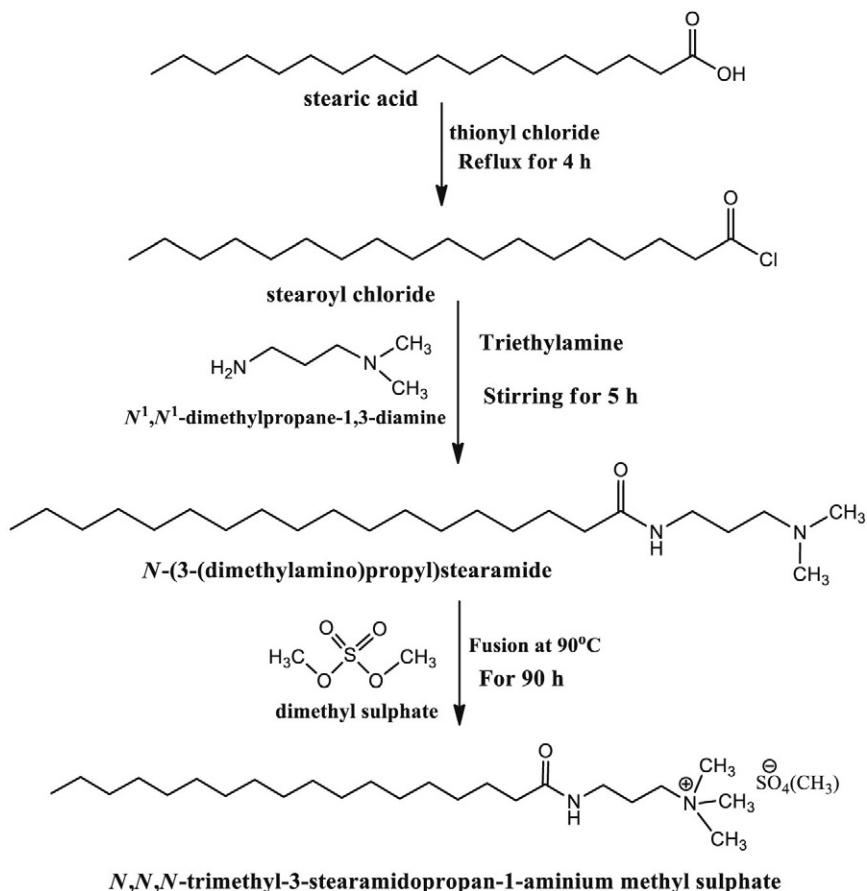
3.1.2. Volatile corrosion inhibitor (VCI)

Volatile corrosion inhibitors (VCIs) are organic compounds that protect metal surfaces by emitting a vapor such as an amine-based compound. The nitrogen on the amine has two electrons that are attracted to the polar metal surface. Once it is attracted to the metal, the rest of the molecule is very hydrophobic and repels water to significantly retard corrosion.

Volatile corrosion inhibitor (VCI) is an inhibitor that has volatile property at normal temperature irrespective of whether it is a solid or liquid. VCI is a compound or mixture of compounds that vapourizes slowly at normal temperature, e.g. nectarine, camphor paradichlorobenzene that are used in homes as a mothproofing agent. The gas vapor that is chemically and physically adsorbed onto a metallic surface



Scheme 19. Synthesis route and chemical structure of zwitterionic gemini surfactant as corrosion inhibitor in acidic environment [91].



Scheme 20. Chemical synthesis of fatty amido-cationic surfactant as corrosion inhibitor in acidic environment [92].

reacts with the metal surface, condenses and hydrolyzed by any moisture to liberate protective ions, thus prevents metal corrosion. The inhibition performance of VCI depends on the volatility of these compounds with fast protective action requiring high volatility while enduring protection requires low volatility.

Quraishi and Jamal [100] synthesized five new organic volatile corrosion inhibitors (VCI) using 1,6-diaminohexane with various acids such as cinnamic acid ($C_9H_8O_2$), nitrobenzoic acid ($C_7H_5O_4N$), phthalic acid ($C_8H_6O_4$), maleic acid ($C_4H_4O_4$), and orthophosphoric acid (H_3O_4P) (Scheme 23), and their inhibiting performance against corrosion of aluminium, zinc, and mild steel was evaluated using weight loss (WL) method and potentiodynamic polarization (PDP) studies. All investigated VCI were reported to exhibit very good inhibition efficiency (IE) for aluminium, zinc, and mild steel.

Zhang et al. [101] developed the synthesis of bis-piperidiniummethyl-urea (BPMU) and mono-piperidiniummethyl-urea (MPMU) as novel volatile corrosion inhibitors (VCIs) (Scheme 24), and their vapor corrosion inhibiting properties were evaluated using volatile inhibiting sieve test (VIS) and vapor inhibiting ability test (VIA), while their volatility were compared by using volatile weight loss test in a closed space. The corrosion inhibition performance of BPMU and MPMU against corrosion of mild steel in thin electrolyte layer was evaluated using electrochemical impedance spectroscopy of a volatile corrosion inhibitor monitor (VCIM). According to their results, BPMU was found to have better corrosion protection effect and lower volatility compared with MPMU. Their results further suggested that that BPMU has more coordination centers to the steel.

Rammelt et al. [102] studied some aspects of the passivation of mild steel in the presence of selected vapor phase corrosion inhibitors (VCIs) with respect to their ability to vapourize by sublimation tests and their role in the inhibition mechanism of mild steel using open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) measurements. It was revealed from their study that the inhibition by VCI compounds mainly depends on their ability to vaporize to a sufficient extent with subsequent protection to the metallic surface. The protection was also found to be strongly influenced by the pH value of the moisture layer on the metallic surface.

In a related study, Kashkovskiy and Kuznetsov [103] studied the protective effect of amines on steel corrosion under simulated conditions of gas condensate fields. It was shown that primary amines are less effective than secondary and tertiary ones in terms of steel protection, especially in vapor phase. They were able to establish from their results the possibility of inhibition of steel hydrogen sulfide corrosion (HSC) in a vapor phase by volatile amines. Recently, Goncharova et al. [104] carried out research on adsorption of VCIs and silanes from vapor-gas phase by ellipsometry and studied the protective effect of adsorption layers on metals. The nanoscale inhibitor films deposition of VCIs on metal surfaces, developed on the basis of Schiff bases and silanes, were reported to provide better corrosion protection than VCIs themselves under the conditions of forced moisture condensation. They further reported that increasing irreversibility is a requisite to strengthening of the protective effect of the nanolayers formed on metal surface.

Very recently, Adelakin et al. [105] investigated the effectiveness of VCI in providing corrosion protection at the underside of AST bottom by determining real-time corrosion rate at the underside of AST using

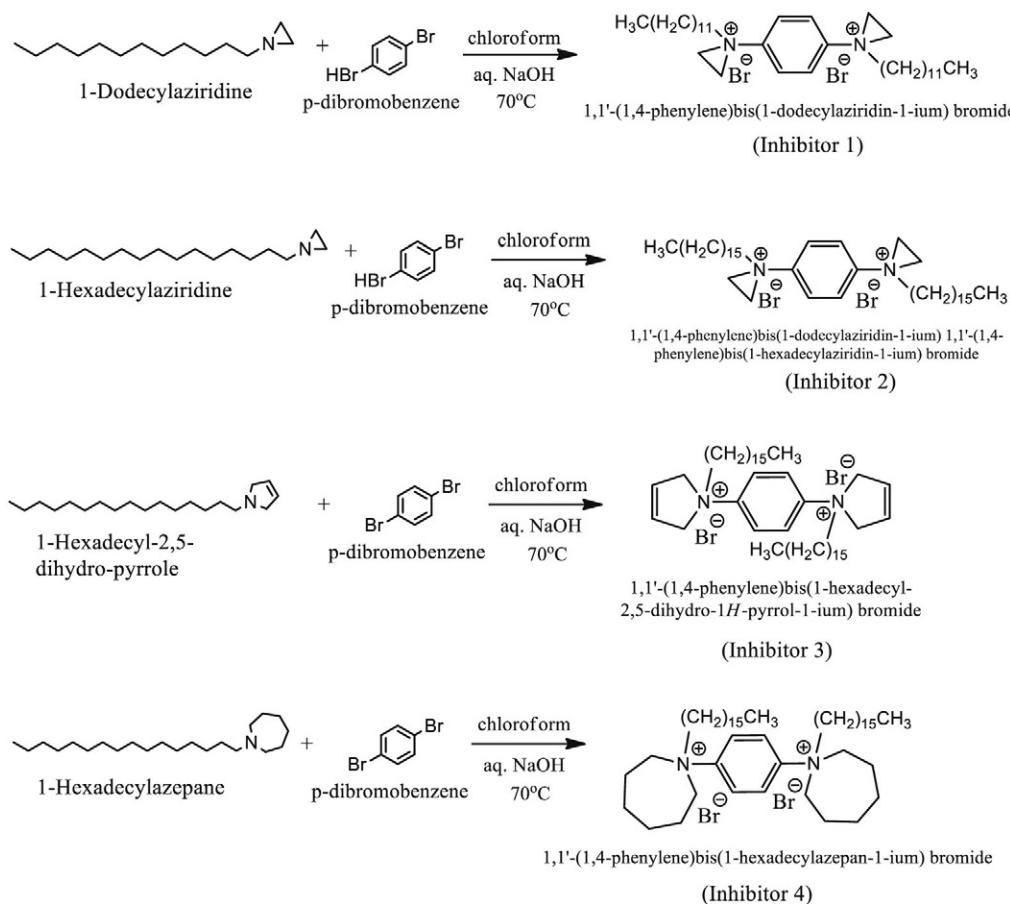
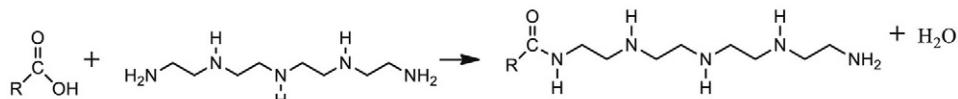
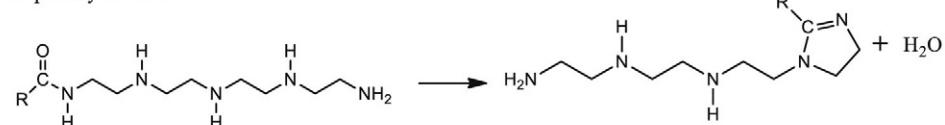
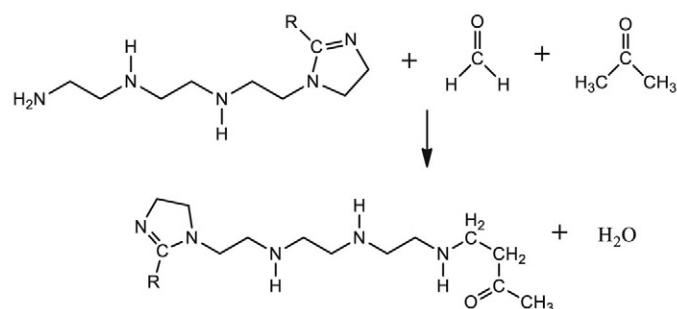
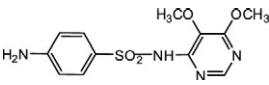
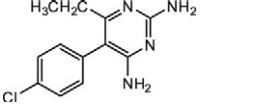
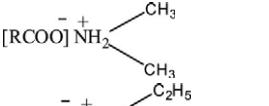
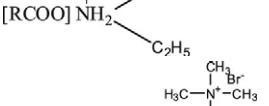
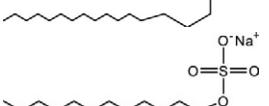
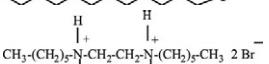
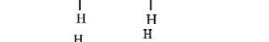
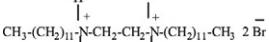
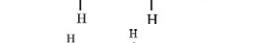
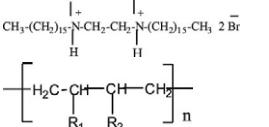
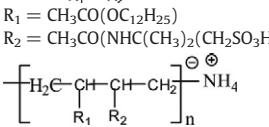
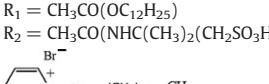
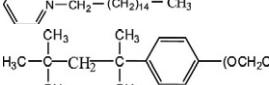
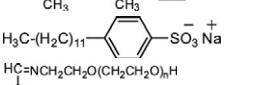
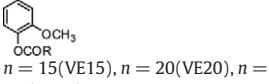
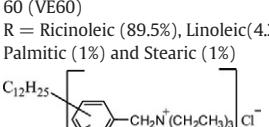
**Scheme 21.** Chemical synthetic routes for the novel base surfactants as corrosion inhibitors in acidic environment [95].**Step 1: Acylation****Step 2: Cyclization****Step 3: Mannich reaction****Scheme 22.** Chemical synthetic steps for Mannich-modified imidazoline (MMI) [96].

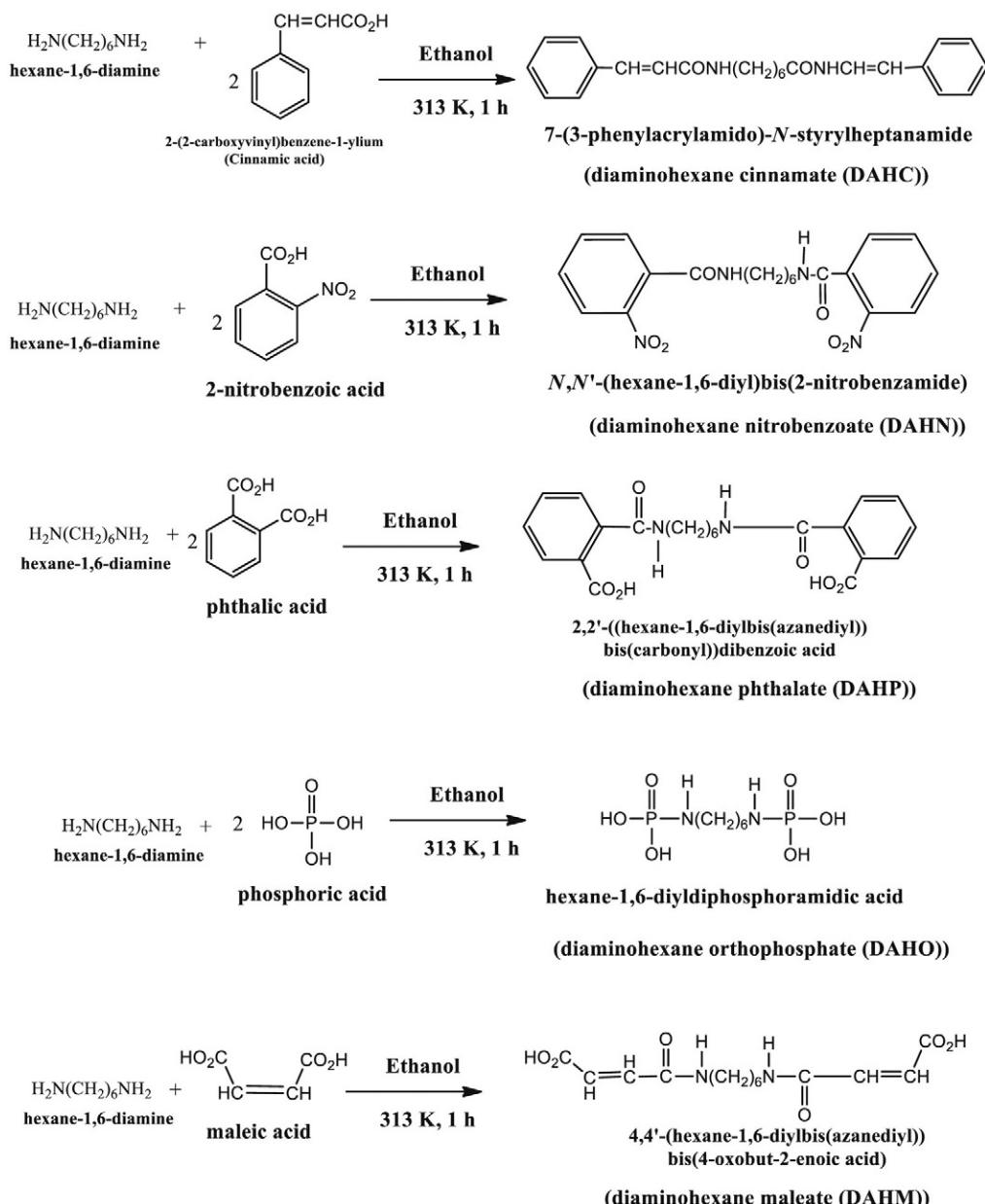
Table 2

Chemical structures of surfactants used as corrosion inhibitors.

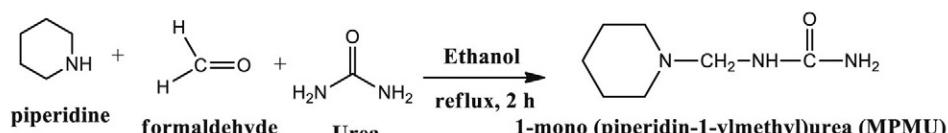
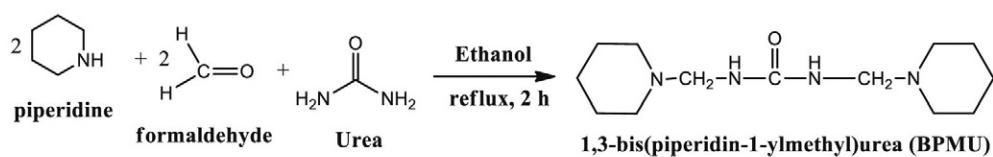
Name	Chemical structure	Metal type	Medium	Reference
Sulfadoxine		Pipeline steel	Crude oil pipeline water	Ngobiri et al. [201]
Pyrimethamine		Pipeline steel	Crude oil pipeline water	Ngobiri et al. [210]
Naphthenic dimethylamine complex (NDMC)		Mild steel	CO2-saturated/NaCl	Abd El-Lateef et al. [211]
Naphthenic diethylamine complex (NDEC)		Mild steel	CO2-saturated/NaCl	Abd El-Lateef et al. [211]
Cetyltrimethyl ammonium bromide (CTAB)		Mild steel	HCl	Yousefi and Javadian [212]
Sodium dodecyl sulfate (SDS)		Mild steel	HCl	Yousefi and Javadian [212]
<i>N</i> -Hexane-diyl-1,2-ethane-bis ammonium bromide (HEAB)		Mild steel	HCOOH	Ansari and Quraishi [213]
<i>N</i> -Dodecane-diyl-1,2-ethane-bis ammonium bromide (DDEAB)		Mild steel	HCOOH	Ansari and Quraishi [213]
<i>N</i> -Hexadecane-diyl-1,2-ethane-bis ammonium bromide (HDEAB)		Mild steel	HCOOH	Ansari and Quraishi [213]
2-Acrylamido-2-methylpropane sulfonic acid/lauryl acrylate copolymer (LPx)		Carbon steel alloy	HCl	Noor El-Din et al. [214]
(2-Acrylamido-2-methylpropane sulfonic acid/lauryl acrylate) copolymer ammonium salt (LPx ammonium salt)		Carbon steel alloy	HCl	Noor El-Din et al. [214]
Cetylpyridinium bromide (CPBr)		mild steel	H2SO4	Tammam et al. [93]
Triton (TX-100)		mild steel	H2SO4	Tammam et al. [93]
Dodecyl benzene sulphonate (DBS)		mild steel	H2SO4	Tammam et al. [93]
Vanillin – derived non-ionic surfactants		Carbon steel	HCl	Tawfik and Negm [86]
Di dodecyl benzyl tri ethyl ammonium chloride		Carbon steel	H2SO4	Tantawy [215]

ER probes. Their study revealed that VCI was able to reduce the corrosion rates of the underside of above ground tank bottoms, with stable condition taking over 12 months and spanning to as long as 24 months to achieve the required effectiveness, which may not be uniform due to micro (local) environment or physical conditions under the tank. The structures of typical volatile corrosion inhibitors used in oil and gas industry are given in Fig. 5.

The corrosion inhibition mechanism of volatile corrosion inhibitor, using nitrite as an example for steel substrate is shown in Scheme 25. The moisture in the air is condensed on the steel surface, and the slowly vapourized nitrite is dissolved into the condensation water to prevent corrodants such as oxygen and seawater from reacting with the steel, thus prevented the steel from corroding.



Scheme 23. Synthesis of volatile corrosion inhibitors [100].



Scheme 24. Synthesis of piperidinium methyl-urea as volatile corrosion inhibitors [101].

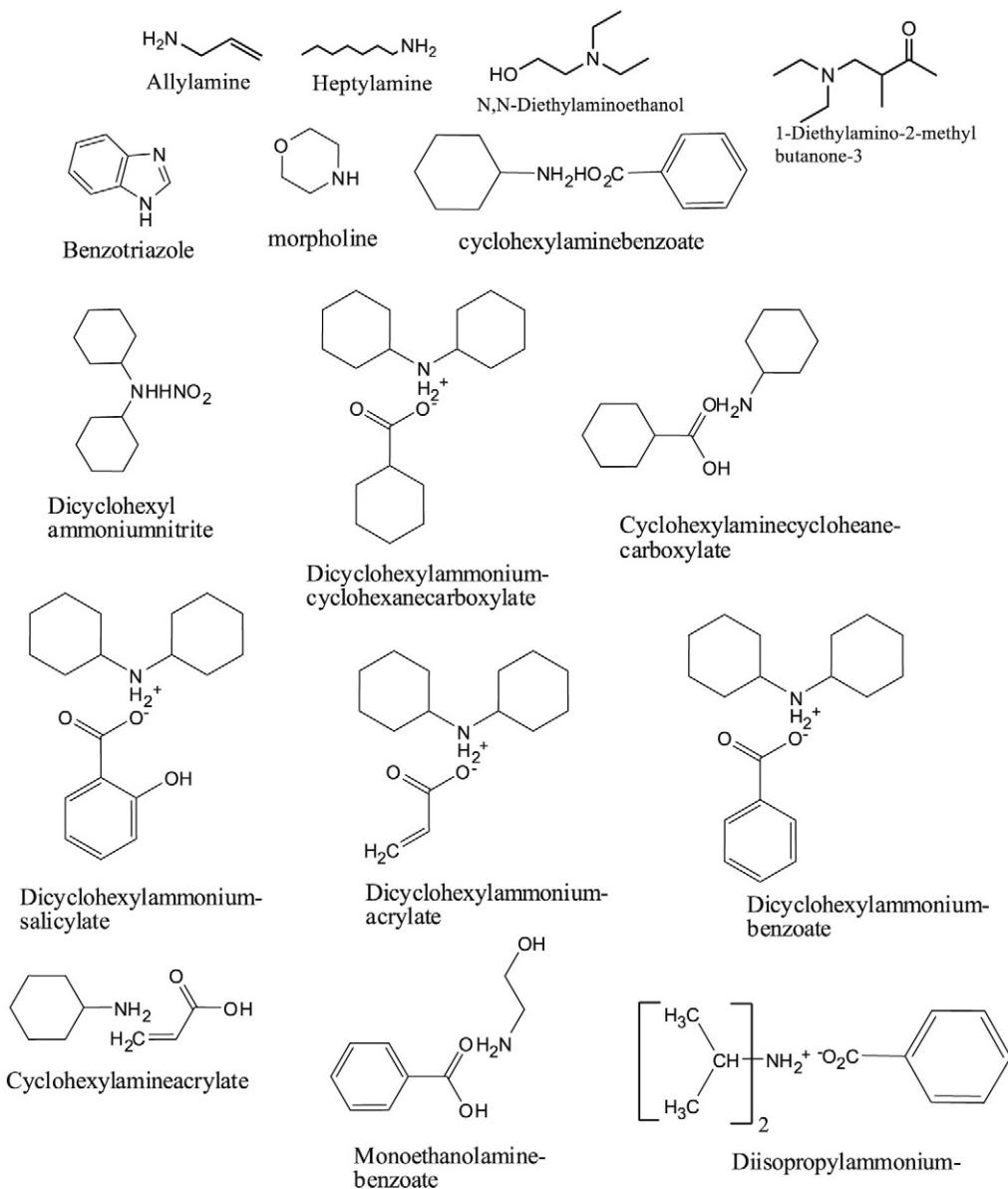
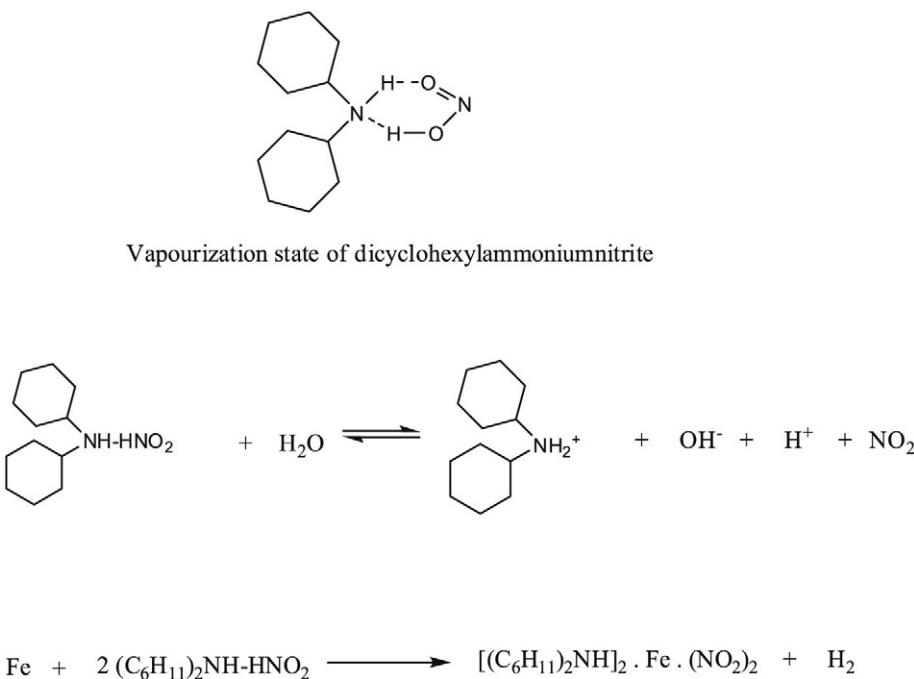


Fig. 5. Structures of typical volatile corrosion inhibitors.

3.2. Green corrosion inhibitor (GCI)

Most of the synthetic organic compounds that are used as inhibitors are not cost-effective and are toxic to humans and the environment. The toxicity of these organic inhibitors has paved way to explore the use of green corrosion inhibitors which are nontoxic, biodegradable and environmentally friendly. A lot of research has been done on development of green corrosion inhibitors [106]. Znini et al. [107] obtained environmentally friendly corrosion inhibitors for the corrosion of steel in H_2SO_4 using essential oils and purified compounds obtained from plant extracts. The inhibitive effect of the extract of Khillah (*Ammi visnaga*) seeds on the corrosion of SX 316 steel in HCl solution was reported by El-Etre [108], where he attributed the anticorrosive performance of this plant extract to the insoluble complexes formed from the interaction between iron cation and Khillah extract. Raja and Sethuraman [109] reported an extensive review of green compounds (natural products) that are applicable as potent corrosion inhibitors, where they concluded that natural substances can serve as impressive corrosion inhibitors in the near future owing to their advantages

which include easy accessibility, eco-friendliness, biodegradability on earth and non-toxicity. Gerengi and Sahin [110] investigated the inhibitory performance of different concentrations of novel plant extract *Schinopsis lorentzii* derivatives against the corrosion of low carbon steel in 1 M HCl solution using Tafel extrapolation, linear polarization, and electrochemical impedance spectroscopy (EIS). It was found that *Schinopsis lorentzii* extract acted as slightly cathodic inhibitor and inhibitory performance increased with increasing concentration of the extract. The adsorption process of the molecules of the extract on the surface of the low carbon steel was reported to involve physisorption and obeyed Temkin adsorption isotherm. Recently, Reyes-Dorantes et al. [111] synthesized fatty amides from crude rice bran oil by mixing one mole of crude oil with 3 mol of aminoethylethanolamine (AEEA), followed by evaluation of their inhibition performance against corrosion of an APIX-70 steel in a CO_2 -saturated solution (3.5% NaCl) using real-time corrosion monitoring and potentiodynamic polarization (PDP) curves. The fatty amides were reported to act corrosion inhibitor at all temperatures tested, and their inhibition efficiency was found to increase with the concentration of added inhibitor. Their inhibitory

**Scheme 25.** Corrosion inhibition mechanism of nitrite, a typical VCI for steel substrate.

performance was attributed to the adsorption of the inhibitor molecules onto metal surface, thus preventing the diffusion of the aggressive ions of the electrolyte to the metal surface.

In recent times, the anti-corrosive performances of natural products such as watermelon rind extract on mild steel in acidic media [112], leaves extract of *Gingko biloba* (GBE) on mild steel in 3.5 wt% NaCl solution saturated with CO₂ [113], *Piper nigrum* extract on mild steel in corrosive medium [114], leaves extract of African *perquetina* on mild steel in sulphuric acid solution [115], peel extract of *Musa paradisica* on mild steel in HCl solution [116], leaves extract of *Nicotiana tabacum* on mild steel in acidic medium [117], bitter leaf root extract on mild steel in sulphuric acid solution [118], leaves extract of African Breadfruit on mild steel and aluminium in 1 M H₂SO₄ [119], turmeric and gingeron on mild steel in acidic medium [120], green extract of *Ligularia fischeri* on mild steel in acidic medium [121], *Phyllanthusamarus* leaf extract (PAE) on mild steel in hydrochloric acid [122], organosolv oil palm (*Elaeis guineensis*) fronds lignin on mild steel in 0.5 M HCl solution [123], *Poupartia birrea* back extracts as a potential green inhibitor for mild steel in 0.5 M H₂SO₄ medium [124] and aminated jojoba oil as green corrosion inhibitors for mild steel in 0.5 N HCl [125] have been reported. These natural products have been found to show good anti-corrosive property for the protection of steel from corrosion. The inhibiting effect of the studied extracts was attributed to the presence of phytochemical constituents present in these extracts which is adsorbed on the surface of the mild steel. Various mechanisms of action have been proposed for the corrosion inhibitory property of these natural products, and were found to be dependent on the structure of the bioactive compounds in the plant extracts. Their anti-corrosive action was suggested to be due to the presence of hetero atomic functional groups in the structure of the bioactive compound, where free electrons on O and N atoms form strong bonds with electrons on the metal surface, thereby confers good inhibition properties to the organic compounds extracted from these plants. The bioactive constituents of natural products vary from one plant species to another but their structures are closely related to their organic counterparts. Some of the compounds isolated from these plants include alkaloids (berberine, ricinine), pyrrolidine, allyl propyl disulphide, 2-hydroxy-1,4-naphthoquinone resin, tannin, coumarin, gallic acid, sterols, lysergic

acid amide, hexuronic acid, neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, reducing and non-reducing sugars, primary and secondary amines, unsaturated fatty acids, bioflavonoids, ascorbic acid, amino acids, flavonoids, pigments, and carotene [126], and structures of some of these compounds are given in Fig. 6.

3.3. Natural corrosion inhibitors

Hamitouche et al. [127] synthesized quaternary ammonium cationic surfactants mixture from light naphtha through chloromethylation of the light naphtha (LN) fraction of the petroleum to afford chloromethylated crude product (CLN), followed by in situ quaternization with triethylamine (TEA) in dimethyl formamide (DMF) to yield white recrystallizable crystals of light naphtha quaternary ammonium salt, (QLN), which is a mixture of *N,N*-diethyl-*N*-alkylarylmethyl ammonium chloride with different alkyl chains and different aryl groups (Scheme 26). The inhibiting performance of the synthesized compound against the corrosion of carbon steel in 1 M HCl solution was then investigated using weight loss (WL) method, potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The inhibiting performance of the cationic surfactant was found to increase with increasing inhibitor concentration and temperature but independent of pH of corrosive medium and immersion time of the sample. The cationic surfactant was reported to act as a mixed (anodic and cathodic) inhibitor and obeyed the Langmuir adsorption isotherm.

Mehdaoui et al. [128] synthesized two new surfactants, gas oil sulfonate (GOS) and kerosene sulfonate (KES) from Algerian petroleum fractions, kerosene (KE), and gas oil (GO) via sulfonation reaction of petroleum fractions with oleum followed by neutralization of sulfonated oils with calcium hydroxide solution (Scheme 27). The inhibiting performance of the surfactants against the corrosion of carbon steel in 1 M HCl was evaluated using potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) spectroscopy. The synthesized anionic surfactants of the two Algerian petroleum fractions (GOS and KES) were reported to inhibit the corrosion of carbon steel in

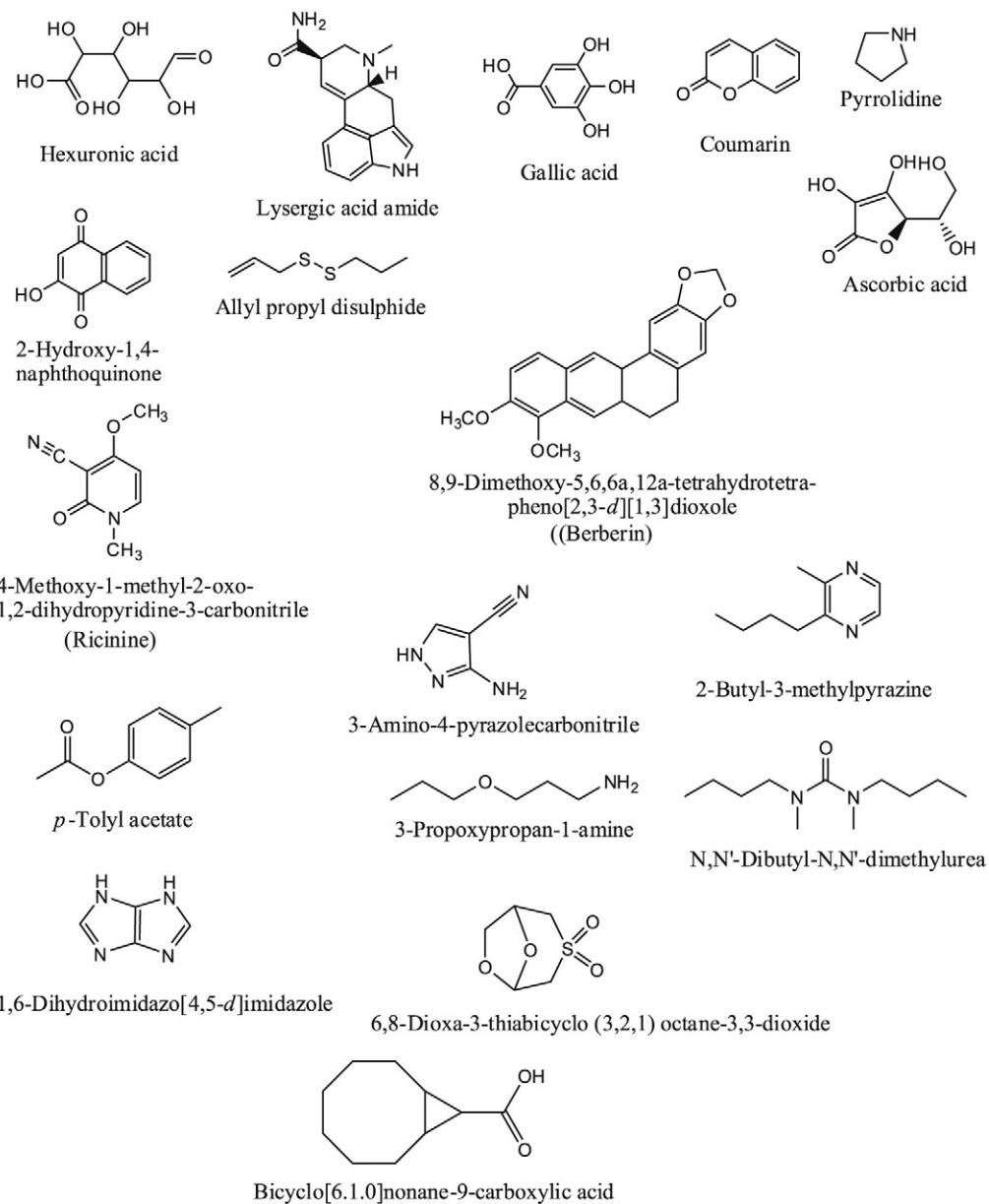


Fig. 6. Structures of active organic constituents in plant extracts.

1 M HCl solution with better performance of the GOS. Both GOS and KES were reported to exhibit mixed-type inhibitors, and their inhibition efficiencies (IE%) were found to increase with inhibitor concentration. The mode of adsorption of the GOS and KES inhibitors on the surface of the carbon steel was found to be fitted to Langmuir adsorption isotherm model.

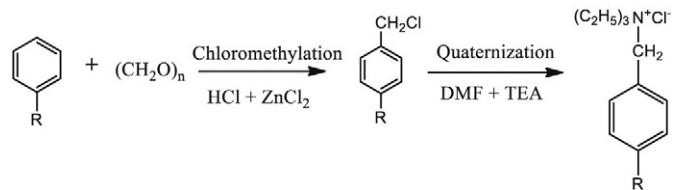
Abd El-Lateef et al. [129] synthesized two natural naphthenate surfactants, naphthenic-dimethylamine and naphthenic-diethylamine

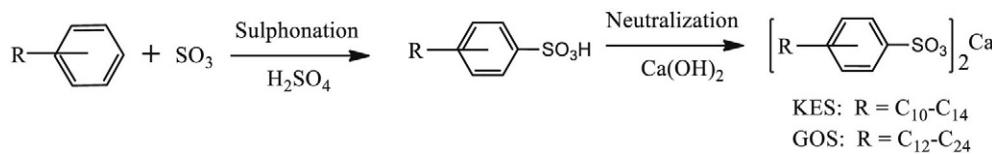
complexes by mixing naphthenic acids isolated from light oil fraction at molar ratio of 1:1 with dimethylamine and diethylamine respectively. The inhibition performance of the two natural naphthenates against corrosion of mild steel in CO₂-saturated 1% NaCl solution was investigated by linear polarization resistance (LPR) corrosion rate and potentiodynamic polarization (PDP) measurements. These compounds were reported to act as inhibitor in the studied medium with naphthenic-diethylamine complex exhibiting the highest inhibition efficiency of 99.76 at 100 ppm. These compounds were also found to behave as mixed inhibitors, affecting both cathodic and anodic corrosion currents, while the adsorption of naphthenate surfactants on the mild steel surface was reported to obey the Langmuir adsorption isotherm model.

3.4. Flow assurance issues in offshore operations

The offshore drilling activities are usually faced with severe technical challenges in flow assurance due to the formation of gas hydrates in flowline, especially when moving towards geological sites of deeper waters and colder temperatures, which are favorable conditions for

Scheme 26. Synthesis of quaternary ammonium cationic surfactants mixture from light naphtha [127].





Scheme 27. Chemical synthesis of inhibitors KES and GOS from Algerian petroleum fractions [128].

gas hydrate formation and stability. Gas hydrates are crystalline, non-stoichiometric clathrate inclusion compounds, consisting of hydrogen-bonded water molecules as hosts and small hydrocarbon gas molecules such as methane, ethane, propane and other gases that may be present (H_2S , CO_2 , N_2), entrapped in the water cavities as guests [130]. They are not chemical compound because of non-existence of strong chemical bonds between water and gas molecules. In offshore production, shut-in and restart operations are particularly critical for hydrate plug formation due to low temperatures, but can occur under steady-state production conditions, such as long deepwater subsea tiebacks. Hydrate formation can restrict flow and even form a solid plug to block all production within a short period. Aside the flow assurance issue of hydrate formation, it can also cause catastrophic failure, leading to equipment damage, injury, and even loss of life.

Despite scientific innovations and technical improvement, flow assurance due to gas hydrate formation in these regions, is still a serious concern for ultradeepwater operations [131]. In this context, it is essential to implement hydrate management strategies for uninterrupted offshore oil and gas production in a safe and cost-effective manner. Chemical inhibition is the most common way to mitigate hydrate formation in offshore oil and gas exploration and the three main methods include thermodynamic hydrate inhibitors (THIs), low dosage hydrate inhibitors (LDHIs) and natural inhibitors. Apart from chemical inhibition method, other options to inhibit hydrate, which is outside the scope of this paper, is to ensure that the system operates outside the hydrate forming region by increasing or decreasing pressure through direct electric heating (DEH).

3.4.1. Thermodynamic hydrate inhibitors

The use of traditional thermodynamic hydrate inhibitors (THIs) such as methanol and monoethyleneglycol (MEG) is highly expensive and conservative [132]. Thermodynamic hydrate inhibitors are used to treat systems with high sub-cooling and/or high water cuts, and require large volumes of methanol or MEG injection with typical rate of 30–60% by volume. They work by shifting the hydrate equilibrium curve to lower temperature and pressure, thereby keeping the system out of the hydrate formation region. This preventive technique requires very high injection rates and large amount of THIs with higher sub-cooling, which thus implies huge capital expenditure (CAPEX) and could cause production shut down [133]. The large volume of MEG consumed in the field and the high financial costs necessitate the need for recycling as an effective and economical solution to long-term production [134, 135]. The recycling of MEG involves regeneration and reclamation processes to remove water and soluble salts, respectively. In many cases, regeneration units are installed to recover most of the injected THIs. The major challenge in the MEG regeneration and reclamation process is the thermal decomposition and degradation of MEG caused by reboiler overheating, leading to fouling, foaming, corrosion, and process upset [136–138].

Liang et al. [139] analyzed the hydrate risks of the well QDN-X under operational conditions during drilling and testing processes, with the following well sections under maximum hydrate risks: normal drilling, 325–1426 m depth (under cooling temperature of 6.5 °C); during drilling stop, 300–1963 m depth (under cooling temperature of 19 °C); during testing stop, 0–1981 m (under cooling temperature of 23 °C). The authors designed hydrate prevention solutions which included addition of sodium chloride and ethylene glycol into drilling fluid during normal

drilling; addition of calcium chloride/potassium formate and ethylene glycol into testing fluid when drilling stops; application of downhole methyl alcohol injection when production rate of natural gas is lower than $25 \times 10^4 \text{ m}^3/\text{d}$; and filling the testing string with testing fluid when the test shuts down for a long time. All the designed solutions were found to meet the requirements of hydrate prevention based on lab experiments and field operations.

Very recently, AlHarooni et al. [140] investigated the extent to which degraded MEG will affect hydrate inhibition, by analyzing methane gas hydrate formation profiles for a variety of solutions of thermally degraded MEG with injection of methyl diethanolamine (MDEA) and film-forming corrosion inhibitor (FFCI) as corrosion inhibitors at a pressure range from 50 to 300 bar using the isobaric method. Thermally degraded MEG with corrosion inhibitors (MDEA and FFCI) was reported to reduce hydrate inhibition performance to different degrees depending on the thermal degradation level. The reduced performance was attributed to the formation of acidic degradation products during thermal exposure [138,141].

3.4.2. Low dosage hydrate inhibitors

In view of enormous financial expenses for hydrate prevention associated with THIs as well as harsher conditions associated with ultradeepwater exploration have necessitated the need for better hydrate inhibition methods and led to the development of low-dosage hydrate inhibitors (LDHIs). In this context, a more robust and economical hydrate management strategies need to be put in place for safe and reliable offshore production of oil and gas. LDHIs consist of kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). Unlike thermodynamic inhibitors, LDHIs do not change thermodynamic equilibrium of hydrates but their surface properties affect the hydrate kinetics and agglomeration. LDHIs are effective at low concentrations, with typical injection rates of 0.5–2.0% by volume [142], and their performances are also dependent on the degree of sub-cooling in the system, i.e. the difference between the hydrate equilibrium temperature and the operating temperature at a given pressure [143].

3.4.2.1. Kinetic hydrate inhibitors. Kinetic hydrate inhibitors (KHIs) are water soluble, low molecular weight polymers whose active groups delay the hydrate nucleation and/or growth and extend the hydrate induction time to exceed the residence time of the reservoir fluid [130]. The induction time again is dependent on the sub-cooling of the system, where higher sub-cooling results in shorter induction times. At higher sub-cooling, the induction times are not sufficient for most offshore applications, hence KHIs have been combined with THIs such as methanol or glycol to extend this sub-cooling limitation, and combinations of thermodynamic and kinetic inhibitors are in use in both offshore and onshore production [130]. In general, KHIs either use alone or in combination with thermodynamic inhibitors, offer an alternative way to control hydrate formation in offshore exploration and have been successfully used in the field for continuous injection applications for over some decades [130]. The three main categories of KHIs developed for field applications include:

- Poly(*N*-vinyllactam) polymers, including a variety of copolymers and grafted polymers, for example, five-ring polyvinylpyrrolidone (PVP) [144]; six-ring polyvinylpiperidone (PVPIP) [145]; seven-ring polyvinylcaprolactam (PVCap) [146];

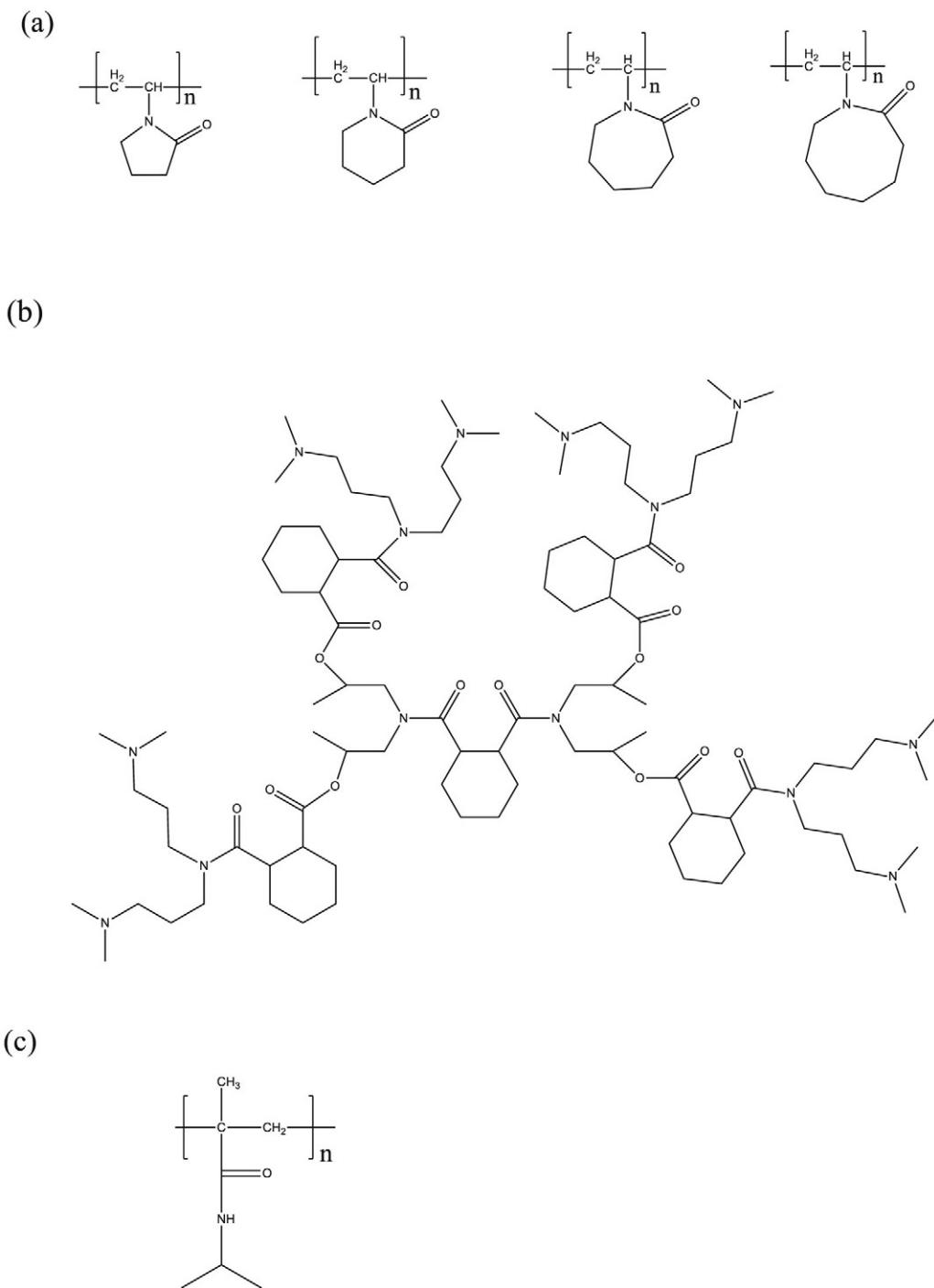


Fig. 7. Structural examples of poly(*N*-vinyl lactam) polymers with increasing lactam ring sizes (a), hyper-branched poly(esteramide) (b) and poly(*N*-isopropylmethacrylamide) (c).

and eight-ring polyvinylazacyclo-octanone (PVACO) [147] (Fig. 7a) and their performances as KHIs were reported to increase with increasing lactam ring size [145,147] with five-and seven-rings being used in commercial KHI formulations.

- Hyper-branchedpoly(esteramide)s [148], with an illustrative structure shown in Fig. 7b.
- *N*-Isopropylmethacrylamide (IPMA) polymers and copolymers [149] (Fig. 7c).

Sharifi et al. [150] evaluated the performance of polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) as kinetic hydrate

inhibitors (KHIs) in the presence of NaCl and *n*-heptane by direct measurement of viscosity changes of gas hydrate slurries formed in situ at high pressure conditions. The addition of KHIs was found to delay hydrate nucleation time with PVP performing more effectively than PVCap, while latter was reported to control the growth and delay agglomeration more effectively than the former. The addition of liquid hydrocarbon (*n*-heptane) to saline solution was found to delay the formation of hydrate at the onset with a reduction in the hydrate crystal growth and a delay in hydrate agglomeration. The addition of KHIs in saline solution in the presence of *n*-heptane was reported to unexpectedly accelerate hydrate nucleation while gas hydrate growth was found to decrease significantly and hydrate particles remaining dispersed in slurry phase, thus minimizing chances of pipeline blockage. Huo et al.

[151] investigated inhibition performance of combined kinetic hydrate inhibitor (polyvinylcaprolactam based) and thermodynamic hydrate inhibitors (methanol and NaCl) in terms of the synergistic effect of the two types of hydrate inhibitors and the effects of pressure and sub-cooling time on the kinetic inhibition effect. The combined systems of PVCap + methanol and PVCap + NaCl were reported to inhibit hydrate formation when the sub-cooling degree was over 10 °C, with better performance of synergistic effect of PVCap + methanol system than that of the PVCap + NaCl system. Pressure was also reported to have significant effect than temperature on the performance of the combined inhibitor systems. The inhibition performance of the combined system was found to decrease with increasing sub-cooling time.

Al-Eisa et al. [152] evaluated performance testing on ready-made polymers, commercial KHIs and newly synthesized polymers using a rocking cell (RC-5) instrument. The inhibiting performance of these KHIs was ascribed to the polymer-water hydrogen bonding interactions. The carbonyl group of the amide in the polymeric inhibitor was also reported to form hydrogen bonding with the hydrate surface to delay the hydrate formation, thereby disrupting the local organization of water clusters around guest gas molecules. These KHIs were found to effectively prevent the formation of gas hydrates of synthetic natural gas with high concentration of H₂S and CO₂ at and beyond sub-cooling temperatures of 4 °C and 5.6 °C, thus maintaining pipeline integrity for various gas fields while lowering total costs of off-shore gas field production.

Recently, Tohidi et al. [153] presented novel developments which will facilitate the return of KHIs, including the results of a testing technique based on inhibition of crystal growth with reproducible results, performance of KHI under shut-in conditions, hydrates formation risk at the top of pipeline, and technique for addressing KHI fouling problems in produced water handling/re-injection (PWRI) and/or MEG regeneration by removing KHIs from produced water prior to PWRI or MEG regeneration. The possibility of predicting the potential suitability of KHI based solution for any specific field application prior to even starting the experimental campaign and/or designing a KHI + THI combination was also evaluated. Their results revealed that there is no risk of hydrate blockage in the bulk of aqueous phase during shut-in conditions provided the system was inside the complete inhibition region (CIR). The amount of hydrates formed at the top of the pipeline was found to be negligible since these hydrates come in contact with the aqueous phase containing KHIs within CIR, hence preventing their growth and could even dissociate [154]. Mono-Ethylene Glycol (MEG) was reported to be an excellent synergist for the KHIs investigated and 1% KHI was used to replace large quantities of MEG to avoid gas hydrate problem, thus providing considerable savings in capital expenditure (CAPEX) due to a significant reductions in the size of MEG regeneration/reclamation units, pipelines and pumps; and operational expenditure (OPEX) due to a significant reduction in the volume of fluid required for heating/boiling (in regeneration/reclamation units). Also a new family of the treatment chemical (TC) was reported to offer a potential solution to the problem of KHI removal from produced waters, which might cause problems related to produced water disposal and processing. Their studies have provided significant economic and environmental impact, as well as extending the life span of petroleum reservoirs.

3.4.2.2. Anti-agglomerants. Anti-agglomerants (AAs) are mostly surfactants, which allow fine hydrate particles to form and disperse in the reservoir fluid to generate transportable slurries of tiny hydrate particles in oil that can flow to the processing facilities. Generally, AAs do not depend on sub-cooling as they allow hydrate to form as very fine crystal dispersed in the oil layer. They are used for continuous injection applications, and most especially in shut-in/start-up scenarios [155]. They have their limitations, including water cut, which typically ranges around 40–60% water cut depending on conditions, and topside emulsion formation because they are surfactants [143,155]. With proper

hydrate performance testing, emulsion tendency testing and formulation, AAs can offer the most cost-effective solution to hydrate control for offshore oil and gas production systems with low-to-moderate water cuts [143,155].

Chua and Kelland [156] synthesized *n*-alkyl-*tri(n*-butyl) ammonium bromide AAs with varying alkyl chain lengths from octyl to octadecyl (C₈–C₁₈) as well as coco (a mixture of chain lengths but mostly in the C₁₂–C₁₆ range), followed by investigation of the influence of the length of the hydrophobic tail, effect of salinity and addition of anionic surfactant on the AA performance. The AA performance of *n*-alkyl-*tri(n*-butyl) ammonium bromides was found to improve with increasing alkyl chain length, which was reported to be valid to a certain extent until the performance began to decrease when the AA must have become too hydrophobic. The best quaternary ammonium salt in the series studied was reported to be *n*-dodecyl-*tri(n*-butyl)-ammonium bromide (DDBAB), followed by coco-*tri(n*-butyl) ammonium bromide (CBAB), *n*-tetradecyl-*tri(n*-butyl)- ammonium bromide (TDBAB), and *n*-hexadecyl-*tri(n*-butyl)- ammonium bromide (HDBAB). The AA performance was also reported to be enhanced with increasing salinity and addition of anionic surfactant, dodecyl sulfate (SDS), particularly at low salinity.

Sun and Firoozabadi [157] demonstrated the effectiveness of a formulation in hydrate anti-agglomeration in a natural gas at low dosage of 100% water cut in both freshwater and brine. The formulation consisted of a nonionic surfactant, a base to increase pH, and an alkane (oil) to eliminate foaming. The three components were found to show synergistic effect to deliver a highly effective performance as hydrate anti-agglomerant. In a related study, Sun et al. [158] threw light on the effectiveness of AA formulation containing 80–89% cocamidopropyl dimethylamine as the effective component, a base and oil (e.g., *n*-octane), through hydrate particle size measurements by the focus beam reflectance measurement (FBRM) in an autoclave setup in both freshwater and brine. The AA formulation was found to reduce hydrate particle size significantly and eliminated large particles. The two additives were found to enhance the effectiveness of the surfactant for anti-agglomeration, where a small amount of *n*-octane was reported to reduce hydrate particle size by a factor of two both in freshwater and brine, which may explain the low viscosity of the hydrate slurries with introduction of a small amount of oil such as *n*-octane in the system. The base helps with elimination of small amounts of hydrogen ions in aqueous solution in situations when acid gas species are present in natural gas. The introduction of 4 wt% NaCl in aqueous phase was found to increase the size of the hydrate particles.

Recently, Saikia and Mahto [159] investigated and compared the hydrate crystal inhibition performance of 1-decyt-3-methyl imidazoliumtetrafluoro borate with the commonly used kinetic inhibitor PVP. The effect of 1-decyt-3-methylimidazoliumtetrafluoroborate on the rheology of base drilling fluid was also studied at a temperature of 2 °C (marine conditions) [160]. Hydrate inhibition efficiency of 1-decyt-3-methyl imidazoliumtetrafluoro borate was reported to be comparable with the commonly used kinetic inhibitor polyvinylpyrrolidone (PVP) and found to be much effective for hydrate inhibition in experimental solution, with or without precursors. The inhibitor was reported to show a better performance against memory effect in the solution. Both 1-decyt-3-methyl imidazolium tetrafluoro borate and PVP were reported to show very encouraging synergistic effect on inhibiting the hydrate crystal formation by increasing the induction time. 1-Decyl-3-methyl imidazolium tetrafluoro borate was found to exhibit anti-agglomerant features and prevented the formation of hydrate block. The authors further suggested that 1-decyt-3-methyl imidazoliumtetrafluoroborate may be used as an effective substitute of PVP for hydrate crystal inhibition in drilling fluid.

Very recently, Lv et al. [161] used a high-pressure viscometer to investigate in-situ viscosities of emulsions and natural gas hydrate slurry, followed by analysis of the effects of different AAs, water cuts,

temperatures and annealing on the viscosity of emulsions and hydrate slurry. They further investigated the variation of system viscosity during hydrate formation from water-in-oil emulsions and equilibrium viscosity of hydrate slurry. Their findings revealed that AA could effectively reduce the sensitivity of slurry viscosity to the volume fraction of the hydrate and temperature, controlled agglomeration and prevented plugging in high water cut systems. The authors further stressed the significance of their study for the application of slurry flow technology to the petroleum industry.

3.4.3. Natural inhibiting components

In multiphase transport systems where crude oils are present, plugging may not be feasible in some cases, even though the system may be within the favorable P-T region of hydrate formation. Several authors have reported the natural ability of some crude oils to inhibit hydrate agglomeration [162–166]. The natural ability is attributed to crude composition and the presence of indigenous hydrate inhibiting components, also called natural inhibiting components (NICs). They are believed to consist of natural anti-agglomerant surfactants with affinity for the hydrate surface, adsorbing to the hydrate by hydrogen bonding interactions as illustrated in Fig. 8. The polar components such as acids, phenols and amine, which are the natural inhibiting components in the oil adsorb to the hydrate surface, creating oil-wet hydrate surface, which is being surrounded by a layer of NICs. This mechanism prevents agglomeration of hydrate particles that may lead to building up of hydrate plugs. The effectiveness of the natural anti-agglomerants has been reported to be dependent on salinity and pH [167]. Although the field of research is still at its infant stage and published material is sparse, several authors laid emphasis on the acid fractions from some crude oils imposing anti-agglomerating effects on hydrates and prevented plugging [168–171].

Recently, Daraboina et al. [172] investigated gas hydrate formation in multiphase mixtures containing an aqueous phase (with dissolved salts), reservoir fluid (crude oil) and natural gas phase using a standard rocking cell (RC-5) apparatus. Three different crude oils at 80%, 70% and 60% water cuts were used to simulate practical conditions in oil and gas pipeline. The effect of crude oil on natural gas hydrate formation was then investigated by observing the hydrate formation temperature in the presence of distilled water (control) at 15.7 °C. The effect of commercial biodegradable kinetic inhibitor Luvicap-Bio on natural gas hydrate formation in the presence of dissolved salts and crude oil was also investigated. The tested crude oils were found to show a clear inhibition effect for hydrate formation which depended on the crude oil types. The variation in crude oil inhibition performance was reported

to probably indicate the existence of a combination of inhibition mechanisms and potentially a competition among inhibition–promotion mechanisms resulting from the influence of crude oil composition (saturates, aromatics, resins and asphaltenes). Inhibition performance was found to increase with an increase in the oil content. The strength of kinetic inhibitor (Luvicap-Bio) was reported not to be affected by salts, but reduced significantly in the presence of crude oil. This study therefore suggested that different inhibition strategies depending on crude oil types and the water cut should be considered for safe operation of sub-sea pipelines in the oil and gas industry.

3.5. Corrosion tests

It is pertinent to know how effective protection of a metal against corrosion can be achieved with addition of corrosion inhibitor to the aggressive environment. There is no set universal standard for the laboratory setups and corrosion testing methods because corrosion cases entail different conditions, ranging from the type of metal used, electrolyte solution involved and corrodants encountered [173].

3.5.1. Metal sample preparation

The choice of metal specimens and surface preparations are very crucial since any impurities and changes in the composition have significant effects on the corrosion results [174]. The metal composition should also be closed to the metals relevant to the corrosion problem in question. For oil and gas industry, low carbon steel (mild steel) with typical chemical composition of 0.16% C, 0.53% Mn, 0.3% Si, 0.055% S, 0.045% P, and 98.91% Fe [175] has been used. Once the metal samples have been cut, it is then degreased using organic solvents like acetone, and ethanol or hot alkaline cleaner to remove any adherent impurities. This is then followed by mechanical polishing with series of emery paper of variable grades starting with 200–400 grit emery papers to remove deep scratches and rough spots on the metal substrate [175], leading to homogeneous appearance of the surface. To achieve a mirror finish, a higher grits reaching up to 1200–1500 grit can be used. Finally, these metals should then be degreased, rinsed thoroughly and dried prior to use [174].

3.5.2. Corrosion test medium

The preferred test medium for laboratory testing of marine corrosion degradation is natural seawater [176], but if not available, a synthetic seawater solution of 3.5 wt% NaCl and substitute ocean water per ASTM D1141 [177] can be prepared from analytical grade reagents. A typical composition of 10 L solution has been prepared by combining

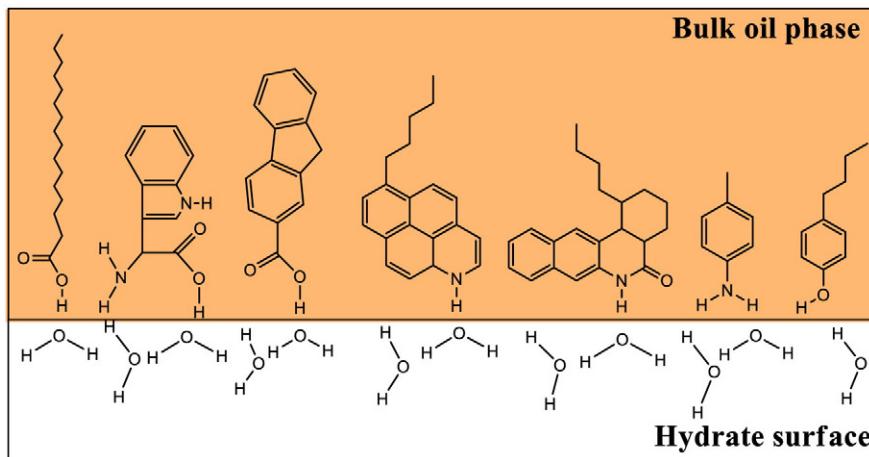


Fig. 8. Illustration of how interactions take place in the crude oil-hydrate interface, where polar, natural inhibiting components in the oil adsorb to the hydrate surface, making it oil-wet [168].

245.34 g NaCl, 40.94 g Na₂SO₄, 77.8 g MgCl₂·6H₂O, 8.112 g anhydrous CaCl₂, 0.296 g SrCl₂·6H₂O, 4.862 g KCl, 1.407 g NaHCO₃, 0.704 g KBr, 0.19 g H₃BO₃ and 0.021 g NaF [177]. To simulate sweet and sour corrosion, these solutions need to be deaerated with nitrogen and saturated with CO₂ and/or H₂S.

3.5.3. Corrosion inhibition efficiency

The corrosion rate can be measured gravimetrically, that is by comparing the weight loss of a metal specimen subjected to corrosion in the presence or absence of inhibitor, by gasometric measurement of the rate of hydrogen gas evolution, by electrochemical methods based either on extrapolation of anodic and cathodic polarization curves (Tafel curves) to their intersection point, linear polarization measurements or electrochemical impedance spectroscopy, and thermometric measurement.

3.5.3.1. Gravimetric method. Gravimetric technique is based on the measurement of weight loss of mild steel coupons in the absence and presence of inhibitor. Metal samples are cleaned and weighed prior to immersion. After a defined time period, corroded metal samples are rinsed thoroughly and weighed again. The corrosion rate (millimeter per year, mm/yr), surface coverage (θ), and corrosion inhibition efficiency (η) can then be calculated using Eqs. (7)–(9) respectively, where w_i is the weight in mg of the metal sample before immersion, w_f is the weight in mg after immersion, A is the total exposed area (cm²), ρ is the density of the specimen (g/cm³), and t is the immersion time (hours) and 87.6 is the conversion factor [178].

$$\text{Corrosion rate (CR)} = 87.6 \left(\frac{w_i - w_f}{\rho A t} \right) \quad (7)$$

$$\theta = \frac{CR_u - CR_i}{CR_u} \quad (8)$$

$$\eta(\%) = \frac{CR_u - CR_i}{CR_u} \times 100 \quad (9)$$

where, CR_u and CR_i are the corrosion rates of uninhibited and inhibited electrolyte solutions respectively.

3.5.3.2. Gasometric method. Gasometric technique is based on the principle that corrosion reactions in aqueous acidic media are characterized by the evolution of gas resulting from the cathodic reaction of the corrosion process, which is proportional to the rate of corrosion [179]. The rate of evolution of the hydrogen gas (R_H) is determined from the slope of the graph of volume of hydrogen gas evolved (V) versus time (t) and the degree of surface coverage (θ) and hence inhibition efficiency ($\eta\%$) can be determined using Eqs. (10) and (11) respectively.

$$\theta = \frac{R_{H_u} - R_{H_i}}{R_{H_u}} \quad (10)$$

$$\eta(\%) = \frac{R_{H_u} - R_{H_i}}{R_{H_u}} \times 100 \quad (11)$$

where R_{H_u} and R_{H_i} are the rates of hydrogen evolution of uninhibited and inhibited electrolyte solutions respectively.

3.5.3.3. Electrochemical methods. Electrochemical-based measurements reveal information regarding the rate of corrosion and mechanism of corrosion protection since corrosion itself is an electrochemical process. The two commonly used electrochemical methods for characterizing the corrosion process and the performance of protective pretreatments include potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS).

3.5.3.3.1. Potentiodynamic polarization. Potentiodynamic polarization (PDP) is an electrochemical measurement, with typical scans shown in Fig. 9 [180], also known as the Tafel curve which is a current-potential

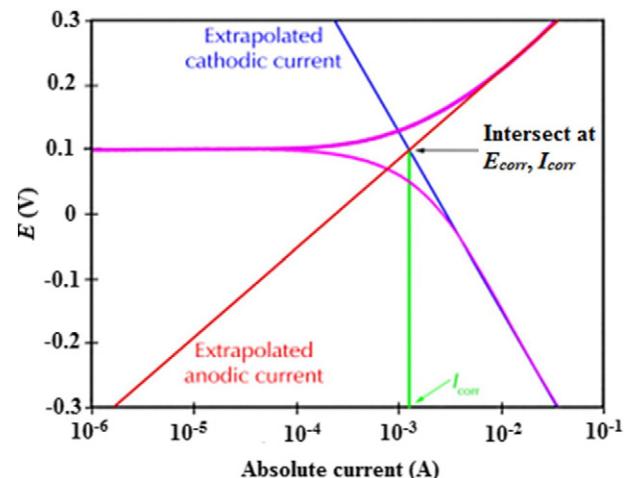


Fig. 9. Typical sample of Tafel plot from a potentiodynamic polarization scan [180].

plot representing the anodic and cathodic reactions in the electrochemical cell. Anodic and cathodic currents as a function of voltage can be represented as extrapolated straight lines shown in Fig. 9. Extrapolating the linear portions of the logarithmic Tafel plot and intersecting these lines result to a point that defines an approximation of the corrosion current I_{corr} and the corresponding corrosion potential E_{corr} .

Thus, I_{corr} is used to calculate the corrosion rate (CR), the degree of surface coverage (θ) and the percentage inhibition efficiency ($\eta\%$) using Eqs. (12)–(14) respectively, where κ is the conversion factor for the right corrosion units, E_q is the sample equivalent weight in grams/equivalent, ρ is density in $\mu\text{A}/\text{cm}^2$, and A is the sample area in cm².

$$\text{Corrosion rate (CR)} = \frac{I_{corr} \times \kappa \times E_q}{\rho \times A} \quad (12)$$

$$\theta = \frac{I_{corr}^u - I_{corr}^i}{I_{corr}^u} \quad (13)$$

$$\eta(\%) = \frac{I_{corr}^u - I_{corr}^i}{I_{corr}^u} \times 100\% \quad (14)$$

where, I_{corr}^u and I_{corr}^i are the corrosion current densities of uninhibited and inhibited electrolyte solutions respectively.

A basic lab setup requires at least a three-electrode electrochemical cell with the metal substrate serving as the working electrode, graphite or platinum as the counter electrode and saturated calomel electrode or Ag/AgCl aqueous electrode as the reference electrode. The counter electrode measures the current while the reference electrode either measures or controls voltage in the system [181]. The open circuit potential (E_{ocp}), which corresponds to the equilibrium potential of the metal is measured at initial stage, which changes as the electrochemical reactions occur until it stabilizes and reaches plateaus. After the E_{ocp} has reached a stable value, a potential is applied from a value under the E_{ocp} to higher potential. Usually, running from −0.2 V to +0.2 V based on the enough E_{ocp} to measure a well-defined Tafel plot should be used. Then, I_{corr} and E_{corr} can be determined from the plots. The corrosion inhibition efficiency can also be determined by measuring the I_{corr} with and without inhibitors. The protection mechanism and classification of inhibitor can then be determined using the E_{corr} shifts from the Tafel plots. If the E_{corr} shifts with and without inhibitor are greater than 85 mV in the anodic or cathodic direction, then the inhibitor can be classified as an anodic or cathodic inhibitor respectively [182,183]. If E_{corr} shifts with and without inhibitors are below 85 mV, then the inhibitor is classified as a mixed-type inhibitor.

3.5.3.3.2. Electrochemical impedance spectroscopy. Electrochemical impedance spectroscopy (EIS) is another electrochemical technique

that provides significant information about corrosion and the protection mechanism offered by the inhibitor. It is also used in monitoring the inhibitor film persistency [184]. In a three-electrode electrochemical cell, small potential perturbations ranging from 5 to 50 mV of AC voltage can be applied in the system over a range of frequencies typically starting from 100 kHz to 10 mHz [185,186]. Each frequency corresponds to a real Z' and imaginary Z'' impedance values whose relationship can be mathematically represented as the Nyquist plot. Depending on the shape of the Nyquist plot, the system is composed of the metal substrate, adsorbed inhibitors, and the electrolyte solution, which can be modeled in an equivalent circuit, where the solution resistance (R_s), polarization resistance (R_{ct}) and double layer capacitance (C_{dl}) can be determined using curve fitting software from the data obtained from the EIS test. These circuit components can provide an idea on the corrosion protection of the inhibitor and its mechanism. A large R_{ct} value typically corresponds to high corrosion protection efficiency while the C_{dl} decreases with better corrosion inhibition. The electrical double layer composed of the metal substrate and the adsorbed ions is considered as a capacitor whose capacitance values decrease whenever the inhibitors adsorb on the metal surface and displace water molecules [187]. The inhibition efficiency is calculated by:

$$I.E(\%) = \frac{R_{ct_i} - R_{ct_u}}{R_{ct_i}} \times 100 \quad (15)$$

where R_{ct_u} and R_{ct_i} are the polarization resistance values corresponding to the uninhibited and inhibited electrolyte solutions respectively.

3.5.3.4. Thermometric method. The thermometric method involves the use of digital thermometer having probe to take temperature reading in the reaction system. The temperature probe is inserted into test tube filled with electrolyte solution and mild steel coupons are carefully dropped in the electrolyte solution while the thermometer probe is pierced through the cork that covers the test tube as shown in Fig. 10.

The temperature variation on thermometer is then monitored at specific time interval until maximum temperature is reached and recorded. The experiment is then repeated in the presence of different concentrations of studied inhibitors. The reaction number (RN) in $^{\circ}\text{C}/\text{min}$ corresponding to the corrosion rate is as given in Eq. (16):

$$RN(^{\circ}\text{C}/\text{min}) = \frac{T_m - T_o}{t} \quad (16)$$

where T_m and T_o are the maximum and initial temperatures of the system respectively, t is the time required to reach the maximum temperature.

The reaction number (RN) can then be used to evaluate the degree of surface coverage (θ) and inhibition efficiency ($\eta\%$) as in Eqs. (17)–(18) respectively;

$$\theta = \frac{RN_u - RN_i}{RN_u} \quad (17)$$



Fig. 10. Thermometric setup.

$$\eta(\%) = \frac{RN_u - RN_i}{RN_u} \times 100\% \quad (18)$$

where RN_u and RN_i are the reaction numbers of uninhibited and inhibited electrolyte solutions respectively.

4. Conclusion

Corrosion inhibitors are the most effective means of controlling the common form of internal corrosion present in oil and gas facilities. Most organic inhibitors exhibit their inhibition performance by physically (physisorption) or chemically (chemisorptions) adsorbed on the metal surface, thus preventing the anodic or cathodic reaction or combination of the two, where they act as mixed-type inhibitor in corrosive media. The inhibitors commonly employed in oil and gas industry are multi-component synthetic organic compounds and phytochemicals of green inhibitors with S, N and O functionalities in their structure. Although oil and gas industry use synthetic organic inhibitor, but are also toxic and persistent, leading to stricter environmental regulation on their usage and thus necessitated the need for alternative inhibitors such as green inhibitors or natural inhibiting components in crude oil fractions, which are inexpensive to produce, environmentally friendly and could be much more effective inhibitor than synthetic organic compounds due to its synergistic mix of bioactive organic compounds ingredients. Furthermore, offshore explorations at ocean depth further offshore and in ultra-deeper waters are favorable conditions for gas hydrate formation and stability, leading to flow assurance issues, necessitate the need for scientific innovations and technical improvement. This paper throws more light on various mitigation strategies for addressing this future challenges in offshore oil and gas developments.

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