Chapter 1

Introduction

Corrosion can be defined in many ways. The one most preferred in literature (1) is the loss of useful properties of material as a result of its chemical or electrochemical reaction with the environment. The corrosion specialist is concerned with the study about the corrosion mechanisms to obtain a better understanding about corrosion and available means for preventing (2) or minimizing damage.

1.1 Corrosion inhibition.

An inhibitor is a substance when added in small concentration to an environment, effectively checks, decreases, or prevents the reaction of the metal with the environment (3). Corrosion inhibitors are added to many systems including: cleaning pads, cooling systems, various refinery units, pipelines, chemical operation, steam generators, ballast tanks, oil and gas production units and many other fields.

Inhibition is usually accomplished by one or more of several mechanisms. Some inhibitors retard the corrosion by adsorption with forming a thin invisible film. Others form visible bulky precipitates which cover the metal surface and protect it from attack (4). Another common inhibitor mechanism, is the effect of the combination of the adsorbed inhibitor and the corrosion product to produce a passive layer on the metal surface.

Other substances, when added, do not interact directly with the metal surface, such inhibitor causes alteration in the environment to be favorable for the formation of protective precipitates or remove the aggressive constituent from the environment. The corrosion rate may also be reduced by other means such as adjusting the pH and temperature, removing dissolved oxygen or lowering the conductivity of the electrolyte.

1.2 Types of inhibitors.

Corrosion inhibitors are substances which when added to the corrosive medium lower the corrosion rate of the metal. Inhibition can result from the retardation of the anodic process, cathodic process or both. Inhibitors can be classified into:

i) Anodic inhibitors.

These are very effective and are widely used. They are anions which migrate to the anode sites of the metal and lead to passivation of the metal surface under favorable conditions. If the anion alone is capable of passivating the metal, the agent has oxidizing properties e.g. nitrite, nitrate and chromate which are named passivators.

ii) Cathodic inhibitors.

Unlike anodic inhibitors, cathodic inhibitors are safe. These are cations which migrate towards cathodic areas of the surface and precipitate either chemically or electrochemically on the surface. Example of cathodic inhibitors is the natural contents of $Ca(HCO_3)_2$ in hard water. The cathodic reaction of the corrosion in neutral aerated solution is the reduction of oxygen, the resulting $(OH)^-$ ions will interact with the inhibitor to precipitate $CaCO_3$ as follow:

$$2Ca(HCO_3)_2 + 2OH^- \rightarrow 2CaCO_3 + 2H_2O \qquad (1.1)$$

which isolates the cathodic area from solution. The inhibitors, which affect cathodic reaction, are cathodic poisons, cathodic precipitants and oxygen scavengers.

iii) Vapour phase inhibitors (5).

These are used for temporary protection of metals in corrosive atmospheres. These are compounds which have low, but significant vapour pressure about (0.1 – 1.0 mmHg) that has corrosion inhibiting properties. They are essentially soluble, filming inhibitors and include nitrate, benzoate and/or carbonate anions attached to suitable heavy organic cation, e.g. dicyclohexyl ammonium nitrate, which is one of the most effective inhibitors of this type.

iv) Adsorption inhibitors (6).

These are mainly organic compounds containing nitrogen, oxygen or sulphur atoms through which they can be adsorbed, usually by chemisorptions on the metal surface (7). Chemisorptions usually occur through donation of electrons from N, S or O functional atoms to the metal atoms on the surface.

Inhibitors can bound to the metal surface to form a coordinate type of link. This process is favored by the presence of vacant orbital of low energy on the metal atoms, as in the case of transition metals. Electron transfer from the adsorbed species is favored by the existence of relatively loosely bound electrons, such as those in anions and neutral organic molecules containing lone pair of electrons or π-electron systems associated with multiple, especially triple, bonds or aromatic rings.

For organic compounds, suitable lone pair of electrons of coordinate bonding occurs in functional groups containing elements of group V and VI of the periodic table. The tendency to form a stronger coordinate bond (and hence stronger adsorption) by these elements increases with decreasing electronegativity in the order: $O < N < S$ (8-10) and depends also on the nature of the functional groups containing these elements.

The degree of inhibition of anodic and cathodic inhibitors depends on the chemical structure of the inhibitor, potential of the metal, and size of molecule.

Kirkov (11) postulated that inhibition efficiency of surface-active compounds appeared to include both chemical and electrochemical factors. The chemical factors influence the formation of the protective surface layer in the metal-corrosive medium interface. The electrochemical factors influence the equilibrium potential on the metal surface and consequently, direct the charge transfer processes.

Hoar (12-13) concluded that adsorption of inhibitor molecules reduces the number of electrode reaction sites and inhibition becomes predominant when the surface was covered with a monolayer film.

v) Precipitation inhibitors.

These are inhibitors, which interfere with anodic and cathodic reactions and are film forming compounds with an action over the metal surface, such as phosphates and silicates.

1.3 The limiting use of inhibitors.

Inhibitors can be used with a great advantage for the protection of metals in many environments. However, it is important to note that inhibitors are generally specific to a given metal, environment and the service conditions. Furthermore, there are certain limitations on the use of inhibitors which should be considered before deciding on their use (14).

i) Inhibitors contaminate the environment and are often toxic; they can not be used in food industries or in any system which could indirectly allow the consumption of inhibitors by human.

ii) They are most useful in closed systems where the corrosive environment is either retained for long periods or recycled.

iii) Inhibitors generally lose their effectiveness as the concentration and temperature of the environment increase. This can be remedied by keeping the concentration of the inhibitor at a level which exceeds the optimum value necessary for protection. This practice reflects a general rule in the use of inhibitors.

1.4 Correlation between inhibition and stability of organic compounds.

The factors which are responsible for inhibition of corrosion by organic compounds depend on the nature of the corroding metal, the composition of the corrosive medium and the condition under which the corrosion process occurs; added to these their chemical properties and structure.

If different kinds of inhibitors are considered separately, the factors responsible for the inhibition action of the organic compounds could be understood better.

i) Inhibition by chemically stable surface active organic compounds.

In many cases the stability of organic compounds as well as their ability to be adsorbed depends on the nature of the corroding metal. It is very difficult indeed to find compounds, which do not undergo any chemical changes in the solution during the course of corrosion process (15). For any a given solution the adsorption of inhibitors depends (16) first of all on the charge of the metal, the potential of the metal and φ scale of potential. In solution, the charge on a metal is relative to the zero charge potential (φ potential). φ potential controls the electrostatic interaction of the metal with dipoles in adsorbed neutral molecules and hence the orientation of the dipole and the adsorbed molecules. Thus, as φ potential becomes more positive the adsorption of anion is favored and as the φ potential becomes more negative the adsorption cation is favored.

ii) Inhibition by surface active chemically unstable organic compounds.

The inhibition efficiency concentration relationship had been considered, and the probability of maximum or minimum had been noted. As a result of interaction with cathodic hydrogen, the significance of the chemical change in the nature of additives was realized. The following three cases have been discussed.

(i) Surface active additives reducible to surface inactive compounds.

(ii) Surface inactive additives reducible to surface active compounds.

(iii) Surface active reducible to new surface active compounds.

The types of chemical transformation are:-

a) Protonation.

Antropov (16-17) in discussing electro-organic reduction process considered the following points as being important with regard to protonation reaction:

(i) It occurs usually on the surface of a metal and can under definite conditions be a rate determining step of the overall reaction.

(ii) Its rate depends on the surface concentration of the organic substance, and therefore on charge on the surface (its φ potential).

(iii) As a result of the opposite effect of electric field and the charge of metal the rate of reduction (protonation) can reach a maximum value at a certain potential of the organic substance.

b) Reduction.

The reduction of organic inhibitors could take place only if the corrosion potential is sufficiently negative. If this condition is fulfilled, then the main principles of the theory of electroreduction of organic compounds (16-17-18) could be applied to that particular case of organic electrochemistry. Thus, the selective reduction of inhibitors on various metals should be expected.

C) Polymerization.

Cathodic reduction under certain conditions may lead to the formation of dimmers or polymers. If polymerization is a surface process, and the formation of copolymers between the inhibitors and corroding metal is possible, the degree of protection should be increased (19).

1.5 Effect of inhibitors on polarization behavior.

One of the most interesting phenomena in corrosion inhibition is that inhibitors do not affect anodic and cathodic reactions to the same degree. Thus one finds, as shown in Figs. (1.1-1.2) that in some instances the cathodic reaction rate is reduced while the anodic reaction rate remains the same or vise versa.

Cathodic inhibition results in a shift of the corrosion potential in the negative direction while anodic inhibition results in a potential shift in the positive direction. While the corrosion potential may give a preliminary indication of the inhibitor mechanism, polarization curves should be recorded for more complete assessment of its mode of action. This is more important since a reduction of the anodic reaction rate, for instance, coupled with an acceleration of the cathodic reaction rate may cause a large cathodic potential shift with no change in the corrosion rate.

Conversely, if both cathodic and anodic reaction rates are reduced to the same extent, no shift in corrosion potential is observed while the inhibition effect is the largest possible. Such relatively simple electrochemical techniques can be considered as useful tools for the rapid assessment of inhibitor activity and for obtaining preliminary information on a possible inhibition mechanism. Even if a system is relatively well behaved, the information value from polarization curves is relatively small and should be combined with more extensive determination of the electrode kinetic parameters, adsorption studies and mass transfer studies.

To elucidate the mechanism of a particular corrosion inhibitor or class of compounds exhibiting inhibitive effects.

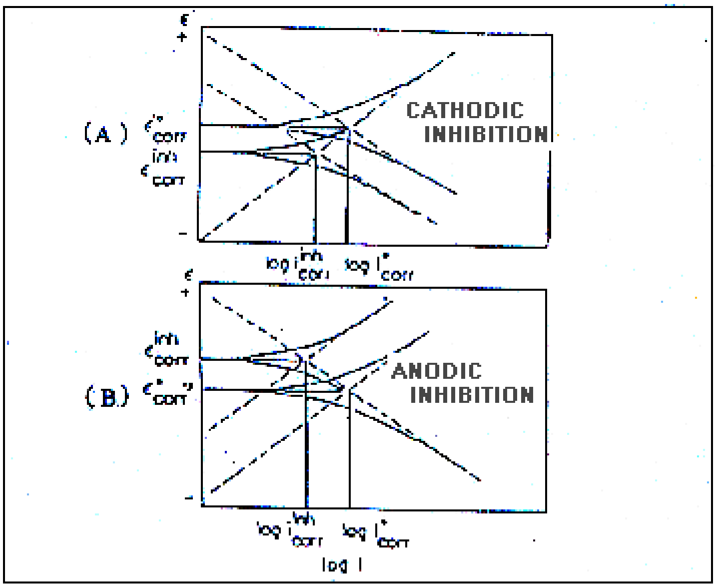

Fig.(1.1): (A) Cathodic inhibition (B) Anodic inhibition.

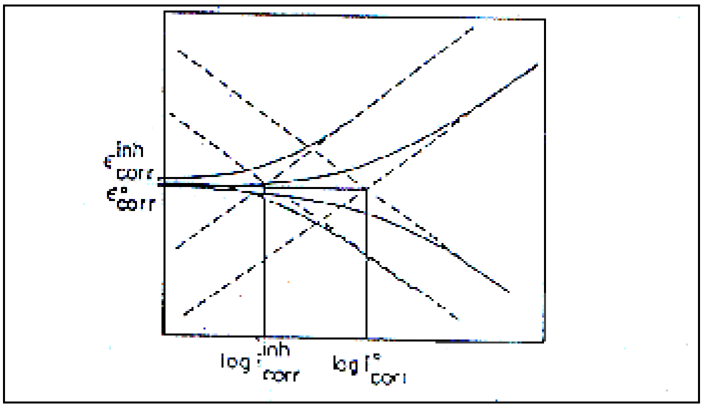

Fig.(1.2): Cathodic and anodic inhibition.

1.6 Factors affecting the adsorption of inhibitor on metals.

i) Electrostatic forces.

Adsorption may take place due to the electrostatic forces between the adsorbed species e.g. ions or dipoles and the electric charge on the metal surface, which is expressed by its potential with zero charge potential rather than hydrogen. The size and magnitude of this potential (φ potential) are very important with respect to adsorption, as discussed before. In addition, φ potential affects the orientation of dipoles and molecules adsorbed on the metal surface.

Antropov (20) has shown that the adsorption of inhibitors on mercury can be related to the adsorption and inhibitive effect of these inhibitors on aluminum. Different free corrosion potentials for different metals can change the behavior of an inhibitor; this may be related to the difference in φ potential.

ii) Functional group and structure of inhibitors.

Some inhibitors can form a coordinate type of link with the metal by electron transfer to the metal. Inorganic compounds of functional groups containing elements of group V and VI of the periodic table, having a suitable lone pair of electrons as functional groups for coordinate bonding. The tendency to stronger coordinate bond formation and hence, stronger adsorption by these elements increases with decreasing the electronegativity in the order O < N< S < Se (21). It depends also on the nature of the functional group and the rest of the molecule, since they affect the electron density on the functional group, which is generally thought to increase the efficiency of an inhibitor as it increases. So, with increasing electron density on the functional group, a stronger coordinate bonding with metal surface is produced hence, greater adsorption.

iii) Interaction of the inhibitor with water molecules.

Due to adsorption process of an inhibitor, water molecules are being removed from the metal surface. During the adsorption process of a molecule, the interaction energy between molecule and water changes as it passes from the dissolved to adsorbed state. This change forms an important part of the free energy of adsorption, i.e. the higher the solvation energy of the adsorbing species, the higher the free energy of adsorption. Increasing the size of the hydrocarbon portion of an organic molecule will increase the solvation energy (16) of an inhibitor leading to decrease the solubility and increasing adsorbability.

iv) Interaction of adsorbed species.

The interaction between adsorbed inhibitor molecules may become significant as the surface coverage of adsorbed species increase. Attractive interactions occur between molecules of the long hydrocarbon chain due to the increase of Van der Waals attractive forces between adjacent molecules leading to stronger adsorption at higher coverage (22).

Synergistic inhibitive effect was observed (23), when a mixture of cationic and anionic inhibitors is used. This is due to the attraction between inhibitive ions of opposite charge, thus increasing the inhibitor efficiency.

With quaternary ammonium cations, presence of halide ions, I^-, Br^- and Cl^-, significantly increase the inhibitive effect (24).

v) Reaction of adsorbed inhibitors.

Adsorbed inhibitors may react forming a new products which act as secondary inhibitors, so that the inhibitive efficiency increases or decreases, for example, sulphoxides can be reduced to sulphides which are more efficient, while thiourea is reduced to HS^- which in turn act as stimulator (25).

vi) Molecular structure of inhibitor.

The inhibition attributable to the initial compound is called (primary inhibitor) and that brought about by the reduction products is (secondary inhibition) (26-27). The inhibition efficiencies calculated for different homologous series of organic compounds have some times underlined the difficulty of attributing the variation in inhibition within seties of mono functional substances to a single molecular property such as electron density.

The possible steric effect including molecular size and mode of interaction which may provide a screening action on the reaction center for the adsorption of the molecule at the metal surface was reported by Altsybeeva and Levin (28). Complexation between the organic molecule and the metal and the stability constant for the resulting complexes were taken into consideration.

The validity of Hammett′s equation (29), later extended by Jaffe (30) and Taft (31), also quantum chemical calculations of electron charge density of individual atoms within a molecular orbital structure on corrosion and inhibition process were investigated (32). A comprehensive approach to corrosion inhibition was suggested by Fouda et al (33). The authors showed that, metallic corrosion inhibition depends not only on the polar effect, the electron charge density of functional groups or adsorption active centers in the molecule, but also on the molecular size of the inhibitor, its mode of adsorption on the metal surface, its heat of hydrogenation and its ability to form insoluble metallic complexes that can be incorporated in the oxide layer, thus reinforcing it or soluble ones that enhance dissolution.

1.7 Adsorption isotherms.

As far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitor at the metal/solution interface is the first step in the action mechanism of the inhibitors in aggressive acid media. Four types of adsorption may take place in the inhibiting phenomena involving organic molecules at the metal/solution interface, namely:

(i) Electrostatic attraction between charged molecules and the charged metal.

(ii) Interaction of electron pairs in the molecule with the metal.

(iii) Interaction of electrons with the metal.

(iv) A combination of all the above (34).

Chemisorption involves charge sharing or charge transfer from coordinate bond. In fact, electron transfer is typical for transition metals having vacant, low energy electron orbital. Concerning inhibitors, electron transfer can be expected with compounds having relatively loose bound electrons (35). This situation may arise because of the presence in the adsorbed inhibitor of multiple bonds or aromatic rings, having a π-bound character (36-42). The inhibition efficiency of homologous series of organic substances, differing only in the hetero atom, is usually in the following sequence: P > Se > S > N >O.

Interpretation may be found in the easier polarizability and lower elecronegativity of the elements on the left in the above sequence (43).

As substitutional adsorption process occurs between the inhibitor molecule, I, in the aqueous phase, and the water molecules adsorbed on the electrode surface, $H_2O_{(s)}$ (44).

$$I_{(aq)} + x\, H_2O_{(s)} \rightarrow I_{(s)} + x\, H_2O_{(aq)} \qquad (1.2)$$

where, x is the size ratio which is the number of water molecules replaced by one molecule of the inhibitor. The above process reaches equilibrium in which the chemical potential μ on the left side is equal to that of the right side.

Now, depending on the expression of (i), as related to the physical model adopted to describe adsorption, one may obtain different expressions of adsorption isotherm.

For instance, the most used expressions are:

i) Frumkin (45).

$$[\theta/1-\theta]\ \exp^{[-2a\,\theta]} = K.C. \qquad (1.3)$$

where (θ) is the degree of coverage, (a), is a molecular interaction parameter depending on the molecular interaction in the adsorption layer and on the degree of heterogeneity of the surface. It can have both positive and negative values and in a measure of the steeples of the adsorption isotherm. The more positive value of (a), the steeper is the adsorption isotherm. This has been interpreted (46) to imply that interactions between molecules with positive (a) value cause an increase in the adsorption energy with the increase of (θ), (K) is the equilibrium constant of the adsorption reaction, and (C) is the inhibitor concentration in the bulk of the solution.

ii) Hill de Boer (47).

$$[\theta/1-\theta]\ \exp^{[\theta/1-\theta]\ [-2a\,\theta]} = K.C \qquad (1.4)$$

iii)Parson (48).

$$[\theta/1-\theta]\ \exp^{[2-\theta/1-\theta]\ [-2a\,\theta]} = K.C \qquad (1.5)$$

iv) Temkin (45).

$$a\theta = \ln K.C \qquad (1.6)$$

v) Flory-Huggins (49).

$$\theta/X(1-\theta)^{x} = K.C \qquad (1.7)$$

where x is the number of water molecules replaced by one molecule of organic adsorbate.

vi) Dahr et al. (49).

$$\theta/[\,e^{(x-1)}(1-\theta)^{x}\,]= K.C \qquad (1.8)$$

vii) Freundlich (50).

$$\theta = K.C^{n} \qquad (1.9)$$

Basically, all above isotherm are of the form: (51)

$$f(\theta, X)\exp^{(-a\theta)} = K.C \qquad (1.10)$$

where f(θ, X) is the configurationally factor which depends essentially on the physical model and assumption underlying derivation of the isotherm (52).

Moreover, all above expressions include the equilibrium constant of the adsorption process, (K) which is related to the standard free energy of adsorption ΔG^o_{ads} by: (45)

$$K=1/55.5 \exp(-\Delta G^o_{ads}/RT) \qquad (1.11)$$

Equations (1.10) and (1.11) have been used to evaluate the most suitable isotherm describing the adsorption inhibitors on the electrode surface.

viii) Langmuir (53).

$$C/\theta = 1/K+C \qquad (1.12)$$

K is the equilibrium constant of the adsorption process.

1.8 Tin.

Tin is an element (54-55) with the symbol Sn (Latin: stannum), atomic number 50 (Fig. 1.3), relative atomic weight 118.71 g.mol^{-1}, electron configuration [Kr] $4d^{10}\ 5s^2\ 5p^2$, melting point 505.08 K and boiling point 2875 K. Tin is a malleable, ductile, highly crystalline, silvery-white metal; when a bar of tin is bent, a strange crackling sound known as the tin cry can be heard due to the breaking of the crystals. This metal resists corrosion from distilled, sea and soft tap water.

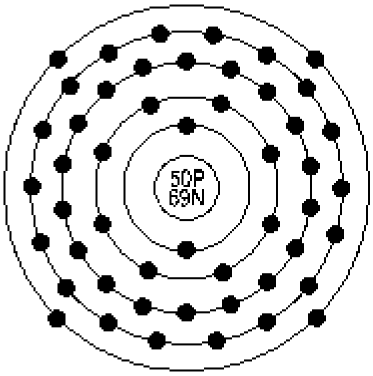

Fig.(1.3): Atomic configuration of tin.

Tin has two allotropes (54) at standard pressure and temperature: gray tin and white tin. Below 13.2°C, it exists as gray or alpha tin, which has a cubic crystal structure similar to silicon and germanium. Gray tin has no metallic properties at all, is a dull-gray powdery material, and has few uses, other than a few specialized semiconductor applications. When warmed above 13.2°C tin changes into white or beta tin, which is metallic and has a tetragonal structure. Converting gray tin powder into white tin produces white tin powder. To convert powdery gray tin into solid white tin the temperature must be raised above the melting point of tin. Gray tin can cause undesirable effects in applications where the metallic properties of tin are important, since metallic white tin will slowly convert to gray tin if it is held for a long time below 13.2°C. The metallic surface of white tin becomes covered with a gray powder which is easily rubbed off. The gray patches slowly expand until all of the tin in the object is converted from the metal to the powder, at which point it loses its structural integrity and may fall to pieces. This process is known as tin disease or tin pest. This transformation may be prevented by the addition of antimony or bismuth.

Tin is a widely sought metal and is used in hundreds of industrial processes (56) throughout the world. In the form of tinplate, it is used as a protective coating for copper vessels, various metals used in the manufacture of tin cans, and similar articles. Tin is important in the production of the common alloys bronze (tin and copper), solder (tin and lead), and type metal (tin, lead, and antimony). It is also used as an alloy with titanium in the aerospace industry and as an ingredient in some insecticides. Stannic sulfide, known also as mosaic gold, is used in powdered form for bronzing articles made of plaster of paris or wood. The United States imports more than one-fifth of the average annual world production of tin. Most of the world's tin is produced by Malaysia, Brazil, Indonesia, Thailand, Bolivia, and Australia.

1.9 Literature survey on corrosion inhibition of tin.

The impedance response of a tin electrode in 4.5 and 6 M H_2SO_4 solutions has been studied (57) at the rest potential, as well as during anodic polarization in the active dissolution and passivation regions. The validity of a model for the active dissolution of tin advanced earlier is proven and extended to explain the mechanism of the open circuit corrosion processes. In the passivation range, the impedance spectra observed are complex, and very dependent on the positive potential and the acid concentration. The high frequency response is ascribed to a barrier-like film formed on the electrode surface, through which ions are transported by high field-assisted migration. The low frequency response suggests an intricate coupling between the passivation and activation-dissolution processes at the film-solution interface.

The anodic behavior of pure tin and a Pb-Sn (10% wt) alloy was studied (58) in sulfuric acid solutions using the ring-disk technique and potential decay measurements. For tin in H_2SO_4 the results show that this metal passivates partly at acid concentrations above 3 M. Tin was found to dissolve mainly as Sn(II) ions, but to some extent also as Sn(IV) if the potential is more than 3 V. The ex-situ analysis of the corrosion layer formed on pure tin showed that the layer consisted mainly of amorphous SnO. The results for the Pb-Sn alloy showed that tin dissolves from or through the corrosion layer formed on the alloy as Sn(II) ions. Tin was found to inhibit the formation of PbO_2. The effect of tin ions dissolved in the solution seemed to be similar to that of tin as an alloying agent. The ring-disk voltammetric measurements showed that a tin-containing compound is formed on the Pb-Sn alloy. This product is probably a mixed Pb-Sn oxide or tin-doped PbO_n.

The anodic behavior of tin in H_2SO_4 solutions, using electrochemical and surface analytical techniques has been studied (59). Ring-disk electrode measurements have provided evidence that tin dissolves as Sn(II) in both active dissolution and passive regions, but these measurements also showed that at sufficiently high anodic over potentials some formation of soluble Sn(IV) takes place in addition to oxygen evolution (60). The surface analysis e.g. scanning electron microscopy (SEM), electron surface for chemical analysis (ESCA) and secondary ion mass spectrometry (SIMS) indicate that the structure of the passivating surface film is mainly amorphous with composition close to SnO.

To obtain a fundamental understanding of the corrosion behavior of lead-free solder, the corrosion behavior of tin-based eutectic alloys in sulfuric and nitric acids saturated with oxygen was investigated (61). The presence of bismuth in a Sn–Bi alloy (43Sn–57Bi (wt%)) slightly accelerated the preferential dissolution of tin instead of dissolving itself in 0.05 M H_2SO_4 and greatly accelerated, in 0.1 M HNO_3 compared with that of pure tin. In both acids, dissolution of both tin and zinc from a Sn–Zn alloy (91Sn–9Zn (wt%)) occurred depending on the ratio of composition, and dissolution of tin from a Sn–Ag alloy (96.5Sn–3.5Ag (wt%)) was accelerated. Dipping tests in H_2SO_4 and HNO_3 of pH 4 showed that dissolution of only zinc and lead occurred, suggesting that the tin-based alloys investigated in this study are preferable to substitutes for lead solders in terms of corrosion resistance.

The electrochemical behavior of tin at different concentrations of nitric acid has been investigated (62). It was found that the rate of corrosion attains its maximum value at about 4 M. The slow rate at high acid concentration is attributed to the formation of stable oxide film.

The electrochemical behavior of a tin electrode in different concentrations of citric acid solutions was studied (63) by electrochemical techniques. The E/I curves showed that the anodic behavior of tin exhibits active/passive transition. Passivation is due to the formation of $Sn(OH)_4$ and/or SnO_2 film on the electrode surface. Addition of NaCl to citric acid solution enhances the active dissolution of tin and tends to breakdown the passivity at a certain breakdown potential. Cyclic voltammetry and galvanostatic measurements allow the pitting potential (E_{pit}) and the repassivation potential (E_{rp}) to be determined. Potentiostatic measurements showed that the overall anodic processes can be described by three stages. The first stage corresponds to the nucleation and growth of a passive oxide layer. The second stage involve pit nucleation and growth and third stage involve repassivation. The impedance spectrum of pure Sn is found to consist of three intersecting capacitive semicircles at the high and medium frequencies with an inductive loop at low frequencies. The capacitive semicircles occurring at the high and medium frequency are due to the dielectric properties of surface oxide film and dissolution of underlying metal, respectively. The inductive loop at low frequencies results from Cl^- ions adsorption at the pitting region. By increasing the potential the pitting corrosion and the fractal dimension of surface due to pitting increase.

Anodic behavior of tin in citrate buffer solution (pH 2−5) was studied (64) using potentiodynamic technique. The current-voltage polarization curves were found to exhibit active-passive transition state; the anodic dissolution of tin in the active region was associated with formation of tin(II) citrate complexes $SnH_xCit^{(1-x)-}$. Chloride ions were shown to retard tin passivation due to the pitting corrosion. The composition of the passive layer formed on tin under its anodic polarization in citrate buffer solution in the presence of chloride ions was investigated using infrared and X-ray photoelectron spectroscopies. According to the experimental data, the passive layer mainly represents coordination compound of tin(II) and citrate ions.

The corrosion behavior of tin in different concentrations of citric acid solutions (0.3–1.0 M, pH=1.8) was studied at 30°C by potentiodynamic technique (65). The E/I profiles exhibit an active passive behavior. The active dissolution involves one anodic peak A associated with a dissolution of the metals as Sn(II) species. The passivity is due to the formation of thin film of SnO_2 and/or $Sn(OH)_4$ on the anode surface. The cathodic sweep shows a small peak C related to the reduction of the passive film. The peak current density I_p of peak A increases with increasing both acid concentration and sweep rate. The effects of adding increasing concentrations of Na_2CrO_4, Na_2MoO_4, $NaNO_3$ and $NaNO_2$ on the corrosion of tin in 0.5 M citric acid at 30°C were investigated. Both CrO_4^{2-} and MoO_4^{2-} ions inhibit the corrosion of tin and the extent of inhibition enhances with their concentrations. Addition of either NO_3^- or NO_2^- ions accelerates the corrosion of tin. NO_3^- ions are more aggressive than NO_2^- ions.

Cyclic voltammetry used to study the influence of systematic additions of citric acid on the E/I curves of tin in 0.5 M $NaClO_4$, in order to verify the film growth in the presence of the organic acid and the inhibition of the pitting corrosion of the metal (66). The minimum concentration of the organic acid needed to change the E/I curves is 10^{-2} M, in the pH range 1.0–4.0. At pH 3.0 and 4.0, the scan rate (υ) dependence on current density, in the potential region of formation and reduction of the film, showed that in a first stage adsorption occurs. In a second stage, the $\upsilon^{1/2}$

dependence found can be explained by ohmic resistance control. The formation of tin/citric acid complexes, in citric acid concentrations higher than 10^{-2} M, is suggested. The pitting inhibition may be due to the formation of a mixed layer of tin oxide and tin citrate complexes on the electrode surface.

The electrochemical behavior of tin in tartaric acid solutions was investigated using potentiodynamic and galvanostatic techniques (67). The anodic behavior of tin exhibits active/passive transition. In the active dissolution potential region, tin dissolves as Sn(II) species, which are subsequently oxidized to Sn(IV). The active dissolution of tin increases with increasing tartaric acid concentration, sweep rate and temperature. Passivation is due to formation of $Sn(OH)_4$ and/or SnO_2 film on the anode surface. The dissolution process is controlled by diffusion. The E/t curves displayed that the time needed to active passive transition increases with increasing acid concentration and temperature but decreases with increasing imposing anodic current density.

The anodic behavior and corrosion of tin in various concentrations of isobutyric acid solutions have been studied (68) by using cyclic voltammetry technique under different experimental conditions. The data reveals that the polarization curves are strongly pH dependent. It is clear that in the pH range from 2.4 to 4 no anodic peak appears. In the pH range from 5 to 6 only one anodic peak appears and the anodic peak current density (I_{PA}) in case pH 5 is greater than that in case pH 6. The anodic excursion spans of tin in isobutyric acid solution (pH 5) are characterized by the occurrence of a well-defined anodic peak (peak A), followed by a passive region. The passivation may be related to the formation and precipitation of oxide film on the electrode surface. The data reveals that increasing isobutyric acid concentration, temperature, and scan rate enhances the anodic peak current density (I_{PA}) and shifts its peak potential towards more positive values. Additions of some polyethylene glycols to the isobutyric acid solution (pH 5) decrease the current density of the anodic peak and shift its peak potential towards the negative direction. These changes depend on the concentration and molecular weight of the polyethylene glycol added.

The anodic behavior of a tin electrode in maleic acid solutions was investigated by potentiodynamic and chronopotentiometric methods (69). Measurements were conducted under different experimental conditions. The results demonstrated that the polarization curves exhibit active/passive transition. In active regions, tin dissolves as Sn^{2+} which is subsequently oxidized to Sn^{4+} and the dissolution process is controlled partly by diffusion of the solution species. The passivity is due to the presence of thin film of SnO_2 on the anode surface formed by dehydration of precipitated $Sn(OH)_4$. The active dissolution of tin increases with increasing acid concentration, temperature and scan rate. The potential transients showed that the passivation time decreases with increasing applied current density. The effect of adding increasing concentrations of CrO_4^{2-}, MoO_4^{2-} and NO_2^{-} ions on the anodic behavior of tin in maleic acid was studied. These ions inhibit the active dissolution of tin and promote the attainment of passivity. The extent of these changes depends upon the type and concentration of the inhibitor.

The corrosion behavior of tin in acetic acid solution of concentration range (2.00-0.001 M) was studied by potentiodynamic polarization technique (70). The corrosion potential, E_{corr}, and the corrosion current, I_{corr}, against pH of acetic acid solution show a linear relationship. The anodic reaction order with respect to OH^- ions is 0.4 while the cathodic reaction order with respect to H^+ is 0.93.

The anodic behavior of tin in 0.05 M solutions of oxalic, citric and tartaric acids in the pH ranges 2.5-6 and at temperature 25-60°C was investigated by potentiostatic technique (71). The polarization curves exhibit two anodic peaks. The peak heights for the two peaks increase with increasing solution pH and temperature. The corrosion of the tin is affected by formation of soluble complex species with organic acid anions and the order of decreasing aggressiveness is oxalic> citric> tartaric acids.

The electrode potentials of tin in citric, malic, oxalic and tartaric acids in solutions of the concentration range appropriate to canned fruits were measured (72). From these measurements the authors estimated the stability constants of the complexes formed by tin with the anions of the cited acids. The stability constants suggested are highest for oxalic, similar to one another for citric and malic acids and a little lower for tartaric acid. Corrosion rates of tin in oxygen-free solutions of the acids fall in the same order as the stability constants, reflecting the influence on the potential of the tin electrode of changes in Sn^{2+} concentration.

The anodic behavior of tin electrode in Na_2CO_3 solutions containing different concentrations of Na_2ClO_4 was studied by potentiodynamic technique and complemented by scanning electron microscope (73). In perchlorate free carbonate solutions; the polarization curves exhibit two anodic peaks assigned to the electroformation of Sn(II) and Sn(IV) species, respectively, prior to the permanent passivation region. The passivity is due to the presence of SnO and SnO_2 layers on the electrode surface. Addition of ClO_4^- ions to the carbonate solution break down the passive layer and initiate pitting corrosion at a certain critical pitting potential. The pitting potential decreases with an increase in ClO_4^- concentration but increases with increasing both Na_2CO_3 concentration and scan rate. Increase the concentration of MoO_4^{2-}, WO_4^{2-} or NO_2^- causes a shift of the pitting potential in the positive direction indicating the inhibition effect of added anions, while addition of NO_3^- anion accelerates the perchlorate pitting corrosion.

Electrochemical impedance spectroscopy (EIS) was used to study the dissolution, passivation and pitting corrosion of tin electrode in aqueous solution of Na_2CO_3 in absence and presence of Cl^- and I^- ions (74). Two simplified equivalent circuits were fitted to the experimental impedance data. The proposed model describes the main features of the characteristic behavior of the electrode process including the formation of passive and active pits. EIS was used to obtain electrolyte resistance, pore resistance, polarization resistance and fractal dimensions of tin electrode in the above-examined solutions. The data indicates that the corrosion rate and the pitting corrosion were increased by the addition of halide ions.

The corrosion and passivation of tin anode in Na_2CO_3 solutions were studied (75) by using potentiodynamic and cyclic voltammetry techniques and complemented by X-ray and scanning electron microscopy. The polarization curves exhibit two anodic peaks assigned to the electroformation of Sn(II) and Sn(IV) species, respectively, prior to permanent passive region. The anodic dissolution reactions are controlled by diffusion. X-ray diffraction showed that the permanent passive layer is duplex and consists of SnO and SnO_2. A multiplicity of cathodic peaks is related to the electroreduction of anodically formed compounds. Addition of Cl^-, Br^- or I^- ions into the carbonate solutions enhances the anodic dissolution of tin to some extent depending upon the sodium carbonate concentration. In passive region, addition of halide ions causes pitting corrosion at a critical pitting potential. The pitting potential decreases with increasing both the halide ions concentration and the scanning rate but increases with increasing the sodium carbonate concentration. SEM examination confirms the occurrence of pitting corrosion

The anodic oxidation of tin in carbonate–bicarbonate solutions covering a wide range of pH and electrolyte composition has been studied by voltammetric techniques and scaning electron microscopy (SEM) (76). The influence of switching potentials, potential scan rate, rotation speed and surface condition are reported. SEM micrographs of the electrode surface show considerable differences in the characteristics of the surface products, whether they were formed in the potential region of the electroformation of stannous oxide and hydroxide or Sn(IV)-containing species which dehydrates into the most stable species. From the dependence of the charges on the potential scan rate it may be inferred that a direct oxidation of Sn(0) to Sn(IV) exists besides the sequence Sn(0) to Sn(II), and Sn(II) to Sn(IV). The effect of the initial surface state on the anodic reactions is better recognized for a rotated electrode. Analysis of the first and second voltammetric cycles through the changes of the anodic current densities with rotation speed, suggest that the initial electrooxidation process at a freshly prepared electrode surface does not follow a dissolution–precipitation mechanism. The formation of soluble corrosion products is enhanced in the potential range of the secondary passivity as the ionic strength of the buffer increases.

The anodic behavior of a tin electrode in NaOH solutions containing different concentrations of $NaClO_4$ was studied by employing potentiodynamic, potential transient under constant current density methods and complemented with scanning electron microscopy (SEM) (77). In perchlorate-free NaOH solutions, the E/I response exhibits active/passive transition. The active region involves two anodic peaks corresponding to the formation of Sn(II) and Sn(IV) species respectively. The permanent passive layer is duplex and consists of SnO and SnO_2. Additions of $NaClO_4$ to the alkali solution, accelerates the active dissolution of tin and tends to breakdown the duplex passive layer at a certain breakdown potential. SEM examination confirms the occurrence of film breakdown. The breakdown potential decreases with an increase in ClO_4^- concentration, but increases with increasing both OH^- concentration and scan rate. The potential–time transients display that the incubation time for pit initiation decreases with increasing both ClO_4^- concentration and anodic current density.

The corrosion behavior of tin in 6 M KOH at room temperature was investigated using cyclic polarization (78). The study revealed a relatively large anodic and cathodic over potentials for water decomposition that depend on the surface structure of the material. Polished tin electrodes also underwent a slow reaction during anodic polarization above the reversible potential for O_2 evolution that involved the formation of a reaction product film. The film was uniform over the surface of the electrodes and contained hydrous potassium titanate. A corrosion product, similar in composition but less uniform in appearance, was formed on tin after 4 months under open-circuit condition in the same solution. Results indicated that the film was formed slowly by a dissolution-precipitation mechanism and that the dissolution step gives rise to an oxidation peak observed in the cyclic voltammogram during anodic polarization. Since the film is formed above the reversible potential for O_2 evolution and since the over voltage for O_2 evolution depends on surface structure, it is not yet clear whether the formation of the corrosion film will complete with electrolysis reactions during the charging of structurally tailored, high surface area, tin electrodes that are under development for ultra capacitor applications.

The corrosion of tin electrode in sodium borate solutions was investigated (79) using cyclic voltammetry and potentiostatic current transient techniques. In absence of halide ions, the E/I response exhibits active/passive transition. The active region involves one anodic peak corresponding to the formation of $Sn(OH)_2$ and/or SnO. Addition of Cl^-, Br^- or I^- ($C \leq 0.01$ M) ions inhibits the active dissolution of tin, but higher concentrations enhance the active dissolution and tend to breakdown the passive film and induce pitting attack. The effect of WO_4^{2-} , MoO_4^{2-} , NO_2^- and NO_3^- as inorganic inhibitors on the pitting corrosion of tin in (0.1 M $Na_2B_4O_7$ + 0.1 M NaCl) solution was studied. The presence of these anions (except NO_3^-) inhibits the pitting corrosion. Chronoamperometry measurements showed that nucleation of pit takes place after an incubation time (t_i). The rate of pit nucleation (t_i^{-1}) increases with increasing halide ions concentration and applied potentials, but decreases with increasing the concentration of the inorganic inhibitors (except NO_3^-). The inhibition efficiency of these inhibitors decreases in the order: $WO_4^{2-} > MoO_4^{2-} > NO_2^-$.

The corrosion and passivation of tin in sodium borate solutions at pH=8.35 were studied by potentiodynamic and cyclic voltammetry techniques (80). The effect of the concentration of borate ion, pH, potential scan rate, successive cyclic voltammetry, switching potential and progressive additions of halide ions on the anodic dissolution and passivation of tin metal are discussed. The primary passivation is attained when the metal is covered with a film of $Sn(OH)_2$ and/or SnO. Permanent passivity occurs when $Sn(OH)_4$ and/or SnO_2 forms a continuous layer on the electrode surface. The anodic dissolution reactions are controlled by diffusion. In all experiments, the aggressive action of the halides decreased in the order $Cl^- > Br^-$. SEM examination confirms the occurrence of pitting corrosion in presence of halide ions. The pitting potential (E_{pit}) decreases with increasing the halide concentration.

The nucleation formation and growth of thin oxide films on tin in a borate buffer solution at pH 8.2 were studied using potentiodynamic and galvanostatic techniques (81). The results indicate reaction controlled kinetics for processes initiating passivity under dynamic conditions. Oxide growth rate is controlled by a nucleation process. Under galvanostatic conditions the behavior of tin resembles in many respects the kinetics of anodization of valve metals. Oxide film growth occurs by an activation-controlled ionic condition under the influence of a high electric field across the film according to an exponential law as on valve metals.

The tin passivation in borate buffer was studied (82) using potentiodynamic curves recorded at high scanning rate (9 V min^{-1}, 3.6 V min^{-1}). The most important feature of these curves is the presence of a current peak at around -1180 mV (SCE) which had not been previously observed. The nature of the passive film formed in the vicinity of this potential was characterized using in situ Mössbauer measurements. On the basis of these results it was concluded that in borate buffer solution:

(a) the passive film formed at more negative range of potentials (-1180 to - 780 mV) is duplex, consisting of highly amorphous $Sn(OH)_2$ or hydrated stannous oxide and SnO_2 or $Sn(OH)_4$; (b) at more positive potentials, the passive layer consists only of Sn(IV) hydroxide or oxide which ensures a more efficient passivation.

The anodic oxidation of tin in 0.2 M borate buffer solution has been studied by potentiodynamic, potentiostatic and galvanostatic techniques(83). It was found that although a large amount of charge is consumed during anodic oxidation, only a fraction of this charge is involved in film growth. The initial stages of metal passivation under dynamic conditions are best described by Mueller's dissolution-precipitation model. Under potentiostatic conditions two different equations describe the kinetics of film formation. For anodic potentials lower than 1.6 V (SCE) a logarithmic dependence holds between cathodic charge and time. At higher potentials, the growth rate is controlled by a nucleation process and the rate law is more complicated. Under galvanostatic conditions the logarithms of the growing time is proportional to the inverse of the cathodic charge. These results are discussed in terms of theories of film growth.

The effect of dichromate, chromate, molybdate, nitrite and nitrate anions on the chloride pitting corrosion of tin in each of the following solutions: Na_2CO_3 (pH = 10.9), $Na_2B_4O_7$ (pH = 8.35) and Na_2SO_4 (pH = 6.8) (each solution containing 0.1 M NaCl) has been studied (84). The potentiodynamic technique was used, complemented by X-ray and SEM. Addition of increasing concentrations $Cr_2O_7^{2-}$, CrO_4^{2-} or MoO_4^{2-} caused a shift of the pitting potential (E_{pit}) in the positive direction indicating the inhibitive effect of the added anions on the pitting corrosion. The absorption characteristic of these anions on the metal surface plays a significant role in inhibition. The NO_2^- anion has a little inhibitive effect of pitting corrosion but the NO_3^- anion is ineffective as an inhibitor, and actually increases pitting corrosion. The pitting corrosion of chloride ions and other aggressive anions in the solutions is completely suppressed at concentration sodium dichromate. The MoO_4^{2-} species limits the growth of the passive film, restricts Cl^- anions and inhibits the pitting corrosion.

The influence of natural honey (chestnut and acacia) and natural honey with black radish juice on corrosion of tin in aqueous and sodium chloride solutions was studied using weight loss and polarization techniques (85). The inhibition efficiency of acacia honey was lower than that of chestnut honey, while the addition of black radish juice increased the inhibition efficiency of both honey varieties. The process of inhibition was attributed to the formation of multilayer adsorbed film on the tin surface. The adsorption of natural honey and honey with black radish on tin was found to follow the Langmuir adsorption isotherm.

The effect of various concentrations (0.5 to 30 ppm) of polyacrylamide samples which have different molecular weights (sample $A=3.4\times10^4$, $B=1.52\times10^4$ and $C=1\times10^4$ g mol^{-1}) and poly(propenoyl glycine)(sample D) which has the same degree of polymerization (D_p) of sample C on the corrosion behavior of tin in 1 M NaCl solution at 20^oC were studied using potentiodynamic polarization technique (86). The various electrochemical parameters (I_{corr}, R_p, E_{pit} and I_p) were calculated from Tafel plots in the absence and presence of these polymers. The data reveal that the inhibition efficiency of polymer C is higher than that of polymer, while the presence of polymer A (the highest molecular weight) accelerates the corrosion of tin in 1 M NaCl indicating that the inhibition decreases with increasing molecular weight. On the other hand, polymer D shows the strongest inhibition efficiency. For the investigated polymer inhibitors B, C and D, it was found that the experimental data fit Flory-Huggins adsorption isotherm. The effect of temperature on various corrosion parameters and the inhibition efficiency was studied for polymer D (10 ppm) in 1 M NaCl over temperature range from 20^oC to 50^oC.

The nature of the oxide layers formed on a Cu-13Sn (wt%) alloy in 0.5 M NaCl aqueous solution was characterized (87) to compare their properties to those obtained on pure copper and pure tin samples. It was found that for Cu-13Sn alloy, Cu_2O and SnO_2 were simultaneously present at the surface, for short immersion times in the NaCl solution. This result was confirmed by XPS measurements. Nevertheless the predominance of copper(I) oxide became clear after 48h immersion. For comparison, similar measurements were performed and discussed in the presence of BTA, an inhibitor of the copper corrosion. Coulometric analyses and impedance measurements showed that the behavior of a Cu-13Sn alloy is very similar to the behavior of pure copper in a 0.5 M NaCl solution with and without BTA. A main difference between the two materials consists in a different thickness of the corrosion layer. The photo electro-chemical method showed interesting possibilities as an in-situ analytical tool in the field of oxide growth, not only on pure metals but also on alloys. The simultaneous presence of SnO_2 and Cu_2O on a Cu-13Sn sample was inferred from this method and checked by XPS measurements, while potentiodynamic experiment was unable to distinguish between the two oxides. A p-type semi conductivity was observed for copper and for bronze at low immersion times in NaCl. Differences appeared for longer immersion times. The semi conductivity remained of the p-type in the case of copper. The differences in the behavior between pure copper and Cu-13Sn alloy were explained in correlation with the growth mechanism of the oxide layer under cationic migration control.

The corrosion behavior of tin in salt solutions at various temperatures and in the presence of air, nitrogen and oxygen atmosphere was investigated (88). For this purpose, model salt solutions containing sodium chloride (2 wt%) and sodium chloride with 0.002 wt% nitrite and nitrate were prepared. The system was chosen to perform the corrosion processes which could take place during the thermal treatment of some food products in tin plate cans, in the presence of oxidizing salts and different atmospheres. Electrochemical investigations were performed using potentiostatic and galvanostatic polarization methods. From the experimental data, the corrosion current, corrosion potential, polarization resistance and electron number were calculated. Auger electron spectroscopy and the XPS technique were used to determine the chemical composition investigations of solid surface. A possible corrosion mechanism was proposed.

The effect of the addition of oxo-anions MoO_4^{2-}, SiO_4^{2-}, HPO_4^{2-} and HCO_3^{-} on the corrosion and passivation of tin in a synthetic medium similar to industrial water has been studied by using electrochemical techniques (89). The results show that tin manifests a passivation phenomenon with breakdown of passivity. Addition of oxo-anions leads to retard a breakdown of passivation and the inhibition of pitting process of tin. The more marked inhibiting effect is obtained in the presence of MoO_4^{2-} and SiO_4^{2-}. The detailed study of the influence of the MoO_4^{2-} shows that the pitting sensitivity of tin decreases when the molybdate concentration increases in solution. Then, these ions offer a good efficiency even at high temperature and for a chloride concentration up to 0.5 M.

The corrosion behavior of tin in Na_2SO_4 solutions at concentrations of 0.1–1.0 M and in the pH range 3–11 was investigated by using potentiodynamic and cyclic voltammetry techniques (90). The voltammograms involve two anodic peaks prior to the initiation of pitting corrosion. The first peak corresponds to the formation of $Sn(OH)_2$ and/or SnO. The second peak correlates to the formation of $Sn(OH)_4$ and/or SnO_2. The pitting initiation can be explained through the adsorption competition between sulphate anions and the passivating species on the passivated electrode surface. The critical pitting potential depends on the sulphate concentration, pH and scan rate. Three cathodic peaks are observed on the negative-going scan, corresponding to the reduction of the dissolved pitting corrosion products, SnO_2 and SnO respectively. Successive cycling has no significant influence on the pitting potential, but leads to a progressive decrease in the heights of the anodic peaks as a result of incomplete reduction during the cathodic sweeping.

The anodic behavior of tin in perchlorate, sulphate, nitrate and acetate solutions was investigated (91) under the influence of acidity and concentration of the electrolyte by potentiodynamic polarization technique. The results showed that the passivation of tin in these solutions is due to the formation of $Sn(OH)_2$ and $Sn(OH)_4$.

Aim of the work

The corrosion behavior of tin in aqueous solutions and its inhibition are very important due to its widespread technological application especially in the manufacture of the cans used for reserving the food stuff, therefore, the study of the corrosion behavior of tin is very important as well as inhibition to prevent the food stuff contamination by its corrosion product.

The work was aimed to:

1) Investigate the corrosion behavior of tin in both $NaHCO_3$ and NaCl solutions.

2) Investigate the inhibiting effect of some inorganic compounds, such as sodium salts of chromate, molybdate, tungstate and phosphate, and some plants extracts as corrosion inhibitors for dissolution of tin in both $NaHCO_3$ and NaCl solutions.

3) Determine the rate of corrosion of tin in absence and presence of some inorganic compounds and some plants extracts by galvanostatic polarization method.

4) Study the pitting corrosion of tin in $NaHCO_3$ and NaCl solutions and the effect of some inorganic compounds and some plants extracts as pitting corrosion inhibitors using potentiodynamic anodic polarization measurements.