The Effect of Organic Compounds on the Electrochemical Behaviour of Steel in Acidic Media. A review.

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This work attempts to detail selected relevant studies on the behaviour of steel in acidic media. Factors affect the inhibition efficiency of the organic compounds in acidic media were discussed; the effect of he structure, the effect of zero- charge potential and the effect of synergistic effect. Different additives of organic compounds with different active centers were used to prevent corrosion in acidic solutions. The behaviour of steel was studied in both mineral acids (sulphuric, hydrochloric and phosphoric) and organic acids.

1. INTRODUCTION

Steel is the most important engineering and construction material in the world. It is used in every aspect of our lives, from automotive manufacture to construction products, from steel toecaps for protective footwear to refrigerators and washing machines and from cargo ships to the finest scalpel for hospital surgery. There are several thousands steel grades published, registered, or standardized worldwide, all of which have different chemical compositions, and special numbering systems have been developed in several countries to classify the huge number of alloys. In addition, all the different possible heat treatments, microstructures, cold-forming conditions, shapes, and surface finishes mean that there are an enormous number of options available to the steel user. Fortunately, steels can be classified reasonably well into a few major groups according to their chemical compositions, applications, shapes, and surface conditions.

Corrosion problems have received a considerable amount of attention because of their attack on materials. The use of inhibitors is one of the most practical methods for protection against corrosion. Several works have studied the influence of organic compounds containing nitrogen on the corrosion of steel in acidic media [1–9], most organic inhibitors act by adsorption on the metal surface [4].

Thermodynamic model is an important tool to study the mechanism of inhibitor on the corrosion of metal, a thermodynamic model for the adsorption process has been suggested [10,11].

It has been known that efficient inhibitors should possess plentiful p-electrons and unshared electron pairs on either nitrogen atoms or sulfur atoms of the inhibitors to the d-orbitals of iron, and by means of transference of electrons chemical adsorption may occur on the steel surface. Thus, the steel corrosion may be suppressed by the protective film on the steel surface.
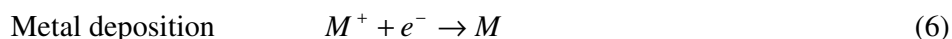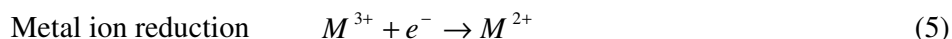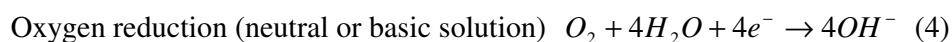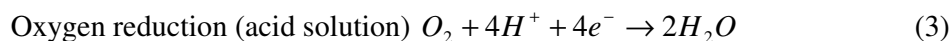
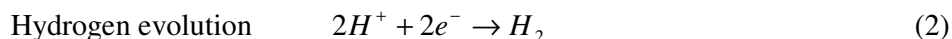## 2. ELECTROCHEMICAL NATURE OF STEEL CORROSION

In iron or steel corrosion, electrochemical reactions may take place as follows:
At the anodic areas

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

When iron corrodes, the rate is usually controlled by the cathodic reaction. There are several different cathodic reactions that are frequently encountered in metallic corrosion. The most common are:

Hydrogen evolution $\quad 2H^+ + 2e^- \rightarrow H_2$ (2)
Oxygen reduction (acid solution) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (3)
Oxygen reduction (neutral or basic solution) $O_2 + 4H_2O + 4e^- \rightarrow 4OH^-$ (4)
Metal ion reduction $\quad M^{3+} + e^- \rightarrow M^{2+}$ (5)
Metal deposition $\quad M^+ + e^- \rightarrow M$ (6)

Hydrogen evolution is a common cathodic reaction since acidic media are frequently encountered. Oxygen reduction is very common, since any aqueous solution in contact with air is capable of reducing this reaction. Metal ion reduction and metal deposition are less common. All the above reactions are consuming electrons.

Since the anodic and cathodic reactions occurring during corrosion are mutually dependent, it is possible to reduce corrosion by reducing the rates of either reaction. So, if the surface of the metal is coated with paint or other conducting film, the rates of both anodic and cathodic reactions will be greatly reduced and corrosion will be retarded. The corrosion behaviour of metals, and thus the corrosion-inhibiting processes as well, depend greatly on the anion composition of the electrolyte.

3. CORROSION PREVENTION BY INHIBITORS

A corrosion inhibitor is a substances that when added in small amounts to a corrosive medium, reduces its corrosivity. Corrosion inhibitors function by interfering with either the anodic or cathodic reactions or both. Many of these inhibitors are organic compounds. It is generally assumed that corrosion inhibition performed by adsorption of the additives (ion or neutral polar molecules) to the

metal-solution interface. It is known that the potential difference between a metal electrode and the solution is due to a non-uniform distribution of electric charges at the interface.

The interaction of ions or neutral molecules at the electrical double layer, changes its properties and structures. The water molecules preadsorbed at the metal surface in contact with the aqueous solution are involved in the successive adsorption processes. According to Bockris [12], the adsorption of an organic substance at the metal-solution interface may be written according to the following displacement reaction.

$$Org_{(sol)} + nH_2O \rightarrow Org_{(ads)} + n\ H_2O_{(sol)} \qquad (7)$$
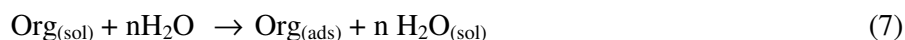
Where n is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. According to Bockris, n is assumed to be independent of coverage or charge of the electrode. Clearly, the value of n will depend on the cross-section area of the organic molecules with respect to that of the water molecule. Adsorption of organic molecule occurs because the interaction energy between the metal surface and the inhibitor is higher than the interaction energy between the metal surface and the water molecules.

Lorenz and Mansfeld [13] classified the modes of inhibition effect of interface inhibitors into three categories: that caused by (i) the geometric blocking effect of adsorbed inhibitive species on the metal surface (ii) the effect of blocking the active sites on the metal surface by adsorbed inhibitive species (iii) the electrocatalytic effect of the inhibitor or its reaction products. It has been discussed [14] in the case of the first mode the inhibition effect comes from the reduction of the reaction area on the surface of the corroding metal, whereas for the other two modes the inhibition effects are due to the changes in the average activation energy barriers of the anodic and cathodic reactions of the corrosion process. Thus, the electrochemical behaviour and the interpretation of the measured electrochemical data will not the same for all the modes. There are many factors affect the inhibition efficiency of the organic compounds in acidic media

3.1. The effect of the structure of organic compounds on their inhibiting properties

Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur, or in some cases selenium and phosphorus. According to Hackerman [15], the inhibiting properties of many compounds are determined by the electron density at the reaction center. With an increase in the electron density at the reaction center, the chemisorption bonds between the inhibitor and the metal are strengthened. Hackerman established the protective properties of pyridine and its derivatives. He found that, the ability of these compounds to reduce corrosion, are actually enhanced at higher electron densities around the nitrogen atom, according to the sequence: pyridine < 3-picoline < 2-picoline < 4-picoline. It is assumed that for organic compounds during the first ionization one of the electrons of the unshared pair is detached, then the ionization potential can serves as a measure of the electron density at the nitrogen atom.

Hackerman et al [16, 17] have been studied the adsorption of organic substances with a long hydrocarbon chain from organic solvents. Theses studies showed that the better the substance is adsorbed, the more effectively it protects the surface.

3.2. The zero- charge potential

The primary event on the inhibiting action of a compound is adsorption. Thus it is very important to predict which substances will be adsorbed on a metal and what potential region the adsorption will occur. If the adsorption is electrostatic in nature, then it will depends on the charge of the metal surface, that is the adsorbate, and the charge of the adsorbent, that is the inhibitor. Thus it is very important to know the electrical properties of both of the components participating in the process. Then it is possible to predict the type of the compounds which will be preferentially adsorbed on the metal surface at the corrosion potential.

The zero charge potential ($\varphi_{z.ch}$) is defined as the metal potential measured against the reference electrode under conditions of zero charge on the metal. At the zero charge potential the ionic double layer is absent at the electrode, At the zero charge potential an electrode is best able to adsorb substance dissolved in the electrolyte. The ability of an electrode to adsorb organic molecules is reduced in the presence of potential difference at the ionic double layer. This is because the field pulls in water molecules having high electric constant, dislodging organic molecules from the surface. Thus the adsorption capacity of an electrode is a maximum close to the zero charge potential.

Antropove [18] proposes a special scale of potential, the initial value of which is the zero charge potential of the surface $\varphi_{z.ch}$. Then the potential φ on this scale will be the difference between the steady stat potential φ_{st} of the electrode and the zero charge potential

$$\varphi_{z.ch:} \qquad \varphi = \varphi_{st} - \varphi_{z.ch} \qquad\qquad (8)$$

For $\varphi > 0$ the metal will be positively charged relative to the electrolyte. In this case a layer consisting primarily of anions will be adjacent to the metal surface on the side of the solution. For $\varphi < 0$, the metal will be negatively charged relative to the solution; in this case the double layer on the side of the solution is mad up of cations. Knowledge of the zero charge potentials of metals and the steady state potentials in a given medium can facilitate considerably the quest for suitable corrosion inhibitor. If the zero charge potential is higher than the steady stat potential of the metal in a given electrolyte $\varphi_{z.ch} > \varphi_{st}$, the metal surface is negatively charged, then the adsorption of cations or positively charged colloid particles will be most likely. For $\varphi_{z.ch} < \varphi_{st}$, the metal surface is positively charged, the adsorption of anions and negatively charged colloid particles is most likely.

3.3. The synergistic effect

Organic cations do not always alter the kinetics of the electrode processes. If salts of organic bases are added to 1 N HCl, there will be a significant change in the rate of hydrogen reduction, as

well as in the ionization of iron. In 1 N H_2SO_4, on the other hand, these same organic cations have only a slight effect. This is because organic cations are not strongly adsorbed on the iron surface; the surface of the iron can be assumed to be positively charged in sulphuric acid, so that ions of like charges are weakly adsorbed. However, if halide ions are introduced into the solution, the situation is changed. The mechanism of action of anion-active substances is connected with the fact that adsorbed anion-active substances create connecting bridges between metal atoms and organic cations.

It was assumed that many organic inhibitors in acidic electrolytes become protonated, changing into cations according to the scheme [19-22]:

$$R_2As + H^+ \rightarrow [R_2AsH]^+ \tag{9}$$
$$R_3P + H^+ \rightarrow [R_3PH]^+ \tag{10}$$
$$R_3N + H^+ \rightarrow [R_3NH]^+ \tag{11}$$
$$R_2S = O + H^+ \rightarrow [R_2SOH]^+ \tag{12}$$
$$(RNH)_2C = S + H^+ \rightarrow [(RNH)_2C = SH]^+ \tag{13}$$

The adsorption of these cations is facilitated in the presence of halide ions, which form intermediate bridges the negative ends of the halogen-metal dipoles being oriented toward the solution.

Halide ions are found [23] to enhance the inhibitive effect of several nitrogen containing compounds of mild steel in acidic solutions. The synergistic influence caused by iodide ions on the inhibition of corrosion of mild steel in H_2SO_4 in the presence of n-hexylamine (n-HA) has been studied [24] using potentiodynamic polarization, linear polarization and a.c. impedance technique. n-HA accelerates the corrosion of mild steel at lower concentrations but inhibits the corrosion at higher concentrations. The addition of iodide ions enhances the inhibition efficiency to a considerable extent. This is due to the synergistic effect, n-HA is adsorbed by columbic interaction on the metal surface, where iodide ions are already adsorbed and thus reduces the corrosion rate.

4. STUDIES IN MINERAL ACIDS

Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. Because of the general aggressivity of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. The development of inhibitors of steels in acid solutions has been the subject of great interest especially from the point of view of their efficiency and applications..

4.1. In sulphuric acid

Sulphuric acid is one of the most aggressive acids of iron and its alloys. The protection of these materials is generally secured by inhibitors used for their rapid action. Organic compounds containing heteroatoms are usually employed [25-30]. They act by adsorption on the metal surface which takes place through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic

rings. The inhibition efficiency should follows the sequence O < N < S < P [31]. The interactions between an organic inhibitor and a metal surface are principally physical adsorption and/or chemisorption. Sulphur and/or nitrogen containing heterocyclic compounds are considered to be effective corrosion inhibitors. Beside amine compounds widely studied in corrosion protection [32-36], thiophene derivatives also offer special affinity to inhibit corrosion of metals in acid solutions [37, 38]. S and/or N atoms adsorb easily on metal surface displacing water molecules as suggested by Bockris and Swinkels [12].

The inhibition of the corrosion of the steel in 0.5 M H_2SO_4 by thiophene compounds was studied [39] by weight loss and electrochemical polarisation. The results obtained reveal that these compounds are very efficient inhibitors. corrosion behaviour of steel is studied in the range from 298 to 353 K without and with thiophene at 10^{-3} M..

The anionic surfactant [*p*-myristyloxy carbonyl methoxy-*p*-sodiumcarboxylate -azobenzene] was used [40] as corrosion inhibitor for mild steel in H_2SO_4. The surface tension at 298K was measured, the critical micelle concentration (CMC) and some surface active parameters were calculated. The inhibition efficiency of this surfactant has been studied by both chemical and electrochemical techniques at 25°C. A significant decrease in the corrosion rate was observed in presence of the investigated inhibitor. The galvanostatic polarization curves showed that, the inhibitor behaves as mixed type but the cathodic effect is more pronounced. The surface morphology of mild steel samples in absence and presence of the inhibitor was examined using scanning electron microscopy.

The inhibition effects of sodium dodecylbenzenesulphonate (SDBS) and hexamethylenetetramine(HA) on the corrosion of mild steel in sulphuric acid solution have been studied [41] using weight loss, electrochemical impedance and Tafel polarisation measurements. For HA, a monotonous increase in inhibition efficiency is observed as a function of concentration. For SDBS, however, an optimum in the inhibition efficiency is observed for a concentration close to 250 ppm, which is ascribed to the formation of hemi-micellar aggregates that provoke inhibitor desorption from the metal/solution interface at higher concentrations. Upon mixing HA and SDBS, concentration regions showing synergistic and antagonistic inhibition behaviour are identified, and it is concluded that electrostatic interactions between adsorbate ions are likely responsible for both phenomena. Langmuir and Frumkin isotherms were tested for relevance in describing the adsorption behaviour of both HA and SDBS.

The corrosion behaviour of 304 stainless steel (SS) in 0.5 M H_2SO_4 solution was studied [42] using potentiodynamic and galvanostatic polarization techniques. Three anodic peaks were observed in the potentiodynamic anodic polarization curves before oxygen evolution. The effects of acid concentrations and voltage scan rate were studied. The inhibitive effect of 4-substituted pyrazole-5-ones toward the corrosion of 304 SS in 0.5 M H_2SO_4 was studied. The inhibition action of these compounds was assumed to occur via adsorption on the steel surface through the active centers contained in their structure. The mechanism of inhibition was interpreted on the basis of the inductive and mesomeric effects of the substituents reveals that, iron ions can be detected and measured by atomic absorption analysis. Gravimetric method was used to study [43] the inhibitory properties of indigo dye during corrosion of mild steel in aerated sulphuric acid solutions at 30–50°C. The effect of

addition of halide salts KCl, KBr and KI was also investigated. The corrosion rates in all systems studied increased with rise in temperature. The inhibition efficiency of indigo dye increased with concentration and synergistically increased on addition of halide salts. Temperature studies revealed increased inhibition efficiency at higher temperatures, which is suggestive of chemisorption mechanism. The inhibitor adsorption characteristics were approximated by Frumkins isotherm and Flory–Huggins isotherm. Activation energy for Fe dissolution in sulphuric acid was observed to reduce from 54.6 kJ mol^{-1} in the uninhibited system to 34.9 kJ mol^{-1} in the inhibited system.

According to Ebenso [44], the inhibitors act at the interphase created by corrosion product between the metal and aqueous corroding solution. Thus the nature of inhibitor interaction and efficiency may be dependent on the chemical, mechanical and structural characteristics of this layer. The study of organic dyes as potential inhibitors in metal–corrodent systems is generating a lot of interest in this laboratory. Such dyes posses molecular structures which recommend them for investigation as possible corrosion inhibitors when compared with reports on other organic inhibitors [45]. In the actual practical application of corrosion inhibitors, single compounds are rarely used, rather, formulations of two or more inhibitors are usually employed [46]. Interestingly, the inhibition efficiency of organic compounds in sulphuric acid solutions has been reported to synergistically increase on addition of halide salts to the solution [47-49].
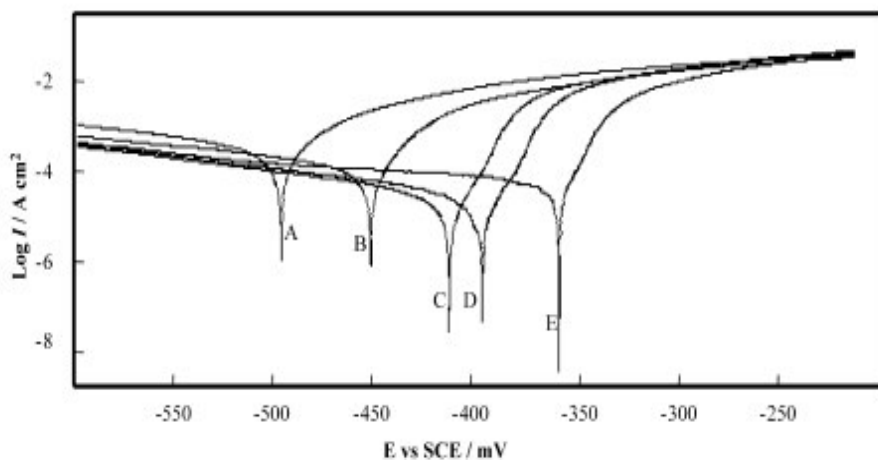
Figure 1. Polarization curves for mild steel in 0.5 M H$_2$SO$_4$ containing 5x10^{-5} M 4-MTHT in the absence and presence of different concentrations of KI. Key: (A) 4-MTHT only, (B) 2 X10^{-4}, (C) 1 X10^{-3}, (D) 2 X 10^{-3} and (E) 1 X10^{-2}M.

The effect of succinic acid (SA) on the corrosion processes of metals and alloys has not been extensively reported [50-52]. SA inhibits the corrosion process of mild steel (with 2.34% Cr) in pH < 4 solutions [53]. The OCP curves were not sufficiently conclusive to clearly characterize SA as a cathodic or anodic type inhibitor. Therefore, SA has been proposed to be a mixed-type inhibitor. The maximum inhibition efficiency was 75% for pH = 3 solutions with 10^{-4} M SA, whereas no inhibitor effect was perceived for pH > 4 solutions. These results have been attributed to the solution composition as function of pH. The corrosion inhibition process in pH < 4 solutions is promoted by the adsorption of non-dissociated SA molecules onto the mild steel electrode surface. For pH ≥ 4, on

the other hand, dissociated species (monohydrogensuccinate and succinate anions) are involved in complexing reactions. The beneficial effect of SA on corrosion of mild steel was also corroborated by optical micrographs taken for coupons immersed in solutions with or without SA.

The inhibition behaviour of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole (4-MTHT) and its synergistic effect with KI for mild steel in 0.5 M H_2SO_4 has been studied [54] using weight loss measurements and different electrochemical techniques such as potentiostatic polarization curves and electrochemical impedance spectroscopy (EIS). The addition of potassium iodide (KI) enhanced the inhibition efficiency considerably. A synergistic effect was observed between KI and 4-MTHT with an optimum mass ratio of [4-MTHT]/[KI] = 4×10^{-2}. The synergism parameters calculated from surface coverage were found to be more than unity. This result clearly showed the synergistic influence of iodide ions on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 by 4-MTHT. The adsorption of this inhibitor alone and in combination with iodide ions followed Langmuir's adsorption isotherm

NaCl can inhibit steel corrosion in sulphuric acid, the poor inhibition efficiency, however, restricts its utilization as a steel corrosion inhibitor in sulphuric acid in reality. As far as o-phenanthroline is concerned, it contains abundant p-electrons in heterocyclic structure and unshared electron pairs in nitrogen atoms, which can transfer the unshared electron pairs to the d-orbitals of ion on steel surface. Obviously, this nitrogen-containing heterocyclic organic compound meets the requirements as a good inhibitor for steel corrosion in acid solution. Now, o-phenanthroline is widely used to chelate with metallic ions in aqueous solutions, but only few investigation has been carried out to test the inhibition properties of o-phenanthroline as an acidic inhibitor [55], the study shows that single o-phenanthroline is not excellent enough as an inhibitor for steel corrosion in sulphuric acid, indicating that single o-phenanthroline can only use as a component of sulphuric acid inhibitor for steel corrosion. NaCl has been used to improve the inhibition efficiency of o-phenanthroline. Synergistic effects have been frequently used in practice [56-61]. Synergism between organic inhibitors and halide ions on metal corrosion in acidic solution has been researched by many authors [57-59]. The corrosion inhibition of cold rolled steel in 0.5 M sulphuric acid in the presence of o-phenanthroline and sodium chloride has been investigated [62] by using weight loss and electrochemical techniques. The experimental data suggest that the inhibition efficiency increases with increasing NaCl concentration in the presence of 0.0002 M o-phenanthroline, but decreases with increasing temperature. A synergistic effect is observed when o-phenanthroline and chloride ions are used together to prevent cold rolled steel corrosion in 0.5 M sulphuric acid. The polarization curves showed that the complex of o-phenanthroline and NaCl acts as a mixed type inhibitor. The experimental results suggested that the presence of chloride ions in the solution stabilized the adsorption of o-phenanthroline molecules on the metal surface and improved the inhibition efficiency of o-phenanthroline.

Fig. 2 shows that the presence of 0.0002 M o-phenanthroline can inhibit both anodic and cathodic corrosion reactions. Compared with the anodic reaction, the cathodic reaction is much greater inhibited by the single o-phenanthroline. Fig. 2 also shows that with the addition of certain amount (0.01–0.3 M) of NaCl, o-phenanthroline drastically inhibits anodic and cathodic reactions, especially, when the concentration of NaCl is bigger than 0.01 M, the inhibition action is more obvious, indicating the existence of synergistic inhibition for steel corrosion. It is found that the corrosion potentials of specimens in 0.5 M sulphuric acid containing 0.0002 M o-phenanthroline and 0.01–0.1 M NaCl are not

found to shift to an anodic or a cathodic direction, showing that in the presence of chloride ion, o-phenanthroline behaves as a mixed type inhibitor for steel corrosion in 0.5 M sulphuric acid.
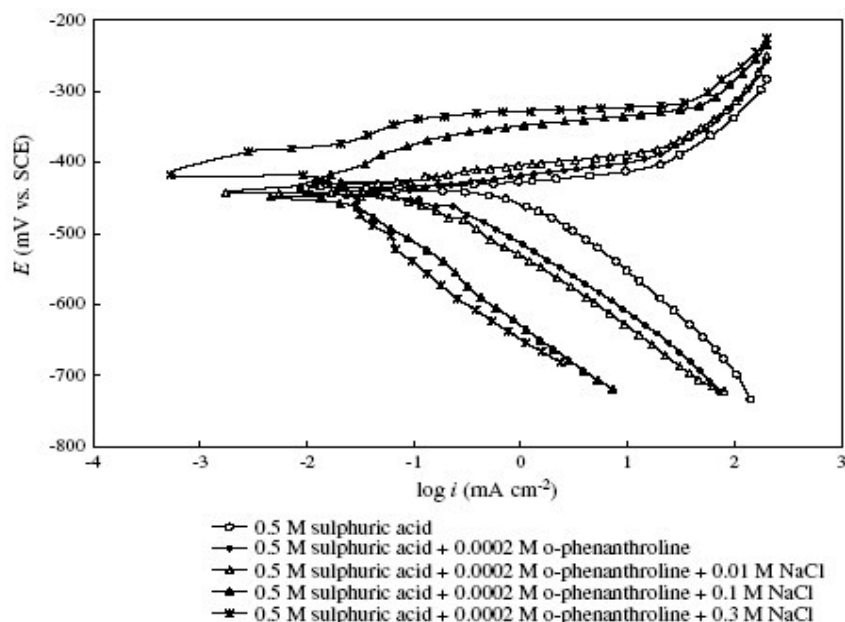
Figure 2. Polarization curves for electrodes in 0.5M sulphuric acid in the absence and presence of various concentrations of inhibitor at 25°C.

Hot acid solutions are generally used for removing mill scales (oxide scales) from the metal surface in various industries at elevated temperatures such as 60°C in hydrochloric acid and up to 95°C in sulfuric acid. To minimize the percentage metal loss during this process, various compounds such as acetylenic alcohols, indoles, thiourea derivatives and dithiazones, etc. are widely used [63-66]. Organic compounds containing nitrogen or sulphur atoms have been reported as superior corrosion inhibitors than those containing nitrogen or sulphur atoms alone [67, 68]. Among these thiourea [$(NH2)_2C=S$] and its derivatives are found in commercial formulations, but because of their toxic nature their use is not safe. A survey of literature [69] reveals that 2-mercaptobenzothiazole is an effective corrosion inhibitor up to 70°C.

A macrocyclic compound, namely 2,3,9,10-tetraphenyl-6,13-dithia-1,4, 5, 7, 8,11,12,14-octaaza-cyclotetradeca-1,3,6,8,10,13-hexaene (PTAT)was synthesized to study [70] the corrosion inhibitive effect on pickling of mild steel in 20%H_2SO_4 at 95°C. The synergistic effect of this compound was studied by weight-loss, potentiodynamic polarization, electrochemical impedance spectroscopy and hydrogen permeation studies. The results of this investigation have shown enhancement in inhibition efficiency (IE) for 500 ppm PTAT in the presence of 0.25% KI as a synergist. Potentiodynamic polarization studies showed that PTAT is a predominantly cathodic inhibitor. The synergistic parameter (S_i) was calculated by using the relation (Eq. (14)) given by Aramaki and Hackerman [32]:

$$S_i = \frac{1 - I_{1+2}}{1 - I_{1+2}^-}$$ (14)

Where $I_{1+2} = (I_1 + I_2) - (I_1 I_2)$ (15)

I_1 is the inhibition efficiency of the anion, I_2 the inhibition efficiency of the cation and I_{1+2}^- the measured inhibition efficiency of the cation in combination with anion.

The synergistic influence caused by iodide ions on the inhibition of corrosion of C-steel in 1 MH_2SO_4 in the presence of some aliphatic amines has been studied [20] using weight loss, potentiodynamic polarization, linear polarization and a.c. impedance techniques. Aliphatic amines used inhibit the corrosion of C-steel and the inhibition efficiency increases by increasing the concentration of the additives and also by addition of iodide ions.

Novel corrosion inhibitors, namely 1-{2-[(2-hydroxyethyl) thio] ethyl} pyrrolidin-2-one (P5) and {[2-(2-oxopyrrolidin-1-yl) ethyl] thio} acetic acid (P4), were synthesized and tested [71] as corrosion inhibitors for steel in 0.5 MH_2SO_4. The effects of P4 and P5 are also compared to their initial reactants 1-vinylpyrrolidin-2-one (P1), 2-mercaptoethanol (P2) and mercaptoacetic acid (P3). The study was carried out by weight loss measurements, potentiodynamic polarisation, linear polarisation resistance (Rp) and electrochemical impedance spectroscopy (EIS) methods. The inhibition efficiency increases with the concentration of P5 to attain 89% at 5 x 10^{-3} M. Polarisation measurements show also that the pyrrolidones act essentially as cathodic inhibitors.

Corrosion inhibition of mild steel in 0.5 M H_2SO_4 in the temperature range 30–60°C using sodium naphthalene disulphonic acid (NDSA) as an inhibitor was studied [72] . The inhibition efficiency increased with the increase in concentration   of NDSA till a critical value which is independent on temperature. The adsorption of inhibitor at 30°C followed Flory–Huggins adsorption isotherm.

Alkali metal halides are found to have a remarkable constructive contribution to the inhibition efficiency of benzoic acid on steel corrosion in 0.5 M H_2SO_4 medium [73]. Inhibition efficiency depends not only on the identity of the anion but also on that of the cation. Halide anions appear to be more effective as the radius gets larger. On the contrary alkali metal cations tend to become less effective with increasing radius of the bare ion. The contributions of the cation and anion to the overall inhibition do not appear to be absolutely summable. Unpredictable contributions might arise from the trace impurities in the batches of the salts and these contributions may be hiding the summable nature of the individual contributions by the alkali metal cations and halide anions. Non-summability may also be due to the fact that each cleaning on the electrode surface brings about a change in the nature of the electrode; because the steel used was not a single crystal.

A non-ionic surfactant, octylphenol polyethylene oxide (OPPEO), was evaluated [74] as an inhibitor for corrosion of low-carbon steel in 0.5 M H_2SO_4. Potentiodynamic and potentiostatic methods and scanning electron microscopy were used to study the inhibition effectiveness of the surfactant. The inhibition efficiency was found to increase with the inhibitor concentration and decrease with temperature. OPPEO showed higher constant protection efficiency near its critical micelle concentration. The activation energy of corrosion was found to be higher in presence than in

absence of the inhibitor. The experimental data were fitted with the Flory–Huggins isotherm at a molecular ratio of 5:1. The Gibbs energy of adsorption decreases with the temperature.

The inhibitive effect of congo red dye (CR) on mild steel corrosion in sulphuric acid solution was studied [75] at different temperatures using gravimetric techniques. The influence of halide additives namely: KCl, KBr and KI on the inhibition efficiency of CR were also investigated. Inhibition efficiency increased with CR concentration but decreased with rise in temperature. Corrosion activation energies of 82.98 and 96.92 kJ mol^{-1} were observed in the absence and presence of CR, respectively. The observed corrosion data suggest that inhibition of mild steel corrosion is due to physical adsorption of the CR molecules on the metal surface, which follow Flory–Huggins isotherm. Inhibition antagonism and synergism were respectively observed at 30 and 60°C on addition of halide salts to inhibited systems containing CR. The inhibition efficiency of CR in the presence of halides increased with rise in temperature and corrosion activation energy in these systems decreased to 40.63 kJ mol^{-1}. These observations indicate a chemical adsorption mechanism, thus suggesting that the halide ions reversed the mechanism of CR adsorption within the concentration range studied. The calculated values of heat of adsorption confirm physisorption and chemisorption mechanisms respectively for CR adsorption in the absence and presence of halides.

Three water-soluble surfactants based on maleic anhydride-oleic acid adduct (MO) were synthesized. They are triethanol ammonium salt of MO adduct (TEASMO), triethanolamine ester of MO adduct (TEAEMO) and polyoxyalkylated MO adduct (POAMO-23). FTIR and 1H NMR confirmed chemical structures. The inhibitive efficiency of corrosion on mild steel in 1 M H_2SO_4 for these surfactants was measured [76] by potentiodynamic technique. The surface and thermodynamic properties of the surfactants were also investigated. The obtained data show that TEASMO exhibit minimum inhibitive efficiency (65%), on the other hand, the obtained maximum inhibitive efficiency was (95%) with POAMO-23.

The inhibition of the corrosion of mild steel in 1.0 M sulphuric acid solution by some ethoxylated fatty acids H_3C-(CH2)-CH=CH-(CH$_2$)$_8$-COO- (CH$_2$CH$_2$O) nH; OL[EO]$_{20}$, OL[EO]$_{40}$ and OL[EO]$_{80}$ has been studied [77] in relation to the concentration of the inhibitors as well as the temperature using chemical (weight loss) and electrochemical (potentiodynamic polarization) techniques. The inhibition efficiency increases with increasing the concentration and the chain length of the inhibitor but decreases with temperature. The inhibition was assumed to occur via adsorption of the fatty acid molecules on the metal surface. The thermodynamic functions of dissolution and adsorption processes were calculated.

The inhibiting action of some polyethylene glycols on carbon steel corrosion, using 3 M sulphuric acid as corroding solution, was evaluated [78] by the weight loss method and polarization and impedance spectroscopy techniques. In order to study the effect of polyethylene glycol structure on the inhibition efficiency, different molar weights (200–10,000 g mol^{-1}) were selected. This work has demonstrated that the polyethylene glycols have an inhibition effect on the corrosion process and the inhibition efficiency is more than 90%. It was shown that polyethylene glycol is adsorbed physically on carbon steel in acid medium.

Benzotriazole derivatives, namely, N-[1-(benzotriazolo-1-yl)alkyl] aryl amine (BTMA), N-[1-(benzotriazolo-1-yl)aryl] aryl amine (BTBA), and 1-hydroxy methyl benzotriazole (HBTA), were

synthesized and their inhibition behaviour on mild steel in 0.5 M H_2SO_4 at room temperature was investigated [79] by various techniques. Potentiodynamic polarization and AC impedance studies were used to investigate the inhibitor mechanism. Benzotriazole derivatives were found to act as mixed type
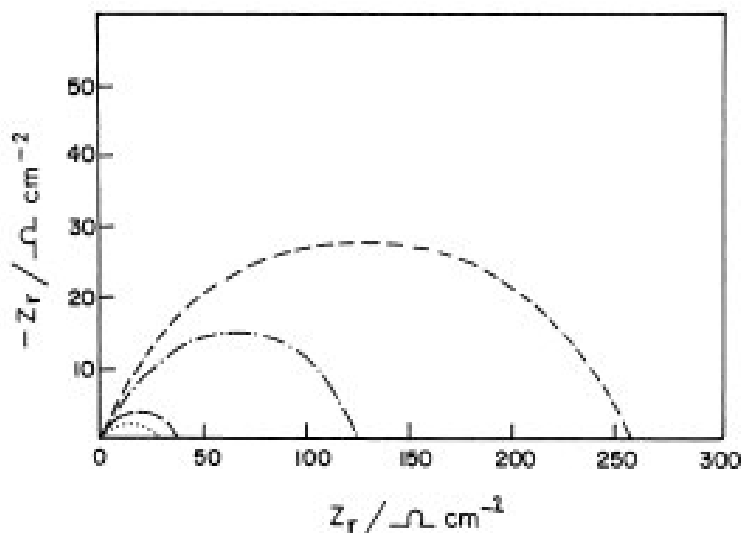
Figure 3. Nyquist diagrams for mild steel in 0.5 M H_2SO_4 containing maximum concentration of benzotriazole derivatives after 10 h. — Blank, ... BTA, — — BTMA, – - - - – BTBA and – – – – HBTA.
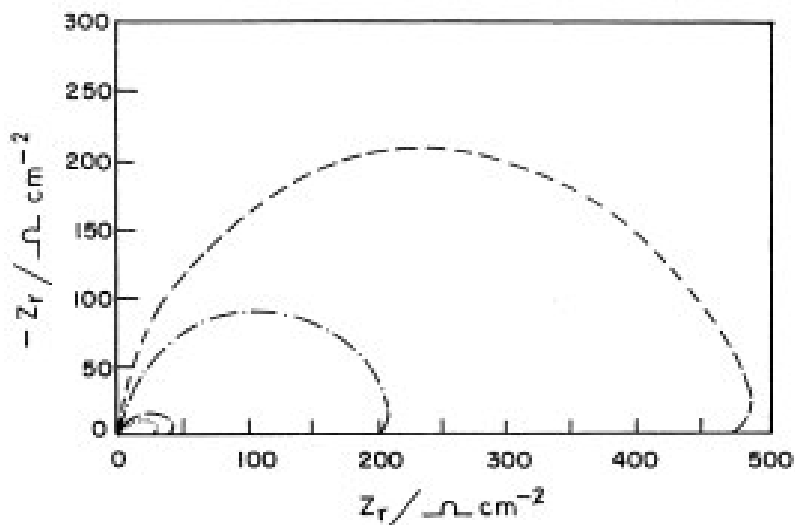
Figure 4. Nyquist diagrams for mild steel in 0.5 M H2SO4 containing maximum concentration of benzotriazole derivatives after 20 h. — Blank, ... BTA, — — BTMA, – - - - – BTBA and – – – – HBTA.

inhibitors. Among the compounds studied, HBTA exhibited the best performance giving more than 95% IE in H_2SO_4 solutions. As the benzotriazole concentration increased, R_{ct} values increased, but C_{dl} values tended to decrease. The decrease in C_{dl} values was caused by adsorption of benzotriazole.

Decrease in C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the benzotriazole derivatives function by adsorption at the metal-solution interface [80]. The change in R_{ct} and C_{dl} values was caused by the gradual replacement of water molecules by the anions of the acid and adsorption of the organic molecules on the metal surface, reducing the extent of dissolution [81]. Figure 3 and 4 show Nyquist diagrams for mild steel in 0.5 M H_2SO_4 in the absence and in presence of a maximum concentration of benzotriazole derivatives after 10 hr. and 20 hr. respectively.

4.2. In hydrochloric acid

Acidization of petroleum oil well is one of the important stimulation techniques for enhancing oil production. It is brought about by using a kind of solution of 15–28% hydrochloric acid. To reduce the aggressive attacks of acid on tubing and casing materials, inhibitors were incorporated to acid solution during acidizing process. A perusal of literature on high-temperature acid corrosion inhibitors indicated that effective corrosion inhibitors during acidization include acetylenic alcohols [82], alkenyl phenones [83], aromatic aldehydes [84], nitrogen containing heterocyclic and their quaternary salts and condensation products of carbonyls and amines [85-88].

Three long chain fatty acid oxadiazoles namely 2-undecane-5-mercapto-1-oxa-3,4-diazole (UMOD), 2-heptadecene-5-mercapto-1-oxa-3,4-diazole (HMOD) and 2-decene-5-mercapto-1-oxa-3,4-diazole (DMOD) were synthesized and were evaluated [89] as corrosion inhibitors for mild steel in 15% HCl by weight loss method. Inhibition tests were also carried out on N-80 steel under similar conditions in 15% HCl containing 5000 ppm of UMOD. The results obtained indicated that oxadiazole derivatives are good corrosion inhibitors. UMOD was found to be the best corrosion inhibitor. It exhibited 94% inhibition efficiency for N-80 steel and 72% inhibition efficiency for mild steel. Potentiodynamic polarization studies carried out at room temperature on mild steel in 15% HCl, containing 500 ppm of oxadiazole derivatives and on N-80 steel in 15% HCl containing 500 ppm of UMOD showed that all the investigated compounds are of mixed type inhibitors.

The effect of two pyrazole-type organic compounds, namely ethyl 5,50-dimethyl-10H-1,30-bipyrazole-3 carboxylate (P1) and 3,5,50-trimethyl-10H-1,30-bipyrazole (P2) on the corrosion behaviour of steel in 1 M hydrochloric acid (HCl) solution was investigated [90] at 308 K by weight loss measurements, potentiodynamic polarisation and impedance spectroscopy (EIS) methods. The inhibition efficiencies obtained from cathodic Tafel plots, gravimetric and EIS methods are in good agreement. Results obtained show that the compound P2 is the best inhibitor and its efficiency reaches 84% at 10^{-3} M. Potentiodynamic polarization studies show that pyrazolic derivatives are cathodic-type inhibitors and these compounds act on the cathodic reaction without changing the mechanism of the hydrogen evolution reaction. The inhibition efficiency of P2 is temperature-dependent in the range from 308 to 353 K and the associated activation energy has been determined. P2 adsorbs on the steel surface according to Langmuir adsorption model. The calculation of the total partial charge of inhibitor atoms is computed.

The inhibition of corrosion of steel in molar hydrochloric acid solution by two bipyrazolic compounds is studied [91] by weight loss and electrochemical polarisation measurements. The two methods give consistent results. The polarisation curves indicate that the bipyrazolic compounds act as mixed-type inhibitors. These compounds are efficient inhibitors.

The corrosion inhibition behaviour of some substituted dithiobiurets, namely, -1,5-diphenyl-2,4-dithiobiuret (DPDTB), 1-tolyl-5-phenyl-2,4-dithiobiuret (TPDTB), 1-anisidyl-5-phenyl-2,4-dithiobiuret (APDTB), 1-chorophe- nyl-5-diphenyl-2,4-dithiobiuret (CPDTB) were studied [92] in 1 to 5 M HCl on mild steel. The characteristics of these compounds are explained in terms of factors such as inhibitor concentration, acid concentration, temperature, immersion time and molecular structure. Potentiodynamic polarization and a.c. impedance techniques were used to investigate the inhibition mechanism. Among the compounds studied APDTB exhibited the best performance giving more than 98% inhibition efficiency (IE) in HCl solutions. DPDTB and CPDTB were found to reduce hydrogen permeation through mild steel in HCl solutions. The adsorption of APDTB was also confirmed by Auger electron spectroscopy (AES).

The influence of thiosemicarbazide(I), phenylthiosemicarbazide Girard's-T(II) and phenylthiosemicarbazide Girard's-P(III) on the corrosion rate of steel in 2 M HCl has been studied [93]. The protection efficiency obtained by weight-loss and potentiostatic polarisation techniques was found to be in good agreement with adsorption measurements at Pt electrode. The behaviour was correlated to the proposed skeletal representation of the adsorption mode of the inhibitors on the metal surface. Electrochemical results indicated that all the compounds investigated acted as cathodic-type inhibitors. The data obtained provide a good fit to both the Temkin adsorption isotherm and the kinetic thermodynamic model recently proposed.

The experiments were carried out according to the following procedures:

1. Activation of Pt electrode in deaerated 0.1M H_2SO_4 by repetitive triangular sweeps while changing the electrolyte repeatedly until the voltammogram acquired its usual shape, Fig.5.

2. The electrolyte was replaced by 0.1M HCl and the voltammogram was recorded, Fig.6.

3. The required inhibitor concentration was then added to the electrolyte and the steady-state voltammogram was recorded. The degree of surface coverage of the Pt electrode with adsorbed additives, was estimated from the hydrogen adsorption–desorption region according to the following equation [94]:

$$\theta = \frac{Q_{Pt}^H - Q_{Pt,ads}^H}{Q_{Pt}^H} = \frac{\Delta Q_{Pt}^H}{Q_{Pt}^H} \tag{16}$$

For elucidation the influence of changes in the molecular structure of the investigated compounds on the protection efficiency, the potentiostatic polarisation curves results obtained show that the order in which the current density decreases relative to a change in molecular structure of the inhibitors is similar to that obtained from weight loss measurement and the reduction of hydrogen adsorption charge at Pt electrodes.
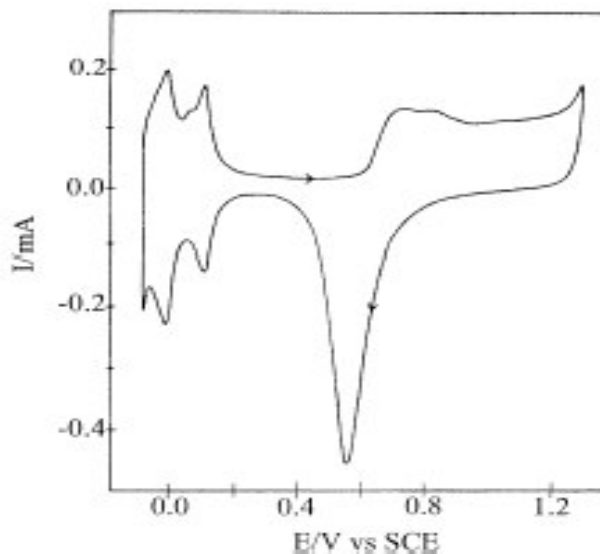
Figure 5. Cyclic voltammogram of Pt electrode in 0.1M H_2SO_4 at room temperature ($v = 100mVs^{-1}$).
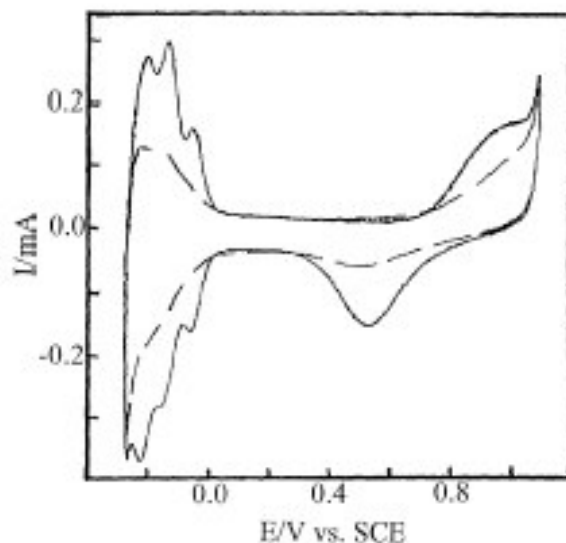
Figure 6. Cyclic voltammogram of Pt electrode in 0.1M HCl in the absence (—) and the presence (- -) of 2×10^{-6} M (compound III).

Several new isoxazolidines having varying degree of steric environment and hydrophobic chain length, prepared efficiently using single-step nitrone cycloaddition reactions, are tested [95] for corrosion inhibition of mild steel in 1 M and 5 M HCl at 50–70° C range by gravimetric and electrochemical methods. All compounds have shown very good corrosion inhibition efficiency in acidic solution. Steric crowding around the nitrogen centers and hydrophobic chain lengths as well as increase in temperature (in the presence of the inhibitor in the higher concentration range 100–400 ppm) are found to increase the inhibition efficiency of the isoxazolidines. Thermodynamic parameters (ΔG_{ads}, ΔH_{ads}, $\Delta S_{ads)}$ for the adsorption process and kinetic parameters for the metal dissolution (or hydrogen evolution) reaction in the presence of one of the isoxazolidines were determined. The

inhibition of corrosion in 1M HCl, influenced by both physi- and chemisorption, was found to be under mixed control, but predominantly under cathodic control.

The adsorption and corrosion inhibition of the gemini surfactants 1,2-ethane bis(dimethyl alkyl (C_nH_{2n+1}) ammonium bromide) (designated as n = 10, 12 and 16) on the steel surface in 1 M hydrochloride acid were studied [96] using the weight loss method. It was found that the adsorption of the gemini surfactants on the steel surface is the main reason to cause the steel corrosion inhibition in hydrochloride acid, and the inhibition efficiency increases with the increase of surfactant concentration and reaches the maximum value near the CMC. A possible adsorption model of gemini surfactant onto the metal surface was also discussed.

The effect of some mercapto-triazole derivatives synthesized in the laboratory containing different hetero atoms and substituents in the organic structures on the corrosion and hydrogen permeation of mild steel in 1.0 M HCl was investigated [97] by weight loss and various electrochemical techniques. Results obtained reveal that all the mercapto-triazole derivatives perform excellently as corrosion inhibitors for mild steel in 1.0 M HCl. Potentiodynamic polarization studies have shown that all these compounds suppress both the anodic and cathodic process and they behave as mixed-type inhibitors. Double layer capacitance and charge transfer resistance values were derived from Nyquist plots obtained from AC impedance studies. Changes in impedance parameters are indicative of the adsorption of these compounds on the metal surface. The inhibition efficiency mainly depends on the nature of the investigated compounds.

The corrosion inhibition characteristics of 2-amino thiophenol (ATP) and 2-cyanomethyl benzothiazole (CNMBT) on two types of steel in 1 M HCl medium were investigated [98] at different temperatures (25, 30, 35, 40 and 50°C). The pitting corrosion behaviour for the same system was studied using a potentiodynamic technique. The pitting corrosion resistance of steel samples increased with increase in concentration of the ATP and CNMBT. Some samples were examined by scanning electron microscopy. The effects of the inhibitors on the general corrosion of the two samples were investigated by using gravimetric and galvanostatic polarization techniques. The inhibition efficiencies increased with increase their concentration but decreased with increase in temperature. Free energies of activation, enthalpies and entropies for the inhibition processes were determined from rate constant data measured and different temperatures at different concentrations of ATP and CNMBT. The inhibition efficiency of CNMBT is higher than that of ATP.

The effect of changing functional groups of some amides and thiosemicarbazone derivatives on their inhibition efficiency has been reported [99] with a view to establishing a relationship between inhibitor efficiency and molecular structure, using the weight loss and hydrogen evolution techniques. The compounds used for this study are urea (U), thiourea (TU), acetamide (A), thioacetamide (TA), semicarbazide (SC), thiosemicarbazide (TSC), methoxybenzaldehyde thiosemicarbazone (MBTSC), 2-acetylpyridine-(4-phenyl) thiosemicarbazone (2AP4PTSC), 2-acetylpyridine-(4-methyl) thiosemicarbazone (2AP4MTSC), benzoin thiosemicarbazone (BZOTSC) and benzil thiosemicarbazone (BZITSC). All the compounds inhibited corrosion to varying degrees. It was found that the molecules which include a thiocarbonyl group, e.g. TU, TA and TSC, have higher inhibition efficiency than the corresponding compounds which do not, e.g. U, A and SC. The results (at 30°C and 40°C) indicate that the order of efficiency of the thiocompounds in solution and the

extent of their tendency to adsorb on mild steel surfaces are as follows: TSC > TU > TA, whereas for the thiosemicarbazone derivatives, the order is BZOTSC > BZITSC > MBTSC > 2AP4MTSC < 2AP4PTSC. Physical adsorption mechanism has been proposed for all the inhibitors except MBTSC, BZITSC and BZOTSC, which are chemically adsorbed.

The effect of sodium n,n-diethyl dithiocarbamate on the corrosion of mild steel in 0·5 M HCl solution was studied [100] using weight loss and potentiodynamic polarisation methods. Experimental data revealed that this compound acted as an inhibitor in the acid environment and, furthermore, that the compound was a mixed type inhibitor, predominating as a cathodic inhibitor. It was found that the inhibition efficiency increased with an increase in concentration at temperatures in the range 303–333 K. The experimental data for the inhibitor fitted the Flory–Huggins adsorption isotherm and the El-Awady thermodynamic kinetic model. The corrosion inhibition mechanism on mild steel in HCl solution was also investigated by infrared spectra and electron probe microanalysis methods. The process of inhibition is attributed to the formation of an adsorbed film on the metal surface, which protects the metal against corrosive agents.

The effect of some prepared compounds, namely pyridine derivatives on the corrosion of carbon steel in 2 M HCl solutions has been studied [101] by electrochemical polarization method (potentiodynamic, Tafel extrapolation) as well as weight loss method. Generally, inhibition efficiency of the investigated compounds was found to depend on the concentration and the nature of the inhibitor. Results obtained from both potentiodynamic and weight loss techniques reveal that these compounds are good inhibitors. The presence of substitution in pyridine ring plays an important role in the percentage inhibition of the compounds under investigation. The adsorption of these compounds on the carbon steel follows a Langmuir adsorption isotherm.

The inhibiting effects of quinoline, 8-hydroxyquinoline, benzo(f)quinoline, quinoline-2-thiol, triphenylbenzyl,and tetrabenzylphosphoniumchloride on the corrosion of mild steel (0·26 wt-%C) in deaerated 3 M HCl solution have been studied [102] using the determination of polarisation curves as well as linear polarisation measurements. Adsorption isotherms and thermodynamic parameters for the adsorption process of the inhibitors were also determined and are discussed. Except for benzo(f)quinoline, which acts as an accelerator of corrosion, the other quinolines act as corrosion inhibitors. T he inhibition was found to be predominantly anodic with quinoline and 8-hydroxyquinoline, while quinoline-2-thiol is a mixed inhibitor. The increase in inhibition efficiency with temperature, the resulting Langmuir adsorption isotherm and the high negative values of the standard free energy of adsorption ΔG°a denoted chemisorption. Triphenylbenzyland tetrabenzylphosphoniumcompounds were found to be inhibitors of the mixed type. High negative values of the standard free energy of adsorption and the resulting Temkin isotherm indicated chemisorption of the phosphonium compounds. The positive values of the standard enthalpy and entropy of adsorption indicated that adsorption of the inhibitors is associated with the desorption of H_2O molecules from the electrode surface. High values of the standard energy of activation of the inhibited corrosion process were interpreted in terms of deactivating coverage.

The inhibiting effect of linear and cyclic thiocarbamides on the corrosion of mild steel in 1 M HCl was studied [103]. The inhibiting effect of the linear and cyclic thiocarbamides was increased

with increasing of concentrations. The adsorption of the compounds obeys Temkin adsorption isotherm. The substances are adsorbed through the sulphure atom which is the adsorption centre.

A corrosion inhibitor namely, 4-salicylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole (SAHMT), has been synthesized and its influence on corrosion inhibition of oil-well tubular steel (N-80) and mild steel in 15% hydrochloric acid (HCl) solution under boiling condition has been studied [104] using weight loss method. Potentiodynamic polarization measurements clearly reveal that the investigated inhibitor is of mixed type and it inhibits the corrosion of both the steels by blocking the active site of the metal. The adsorption of the inhibitor on the metal surface from 15% HCl has been found to obey Temkin's adsorption isotherm. The performance of the SAHMT was compared with that of propargyl alcohol (PA), a standard corrosion inhibitor for acidization.

The inhibition effect of vanillin (4-hydroxy-3-methoxy-benzaldehyde) and protocatechualdehyde (3,4-dihydroxy-benzaldehyde) in hydrochloric acid medium on steel with known composition has been investigated [105]. It has been determined using, weight loss, polarization and impedance methods that the corrosion rates decrease and percentage inhibition efficiencies and surface coverage degrees increase with increasing additive concentration. On the other hand inhibition efficiencies are seen to increase with decreasing in temperature. Polarisation studies indicate the compounds studied to be mixed inhibitors.

The efficiency of 2,5-bis(n-methoxyphenyl)-1,3,4-oxadiazoles (n-MOX), as corrosion inhibitors for mild steel in 1 M HCl and 0.5 M H_2SO_4 have been determined [106] by weight loss measurements and electrochemical studies. The results showed that these inhibitors revealed a good corrosion inhibition even at very low concentrations. Comparison of results among those obtained by the studied oxadiazoles showed that 2-MOX was the best inhibitor. It is found to behave better in 1 M HCl than in 0.5 M H_2SO_4. Polarisation curves indicate that 2-MOX is a mixed inhibitor in 1 M HCl, but in 0.5 M H_2SO_4, the inhibition mode of 2-MOX depends on the electrode potential and acts essentially as a cathodic inhibitor. The inhibition efficiency slightly increases with temperature in the range from 25 to 60°C, the associated activation energy have been determined. The addition of 2-MOX leads to decrease this activation energy. The adsorption of 2-MOX on the mild steel surface in both acidic media follows a Langmuir isotherm model. Significant correlations are obtained between inhibition efficiency with the calculated chemical indexes, indicating that variation of inhibition with structure of the inhibitors may be explained in terms of electronic properties.

2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole (DAPT) was synthesized and its inhibiting action on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 at 30°C was investigated [107] by various corrosion monitoring techniques. A preliminary screening of the inhibition efficiency was carried out using weight loss measurements. At constant acid concentration, inhibitor efficiency increases with concentration of DAPT and is found to be more efficient in 0.5 M H_2SO_4 than in 1 M HCl. Potentiostatic polarization studies showed that DAPT is a mixed-type inhibitor. The effect of temperature on the corrosion behaviour of mild steel in 1 M HCl with addition of DAPT was studied in the temperature range from 25 to 60°C. Its was shown that adsorption is consistent with the Langmuir isotherm for 30°C.

Propargyl alcohol (2-propyn-1-ol or PA) which is used as an inhibitor for carbon steel in acidizing of oil wells, in chemical cleaning and acid pickling of heat-transfer equipment, removing of scales in metallurgy were conducted in either HCl or H_2SO_4 solutions [108-110].

4.3. In phosphoric acid

Phosphoric acid solutions are used in pickling of delicate and costly components and precision items where re-rusting after pickling has to be avoided [111]. Only a few papers have been devoted to the inhibition of mild steel corrosion in H_3PO_4 solutions, particularly at concentration levels as experienced during production of the acid by what is known as the dihydrate and hemi-hydrate wet-method processes. Schweinsberg et al. [112] found that both, polyvinylpyrrolidone and polyethylenimine are effective inhibitors for the corrosion of low carbon steel over a wide concentration range of aqueous H_3PO_4 solutions.

The corrosion behaviour of mild steel in H_3PO_4 was studied by various electrochemical techniques, namely linear polarization resistance (Rp), polarization curves (Tafel plots) and electrochemical impedance spectroscopy (EIS). The action of Propargyl alcohol PA as an inhibitor was also examined [113] over a wide range of acid concentrations and solution temperatures. Figure 7 shows the Potentiostatic polarization curves of mild steel corrosion in different concentrations of H_3PO_4 solutions at 50°C, whereas Fig.8. shows Arrhenius plots for mild steel corrosion in H_3PO_4 solutions. The results obtained from both polarization curves and EIS proved that PA greatly inhibits the hydrogen evolution reaction on mild steel in H_3PO_4 solutions at temperatures $\geq$ 40°C (Fig.9) and inhibition occurs by adsorption of PA molecules. The most favourable adsorption mode is one in which carbon atoms forming the triple bond interact with the iron atoms. Inhibition of the cathodic reaction suggests that adsorption of the inhibitor is most favourable at a surface partially covered by hydrogen. A similar mode of inhibition by PA was proposed by
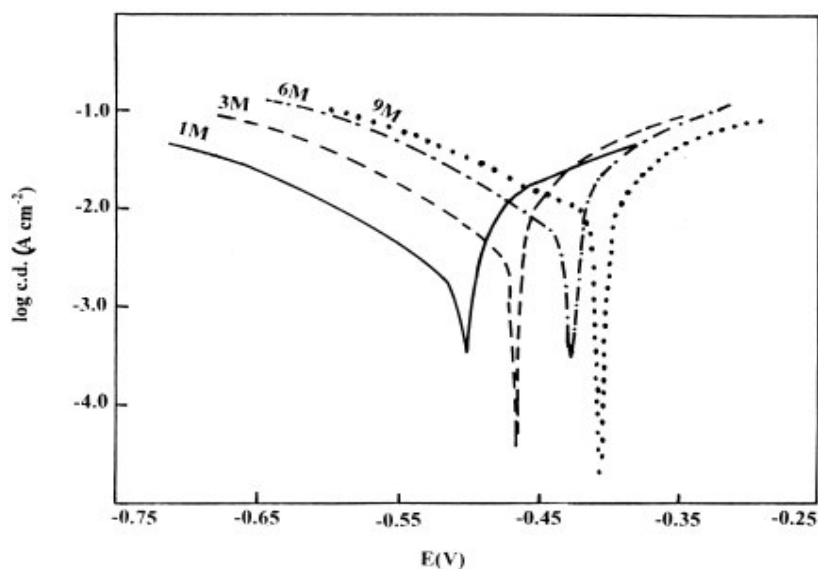
Figure 7. Potentiostatic polarization curves of mild steel corrosion in H_3PO_4 solutions at 50°C.
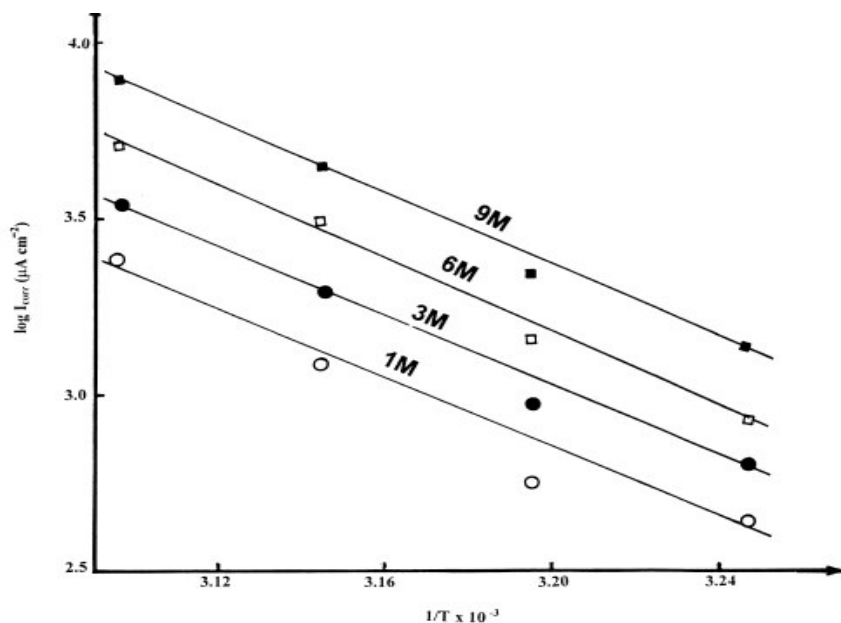
Figure 8. Arrhenius plots for mild steel corrosion in H_3PO_4 solutions.
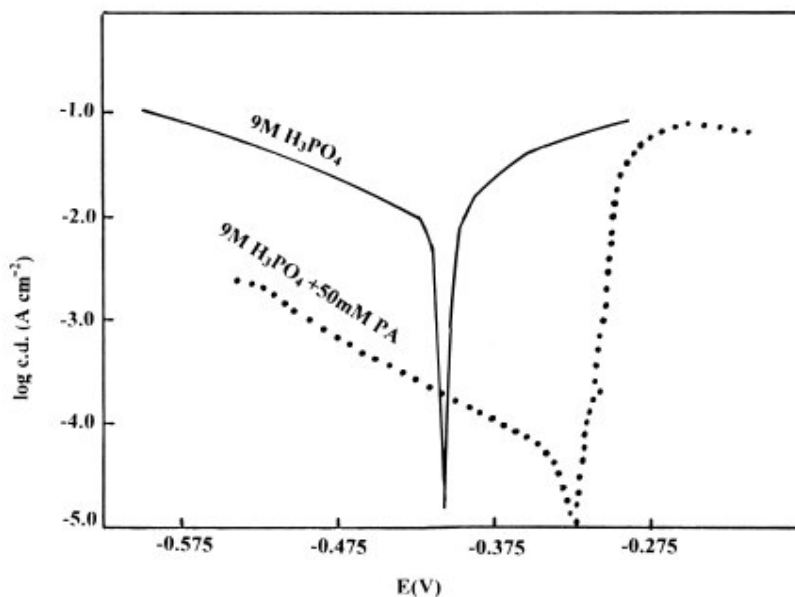
Figure 9. Potentiostatic polarization curves of mild steel corrosion in 9 M H_3PO_4 solution without, and with, 50 mM PA at 50°C.

Hackerman et al. [114,115] and Bockris and Yang [116]. The results of this work present no indications of the formation of a polymer film of PA on the steel surface in the presence of PA, no significant change in values of b_c and the impedance spectra recorded at either E_{corr} or 100 mV vs. E_{corr} have only one capacitive loop.

The effect of some quaternary N-heterocyclic compounds on the corrosion of mild steel in solutions of phosphoric acid (H_3PO_4) has been investigated [117] in relation to the concentration of the

inhibitor and acid as well as temperature by various monitoring corrosion techniques. Surface morphology was studied by scanning electron microscopy (SEM). Results obtained revealed that these compounds are good mixed-type inhibitors without changing the mechanism of the corrosion process. In general, at constant acid concentration, inhibitor efficiency increased with concentration of the inhibitor. On the other hand, at constant inhibitor concentration, inhibitor efficiency decreased with concentration of the acid up to a critical concentration above which it started to increase (Fig.10). Results from hydrogen evolution (HE) and mass loss (ML) measurements are in good agreement (table1)
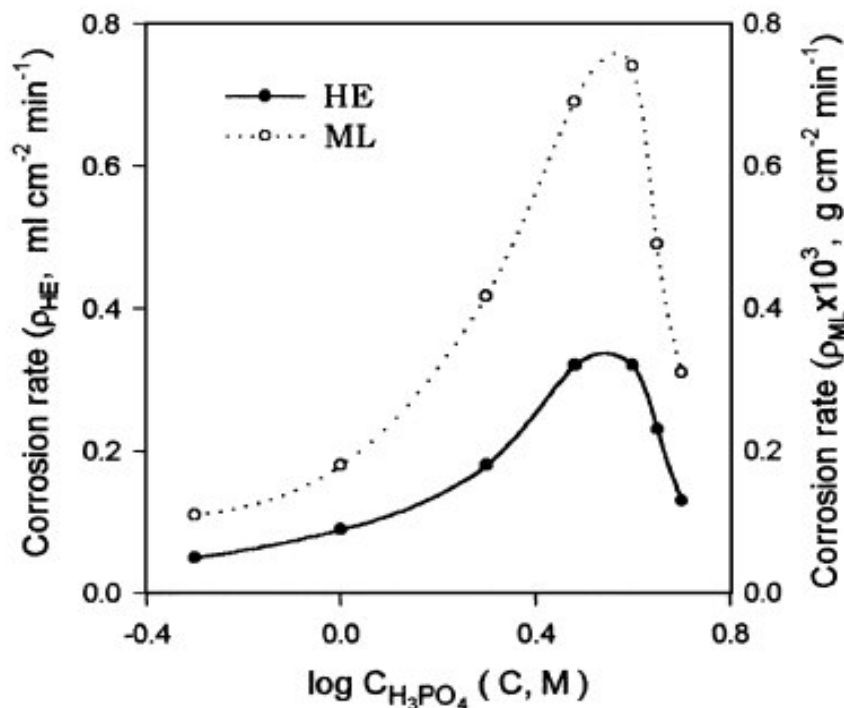

Figure 10. Variation of corrosion rate with the logarithmic concentration of H3PO4.

Table 1. Inhibition efficiencies for different concentrations of the studied compounds in 2.0M H_3PO_4 from HE and ML measurements

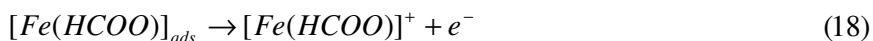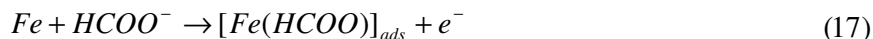| Conc. (M)	Inh.%					
	Compound I		Compound II		Compound III	
	HE	ML	HE	ML	HE	ML
1.0×10^{-5}	–	–	–	–	14.95	16.91
2.5×10^{-5}	–	–	–	–	35.32	36.42
5.0×10^{-5}	32.39	26.22	33.98	36.08	59.59	60.16
1.0×10^{-4}	39.79	36.58	42.83	42.55	78.52	79.94
1.5×10^{-4}	–	–	58.10	59.14	97.68	98.27
2.5×10^{-4}	57.39	56.10	74.91	75.66	99.26	98.99
5.0×10^{-4}	72.00	70.77	89.55	89.38	99.26	99.95
1.0×10^{-3}	87.32	87.27	96.56	95.91	–	–
2.5×10^{-3}	97.18	96.49	–	–	–	–

The corrosion rates of steel in concentrated phosphoric acid (1.0–11.0 M) were determined [118] by the weight loss method, at three temperatures 298, 308 and 323 K. Results obtained show that corrosion rate increases with both acid concentration and temperature. The activation energies, enthalpies and entropies of the dissolution process were determined.

3,5-Bis (n-pyridyl)-4-amino-1,2,4- triazoles (n-PAT), a new class of compounds containing nitrogen and aromatic rings, were investigated [119] on the inhibition of mild steel in H_3PO_4 solutions by weight loss and potentiodynamic polarization methods.

5. STUDIES IN ORGANIC ACIDS

Corrosion studies on metals in organic acid solutions are scarce in comparison with similar studies in mineral acids [120-122]. Mild steel is used in fabrication of reaction vessels, storage tanks etc. by industries, which either manufacture or use organic acids as reactant. Organic acid ranks among the most important chemicals in industry today. The reactive carboxyl group makes them a basic building block for many compounds such as drugs, pharmaceuticals, plastics and fibers. Despite the importance of organic acids in industry, few corrosion studies of these acids   [123-126] have been made. However, at high temperatures, the acids can dissociate, forming more aggressive ions that can cause faster corrosion than might otherwise be expected. A variety of organic compounds containing heteroatoms such as O, N, S and multiple bonds in their molecule are of particular interest as they give better inhibition efficiency than those containing N or S alone [127-131].

The corrosion of mild steel in nonaqueous and aqueous solution may be considered in the following steps [132]:

$$Fe + HCOO^- \rightarrow [Fe(HCOO)]_{ads} + e^- \qquad (17)$$

$$[Fe(HCOO)]_{ads} \rightarrow [Fe(HCOO)]^+ + e^- \qquad (18)$$

$$[Fe(HCOO)]^+ + H^+ \leftrightarrow Fe^{++} + HCOOH \qquad (19)$$

The evolution of hydrogen occurs as the cathodic reaction by the following mechanism:

$$M + HCOOH + e^- \rightarrow MH_{ads} + HCOO^- \qquad (20)$$

$$MH_{ads} + MH_{ads} \rightarrow H_2 + M \qquad (21)$$

The adsorption of formate ions on the surface of iron is a prerequisite for the anodic dissolution to occur; thus the rate of corrosion should depend on the concentration of formate ion in the solution. The conductance of formic acid solution gradually increases in the concentration range 5%–20%. As a result, the extent of adsorption of formate ion, as well as the rate of Step 7 increases and, consequently, the rate of corrosion will also increase. The triazoles inhibit the corrosion by controlling both the anodic and cathodic reactions. In acidic solutions these compounds exist as protonated species. These protonated species adsorb on the cathodic sites of the mild steel and decrease the evolution of

hydrogen. The adsorption on anodic sites occurs through the p-electrons of aromatic rings and the lone pair of electrons of nitrogen and sulfur atoms which decrease the anodic dissolution.

Sekine et al [133] investigated the corrosion behaviour of mild steel in various organic acids; glycolic, lactic, malic, tartaric and citric acids using electrochemical measurements. The corrosion rate of mild steel was decreased in the following order:

Malic > tartaric > lactic > citric > glycolic acid. The corrosion rate of mild steel in aqueous solutions of the acids under investigation was increased with increasing of the concentration, but in glycolic acid solution the corrosion rate was kept constant in such a corrosion rate. This was attributed to the adsorption of glycolic acid on the steel surface forming a layer of a low solubility from iron ions-glycolic acid salt, thus the corrosion of steel is inhibited by this formation.

5-Heptadec-8-enyl-4-phenyl-4H–[1,2,4] triazole-3-thiol (HPTT), 4-phenyl-5-undecyl-4H–[1,2,4] triazole-3-thiol (PUTT), and 5-dec-9-enyl-4-phenyl-4H–[1,2,4] triazole-3-thiol (DPTT) were synthesized and their influence on the inhibition of corrosion of mild steel in 20% formic acid was investigated [134] by weight loss and potentiodynamic polarization techniques. The inhibition efficiency of these compounds was found to vary with their nature and concentration, temperature and immersion time. The values of activation energy and free energy of adsorption of the triazoles were calculated to investigate the mechanism of corrosion inhibition. Good inhibition efficiency (>90%) was found even at lower concentration (i.e., 25 ppm) in acid solution. The adsorption on mild steel surfaces was found to obey Temkin's adsorption isotherm. Potentiodynamic polarization results revealed that the compounds studied are mixed type inhibitors. Electrochemical impedance spectroscopy was also used to investigate the mechanism of the corrosion inhibition.

Selected thiourea derivatives have been synthesized and evaluated [135] as corrosion inhibitors of mild steel in 20% formic acid by weight loss and potentiodynamic polarization methods All of these compounds have shown very good inhibition efficiency (IE) in the formic acid. IE of these compounds has been found to vary with the concentration of the compounds, solution temperature, immersion time and concentration of the acid solution. The adsorption of these compounds on the steel surface from the acid has been found to obey Temkin's adsorption isotherm. The potentiodynamic polarization studies revealed that all the compounds are mixed type inhibitors.

SAE 1018 carbon steel in buffered acetic acid (HAc) solutions containing chlorides, with and without H_2S, was studied [136]. Polarization curves obtained by different electrochemical techniques, indicate negligible modification of anodic slopes when adding H_2S; however, the cathodic branch is more sensitive showing an accelerated reduction reaction in the presence of H_2S. Interface characterization was performed by electrochemical impedance technique (EIS) in the absence and presence of H2S and near to the corrosion potential (E_{corr}). Analysis of results shows no film of corrosion products, since the impedance spectra characteristics indicate a great activity of steel in the solutions studied, with differences only at low frequencies. The adsorbed complexes formed in the solution containing HAc, acetate and chlorides control the corrosion process and prevent passive film formation, even in the presence of H_2S.

2-(N,N-dimethylamino) benzylidene imino-4-(4-methyl phenyl)-1,3-thiazole (DIMPT), 2-benzylidene imino-4-(4- methyl phenyl)-1,3-thiazole (BIMPT), 2-salicylidene imino-4-(4-methyl phenyl)-1,3-thiazole (SIMPT) and 2-cinnamylidene imino-4-(4-methyl phenyl) -1,3-thiazole (CIMPT)

were synthesized in the laboratory and their influence on the inhibition of corrosion of mild steel in 20% formic acid and 20% acetic acid was investigated [137] by weight loss and potentiodynamic polarization techniques. The inhibition efficiency of these compounds was found to vary with their nature and concentration, temperature, immersion time and acid concentration. The values of activation energy and free energy of adsorption of the thiazoles were calculated to investigate the mechanism of corrosion inhibition. The adsorption of all the thiazoles on mild steel surface was found to obey Langmuir adsorption isotherm. The potentiodynamic polarization result revealed that the compounds studied are mixed type inhibitors. Electrochemical impedance spectroscopy was used to investigate the mechanism of corrosion inhibition.

Phenyl phthalimide derivatives were used [138] as corrosion inhibitors for the dissolution of iron and c-steel on 0.1 M oxalic acid. The inhibition efficiency of these compounds was o increased with increasing of concentration. The inhibiting effect was attributed to a chemisorption of the molecules as a result of charge transfer from the inhibitor molecule to the metal surface.

The effect of (0.05 M) tartaric and malic acids on the behaviour of c-steel in the presence of Fe^{2+} ions at pH 2.8 was studied [139] by measuring the corrosion potential and the corrosion rates by the galvanostatic polarization technique. The extent to which corrosion is promoted depends on the concentration of Fe^{2+} ion. Tartaric acid has a more pronounced effect on the corrosion rate. The activation energy of hydrogen evolution was found to be 5.46 and 4.55 Kcal mol^{-1} for tartaric and malic acid respectively. The activation energies for the overall corrosion process at the corrosion process was found to be 5.6 and 5 Kcal mol^{-1} for tartaric and malic respectively. These are characteristic of a diffusion controlled process.

6. CONCLUSIONS

Compounds containing nitrogen, oxygen, sulphur and phosphorous in the conjugated system have particularly been reported as efficient corrosion inhibitors. These compounds can adsorb on the steel surface blocking the active sites and thereby decreasing the corrosion rate. They control corrosion, acting over the anodic or the cathodic surface or both.

The selection of a suitable inhibitor for a particular system is a difficult task because of the selectivity of the inhibitors and wide variety of corrosive environment. The choice of the inhibitors was based on the fact that these compounds contains electrons and heteroatoms such as N, O and S, which involve greater adsorption of the inhibitor molecules onto the surface of mild steel. It has been observed that the adsorption of corrosion inhibitors depends mainly on certain physico-chemical properties of the molecule such as functional groups, steric factors, aromacity, electron density at the donor atoms and p orbital character of donating electrons [140-143], and also on the electronic structure of the molecules [144, 145].

The potential of zero charge (pzc) plays an important role in the electrostatic adsorption process. The potential difference between the corrosion potential and the pzc of a corroding metal was introduced by Antropov to assess the influence of the charge and the nature of the metal on organic adsorption [146]. The adsorption of cation is favored if the net charge is negative. However, the

adsorption of anion is favored if the net charge is positive. This kind of adsorption refers to physical adsorption. Furthermore, adsorption of some ions has been suggested to involve not only electrostatic interaction but also partial charge transfer leading to a covalent bond formation.

References

1. P. Chatterjee, M.K. Benerjee, K.P. Mukherjee*, Ind. J. Technol*. 29 (1991) 191.
2. M. Elachouri, M.S. Hajji, S. Kertit, E.M. Essassi, M. Salem, R. Coudert, *Corros. Sci*. 37 (1995) 381.
3. B. Mernari, H. Elattari, M. Traisnel, F. Bentiss, M. Larenee, *Corros. Sci*. 40 (1998) 391.
4. F. Bentiss, M. Traisnel, M. Lagrenee, *Corros. Sci*. 42 (2000) 127.
5. L. Elkadi, B. Mernari, M. Traisnel, F. Bentiss, M. Lagrenee, *Corros. Sci*. 42.   (2000) 703.
6. A. Elkanouni, S. Kertit, A. Ben Bachir, *Bull. Electrochem*. 12 (1996) 517.
7. R. Walker, *Corros. Sci*. 31 (1975) 97.
8. S. Kertit, B. Hammouti, *Appl. Surf. Sci*. 93 (1996) 59.
9. F. Bentiss, M. Lagrenee, M. Traisnel, J.C. Hornez, *Corros. Sci*. 41 (1999) 789.
10. E. Khamis, *Corrosion* 46 (1990) 476.
11. T.P. Zhao, G.N. Mu, *Corros. Sci*. 41 (1999) 1937.
12. J.O'M Bockris, D.A.J. Swinkels, *J. Electrochem. Soc*., 111 (1964) 736
13. W.J. Lorenz, F.Mansfeld., in: proceeding of the 6th Symposium on European Inhibition of Corrosion, University of Ferrara, Ferrara, 1985, p. 23.
14. C. Cao, *Corros. Sci*., 38 (1996) 2073.
15. R.R. Annand, R.M. Hurd, N. Hackerman, *J.Electrochem. Soc*., 112 (1965) 1968
16. E.Z. Cook, N. Hackerman, *J. Phys. Chem*., 55 (1951) 549.
17. J. Bordeaux, N. Hackerman, *J. Phys. Chem*., 61 (1957)1329.
18. L.I Antropove, *Zhurn. Fiz. Khim*., 37 (1963) 965.
19. N. Hackerman, E.S.Jr. Snavely, J.S..Jr, Payne, *J. Electrochem. Soc*. 113(1966) 677.
20. T. Murakawa, T. Kato, S. Naguara, N. Hackerman, *Corros. Sci*., 8 (1968) 483.
21. A.S. Fouda, H.A. Mostafa, F. El-Taib, G.Y. Elewady, *Corros. Sci*., 47 (2005) 1988.
22. S.A.Abd El-Maksoud, *Journal of Electroanal. Chem*. 565 (2004) 321.
23. Z.A. Iofa, Proc. Second Eur. Symp. Corr., Inhib., 1965, Univ. Ferrera, p.151, 1966
24. S. Muralidharan, S. Syed Azim, L.John Berchmans, S.V.K. lyer, *Anti-Corrosion Methods and materials*, 44 (1997) 30.
25. A. Chetouani, B. Hammouti, A. Aouniti, N. Benchat, T. Benhadda, *Prog. Org. Coat*. 45 (2002) 373.
26. K. Bekkouch, A. Aouniti, B. Hammouti, S. Kertit, *J. Chim. Phys*. 96 (1999) 838.
27. S. Kertit, K. Bekkouch, B. Hammouti, *Rev. Metall*. 97 (1998) 251.
28. D. Bouzidi, S. Kertit, B. Hammouti, M. Brighli, *J. Electrochem. Soc. India* 46 (1997) 23.
29. S. Kertit, B. Hammouti, M. Taleb, M. Brighli, *Bull. Electrochem*.13 (1997) 241.
30. S. Kertit, B. Hammouti, *Appl. Surf. Sci*. 93 (1996) 59.
31. J.G.N. Thomas, Proceedings of the Fifth European Symposium on Corrosion Inhibitors, Ann. Univ., Ferrara, Italy, 1980–1981, p. 453.
32. K. Amaraki, N. Hackerman, *J. Electrochem. Soc*. 116 (1969) 568.
33. N. Hackerman, D.D. Justice, E. McCafferty, *Corrosion* 31 (1975)240.
34. S.L. Granese, *Corrosion* 44 (1988) 322.
35. G. Banerje, S.N. Malhotra, *Corros. Sci*. 48 (1992) 10.
36. H. Kaeshe, R. Narayan, *J. Electrochem. Soc*. 105 (1985) 191.
37. A.A. Samarkandy, A.O. Al-Oubi, R.M. Khalil, A.A. Abdel Fattah,*Bull. Electrochem*.17 (2001) 111.

38. B. Mernari, L. El Kadi, S. Kertit, *Bull. Electrochem.* 17 (2001) 115.
39. M. Bouklah, B. Hammouti, A. Aouniti, T. Benhadd, *Prog. Org. Coat.* 49 (2004) 225.
40. M.A. Migahed, E.M.S. Azzam, A.M. Al-Sabagh, *Mat. Chem. Phys.*,85 (2004) 273.
41. Mirghasem Hosseini, Stijn F.L. Mertens, Mohammed R. Arshadi, *Corros. Sci.*, 45 (2003) 1473.
42. M. Abdallah, *Mat. Chem.Phys.*, 82 (2003) 786.
43. E.E. Oguzie, C. Unaegbu, C.N. Ogukwe, B.N. Okolue , A.I. Onuchukwu, *Mat. Chem.Phys.*, 84 (2004) 363.
44. E.E. Ebenso, *Mat.. Chem. Phys.* 9672 (2002) 1–8.
45. W.M. Morgans, Outlines of Paint Technology, vol. 3, Edward Arnold, London, 1990, p. 127.
46. A.A. Hosary, R.M. Saleh, Progress in the Understanding and Prevention of Corrosion, vol. 2, Institute of Materials, 1993, pp.911–915.
47. T. Horvath, E. Kalman, Progress in the Understanding and Prevention of Corrosion, Institute of Materials, 1993, pp. 923–926.
48. S.M. Beloglazow, Progress in the Understanding and Prevention of Corrosion, vol. 2, Institute of Materials, 1993, pp. 906–910.
49. G.K. Gomma, *Mater. Chem. Phys.* 55 (1998) 241
50. S. Sankarapapavinasam, F. Pushpanaden, M.F. Ahmed, *Bull. Eletrochem.* 5 (1989) 319.
51. A.A. Mazhar, S.T. Arab, E.A. Noor, *Bull. Eletrochem.* 17 (2001) 319.
52. B.A. Smith, L.J. Turbini, *J. Electron. Mater.* 28 (1999) 1299.
53. F.C. Giacomelli, C. Giacomelli, M.F. Amadori, V. Schmidt, A. Spinelli ,*Mater. hem. Phys.* 83 (2004) 124.
54. S.N. Banerjee, S. Misra, *Corrosion* 45 (1989) 780.
55. F. Bentiss, M. Bouanis, B. Mernari, M. Traisnel, M. Lagrenee, *J. Appl. Electrochem.* 32 (2002) 671.
56. E.E. Ebenso, *Mat. Chem. Phys.* 79 (2003) 58.
57. Y. Feng, K.S. Siow, W.K. Teo, A.K. Hsieh, *Corros. Sci.* 41 (1999) 829.
58. E. Khamis, E.S.H. El-Ashry, A.K. Ibrahim, *Br. Corros. J.* 35 (2000) 150.
59. M. Hosseini, S.F.L. Mertens, M.R. Arshadi, *Corros. Sci.* 45 (2003) 1473.
60. S. Rajendran, B.V. Apparao, N. Palaniswamy, *Electrochim. Acta* 44 (1998) 533.
61. T. Du, J. Chen, D. Cao*, Br. Corros. J.* 35 (2000) 229.
62. Xueming Li , Libin Tang, Lin Li , Guannan Mu, Guangheng Liu, *Corros. Sci.*,48 (2006) 308.
63. A. Frignani, C. Monticelli, G. Trabanelli, *Corrosion* 34 (3) (1999) 214.
64. G. Moretti, G. Quartarone, A. Tassan, A. Zingales, *Br. Corros.* J.31 (1) (1996) 49.
65. Z.D. Stankovic, M. Vukovic, *Electrochim. Acta* 41 (16) (1996) 2529.
66. A. singh, R.S. Chaudhary, *Br. Corros. J.* 31 (4) (1996) 300.
67. B.A. Abd-El-Nabey, E. Khamis, G.E. Thompson, J.L. Dawson, Surf.Coat. Technol. 28 (1986) 67.
68. A. Raman, P. Labine, Reviews on Corrosion Inhibitor Science Technology, Vol. .11, NACE, Houston, TX, 1986, p. 20.
69. G. Schmidt, *Br. Corros. J.* 19 (1984) 165.
70. M.A. Quraishi, Jaya Rawat, *Materials Chem. Phys.* 70 (2001) 95.
71. M. Bouklah, A. Ouassini, B. Hammouti, A. El Idrissi, *Appl. Surf. Sci.* 252(2006) 2178.
72. F. M. Bayoumi , W. A. Ghanem, *Mat. Lett.* 59 (2005) 3806.
73. S. Bilgic, H. Yılmaz, *Mat. Chem. Phys.* 79 (2003) 5.
74. A.S. Algaber, E. M. El-Nemma, M. M. Saleh *, Mat. Chem. Phys.* 86 (2004) 26.
75. E.E. Oguzie, *Mat. Chem. Phys.* 87 (2004) 212.
76. M.M. Osman, R.A. El-Ghazawy, A.M. Al-Sabagh, *Mat. Chem.Phys.* 80 (2003) 55.
77. E.E. Foad El Sherbini, *Mat. Chem. Phys.* 60 (1999) 286.
78. H.Ashassi-Sorkhabi, N. Ghalebsaz-Jeddi, *Mat. Chem. Phys.* 92 (2005) 480.
79. S. T. Selvi, V. Raman and N. Rajendran, *J. Appl. Electrochem.* 33 (2003) 1175.
80. E.Mc. Cafferty and N. Hackerman, *J. Electrochem. Soc.* 119 (1972) 146.

81. S. Muralidharan, K.L.N. Phani, S. Pitchumani, S. Ravichandran, S.V.K. Iyer, *J. Electrochem. Soc*. 142 (1995) 1478.
82. K.D. Neemla, R.C. Saxena, A. Jayaraman, *Corros. Prev. Cont*. 6 (1992) 69.
83. W. Frenier, F.B. Growcock, V.R. Lopp, *Corrosion* 44 (1988) 590.
84. F.B. Growcock, W.W. Frenier, *Proc. Electrochem. Soc*.86–87 (1986) 104.
85. M.A. Quraishi, D. Jayaperumal, S. Subramanian, S.M. Natesan, G.Venkatachari, K. Balakrishnan, *Bull. Electrochem*. 12 (1996) 100.
86. M.A. Quraishi, M.Q. Ansari, S. Ahmad, G. Venkatachari, *Bull. Electrochem*. 13 (1997) 257.
87. M.A. Quraishi, S. Ahmad, M.Q. Ansari, *Br. Corros. J*. 32 (1997) 297.
88. M.A. Quraishi, D. Jamal, *Corrosion* 56 (2000) 156.
89. M.A. Quraishi, D. Jamal, *Mat. Chem.Phys*. 71 (2001) 202.
90. K. Tebbji, B. Hammouti, H. Oudda, A. Ramdani, M. Benkadour, *Appl. Surf. Sci* 252 (2005) 1378.
91. K. Tebbji, A. Aouniti, M. Benkaddour, H. Ouddac, I. Bouabdallah, B. Hammouti , A. Ramdani, *Prog. Org. Coat*. 54 (2005) 170.
92. M.A. Quraishi, J. Rawat, M. Ajmal, *J. Appl. Electrochem*. 30 (2000) 745.
93. A.A. El-Shafei, M.N.H. Moussa, A.A. El-Far, *Mate. Chem. Phys*. 70 (2001) 175.
94. A.A. El-Shafei, M.N.H. Moussa, A.A. El-Far, *J. Appl. Electrochem*. 27 (1997) 1075.
95. El-Shareef , R.F. Al-Ghamdi , *Corros. Sci*. 47 (2005) 2659.
96. Ling-Guang Qiu, An-Jian Xie, Yu-Hua Shen, *Corros. Sci*. 47 (2005) 273.
97. Hui-Long Wang , Rui-Bin Liu, Jian Xin, *Corros. Sci*. 46 (2004) 2455.
98. S.S. Abd EL-REHIM, S.A.M. Refawy, F. Taha, M.B. Saleh, R.A. Ahmed, *J. App. Electrochem*. 31 (2001) 429.
99. E.E. Ebenso, U.J. Ekpe, B.I. Ita, O.E. Offiong, U.J. Ibok, *Mat. Chem. Phys*. 60 (1999) 79.
100.   H.B. Fan, C.Y. Fu, H.L.Wang, X.P. Guo, J.S. Zheng, *Br. Corros.J*. 37 (2002) 122.
101.   S.A. Abd El-Maksoud, A.S. Foud, *Mat. Chem. Phys*. 93 (2005) 84.
102.   M. S. Abdelaal, M. S. Morad, *Br. Corros. J*. 36 (2001) 253.
103.   A.S. Stoyanova, E.I. Sokolova, S.N. Raicheva, *Corros. Sci*. 39 (1997) 1595.
104.   M.A.Quraishi, D. Jamal, *Mat. Chem. Phys*. 68 (2001) 283.
105.   K.C.Emregül, M. Hayval, *Mat. Chem. Phys*. 83 (2004) 209.
106.   F. Bentiss, M. Traisnel, N. Chaibi, B. Mernari, H. Vezin d, M. Lagrenee, *Corros. Sci*. 44 (2002) 2271.
107.   F. Benttss, M. Traisnel, M. Lagrenee, *J. App. Electrochem*. 31 (2001) 41.
108.   G.L. Foster, B.D. Oakes, C.H. Kucera, *Ind. Eng. Chem*. 51 (1959) 825.
109.   F. Zucchi, G.L. Zucchi, G. Trabanelli, Proceedings of the 3rd Eur. symp. on orrosion inhibitors, Ann. Univ. Ferrara, N.S. Sez. V, suppl. N.5 1970, pp. 121.
110.   I.L. Rozenfeld, Corrosion Inhibitors, McGraw-Hill Inc., New York, NY, 1981, pp. 138 and 193.
111.   V.S. Muralidharan, K.S. Rajagopalan, *Corros. Sci*. 19 (1979) 207.
112.   Y. Jianguo, W. Lin, V. Otieno-Alego, D.P. Shweinsberg, *Corros. Sci*. 37 (1995) 975.
113.   M.S. Morad, *Mat. Chem. Phys*. 60 (1999) 188.
114.   M. Bartos, S.D. Kapusta, N. Hackerman, *J. Electrochem. Soc*. 140 (1993) 2604.
115.   P. Kuteg, J. Vosta, J. Pancir, N. Hackerman, *J. Electrochem. Soc*. 142 (1995) 1847.
116.   J.O'M. Bockris, B. Yang, *J. Electrochem. Soc*. 138 (1991) 2237.
117.   E.A. Noor, *Corros. Sci*. 47 (2005) 33.
118.   M. Benabdellah, B. Hammouti, *Appl. Surf. Sci*. 252 (2005) 1657.
119.   L. Wang, *Corros. Sci*. 48 (2006) 608.
120.   I.A. Sekine, A. Masuko and K. Senoo, *Corros. Sci*. 43 (1987) 553.
121.   V.B. Singh and R.N. Singh, *Corros. Sci*. 37 (1995) 1399.
122.   I. Sekine, S. Hatakeyama and Y. Nakazawa, *Corros. Sci*. 27 (1987)275.

123.   E. Heitz, 'Corrosion of Metals in Organic Solvents', (New York, NY: Plenum Press, 1974), p. 226.
124.   I. Sekine, H. Ohkawa, and T. Hank, *Corros. Sci*. 22 (1982) 1113.
125.   I. Sekine and A. Chinda, *Corrosion* 40 (1984) 95.
126.   M.M. Singh and A. Gupta, *Mat. Chem. Phy*. 46 (1996) 15.
127.   S. Muralidharan and S.V.K. Iyer, *Anti-Corros. Met. Mater*. 44 (1997) 100.
128.   M.A. Quraishi, M.A.W. Khan and M. Ajmal, *Anti-Corros. Met. Mater*. 43 (1996) 5.
129.   B. Hammouti, A. Aouniti, M. Taleb, M. Bright and S. Kertit, *Corrosion* 51 (1995) 411.
130.   N. Al-Andis, E. Khamis, A. Al-.Mayouf and H. Aboul-Enein, *Corros. Prev. Cont*. 42 (1995) 13.
131.   B.A. Abd-El-Nabey, E. Khammis, M.Sh. Ramadan and A. El-Gindy, *Corrosion* 52 (1996) 671.
132.   M.M. Singh and A. Gupta, *Mat. Chem. Phys*. 46 (1996) 15.
133.   I. Sekine, T. Hayakawa, T. Negishi, M. Yuasa*, J. Electrochem. Soc*., 137 (1990) 3029
134.   M.A. Quraishi, F.A. Ansari, *J. App. Electrochem*. 33: (2003) 233.
135.   M.A. Quraishi, F.A. Ansari, D. Jamal, *Mat. Chem. Phys*. 77 (2002) 687.
136.   M.A. Veloz, I. Gonzalez, *Electrochim. Acta* 48 (2002) 135.
137.   M.A. Quraishi, H.K. Sharma*, J. App. Electrochem*. 35 (2005)33.
138.   M. Abdallah, H.E. Megahed, *Monatshefte fuer Chemie*, 126 (1995) 519.
139.   G.K. Gomaa, *Mat. Chem. Phys*., 52 (1998) 200.
140.   E. Khamis, *Corrosion* 46 (1990) 476.
141.   E. Stupnisek-Lisac and S. Podbrscek, *J. Appl. Electrochem*. 24 (1994) 779.
142.   G. Schmitt and K. Bedbur, *Werkst. Korros*. 36 (1985) 273.
143.   E. Stupnisek-Lisac and M. Metikos-Hukovic, *Br. Corros. J*. 28 (1993) 74.
144.   S.L. Granese, B.M. Rosales, C. Oviedo and J.O. Zerbino, *Corros. Sci*. 33 (1992) 1439.
145.   S.L. Granese, *Corrosion* 44 (1988) 322.
146.   L.I. Antropov, Inhibitors of Metallic Corrosion and the φ-scale of Potentials, 1st International Congress on Metallic Corrosion, Butterworths, London, 1962, pp. 147–156.