

Inhibition of carbon steel corrosion in closed-loop-water heating/cooling systems using sodium caprylate as an environmentally-friendly corrosion inhibitor

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ABSTRACT

Carbon steel (CS) is widely used in water transporting systems because of its exceptional mechanical properties. However, CS is highly prone to corrosion, and uniform corrosion is the most common form of corrosion that affects CS. The internal corrosion of CS equipment is the main reason behind the failure of a closed loop water heating/cooling system. Water quality parameters like dissolved salts and gases, low pH, high temperature, galvanic and microbial activity greatly affect the rate of internal corrosion. Thus, it is important to mitigate internal corrosion of CS. One common way of mitigating corrosion is by using corrosion inhibitors. However, the commercially available corrosion inhibitors are found to be toxic and current research is focused on developing environmentally-friendly corrosion inhibitors.

The objective of this work is to investigate the possibility of using sodium caprylate (SC) as an environmentally-friendly corrosion inhibitor for closed-loop-water heating/cooling system with CS as the substrate (material of construction) and the Montreal tap water as the electrolyte, under various conditions; concentration of SC, water temperature and pH, and time. Four electrochemical techniques and scanning electron microscopy were employed in the study.

The results revealed that SC offered a 96% corrosion inhibition efficiency at 10mM concentration and at pH 8 and room temperature (295 K). The inhibition efficiency was found to be SC concentration dependent. Two distinctive regions of efficiency (lower/high) were identified, with the sharp transition occurring when going from 6.28mM to 6.3mM of SC in the water. The corresponding low-to-high corrosion inhibition efficiency transition can be linked to the abrupt change in surface concentration and orientation of SC. Experiments at varying temperature revealed that SC can also efficiency inhibit corrosion up to 333K. The inhibitor can also efficiently inhibit corrosion in the pH range form 7-10 pH. The kinetics study showed that adsorption SC onto the CS surface is very quick (within a couple of minutes). Furthermore, surface analysis study using SEM showed that for CS kept in 10 mM SC solution for 30 days at 295 K, there was negligible corrosion as compared to the sample that was kept in the inhibitor-free solution. In conclusion, SC can efficiently be used as a corrosion inhibitor for water heating/cooling systems made of CS, up to 333K.

ABRÉGÉ

L'acier au carbone (AC) est couramment utilisé dans les systèmes de transport d'eau à cause de ses propriétés mécaniques exceptionnelles. Cependant, l'AC est très susceptible à la corrosion, et la corrosion uniforme est la forme de corrosion la plus commune qui l'affecte. Cette corrosion interne d'équipement en AC est la cause principale de défaillance des systèmes de chauffage/refroidissement à boucle fermée. Les paramètres de qualité d'eau comme la quantité de sels et gaz dissous, le niveau de pH, la température, et l'activité galvanique et microbienne affectent le taux de corrosion interne. Ainsi, il est important de réduire la corrosion interne de l'AC. Une façon courante de réduire la corrosion est d'utiliser des inhibiteurs de corrosion. Cependant, les inhibiteurs de corrosion commerciaux sont toxiques et la recherche actuelle est concentrée sur le développement d'inhibiteur de corrosion écologiques.

L'objectif de cette thèse est d'investiguer la possibilité d'utiliser le caprylate de sodium (CS) comme inhibiteur de corrosion écologique pour les systèmes de chauffage/refroidissement à boucle fermée en utilisant de l'AC comme matériel de construction et l'eau courante de la ville de Montréal comme électrolyte sous des conditions variables: concentration de CS, température de l'eau, pH, et temps d'utilisation. Quatre techniques électrochimiques et la microscopie électronique à balayage ont été utilisées dans cette étude.

Les résultats ont démontré que le CS a offert une efficacité d'inhibition de corrosion de 96% à une concentration de 10 Mm, un pH de 8, et à température ambiante (295 K). Cette efficacité d'inhibition dépend de la concentration du CS. Deux régions d'efficacité distinctes (basse/élevée) ont été identifiées, la nette transition entre les deux étant située entre 6.28 mM et 6.3 mM de CS dans l'eau. La transition correspondante d'un bas à haut niveau d'efficacité d'inhibition de corrosion peut être reliée à l'abrupt changement dans la concentration de surface et l'orientation du CS. Des expériences à températures variable ont démontré que le CS peut inhiber la corrosion de manière efficace jusqu'à une température s'élevant à 333K. L'inhibiteur peut également inhiber la corrosion du CS sur la surface d'AC était très rapide (moins que deux minutes). De plus, l'analyse de surface par microscopie électronique à balayage a démontré que, pour de l'AC préservé dans une solution de CS a 10mM pendant 30 jours à 295 K, la corrosion était négligeable relativement à un

échantillon préservé dans une solution dépourvue d'inhibiteur. En conclusion, le CS peut être utilisé efficacement comme inhibiteur de corrosion pour les systèmes de chauffage/refroidissement en AC, pour des températures s'élevant jusqu'à 333 K.

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CHAPTER 1: Introduction

Water is regarded as a special engineering material. It is widely used as a cooling fluid in various industrial and domestic processes to remove undesired heat from the surfaces of heating equipment. It is also used for heating (e.g. water-heaters in domestic and industrial buildings, etc.). However, there is scarcity of clean water all around the globe due to rising population and increasing development. Thus, it is important to reuse water as many times as possible for both domestic and industrial processes. In a closed-loop-water system, a fixed volume of water is recirculated in a closed cycle and it undergoes alternate heating and cooling without being exposed to air. Thus, a very little loss of water takes place over time and this helps in reducing water usage. This thesis is mainly focused on closed-loop water heating/cooling systems like the central heating system installed in apartments, hospitals, universities etc. A central heating system comprises of a heat source in the form of a boiler or a heat exchanger and a heat sink which is the radiator. Water is circulated in between the heat source and the heat sink. The heating equipment of a central heating system are made of various alloys like stainless steel, aluminum, copper and carbon steel. Due to low cost and exceptional mechanical properties, one of the most widely used alloys for making heat exchangers, radiators, boilers, pipes that build-up the closed-loop heating/cooling systems is carbon steel. [1-5].

However, closed-loop heating/cooling systems are highly prone to internal corrosion of the carbon steel equipment. Presence of water in the equipment of closed-loop water heating/cooling systems make them susceptible to internal corrosion. In United States, the annual losses sustained due to corrosion problem in industrial and government sector are approximately 276 billion USD or 3.1% of its Gross Domestic Product (GDP). The destructive effect of corrosion is a significant issue in the maintenance and operation of closed-loop-water heating/cooling system. Corrosion in closed-loop-water heating/cooling systems occur due to water quality parameters like dissolved oxygen and other gases, dissolved salts, high temperature, low pH and galvanic activity between two dissimilar metals and microbial activity. Dissolved oxygen is one of the primary factor that affects the rate of internal corrosion. Also, due to presence of high temperatures in the heating systems like boilers and heat exchangers, rate of internal corrosion accelerates as the dissolved oxygen in the system reacts with metallic surface at a faster rate. In other words, corrosion is an

electrochemical reaction which involves movement of electrons from the anodic site to the cathodic site in presence of an electrolyte. Because of corrosion, the erosion and loss of the metallic structure occurs. However, loss of a metal does not imply the loss of the metal only, it also takes into consideration the amount of energy used, amount of water lost due to leakage and failure of equipment and the human labour associated with fabrication of the entire metallic system. And thus, re-fabrication of the metallic structure damaged by corrosion would require investment of all these resources which estimates to millions of dollars and this is accounted as direct economic loss. However, indirect economic losses like shutdown of the entire process plant, loss of products, like leakage of water to the environment, loss of efficiency leading to minimized heat transfer caused by clogging of pipes due to presence of corrosion products and contamination of water, are accounted as additional costs related to corrosion problem. [5-6]

Therefore, it is important to mitigate corrosion. There are various ways to reduce the internal corrosion attack of carbon steel machinery; however, the best option is use of corrosion inhibitors. Some of the widely used corrosion inhibitors for water systems made of ferrous alloys are molybdate, nitrites, chromates and polyphosphates, which are discussed elaborately in Chapter 2. However, it is seen that the commercially available corrosion inhibitors for aqueous systems possess toxic properties and their use has become a big concern due to environmental rules and regulations. Hence, in the recent times the focus has shifted towards development of such corrosion inhibitors which are derived from natural sources, like plants. Also, in recent times organic molecules, that are bio-degradable and environmentally compatible like the carboxylates are receiving acceptance as corrosion inhibitors. Moreover, a corrosion inhibitor should also be readily available and be of low cost.

Thus, this thesis report is mainly focused on investigation of Sodium Caprylate (SC) as an environmentally-friendly corrosion inhibitor for inhibiting internal corrosion in closed-loop-water heating/cooling system. SC is an organic molecule and comprises of carboxylate group as the functional group. The reason for choosing SC as the green inhibitor is that carboxylate group is non-toxic and readily bio-degradable in nature and being a straight chain carboxylate, it has shown good inhibition towards number of alloys, especially carbon steel. [7] This current work mainly investigates the interaction of SC with the carbon steel surface under various experimental conditions like; varying concentration of SC, pH and temperature, and measures the inhibition

efficiency of the corrosion inhibition process under these conditions. The electrolyte used for this thesis is the Montreal tap water. Also, this work investigates the kinetics of the SC adsorption process and studies the topography of the carbon steel substrate in an un-inhibited and inhibited solution using Scanning Electron Microscopy (SEM).

The thesis is divided into six chapters. Firstly, in Chapter 2: Background and Literature, elaborate discussions and reviews are done w.r.t to corrosion problem in closed-loop-water heating/cooling systems. Also, discussion about various corrosion controls methodologies and environmentally-friendly corrosion inhibitors is presented. In Chapter 3, main objectives of this thesis work are presented. Chapter 4 gives an overview of the experimental procedures, chemicals/ materials and solutions and the various electrochemical and surface characterization techniques that are extensively used in this work. Chapter 5 presents and discusses the results obtained. Finally, Chapter 6 summarizes the major conclusions related to this thesis.

CHAPTER 2: Background and Literature Review

Corrosion is a spontaneous process which starts at the surface of the metallic structures and causes damage to the metallic structures by unintended chemical or electrochemical actions. The main reason why a corrosion reaction occurs is "to lower the free energy of the system." When metals are formed from their ores, they possess higher free energy than their ores. Metals tend to revert to the state of low energy and transform back to their ores, i.e. the native oxide state in most cases, by the spontaneous process of corrosion.[5] Depending on the type of metal and the environment in which they are placed, most metals have the tendency to get oxidized. However, some of them easily get oxidized as compared to others, which can be evaluated with the help of Galvanic series. While deciding the corrosion resistance performance of any alloy, composition and microstructure of the alloy are the two important factors. From microscopic point of view, metallic surfaces are not homogeneous. They are rough or irregular in nature and because of these irregularities, surfaces possess different chemical and energetical properties. Grain boundaries are such areas of atomic mismatch between two adjacent microscopic regions. These regions of mismatch or imperfection possess greater energy state and higher chemical reactivity and are considered active sites for onset of corrosion. [8]

Corrosion can be classified into three types based on the mechanism of their reaction; chemical, electrochemical and physical corrosion. Chemical corrosion reaction is a heterogeneous reaction that is based on basic laws of chemical kinetics. It refers to corrosion of metals dipped in non-electrolyte/dry gases and it is not accompanied by flow of electrons. Physical corrosion reaction is based on metallic corrosion reaction of a solid metal kept in contact with a liquid metal. Electrochemical corrosion reactions involve flow of electric current and involve two set of spontaneous reactions namely anodic reaction and cathodic reaction. The anodic reaction involves oxidation reaction which leads to dissolution of the metal. The cathodic reaction can be of various types depending on the type of environment; reduction of metal, deposition of metal, consumption of oxygen and evolution of hydrogen.[9]

The corrosion reaction occurring in presence of water is mostly electrochemical in nature. In order, for corrosion attack to initiate on the surface of the alloy kept in water medium, there must be a difference in potential at various regions of the surface to facilitate flow of electricity from region of high potential to region of low potential across the metallic surface. The surface of iron alloys for example steel gets divided into two regions namely anodic (iron dissolution occurs) and cathodic (where a reduction reaction happens) as shown in **Figure 2.1** below.



Fe(s) (iron)



There are four essential components for an electrochemical reaction - 1) anodic part or low potential region, 2) cathodic part or high potential region, 3) electrically-conducting material and 4) an electrolyte, all kept in direct contact with each other. Corrosion is categorized into eight forms namely uniform corrosion, galvanic corrosion, stress corrosion, pitting corrosion, crevice corrosion, intergranular corrosion, selective leaching and erosion corrosion. The main objective of this report is to study uniform corrosion, which leads to uniform depletion of the metallic surface without any appreciable localized damage.

2.1 Corrosion and water quality

Water is widely used in industrial and domestic processes as a heat transfer medium or a cooling medium to remove heat from heat transfer equipment and for production of steam. Water finds applications with regards to hot processes due to its high heat capacity. [1] However, non-deionized cooling water is corrosive to most alloys as it is not pure. Water quality greatly influences the corrosivity of water. Various factors like concentration of dissolved gases and salts,

pH, temperature, bacterial growth, scale deposition that have an impact on water quality are described elaborately in the section below: [5-6]

1. **Dissolved gases:** Dissolved Oxygen (DO) comes from ambient air and is excessively present in water. The rate of carbon steel corrosion is proportional to oxygen content in water and DO plays an important role in the composition of corrosion films on carbon steel surface. It boosts up the reduction reaction by acting as the main electron acceptor. It is a cathodic depolarizer or a strong oxidant which causes oxidation of the metal at the anode and reacts with hydrogen at the cathode, which accelerates the corrosion attack. Solubility of oxygen varies with pressure, concentration of electrolytes and temperature of water. In comparison to oxygen, carbon dioxide is more soluble in pure water (1.3 gL⁻¹ at 303 K). It converts to Carbonic acid (H₂CO₃) as shown in the reaction below and brings down the solution to pH 6 where acid attack can prevail.

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$
(2.1)

 CO_2 has more impact in boiler condensate systems, where H_2CO_3 reacts with steel to produce ferrous bicarbonates, which are highly soluble salts and can result in thinning of the iron alloy. Chlorine is not naturally found in cooling waters; it is added for biological control. Ammonia also can affect heat transfer equipment. It has detrimental effects on copper alloys, however it does not affect iron alloys. [5,10]

2. pH: It is defined as the hydrogen ion (H⁺) concentration in a solution. Low pH implies more number of hydrogen ions and higher pH implies low number of hydrogen ions. Low pH or acidic solutions increase the rate of corrosion due to high supply of hydrogen ions. For closed loop systems, pH is maintained at pH 8.5 to pH 9; in boiler systems water has a pH of 11. Uniform corrosion is the predominant form of attack in acidic medium, i.e. pH 5 and below. With increase in pH, i.e. above pH 4, iron oxides precipitate from the solution leading to formation of deposits. These deposits obstruct the diffusion of oxygen towards the metal surface, resulting in decrease of corrosion. Also, with increase in pH, the nature of the iron oxide deposits transform from loosely adhering form (at pH 6) to hard and persistent form at pH 8. To bring down the rate of corrosion to a manageable limit of less than 0.13 mm yr⁻¹, in case of aerated water systems made of steel within pH range of 6.5

to 9, chemical treatment is required. When the pH of waters containing moderate levels of calcium increases, $CaCO_3$ scales are formed, which reduce mass transfer of oxygen to the metal surface along with formation of a heat transfer barrier.[5]

- 3. **Temperature:** Temperature plays an important role in corrosion reaction. The rate of corrosion reaction for a given oxygen concentration doubles with every 303 K rise in temperature approximately, when the corrosion reaction is controlled by diffusion of oxygen. In an open system as the dissolved oxygen can escape, the rate of corrosion reaction increases with increase in temperature to about 353 K and then falls to a very low rate near about the boiling point. This occurs because of low solubility of oxygen in water at higher temperatures. However, in a closed system the dissolved oxygen cannot escape and thus the rate of corrosion increases until the entire oxygen reserve is consumed.[6]
- 4. Microbial activity: Most engineering alloys with exception of titanium along with high nickel-chromium alloy are damaged due to corrosion caused by microbial activity. Microbes stick to the metal surface and form a biofilm which accelerates the corrosion attack. This type of microbial growth is referred to as biofouling and it has various detrimental effects. Water recirculation systems are an ideal environment for growth and proliferation of microorganism like algae, bacteria and fungi. They can interrupt the flow of water through heating equipment like heat exchangers and other similar conduits. Biofouling interferes with heat transfer by significantly reducing heat transfer efficiency, contributes to internal corrosion and leads to damage of the entire water circulating system. Massive growth of microbes hinders proper water distribution by plugging of screens and interfere with pump suction. [5-6]
- 5. **Dissolved salts:** The dissolved constituents in water can have great impact on water quality. The conductivity of water increases due presence of dissolved salts, which influences the corrosion rate as well as scale formation. Hardness ions like calcium and magnesium along with HCO₃⁻ impart inhibition to corrosion attack and it is seen that soft waters with lower concentration of calcium and magnesium is more corrosive than hard waters with higher amount of calcium and magnesium ions. Chloride and sulphate ions are harmful for iron alloys. Cl⁻ ions being small and highly mobile migrate towards the anodic

site and neutralize the Fe^{2+} ions which are produced when iron dissolves. Cl^- ions can adsorb on the metallic surface and interfere with the formation of passive film, which leads to uniform corrosion in carbon steel. Sulphate ions do not possess film piercing abilities like Cl^- ions and they are elusive in their effect on corrosion. Other ions that are commonly found in cooling water systems are manganese, sulfide, phosphate and nitrites. [2,5-6]

- 6. Scaling and fouling deposits: A scale can be defined as a crystalline growth of insoluble salts or oxide which adheres on the surface of heat exchanger. The rate of scale formation is determined by certain variables like temperature, concentration of scale-forming species, pH, water quality and hydrodynamic parameters. In general, solubility of scales increase with rise in temperature, however CaCO₃ and CaSO₄ follow a reverse trend. CaCO₃ is the most common scale formed in cooling water systems and it acts as a heat transfer barrier. Loose and insoluble materials suspended in water in the form of water borne deposits are called foulants. Some examples of such foulants are migrated corrosion products, clays, silts, suspended sand particles, biological matter, twigs etc. They interfere with water flow of a cooling system and lead to reduction in heat transfer.[5]
- 7. **Galvanic activity:** When a metal meets another metal in a corrosive and conducting environment, galvanic corrosion is initiated. The corrosion reaction occurs because of potential difference that exists between the two metals, the more noble metal acts as the cathode and the active metal corrodes by acting as an anode.[11]

2.2 Corrosion in closed-loop-water-heating/cooling systems

Due to rise in population worldwide and increasing development, it is important to utilize the limited water supplies in a proper way. In a closed-loop water system, water is constantly recirculated and it alternately undergoes heating and cooling without being exposed to air. Since it is a closed-loop system, a very small amount of water is lost over time. Thus, one of the biggest advantage of a closed-loop-water system is that water is reused again and again and makeup water is minimum. [1,5,12].

Closed-loop-water-heating systems deliver warmth to the interior of homes, hospitals, universities etc. One most common example of a closed-loop-water-heating/cooling system is the central heating system. A central heating system comprises of an energy source or fuel supply, a heat exchanger or boiler for heating water, a pump to circulate water and a radiator to release heat to the interior spaces. A typical design of a radiator contains two mild steel separate sheets of 1-2 mm thickness. The water pipes are generally made of iron and copper alloys. The heating modules present in boilers are made of steel, mild steel, copper and aluminum alloys. Steam boilers are constructed into various designs and mostly they are made of low carbon steel. The mains water is in the pH range of 6.5-8. The closed-loop water cooling systems that are used for extracting heat from the heating equipment are generally kept at basic to neutral pH. The maximum temperature at exit point of the boiler is 353 K. [2,13]

However, internal corrosion is a very big concern in these closed-loop systems. Central heating systems are attacked by corrosion due to various reasons like - 1) use of mixed metallurgy, 2) excessive use of flux leading to high chloride level, 3) microbial activity and 4) nucleate boiling that occurs on the surface of heat exchangers and boilers. Even though the dissolved oxygen concentration is very low in closed-loop water systems, corrosion attack continues in machinery made of cast iron and aluminum. In closed-loop water systems, oxygen enters the system through pump seals, design faults and poor joints on the negative pressure region of the pump. To protect boilers from internal corrosion, initial step is the removal of dissolved oxygen. Generally, the dissolved oxygen content prevalent in waters of heating systems becomes nil and the water is saturated with oxygen only when the water system is first filled up. Steel corrodes to small extent, while consuming the little amount of dissolved oxygen that is present before the water gets deaerated. At steady state the oxygen concentration is about 0.3 mg l⁻¹ and the corrosion attack is negligible in systems like central heating systems. Under such conditions, the lifespan of radiators and heat exchangers are more than 30 years. However, when fresh oxygen gets into the closedloop system due to design faults and other factors, the heating equipment falls apart only after 2 years of service. [2,14]

Other than dissolved oxygen, temperature is one of the main factors that accelerates the rate of corrosion in closed-loop systems. In a closed-loop system, the rate of corrosion attack increases linearly with temperature as oxygen cannot escape from the system. With increase in

temperature, the rate of oxygen diffusion towards the metal surface increases, this boosts up the cathodic reaction as more amount of oxygen is present and thereby increases the corrosion attack. [5] In mild steel, rate of corrosion is about 0.05-0.15 mm year⁻¹ at 288 K. When the temperature gets closer to 343 K, the rate of corrosion is 1.8 times greater and thus the corrosion rate goes up by 0.09-0.27 mm year⁻¹. [2]

Mineral scale deposits can cause major operational problems in water circulating systems. Silica and magnesium are highly un-desirable as they cause deposit formation and lead to catastrophic failures related to operations of process plants. The deposits bring about reduction in heat transfer rates in heating equipment such as boilers, heat exchangers, steam generators etc. Boiler operating conditions that lead to metal oxide formation and inorganic deposits on the water side of a boiler, causes local overheating, increased fuel consumption along with additional precipitation of solutes from water.[1] For mixed metallurgy comprising of two alloys like carbon steel and aluminum, the water chemistry is much more challenging since minimum corrosion rate is provided at two different pH ranges: pH 6.5 to pH 8.5 for aluminum and > pH 9 for carbon steel. [15]

Heating systems get contaminated due to presence of bacteria and the most common anaerobic bacteria is sulphate reducing bacteria (SRB), which grows in the pH range of 5-10 and temperature range of 278-323 K. It can convert sulphate ions into sulphide ions, which can accelerate the cathodic corrosion reaction and thus bring about corrosion of steel even in neutral oxygen free solutions. [2] Corrosion along with salt deposits and biofouling collectively cause deterioration to the metallic surface and cause loss of thermal exchange capacity which decreases the thermal efficiency of the entire circuit leading to severe economic losses. [16]

2.2.1 Carbon steel corrosion in closed loop water heating/cooling systems

Carbon steel is a very important alloy of iron. Low cost, exceptional mechanical properties and easy fabrication into pipes, boilers, heat exchangers make it the most widely used material of construction for most domestic and industrial processes. [17-22]. However, it is observed that water recirculating equipment made of carbon steel are highly susceptible to internal and various other forms of corrosion. Since the water recirculating systems are fabricated for longer service

life, maintaining them in good condition is of great concern. [23] Water chemistry variables like dissolved oxygen, temperature fluctuations, salts, other dissolved gases, microbial & galvanic activities impact the rate of internal corrosion. Carbon steel is generally damaged by uniform or general form of corrosion. Uniform corrosion is defined as uniform dissolution/depletion of the entire exposed metal surface. The metal surface becomes thinner and then ultimately it disintegrates and falls apart. [24] Corrosion in cooling and heating water systems have harmful impact on the health of human beings and animals besides having negative environmental impact and economic losses. The cathodic and anodic reactions of carbon steel in neutral aqueous medium are mentioned below [25].

Anodic reaction: It is that part of the corrosion reaction where oxidation of the metal takes place and metal losses electrons as shown below:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{2.2}$$

$$\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{e}^{-} \tag{2.3}$$

Cathodic reaction: It is the electrode where reduction reactions take place, where electrons are accepted as shown below for neutral solutions.

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2} \tag{2.4}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2.5}$$

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$
 (2.6)

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$$
 (2.7)

where Eqs. (2.4) and (2.6) occur at low pH, and (2.5) and (2.7) happen in the alkaline environment. Also, if oxygen is dissolved in the electrolyte, then its reduction is a preferential cathodic reaction.

Final corrosion product reaction for ferrous material is given as:

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$$\mathrm{Fe}^{2+} + 2\mathrm{OH}^{-} \to \mathrm{Fe}(\mathrm{OH})_2 \tag{2.8}$$

The primary corrosion products of carbon steel in aqueous medium are given below [26] 1) Fe_2O_3 or $Fe(OH)_2$: Hydrous ferrous oxide or hematite is the most common form of rust which is reddish-brown in colour.

2) Fe₃O₄xH₂O: Ferrous ferrite or hydrated magnetite, which is greenish or deep blue in colour.

3) Fe₃O₄: Magnetite which is black in colour.

In nearly neutral solutions, dissolved oxygen causes appreciable amount of internal corrosion of iron pipes. There are three rate determining steps, when oxygen induced corrosion of iron pipes is involved as given below [27]:

- 1) Oxygen diffusion to the metal surface.
- 2) Electron transfer reactions at the anodic sites.
- 3) Transportation of corrosion product from metal surface to the bulk.

The cathodic reactions (2.6) and (2.7) and the anodic reaction (2.2) are both influenced by the presence of dissolved oxygen. The dissolved oxygen reacts with H⁺ that are adsorbed on the iron surface. The anodic reaction that brings about oxidation of iron, proceeds rapidly in the presence of dissolved oxygen that encounters the metal surface. Thus, rusting films comprise of three layers of iron oxides in different states of oxidation. Ferrous hydroxide, $Fe(OH)_2$ that is formed as shown in equation (2.8), makes up the diffusion-barrier layer existing next to the metallic surface through which oxygen diffusion takes place. The pH range of saturated ferrous hydroxide is in the range of pH 9.5, because of which the iron that corrodes in pure water is always in the alkaline range. Due to contact with dissolved oxygen, the outer surface of the film gets converted to hydrous ferric oxide (orange to reddish brown in colour) as given in the reaction below:

$$\operatorname{Fe}(\operatorname{OH})_{2} + \frac{1}{2}\operatorname{H}_{2}\operatorname{O} + \frac{1}{4}\operatorname{O}_{2} \to \operatorname{Fe}(\operatorname{OH})_{3}$$

$$(2.9)$$

Ordinary rust mostly comprises of hydrous ferric oxide. The pH range is nearly neutral for saturated Fe(OH)₃. Hydrous ferric oxide exists as non-magnetic α Fe₂O₃ or in the form of magnetic

 γ Fe₂O₃. The magnetic hydrous ferrous ferrite, i.e. Fe₂O₄x*n*H₂O converts to a black intermediate layer in between Fe₂O₃ and FeO. [6]

The most widespread corrosion compounds that are formed in case of central heating systems are H_2 and Fe_3O_4 . H_2 can cause gas-locking of the pipes whereas Fe_3O_4 leads to blockage and seizure of circulating pumps. A well-designed heating system has < 0.1 ppm of O_2 , implying it is in the de-aeration range after the oxygen in the initial charge of water is fully consumed. However, there is always a small amount of aeration due to make-up water and faulty designs. In de-aerated waters, mainly the following reaction occurs:

$$3Fe(OH)_2 \longleftarrow Fe_3O_4 + H_2 + 2H_2O \tag{2.10}$$

The reaction (2.10) is termed as Schikorr reaction. The $Fe(OH)_2$ gets decomposed above 373 K in de-aerated water, however decomposition is slower in waters at 333 K. At first, a substantial amount of Fe₃O₄ circulates in the heating system in the form of sludge and then it gets deposited on the pumps and radiators. The high amount of corrosion products in the solution such as FeOH⁺ and Fe(OH)₂ result in formation of sludge and finally Fe₃O₄ is formed by the Schikorr reaction. The presence of copper ions catalyzes the Schikorr reaction occurring in central heating systems. In a study done for a model central heating system, it was found that even though protective conditions prevailed in the model system after 2 months, the formation of Fe₃O₄ and H₂ continued for many service years. The presence of aggressive ions may interrupt with the formation of protective films in the boiler. The interiors of the failed boilers depict that varying corrosion products were present and the corrosion attack occurred due to many different conditions, with one prime factor being the concentration of dissolved oxygen. In an actual central heating system, poor design practices and construction shortcomings can cause a higher level of aeration than prevalent in the model system, leading to faster corrosion rates. Some parts of the central heating system get aerated due to faulty design and this is the main reason behind failure of a central heating system. [28, 29] Also, presence of sulfate-reducing bacteria in naturally deaerated systems leads to abnormally high rate of iron corrosion. When the pH range is on the acidic side, i.e. less than pH 4, the ferrous oxide film gets dissolved and because of that the metal surface comes in direct contact with the aqueous medium.

The rate of iron corrosion decreases due to passivity of iron in presence of alkaline medium and dissolved oxygen. In the range of pH 4-10, the rate of corrosion only depends on the rate of diffusion of oxygen to the cathodic sites that are available. Presence of dissolved salts also impacts the rate of corrosion reaction in water systems made of iron. In presence of sodium chloride, the conductivity of the solution increases. Iron corrodes rapidly in dilute solutions of sodium chloride as more dissolved oxygen can reach the cathodic sites. Whereas above 3% NaCl, the amount of dissolved oxygen decreases and thus the corrosion attack decreases. Other than NaCl, KCl, LiCl, KI, NaBr also affect the corrosion reaction in similar manner. Chlorides are slightly more corrosive as compared to Na, K and Li. [6].

2.3 Corrosion Protection

The metallic structures made of iron, copper, aluminum, zinc alloys are characteristically unstable. Free metals are less stable as compared to ionic solutions and their hydroxides, oxides and many other salts under various environments to which these metals are being exposed. As mentioned in the earlier sections, thermodynamics favor the conversion of metals to their oxide or salt form. [5] Thus, to retain the physical properties of a metal and its alloys, it is important to protect the metal from corrosion attack caused due to the surrounding environment. Economic losses, safety and conservation are three reasons why corrosion protection is important. Material loss, damage of machinery and loss of efficiency is accompanied by economic losses every year worldwide. Corrosion attack leads to compromise in safety. Equipment failure of, for example pressure vessels, boilers, metallic containers, has catastrophic consequences. Re-fabrication of corroded equipment leads to investment of resources in the form of money, time, manpower and metal. [6] There are various ways of mitigating corrosion in metallic structures that are exposed to atmosphere, water, salt water, acids and other hostile environments. The main objective of these protective methods is to reduce the rate of corrosion attack to a tolerable level, so that the material can achieve its desired or normal life span. However, in only few rare cases corrosion protection strategies can eliminate the corrosion attack completely. There are various ways to mitigate corrosion and some of the widely-used corrosion mitigation strategies are discussed below:[5-6,30]

- **Proper material selection:** Corrosion attack can be handled by proper material selection, proper design of the equipment, control over operating conditions within the design range and using suitable corrosion control measures. Proper selection of materials can possibly minimize corrosion due to use of a less expensive material along with passivation methods and other corrosion control surface treatments. Proper evaluation while selecting materials of construction and deciding ways to mitigate corrosion have direct impact on the economics of a water system. Materials having good corrosion resistance should always be considered and a proper background check about the physico-chemical and mechanical properties of the material as well as knowledge about cost, fabrication technique and heat treatments techniques are also important factors.[30]
- Corrosion inspection and monitoring: Some authors agree that corrosion damage is related to human error or in other words poor management. Lack of monitoring, insufficient review of design and inattention to technical shortcomings and warnings lead to initiation of corrosion attack. Thus, it is important to have a well managed system to tackle technical corrosion issues and provide active human response to handle them. To ensure unabated operations of industrial processes at minimum cost, corrosion inspection should be carried out from early stages of design until the period of shutdown. Corrosion engineers or experts, along with plant managers should conduct inspections from time to time and ensure that facilities are fit for service and equipment are working at proper conditions. Techniques like weight loss measurements must be employed to evaluate corrosion rate. Other modern electrochemical techniques like Electrochemical Impedance Spectroscopy(EIS), Linear Polarization Resistance (LPR) must be used to inspect changes in physical dimensions and properties of the materials. [31-33]
- **Coating:** Due to application of a coating to carbon steel or any other metal, a protective barrier is formed on top of the material which slows down the corrosion attack. Coating involves all corrosion control and prevention methods such as sacrificial protection/inhibition which involve modification of environment and development of

corrosion resistant materials. There are various ways to classify coatings. Coating material can be metallic, organic or inorganic in nature. In case of metallic and inorganic coatings, a very thin coating can provide satisfactory barrier between the metallic surface and the corrosive environment. Electrodeposition, cladding, hot dipping is used for coating metals whereas coating techniques like spraying, diffusion or chemical conversion is used for inorganic materials. Organic coatings like paints, lacquers and varnishes provide better corrosion protection as compared to other types of coatings. However, for an organic coating, apart from proper application procedure, surface preparation, type of primer coat and topmost coat are very important factors. If the metallic surface is not properly prepared, the paint coating may peel off because of poor bonding. Also, when the primer does not adhere with top coat, early failure occurs. Coatings are also classified as metallic and non-metallic coatings. Non-metallic coatings for example paints, oils, waxes, lacquers are relatively inert and electrically non-conductive in nature. On the other hand, metallic coatings like for example Al, Zn-Al coatings are conductive and they play a more active role in mitigation and control of corrosion rate.[9]

- Cathodic protection: Cathodic protection is mostly used as the secondary method of corrosion control, when primary corrosion protection technique is a coating. Generally, a coating is 50%-99% efficient depending upon the procedure of installation and type of coating. The efficiency reaches 100% when cathodic protection is applied as the secondary mode of corrosion control. The basic principle of Cathodic Protection is connecting an anode externally to the metal to be protected and then passing a positive DC current through them so that the coated metal becomes a cathode and the corrosion process is not initiated. Cathodic Protection is a standard protection that is applied for ship hulls, pipelines and water storage tanks. There are two methods of Cathodic Protection; Cathodic or Impressed Current and Sacrificial Anodes. [34-35]
- Anodic protection: Anodic Protection is a technique of corrosion control that is used for process industries to solve the problem of corrosion and contamination. Anodic Protection principle is based on the ability of certain metals and alloys to act in the passive mode in various corrosive environments. A positive current is impressed on them while their

potential is maintained by means of a potentiostat, that has a pre-determined range of potential where the passive film is stable. Anodic Protection reduces corrosion rate to a great limit and enables use of cheaper materials for various severe applications. The principles of designing related to Anodic Protection are still being developed. Electrochemical, physical and geometric parameters must be taken into considerations while considering designing of such a system.[36]

• Corrosion Inhibitors: Corrosion inhibitors are substances which can lower the corrosion attack even when they are applied in very low concentration. The mechanism behind decrease in corrosion is that the inhibitor chemically or physically adsorbs onto the metallic surface and forms a protective layer and thereby minimises corrosion attack by blocking aggressive ions from meeting the metallic surface or slowing down the kinetics of either the cathodic or anodic reaction, or both. In most cases corrosion inhibitors are not pure substances, they are mixtures or by-products. Commercial inhibitors contain active ingredients as corrosion inhibitors along with surfactants, biocides and emulsifiers. Certain examples of inorganic corrosion inhibitors are molybdates, nitrates, phosphates and silicates. [37-47]

2.4 Corrosion Inhibitors

To ensure that closed loop water systems are sustained and operated at optimum conditions, it is essential to maintain good water conditions from the initial phase till the shutdown phase. Corrosion attack leads to great deal of economic losses, hence best way to reduce the losses associated with corrosion is by prevention. As mentioned in earlier section, corrosion inhibitors are chemical substances, which when added to any kind of environment i.e. aqueous solutions, oils, fuels and atmospheric, reduce the rate of corrosion by forming a protective layer on top of the metallic structure. Mitigation of corrosion attack occurs due to the following reasons [48-51].

- Adsorption of ions/molecules onto the metallic/alloy surface and formation of an 'insulating' layer.
- 2) Reduced rate of anodic or cathodic reaction.

- 3) Decreased rate of diffusion of corrosive species to the metallic surface.
- 4) Decreased electrical resistance of the metallic surface.

A deep knowledge about the chemical behaviour and corrosion processes occurring in the system are necessary for successful application of an inhibitor. Selection and concentration of an inhibitor depends on various factors like type of the system, water quality, temperature, water velocity, applied stress, metallic composition and presence of galvanic couples. In most cases, inhibitor formulations comprise of fatty acids and nitrogen-containing precursors. [5]

Basic inhibition mechanism of organic molecules is that they mostly adsorb onto the metallic surface by displacement of water molecules from the surface. The electron transfer from the inhibitor to the metal occurs due to the availability of lone pairs and/or π -electrons on the inhibitor molecules. The presence of hetero atoms like O, N and S (higher basicity and electron cloud), act as the active centers for the process of adsorption to occur. O<N<S<P is the general inhibition efficiency sequence. [48]

Even though there are various ways to mitigate corrosion, use of corrosion inhibitors have gained wide popularity. As compared to other methods of corrosion protection, corrosion inhibitors are generally considered as the most promising, practical and cost effective method to mitigate corrosion. As per estimation, the U.S demand for corrosion inhibitors would rise to 4.1% yearly to \$2.5 billion USD in 2017. Inhibitors are applicable in many commercial applications and industrial systems like cooling systems, boilers and water processing plants, pipelines, oil and gas production units, etc. There are three basic ways of application of inhibitors namely 1) Continuous treatment, 2) Intermittent treatment and 3) Squeeze treatment. Cost, easy availability and impact on the environment are certain important factors that are needed to be considered while selecting an inhibitor. [5,49].

However, due to hazards related to synthetic inhibitors, nowadays focus has shifted towards naturally occurring compounds. For the sake of health, environment and safety, use and disposal of corrosion inhibitors must follow strict rules and regulations. The market trend of corrosion inhibitor has changed and certain widely used inhibitors in industrial applications are being unused. It is because of the high toxicity of the corrosion inhibitors like chromate, phosphate and arsenic, which might cause serious harm to health and the environment. The inhibitors that contain hexavalent chromium Cr^{6+} , is a common carcinogenic chemical and it can cause severe degree of toxicity or pollution to the surrounding environment. [6,48,50].

The new trend of research shifted towards development of natural products as corrosion inhibitors. Researches has been going on with the motive of developing environment friendly corrosion inhibitors. Green corrosion inhibitors are organic compounds that are biocompatible in nature since they are derived from natural sources like plants, leaves, flowers, seeds, bark of extracts, organic molecules. They act by adsorbing on the metal surface by forming a film that minimizes the interaction between the metallic surface and the corrosive environment. [52] Also, they are inexpensive and come from renewable resources; hence they are an attractive alternative for the commercial corrosion inhibitors. Elaborate description about green corrosion inhibitor is available in Section 2.6. Corrosion inhibitors can be classified as anodic/cathodic inhibitors, mixed inhibitors and organic inhibitor. [48-49,53].

2.4.1 Anodic Corrosion Inhibitor

Anodic inhibitors, also referred to as passivation inhibitors work by reducing the anodic reaction. In other words, by blocking the anodic reaction and causing the natural reaction of passivation of metallic surfaces that leads to the formation of a film adsorbed onto the surface. The anodic inhibitors interact with corrosion product that is formed initially and results in formation of an insoluble film on the metallic surface. This makes the metallic surface go into the passivation range. They mainly affect the anodic corrosion reaction and the corrosion potential of the metal is dragged to more positive values. Anodic inhibitors are applied in near neutral pH medium where sparingly soluble products of corrosion like hydroxides and oxides are obtained. At high concentrations of the inhibitor, the metal gets passivated when the primary cathodic current density increases w.r.t critical current density at the anode. Generally anodic inhibitors are most effective at an optimum concentration. Improper amount of inhibitor might result in incomplete film formation on top of the metal surface, that can lead to localized attacks. They can be categorized into two types: 1) oxidizing ions, namely chromate and nitrite that can passivate steel in the

absence of dissolved oxygen. Chromates are widely used in recirculation-cooling systems 2) nonoxidizing ions, such as phosphate, tungstate, and molybdate, on the contrary that require the presence of oxygen to passivate steel. [5-6, 37,49]

2.4.2 Cathodic Corrosion Inhibitor

Cathodic inhibitors deaccelerate the oxygen reduction reaction on the surface of steel by precipitating salts that have poor solubility in solutions. Due to reduction of oxygen supply for continuation of the corrosion process, the rate of corrosion reaction and corrosion potential decrease. They do not have any direct effect on the anodic reaction, but inhibit the cathodic reaction. Cathodic inhibitors are strong acceptors of protons. These inhibitors comprise of such metal ions that can initiate a cathodic reaction due to alkalinity, which results in formation of insoluble compounds that can precipitate selectively on the cathodic sites. They also form a compact and adherent film over the surface, which restricts the diffusion of reducible species, i.e. oxygen diffusion and conductive electrons, thus minimizing the rate of the corrosion reaction. Some common examples are magnesium, zinc and nickel that can react with the hydroxyl ion of the water system, leading to formation of Zn(OH)₂, Mg(OH)₂ and Ni(OH)₂, and other examples are carbonates, polyphosphates. [5,37]

2.4.3 Mixed Corrosion Inhibitor

Generally, 80% inhibitors fall under this category. Mixed inhibitors are those inhibitors which can repress both the anodic and cathodic corrosion reactions, which take place by the inhibitor molecule adsorbing onto to the entire surface of metal or alloy like steel, leading to the formation of a thin protective coating or film. They lower down the corrosion attack without causing a change in the corrosion potential. Examples of mixed inhibitors are organic substances containing polar groups with nitrogen, Sulphur and hydroxyl. [37]

2.4.4. Organic Corrosion Inhibitor

Organic compounds that contain heteroatoms like nitrogen, oxygen, sulphur and phosphorous, their π electrons in triple or conjugated double bonds can act as good inhibitors because of their capability to adsorb onto the metal surface. The performance of organic inhibitors depends on the chemical structure as well as physico-chemical properties of the organic compound like functional group, electronic structure of the molecule, electronic cloud of the donor atom. Chain length and size of the molecule, ability of cross-linking, strength of bonding to the substrate and solubility in the given environment, are certain factors that can affect the action of an organic inhibitor. The adsorption process can occur in two ways-

1) Physisorption: It requires electrostatic forces between the ionic charge or dipole of the adsorbed species and the electric charge present at the metal/solution interface. The heat or energy of this adsorption process is low and is unsuitable at higher temperature conditions. The interaction can also involve some other forces, such as van der Waals forces, hydrogen bonding.

2) Chemisorption: It involves formation of coordinate bonds by sharing or transferring charge between the inhibitor molecules and the metal surface. This type of adsorption is much stronger as compared to physisorption, having a greater heat of adsorption. Also, it is irreversible in nature and is stable at high temperature conditions. Some common examples of organic corrosion inhibitors are carboxylate compounds like sodium decanoate. [37,48-49].

2.5 Corrosion inhibitors for ferrous alloys in water and steam systems

One of the most common ways of mitigating internal corrosion in water circulating systems is by using corrosion inhibitors. The selection of corrosion inhibitors for water systems depends on the type of water system in concern: once through system, open recirculating system or closed-loop system.[5] Also, because of tightening of the environmental regulations, the scope of using compounds and their maximum concentration has limits. The efficiency of the inhibition process can only be understood well, if proper knowledge of the chemical interaction occurring amongst

the inhibitors, other dissolved chemicals and products of the corrosion reaction are studied well. Other factors that influence the evaluation and effectiveness of the inhibition process include initial water quality, type and concentration of the inhibitor in use, condition of the machinery and piping to be tested and the period of the corrosion testing. A multi-functional (i.e. along with prevention of corrosion, it should also be able to stop the formation of scale and bacterial growth) corrosion inhibitor is considered a worthy candidate for the inhibition process.[40] The most common way to classify inhibitors for water and steam systems made of iron alloys is by dividing them as inorganic and organic inhibitors.

2.5.1 Inorganic corrosion inhibitors

Calcium carbonate: The most widely known natural inhibitor is calcium carbonate. Other than causing the problem of scale formation on heat exchangers, $CaCO_3$ can reduce rate of corrosion in steel. Water is termed stable at a given temperature when insoluble deposits of calcium carbonate are not present and when the water does not act aggressively on material of construction. The stability of water can be described using Saturation Index as given below:

$$SI_{L} = pH - pH_{s} \tag{2.11}$$

where pH represents the pH of the actual water, pH_s represents the same composition of water that contains the equilibrium concentration of carbonic acid compounds. If pH< pH_s, the free CO₂ concentration in the water exceeds the equilibrium value, carbonate film does not deposit on the walls of pipes or equipment. If pH> pH_s, calcium carbonate is precipitated from solution and can decrease or eliminate corrosion. The negative effect of this is that the carbonate film represents an additional (unwanted) resistance for heat transfer.[40]

SiO₂ (Silica): It is another natural inhibitor that provides satisfactory protection against steel even when SiO₂ concentration is as low as 4-8 mgL⁻¹. However, silica has certain disadvantages like their tendency to form soluble deposits in presence of calcium and iron ions.

Chromates: Since it is applicable for a wide range of pH, chromate is widely used for treatment of ferrous and non-ferrous materials. The oxidation of iron leads to the formation of a

protective film producing a mixed oxide given as $(Cr_2O_3 + Fe_2O_3)$. It is suitable for protection at only a specific concentration as it is sensitive to ions like Cl⁻ and sulphate. When applied at low concentrations, pitting corrosion might occur. Chromate has "self -healing" capacity and whenever the protective film breaks it can relocate or transport to the site of broken film and re-create the film. However, as it possesses carcinogenic properties, its usage has decreased in recent times, and in some countries, it is ever forbidden. Recirculating water systems are treated with 0.04-0.2% of sodium chromate (Na₂CrO₄) with an alkali at pH 8. Chromate is generally consumed very slowly and it should be added periodically to maintain the concentration above the critical value. [5,40,54]

Nitrite: Widely used for closed loop systems, Sodium Nitrite (NaNO₂) is an anodic inhibitor and the protective action of other inhibitors like molybdate can be enhanced by it. Presence of aggressive ions like chloride ions and sulphate ions regulate its inhibition efficiency. Nitrite is used exclusively or along with pH buffers and high dosage is required to achieve good protection. It is unsuitable for open systems due to the possibility of conversion to nitrate, with impact on microorganisms and its incompatibility with regards to biocides [5,40,54]

Karim et al. [22] studied the corrosion protection of mild steel in simulated cooling water (SCW) by using sodium nitrite in presence of chloride ion. The authors observed that nitrite inhibited mild steel corrosion in near neutral and alkaline (pH 6 and above) SCW whereas the corrosion rate increased in acidic media (pH 4 and below). The inhibition activity increased with the increase of nitrite concentration up to 500 ppm, reaching a constant at pH 6 and above. Also, for stagnant SCW conditions, highest corrosion inhibition was observed at pH 8 for wide range of concentration of NaNO₂.

Molybdate: Application of Molybdate for protection against corrosion for cooling water present in open recirculating systems and closed loop systems is well reported. It works better in presence of oxygen and transforms Fe_2O_3 to Fe_3O_4 . Molybdates are very good in corrosion protection for both soft water and hard water. Some disadvantages related to Molybdate is its high expense and accumulation in sludge for waste treatment plants. Molybdate provides the best protection for steel. Application of Molybdate in closed loop systems needs an oxidizing salt like NaNO₂. It is also less toxic than chromate; however, its oxidizing properties are inferior as compared to chromates. In neutral medium, presence of another oxidant is necessary as the oxidizing property of molybdate is absent for steel. Presence of MoO_2 black film at pH range greater than pH 5, indicates the reduction reaction of molybdate ion. [40,54-55].

Saremi et al. [56] studied the impact of molybdate concentration and hydrodynamic effect on mild steel corrosion inhibition in simulated cooling water and achieved good inhibition efficiency. They observed that the inhibition efficiency of molybdate raised up when both its concentration and velocity of water circulation were increased. The two determining factors were adsorption of molybdate and oxygen ions on the metallic surface, that formed a preventive layer with a greater resistance to charge transfer and lesser permeability.

Polyphosphates: These are non-toxic, less expensive type of inhibitors that can inhibit corrosion of iron alloys even when applied at low concentrations. They are widely used for inhibition of corrosion and scale formation for water treatment in water circulating systems. However, they have disadvantages as they might enhance the corrosion reaction when applied at high concentration. This occurs due to formation of complexes that are soluble with metal cations and that might lead to activation of local corrosion reaction of steel, particularly in alkaline environment. Also, they have the tendency of converting to orthophosphate due to hydrolysis, that can stimulate deposits formation. Their stability decreases with increasing pH and content of calcium ions. They perform a dual function of protecting steel and preventing deposition of calcium carbonates. [40]

2.5.2 Organic corrosion inhibitors

Phosphonic acids: Cooling water systems widely use phosphonic acids for the anticorrosion treatment. Some examples are HPA- Hydroxyphosphonoacetic acid, HEDP- 1hydroxyethane-1,1-diphosphonic acid. They are widely used for water treatment because of their low cost and low toxicity. They protect the metal from corrosive environments due to formation of complexes. Solution temperature has impact on the protection offered by phosphonic acids. Also, hydrophilic chelating agents have negative impact on the corrosion reaction and they lead to localized corrosion. [40]

1,2,3-benzotriazole (BTA): It is one of the most commonly used inhibitors for water treatment applications. It has relatively high solubility in water and alcoholic media, high thermal stability and ability to arrange into sparingly soluble compounds with various metal cations. BTA is mostly applicable for copper and its alloys, it is also able to form protective layers of polymeric complex compounds on iron and other metal alloys. [40]

Mercapto and thiazoles: They are applied for acidic media; however, they can also exhibit protective film forming properties in the neutral pH range for copper, steel and aluminum alloys.

Carboxylates: Carboxylates are suitable for application in aqueous medium. They are very effective, non-toxic and bio-degradable corrosion inhibitors. They are capable of inhibiting corrosion of not only ferrous alloys, but also non-ferrous alloys. Also, they can act as multifunctional reagents that have anticorrosion ability along with biocidal activity and antiscaling property. The most widely studied carboxylate inhibitors contain salts of aromatics and fatty carboxylic acids. Sodium Benzoate is an aromatic carboxylate that can reduce corrosion in iron alloys and non-ferrous metals. Addition of an additional functional group to the benzene ring improves the efficiency of the aromatic carboxylate. For example, sodium anthranilate is one of the best inhibitor for preventing de-passivation of iron. Lower aliphatic carboxylates can stimulate the corrosion of metals and lead to de-passivation due to hydrophilicity of anions. With increasing length of the hydrocarbon chain, the inhibition properties increase because of increase in hydrophobicity and surface activity. The corrosion in mild steel was reduced when the chain length 'n' increased from zero to eight, when salts of mono and di-carboxylic acids were used in aqueous medium at greater or equal to pH 7. Some examples of carboxylate salts are sodium decanoate and sodium oleate. However, due to certain factors like instability in the presence of salts imparting hardness of water, micelle formation and potential of foaming, carboxylates have limited

application in water cooling-heating systems despite of their high corrosion inhibition efficiency. [7,40]

2.5.3 Miscellaneous

At room temperature, corrosion of iron is nearly negligible in aqueous medium that is free of dissolved oxygen. One practical means to reduce corrosion of iron or steel in contact with water is to reduce the content of dissolved oxygen. Deactivation and de-aeration are the two ways in which dissolved oxygen can be removed. Deactivation involves chemical reaction of oxygen and de-aeration involves distilling oxygen off the suitable equipment. Strong reducing agents like sodium sulfite (Na₂SO₃) and hydrazine (H₂N₂) acts as corrosion inhibitors and they bring about removal of oxygen. However, hydrazine is identified as a possible carcinogen. The oxygen scavenging reaction of sodium sulfite is given below:

$$\frac{1}{2}O_2 + Na_2SO_3 \rightarrow Na_2SO_4$$
 (2.12)

Two other scavengers of oxygen are carbohydrazide and diethyhyroxlamine (DEHA). Other than reducing the dissolved oxygen content, they also form a protective film on top of iron and copper. The minor amount of hydrogen formed when steel encounters water can be minimized by treating water with NaOH and Na₃PO₄ at pH range of 8.5. Zinc polyphosphate is used since more than 60 years for controlling corrosion of steel in municipal water systems. Rise in saturation index i.e. the measure of alkalinity and calcium content of water effectively reduces the corrosion in hot-water systems. Addition of lime Ca(OH)₂ and soda ash Na₂CO₃ can raise the saturation index. Sodium silicate treatment is applied in soft-water areas. Presence of silicates offer passivity of iron at pH 10 and leads to reduction of corrosion rate to 0.1-0.7 gm⁻²d⁻¹. Sodium hydroxide offers similar passivity and low corrosion rate at a higher pH range of 10-11. Zinc salts can combine with organic and inorganic anions like chromates and polyphosphates and provide synergistic corrosion inhibition action [6,40,54]

2.6 Green Corrosion Inhibitors
Even though the inhibition efficiency for protection of metals is very high, most of the corrosion inhibitors that are commercially available are found to possess toxic and carcinogenic properties. [57-62] For example, one very commonly used corrosion inhibitor for recirculating water systems, for engine-cooling systems made of steel, copper, aluminum and brass is sodium chromate (Na₂CrO₄) [6]. However, hexavalent chromium ion is a human carcinogen linked with lung cancer. Chromate exposure mostly occurs through inhalation or ingestion and skin contact . The molecular debris associated with the reduction process of Cr^{6+} to Cr^{3+} leads to critical changes in DNA. The main regulatory agency that takes care of chromium uses and emissions is Environmental Protection Agency (EPA). The current limit for public health service exposure for chromate is 0.05 mg l⁻¹. [50,63]

Also, Sodium Tungstate(Na₂WO₄), Vandates (NaVO₃), Nitrates(NaNO₂), were used for protection of metallic structures made of ferrous and non-ferrous metals, however their application is decreasing due to their toxic properties. Molybdate salts were used in open type recirculating water systems as a replacement of chromates, however they are very expensive [64]. Moreover, phosphates, sulfites and amines are used for hot water systems; however as they are toxic, their usage enables the system to operate at low inorganic salt concentrations, which ultimately leads to discharge of a large amount of water into water bodies. This increases the environment footprint due to increase in discharge of water and higher amounts of energy consumption [65]. Also, benzotriazole (BTA) and some of the heterocyclic compounds also possess toxic properties. The harmful effects of the toxic inhibitor may lead to temporary or permanent failure to lungs, kidneys and liver, causing serious trouble to enzyme system of the body. The toxicity of the inhibitor might be exhibited during its synthesis or its application phase.[52]

Thus, the increasing environmental concern worldwide is likely to affect the choice of corrosion inhibitors in future. Corrosion inhibitors which are less toxic, cheaper and biodegradable in comparison to the current formulations have a growing market world-wide. High performance and environment friendly corrosion inhibitors must be developed for boilers and hot water systems, as protection against corrosion is needed at aggressive operating conditions like high pressure and temperature and high dissolved salts concentration. In recent times, focus has now shifted towards "greener" molecules, implying naturally occurring and bio-compatible molecules, which have a low environment footprint and which are devoid of any heavy metals or toxic compounds. Also,

being derived from renewable sources, they are readily available and thus can be produced at low cost using simple procedures. Some examples of naturally occurring products are plant origin products like seeds, bark, pigments, non-toxic synthetic compounds like dyes, organic compounds like pyridine, Schiff base compounds, rare earth metals etc.[66-73] In following paragraphs, green corrosion inhibitors applicable for ferrous alloys are discussed.

In the work [65], TGWT tannins were used for treatment of steam boilers mostly fabricated from aluminum and carbon steel. Tannins are large polyphenolic naturally occurring product that are environmentally-friendly. They can participate in strong complex formation with metal ions and macromolecules.TG 3000 tannins readily adsorbed onto the metallic surface and reached equilibrium in 15 minutes. The corrosion inhibition efficiency was found to be 80% for aluminum (at pH 7-9 range) and mild steel (at pH 10-11 range). Electrochemical techniques and QCM-D method proved that TG 3000 tannins formed a rigid protective layer on top of the aluminum and mild steel surface.

Manimegalai and Manjula [51], studied the corrosion inhibition for carbon steel in aqueous medium containing 60ppm of Cl⁻ ions by using *Sargassum swartzii* (brown algae). Brown algae is a large group of multicellular algae, mostly used in food and medicine industries and industrial purposes. Weight loss method was conducted at 303K-343K. It was found that inhibition efficiency increased with increase in inhibitor concentration; however it decreased with rise in temperature. Physical adsorption took place, indicating a strong and spontaneous adsorption of the SS extract on the metallic surface.

In this work [41], electrochemical and weight loss techniques were employed to study the corrosion inhibition of L- ascorbic acid(AA) on carbon steel at a pH 2-6 solution. L-Ascorbic acid(AA), a type of vitamin C, is a readily obtainable and water-soluble molecule that shows corrosion inhibition characteristics. Surface of carbon steel was studied using optical microscope analyses. The maximum inhibition efficiency of 69% was obtained for 10⁻³ mol dm⁻³ of AA, at pH 4. Results show that AA acts in the form of a mixed-type inhibitor.

2.7 Selection of corrosion inhibitors for closed loop-water-heating/cooling systems

For successfully applying inhibitors, it is important to acquire knowledge and understanding about their chemical behaviour and the corrosion processes occurring in the system under consideration. The type and concentration of the inhibitor depends on water quality, temperature fluctuations, presence of galvanic couples, presence of stress or crevices and debris. The installation where inhibitors are used vary from small to big, closed loop systems or open loop water recirculating systems which make use of millions of gallons of water per day. The primary criteria for evaluation of an inhibitor is its efficiency. Before applying an inhibitor in the field, specific set of laboratory experiments are done. There are three steps involved in evaluation and selection of corrosion inhibitors as given below [33]:

- Laboratory evaluation methodologies: The laboratory testing must be carried out at conditions which can simulate the operational conditions prevalent in the field, such as composition of the material, environment (acidic, basic or neutral), temperature, flow, pressure, way of the adding the inhibitor i.e. batch or continuous. Also, the oratory techniques should be such that they simulate variables which can influence inhibitor performance. The screening procedure for inhibitors in the laboratory involves two parts:
 methodology: experimental setup for generation of corrosion and 2) measuring techniques: they determine the corrosion rate and inhibition efficiencies. Wheel test, Rotating Cylinder Electrode are some examples of such techniques.
- 2) Measuring techniques: They include the corrosion rates measuring methods and are classified as destructive and non-destructive techniques. In a destructive measuring technique corrosion is made to occur forcefully by using potentio-dynamic and polarization methods. On the other hand, non-destructive techniques include linear polarization resistance (LPR), Electrochemical Impedance Spectroscopy (EIS) and they can be used for repeated measurements at varying time intervals.

3) **Test for compatibility:** Due to economic considerations, it is important to wisely choose materials for corrosion protection. The corrosion inhibitor should be cheap, as maintenance cost and operational costs are also involved. In selecting material its environmental impact must be evaluated elaborately; the corrosion inhibitor should be bio-compatible. Other steps include quality control tests and field evaluation test like mass counts, visual inspection etc. [5,33].

2.7.1 Sodium Caprylate: Green Inhibitor for closed-loop-water-heating/cooling systems



Figure 2.2: 3D model of Sodium Caprylate

(Courtesy: https://commons.wikimedia.org/wiki/File:3D_Sodium_caprylate.png)

Due to toxicity of the widely available corrosion inhibitors in the market, the focus has now shifted towards development of environmentally- friendly corrosion inhibitors. As closed loop water recirculating systems mostly use corrosion inhibitors for corrosion protection, use of toxic chemicals and formulations for treatment of internal corrosion has become a serious concern. Research has been going on world-wide to develop bio-compatible and less toxic chemicals for corrosion inhibition in closed-loop-water systems.

The organic molecule that is studied in this work is sodium caprylate (SC) as given in the **Figure 2.2** above. Its molecular formula is $C_8H_{12}NaO_2$ and molecular weight is 166.196 gmol⁻¹.

SC is a sodium salt of fatty acid that is prepared by the process of saponification. SC is derived from Caprylic acid, which is an eight-carbon saturated fatty acid and it is also known as Octanoic acid. Caprylic acid is a natural product which is found in the milk of various mammals. SC comprises of carboxylate group as its functional group and is a good surfactant that can strongly adsorb at air/water interface. SC is mainly used as soap or a cleansing agent, foaming agent or an emulsifier. Carboxylates are environmentally safe molecules as they are readily bio-degradable, are less toxic and have proved to be suitable inhibitors for aqueous media applications. The structure of the carboxylates is such that they can accommodate other functional groups such as amino acids and thus can perform as multi-functional reagents which have anti-scaling and biocidal properties. The most widely accessible and studied amongst carboxylate inhibitors are the salts of aromatic compounds and fatty carboxylic acids. [7, 57]

SC being a surfactant, is an amphiphilic molecule. Amphiphilic molecule comprises of a hydrophobic (away from water) and hydrophilic (water loving) part. In case of SC, the hydrophilic group is the carboxylate functional group and the tail of eight carbon chain make up the hydrophobic part. SC forms a protective film on top of the metal surface through adsorption (chemisorption or physisorption) via its functional group as shown in the Figure 2.3 below. The protective film is called a self-assembled monolayer or SAM. SAM is a spontaneous process that occurs when a substrate is dipped in a solution of surfactant. Due to adsorption of the surfactant on the metallic surface, a highly ordered and stable structure of monolayer or bilayers is formed, which insulates the substrate from the corrosive environment, which in turns results in a decrease of corrosion rate. The formation of SAM take place even when the concentration of the inhibitor is in ppm. Thus, it is a very cost effective procedure for mitigation of corrosion.[57] However, SC forms micelles and vesicles when used at higher concentrations than Critical Micelle Concentration (CMC). The physico-chemical properties of the surfactant molecule are highly affected below and above the CMC value. The CMC of a surfactant is the concentration at which the physical and chemical properties of surfactant solutions show an abrupt variation. The CMC value is an important parameter that determines the effectiveness of a surfactant molecule as corrosion inhibitors. Below the CMC value, surfactant molecules or monomers interact with the exposed substrate by adsorption, the interfacial aggregation decreases the surface tension and it is related to the corrosion inhibition process. However, above the CMC value, the metallic surface

becomes covered with a protective layer or an adsorbed monolayer. Additional surfactant concentrations in the solution would result in the formation of micelles or multiple adsorbed layers. The values of corrosion current density j_{corr} (Acm⁻²) and the surface tension are not altered near about the CMC value. [74] The CMC value of Sodium Caprylate is 351mM at 298K for a solution made of de-ionized water. [75-78].



Figure 2.3: SAM formation on top of carbon steel substrate

Per literature survey, SC was used for corrosion inhibition of carbon steel in a cooling system media. The tested concentration of SC ranged from 10 to 700 ppm. Starting at 400 ppm, the rate of corrosion reaction on carbon steel reduced very sharply. The adsorption process of the inhibitor molecule on the carbon steel followed Langmuir isotherm. Fourier transform infrared (FTIR) spectra was used to analyze the protective film on carbon steel when SC was present at higher concentration. Also, it was revealed that SC was adsorbed on to the metallic substrate via its functional group.[7]

CHAPTER 3: Objectives

The main objective of this thesis work is to investigate the possibility of using Sodium Caprylate (SC) as an environmentally-friendly organic corrosion inhibitor for treatment of G1117 low carbon steel used in closed-loop-water heating/cooling systems. The electrolyte used for investigating the corrosion inhibition efficiency of SC is Montreal tap water.

3.1 Specific Objectives

The specific objectives of the research are given below:

- To investigate the corrosion inhibition efficiency at varying concentrations of SC by using four electrochemical techniques namely Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS), Polarization Resistance (PR) and Tafel Polarization (TP) technique. To finalize an optimum concentration of SC based on the results of efficiency obtained by the four techniques.
- ii) To investigate the influence of temperature and pH on the corrosion inhibition efficiency of SC.
- iii) To study the kinetics of the adsorption process of SC on the carbon steel substrate.

CHAPTER 4: Experimental Procedures and Materials

This chapter elaborately describes the materials, solutions, experimental methodology and the research techniques that are used for the experiments done for this thesis.

4.1 Materials and solutions

The molecule that is studied as the corrosion inhibitor is Sodium Caprylate(SC) [purity of 99%, Product No: 1001833424, SIGMA.]. Montreal tap water is used as the electrolyte. For adjusting the pH of the Montreal tap water, $0.5M H_2SO_4$ solution [purity of 98% and Product No 1-800-234-7437] and 8M NaOH (purity of 97% and Product No: 1310-73-2) solution are used. The chemical composition (weight %) of the working electrode, i.e. G1117 low carbon steel is given as Fe= balance, C= 0.14-0.20, Mn=1.00-1.30, P=0.04 and S= 0.08-0.13. [72]

4.2 Three Electrode-electrochemical setup

For all the corrosion experiments a three-electrode electrochemical cell is used. Saturated Calomel Electrode (SCE) is used as the reference electrode and all the potentials are reported in this work are quoted w.r.t (SCE). A graphite rod is used as the counter electrode. The working electrode is made from a carbon steel button, whose chemical composition is outlined above. The carbon steel button is obtained from a carbon steel rod that is purchased from McMaster-Carr Company (part No 8290T14). Its diameter is 5/8" (equivalent to 1.59 cm). A Teflon holder is used for holding the working electrode sample while conducting the corrosion experiments. The exposed surface area of the WE is 1.039 cm². A thin plastic hollow rod is used as the means to purge Argon gas into the solution. A schematic diagram of a three-electrode setup is given below in **Figure 4.1**. For conducting experiments with temperature variation, the same setup is used, however the cell is placed in a water bath (Company: Poly ProBath). Thermometers are used to measure the temperature. The setup is easy to assemble. However, the reference electrode, counter electrode, Teflon holder must be rinsed thoroughly every time, before immersing them into the solution inside 250 ml beaker to avoid contamination of the electrolyte.



Figure 4.1:Schematic of a three-electrode cell; 1) Teflon Holder, 2) Working Electrode, 3) Graphite rod, 4) Standard Calomel Electrode, 5) Argon bubbler 6) 250 ml beaker

4.3 Experimental equipment and Software

Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS), Linear Polarization techniques for polarization resistance and Tafel polarization measurements are performed using software GPES v. 4.9 (for OCP and polarization techniques) and FRA 2 (for EIS), which are controlled by an AUTOLAB potentiostat/galvanostat/FRA PGSTAT 30. For every set of experiment, OCP is the first experiment that is conducted after immersing the freshly polished working electrode in the solution. For OCP, the potential of the working electrode is recorded under the condition of no external current for 7200 seconds, until a steady state potential is obtained. Next, EIS measurements are carried out at open circuit potential, E_{oc} . EIS measurements are performed over a frequency range of 50 kHz to 50 mHz using a \pm 10mV AC voltage amplitude. After, EIS measurements, polarization resistance (PR) measurement is carried out within a potential window of \pm 20mV w.r.t E_{oc} and a step potential of 0.45mV and scan rate of 1.5 mVs⁻¹. As last, the Tafel polarization measurement is carried out within a window of \pm 200mV w.r.t E_{oc} and same scan rate and step potential are used as that in the polarization resistance method. To evaluate the topography of the CS samples, a scanning electron microscopy (FEI Quanta Environmental Scanning Electron Microscopy (ESEMTM)) is employed.

4.4 Experimental methodology

First, the solution for the experiment is prepared by adjusting the pH of the Montreal tap water. After the adjustment of pH next step is addition of powdered form of SC to the 200 ml of solution to achieve a desired SC concentration. Then, the solution is sonicated for 5 minutes. After that, 200 ml of the prepared solution is put in a 250-ml beaker and deep argon bubbling is initiated for a span of one hour. In the meantime, the working electrode preparation steps are completed. The carbon steel button is first wet-polished with 120- grit paper and then with a 600-grit paper. After the second polishing the CS button is dipped in an ethanol bath and sonicated for 5 minutes. In the mean-time, the Teflon holder assembly is washed using reverse-osmosis (RO) water. The CS button is taken out from the ethanol bath and dried using argon gas. After putting the CS button into the Teflon holder, the Teflon holder is sealed with a parafilm so that the exposed surface of CS button cannot encounter the solution at the time of being immersed into the solution. After immersing the Teflon holder into the solution, with the help of a tweezer the parafilm layer is withdrawn. First, OCP measurements are started for 7200 seconds, followed by, EIS, PR and Tafel measurements in the sequential order.

The argon gas used for de-oxygenating the solution is of 99.998% purity and the bubbling rate is 3-5 bubbles/ second for 3600 seconds and once OCP is started the bubbler is adjusted to a shallow height and bubbling rate is 2-3 bubbles/second. The SC concentrations being tested are 1mM, 5mM, 6mM, 6.25mM, 6.28mM, 6.3mM, 6.5mM, 7mM, 8mM, 10mM, 12mM and 17mM. However, the very first set of experiments are done using 0mM concentration of SC at pH 8 Montreal tap water and at 295 K (control measurements in the absence of inhibitor). The measurements are also done at temperatures ranging from 295K to 333K and pH range of pH 7 until pH 10. All these measurements are done in the absence and presence of inhibitor in the solution.

For the inhibitor adsorption kinetics measurements, only PR experiment is performed without prior testing of OCP or EIS measurements. The PR experiments are started right after the CS working electrode is immersed in a solution in absence and presence of the inhibitor at time intervals of 2, 5, 10, 15, 20, 40, 60, 90, 180 minutes at 295K and pH 8 Montreal tap water. For long-term immersion experiments, CS buttons are immersed in solution (0mM and 10mM SC

concentrations) for 30 days at 295 K with pH of the solutions at pH 8. At the end of 30 days, the CS buttons are taken out and thoroughly rinsed with de-ionized water and dried with argon gas before SEM images are taken.

CHAPTER 5: Results and Discussions

This section is dedicated to the discussion of experimental results done using various electrochemical procedures to establish the possibility of using SC as an environmentally-friendly corrosion inhibitor for closed-loop water heating/cooling system. As shown in the Figure 2.2, SC is a straight chain aliphatic carboxylate. Due to low toxicity and readily bio-degradable properties, carboxylates are worthy candidates as corrosion inhibitors for mildly saline, aerated and nearly neutral aqueous solutions. [7]. Also, a close look at the structure of SC reveals that it is a surfactant molecule. It comprises of (-COOH) as the hydrophilic head group, which is electron rich due to presence of unpaired electrons on the two oxygen atoms. Thus, it can share the unpaired electrons with the *d*-orbitals of carbon steel (i.e. iron) resulting in adsorption of the inhibitor molecule onto the metal surface. Furthermore, the long alkyl chain is hydrophobic in nature and it can act as a barrier for transport of water molecules and other corrosive ions from the bulk of the solution to the CS surface. In other words, due to the adsorption of the head group onto the CS metal surface and presence of this alkyl chain, a protective film or a self-assembled-monolayer (SAM) can be formed on top of the metal surface that results in inhibition of corrosion attack as shown in Figure **2.3.** It is hypothesized that with increase in the concentration of SC in solution, the inhibition efficiency should increase or the rate of corrosion reaction should decrease, due to the increased surface coverage of CS by SC. [60,72]

The following sections would elaborately discuss the results obtained due to interaction of SC onto the CS at various experimental conditions. At first, the effect of SC concentration on Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS), Polarization Resistance (PR) and Tafel Polarization (TP) plots would be discussed. Then an optimum concentration of SC would be selected to study the effect of temperature, pH of the solution on the corrosion rate, and then the kinetics of adsorption process would be presented. Last section is dedicated to the study of topography of CS under inhibited and un-inhibited conditions using Scanning Electron Microscopy (SEM).

5.1 Effect of Sodium Caprylate concentration

First set of experiments involved studying the inhibition efficiency of SC by varying its concentration under fixed temperature of 295 K and at pH 8 Montreal tap water . Following sections are dedicated to discussions based on results obtained from Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS) Polarization Resistance (PR) and Tafel Polarization (TP) under varying SC concentrations. Four different techniques are studied to validate the results obtained from each one of them and to better understand the corrosion inhibition process.

It should be kept in mind that a strict sequence has been maintained while carrying out these four different types of electrochemical techniques. At first, OCP measurements are carried out for 7200 seconds and then EIS and PR measurements are done. EIS and PR experiments are non-destructive in nature, implying they have a small potential window w.r.t Open Circuit Potential, E_{oc} , i.e. EIS \pm 10mV vs E_{oc} and for PR \pm 20mV vs E_{oc} . On the other, during Tafel Polarization experiments, the potential window is larger i.e. \pm 200mV vs E_{oc} , implying corrosion is forced to occur and hence it is a destructive test. [60] This sequence of electrochemical measurements is first done for a control experiment (without the presence of inhibitor in the electrolyte). After obtaining consistency in the results for the control runs, concentration of SC is varied. The concentrations of SC being tested are 1mM, 5mM, 6mM, 6.25mM, 6.28mM, 6.3mM, 6.5mM, 7mM, 8mM, 10mM, 12mM and 17mM. Every set of experiments are repeated until three consistent results are obtained.

5.1.1. Effect of Sodium Caprylate concentration on Open Circuit Potential (OCP)

OCP i.e. E_{oc} is the first set of experiment done after immersing the freshly polished CS electrode into the solution. Special care must be taken to stabilize the OCP before proceeding with Impedance and Polarization experiments. Thus, after various trials, OCP is recorded for 7200 seconds for all sets of experiments, since it is observed that more than 3600 seconds are required to reach a steady state (or equilibrium state).

Open Circuit Potential is an important test as it indicates the thermodynamic tendency of the working electrode to participate in a corrosion reaction with the surrounding medium. The electrochemical potential of a metal dipped in an aqueous solution is a function of its inherent reactivity and the oxidizing power of the surrounding solution. While, measuring the OCP, there is no external load on the circuit and no current flows through the circuit. Figure 5.1 shows the variation of OCP versus time of CS in the Montreal tap water of pH 8 recorded in the absence (0mM) of SC inhibitor in the solution i.e. control experiment and in the presence of 10 mM of SC in the solution at 295 K. In the absence of inhibitor, the OCP stabilizes at around -0.775 V vs SCE. However, when the inhibitor is present in the solution, OCP shifted to more positive values, indicating a decrease in tendency of CS to corrode. Figure 5.2 represents the behaviour of OCP with increasing concentration of SC. It can be observed that the behaviour can be divided in two SC-dependent concentration regions. Namely, with an increase in SC concentration to 6.28 mM, OCP values remained constant, which indicates that the presence of SC in the solution did not influence the corrosion behaviour of CS. An abrupt increase in OCP is obtained when the concentration of SC was 6.3 mM, and the values remained constant up to 17 mM. This increase indicates a decrease in tendency of CS to corrode. The behaviour in Figure 5.2 also indicates that the system behaves completely differently in the two corresponding SC concentration ranges.



Figure 5.1: Typical $E_{oc}(V)$ recorded versus time for CS in two solutions:0 mM SC (-) and 10 mM SC (...) at 295 K and Montreal tap water at pH 8.



Figure 5.2: Variation of $E_{oc}(V)$ with increasing concentration of SC(mM) at 295K and Montreal tap water at pH 8.

5.1.2. Effect of Sodium Caprylate concentration on Electrochemical Impedance Spectroscopy (EIS) behaviour

To further explore the behaviour of the system, Electrochemical Impedance Spectroscopy (EIS) measurements is done. **Figure 5.3** shows the EIS spectra of the CS working electrode recorded in absence (0mM) and presence of 10 mM of SC in the solution at 295K and Montreal tap water at pH 8, in the form of a Nyquist plot. The diameter of the semicircle is proportional to the corrosion resistance. As it can be seen, when SC is added to the solution, the corrosion resistance significantly increased. This implies that the CS is getting protected against corrosion attack by the action of SC.



Figure 5.3: Typical Nyquist plots of CS recorded in the absence (0mM) of SC in the solution and in the presence of 10mM of SC in the solution at 295K and Montreal tap water at pH 8.Symbols represent the experimental data and solid lines represent the modelled spectra.

For extracting qualitative information, an analysis termed as nonlinear least-squares (NLLS) fit is used for modelling the EIS spectra in the form of electrical equivalent circuits (EECs), which are shown in **Figure 5.4**[60,72]. In these EECs, R_{el} stands for the ohmic resistance between the reference electrode and the working electrode, R_1 is the corrosion resistance, CPE is the double-layer capacitance and it represents a so-called constant phase element (CPE); the use CPE is needed in cases when the metal surface is nonhomogeneous in terms of the surface charge distribution. In the current case, CPE represents the non-perfect capacitor. Here, the most important parameter is R_1 or the corrosion resistance, which is inversely proportional to the kinetics of corrosion reactions. Thus, the higher the value of R_1 , better the corrosion protection of SC is (higher corrosion inhibition efficiency). The physical meaning of EEC element C in **Figure 5.4(b)** is currently not clear to the author of this thesis, but its use in the modelling process is needed (see below).

The EEC in **Figure 5.4(a)** is used to fit the EIS spectra in absence of SC, and as seen in **Figure 5.3**, the agreement between the modelled (line) and experimental values (symbols) is very good.

However, in presence of SC, the same EEC did not result in a good agreement between the modelled and experimentally obtained results, and the EEC in **Figure 5.4** (b) is used instead. Again, **Figure 5.3** demonstrates that the agreement between the modelled (line) and experimental values (symbols) is very good (it should be noted that this is the case at all other SC concentrations used in this work). **Table 5.1** lists EEC parameter values obtained by fitting the EIS data for varying concentration of SC.



Figure 5.4: EEC models used to fit EIS data for (a) CS electrode in blank solution and (b) CS electrode immersed in an electrolyte containing Sodium Caprylate. R_{el} :electrolyte (ohmic) resistance; CPE: double layer capacitance, R_1 : Corrosion resistance.

Table 5.1: EIS parameters for CS substrate dipped in solution of increasing concentration of SC at pH 8 Montreal tap water and 295K.

SC(mM)	0	1	5	6	6.25	6.28	6.3	6.5	7	8	10	12	17
$\mathbf{R}_{\mathrm{el}}\left(\Omega ight)$	1929	1572	986	895	886	907	868	909	851	767.3	672	617	473
±SD	7	14	11	5	26	26	11	10	9	0.6	5	4	16
CPEX10 ⁶	310	254	249	190	119	193	31	43	41	36	48	26	35
$(\Omega^{-1}s^{n1})$													
±SD	20	30	39	10	40	14	3	5	9	5	9	1	7
n	0.767	0.696	0.694	0.715	0.732	0.721	0.746	0.738	0.742	0.734	0.746	0.694	0.718
±SD	0.015	0.019	0.038	0.033	0.016	0.026	0.026	0.024	0.035	0.009	0.009	0.017	0.007
C(µF)	-	35	39	32	33	32	14	15	14	15	13	13	12
±SD		8	9	6	5	4.32	0.4	1	3	1	1	2	1
$\mathbf{R}_1(\mathbf{\Omega})$	3540	3913	4173	4533	4780	5097	14733	99267	92233	154733	147067	143633	136750
±SD	52	165	352	474	317	641	8016	1332	5227	6586	12305	17054	27365

Let's first discuss the CPE trend. The **Table 5.1** shows that CPE gradually decreases as the concentration of SC in the solution increases. Given that CPE represents the double-layer capacitance, this is an expected trend. Namely, the electrochemical double layer capacitance can be resembled in the form of a two-plate condenser capacitance C_{DL} (Fcm⁻²) as given below:

$$C_{\rm DL} = \varepsilon_0 \, \varepsilon_r \, A/l \tag{5.1}$$

Where $\varepsilon_0 = 8.854 \text{ X } 10^{-12} \text{ Fm}^{-1}$, is the vacuum permittivity, the relative permittivity of the dielectric between the plates is given by ε_r , A is the surface area of the plate in (m²) and *l* is the separation between the plates in (m). As seen in the table through the decrease in CPE, as the concentration of SC increases, formation of an adsorbed film of SC takes place on the CS surface, which blocks the CS surface and decreases the surface area available for the charge storage. However, when the concentration of SC reached 6.3mM, the CPE value dropped suddenly and then remained relatively constant. This behavior is in accordance with the OCP trend in **Figure 5.2** and will be explained later in the thesis.

Further, although the meaning of element "C" in the EEC is not known, the trend in its behavior with SC concentration resembles that one of OCP and CPE. However, the most important parameter to consider is R_1 or the corrosion resistance. It can be seen in **Table 5.1** that, with increase in the concentration of SC, the value of R_1 began to increase, which implies that the SC protective film formed due to adsorption of SC is successful in inhibiting corrosion. The corresponding corrosion inhibition efficiency, η , can be calculated by using equation 5.2 as given below:

$$\eta = (1 - \frac{R_o}{R_i}) X100\%$$
(5.2)

Where, R_o is the resistance of the controlled or blank solution, R_i is the resistance in presence of the inhibitor measured in Ω .

Figure 5.5 shows the dependence of corrosion inhibition efficiency obtained from R_1 values on the SC concentration. The trend is very similar to that one of OCP (Figure 5.2). With

an increase in SC concentration, the corrosion inhibition efficiency gradually increases reaching ca. 31% at SC concentration of 6.28 mM. With further increase in SC concentration, the corresponding inhibition efficiency sharply increases to ca. 96%, and it then remains relatively constant (the maximum efficiency obtained is 98%). Discussion and comments regarding this peculiar trend observed w.r.t to the efficiency (and also OCP and CPE) will be presented in section **5.1.5.**



Figure 5.5: Corrosion inhibition efficiency of SC against blank solution calculated from corrosion resistance R_1 values obtained by EIS as a function of SC concentration at 295 K and pH 8 Montreal tap water.

5.1.3. Effect of Sodium Caprylate concentration on Polarization Resistance (PR)

From the previous two sections, it was observed that with increase in concentration of SC, the corrosion inhibition efficiency increased, which meant better protection against corrosion. To further support and validate the results obtained from OCP and EIS measurements, PR measurements are carried out. A typical example of polarization resistance plot for 0mM and 10mM concentrations of SC at 295K and Montreal tap water at pH 8 is shown in **Figure 5.6**. The inverse of the slope is directly proportional to the corrosion resistance of the system. **Figure 5.7** represents the trend of corrosion inhibition efficiency calculated from PR values using eqn. 5.2 at various concentrations of SC at 295K and Montreal tap water of pH 8. It should be noted that while

calculating the efficiencies of polarization resistance, the PR plots were corrected with regards to uncompensated resistance iR, which is the resistance between the WE and RE and in another words $R_{el}(\Omega)$, that was obtained from EIS results (**Table 5.1**).



Figure 5.6: Typical polarization resistance plots of CS measured in absence i.e. 0mM and presence of 10 mM SC at 295 K in the Montreal tap water of pH 8.



Figure 5.7:Corrosion inhibition efficiency of SC against blank solution calculated from polarization resistance values obtained from PR measurements, as a function of SC concentration at 295 K and pH 8 Montreal tap water.

It is clear from **Figure 5.7** that the inhibition efficiency trend is almost the same as that one presented in **Figure 5.5**, and it could, thus, be explained in the same manner. This also validates the techniques used and demonstrates the reliability of data.

5.1.4 Effect of Sodium Caprylate concentration on Tafel Polarization (TP) plots

The last set of experiments with variable SC concentration involved Tafel polarization measurements, which are done to further verify the results obtained from PR and EIS measurements. As already mentioned earlier, Tafel polarization is a destructive test, where corrosion is forced to occur and hence it is conducted at the very end. This experiment helps to study the recorded current response and the kinetic parameters that are related to the rate of the partial and overall corrosion reactions, in presence and absence of the inhibitor in the electrolyte. Figure 5.8 shows an example of a Tafel polarization plots recorded in the absence of SC in the solution (control) and in the presence of 10mM of SC in the solution at 295K and Montreal tap water at pH 8. In this figure, the cathodic branch is given by the branch of Tafel plot lying potentials negative of OCP (the sharp negative 'spike' on the graph). The cathodic branch is related to the hydrogen evolution or reduction of oxygen reaction occurring on the CS surface. Since the electrolyte, in the current case, was deoxygenated by argon, the cathodic branch (cathodic corrosion reaction) represents the hydrogen evolution reaction. The anodic branch lies towards the potentials positive of OCP, where the actual iron dissolution reaction occurs. Since the two partial corrosion reactions are under kinetic control, the cathodic and anodic current branches show linear regions as shown in the Figure 5.8 below. [60] The point of intersection of the extrapolated linear parts (Tafel slopes) lies at the corrosion potential E_{corr} and it yields the total corrosion current density j_{corr} (A cm⁻²), while the slopes of the two linear parts are termed as "Tafel slopes".



Figure 5.8: Typical tafel polarization curves recorded in the absence(0mM) and presence of 10mM SC in the Montreal tap water of pH 8 and at 295 K.

In **Figure 5.8**, it is seen that when SC is present in the solution, the currents in the entire potential region decrease relative to those in the absence of SC in the solution. This indicates that SC inhibits both the cathodic and anodic corrosion reaction, thus acting as a mixed type of corrosion inhibitor.

Table 5.2:Tafel parameters for CS substrate dipped in solution of increasing concentration of SC at pH 8 Montreal tap water and 295 K.

SC(mM)	0	1	5	6	6.25	6.28	6.3	6.5	7	8	10	12	17
jcorr X10 ⁶	3.4	2.95	2.71	2.41	2.856	2.649	0.173	0.314	0.180	0.236	0.2890	0.1594	0.2059
(A cm ⁻²)													
±SD	0.2	0.19	0.087	0.199	0.236	0.344	0.0118	0.071	0.037	0.023	0.0253	0.0291	0.0404
β _c (Vdec ⁻¹)	0.167	0.135	0.153	0.165	0.173	0.160	0.113	0.111	0.112	0.112	0.107	0.117	0.110
\pm SD	0.007	0.031	0.031	0.022	0.021	0.030	0.013	0.006	0.013	0.007	0.009	0.005	0.006
$\boldsymbol{\beta}_{a}(Vdec^{-1})$	0.085	0.090	0.085	0.084	0.086	0.089	0.274	0.257	0.133	0.277	0.235	0.199	0.222
\pm SD	0.002	0.005	0.007	0.005	0.006	0.004	0.118	0.008	0.032	0.071	0.013	0.060	0.053
R _T -iR													
$(\Omega \text{ cm}^2)$	6471	7883	8695	10335	8715	9355	193275	110967	147333	145700	110733	199717	156767
\pm SD	250	248	351	990	750	744	8624	24581	14354	13922	6276	18955	22823
Ecorr (V)	-0.79	-0.81	-0.80	-0.79	-0.79	-0.801	-0.225	-0.269	-0.217	-0.249	-0.235	-0.218	-0.225
\pm SD	0.003	0.013	0.012	0.008	0.010	0.0070	0.0132	0.011	0.017	0.020	0.040	0.019	0.020

To quantify the behaviour of the system in terms of the kinetics of corrosion reactions, the Tafel plots recorded at various SC concentrations are analyzed and the corresponding kinetic values are presented above in **Table 5.2**: corrosion resistance from Tafel Polarization $R_T (\Omega \text{ cm}^2)$, corrosion current density j_{corr} (Acm⁻²) at corrosion potential E_{corr} (V) and Tafel slopes, namely anodic slope β_a and cathodic slope β_c in (Vdecade⁻¹). It should be noted that while calculating the efficiencies of Tafel resistance R_T , the Tafel plots are corrected with regards to uncompensated resistance *iR*, which is the resistance between the WE and RE and in another words R_{el} , that is obtained from EIS results.

From **Table 5.2**, it can be observed that the value of j_{corr} decreases with an increase in the concentration of SC, implying decline in the rate of corrosion on the CS surface due to adsorption of the inhibitor molecule. The E_{corr} value has also shifted towards positive potential which also implies protection against corrosion due to the presence of the inhibitor molecule. Looking at the values of the Tafel plot slopes, both the anodic and cathodic slope values remain unaffected by the SC concentration going from 0 to 6.28 mM, but then suddenly change and again remain almost constant. This behaviour is in accordance with the OCP, PR, and capacitance behaviour discussed previously in the thesis. The change in the cathodic slope value indicates a change in the hydrogen evolution reaction mechanism, and the same can be claimed for the anodic reaction where the change in the iron dissolution (corrosion) mechanism is observed. Further, the trend of R_T values is very similar to that from EIS and PR measurements, and a sudden increase at 6.3mM of SC is observed. In conclusion, the trend of all kinetic values in the table is in accordance with the trends obtained from OCP, PR and EIS measurements.

Figure 5.9 and **Figure 5.10** represent the corrosion inhibition efficiencies calculated from R_T (using eqn. 5.2) and j_{corr} (using eqn. 5.3) values respectively with varying concentrations of SC at pH 8 and 295 K (the efficiency values are calculated by comparing either the corrosion current

density or Tafel polarization resistance values in the absence and presence of SC in the solution). Efficiency w.r.t to j_{corr} is calculated by using:

$$\eta = \left(1 - \frac{j_{corr,i}}{j_{corr,o}}\right) X 100\%$$
(5.3)

Where, $j_{corr,i}$ (Acm⁻²) is current density when inhibitor is present and $j_{corr,o}$ (Acm⁻²) is the current density of the controlled experiment. The efficiencies obtained for j_{corr} and R_T follows the similar trend that is observed during OCP, EIS and PR measurements. Hence, this proves the consistency of results obtained with the help of all the four electrochemical techniques.



Figure 5.9: Corrosion inhibition efficiency of SC against blank solution calculated from Tafel polarization resistance R_T obtained from Tafel polarization curves, as a function of SC concentration at 295 K and pH 8 Montreal tap water.



Figure 5.10: Corrosion inhibition efficiency of SC against blank solution calculated from current density j_{corr} values obtained from Tafel polarization curves, as a function of SC concentration at 295 K and pH 8 Montreal tap water.

5.1.5 Compilation of the results obtained from EIS, PR, TP

From the efficiency plots obtained from EIS, PR and TFL experiments i.e. **Figures 5.5**, **5.7**, **5.9** and **5.10** it is observed that inhibition efficiency of SC is dependent on its solution concentration. All the three electrochemical experiments yielded almost similar behavior, and **Figure 5.11** represents the compilation of corrosion efficiency values obtained from all the three experimental techniques (i.e. four sets of corrosion inhibition efficiency values). As mentioned before, the trend can be divided in two SC-concentration dependent regions: <6.28 mM and >6.3 mM.



Figure 5.11: Corrosion inhibition efficiency by SC calculated from PR, EIS and Tafel measurements as a function of SC concentration at 295 K, pH 8 Montreal tap water.

Namely, there is a sharp increase in the corrosion inhibition efficiency obtained when the concentration of SC increases from 6.28 mM to 6.3mM. This is an interesting trend for an efficiency vs concentration plot, especially when the applied concentration of SC is significantly lower than its CMC value, i.e. 351mM in de-ionized water [77]. It can be speculated that, for SC concentration below 6.28mM, the protective SC layer formed on top of the exposed CS surface is amorphous / disordered, as schematically shown in **Figure 5.11** Within this SC concentration region, the surface coverage by SC is also low, and thus the corrosive electrolyte can penetrate through the layer to the surface and cause the corrosion of the surface, albeit at a lower extent than when the surface is completely 'naked' (no inhibitor in the solution). However, with an increase in concentration of SC from 6.28 mM to 6.3mM, the SC monolayer gets re-oriented and becomes more condensed and structured, which results in higher protection against corrosion and hence the corrosion inhibition efficiency abruptly increased. Also, there is a possibility that a bilayer or a multilayer protective film is formed on top of the CS substrate, as schematically shown in **Figure**

5.11. [79-80]. The trend observed in **Figure 5.11**, is termed as S-shaped isotherm in certain literature and it was reported that a sharp increase in adsorption was observed at concentrations much below CMC [81]. The rise in the efficiency can be accounted by changes in the conformation of the adsorbed inhibitor molecule, i.e. horizontal orientation w.r.t CS surface at lower concentration and perpendicular orientation at higher concentrations. These studies are based on corrosion inhibition by organic surfactants for carbon steel in acidic medium [82]. Also, with regards to the results obtained in this report, the trend of SC inhibition efficiencies can be interpreted in terms of hemimicelles and admicelles. Per this theory, there is a sharp increase in slope of adsorption isotherm of surfactant molecules when 2D aggregates called hemimicelles start forming on the surface of the substrate. The concentration at which hemi-micelles are formed is termed as hemi-micelle concentration (H.M.C) and it is of the order of 1/100 of the C.M.C and happens at a surface coverage of approximately 1/100 of a monolayer [83]. However, further experiments must be performed to study the actual mechanism behind the sudden jump in the corrosion inhibition efficiency. Using, studies like PM-IRRAS the structure of the SC protective layer on top of CS substrate could be investigated.

Since, a very high corrosion inhibition efficiency was observed from 6.3mM SC concentration until 17mM, 10 mM SC concentration is chosen as the optimum concentration for further experiments.

Note: While carrying out experiments with 6.3mM, 6.5mM and 7mM of SC concentrations at Montreal tap water of pH 8 and 295 K, the results obtained from OCP, EIS, PR and Tafel Polarization showed fluctuations. This could be because of some faulty experimental condition or due to re-organization of the monolayer on top of the CS substrate. Thus, these concentrations can be termed as the region of "transition", where re-growth or re-organization of the monolayer occurred. In addition, the salt concentration in the Montreal tap water changes from day to day, and thus its corrosivity.

5.2 Effect on temperature

To evaluate the effect of temperature on the corrosion inhibition efficiency of SC, PR experiments are carried at varying temperatures in the absence and presence of SC at 10mM concentration at pH 8 Montreal tap water. In **Figure 5.12**, the efficiency calculated from polarization resistance (using eqn. 5.2) is given. It can be observed that with an increase in temperature, the inhibition efficiency of PR only slightly decreases up to 313K, and then at 333K it suddenly decreases to 86%. This is expected given that the protection of the CS surface by SC inhibitor depends on the surface coverage by SC and orientation of SC molecules on the surface. With an increase in temperature after 313K, it appears that the surface coverage by SC decreased, which then resulted in an increase in corrosion rate. Nevertheless, even at 333K the protection of the surface is relatively high, indicating a good performance of SC.



Figure 5.12: Corrosion inhibition efficiency by SC calculated from PR measurements as a function of temperature for SC concentration of 10mM at pH 8 Montreal tap water.

Temperature varying experiments can also be used for determination of activation energy (E_a) employing the Arrhenius equation:

$$\ln(CR) = -E_a/RT + \ln A \tag{5.4}$$

where E_a (J mol⁻¹) depicts the apparent activation energy, R (8.314 J mol⁻¹ K⁻¹) is the universal gas constant, T (K) is the absolute temperature, CR represents the corrosion rate and A (A cm⁻²) is the pre-exponential factor. The equation (5.4) can also be represented in terms of inverse of the polarization resistance PR⁻¹(Ω ⁻¹) as shown in equation (5.5), since CR can be represented w.r.t to corrosion current I_{corr} (Amperes), where I_{corr} is again inversely related to PR.[84]

(5.5)

 $\ln(PR^{-1}) = -E_a/RT + \ln A$

In equation 5.5, the inverse of the polarization resistance is directly related to the kinetics of corrosion reactions. **Figure 5.13** gives the plots for $\ln(PR^{-1})$ vs (T^{-1}) in absence and presence of SC at 10mM and shows the dependence of corrosion resistance on temperature represented in equation 5.5. The value of E_a is obtained from the slope of the lines as given in **Figure 5.13**, i.e. E_a value for 10mM solution is 47.1 KJ mol⁻¹ and that one for 0mM SC solution is 22 KJ mol⁻¹. The E_a value is higher for the inhibited solution as compared to the blank solution. This implies that SC not only protects the surface from corrosive species by adsorption (the surface coverage effect), but also increases the activation energy related to the corrosion reactions.



Figure 5.13:Arrhenius plot for CS at 0mM and 10 mM SC in Montreal tap water at pH 8 and varying temperatures. Results are obtained from PR measurements.

5.3 Effect on pH

The effect of pH was studied on the corrosion of carbon steel in the absence and presence of 10mM concentration of SC in the Montreal tap water at 295K. The pH of water is adjusted to pH 7, pH 8, pH 8.5, pH 9 and pH 10. pH adjustments for pH8, pH 9 and pH 10 are done using 8M NaOH and pH 7 is adjusted with the help of 0.5M H₂SO₄. From **Figures 5.14 and 5.15**, it can be observed that even with variation in pH range from pH 7 to pH 10, the corrosion inhibition efficiencies(using PR and Tafel polarization measurements) that are yielded are high. However, although the behaviour is pH dependent, the variation is rather random, without displaying any particular trend. In conclusion, it can be claimed that SC performed efficiently in the pH range from 7 to 10.



Figure 5.14:Corrosion inhibition efficiency of SC calculated from PR measurements as a function of pH for SC concentration of 10 mM at 295 K.



Figure 5.15:Corrosion inhibition efficiency of SC calculated from j_{corr} (Acm⁻²) obtained from Tafel polarization measurements as a function of pH for SC concentration of 10 mM at 295 K.

5.4 Kinetics of adsorption of Sodium Caprylate

The SC adsorption kinetics experiments are done by measuring the polarization resistances in the absence of SC in the solution and in the presence of 10 mM of SC in the solution, employing the polarization resistance technique at varying time intervals at 295 K and pH 8 Montreal tap water. A plot of the resulting corrosion inhibition efficiency (obtained by using eqn. 5.2) is given in **Figure 5.16**. It can be seen that after two minutes of adsorption, the inhibition efficiency reaches 81%, demonstrating a very quick SC adsorption process. However, this point should be taken with caution due to the time scale of the measurement; the actual linear polarization scan takes 80 seconds to complete. However, when this point is dismissed, the trend in the figure shows a typical adsorption kinetic behaviour. Namely, with an increase in time, the surface coverage by SC first sharply increases and then gradually reaches a plateau (not attained within the time frame of the present experiment), representing a quazi-equilibrium.



Figure 5.16: Corrosion inhibition efficiency by SC against blank solution calculated from PR measurements as a function of time for SC concentration of 10mM at 295 K, pH 8 Montreal tap water. The graph can be related to the kinetics of SC adsorption.

5.5 Effect of long-term Sodium Caprylate corrosion protection efficiency

The effect of long-term immersion of CS in pH 8 Montreal tap water at 295 K is investigated in absence and presence of Sodium Caprylate at 10mM. The investigation is done by studying the topography of the carbon steel samples using Scanning Electron Microscopy (SEM) technique for different duration of time. **Figure 5.17**, shows the SEM image of a freshly-polished and dry CS surface (this CS sample is not immersed in the electrolyte before the SEM image was taken). This figure serves as a reference for comparison of SEM images given in **Figure 5.18**.



Figure 5.17:Scanning Electron Microscopy (SEM) image of a freshly polished CS surface.

The **figure 5.18(a)** represents the SEM image of a CS sample that is kept in a 0 mM SC solution of pH 8 Montreal tap water at 295 K for 30 days (unprotected sample). It can be seen that the surface is extensively covered by corrosion products.



Figure 5.18: (a) SEM image of a CS sample kept in 0mM SC solution for 30days at 295 K, pH 8 Montreal tap water, (b) SEM image of a CS sample kept in 10mM SC solution for 30 days at 295 K, pH 8 Montreal tap water.

On the other hand, the sample in **Figure 5.18(b)** looks negligibly affected by corrosion, which implies that 10mM concentration of SC solution could protect the CS sample for a span of 30 days at 295 K, pH 8 Montreal tap water.

CHAPTER 6: Conclusions

The possibility of using Sodium Caprylate as a corrosion inhibitor for closed-loop-water heating/cooling systems was investigated using OCP, EIS, PR, Tafel Polarization and SEM techniques and following conclusions were drawn:

- 1) SC gave 96% corrosion inhibition efficiency when applied at 10mM concentration. All the four electrochemical techniques gave good agreement and results showed consistency.
- 2) There was a sudden jump in the corrosion inhibition efficiency when SC concentration increased from 6.28mM to 6.3mM, which was prescribed to structural changes of SC molecules on the CS surface and/or due to the formation of a multi-layered SC structure.
- SC showed a corrosion inhibition efficiency of 86% at a temperature range of 333 K, implying it is applicable for high temperature applications like closed-loop-water heating/cooling systems.
- The kinetics of adsorption process revealed that SC adsorption process is very quick and it readily starts protecting the carbon steel surface after 2 minutes.
- 5) SC showed high inhibition efficiency in the pH range between pH 7 to pH 10.
- 6) Scanning Electron Microscopy studies showed that SC protected the carbon steel sample for a span of 30 days at 295 K with negligible corrosion occurring on its surface
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