STUDY OF SOME IMIDAZOLIUM BASED IONIC LIQUIDS AS GREEN CORROSION INHIBITOR ON MILD STEEL IN ACIDIC MEDIUM

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Submitted by
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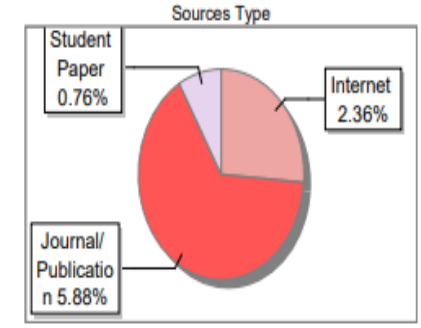

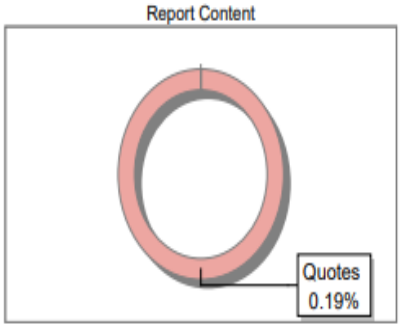

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ABSTRACT

The corrosion is a world-wide severe material science problem due to having social and economic impact. The prevention techniques become more realistic because the completely removal of corrosion is not possible. One of very important prevention method is use of corrosion inhibitor. Corrosion inhibitor is a chemical substance added to the corrosive environments which is reduce the corrosion rate of metal and alloys by formation of protective layer or increasing the electrical resistance on metal surface.

As a contribution to the current interest in finding out environment friendly more efficient corrosion inhibitors the present thesis focuses on the synthesis and characterization of some imidazolium based ionic liquids and their application as green corrosion inhibitors for mild steel corrosion in 0.5 M H_2SO_4 medium. Mild steel material is extensively used in various industries due to low cost, easy availability, high tensile strength, good malleability, high ductility, and many other properties. One such attractive strategy involves ionic liquids due to their fascinating properties such as low volatility, non-flammability, non-toxic nature, high thermal and chemical stability and their ability to adsorb on the metallic surface. Henceforth, the present work also explored the effect of different alkyl chain length and effect of different anions of imidazolium based ionic liquids on mild steel surface in 0.5 M H_2SO_4 medium. These ionic liquids were synthesized using a well-established green microwave irradiation method. The thesis work conducted is described in the following chapters:

CHAPTER-1: INTRODUCTION AND REVIEW OF LITERATURE

The purpose of this chapter to provide a primary information about the corrosion, it's historical background, causes, phenomenon, types of corrosion, its social and economic impact on development and the factors which play important role in corrosion process. This chapter also discuss the basic mechanism of corrosion and methods which can use to protect the material such as protective layer formation, selection of material, inhibitors and reduction of destructiveness of corrosive material.

CHAPTER-2: MATERIALS, METHODS AND METHODOLOGY

This chapter provides information about the conventional methods and advanced instruments, tools, materials and techniques used during the experimental works to

obtain objectives of present research studies. It also presents the outline of experimental setup and make our study replicable.

CHAPTER-3: SYNTHESIS AND CHARACTERIZATION OF SOME IMIDAZOLIUM BASED IONIC LIQUIDS

This chapter focuses on the synthesis and structure confirmations of imidazolium based ionic liquids with different alkyl chain of cationic part and different anions namely 1-Ethyl-3-ButylImidazolium Bromide [BuEImBr], 1-Ethyl-3-PentylImidazolium Bromide [PEImBr], 1-Ethyl-3-BenzylImidazolium Bromide [BzEImBr], 1-Ethyl-3-BenzylImidazolium chloride [BzEImCl]. All four ionic liquids are synthesized by the help of microwave assisted synthesizer and characterized by various spectroscopic technics such that ^{1}H NMR, ^{13}C NMR, IR and Mass Spectrometry.

CHAPTER-4: IMIDAZOLIUM-BASED IONIC LIQUIDS OF DIFFERENT CATION AS GREEN CORROSION INHIBITOR

Ionic liquids are widely used in various fields of industries due to their low volatility, non-toxic, high adsorption ability, eco-friendly and least expensive nature. In the past decades the use of ionic liquids as corrosion inhibitor is the topic of interest of research in the field of material science. Various chemical variants of ionic liquids are available among of these Imidazole based ionic liquids reported as excellent corrosion inhibitor on mild steel material. In this chapter the effect of side alkyl chain length was investigated on inhibition efficiency & corrosion rate of two imidazolium based ionic liquids having different cations namely: 1-Ethyl-3-Butylimidazolium Bromide [BuEImBr] and 1-Ethyl-3-Pentylimidazolium Bromide [PEImBr]. The various advanced techniques such as gravimetric measurement, potentiodynamic polarization measurement, electrochemical impedance spectroscopy, scanning electron microscopy were used for inhibition efficiency measurement. The obtained results from the all described techniques were in consonance to each other.

CHAPTER-5: IMIDAZOLIUM-BASED IONIC LIQUIDS OF DIFFERENT ANIONS AS GREEN CORROSION INHIBITOR

This chapter deals with the corrosion inhibition properties of imidazolium based ionic liquids containing different anion [BzEImBr] and [BzEImCl]. Chapter provide the strong evidences for the metal inhibitor interaction. Various advanced methods such

that weight loss, electrochemical measurements used for determine corrosion parameters. Surface morphology of mild steel surface was studied by the use of SEM (scanning electron microscopy) in absence and presence of inhibitor in 0.5 M sulphuric acid solution. Kinetical and thermodynamic parameters help to describe inhibition mechanism and determining temperature effects.

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DECLARATION

I, **Ashish Rathore**, hereby certify that the research work presented in my Ph.D. thesis entitled **"Study of Some Imidazolium based Ionic Liquids as Green Corrosion Inhibitor on Mild Steel in Acidic Medium "** which is carried out by me under the supervision of **Dr. Sushil Kumar Sharma** and submitted in the partial fulfillment of the requirement for the award of the degree of Doctor of Philosophy of the University of Kota, represents my ideas in my own words and where others' ideas or words have been included in this thesis, I have adequately cited and referenced the original sources.

The work presented in this thesis has not been submitted elsewhere for the award of any degree or diploma from any other institution or university in India or abroad. I declare that I have adhered to all the principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea / data / fact / source in my submission.

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This is to certify that the above statement made by **Mr. Ashish Rathore** (Registration Number RS/2525/20) is correct to the best of my knowledge.

Date: **Dr. Sushil Kumar Sharma**
Place: Research Supervisor

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"सरस्वति महाभागे विद्ये कमललोचने। विद्यारूपे विशालाक्षि विद्यां देहि नमोऽस्तु ते।।"

हे! महा भाग्यवती, ज्ञानदात्री, ज्ञानरूपा कमल के समान विशाल नेत्र वाली सरस्वती माँ मुझे विद्या प्रदान करें ।मैं आपको प्रणाम करता हूँ।

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This thesis reflects not only my work but also the collective support of everyone who has touched my life academically and personally. The journey has taught me the value of questioning and the importance of diverse perspectives in enriching our understanding of complex philosophical issues.

Ashish Rathore

CONTENTS

LIST OF ABBREVIATIONS

AC	Alternative current
AE	Auxiliary electrode
BuEImBr	1-Ethyl-3-Butylimidazolium Bromide
BzEImBr	1-Ethyl-3-Benzylimidazolium Bromide
BzEImCl	1-Ethyl-3-Benzylimidazolium Chloride
CE	Counter electrode
CI	Corrosion inhibitor
Conc.	Concentration
C_R	Corrosion rate
DC	Direct current
EDS	Energy dispersive x-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
FE-SEM	Field emission – scanning electron microscopy
IE	Inhibition efficiency
IGC	Intergranular corrosion
ILs	Ionic liquids
ImILs	Imidazolium-based ionic liquids
MS	Mild steel
OCP	Open circuit potential
OGCIs	Organic green corrosion inhibitors
PEImBr	1-Ethyl-3-Pentylimidazolium Bromide
PDP	Potentiodynamic polarization
PR	Polarization Resistance
RE	Reference electrode
SC	Stress corrosion

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Chapter – 1

INTRODUCTION AND REVIEW OF LITERATURE

Abstract

The purpose of this chapter to provide a primary information about the corrosion, it's historical background, causes, phenomenon, types of corrosion, its social and economic impact on development and the factors which play important role in corrosion process. This chapter also discuss the basic mechanism of corrosion and methods which can use to protect the material such as protective layer formation, selection of material, inhibitors and reduction of destructiveness of corrosive material.

1.1 Concept of corrosion

The "corrosion" word is originated by the Latin word "corrodere" which means "to gnaw away" (to eat away) [1-2]. After 1960s the term 'corrosion' correlates the oxidation of all natural, synthetic, biomaterial and nanomaterials [3]. Corrosion is a universal phenomenon in which the material converted into chemically more stable form such as hydroxides, oxides, etc. Corrosion is naturally occurring, non-reversible, electrochemical redox process between metal and corrosive environment [4-6].

The researchers and material scientists define the corrosion in their work.

The international standard organization define corrosion as "corrosion is a physiochemical reaction between metal and its surrounding environment to modified the properties of metal" generally the functional properties of metal is degraded in this process [7].

According to Fontana," corrosion is destruction or deterioration in the material properties by electrochemical reaction with corrosive environments" [8].

The British scientist U.R. Evans (1923) known as `father of corrosion science` said that corrosion is largely an electrochemical phenomenon it may be define as destruction by electrochemical or chemical agents [9].

The international union of pure and applied chemistry define the corrosion as "An irreversible interfacial reaction of a material with its environments which results in consumption of material or in dissolution into the material of a component of the environment" [10].

The metal- environment interaction on the environment is often more important than the actual deterioration of metal for example lead pipes cannot used in water supply, galvanized steel may not use in the foodstuff due to the toxicity of lead and zinc salt

respectively. To avoid these types of issues selection of material with environmental combination is major point of interest [11-12].

The following are the main concepts in the definition: degradation, material, reaction, and environment which can be explained as follow [11,13-14].

Metal – chemical composition, macroscopic and microscopic heterogeneities, physical characteristics like stress, tensile strength etc.

Environment – chemical nature, concentrations, impurities, pressure, temperature, velocity, impingement etc.

Metal–Environment interface – kinetics of metal oxidation and dissolution, nature and location of corrosion products, film growth and film dissolution etc.

1.2 Historical background of corrosion study

The historical background of corrosion is too old, in ancient, corrosion is commonly known as rust, and it was defined as a phenomenon by which the material destroys own beauty and luster. In AD 23-76 first of all roman philosopher Pliny and elder wrote about the iron destruction in their essay "Ferrum corrumpitar" [15]

Many scientists and authors are in row who mentioned corrosion in their writings [16-17].

- Herodotus (5^{th} century) and Davy (1824) suggest the methods for protection of iron by using tin and zinc respectively.
- In 1788 Austin noticed the alkaline nature of water when it reacts with iron.
- Thenard explain corrosion as electrochemical phenomenon in 1819.
- In 1829 Hall established that iron does not rust in the absence of oxygen.
- Willis R. Whitney published first paper in 1903 on corrosion as a convincing proof that the corrosion is an electrochemical process.
- The second decades of 20^{th} century the research developed in the field of microbial corrosion, corrosion fatigue, stress corrosion, cracking.
- During 1920s researchers also take interest in the corrosion study of nonferrous metals.
- A new branch of corrosion engineering developed by the industrial support to the study of fundamental of corrosion.
- In 1924 a British scientist U.R. Evans published a book "The corrosion of metals" which gave much impetus to this new field of research.

- A corrosion division established in 1942 by electrochemical society L.G. Vande Bogart elected as a first president.
- The national association of corrosion engineering (NACE) founded in 1945.
- 1948 H.H. Uhlig edited corrosion handbook. Approx. 24,854 copies have been sold of this book by the end of 2001.
- During 1950 to 1960 the interest developed in high temperature corrosion, corrosion protection of metals and semiconductors.
- Stern and Geary extend the work on corrosion protection by deriving a equation which shows that the corrosion rate is inversely proportional to the slope of the polarization curve.
- Many surface analytical technologies adapted for corrosion analysis by the end of 1990s.
- During the last twenty to thirty years, the corrosion division extend their interest to address current technical problems, corrosion in non-aqueous solvent, sensors for corrosion detection and in the field of corrosion protection by coating and inhibitors.

1.3 Cause of corrosion

The starting form of metals are minerals and ores. When the metals are exposed in the environment, they would revert back to their natural form such as oxides, hydroxides, sulphides etc. thus metal represent a state that having higher energy and it tried to decrease their energy by spontaneously reacting to form compounds that have great thermodynamic stability. The amount of energy which are freed by corrosion varies from metal to metal. It is relatively high for metals such as aluminum, iron and magnesium and relatively low for copper, gold and silver. For example, when iron and steel come in contact of moisture and air it forms rust or iron oxide film on the iron surface [18-19].

The negative values of Gibbs free energy for the corrosion reaction tends to convert metal into the corrosion product. The Pilling Bedworth ratio parameter also used to predict the extend of oxidation of metal [20].

1.4 Classification of corrosion process

The corrosion process can be classified mainly on the basis of the corrosive environments, mechanism and surface appearance. These can be illustrated in the following **Table 1.1**.

Table 1.1: Classification of corrosion process

Base of classification	Types	Features
Corrosive environments	Dry Corrosion	In this type of corrosion, the metal is directly reacted with the atmospheric air or oxygen, halogens, hydrogen sulphide, nitrogen, sulphur dioxide etc. in absence of moisture.
	Wet Corrosion	Wet corrosion is taking place when the metal is directly contact with the moisture or electrolytic solution. The corrosion reaction occurs at the metal- electrolytic interface. It creates cathodic and anodic sites at the metal.
Corrosion mechanism	Electrochemical Corrosion	It occurs in wet condition with large numbers of anodic and cathodic sites.
	Chemical Corrosion	It takes place in dry condition by the direct attack of environment on metal.
Surface appearance	Uniform Corrosion	This type of corrosion affects the entire surface of material.
	Localized Corrosion	In this type of corrosion, a specific area of material is affected.

1.5 Form of corrosion

Due to the different material and environmental condition corrosion affect the material in variety of ways. Corrosion scientists described the various forms of corrosion on the basis of appearance and change in the physical properties of material [21-24].

1.5.1 ***Uniform corrosion***- In this type of corrosion form large surface area is uniformly attacked by corrosive environment and result is that the metal is distorted uniformly and metal losses in an even corrosion rate. A corrosion film is form on the metal surface. **Figure 1.1**

Figure 1.1: Uniform corrosion
(https://armoloy.com/wp-content/uploads/2023/10/uniform-corrosion.jpg)

1.5.2 ***Galvanic corrosion*** **–** It is also known as bimetallic corrosion. It occurs when two conductive metals are electrically connected to each other and present in an electrolytic corrosive environment, the metal with lower reduction electrode potential undergo corrosion, due to the strong driving force for dissolution generated by potential difference between metals. Metal which has lower reduction electrode potential according to the galvanic series act as anode. This type of corrosion can be protected by using insulating material on metals. **Figure 1.2**

Figure 1.2: Galvanic corrosion
(https://armoloy.com/wp-content/uploads/2024/11/galvanic-corrosion-on-washer-and-nut.jpg)

1.5.3 ***Crevice corrosion*** **–** It is the localized form of corrosion occurs in the narrow junction gap of metal-metal or metal-nonmetal due to trapped a small number of electrolytes in crevice. In this type of corrosion form a concentration cell is form between the junction gap and electrolyte, in which electrolyte act as cathode while the gap between metal act as anode. This form of corrosion seems in crevice of pipes in presence of moisture. This type of corrosion can be prevented by use welded joints. **Figure 1.3**

Figure 1.3: Crevice corrosion
(https://orapiasia.com/wp-content/uploads/crevice-corrosion-causes-1-1024x482.jpeg)

1.5.4 ***Pitting corrosion*** **–** It is an extreme case of localized corrosion in steel, aluminum etc. it Generated due to the breakdown of protective film. It is not easy to detect in general inspection because pit is covered by corrosive material. Generally, the aggressive anions such that halides and sulphates break the protective film and generate pit on metal surface. **Figure 1.4**

Figure 1.4: Pitting corrosion
(https://assets.efficientplantmag.com/wpcontent/uploads/2017/06/1706rmcasset.jpg)

1.5.5 ***Erosion corrosion*** – In this form of corrosion, mechanical force is work as a driving force for corrosion. It occurs when the corrosive medium is flow on the metal surface and a markable increment is observe in corrosion rate when the flowing rate is reached to critical velocity, this type of corrosion observed in all type of equipment's like pumps bends and valves etc. it can be reduced by proper designing and cathodic protection. **Figure 1.5**

Figure 1.5: Erosion corrosion
(https://armoloy.com/wp-content/uploads/2024/11/erosion-corrosion-of-old-pipe.jpg)

1.5.6 ***Stress corrosion (SC)*** **–** This type of corrosion is combining effect of static tensile stress and corrosive environment. Corrosive environment, temperature and pH affected the stress corrosion. SC can be prevented by use of inhibitors. **Figure 1.6**

Figure 1.6: Stress corrosion
(https://us.sfs.com/images/640/7093%20%20US/Resource%20Hub/Learn%20More%20%20Industry/Stress%20corrosion%20cracking%20prevent/brown%20corrosion%20crack.jpg)

1.5.7 ***Biological corrosion*** – The term biological corrosion referred for the degradation of metal by living organism. Macro or microorganisms directly or indirectly affect the corrosion by influencing anodic or cathodic reaction, producing corrosive environment, create electrolytic cells and by altering the composition of corrosive media. **Figure 1.7**

Figure 1.7: Biological corrosion
(https://www.luminultra.com/wp-content/uploads/mic-passman-figure-3.jpeg)

1.5.8 ***Selective leaching*** – It is the removal of reactive metal from a solid alloy composition, for examples dezincification of brass, selective leaching of iron from gray cast iron. **Figure 1.8**

Figure 1.8: Selective leaching
(https://upload.wikimedia.org/wikipedia/commons/thumb/7/7f/Spongiose500.jpg/220px-Spongiose500.jpg)

1.5.9 ***Inter-granular corrosion (IGC***)- It is a specific type of corrosion form also known as inter crystalline corrosion in which corrosion take place at the boundaries of grain due the presence of impurities, it is act as anode while the main body of grains protected because of act as cathode. For each alloy system the mechanism is differ of IGC. It can be reduced by the addition of some specific metals which can form strong carbide such as niobium and tantalum. **Figure 1.9**

Figure 1.9: Intergranular corrosion
(https://mohammad0044.wordpress.com/wpcontent/uploads/2014/11/f117-2.jpg)

1.6 Corrosion rate and factors affecting the corrosion rate

The metal and nonmetal can be compared on basis of their corrosion resistance nature, to make it more relevant several researchers expressed the quantitative expression of rate of attack for each material in their literature such as- percentage weight loss, milligrams per square centimeter per day, gram per square inch per hour but they do not used to expressed the life of a component, the `mils per year` is the most desirable way to expressed the rate of corrosion which can be readily calculated by the weight loss of metal during the corrosion test. the other units of corrosion rate are as follow- Inches per year (ipy), Milli meters per year (mm/yr.), Micro meters per year (μm/yr.), Milligrams per square Deci meter per day (mdd).

The loss of material per unit surface and per unit time is define as corrosion rate. for a uniform corrosion, average corrosion rate can be calculated by faraday law [25]. The corrosion rate mainly affected by both the metal and the corrosive environments [26-27]. Factors which are affect the rate of corrosion categorized as-

1.6.1 Factors related to the metals - The selection of metal plays an important role in corrosion process. The corrosion and its nature directly depend on metal which used as material, some factors related to metals discussed as follow [28-30].

a. **Physical state of metal-** The corrosion rates are higher of stressed metals in compare to the non-stress metals. For examples the corrosion rate is fast in joints, bends, valves and rivets of boiler.

b. **Reduction potential position in electrochemical series-** The electrochemical series is the increasing order of reduction electrode potential hence when two different metals are linked electrically in electrolytic solution then the corrosion rate of the metal which is present high in the series or having low reduction electrode potential gets highly corroded while another metal is protected. The rate of corrosion depends on the potential difference between the metals, higher the potential difference the rate is also higher.

c. **Impurities in metal**- Impurity is heterogeneity of a pure metal which creates small galvanic cells due to this the anodic part of metal gets corroded and the corrosion rate increases with increasing the impurity.

d. **Relative areas of cathode and anode-** The ratio of anode and cathode area play important role in electrochemical reaction. Larger the cathode area leads the faster consumption of electrons, hence small ratio of anode / cathode, the rate of corrosion is high.

e. **Hydrogen overvoltage-** In the electrochemical corrosion process hydrogen gas is evaluated at cathode. higher overvoltage of hydrogen decreases the rate of cathodic reaction, or reduce the rate of overall corrosion reaction.

f. **Nature of metal surface film –** The metal surface reacts with atmosphere and form oxide film on metal surface. It is a corrosion product, if the corrosion products are insoluble and non-porous the rate of corrosion is decrease while the corrosion rate is increase if the surface film is volatile or soluble in nature.

g. **Nature of corrosion product**- The corrosion product is present on metal surface which is act as a barrier between metal and corrosive environment for further attack. So, if corrosion product has nonvolatile, non-porous and insoluble nature it restricted the father attack of electrolyte.

1.6.2 Factors related to the environments -The rate of corrosion is also depending on the nature of corrosive environment or electrolyte [31-33] the aggressive nature of

electrolyte usually increases the corrosion rate, the factors which are directly related to the environments are discussed as [34-36]

a. **Oxygen concentration of electrolyte-** As usually the rate of corrosion is increase on increasing the oxygen concentration in the environment but the formation of non-porous oxide layer on the metal surface is decrease the rate of corrosion.
b. **Impurity of corrosive environments-** The corrosiveness is considerably increase on increasing the impurity in atmosphere. For example, oxide of nitrogen catalyzed the oxidation of sulfur to form sulphuric acid which increase the rate of corrosion.
c. **Temperature-** Usually, high temperature increases the dissolution of oxygen and concentration of ions in atmosphere which leads the rate of corrosion.
d. **Conductivity of electrolyte –** The conductivity of electrolyte is directly related to the flow of electrons or corrosion current density, which increase the rate of corrosion.
e. **pH of the corrosive environment-** The corrosive nature of any metal depends on the nature of the corrosive environment, in the acidic medium the evaluation rate of hydrogen gas on cathode increased which leads the faster corrosion rate.
f. **Humidity-** On increasing moisture in atmosphere the rate of corrosion is significantly increase because it provides a furnished electrolytic environment to the electrochemical corrosion.
g. **Fluid velocity-** Higher the relative velocity between the medium and corrosion surface accelerates the corrosion rate due to the diffusion of soluble corrosive product film on metal surface.

1.7 Electrochemical theory of corrosion

The British scientist U.R. Evans described ‘corrosion’ mainly an electrochemical phenomenon. According to this theory metal is react electrochemically with the water, oxygen and other substances present in the aqueous electrolytic solution. Electrochemical theory of corrosion based on the electron transfer between the metal and electrolyte. Oxidation proceed at the anodic sites while the reduction take place at the cathodic sites. Electrochemical corrosion can be explained by the following oxidation-reduction reactions [37].

Anodic reactions- Electrons are released at the metal surface anodic sites by the oxidation of metal atoms.

$$M \rightarrow M^{n+} + ne^-$$

Cathodic reaction- The reduction takes placed at the cathodic sites which are depends on the electrolyte. Some of common cathodic reactions are as follows-

- Hydrogen Evolution in acidic solution

$$2H^+ + 2e^- \rightarrow H_2$$

- Hydrogen Evolution in neutral and basic solution

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

- Oxygen reduction in acidic solutions

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

- Oxygen reduction in neutral and basic solution

$$O_2 + H_2O + 4e^- \rightarrow 4OH^-$$

- Metal reduction and metal deposition

$$M^{2+} + e^- \rightarrow M^+$$

$$M^+ + e^- \rightarrow M$$

Oxygen involving corrosion reactions known as oxygen type corrosion for example iron immersed in water in presence of oxygen.

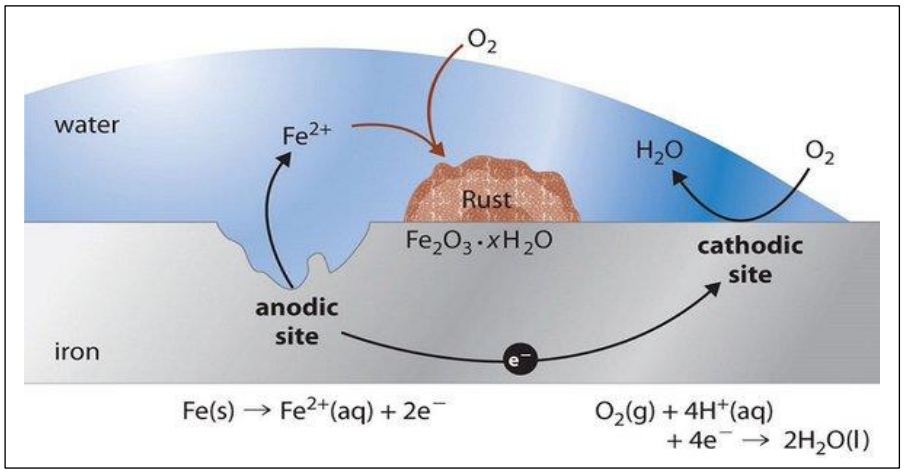

Figure 1.10: Corrosion mechanism
(https://qph.cf2.quoracdn.net)

1.8 Cost of corrosion

Corrosion is a universal process. It is directly and indirectly affected the growth of a nation. In 1970s and 1980s the governments of several nations started to study the cost

of corrosion and they observed that many times, for an industrial nation the cost of corrosion is greater than the cost of natural disasters in a financial year.

There are three aspects of impact of corrosion on human life first is the human injury or death, second is the contamination of earth environment and third is the financial costs. A lot of cases of human injuries and deaths are listed due to the failures in boiler tanks, pressure basins, motor turbines, building damage etc. some of them are listed as follow [38-40].

- Sinking of River Queen ship accident in 1967 at USA,
- In 1970 platform collapse in North Sea, Mexico fire and explosion due to the petrol leaking in a valve, oil leakage from a pipeline in Russia in 1997.
- The chemical plant explosion in Bhopal in 1984, it is reported that steel pipes corroded and water leaked into tanks containing methylisocyanate (MIC) the iron corrosion products provided a catalyst for a reaction, which blew apart the plant allowing the methylisocyanate and other toxic gases to escape, killing over 8000 people.
- Berlin Congress Hall Collapse, 1980.
- Failure of Aloha Airline Flight in 1988.
- Failure of Livestock Facilities a reinforced concrete support column in a swine barn in Ontario, Canada failed, causing the barn to collapse and killing 250 hogs.
- In march 2006, Prudhoe Bay Oil Pipeline Leaked due to the corrosion and approximately one million litters of crude oil leaked from a corroded transit pipeline in Northern Alaska.
- In 2007, a 25-year-old sewage pipe running adjacent to the Buena Vista Lagoon in California was leaked due to the developed a 24 cm diameter hole. it is estimated that 7.3 million gallons of raw sewage spilled into the lagoon.

The production process and product become more complex and expensive due to the corrosion failures. In 1949 Uhlig provide an economic insight, according to this annually losses are estimating US $5.5 billion. In 1978 alone in USA the significant contribution due to the corrosion is approximately 5% of the national GDP [41]. The corrosion cost is estimated 3-4 % of GDP in industrialized nation [42]. In 2013 NACE international conducted a worldwide study on corrosion costs and preventative strategies, which was utilized in the World Bank economic sector and global Gross Domestic Product (GDP) data to relate the cost of corrosion. This study showed that

the estimated global cost of corrosion was approximately 3.4% of the GDP, for India it is 4.2 % of GDP [43]. In June 2021, it was reported by international zinc association (IZA) that the annual loss in India due to corrosion is equivalent to 5-7 % of GDP. The direct and indirect economic losses of corrosion can be described by the following diagram-

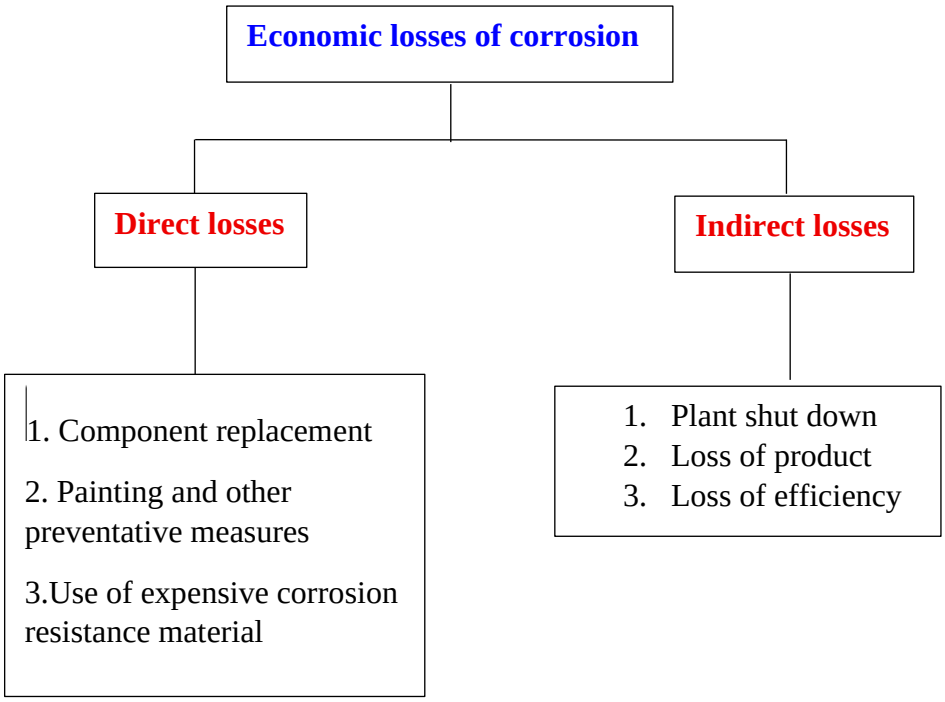

Figure 1.11: Economic losses of corrosion

1.9 Corrosion prevention methods

The prevention of corrosion become more significance because the completely eradication of corrosion is impossible or difficult to achieve. To reduce the economic loss, human safety and environment concern is the primary significance of corrosion control. Several methods of corrosion protection have been reported in literatures such that material selection and designing, coating, inhibitors, cathodic protection. The main strategy behind the prevention of corrosion or corrosion control is selection of material, designing the material and reducing the aggressive nature of corrosive environment [3,44-45]. The some of corrosion prevention methods discussed below. [46]

1.9.1 Selection of material- There is a strong relation between the corrosion of metal or alloy and the environment, the corrosion behavior of each metal and alloy is unique and directly proportional to the corrosivity of environment and inversely proportional to the corrosive resistance of material, hence the selection of material is most common way to control corrosion. The selection of material based on some properties such that smoothness to deliver, cost and corrosion resistance property [47]. According to V. Cicek [30] materials can be classified as ferrous and non-ferrous, Carbon steel and steel alloys referred as ferrous material, which are commonly used in manufacturing due to low cost, good mechanical property and applicability for protective coating and fabrication. Other metals then iron and alloys included in non-ferrous material such that **Aluminum** is broadly used due to its light weight but it has high corrosion resistance nature. Alloying decreases the corrosion resistance of aluminum by forming a protective film of aluminum oxide on its surface. **Tungsten** has highest melting point in all metals and good strength at high temperature. It also shows good resistance to acids and alkalis. **Tantalum** is use in handling commercially pure solutions due to superior corrosive resistance nature. **Titanium and its alloy** were firstly using as structural metal in 1952. It has high corrosion resistance and form protective film of TiO_2. They were firstly adapted in aircraft and ordnance now utilized in missiles and chemical process due to high strength-to-weight ratio. **Copper and its alloy** in pure form, copper has limited uses due to low strength and smooth surface but its alloy widely used in sea water environment such as pumps and piping [48].

1.9.2 Material designing - The designing of material is as important as selection of material. The mechanical performance, function and cost of the product are depended on the designing of a material. It is based on the construction. The considerable area which required attention at designing stage are described below [49-50]

- Bimetallic contact
- Welding
- Metals in contact with moisture absorbent materials
- Inaccessibility
- Areas of condensation
- Features which reduce the paint thickness
- Oil, grease and rust patches

- Fluid movements
- Joints

1.9.3 Cathodic and anodic protection – Anodic protection technique is based on the electrode kinetics principles. It controls the electrode potential in a zone where the metal is passive state. Mainly anodic current decreases the rate of hydrogen evolution to a structure. Potentiostat require to maintain the constant electrode potential to a metal. The anodic protection is applicable in extreme corrosive environment and also have low current requirement. On other hand cathodic protection is widely used to protect mild steel, water or fuel pipe lines, fuel tanks and ships. In this technique corrosion of a metal controlled by making it the cathode of an electrochemical cell. It requires high current which increases with corrosivity of environment. So cathodic protection is practically not applicable in aggressive corrosive medium [45,51].

1.9.4 Coating – Coating provided a way to increase the performance capacity and life time of material. The coating can be use individually and in combinations. There are basically three methods by which coating provide the protection to material barrier, chemical inhibition and galvanic (sacrificial) protection. [13] Barrier protection completely isolate the material to the corrosive environment, in chemical inhibition coating released inhibitors which have ability to retard the corrosion while in the sacrificial protection of material refers to a coating in which the coating material have faster corrosion rate, act as sacrificial anode and substrate act as cathode in corrosion cell. In general rule thicker the coating provides the longer protection to substrate while a pin hole accelerates the corrosion failure. The coating can be classified as follows [13, 52-53].

A. **Organic coating –** This type of coating provides a protective barrier against corrosion and most commonly used for protecting different metals i.e., aluminium, zinc and steel [54]. Paints, resins, varnishes plastic and rubber coating are widely used in industries as a defensive coating. It has insulator nature which do not permit air and moisture to arrive at metallic surface and also have pigments which act as inhibitor. Recently the polymer coating shows great potential as the corrosion potential system. Before utilized this type of coating the metal surface to remove dust and impurity cleaned properly.

B. **Metallic coating** – This type of coating has two types of functions first is act as barrier and the second is the providing cathodic protection by galvanically corroding. In this type of coating the substrate coated by another metal. On the basis of coating metal, metallic coating divided into two classes first is the nobler or cathodic coating which provide the corrosion protection by the more corrosion resistance compare to the substrate while in the sacrificial or anodic coating the coating oxidizes rather than the substrate for example leads, copper and silver provide the nobler or cathodic protection and zinc and cadmium provide the anodic protection. There are many processes of metal coating on steel surface [22, 55].

- Hot dipping
- Thermal spraying
- Electrochemical and chemical vapor deposition
- Metal cladding
- Cementation

C. **Inorganic coating –** Coating of natural compounds of earth strata such as concrete, glass, porcelain enamels, zinc silicates are included in the inorganic coatings. several process such as anodizing, enamelling, surface conversion, phosphating etc. used in inorganic coating. It secures the metal against acids, alkalis and erosion corrosion at high temperature. Vitreous enamels coating is used to protect against high temperature gases and the enamels coated steel have very long life [56]

1.9.5 Use of inhibitor- Inhibitors gain considerable practical importance due to having both metallic prevention and corrosive environment reduction nature [57]. inhibitors are the substances which small concentration added in corrosive medium to decrease the corrosion rate. Inhibitor slow the corrosion rate by [58-59]

- Retarding either the anodic or cathodic reactions.
- Reducing the movement or diffusion of ions to the metallic surface.
- Increasing the electrical resistance of the metallic surface.

1.10 Corrosion inhibitor

There are several methods of corrosion protection but the use of corrosion inhibitors is commonly used due to its inexpensive nature, longevity and low interfere effect on the substance compare to others [60-62]. Inhibitors had a great acceptance in industries due to having environment friendly nature. The inhibitors have some characteristics such

that good adsorption ability on metal surface, capability of protective film formation, ability to retard the anodic and cathodic or both reaction on metal surface, ability of increase electrical resistance on metal surface and reducing nature of aggressiveness of corrosive environment [63-65]. Some general characteristics which determine the performance and applicability of various corrosion inhibitors are as follow [66-67].

- Presence of a functional group to donate lone pair
- Large structure with active chemical groups
- Ability to cover large surface area
- Cost effectiveness
- Non-toxic, less hazardous

1.10.1 Classification of corrosion inhibitor- There are several ways to classified corrosion inhibitors on the basis of their nature, corrosive environments, interaction with metals and inhibition mechanism. It can be easily understood by following diagram.

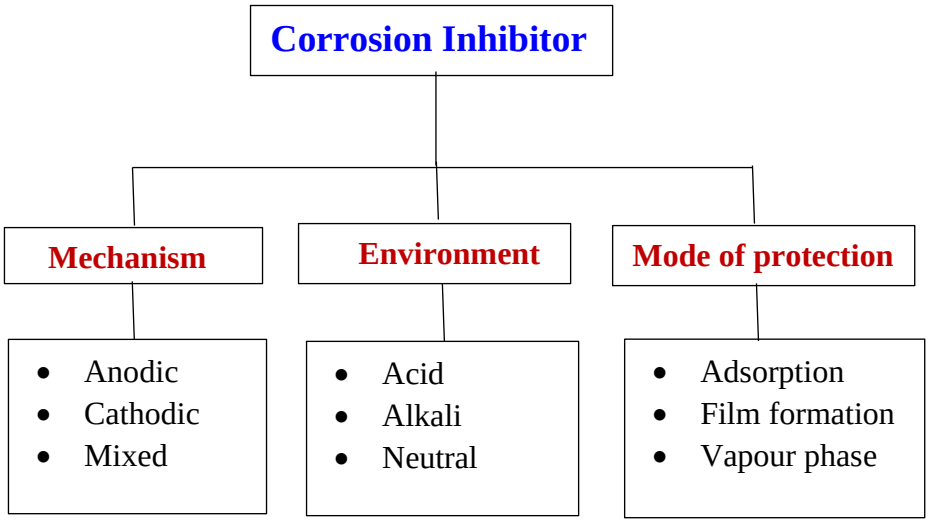

Figure 1.12: Classification of corrosion inhibitor

a. **Anodic inhibitors** retard the metal dissolution reaction at anode. In presence of anodic inhibitors, the corrosion potential displaced in the positive direction. They are also called passivating inhibitors. They form a thin protective film along the anode. If the concentration of anodic inhibitors is low, it stimulates the pitting type of corrosion so it is denoted as dangerous. Anodic inhibitors are two types [68-69].

- Oxidizing anodic inhibitors- that type of anions passivate steel in absence of oxygen such as chromates and nitrates.
- Non-oxidizing anodic inhibitors- the inorganic anions such as phosphates, tungstate required the presence of oxygen to passivate the steel.

b. **Cathodic inhibitors** retard the evolution of hydrogen gas by diffusion of the hydrogen ions at cathode in acidic solution. The cathodic inhibitor precepted on cathodic site and form a protective film barrier. Cathodic inhibiters are fall into three categories cathodic precipitates, oxygen scavengers, and hydrogen poisons. The carbonates of magnesium and calcium which is present in natural water precepted on cathodic area in form of protective layer similarly zinc also act as precepted in form of zinc hydroxides.

$$Ca^{+2} + 2HCO^{-}{}_3 + OH^{-2} \rightarrow CaCO_3 + HCO^{-}{}_3 + H_2O$$

$$Zn^{+2} + OH^{-} \rightarrow Zn(OH)_2$$

Oxygen scavengers are the based on the removal of dissolved oxygen for examples hydrazine and sodium sulphite, while the hydrogen poisons are interfered with the evolution of hydrogen gas such that the salts of arsenic and antimony [70].

c. **Mixed type inhibitors** deal with the both anodic and cathodic types of reactions. the mechanism of mixed type of inhibitors is based on the formation of hydrophobic film. The adsorption of inhibitors depends on the ionic charge and chemical composition of inhibitors which is affected by the temperature and pressure factors. Mixed inhibitors inhibit the corrosion by controlling the both anodic and cathodic reaction [71].

d. **Acidic environment inhibitor** known for involving the reduction of electropositive ions and deposition on the metal surface by lowering the over potential of cathodic reaction. Recently it is reported that the inhibitors having heavy metal ions with organic compound containing heteroatoms with multiple bonds found to be good corrosion inhibitor for iron in acidic medium [72-73].

e. **Alkali environment inhibitor,** the protective film of oxides and hydroxides on metal surface are soluble in alkaline medium. Hence the inhibitors which content organic molecules such as substituted phenols and naphthol, beta-diketones and thiourea expend the pH stability rang of protective film. these types of inhibitors

decrease the corrosion rate by decreasing the diffusion rate of reactants on metal surface [74-75].

f. **Neutral environment inhibitor,** in the neutral corrosive medium surface-active chelating inhibitor found to be efficient corrosion inhibitor due to the interaction with oxide covered metal surface and prevention of oxygen reduction at cathodic site [76].

g. **Adsorption inhibitor** this type of inhibitor has a wide range of inhibitors. Adsorption inhibitors adsorbed on metal surface and show inhibition by affecting the both anodic and cathodic site. Specially used in the industries where acids are used as a cleaning, descaling and picking agents. Adsorption inhibitors have some special structural characteristics like heteroatoms, multiple bonds etc [77-78].

h. **Film formation inhibitor** they inhibit the corrosion by forming a barrier film which are not straight forward like adsorption inhibitor while specific either to the cathodic or to the anodic. For example, benzoate is an anodic film forming inhibitor while the zinc and calcium salt is cathodic film forming inhibitor [79].

i. **Vapour phase inhibitor** they are volatile in nature so easy to transported in desirable side hence used in the critical machine parts. The vapour pressure of these inhibitors is usually between 10^{-7} to 10^{-2} mm mercury at room temperature. For examples the dicyclohexylammonium nitrite and cyclohexylamine chromate act as vapour phase inhibitor for copper and brass respectively [80-81].

1.10.2 Selection of corrosion inhibitors

Economically, the selection of corrosion inhibitors in combination of material and medium is preferable strategy for corrosion control [82]. There are several factors which influence the performance of inhibitors such as microstructure of metal, chemical composition, pre-corrosion etc. The microstructure components directly affect the adsorption, mechanical properties, corrosion resistance of the material as well as the inhibition efficiency of inhibitors [83-86]. For industrial use of inhibitor usually the selection process based on the laboratory and field testing. The grade of inhibitor is represented by inhibition efficiency which are expressed by following equation number (1.1).

$$\text{Inhibitor Efficiency (\%)} = \frac{C_{R_{unInhibited}} - C_{R_{Inhibited}}}{C_{R_{Inhibited}}} \quad (1.1)$$

$C_{R_{unInhibited}}$ = corrosion rate of the uninhibited system, $C_{R_{Inhibited}}$ = corrosion rate of the inhibited system

The number of factors such as mode of interaction, adsorption sites, charge density, flow rate, viscosity, eco-friendly nature etc. affect the inhibition efficiency which play an important role in the selection of inhibitor [87].

In the past few years compounds that contain heteroatoms N, S, O, P with aromatic ring and pi-electron containing functional group gain more attention and show good inhibition efficiency in acidic media due to economical, convenient, and effectiveness [88-89].

1.11 Ionic liquid as green corrosion inhibitors

1.11.1 Green corrosion inhibitor and general characteristics

After the initial report of use of organic inhibitors as a corrosion inhibitor published by speller, many inorganic and organic substances investigated for this purpose but the growing issue for use these inhibitors was the toxic and harmful nature for our environments. For example, Cr (IV) labeled as carcinogen. These issues prompted the research of green corrosion inhibitors who are interested in eco-friendly technology [26,90].

Green corrosion inhibitors are the combination of one or more than one substance which are naturally occurring or synthesized by ecofriendly techniques, biodegradable in environments and do not content heavy metals or other toxic compounds. For examples plant extract, natural polymers, Ionic liquids are considered as a green corrosion inhibitor [91-93].

To promote the green synthesis and ecofriendly techniques in chemistry, in 1998 P.T. Anastas and J.C. warner announced the “12 principles of green chemistry” which are as follows [94].

a. **Prevention of waste**- It’s better to prevent waste formation than to treat and clean-up it.
b. **Atom economy**- The method of synthetization should be designed to maximize the incorporation of all materials used in process into the final product.

c. **Non-toxic and less hazardous synthesis**- Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

d. **Design eco-friendly chemicals-** The design of chemicals products should be preserved efficacy of function while reducing toxicity.

e. **Benign solvents and auxiliaries-** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.

f. **Design for energy efficiency**- Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

g. **Use of renewable feedstock`s-** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

h. **Reduce derivatives-** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

i. **Catalysis-** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

j. **Design for degradation-** Chemical products would be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

k. **Real-time analysis for pollution prevention-** Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

l. **Inherently benign chemistry for accident prevention-** Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

1.11.2 Historical background of ionic liquid

There are several beginnings in story of discovery of Ionic liquids in which the earliest was Paul Walden, in 1914 he reported the physical properties a molten salt Ethyl ammonium nitrate [$EtNH_3$] [NO_3] which is liquid and has a melting point of 12^0C. In 1934 ionic liquids is appear in a patent for formation of different viscosity solution

formed by mixing of cellulose and halide salt of nitrogen containing bases at above 100^0C. In 1951 Hurley and Weir discovered 1-ethylpyridinium bromide-aluminium chloride ($[C_2py]Br\text{-}AlCl_3$). Bernard Gilbert give detail studied of the physical and chemical properties of ionic liquids made from 1-butylpyridinium chloride and aluminium (III) chloride. In 1982 Wilkes and Hussey found imidazolium as a most stable cation by comparing several heterocycle cations, later Seddon and Hussey investigated metal complexes in ionic liquids. In 1992 Wilkes and Zaworotk developed Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. Howarth synthesised an imidazolium-based ionic liquid and described its use in solvent based Diels-Alder reaction in 1997. In 20^{th} century a lot of interest increased in the field of ionic liquid and its applications such that catalytic reaction, electrochemistry, solvent chemistry etc [95-96].

1.11.3 Ionic liquid and general characteristics

Ionic liquid is a molten salt completely comprised by novel anion and cation which contains heteroatoms such as N, O, P, S etc. The melting point of ionic liquids is below the boiling point of water at room temperature. It is also known as ionic fluid, liquid ionic salt, molten salt and neoteric solvent [97-99]. Recently ionic liquids are designed on based of their specific application in field of synthesis, chemical transformation, separation, extraction and catalyst by the selection of proper cation and anions [98]. The cationic part of ionic liquids consists by large organic compound with appositive charge while the anionic part is consisting by small inorganic or atoms groups with negative charge. The common cation and anion groups are listed below in **Figure 1.13 and 1.14**. Due to the different in size the bond between the cation and anion is very week and columbic in nature their physio-chemical properties vary with the change in their structures [100-101].

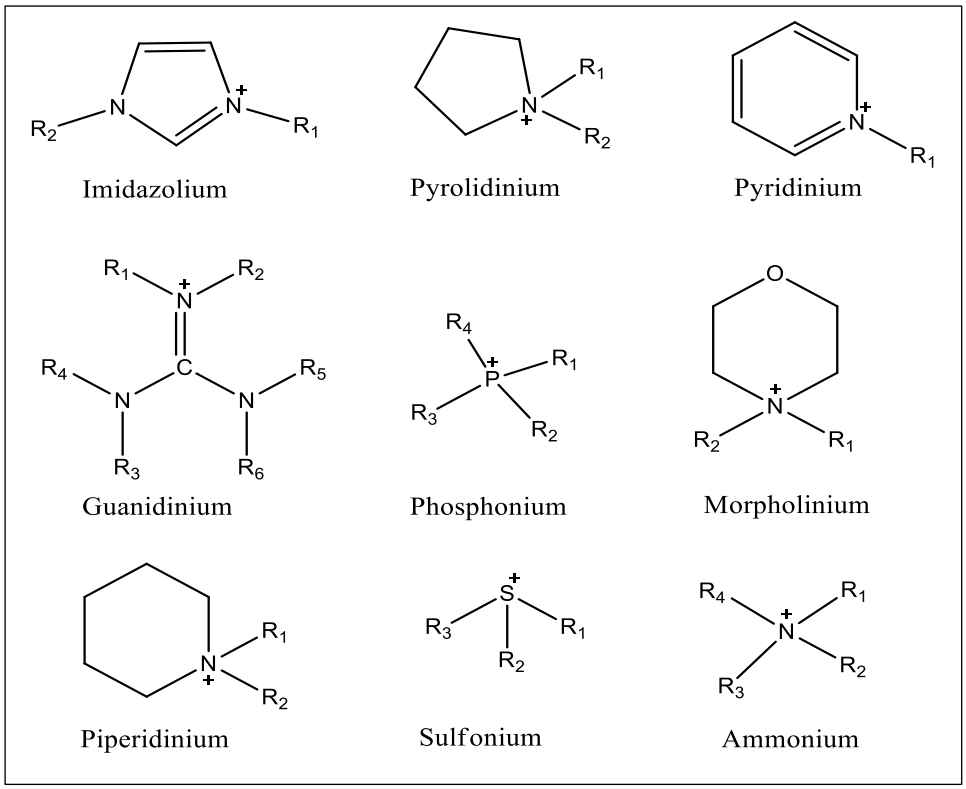

Figure 1.13: Structure of common cations used in ionic liquids

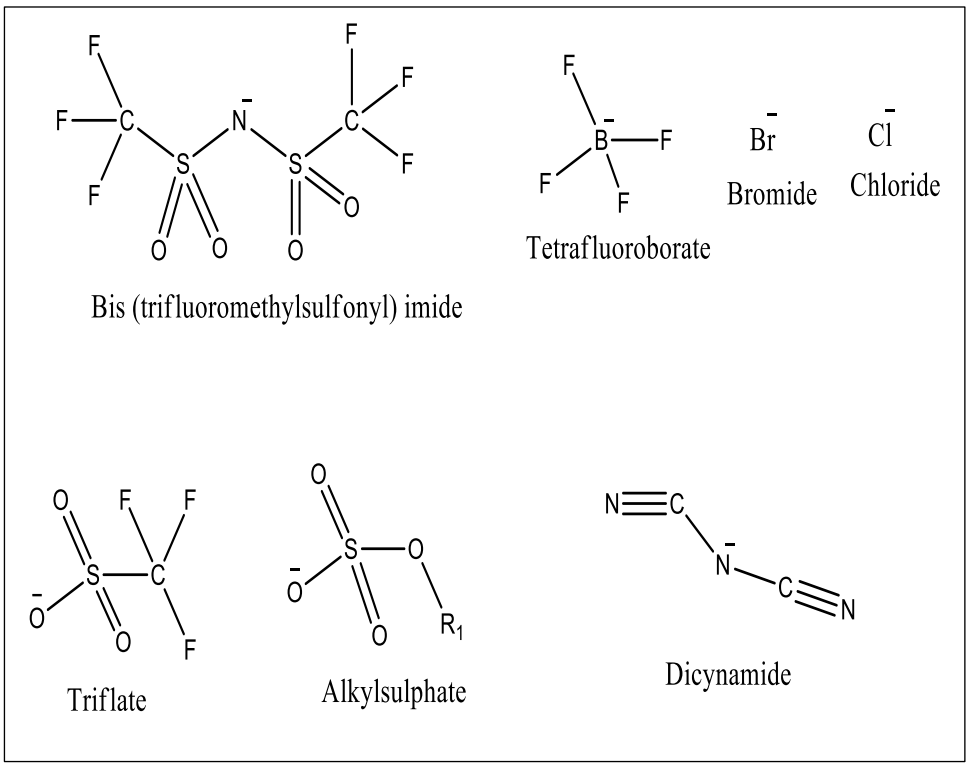

Figure 1.14: Structure of common anions used in ionic liquids

Ionic liquids are attractive replacement of traditional organic solvents due to its various properties such as [102].

- They are highly polar in nature.
- Ionic liquids are non-volatile and have negligible vapor pressure.
- They are stable and resistance to heat up to the 300^{o}C.
- They show high electrical conductivity.
- They are liquid in a wide range of temperature up to the 200 ^{o} C.
- They are designer solvents; they can be prepared for a specific designation objective.

1.12 Ionic liquids as a green corrosion inhibitor for mild steel (Literature)

To increase the ecological awareness development and use of environment friendly material is essential requirement of every field of science. Low concentrated acids are widely used in industries as a cleaning and pickling agents [103]. Mild steel, is now the most common form of steel and highly used because its relatively cheap and good mechanical properties. But the challenge is that mild steel has low corrosion resistance especially in acidic environments [104]. To remove this problem researchers focused to developed mild steel corrosion inhibitors in acidic medium. Development of organic inhibitors, plant-based inhibitors, drug inhibitors etc. are the results of this research but they having own limitations. To improve the inhibition efficiency, handling capabilities and environment friendly nature research oriented a new class of corrosion inhibitor: Ionic liquids. Last of two decades ionic liquids are extensively used in industries as well as in academia due to variety of applications and their inhibitive properties. Ionic liquids show high applicability as a corrosion inhibitor for mild steel material in acidic medium. Our research is focused to determine the structural effect of ionic liquids on their inhibition efficiency. To make a strong background for synthesis and corrosion inhibition application of ionic liquids on mild steel in acidic medium the literature of previous ten years is described as.

Zheng et al. (2014) investigated corrosion inhibition efficiency of amino acid ionic liquid, 1-octyl-3-methylimidazolium l-prolinate ([Omim]Lpro) for mild steel surface in 0.5M sulphuric acid medium. The experimental results of PDP method reveals that it is act as mixed type of inhibitors with a predominantly cathodic action. The maximum inhibition efficiency 80% obtain at 10mM concentration. Quantum chemical calculation helps to explain the inhibition mechanism. El-Awady thermodynamic-kinetic model and Flory–Huggin's isotherm equations were best fitted adsorption isotherm for studied ionic liquid [105].

Velrani et al. (2014) reported the influence of 1-butyl-3-methylimidazolium chloride (1-BMIC) ionic liquid as corrosion inhibitor on mild steel in 2 M H_2SO_4 medium. Weight loss study, potentiodynamic polarization and electrochemical impedance study used to note the effect of concentration and effect of temperature on inhibition efficiency. PDP study also reveal the mixed type of inhibition nature of (1-BMIC). Freundlich adsorption isotherm model found to as a best fitted model for adsorption of (1-BMIC) on mild steel surface. The highest inhibition efficiency 83.39 % obtained at 0.001M concentration of 1-BMIC [106].

Lozano et al. (2014) studied the two imidazolium based ionic liquid 1,3-dibencilimidazolio acetate (DBImA) and 1,3-dibencilimidazolio dodecanoate (DBImL) as corrosion inhibitor on mild steel in 1.0 M HCl and 1.0 M H_2SO_4 medium. The inhibition efficiencies were increase with the increase concentration and optimum inhibition efficiency was found 11% and 30% in 1.0 M H_2SO_4 medium for (DBImA) and (DBImL) respectively. Similarly in 1.0 M HCl medium the optimum inhibition efficiency was 82% and 88% for (DBImA) and (DBImL) respectively. The results from Tafel plots, electrochemical impedance spectroscopy and SEM revealed a high inhibition effectiveness in HCl medium for both ionic liquids. The PDP study confirm the physisorption. Langmuir model best fitted model in both acidic solution for both ILs [107].

Kowsari et al. (2014) investigated a task specific ionic liquid namely**:** 1-methyl-3-(2-{2-[2-(1-methyl-1-H-imidazol-3-ium-3-yl)ethoxy}-ethyl-1H-imidazol-3-ium dichloride as corrosion inhibitor on low carbon steel in 1.0 M HCl solution. Weight loss measurements (WL), potentiodynamic polarization test (PDP), electrochemical impedance spectroscopy (EIS) techniques used for concentration effect on inhibition efficiency while scanning electron microscope (SEM), atomic force microscope (AFM) used for surface morphological study. The PDP study also indicated that it is mixed

type of inhibitor with anodic dominance. The highest inhibition efficiency was 77.6% obtained at 200 mg/L concentration of IL [108].

Molchan et al. (2014) examined the corrosion behaviour of 1-alkyl-3-methylimidazolium tricyanomethanide ([C$_n$mim]TCM, n = 2, 4, 6 and 8) as a function of alkyl chain length in the cation on mild steel. The finding results suggest that the cation with longer alkyl chain reduce the mild steel dissolution. The corrosion inhibition efficiency was found to be significantly increased for the [C$_n$mim]TCM ILs with the longer length of alkyl chain in the cation [109].

Acidi et al. (2014) determined the corrosion inhibition nature of three promising ionic liquids namely, 1-ethyl-3-methylimidazolium tetrafluoro borate [EMIM][BF_4], 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [EMIM][Otf] and 1-Butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][Otf] in aqueous monoethanolamine system. The obtained results revealed that the Inhibition efficiency decreases in the order [EMIM][BF_4], [EMIM][Otf], and [BMIM][Otf. [EMIM][Otf] and [BMIM][Otf] showed poor inhibition ability compared to [EMIM][BF_4], which may be due the stronger interaction of carbon dioxide to [EMIM][BF_4] [110].

Zheng et al. (2015) examined the corrosion inhibition performance and mechanism of two ionic liquids named as 1-octyl-3-methylimidazolium bromide ([OMIM]Br) and 1-allyl-3-octylimidazolium bromide ([AOIM]Br) for mild steel in 0.5 M H_2SO_4. According to electrochemical measurements given ILS act as modest cathodic inhibitor. ([AOIM]Br) showed better inhibitive nature due to the electron donating effect of allyl group. Both ILS follow the El-Awady thermodynamic–kinetic model of adsorption and theoretical calculations was used to explain the mechanism of inhibition [111].

Mashuga et al. (2015) studied the mild steel corrosion inhibition in 1M HCl solution by some ionic liquids, namely 1-hexyl-3-methylimidazolium trifluoromethanesulfonate [HMIM][TfO], 1-hexyl-3-methylimidazolium tetrafluoroborate [HMIM][BF_4], 1-hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF_6], and 1-hexyl-3-methylimidazolium iodide [HMIM][I]. electrochemical experimental results indicated that all ionic liquids having appreciably high inhibition efficiency and behaved as mixed type of inhibitors at 303 K. According to the thermodynamic data all ionic liquids spontaneously adsorbed on mild steel surface and form Fe/ILS complexes. Adsorption study results revealed that [HMIM][TfO], [HMIM][BF_4] and [HMIM][I] obeyed Langmuir adsorption isotherm, while [HMIM][PF_6] better fit with Temkin adsorption isotherm [112].

Yousefi et al. (2015) studied the corrosive resistance behaviour of six ionic liquids with different counter ions and chain length namely 1-ethyl-3-methylimidazolium chloride (EMIm Cl), 1-butyl-3-methylimidazolium chloride (BMIm Cl), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIm PF_6), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm BF_4), 1-butyl-3-methylimidazolium bromide (BMIm Br), and 1-hexyl-3-methylimidazolium chloride (HMIm Cl) on mild steel in hydrochloric solution. Potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), atomic force microscopy (AFM), dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FT-IR) and quantum chemical calculations were used for investigating the corrosion inhibition efficiency and surface morphology. Among the all-ionic liquids (HMIm Cl) exhibited the best inhibition efficiency. While in case of different anions the synergistic effects of studied anions increase in the following order $PF_6^- > BF_4^-$ $>Br^- >Cl^-$ [113].

Sasikumar et al. (2015) investigated some imidazolium based ionic liquids namely 1-ethyl-3-methylimidazolium tetrafluoroborate $[EMIM]^+[BF_4]^-$, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate $[BDMIM]^+[BF_4]^-$ and 1-decyl-3-methylimidazolium tetrafluoroborate $[C_{10}MIM]^+[BF_4]^-$ as corrosion inhibitor on mild steel in 1.0 M HCl solution by using experimental and theoretical techniques. Polarization measurements showed that all ILs show mixed type of inhibition with obeyed Langmuir adsorption isotherm model. The maximum inhibition efficiency was 98.08% obtained at 500 ppm concentration for $[C_{10}MIM]^+[BF_4]^-$ [114].

Yang et al. (2015) examined the corrosion inhibition performance of 1-decyl-3-methylimidazolium chloride (DMICl) on mild steel in NaCl solution at pH 3.8 and 6.8. Open circuit potential, polarization curves and impedance spectroscopy used to investigate inhibition efficiency. The Scanning electron microscopy (SEM), energy dispersive spectroscopy and X-ray photoelectron spectroscopy data indicated the presence of inhibitive layer on mild steel surface [115].

Hanza et al. (2016) investigated the corrosion inhibition effectiveness of imidazolium based ionic liquid 1,4-di [1′-methylene-3′-methyl imidazolium bromide]- benzene for mild steel in 1M sulphuric acid solution. The electrochemical measurement data suggested that inhibition efficiency increases with the concentration of ionic liquids. The physisorption mechanism was confirmed by the thermodynamic data obtained by Langmuir adsorption isotherms [116].

Yesudass et al. (2016) examined the corrosion inhibition properties of alkyl imidazolium based ionic liquids (ILs) namely 1-ethyl-3-methylimidazolium ethylsulfate $[EMIM]^+[EtSO_4]^-$, 1-ethyl-3-methylimidazolium acetate $[EMIM]^+[Ac]^-$, 1-butyl-3-methylimidazolium thiocyanate $[BMIM]^+[SCN]^-$, 1-butyl-3-methylimidazolium acetate $[BMIM]^+[Ac]^-$ and 1-butyl-3-methylimidazolium dicyanamide $[BMIM]^+[DCA]^-$. The PDP results indicated that inhibitors inhibit both the anodic mild steel dissolution and cathodic hydrogen evolution reactions hence they act as mixed type inhibitor. SEM results confirmed the protective layer formation on mild steel. The thermodynamic and kinetic study revealed the physisorption and chemisorption of ionic liquid on mild steel surface. They obeyed the Langmuir adsorption isotherm model of adsorption. Quantum chemical calculations, Quantitative structure-activity relationship (QSAR) analyses and Monte Carlo simulations studies were used to correlate experimental results [117].

The newly synthesized ionic liquid 3-(4-chlorobenzoylmethyl) methyl-benzimidazolium bromide ($[BMMB]^+ Br^-$) was investigated by **Kannan et al. (2016)** as a corrosion inhibitor on carbon steel in 1 M HCl solution. Polarization study confirmed the mixed type of inhibition nature of ($[BMMB]^+ Br^-$). The impedance of metal dissolution was increased with the increasing concentration and temperature. Adsorption of $[BMMB]^+ Br^-$ on carbon steel follows Langmuir model of adsorption isotherm. Thermodynamic properties suggested that $[BMMB]^+ Br^-$ has both physical and chemical adsorption behaviour [118].

Chong et al. (2016) studied an organic salt comprising a protic imidazolinium cation and a 4-hydroxycinnamate anion as a corrosion inhibitor on mild steel in aqueous 0.01 M NaCl solution of different pH conditions. The polarization study results show that the inhibition efficiency was 86%, 72% and 84% in basic, acidic and neutral pH respectively [119].

Deyab et al. (2017) synthesized and characterized four ionic liquids, namely 3-Decyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate (IL1), 3-Dodecyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate (IL2), 3-Decyl-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate (IL3) and 3-Dodecyl-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate (IL4) as corrosion inhibitor for carbon steel in 1 M hydrochloric solution. The corrosion inhibition performance was evaluated by using PDP and EIS measurements. The order of the inhibition efficiency was as follows:

IL4 > IL3 > IL2 > IL1 and all ILs well fitted with the Temkin adsorption isotherms [120].

Sheety et al. (2017) synthesized the inexpensive corrosion inhibitor, 1.3-bis[2-(4-methoxyphenyl)-2-oxoethyl]-1*H*–benzimidazol-3-ium bromide (MOBB) for 6061 Al-15 vol% $SiC_{(P)}$ composite in 0.1 M HCl and 0.1 M H_2SO_4 media at temperatures range 30^0C to 50^0C. The structure of MOBB was confirmed by FTIR, NMR, LC-MS (Liquid chromatography mass- spectrometry) and XRD techniques. According to the adsorption energy results, it showed the chemisorption and follows the Langmuir adsorption isotherms. The inhibition efficiency was obtained 98.7% in HCl and 98.8 % in sulphuric acid. The potentiodynamic polarization results revealed that it was behave as mixed type of inhibitor predominantly cathodic inhibitor [121].

Velusamy et al. (2017) investigated two imidazolium based ionic liquids namely 1-octyl-3-methyl imidazolium chloride ($[OMIM]^+[Cl]^-$) and 1-butyl-3-methyl imidazolium chloride ($[BMIM]^+[Cl]^-$) as corrosion inhibitor on mild steel in various completion brine fluids. The results indicated that the IL with longer alkyl chain exhibited better inhibition efficiency than the other IL and ionic liquids can be explored to develop anti-corrosive completion fluids suitable for oil and gas industries [122].

Three novel amino acids based corrosion inhibitors for mild steel in 1.0 M HCl medium namely 2-(3-(carboxymethyl)-1H-imidazol-3-ium-1-yl)acetate (AIZ-1), 2-(3-(1-carboxyethyl)-1H-imidazol-3-ium-1-yl)propanoate (AIZ-2) and 2-(3-(1-carboxy-2-phenylethyl)-1H-imidazol-3-ium-1-yl)-3-phenylpropanoate (AIZ-3) were synthesized by **Srivastava et al. (2017).** The study revealed that maximum inhibition efficiency was obtained 96.08% at 200ppm concentration. PDP study suggested that AIZ-1 act as cathodic inhibitor while AIZ-2 and AIZ-3 show mixed type of inhibition. All three ILs follow the Langmuir model of adsorption isotherm [123].

Guo et al. (2017) studied two imidazolium based ionic liquids with different anions namely 1-vinyl-3-aminopropylimidazolium hexafluorophosphate ($[VAIM][PF_6]$) and 1-vinyl-3-aminopropylimidazolium tetrafluoroborate ($[VAIM][BF_4]$) as a corrosion inhibitor on Q235 carbon steels in 1.0 M HCl medium. At 45^OC. the maximum inhibition efficiency was 90.53% and 54.01% respectively. The inhibition efficiency of ($[VAIM][BF_4]$) decrease with increasing temperature while opposite trend obtained for ($[VAIM][PF_6]$). The important key point of the study was that the ($[VAIM][PF_6]$) obeyed Langmuir model of adsorption isotherm while ($[VAIM][BF_4]$) fitted with EI-Awady kinetic-thermodynamic adsorption isotherm [124].

Feng et al (2018) studied the corrosion inhibition ability of three ionic liquids with different anionic chain length 1-vinyl-3-methylimidazolium iodide ([VMIM]I), 1-vinyl-3-proplylimidazolium iodide ([VPIM]I) and 1-vinyl-3-butylimidazolium iodide ([VBIM]I) on X70 steel in 0.5 M H_2SO_4 solution at 298 K. The all-electrochemical measurements show that all three ILS shows mixed type inhibition. The order of inhibition efficiency was [VMIM]I < [VPIM]I < [VBIM]I which indicate that the inhibition efficiency increase with increasing alkyl chain length attached to the imidazolium ring. All three ILs showed physisorption as well as chemisorption and followed the Langmuir adsorption isotherms [125].

El-Hajjaji et al. (2018) reported two ILs based on pyridazinium which name 1-(-ethoxy-6-oxohexyl) pyridazine -1-ium bromide and 1- (2-bromoacetyl) pyridazinium bromide as corrosion inhibitor for mild steel in 1 M HCl solution. Ultrasound irradiation method was used to synthesized both ILs while the inhibition performance was measured by electrochemical impedance (EIS) and molecular dynamic simulation methods. The obtained results indicate that inhibition efficiency and charge transfer resistance (R_{ct}) increase while the double layer capacitance (C_{dl}) decreased with the increasing concentration of ILs. The adsorption data for both ILs fitted in the Langmuir adsorption isotherms [126].

Nessim et al. (2018) synthesised and characterized three ionic liquids namely 3,3′-(1,4-phenylenebis(methylene))bis(1-octyl-1*H*-imidazol-3-ium) bromide, 3,3′-(1,4-phenylenebis(methylene))bis(1-decyl-1*H*-imidazol-3-ium) bromide and 3,3′-(1,4-phenylenebis(methylene))bis(1-dodecyl-1*H*-imidazol-3-ium) bromide as IL_1, IL_2, and IL_3. Elemental analysis, IR, and ^{1}H-NMR spectroscopy tools were used for characterization furthermore all three ionic liquids were tested as corrosion inhibitor for stainless steel in 0.5 M H_2SO_4 solution by using electrochemical techniques. According to the obtained results the optimum inhibition efficiency was 90.7%, 97.3% and 82.6% for IL_1, IL_2, and IL_3 respectively with mixed type of inhibition [127].

Azeez et al. (2018) examined three ionic liquids namely: 1-Methyl-3-propylimidazolium iodide (MPIMI), 1-butyl-3-methylimidazolium iodide (BMIMI) and 1-hexyl-3-methylimidazolium iodide (HMIMI) as corrosion inhibitors for mild-steel corrosion in 1 M HCl solution. PDP study revealed that these ILs acted as mixed-type inhibitors. The negative values of Gibbs free energy supported the spontaneous physical adsorption of these inhibitors. The maximum inhibitions efficiency was obtained 93.1%, 87.8% and 80.4% at 5×10^{-3} M concentration for

HMIMI, BMIMI and MPIMI, respectively. Surface morphology confirmed the electrochemical results [128].

Yousefi et al. (2018) investigated the corrosion inhibition performance of sodium dodecyl sulfate (SDS) in the presence of imidazolium-based ionic liquid, 1-methylimidazolium trinitrophenoxide ([MIm][TNP]) as an additive on mild steel in 2 M HCl solution. Advanced investigation tools such that electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), scanning electron microscopy (SEM), atomic force microscopy (AFM) and quantum chemical calculations were used for corrosion inhibition study. Negative values of Gibbs free energy verify the spontaneous adsorption of IL on the steel surface. Thermodynamic data confirmed Langmuir adsorption isotherm. SEM images revealed the formation of protective film on mild steel surface [129].

Li et al. (2019) investigated the corrosion inhibition property of 4,6-dimethyl-2-mercaptopyrimidine (DMPP) on mild steel in 0.5 M sulphuric acid medium by using electrochemical technique. Langmuir adsorption isotherm is fitted for adsorption of applied IL on mild steel surface. The maximum inhibition efficiency was obtained 99.8% at 0.5mM [130].

Luna et al. (2019) reported the corrosion inhibition behaviour of 1-ethyl 3-methylimidazolium thiocyanate, $(EMIM)^{+}(SCN)^{-}$ ionic liquid on API 5 L X52 steel immersed in 0.5 M H_2SO_4 and 0.5 M HCl aqueous solutions. Gravimetric experiment, PDP, EIS techniques were used to study. The inhibition efficiency was found 82.9% and 77.4% for H_2SO_4 at 75 ppm and HCl at 100 ppm concentrated solution. IL followed the Langmuir adsorption model in both corrosive medium and surface adsorption was confirmed by EDS and X-ray photoelectron spectroscopy which indicate the physisorption as well as chemisorption. The higher value of activation energy for H_2SO_4 revealed that IL is better inhibitor in H_2SO_4 solution compare to HCl solution [131].

Jannat et al (2019) synthesized dicationic ionic liquid 1,4- (Divinyl-imidazolium bromide) butane to investigate the corrosion inhibition ability on steel in 1 M sulphuric acid medium. The corrosion inhibition effectiveness was demonstrated by PDP and EIS measurements. The surface adsorption was confirmed by SEM/EDX analysis. Langmuir adsorption model was followed by the IL. The inhibition mechanism was studied by quantum chemical analysis [132].

Panchratna et al (2019) studied the anticorrosion behaviour of a green ionic liquid 3-(4-fluorobenzyl)-1-methyl-1*H*-imidazol-3-ium bromide [FBMIm]Br for mild steel in 0.5 M sulphuric acid medium. The structure was confirmed by various spectroscopic techniques FT-IR, ^{1}H NMR, and ^{13}C NMR. The results of PDP and EIS experiments revealed the high corrosion inhibition efficiency 98.90% & 99.48% respectively for 0.01M concentration of IL. Polarization curves showed the mixed mode of inhibition and mild steel surface adsorption followed the Langmuir adsorption very nicely. The formation of protective film layer was confirmed by SEM and AFM observation [133].

Ahmad et al. (2019) synthesized and characterized new indolium based ionic liquids methoxy-1,2,3,3-tetramethyl-3*H*-indolium iodide (IBIL-I), 1-(2-carboxyethyl)-2,3,3-trimethyl-3*H*-indolium iodide (IBIL-II), 2,3,3-trimethyl-1-(pyren-2-ylmthyl)-3*H*-indolium iodide (IBIL-III), 1-(3-ethoxy-3-oxopropyl)-2,3,3-trimethyl-3*H*-indolium bromide (IBIL-IV) and 1-(2-ethoxy-2-oxoethyl)-2,3,3-trimethyl-3*H*-indolium bromide (IBIL-V) to investigated the corrosion inhibition behaviour on mild steel in 0.5 M sulphuric acid medium by using polarization measurements and cyclic voltammetry. The results indicated that IL which have bromide as anionic head was more efficient compare to those which have iodine. According to Electrochemical data IBIL-IV has highest inhibition efficiency and acted as mixed type of inhibitor. Thermodynamic data favoured the Langmuir adsorption isotherms [134].

Talari et al. (2019) synthesized two imidazole based ionic liquids namely thiazole-4-carboxylic acid (TCA) and 2-methyl-1,3-thiazole-4-carboxylic acid (MTCA) to investigated the corrosion inhibition performance on mild steel in 0.1M HCl medium at 25^{0}C.The results revealed that corrosion inhibition efficiency increased with increased concentration of inhibitor and at 150 ppm concentration the inhibition efficiency obtained approximately 90% for both ILs. Both ILs followed the Langmuir adsorption isotherms. Theoretical quantum chemical calculation and Monte Carlo simulation were employed to determine the most stable configuration, the adsorption sites, and the interaction energies of both ILs [135].

Lozada et al (2020) investigated the corrosion inhibition properties of two ionic liquids namely 1,2-dimethyl-3-butylimidazolium iodide ($[DBIM]^{+}I^{-}$) and 1,2-dimethyl-3-propylimidazolium iodide ($[DPIM]^{+}I^{-}$) on API 5L X52 steel in 1 M H_2SO_4 solution. The inhibition efficiency order was found as ($[DBIM]^{+}I^{-}$) > ($[DPIM]^{+}I^{-}$). Electrochemical results revealed that inhibition efficiency was increase on increasing

alkyl chain length of ILs. The maximal range of inhibition efficiency of ILs was 91 to 95 % [136].

Praveen et al. (2020) examined the corrosion inhibition nature of ionic liquid 1-Methyl-3-propylimidazolium iodide (MPII) on Mild Steel in 1 M H_2SO_4 by experimental and computational study. The PDP results revealed that given IL acts as a mixed type inhibitor with a high inhibition efficiency of 91% at 298 K. Morphology and topography of the Mild Steel surface in presence and absence of inhibitor were investigated by SEM. Various thermodynamic parameters were used to project the inhibition mechanism. Molecular dynamic simulation, EIS, and DFT methods used to confirm the inhibitor interaction with metal surface [137].

Zunita et al. (2020) examined the corrosion inhibition abilities of some imidazole based ionic liquids namely, 1,3-dipropyl-2-(2-propoxyphenyl)-4,5-diphenylimidazole iodide (IL1) and 1,3-dibutyl-2-(2-butoxyphenyl)-4,5-diphenylimidazole iodide (IL2) for carbon steel in brackish water media (1% NaCl solution). The corrosion inhibition effect of these ILs were studied with different concentrations and temperature range between 25^0 C to 55^0 C. The results showed that both ILs follow Langmuir adsorption isotherm. The Gibbs free energy for adsorption was obtained −35.04 and −34.04 kJ/mol for IL-1 & IL-2 respectively. Thermodynamic data confirmed the physisorption on carbon steel surface [138].

El-Aoufir et al. (2020) evaluated the corrosion inhibition performance of different alkyl chain length bearing 1,2,4-triazole derived two ionic liquids, 5-octylsulfanyl-1,2,4-triazole (TR8) and 5-decylsulfanyl-1,2,4-triazole (TR10) for mild steel corrosion in 1.0 M HCl solution. Experimental evolution was done by weight loss (WL), potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) while theoretical evaluation done by density functional theory method (DFT). Inhibition mechanism was explored by the help of molecular dynamic simulation method. Scanning electron microscope (SEM) and atomic force microscopy (AFM) confirmed the protective layer formation on mild steel surface. EIS results revealed that the optimum inhibition efficiency was 92% and 88% for TR10 and TR8, respectively. Both ILs followed the Langmuir modal of adsorption isotherms [139].

Nkuna et al. (2020) studied the corrosion potential of three ionic liquids on mild steel in 1M HCl medium in which one of based on imidazolium ion namely 1-Ethyl-3-methylimidazolium ethyl sulfate (EMIM)(ESO_4). The adsorption energy was found -

3.04 kcal mol^{-1}. The optimum inhibition efficiency was 83.36% at 0.008 M concentration [140].

Ardakani et al. (2020) examined imidazolium derived polymeric ionic liquid namely [3-butyl-1-vinylimidazolium bromide] as corrosion inhibitor on mild steel in 1 M HCl solution. Tafel plot, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) measurements and quantum chemical calculation were used to analyse the inhibition effect. The taffel results indicated the mixed type of inhibition with predominantly cathodic type. The study revealed that the corrosion inhibition efficiency of the PIL exceeded 96% [141].

El-Hajjaji et al. (2021) synthesized two ionic liquids to investigate the corrosion inhibition properties on mild steel surface in 1M hydrochloric corrosive medium. Ionic liquids were named as 1-phenethyl-3-(3-phenoxypropyl)-1H-imidazol-3-ium bromide [Imid-3PE] Br, and 1-phenethyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium bromide [Imid-4PE] Br. The results of PDP experiments revealed that both ILs behaved as mixed type of inhibitors. According to EIS study the inhibition efficiency at optimum concentration was obtained as 95.8% for [Imid-3PE] Br and 96.7% for [Imid-4PE] Br. The physisorption and chemisorption was confirmed by the Langmuir adsorption isotherms and various thermodynamic parameters [142].

Zeng et al. (2021) investigated three ecofriendly corrosion inhibitors, 1-propyl-3-methylimidazolium bromide ([PrMIm]Br), 1-aminopropyl-3-methylimidazolium bromide ([APMIm]Br) and 1,4-bis(3-methylimidazolium-1-yl) butane dibromide ([BMImB]Br_2) for mild steel in sulphuric acid medium by using various techniques like weight loss method, PDP, EIS, SEM etc. The obtained results revealed that the ([BMImB]Br_2) showed highest corrosion inhibition efficiency 92.9 % at 303K. The order of inhibition efficiency was as follows [BMImB]Br_2 > [APMIm]Br > [PrMIm]Br. Weight loss experiment showed that [BMImB]Br_2 and [APMIm]Br act as good inhibitors at high temperature. All ILs followed the Langmuir adsorption isotherms model and show physisorption as well as chemisorption [143].

El-Katori et al. (2021) synthesized three ionic liquids namely (3-(2-ethoxymethyl)-1-octyl-1H-imidazol-3-ium chloride, 1-decyl-3-(2-ethoxymethyl)-1H-imidazol-3-ium chloride and 1-dodecyl-3-(2-ethoxymethyl)-1H-imidazol-3-ium chloride). Their structure was confirmed by FT-IR, ^{1}H NMR, and ^{13}C NMR spectra. The anti-corrosive properties of all ILs were studied on stainless steel in 2 M HCl solution by various

electrochemical measurements. The obtained results revealed that ILs behaves as mixed type of inhibitor and DFT and Monte Carlo simulation methods used to discuss the relation between structure and inhibitive action [144].

Cui et al. (2021) examined the corrosion inhibition performance of five imidazolium based ionic liquids named as (a) 1-propyl-3-methylimidazolium bromide [Pmim]Br, (b) 1-carboxyethyl-3-methylimidazolium bromide [COOHemim]Br, (c) 1-hydroxyethyl-3-methylimidazolium bromide [OHemim]Br, (d) 1-allyl-3-methylimidazolium bromide [Amim]Br, and (e) 1-aminoethyl-3-methylimidazolium bromide [NH2emim]Br. in H_2S and HCl medium by using electrochemical experiments, weight loss measurement, morphology analysis, and quantum chemical calculation method. The obtain results indicated that [Amim]Br has strong inhibition ability among the all ILs. Their inhibition efficiency decreases with increasing temperature. All ILs followed the Langmuir adsorption isotherm modal [145].

Costa et al. (2021) deals with the corrosion inhibition application of imidazole & four ionic liquids, 4-(imidazole-1-il)-phenol (PHEN), [4-(1*H*-imidazole-1-yl)-phenyl]methanol (METH), 2-(1*H*-imidazol-1-yl)-1-phenylethan-1-one (ETHAN) and 4-(1*H*-imidazole-1-yl)benzaldehyde (BENZ) on carbon steel in acidic medium. According to the electrochemical and gravimetric results the obtained order of inhibition efficiency was BENZ > ETHAN > METH > PHEN > IMI. DFT methods used to show the hardness of the inhibitor molecules and hardness is inversely promotional to inhibition performance hence softness leads to anticorrosion properties. Monte Carlo method (MC) was used to calculate the adsorption energies while Compass force field was selected towards obtaining the solvation energy between inhibitor and metallic surface which is show the inverse correlation with corrosion inhibition [146].

Rashed et al. (2022) synthesized three ionic liquids namely 1-butyl-1-methyl-pyrrolidinium Imidazolate (BMPyrIM), 1-butyl-3-methyl-imidazolium Imidazolate (BMImIM), and bis (1-butyl-3-methyl-imidazolium Imidazolate) (BBMImIM) to studied the cationic and dimeric effect of imidazolium based ionic liquid on mild steel in 1.0 M HCl solution by using potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), surface and structural (scanning electron microscopy (SEM)), Energy-dispersive X-ray spectroscopy (EDS), Atomic force microscopy (AFM) and Fourier Transform Infrared Spectroscopy (FTIR) and theoretical techniques (Density functional theory (DFT). The PDP result indicate that ILS behaved as mixed

type of inhibitor. The inhibition efficiency at optimum concentration was 98.6%, 94.3% and 92.4% for BBMImIM, BMImIM and BMPyrIM respectively. The SEM, EDS and AFM study confirmed the protective film formation on mild steel surface and the protection obey the Langmuir adsorption isotherm [147].

Kumar et al. (2022) investigated the imidazole based ionic liquid as corrosion inhibitor namely 1-hexyl-3-methylimidazolium tetrafluoroborate (HMIM.BF_4) on mild steel surface. The results revealed that it behaved as cathodic type of inhibitor and also showed chemisorption and physisorption nature. The inhibition efficiency increases on increasing inhibitor concentration which is maximum 96.27% at 300 ppm. The HMIM.BF_4 obeyed Langmuir and Temkin adsorption isotherms [148].

Nahle et al. (2022) studied the corrosion inhibition effect of cation of two imidazole based ionic liquids 3-(4-hydroxybutyl)-1-phenethyl-1H-imidazol-3-ium chloride **(**[HB-Imid] Cl), and 3-(2-chlorobenzyl)-1-phenethyl-1H-imidazol-3-ium chloride **(**[CB-Imid] Cl**)** on mild steel in 1.0 M HCl solution. Electrochemical techniques used for experimental study while DFT and molecular dynamic simulation used for explain theoretical approach. The results of experimental study indicated that both ILs categorised as mixed type inhibitors and the inhibition efficiency was obtained approx. 95 % at highest concentration 1.0×10^{-3} M. Both inhibitors were followed Langmuir model of adsorption isotherms and adsorbed on mild surface trough the physical and chemical bonds. The formation of protective layer formation confirmed by SEM and EDX examination [149].

Wang et al. (2022) investigated five fatty acid based ionic liquids (FAILs) with various anionic alkyl chain namely methyltrioctylammonium butyrate ($[N_{8881}][C_{4:0}]$), methyltrioctylammonium caproate ($[N_{8881}][C_{6:0}]$), methyltrioctylammonium octanoate ($[N_{8881}][C_{8:0}]$), methyltrioctylammonium laurate ($[N_{8881}][C_{12:0}]$) and methyltrioctylammonium palmitate ($[N_{8881}][C_{16:0}]$) as corrosion inhibitors on mild steel surface in 1 M HCl test solution. The study focused on the effect of anionic alkyl chain length on inhibition efficiency to synthesised effective and eco-friendly ionic liquids. to get the results of the present study weight loss measurement, electrochemical study with PDP and EIS, scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, x-ray diffraction was used. The results reveals that the all ILs are effectively adsorbed and formed protective film on mild steel surface. The methyltrioctylammonium octanoate [N_{8881}] [$C_{8:0}$] IL form most compact

film among the all ILs which analysed by molecular dynamic simulation and get highest inhibition efficiency 96.94% compare [150].

Tecuapa-Flores et al (2022) reported corrosion inhibition behaviour of N, N'-bis (carboxilicmethyl)benzimidazolium based IL for carbon steel. The corrosion inhibition in IL on electrode was analysed by x-ray diffraction, SEM and EDS. Corrosion current density was reduced significantly for ILS and impedance spectroscopy revealed that the solution resistance was increase compare to blank [151].

Hajjaji et al. (2023) investigated the corrosion inhibition efficiency of imidazolium based ionic liquids derivatives of different alkyl chain length [Eth-IM^+, Br^-]**,** [Met-IM^+, Br^-] and [Prop-IM^+, Br^-] on mild steel in 1 M HCl. Electrochemical Impedance Spectroscopy, Potentiodynamic polarization techniques were used as experimental studies. While DFT (Density Functional Theory) was used for Theoretical calculations. The results reveal that all three ILs have excellent inhibition efficiency greater than 90 %. The mixed type of inhibition behave was proved by electrochemical experiments. SEM and EDX results indicated the formation of protective layer at mild steel surface [152].

Asfour et al. (2023) synthesized and chemically elucidated benzimidazolium chloride based polymeric ionic liquids namely 1,3-diheptyl-2-(2-phenyl-propyl)-3*H*-benzimidazol-1-ium chloride (IL1), 1,3-dioctyl-2-(2-phenyl-propyl)-3*H*-benzimidazol-1-ium chloride (IL2), and 1,3-Bis-decyl-2-(2-phenyl-propyl)-3*H*-benzoimidazol-1-ium chloride (IL3) by using Fourier transform infrared spectroscopy, ^{1}H NMR, ^{13}C NMR, and elemental analysis tools. They also investigated the corrosion inhibition efficiency on carbon steel in 1 M HCl medium. The inhibition efficacy of the synthesized ILs was obtained 79.7%, 92.2% and 96.9%, for IL1, IL2 and IL3 respectively at 250 ppm and 303 K. The PDP results demonstrated that the all three ILs acting as mixed type of inhibitor. Langmuir adsorption isotherm model was confirmed as the best fitted isotherm [153].

Three ionic liquids with different alkyl chain were investigated by **Haldhar et al. (2023).** 1-(2-methoxy-2-oxoethyl)-3-methylimidazolium bromide (ILR1), 1-(2-ethoxy-2-oxoethyl)-3-methylimidazolium bromide (ILR2), and 1-(2-propoxy-2-oxoethyl)-3-methylimidazolium bromide (ILR3) were studied as corrosion inhibitors in 1 M HCl at 298 K. The practical and theoretical results demonstrated that the inhibitory action improves with the length of the alkyl chain and the order of corrosion resistance

was ILR1 < ILR2 < ILR3. The maximum inhibition efficiency was 95% obtained for ILR3 [154].

Chihbi et al. (2024) studied the two ecological ionic liquids derivatives based on imidazolium namely, 3-(2-ethoxy-2-oxoethyl)-1-phenethyl-1H-imidazol-3-ium-chloride [OE-IM^+, Cl^-] and 3-(4-ethoxy-4-oxobutyl)-1-phenethyl-1H-imidazol-3-ium-chloride [OB-IM^+, Cl^-] as corrosion inhibitor on mild steel in 1 M HCl medium by theoretical and experimental calculations. For the same concentration the order of inhibition efficiency was found as [OE-IM^+, Cl^-] < [OB-IM^+, Cl^-]. The results indicated that the performance effectiveness increase as the length of alkali chain was increase [155].

Ghiaty et al. (2024) examined Tetra-cationic ionic liquids 2-(4-dodecyldimethylamino) phenyl)-1,3-bis (3-dodecyldimethylammnonio) propyl) bromide-1-H-imidazol-3-ium acetate (DDAP-ImA) and 2-(4-hexyldimethylamino) phenyl)-1,3-bis(3-hexcyldimethylammnonio) propyl) bromide-1 H-imidazol-3-ium acetate (HDAP-ImA) as high potential corrosion inhibitor for steel in 1 M HCl solution. It was observed that the increasing alkyl chain length from hexyl to dodecyl tetra-cationic for HDAP-ImA and DDAP-ImA changes the morphology from amorphous to crystalline transition [156].

Liu et al. (2024) studied the five kind of imidazolium based ionic liquid with different alkyl chain length 1-alkyl-3-methylimidazolium bromide ($[C_x ami]Br$) x = 8, 10, 12, 14 and 16 as corrosion inhibitor on Q235 steel in 1 M HCl medium. Weight loss, potentiodynamic polarization and surface analysis tools used for inhibition study. The obtained results indicated that all five types of inhibitors acted as a mixed type of inhibitor with best fitted Langmuir adsorption isotherm model. The highest inhibition efficiency was 95.17% obtained for the ($[C_{16} ami]Br$) at 0.005 mM concentration [157].

Ratnani et al. (2024) synthesized and characterized 1-Heptyl-3-methylimidazolium bromide [HMImBr] and 1-Benzyl-3-methylimidazolium bromide [BzMImBr] to use as a green corrosion inhibitor on mild steel surface in 0.5 M sulphuric acid medium. Weight loss and electrochemical study revealed that the inhibition efficiency increase as the concentration of the ILs increase. [BzMImBr] showed better inhibition efficiency then the [HMImBr] due to having aromatic ring structure. The PDP study indicate the mixed type of inhibition and data of Gibbs free energy demonstrated the physisorption. SEM, EDS and AFM study used to analyse surface morphology [158].

1.13 Aims and objectives of present study

The aim of this research work is to study the effect of following ionic liquids with common anions namely 1-Ethyl-3-ButylImidazoliumBromide [BuEImBr], 1-Ethyl-3-PentylImidazolium Bromide [PEImBr] and common cations namely 1-Ethyl-3-BenzylImidazolium Bromide [BzEImBr], 1-Ethyl-3-BenzylImidazolium Chloride [BzEImCl] as corrosion inhibitor. It has been found that the corrosion inhibition abilities of ionic liquids depend on the molecular structure of the ionic liquids and their interaction with the metal surface. The study will use advance electrochemical techniques potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy for surface morphological examination. The main research objectives are described below-

- To synthesized and characterized ionic liquids based on imidazolium.
- To study the effect of concentration of ionic liquids, immersion time and temperature on the corrosion rate and inhibition efficiency.
- To propose possible mechanisms, type of adsorption and adsorption isotherm for the corrosion inhibition.
- To apply thermodynamics, kinetics and adsorption principles for study the inhibition potentials of the ionic liquids.
- To study the nature of adsorption of different ionic liquids on metal surface and surface morphology of the mild steel by using by scanning electron microscopy (SEM).

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Chapter - 2

MATERIAS, METHODS AND METHODOLOGY

Abstract

This chapter provides information about the conventional methods and advanced instruments, tools, materials and techniques used during the experimental works to obtain objectives of present research studies. It also presents the outline of experimental setup and make our study replicable.

2.1 Materials: -

To study the anti-corrosion behaviour of ionic liquid on metal mild steel is one of the materials which are mostly and widely used in industries such as gas and petroleum pipes, tanks, infrastructures, automobiles, tools etc due to easy availability, cheap cost, good malleability, high tensile strength and ductility [1-3]. Some acids such as nitric acid, sulphuric acid, hydrochloric acids, acetic acid etc are used in industries in many purposes like souring agent, cleaning agent, recycling process of water, to sterilize canned food, scrubbing, acid pickling and various petrochemical process [4-6]. Sulphuric acid often used for wastewater treatment because its breakdown the contaminants chemical pollutants into inert compounds and non-corrosive nature, low cost [7-8].

2.1.1 Preparation of mild steel test specimen:

The metallic material mild steel (MS) used for all experiments was purchased from Mahesh iron work Kota, Rajasthan. Table 2.1 represent the chemical composition of mild steel material was determined with the help of FE-SEM EDS. EDS chemical composition and Elemental mapping analysis illustrated in **Figure 2.1 and 2.2** respectively.

Table 2.1: Chemical composition of mild steel material

Elements	Fe	C	O	Zn	Cu
Weight %	94.64	3.77	0.50	0.37	0.35

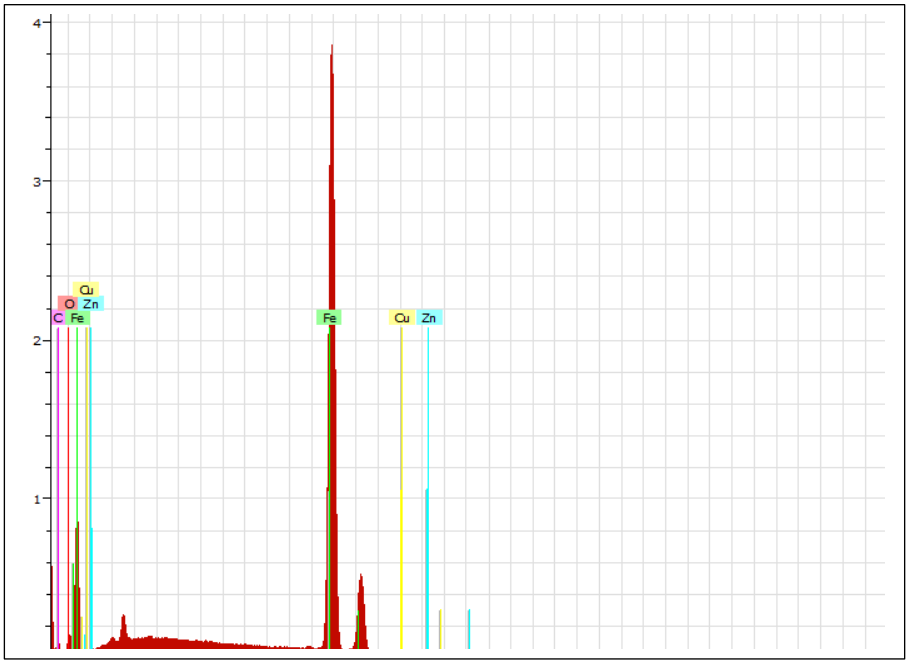


Figure 2.1: EDS graph of chemical composition of plain mild steel sample

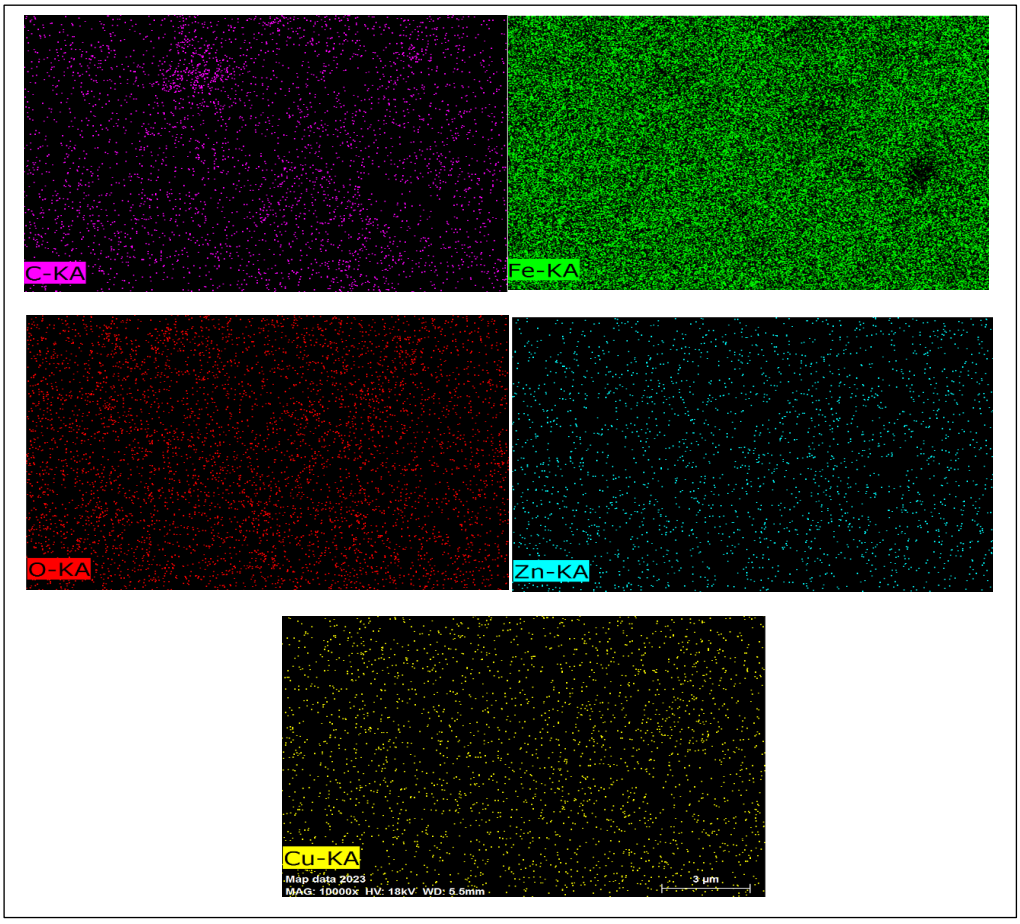


Figure 2.2: Elemental Mapping of mild steel sample

2.1.1.1 Test specimen for weight loss study: - For gravimetric (Weight-loss) study of corrosion, the mild steel sheet is mechanically cut into the rectangular shape strips with the help of cutter which is represented in **Figure 2.3**. The dimension of the strips was 3.6 cm x 2.3 cm x 0.3 cm (Length x Width x Thickness). To hanging the strips into the test solution there were employed a uniform hole diameter at the one end of strips. Before the use of mild steel strips were abraded by the emery papers of different grades (80, 220, 320, 400, 600, 800, 1000, 1200) degreased with acetone (99%, fisher scientific), rinsed with double distilled water, and then air-dried in moisture free desiccator.

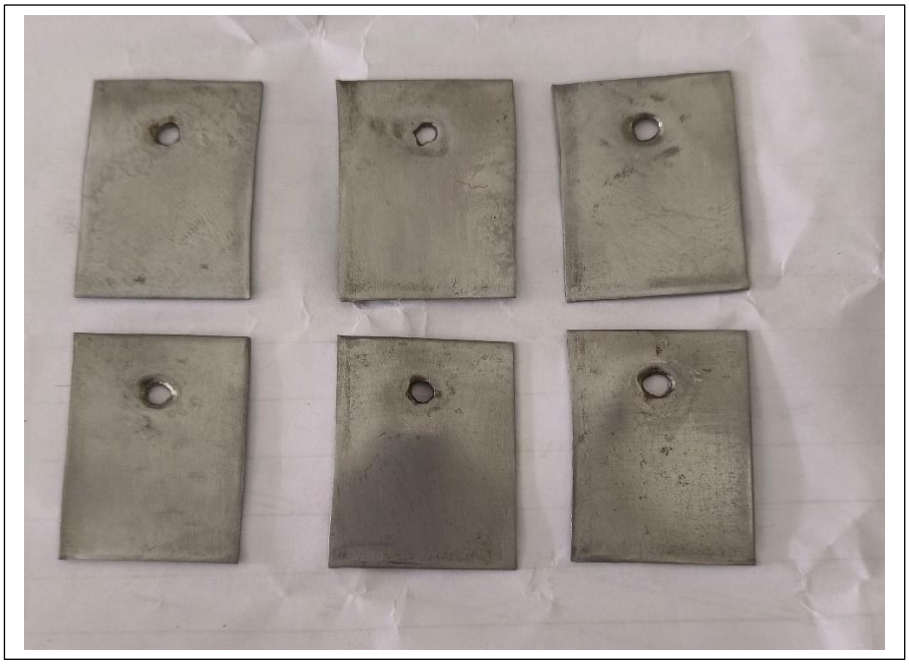


Figure 2.3: Mild steel sample for weight loss experiment

2.1.1.2 Test specimen for electrochemical and surface morphological study:- The mild steel strips which have same chemical composition with $1cm^2$ working area were used for all electrochemical experiments whereas mild steel strips of dimension 1.0 cm x 1.0 cm x 1.0 mm (Length x Width x Thickness) and cubic shape were used to surface morphological study which was abraded by emery papers of different grades, clean and rinsed by water and acetone then dried in desiccator before used.

2.1.2 Preparation of corrosive medium

The present research work was performed in sulphuric acid media which was purchased from fisher scientific India Pvt. Ltd. Molecular formula of sulphuric acid is H_2SO_4, molecular weight is 98.08 g/mol. purity of the acid is 97% and density is 1.834 gmL^{-1}

at 293 K. The stock solution of corrosive test solution 0.5 M H_2SO_4 prepared by diluting the concentrated sulphuric acid by double distilled water then it was converted into different concentrations of corrosion inhibitor solutions such that 200 ppm, 400 ppm, 600 ppm, 800 ppm and 1000 ppm with adding test inhibitor. Sulphuric acid is the best choice to choose as corrosive media because of having large rang of application such as domestic cleaner, electrolyte in lead acid batteries, fertilizers production, oil and petroleum refining, waste water treatment, dehydrating agent, production of dyes, detergents, insecticides, in pharmaceutical industries etc. [9-10].

2.1.3 Corrosion inhibitors used for investigation

In the present research work we were synthesized four imidazolium based ionic liquids to study the effect of alkyl chain length and the effect of different anions on their efficiency of corrosion inhibition in 0.5 M H_2SO_4 corrosive medium. The names of ionic liquids are 1-ethyl-3-butylimidazolium bromide (BuEImBr), 1-ethyl-3-pentylimidazolium bromide (PEImBr), 1-ethyl-3-benzylimidazolium bromide (BzEImBr) and 1-ethyl-3-benzylimidazolium chloride (BzEImCl). All ionic liquids were synthesized by CEM DISCOVER (USA) microwave reactor. The synthesis scheme and the characterization of above ionic liquids are widely discussed in the chapter -3.

2.2 Methods and methodology

2.2.1 Characterization techniques used for ILs

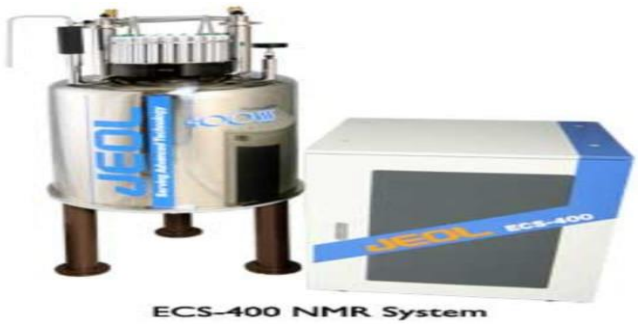
All ionic liquids were characterised by following techniques such as the IR samples were prepared in KBr pellets and recorded by FTIR spectrophotometer –ATR Alpha-T (Bruker, Germany).

The ^{1}H NMR spectra of samples obtained by ECS JEOL Resonance, Japan spectrometer, operate at a frequency of 100 MHz.

The ^{13}C NMR spectra were examined by ECS JEOL Resonance, a Japan spectrometer having 400 MHz frequency by using $CDCl_3$ as a solvent.

The high-resolution Xevo G2-SQT mass spectrometer (Waters, USA) employ to measure the molecular weight of the ionic liquids.

Figure: 2.4 Illustrated the instruments used in the characterization



NMR- Spectrometer

FT-IR Spectrophotometer-ATR **Mass- spectrometer**

Scanning electron microscope

Figure 2.4: Instruments used for characterization

2.2.2 Weight loss measurements

The gravimetric measurement for corrosion study was firstly described by Mattson. It is simplest and longest method [11]. It is widely used in corrosion study due to having a lot of advantage such that no sophisticated tools and instrument is required, low cost and applicability to all form of corrosion in all corrosive environments. For weight loss measurements rectangular shape mild steel strips with dimension 3.6 cm x 2.3 cm x 0.3cm (L x W x T) were used. Mild steel strips abraded by the emery papers of different grades (80, 220, 320, 400, 600, 800, 1000, 1200) degreased with acetone (99%, fisher scientific), rinsed with double distilled water, and then air-dried in moisture free

desiccator. Strips were weighted (W_1) by the help of electronic balance (CX220, citizen) **Figure 2.5** with an accuracy ± 0.01 mg before deep in the test solution.

Glass hook represented in **Figure 2.6** used to hang the mild steel strips into beaker which containing 100 ml of test solution with different concentration of inhibitors for different immersion time at various temperature using thermostat water bath. After the immersion time periods mild steel strips were removed from the test solution, washed and degreased by water and acetone then dried in desiccator. After this, strips were weighted to recorded final weight (W_2). Weight loss was calculated by (W_1-W_2). Weight loss study was applied to calculate corrosion rate and corrosion inhibition efficiency at different immersion time (12h, 24h, 36h, 48h) and various temperature (303 K, 313 K, 323 K, 333 K) in presence and absence of inhibitors.

Figure 2.5: Weighing Balance used to weighing mild steel coupons

Figure 2.6: Glass hook used to hanging of mild steel coupon in corrosive solution

2.2.3 Electrochemical measurements

The electrochemical work station Autolab PGSTAT 204 used for all electrochemical measurement was purchased from Metrohm (Netherlands) and Nova1.10 electrochemical software used to analyse data. The instrumentation has a conventional three electrode setup which is described below and illustrated in **Figure 2.9** [12]

(i) ***Working electrode,*** it is the primary electrode which corrosion rate being measured so it should be prepared with carefully. It is assembled between the gasket and reference electrode. A mild steel strip of 1 cm^2 working area used as working electrode (WE) for this study.

(ii) ***Counter electrode,*** it is made up of inert material for example platinum or graphite. It is used to measure cell current. A graphite rod shown in **Figure 2.7** used as a counter electrode (CE) for electrochemical study of corrosion.

(iii) ***Reference electrode,*** it has stable and reproducible potential. For reference electrode a small anodic potential produce reduction reaction while a small cathodic potential produce oxidation reaction. It is introduced to avoid the measurement error in the potential due to the polarization of ions in the solution. For present study Ag/AgCl(3MKCl) electrode used as the reference electrode (RE). **Figure 2.8**

Figure 2.7: Graphite rod as Counter Electrode

Figure: 2.8 Ag/AgCl(3MKCl) electrode as the Reference Electrode

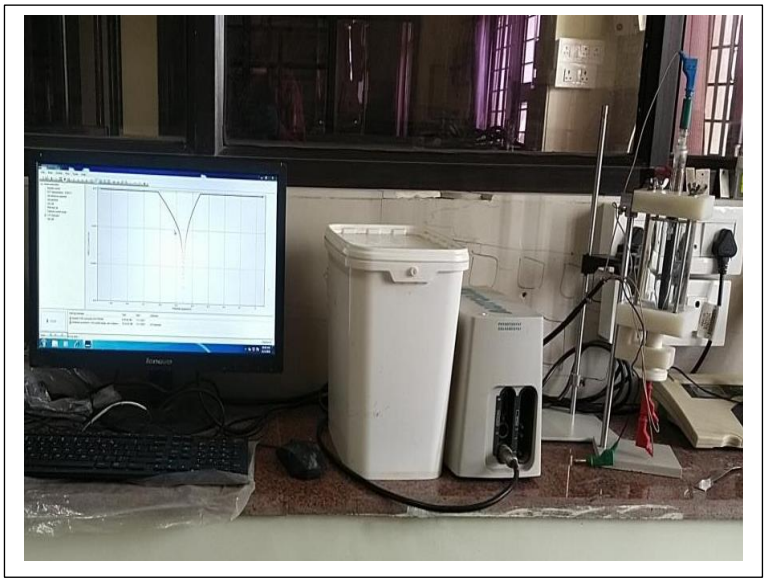


Figure 2.9: Experimental setup for electrochemical experiment

Procedure: To plot Tafel curves or potentiodynamic current-potential curves a Potentiostat /Galvanostat Autolab-204 Metrohm used. The finely polished mild steel coupon with 1 cm^2 area immersed in the test solution of 1000 ml and allowed to obtained steady state open circuit potential (OCP) for 30 minutes then curves recorded by polarizing the working electrode to -500 mV cathodically and +500 mV anodically with respect to the OCP at a scan rate of 1 mV s^{-1}. The setup was allowed to obtain fairly stable open circuit potential (OCP) to conducted linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). The EIS analysis was carried out immediately after LPR without any surface treatment of working electrode.

2.2.3.1 Potentiodynamic polarization (PDP) measurements

This technique helps to monitoring long term corrosion. It used to determine or measure the instantaneous corrosion rate. This technique based on this fact that small shift in the potential of corroding electrode is directly proportional to the corrosion current density which can be easily converted into the corrosion rate. The resistance (Rp) determined by the ratio of applied potential and the resulting current response which is inversely proportional to the corrosion rate. Rp is the transition resistance for metal ion dissolution in the corrosive solution from the metal surface. Corrosion rate can be determined by the Rp with the help of stern-Geary equation [13-14].

$$R_p = \left(\frac{\Delta v}{\Delta I}\right)_{E_{corr}} \quad (2.1)$$

$$i_{corr} = \frac{B}{R_p} \quad (2.2)$$

Where i_{corr} = corrosion current density (A /cm^2), R_p = Polarisation Resistance (Ω cm^2) and B = stern-Geary constant.

$$B = \frac{(b_a \,.\, b_c)}{2.3\,(b_a + b_c)} \quad (2.3)$$

b_a = the anodic Tafel slope, b_c = the cathodic Tafel slope.

The % inhibition efficiency can also be calculated by the help of following equation [15].

$$\%IE = \frac{R_{P_{unInhibited}} - R_{P_{Inhibited}}}{R_{P_{UnInhibited}}} \; X\; 100 \quad (2.4)$$

The taffel extrapolation method also used to determine the inhibition efficiency. Julian Tafel found the linear relationship between the E and log(i) for sufficiently large potential polarized electrode. This region in which this relation is exist known as Tafel region. The mathematical relation is given by the equation (2.5).

$$i = i_{corr}\left[\exp\left\{\frac{2.303(E-E_{corr})}{ba}\right\}\right] - \left[\exp\left\{\frac{2.303(E-E_{corr})}{bc}\right\}\right] \quad (2.5)$$

i = corrosion current, i_{corr} = current at corrosion potential, E_{corr}= corrosion potential, b_a = the anodic Tafel slope, b_c = the cathodic Tafel slope.

$$\%IE = \frac{i_{corr_{unInhibited}} - i_{corr_{Inhibited}}}{i_{corr_{UnInhibited}}} X\ 100 \quad (2.6)$$

2.2.3.2 Electrochemical impedance spectroscopy (EIS)

Impedance is the amplitude of current for a given voltage means it is a proportionality factor between the current and voltage. EIS study was used to analyse protective film layer and mechanism of corrosion protection. The impedance data were analysed by using Nyquist and Bode plots and impedance parameters such as charge transfer resistance R_{ct}, solution resistance R_s and double layer capacitance C_{dl} in absence and presence of different concentration of inhibitors obtained by fitting the experimental data. Zsim software used for the fitting and simulation of Nyquist plots. Nyquist plot compare the impedance magnitude and phase angle. The increment in the diameter of semi-circle loop indicates the formation of protective layer on mild steel surface. Bode and Bode phase plot used to show electrochemical reaction dominance and improvement in the phase angle with the increment in the concentration of ILs. The inhibition efficiency of the inhibitors can be determined by the AC impedance method by the following equation (2.7) [16-17].

$$\%\ IE = \left[\frac{\left[R_{ct_{Inhibited}} - R_{ct_{unInhibited}}\right]}{R_{ct_{Inhibited}}}\right] X\ 100 \quad (2.7)$$

Where R_{ct} is the resistance to charge transfer in an unconstrained solution, and $R_{ct(inh)}$ is the resistance to charge transfer in an inhibited solution.

2.2.4 Surface analyses SEM and EDS spectroscopy

The Nova Nano Fe-SEM 450(FEI) scanning electron microscope with EDS energy dispersive X-ray spectroscopy used to determine the chemical composition and the image of surface morphology of inhibited and corroded mild steel sample. To prepare the sample for surface morphological analysis 1.0 cm x 1.0 cm x 0.10 cm (L x W x T) dimension mild steel coupon is used. This coupon is abraded with emery papers of different grades, cleaned and degreased with double distilled water and acetone then dried in desiccator before used. these samples immersed in the 100 ml of the test solution of 0.5 M H_2SO_4 without inhibitor and 100 ml test solution of optimum concentration of inhibitor for 24 hours at 303 K temperature. After this samples are washed with double distilled water and acetone then dried in desiccator. **Figure 2.10**

Figure 2.10: Mild steel sample for SEM study

2.3 Calculation of various parameters

2.3.1 Calculation of corrosion rate

The corrosion rate for mild steel coupon in absence and presence of various concentration of inhibitors at different temperature was calculated by the following equation (2.8) [18-19].

$$C_R = [\frac{87.6\ X\ \Delta W}{AtD}] \qquad (2.8)$$

Where C_R = corrosion rate in mmy^{-1}, ΔW = weight loss of mild steel in mg, A = area of the MS specimen (in cm^2), t = time (in hrs.), and D = density of mild steel (7.85 g/cm^3).

2.3.2 Calculation of inhibition efficiency

The inhibition efficiency of inhibitors can be easily determined by the help of surface coverage area of mild steel coupon by inhibitor. The calculation of surface coverage area and % of inhibition efficiency was given by following equations 2.9 and 2.10 respectively [20].

$$\text{Surface coverage } (\theta) = [\frac{(W0 - Wi)}{W0}] \qquad (2.9)$$

$$\%IE = [\frac{[(W0 - Wi)}{W0}]X100 \qquad (2.10)$$

Where Wo is the weight loss in absence of inhibitor, Wi is the weight loss in presence of inhibitor.

2.3.3 Evaluation of activation and thermodynamic parameters

The evaluation of various activation and thermodynamic parameters such as activation energy (E_{act}), enthalpy of adsorption (H_a) and entropy of adsorption (S_a) can be calculated by plot the graph according to the following Arrhenius equation and transition state theory equation (2.11) and (2.12) respectively.

$$ln\ C_R = ln\ A - \left(\frac{Ea}{RT}\right) \qquad (2.11)$$

C_R =Corrosion rate, Ea = Energy of activation, T = Absolute temperature, R = Universal gas constant, and A = Frequency factor.

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta Sa}{R}\right) \exp -\left(\frac{\Delta Ha}{RT}\right) \qquad (2.12)$$

Where h = Planck's constant, N = Avogadro's constant, ΔH_a = enthalpy of activation, and ΔS_a = entropy of activation

The activation energy of adsorption evaluates by the slope of the graph between $ln(C_R)$ and 1/ T. similarly enthalpy of adsorption (H_a) and entropy of adsorption (S_a) can also be calculated by the help of slop and intercept of the graph between $ln\frac{C_R}{T}$ and 1/T.

The standard free energy (ΔG^0_{ads}) for the adsorption of inhibitors on the mild steel surface was calculated using equation (2.13)

$$\Delta G_{ads} = -RT\ ln\ (55.5K_{ads}) \qquad (2.13)$$

The nature of interaction between the ionic liquid (IL) and mild steel surface was evaluated by the adsorption isotherms. Adsorption isotherms represent the variation in the adsorption of inhibitor on mild steel surface at constant temperature with respect to pressure and concentration. The best fitted adsorption isotherms model observed by the regression value (R^2). The adsorption isotherms model for which the regression value close to unity was considered as best fitted. The various adsorption isotherms model was mentioned following [21-22].

1. **Langmuir adsorption isotherm**

$$\frac{C_{Inh}}{\theta} = C_{Inh} + \frac{1}{K_{ads}} \quad (2.14)$$

C_{inh}= Concentration of inhibitors, K_{ads} =Adsorption equilibrium constant, θ = Degree of surface coverage

On plotting C_{inh}/θ versus C_{inh}, if a straight line is obtained the adsorption process follows Langmuir adsorption isotherm.

2. **Freundlich adsorption isotherm**

$$\theta = K_{ads} C_{inh}^{n} \quad (2.15)$$

$$log\theta = logK_{ads} + nlogC_{inh} \quad (2.16)$$

0<n<1: n = empirical constant, θ is the degree of surface coverage, C_{inh}= Concentration of inhibitors, K_{ads}= Adsorption equilibrium constant

If a straight line is obtained on plotting log (θ) versus log (C_{inh}) than the adsorption process follows Freundlich adsorption isotherm.

3. **Temkin adsorption isotherm**

$$-2a\theta = ln\, K_{ads} + ln\, C_{inh} \quad (2.17)$$

Where θ = Degree of surface, C_{inh} = Concentration of inhibitors K_{ads}= Adsorption equilibrium constant.

4. **El-Awady's adsorption isotherm**

$$log\, \frac{\theta}{(1-\theta)} = \log K + y \log C \quad (2.18)$$

where C is the concentration, θ is the degree of surface coverage, K is the equilibrium constant, y is the number of active sites.

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Chapter - 3

SYNTHESIS AND CHARACTERIZATION OF SOME IMIDAZOLIUM BASED IONIC LIQUIDS

Abstract

This chapter focuses on the synthesis and structure confirmations of imidazolium based ionic liquids with different alkyl chain of cationic part and different anions namely 1-Ethyl-3-ButylImidazolium Bromide [BuEImBr], 1-Ethyl-3-PentylImidazolium Bromide [PEImBr], 1-Ethyl-3-BenzylImidazolium Bromide [BzEImBr], 1-Ethyl-3-BenzylImidazolium chloride [BzEImCl]. All four ionic liquids are synthesised by the help of microwave assisted synthesizer and characterised by various spectroscopic technics such that ^{1}H NMR, ^{13}C NMR, IR and Mass Spectrometry.

3.1 Introduction

In the sense of green chemistry, research and application of green chemistry principles focus to development ecofriendly and cleaner processes. The use of ionic liquids in academia and industries as solvent, catalysts and efficient chemical transformation is ever-growing research in the present scenario. A large number of combinations of cations and anions provided uniqueness and attractiveness to ionic liquids to work in several fields. There are mainly two methods to synthesis ionic liquids, metathesis and acid base neutralization. Earl and Seddon developed a method to prepare imidazolium cation based ionic liquids in which alkyl imidazolium halides was prepared by quaternization of heterocyclic compound with appropriate alkyl halides. This product directly used in the anion metathesis [1-3]. In the current research works to get the better results of quaternization reaction and avoid the contamination, non-conventional methods such that microwave and ultrasound techniques used in the synthesis. This route provides better yields and suitable for synthesis water soluble ionic liquids [4-7]. Microwave irradiation is a non-conventional heating source which provides fast, efficient, solventless and environment friendly methodology for ionic liquids synthesis [8-9]. In present work microwave irradiation used to ionic liquids synthesis and IR, ^{1}H-NMR, ^{13}C-NMR, Mass-Spectrometry, spectroscopic techniques used for structural confirmation of synthesised ionic liquids.

3.2 Advantage of Microwave assisted synthesis comparison with conventional method

In 2001 Verma and Namboodiri first time used microwave irradiation to synthesis ionic liquids further Pal and Kumar synthesised a variety of imidazolium based ionic liquids

by using microwave irradiation in 2006 [10,11]. Following advantages of microwave synthesis are as follows [12-15].

- Rapid or less time-consuming process
- Solvent less process
- Increment in reaction rate and yield
- High atom economy
- Flexible reaction scale
- Energy efficient or rapid energy transfer
- Convenient reactor size
- Explore greener alternatives
- Easy to handling
- Selective heating
- No byproducts formation
- Absolute control on reaction parameters

3.3 Equipment and chemicals

The equipment and all analytical grade (AR) chemicals and solvents which were used for synthesis purpose described below.

1. **Acetone (C_3H_6O)**

   It was used as solvent and washing agent for mild steel coupon. For purpose of present work used acetone was made by Fisher Scientific with 99% purity and molecular weight 58.08.

2. **Ethyl acetate ($C_4H_8O_2$)**

   It was used as purification reagent in ionic liquids synthesis. For present work purpose used Ethyl acetate was made by Fisher Scientific with 99% purity and molecular weight 88.11.

3. **1-Ethylimidazole ($C_5H_8N_2$)**

   For Microwave synthesis of ionic liquids, 1-Ethylimidazole was used as a reactant. It was directly purchased from market which was made by Tokyo Chemical Industry, Japan with 98% purity, molecular weight 96.13 and density 0.993 gm/ml.

4. **1-Bromobutane (C_4H_9Br)**

   It is a colourless liquid which is insoluble in water and soluble in organic solvents. In the present research work it was used as a source of butyl group for synthesis of [BuEImBr]. It was made by Loba Chemie Pvt. Ltd. with 98% Purity, molecular weight 137.03 and density 1.27 gm/mL.

5. **1-Bromopentane ($C_5H_{11}Br$)**

   It is a colourless liquid which was used in the synthesis of ionic liquid [PEImBr]. It was made by Loba Chemie Pvt. Ltd with 98% Purity, molecular weight 151.04 and density 1.21 gm/mL.

6. **Benzyl Bromide ($C_6H_5CH_2Br$)**

   It is a colourless liquid used to introduced benzyl group in the organic synthesis. It was made by Alfa Aesar with 99% Purity, molecular weight 171.03 and density 1.44 gm/mL.

7. **Benzyl Chloride (C_7H_7Cl)**

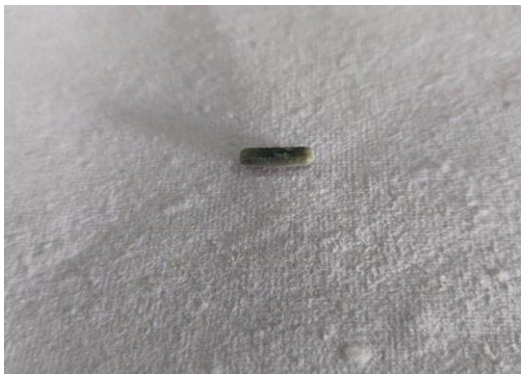
   It is a colourless liquid with an irritating Odor and slightly soluble in water. It was made by Loba Chemie Pvt. Ltd. with 99% Purity, molecular weight 126.58 and density 1.1 gm/mL.

A closed vessel with magnetic stirrer used as reaction container. Single-mode microwave reactor, Discover, CEM (USA) used for microwave synthesis of ionic liquids. All chemicals were measured with the help of F3 Finnpipette of rang 100µL to 1000µL made by Fisher Scientific. At last, the synthesised ionic liquids were dried in a vacuum oven, 106, Lepro international (India). All equipment and chemicals used for synthesis purpose was shown in **Figure 3.1 and 3.2** respectively.

(a) Microwave Reactor

(b) Vacuum Oven

(C) Microwave Vessel



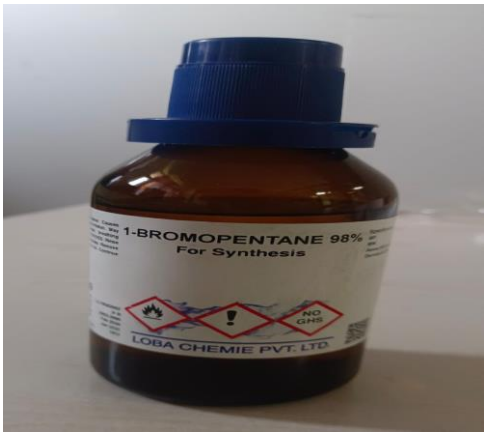
(D) Megnatic Niddle

Figure 3.1: Equipment used in synthesis

(a) Acetone

(b) 1-Ethylimidazole

(c) 1-Bromobutane



(d) 1-Bromopentane

(e) Benzyl bromide

(f) Benzyl chloride

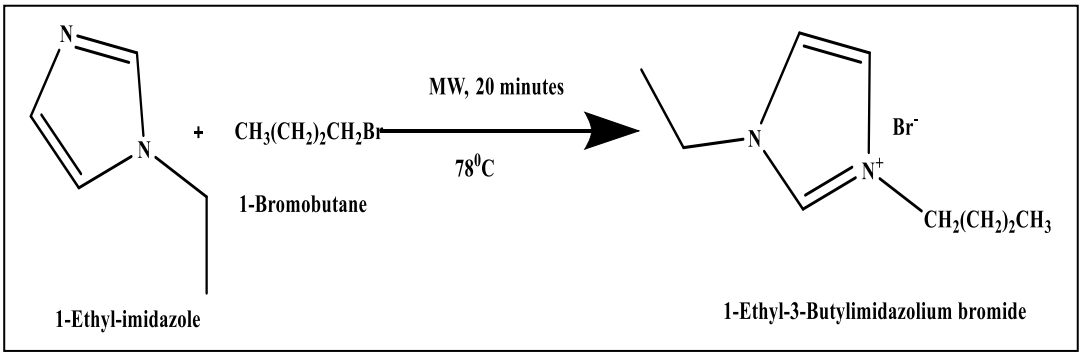
Figure 3.2: Chemicals used in synthesis

3.4 Microwave assisted synthesis of imidazolium based ionic liquids

The controllable single-mode microwave reactor made by Discover, CEM(USA) used for microwave irradiation synthesis, depicted in **Figure: 3.1 (a)** equipped with magnetic stirrer was set at 44 psi pressure, 78^0C temperature, 240 W power control and medium range of stirring. Take equimolar mixture of reactant with the help of Finnpipette in closed vessel and subjected to microwave reactor with make all setup of device.

3.4.1 Synthesis of 1-Ethyl-3-Butylimidazolium Bromide [BuEImBr]

To synthesis of [BuEImBr] ionic liquid take 0.025 moles or 2.4202 ml of 1-Ethylimidazole in a dried closed vessel followed by the drop wise addition of 0.025 moles or 2.6972 ml 1-Bromobutane with the help of Finnpipette. Vessel was subjected to microwave reactor for 20 minutes at 78^0C. Scheme 3.1 described the chemical reaction. After completion of the reaction brown-yellowish viscos liquid with M.P. 84^0C was obtained as a product shown in **Figure 3.3** which was washed by Ethyl Acetate and dried in vacuum oven at 60^0C for overnight. The scheme 3.1 represent the synthesis of the [BuEImBr]**.** The yield of the reaction was obtained 94.36%.



Scheme-3.1: synthesis of 1-Ethyl-3-Butylimidazolium Bromide

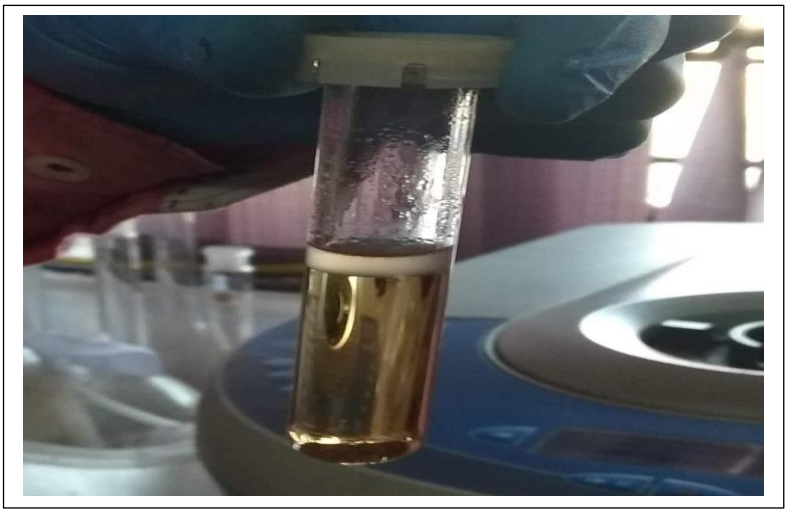
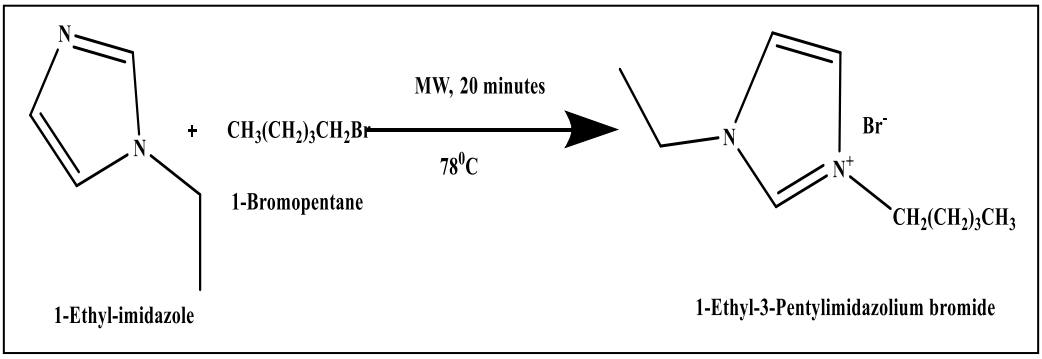


Figure 3.3: Synthesised 1-Ethyl-3-Butylimidazolium Bromide

3.4.2 Synthesis of 1-Ethyl-3-Pentylimidazolium Bromide [PEImBr]

To synthesis of [PEImBr] ionic liquid take 0.025 moles or 2.4202 ml of 1-Ethylimidazole in a dried closed vessel followed by the drop wise addition of 0.025 moles or 3.1001 ml 1-Bromopentane with the help of Finnpipette. Vessel was subjected to microwave reactor for 20 minutes at 78^0C. Scheme 3.2 described the chemical reaction. After completion of the reaction brown-yellowish viscos liquid with M.P. 87^0C was obtained as a product shown in **Figure 3.4** which was washed by Ethyl Acetate and dried in vacuum oven at 60^0C for overnight. The scheme 3.2 represent the synthesis of the [PEImBr]**.** The yield of the reaction obtained 95.42%.



Scheme-3.2: Synthesis of 1-Ethyl-3-Butylimidazolium Bromide

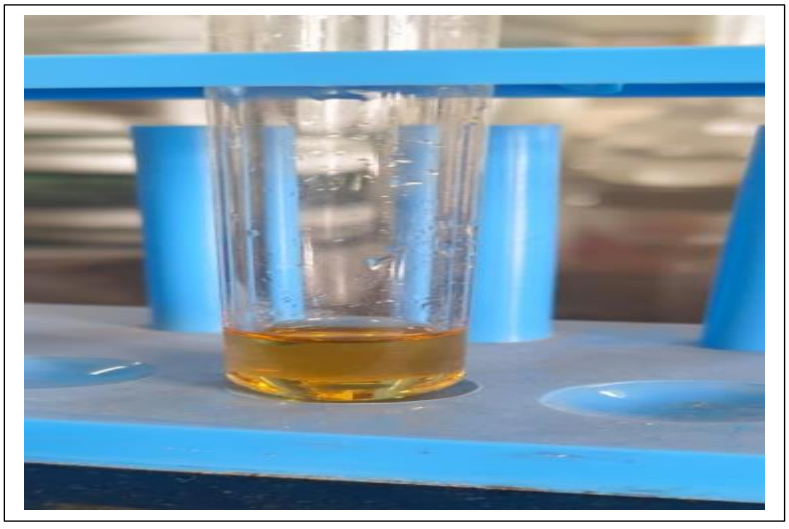
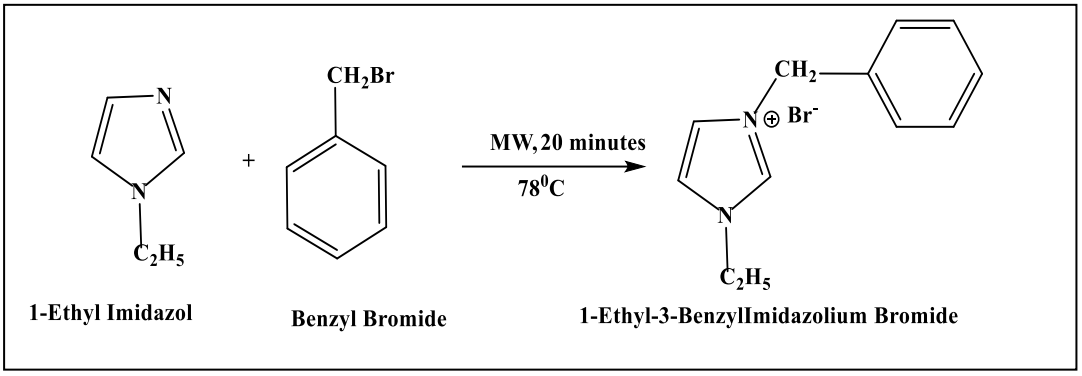


Figure 3.4: Synthesised 1-Ethyl-3-Pentylimidazolium Bromide

3.4.3 Synthesis of 1-Ethyl-3-Benzylimidazolium Bromide [BzEImBr]

To synthesis of [BzEImBr] ionic liquid take 0.025 moles or 2.4202 ml of 1-Ethylimidazole in a dried closed vessel followed by the drop wise addition of 0.025 moles or 2.9694 ml Benzyl Bromide with the help of Finnpipette. Vessel is subjected to microwave reactor for 20 minutes at 78^0C. Scheme 3.3 described the chemical reaction. After completion the reaction dark brown-orange viscos liquid with M.P. 97^0C was obtained as a product shown in **Figure 3.5** which was washed by Ethyl Acetate and dried in vacuum oven at 60^0C for overnight. The scheme 3.3 represent the synthesis of the [BzEImBr]**.** The yield of the reaction obtained 92.55%.

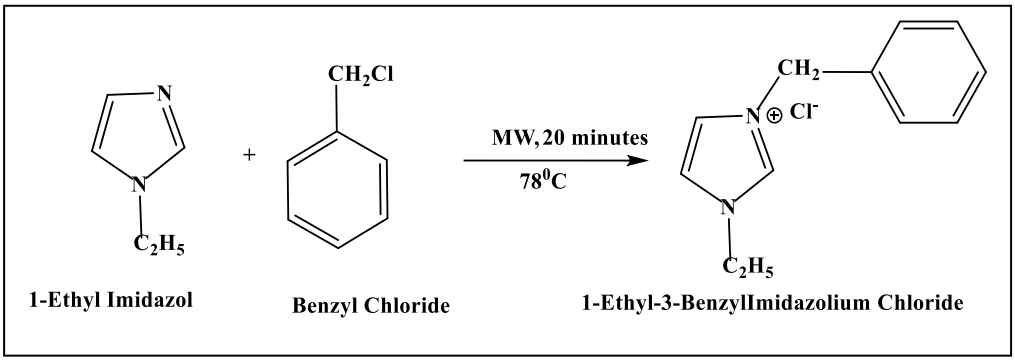


Scheme-3.3: Synthesis of 1-Ethyl-3-Benzylimidazolium Bromide

Figure 3.5: Synthesised 1-Ethyl-3-Benzylimidazolium Bromide

3.4.4 Synthesis of 1-Ethyl-3-Benzylimidazolium Chloride [BzEImCl]

To synthesis of [BzEImCl] ionic liquid take 0.025 moles or 2.4202 ml of 1-Ethylimidazole in a dried closed vessel followed by the drop wise addition of 0.025 moles or 2.8770 ml Benzyl Chloride with the help of Finnpipette. Vessel is subjected to microwave reactor for 20 minutes at 78^0C. Scheme 3.4 described the chemical reaction. After completion the reaction dark brown-orange viscos liquid with M.P. 83^0C was obtained as a product shown in **Figure 3.6** which was washed by Ethyl Acetate and dried in vacuum oven at 60^0C for overnight. The scheme 3.4 represent the synthesis of the [BzEImCl]**.** The yield of the reaction obtained 95.27%.



Scheme-3.4: Synthesis of 1-Ethyl-3-Benzylimidazolium Chloride

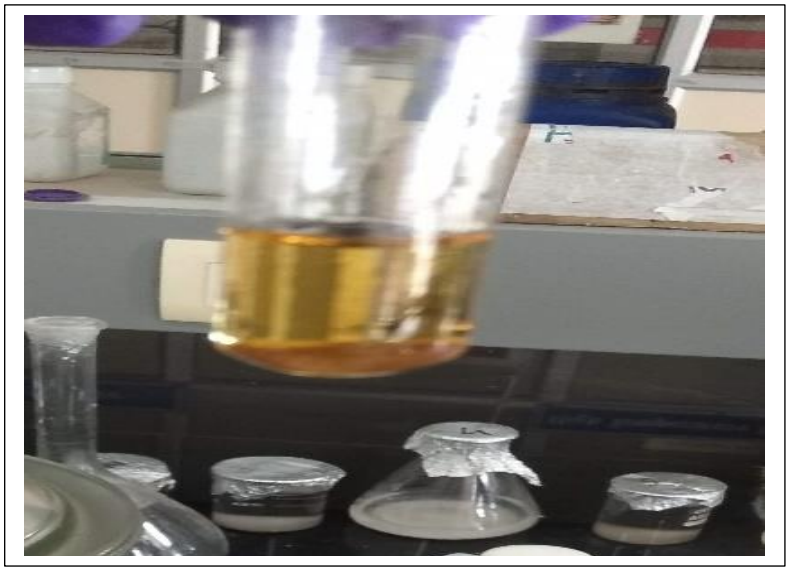


Figure 3.6: Synthesised 1-Ethyl-3-Benzylimidazolium Chloride

3.5 Characterization of synthesized ionic liquids

The structural confirmation of synthesised ionic liquid was done by ^{1}H-NMR, ^{13}C-NMR, IR and Mass Spectrometry. ^{1}H-NMR spectra were measured in $CDCl_3$ solvent by ESC 400 MHz, JEOL, Resonance, Japan on δ scale. TMS was used as internal reference. ^{13}C-NMR was measured by ESC 100 MHz, JEOL, Resonance, Japan in $CDCl_3$ solvent. An IR spectrum was recorded by using ATR (Alpha-T, Bruker). Xevo G2-SQT (Water USA) was used to take Mass spectra.

3.5.1 Characterization of 1-Ethyl-3-Butylimidazolium Bromide [BuEImBr]

^{1}H-NMR (400 MHz, $CDCl_3$) spectra exhibited the peaks at δ: 0.82 (t, 3H), 1.47 (m,5H), 1.78(m, 2H), 4.3 (m, 4H), 7.46 (d, 1H), 7.57 (d, 1H), 10.27 (s, 1H) [**Figure 3.7**]

^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.4 (CH_3), 15.7 (CH_3), 19.4 (CH_2), 32.1 (CH_2), 45.2 (N- CH_2), 49.7 (N^+- CH_2), 122.1 (N-CH), 122.4 (N^+-CH), 136.4 (N^+=CH-N) [**Figure 3.8**]

MS (ES^+) m/z peaks was found at 153.1274 [**Figure 3.9**]

FTIR (v_{max} 525-4000 cm^{-1}) 3130 (w), 2934, 2958(s), 2872(s), 1461-1562(s), 1250-1382(m), 1400-1500 (m), 769-832(m), 634-686 (S) [**Figure 3.10**]

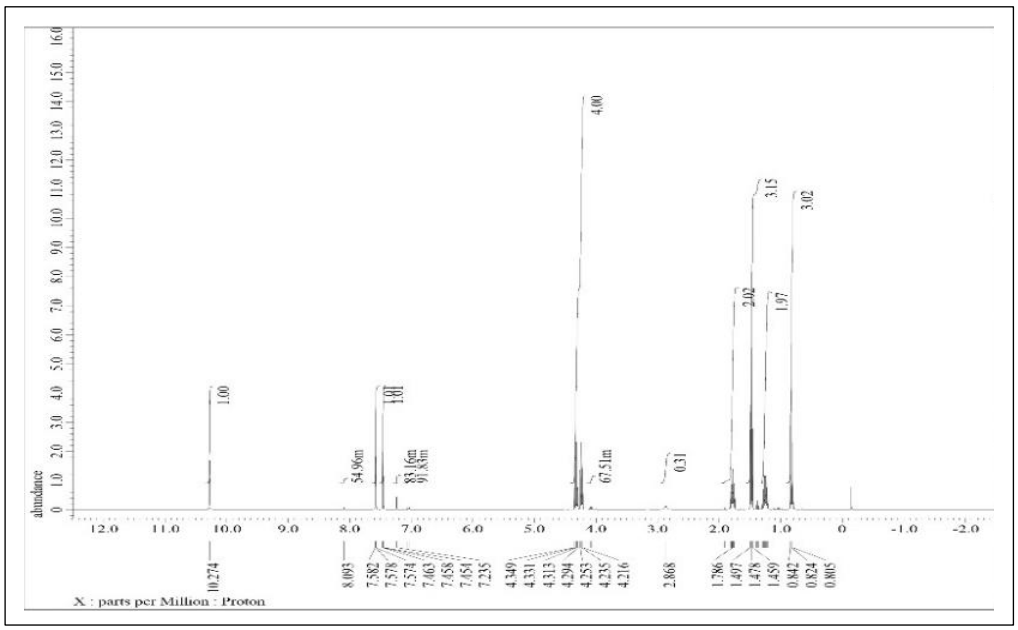


Figure 3.7: ^{1}H-NMR Spectra of 1-Ethyl-3-Butylimidazolium Bromide

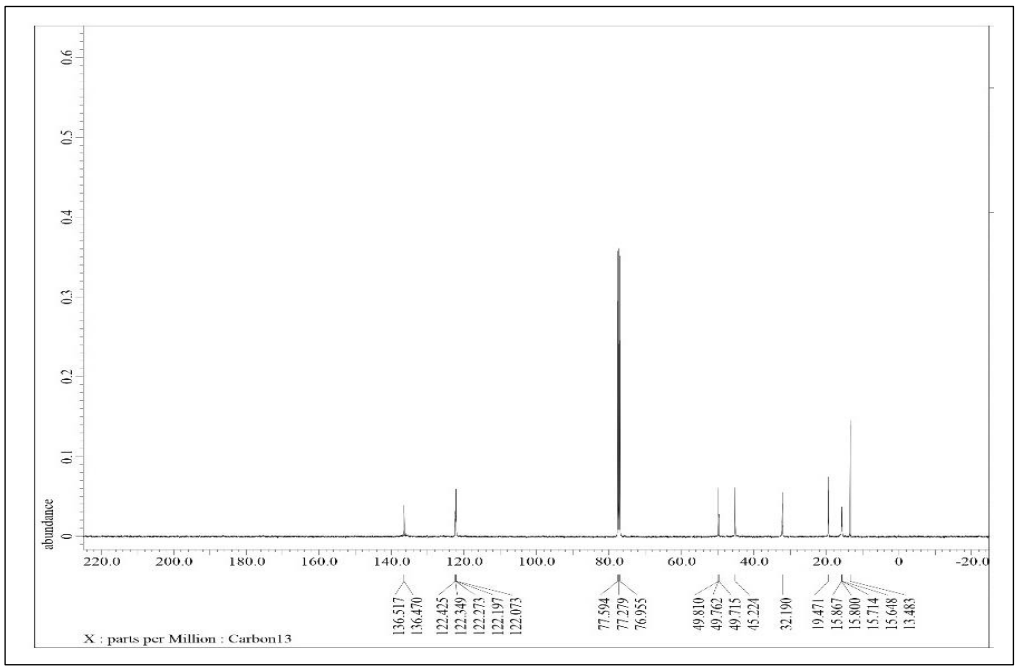


Figure 3.8: ^{13}C-NMR Spectra of 1-Ethyl-3-Butylimidazolium Bromide

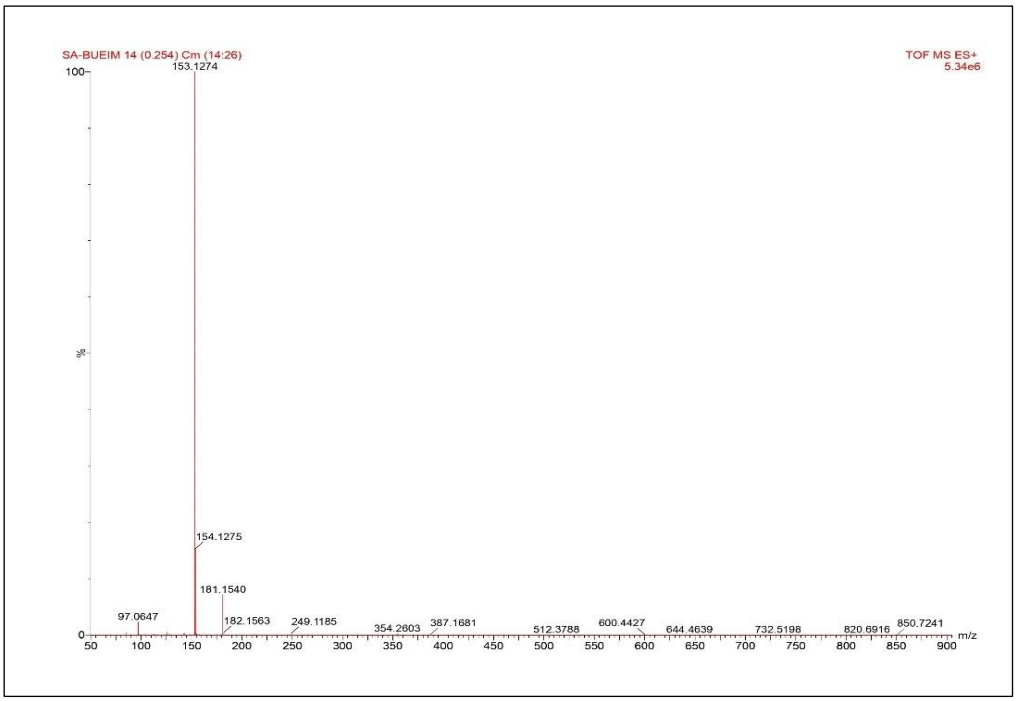


Figure 3.9: Mass Spectra of 1-Ethyl-3-Butylimidazolium Bromide

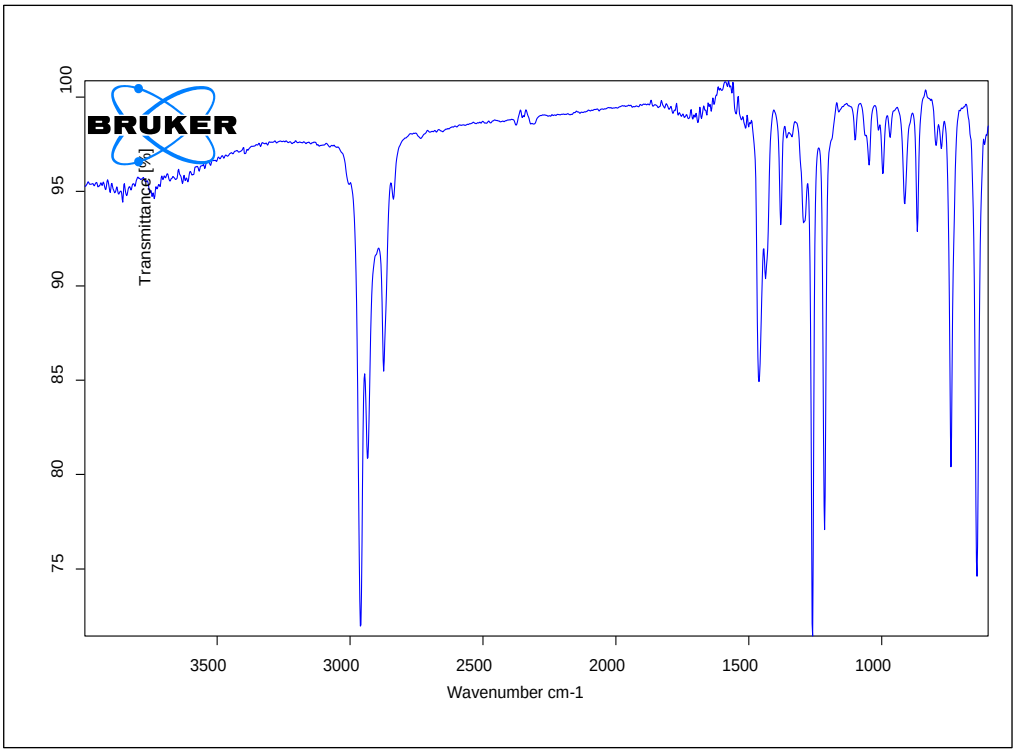


Figure 3.10: IR Spectra of 1-Ethyl-3-Butylimidazolium Bromide

3.5.2 Characterization of 1-Ethyl-3-Pentylimidazolium Bromide [PEImBr]

^{1}H-NMR (400 MHz, $CDCl_3$) spectra exhibited the peaks at δ: 9.96 (s, 1H), 7.44-7.45(d, 1H), 7.29-7.30(d, 1H), 3.99-4.14 (m, 4H), 0.48-0.51 (t,3H), 0.57-1.2 (m, 7H), 1.23-1.60 (m, 2H) [**Figure 3.11**]

^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.6 (CH_3), 15.6 (CH_3), 21.8 (CH_2), 28.0 (CH_2), 29.7 (CH_2), 44.9 (N-CH_2), 49.7 (N^+-CH_2), 123 (N-CH, N^+-CH) 136.0 (N^+=CH-N) [**Figure 3.12**]

MS (ES^+) m/z peaks was found at 167.1636 [**Figure 3.13**]

FTIR (V_{max} 525-4000 cm^{-1}) 3056 (w) 2931, 2956, 2860(s) 1456-1562(s) 1250-1380(m) 1400-1500(m) 752-825(m) 633-685(S) [**Figure 3.14**]

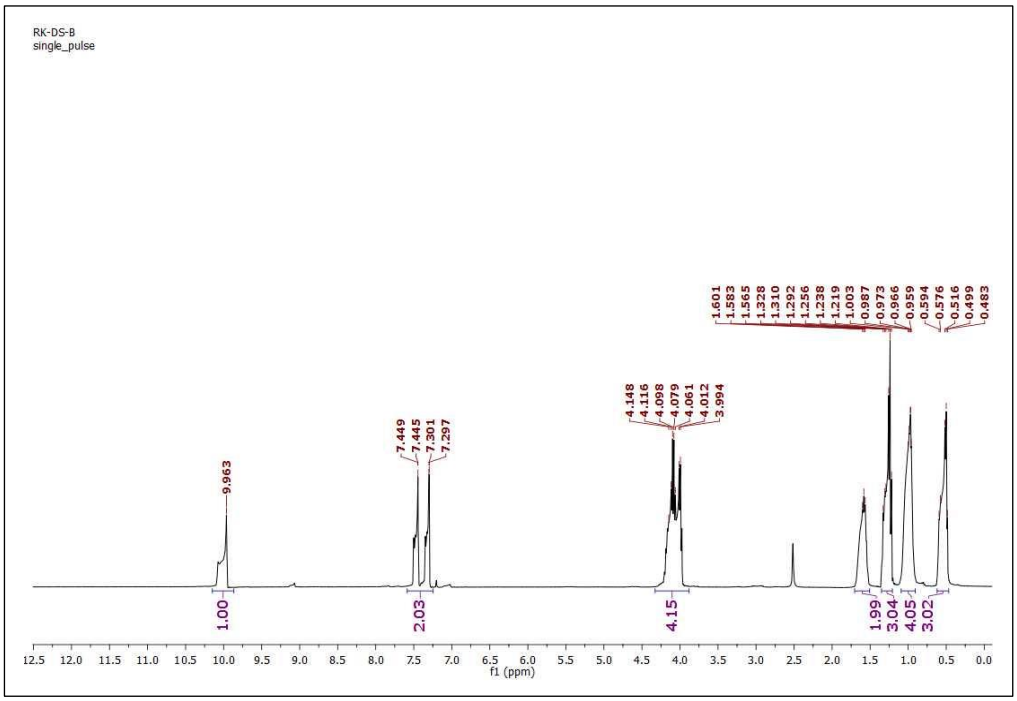


Figure 3.11: ^{1}H-NMR Spectra of 1-Ethyl-3-Pentylimidazolium Bromide

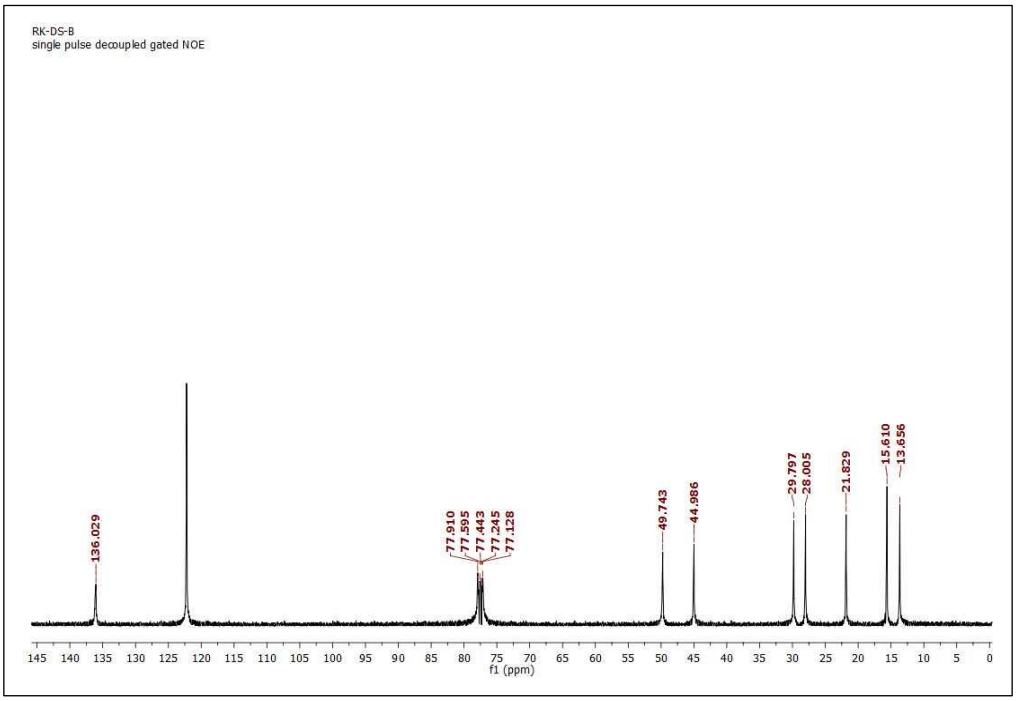


Figure 3.12: ^{13}C-NMR Spectra of 1-Ethyl-3-Pentylimidazolium Bromide

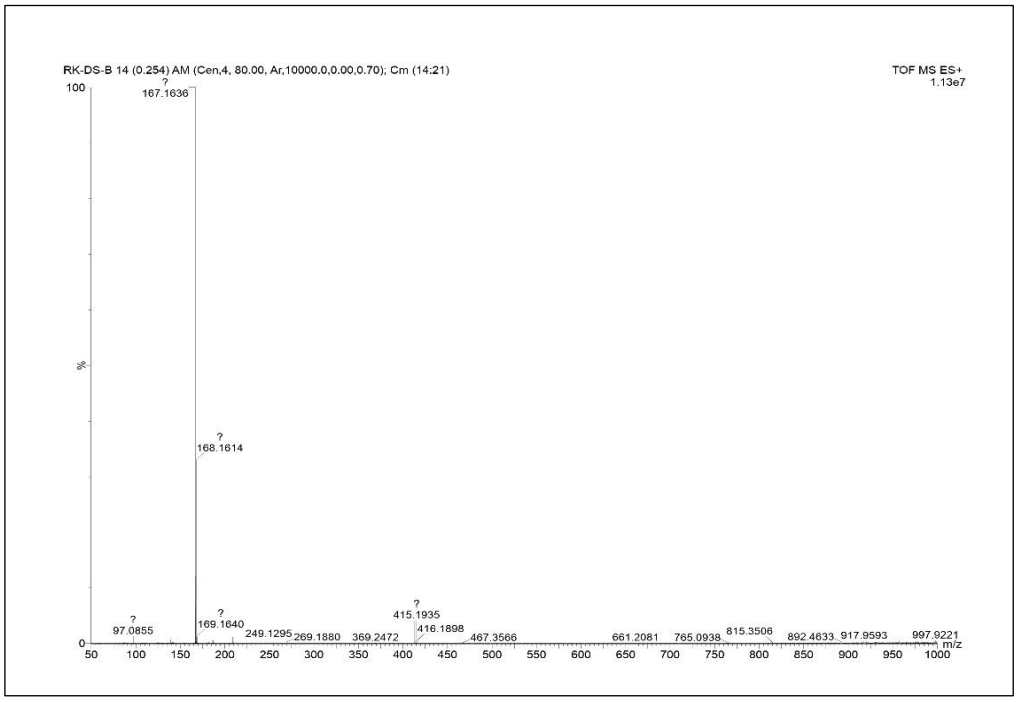


Figure 3.13: Mass Spectra of 1-Ethyl-3-Pentylimidazolium Bromide

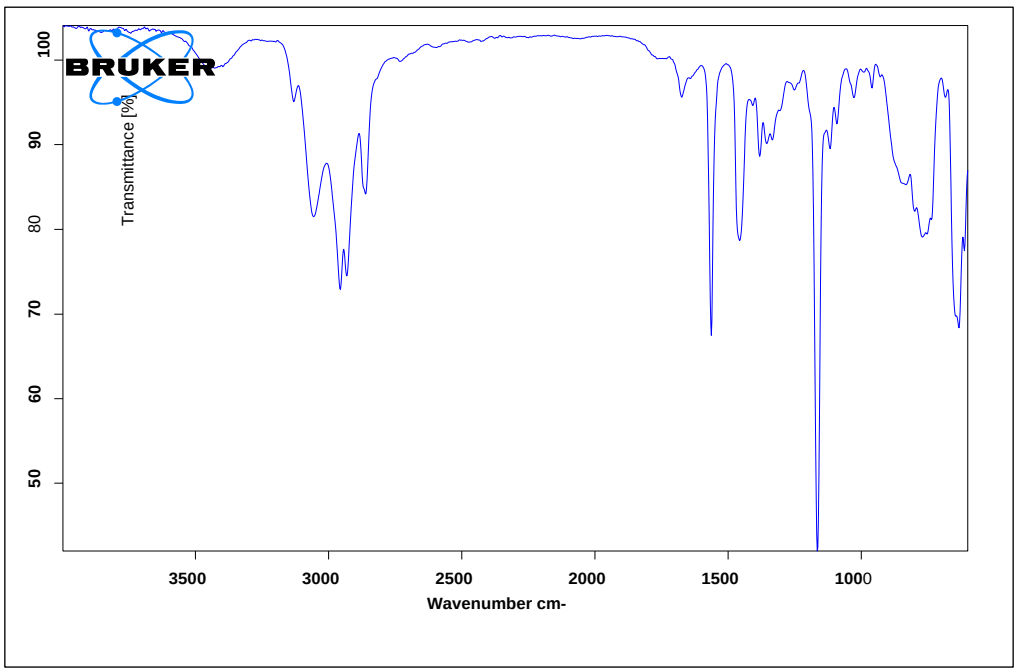


Figure 3.14: IR Spectra of 1-Ethyl-3-Pentylimidazolium Bromide

3.5.3 Characterization of 1-Ethyl-3-Benzylimidazolium Bromide [BzEImBr]

^{1}H-NMR (400 MHz, $CDCl_3$) spectra exhibited the peaks at δ: 1.37-1.40 (t, 3H), 4.25-4.31 (m, 2H), 5.51 (s, 2H), 7.25-7.97 (m, 7H), 10.4 (s, 1H) [**Figure 3.15**]

^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.5 (CH_3), 45.3 (N-CH_2), 53.1 (N^+-CH_2) 122.0,122.1 (CH of imidazole ring) 129.0,129.3 (CH of benzyl ring) 133.2 (C of benzyl ring) 136.4 (N-CH-N^+) [**Figure 3.16**]

MS (ES^+) m/z peaks was found at 187.1098 [**Figure 3.17**]

FTIR (V_{max} 525-4000 cm^{-1}) 3054 (w), 2969, 2978 (s), 2823(s) 1475-1600(s), 1200-1350(m), 1400-1500(m), 1000-1250(s), 690 – 715(s) [**Figure 3.18**]

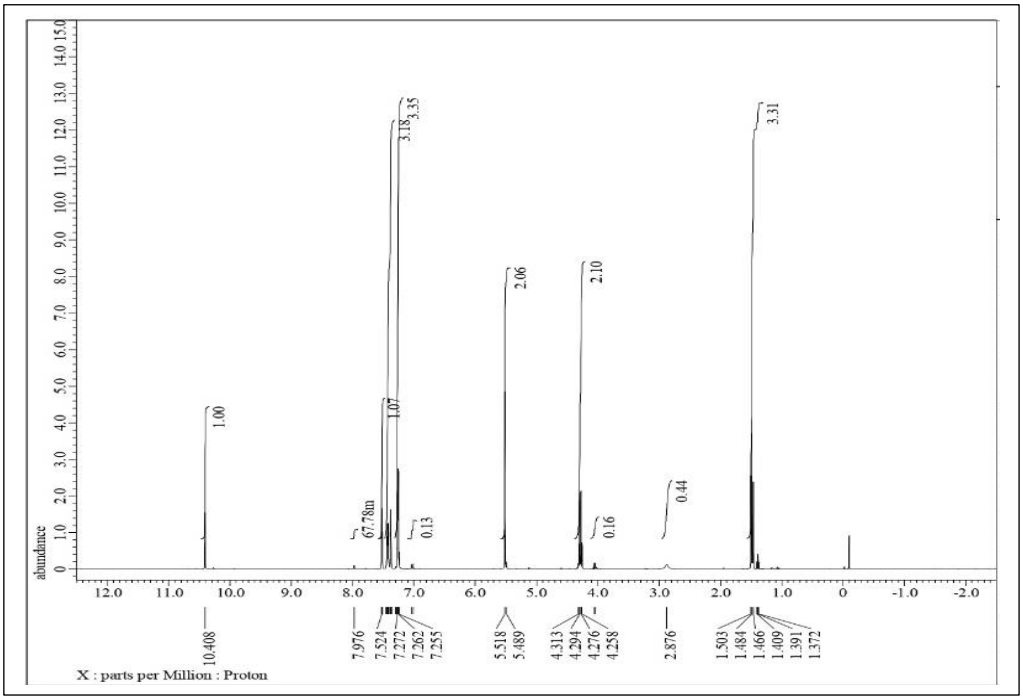


Figure 3.15: ^{1}H-NMR Spectra of 1-Ethyl-3-Benzylimidazolium Bromide

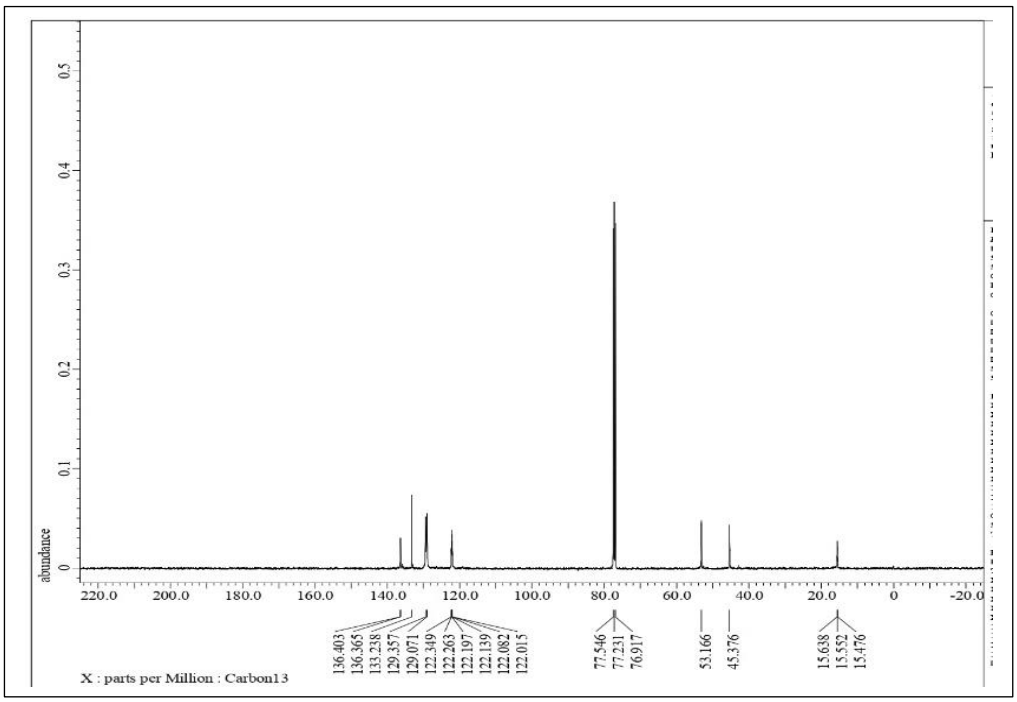


Figure 3.16: ^{13}C-NMR Spectra of 1-Ethyl-3-Benzylimidazolium Bromide

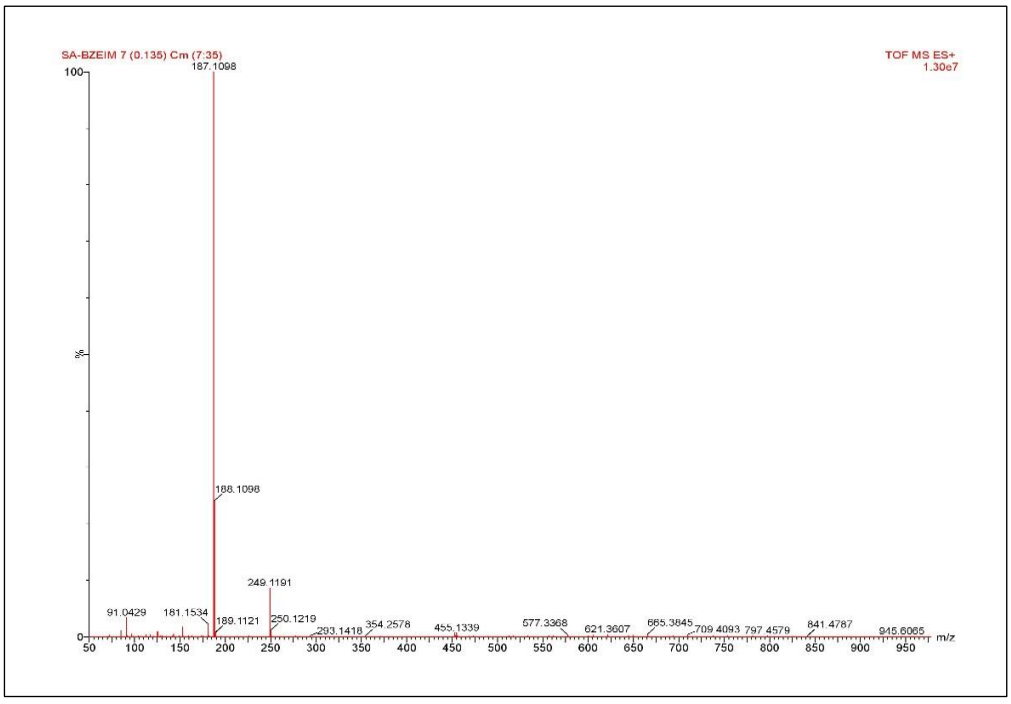


Figure 3.17: Mass Spectra of 1-Ethyl-3-Benzylimidazolium Bromide

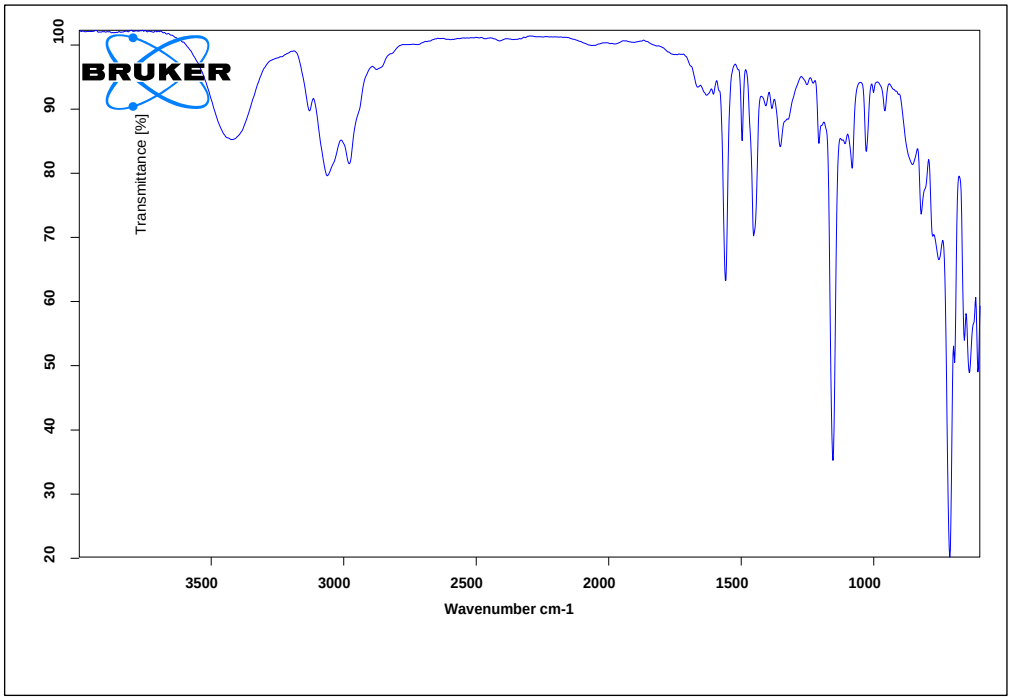


Figure 3.18: IR Spectra of 1-Ethyl-3-Benzylimidazolium Bromide

3.5.4 Characterization of 1-Ethyl-3-Benzylimidazolium Chloride [BzEImCl]

^{1}H-NMR (400 MHz, $CDCl_3$) spectra exhibited the peaks at δ: 1.17-1.21 (t, 3H), 3.98-4.06 (m, 2H), 5.2 (s, 2H), 6.96-7.38 (m, 7H), 10.2 (s, 1H) [**Figure 3.19**]

^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.3 (CH_3), 44.8 (N-CH_2), 52.7 (N^+-CH_2) 121,122 (CH of imidazole ring) 128,129 (CH of benzyl ring) 133.4 (C of benzyl ring) 136.3 (N-CH-N^+) [**Figure 3.20**]

MS (ES^+) m/z peaks was found at 187.1307 [**Figure 3.21**].

FTIR (V_{max} 525-4000 cm^{-1}) 3063(w), 2969, 2978(s), 2823(s), 1475-1600(s), 1200-1350(m), 1400-1500(m), 1000-1250(s), 690 – 715(s) [**Figure 3.22**].

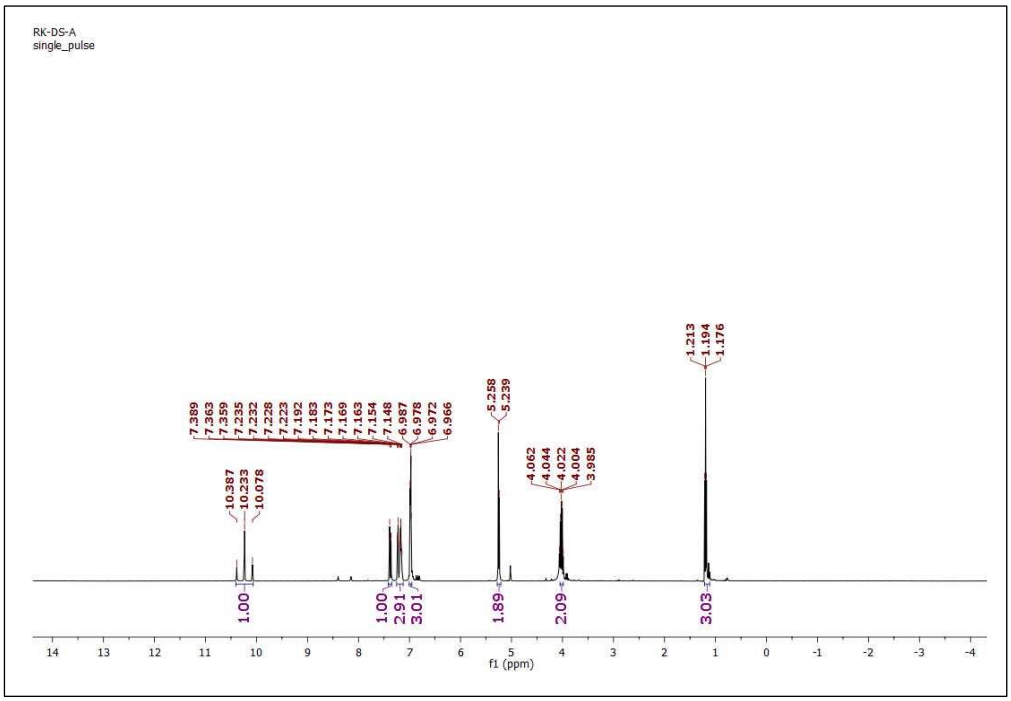


Figure 3.19: ^{1}H-NMR Spectra of 1-Ethyl-3-Benzylimidazolium Chloride

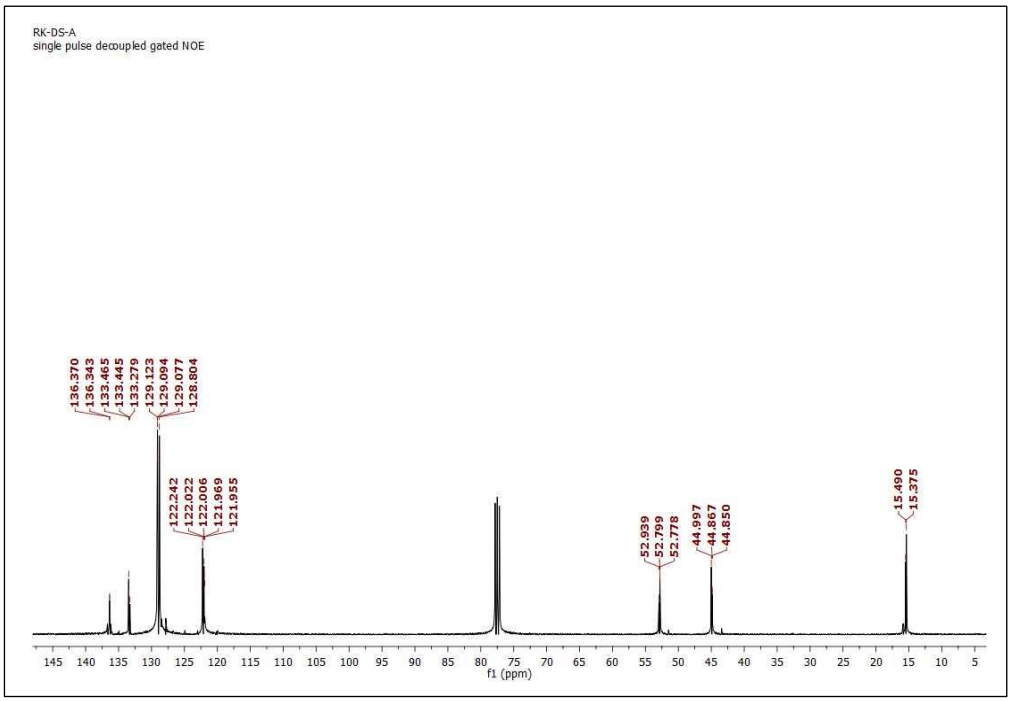


Figure 3.20: ^{13}C-NMR Spectra of 1-Ethyl-3-Benzylimidazolium Chloride

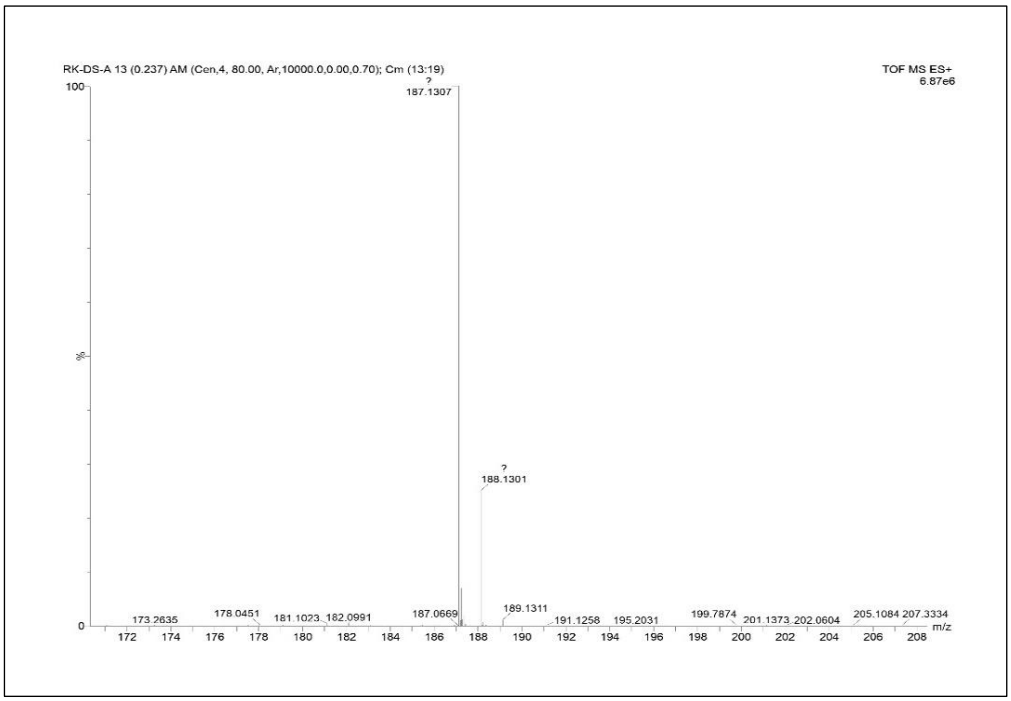


Figure 3.21: Mass Spectra of 1-Ethyl-3-Benzylimidazolium Chloride

Figure 3.22: IR Spectra of 1-Ethyl-3-Benzylimidazolium Chloride

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Chapter – 4

IMIDAZOLIUM-BASED IONIC LIQUIDS OF DIFFERENT CATION AS GREEN CORROSION INHIBITOR

Abstract:

Ionic liquids are widely used in various fields of industries due to their low volatility, non-toxic, high adsorption ability, eco-friendly and least expensive nature. In the past decades the use of ionic liquids as corrosion inhibitor is the topic of interest of research in the field of material science. Various chemical variants of ionic liquids are available among of these Imidazole based ionic liquids reported as excellent corrosion inhibitor on mild steel material. In this chapter the effect of side alkyl chain length was investigated on inhibition efficiency & corrosion rate of two imidazolium based ionic liquids having different cations namely: 1-Ethyl-3-Butylimidazolium Bromide [BuEImBr] and 1-Ethyl-3-Pentylimidazolium Bromide [PEImBr]. The various advanced techniques such as gravimetric measurement, potentiodynamic polarization measurement, electrochemical impedance spectroscopy, scanning electron microscopy were used for inhibition efficiency measurement. The obtained results from the all described techniques were in consonance to each other.

4.1 Gravimetric measurements

It is quantitative methods to monitoring corrosion in metallic materials. Gravimetric method is classical and simplest method which is based on the weight loss value. Various corrosion parameter and factors affecting that such as effect of concentration of ILs, effect of immersion periods and effect of temperature have been evaluated by this technique [1]. The calculation of weight loss of mild steel evaluated by the difference of weight before and after the immersion of mild steel coupon in corrosive solution. The obtained data inputted in the known formula to calculate the corrosion rate and inhibition efficiency according to the set standard by national association of corrosion engineer's standard [2]. There are several attractive features that account for its sustainable popularity [3].

- It is applicable to all environment gases, liquids, solids.
- Visual inspection of corrosion can be possible in this technique.
- Corrosion product can be observed and analysed in this technique.
- Corrosion rate and inhibitor performance can be easily determined by this technique.
- Localised corrosion can be easily identified by this technique.
- No sophisticated instrument is required to obtain a result.

4.1.1 Experimental process for gravimetric measurements

The gravimetric measurements of mild steel were carried out with the help of 3.6 x 2.3 x 0.3 (Length x Width x Thickness) rectangular shape mild steel coupons with a spherical hole uniform diameter, glass hooks, beaker and experimental solutions of different concentrations. Firstly, coupons were abraded by different grades of emery papers (80, 220, 320, 400, 600, 800 and 1000), cleaned with double distilled water, degreased by acetone and dried in desiccator to provide an excellent surface for evaluation. After weighing, coupons were hanged with the help glass hooks into a beaker containing 100 ml of test solution with different concentration of ILs. As illustrated in **Figure 4.1**. After 3-hour exposure coupons were remove from the test solutions and washed by double distilled water and degreased by acetone to remove corrosion products, dried in desiccator and reweight. The difference between weight before corrosion and after exposure was calculated and easily converted in the form of corrosion rate and inhibition efficiency. All measurements carried out four different temperatures (303 K, 313 K, 323 K, 333 K) **Figure 4.2**.

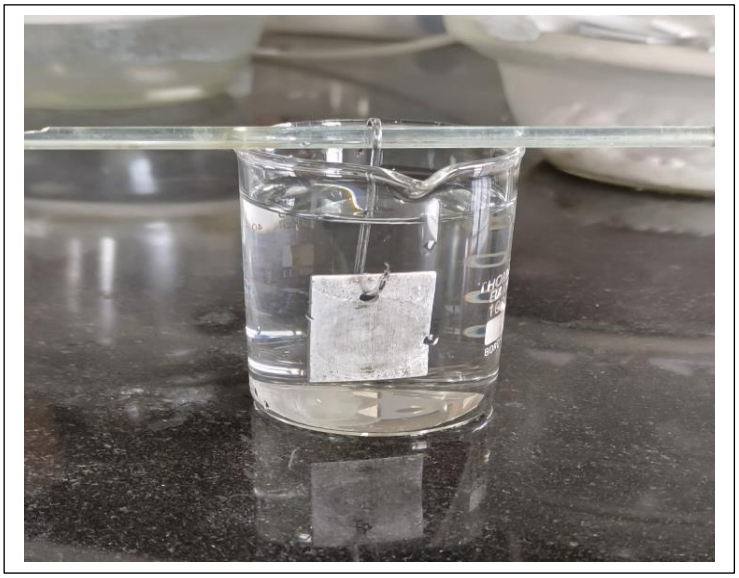


Figure 4.1: Experimental setup of gravimetric analysis of corrosion parameters

Figure 4.2: Gravimetric measurements (weight loss) in laboratory at different temperature (303 K, 313 K, 323 K, 333 K)

4.1.2 Determination of Gravimetric parameters

There are three main parameters weight loss, corrosion rate and inhibition efficiency which were calculated with the help of gravimetric measurement [4].

4.1.2.1 Weight loss (WL)

The weight loss value is the major parameter of this technique which affect the corrosion rate and inhibition efficiency. It can be determined by the following equation 4.1.

$$\Delta W = W_1 - W_2 \qquad (4.1)$$

W_1 is weight of coupon before immersion, W_2 is weight of coupon after immersion

4.1.2.2 Corrosion rate (C_R)

The corrosion rate in mmpy was determine with the help of weight loss value by well-known engineering formula 4.2 [5].

$$C_R = [\frac{87.6\ X\ \Delta W}{AtD}] \qquad (4.2)$$

C_R = corrosion rate in mmpy, ΔW= weight loss of material in gram, A = exposure surface area of coupon in cm^2, t = exposure time in hour, D = density of mild steel coupon (7.86 g cm^{-3})

4.1.2.3 Inhibition efficiency (IE)

The corrosion inhibition performance of ILs represent by percentage inhibition efficiency (% IE) which calculated by the help of weight loss value obtained in the absence and present of different concentrations of ILs. Equation (4.3) helps to determine % IE [6].

$$\%IE = [\frac{[(W0 - Wi)}{W0}]X100 \qquad (4.3)$$

W_0 = weight losses without inhibitor, W_i = weight losses with inhibitor

Surface coverage can also determine by % inhibition efficiency by following equation (4.4)

$$\theta = \%\ IE / 100 \qquad 4.4)$$

Θ = surface coverage

4.1.3 Evaluation of gravimetric parameters

The various parameters such as corrosion rate (C_R), inhibition efficiency (%IE) thermodynamic and kinetic parameters, energy of adsorption (ΔG^0_{ads}), Activation energy (E_a), Enthalpy of adsorption (ΔH_a) and entropy of adsorption (ΔS_a) were determined with the help weight loss experiments at different temperatures and different concentration for both ionic liquids [BuEImBr] and [PEImBr]. The summarized data of weight loss measurements are illustrated in the tables from 4.1 to 4.8.

Table 4.1: Effect of different concentration of [BuEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 303 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	3.7867	3.4447	0.342	158.62	---	---
200	4.341	4.1252	0.2158	102.65	0.36900	36.90
400	4.1119	3.9271	0.1848	85.49	0.45964	45.96
600	4.3324	4.197	0.1354	63.11	0.60409	60.40
800	4.1726	4.0891	0.0835	38.72	0.75584	75.58
1000	4.1779	4.1393	0.0386	18.22	0.88713	88.71

Table 4.2: Effect of different concentration of [BuEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 313 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.3648	3.7175	0.6473	300.22	---	---
200	4.3123	3.8776	0.4347	201.61	0.32844	32.84
400	4.3323	3.9507	0.3816	177.87	0.41047	41.04
600	4.3524	4.0495	0.3029	142.98	0.53205	53.20
800	4.0447	3.8185	0.2262	104.91	0.65054	65.05
1000	4.3378	4.215	0.1228	57.38	0.81028	81.02

Table 4.3: Effect of different concentration of [BuEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 323 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.0316	2.9728	1.0588	491.08	---	---
200	3.9561	3.2056	0.7505	352.48	0.29117	29.11
400	4.126	3.4437	0.6823	315.66	0.35559	35.55
600	4.3215	3.7273	0.5942	275.59	0.43879	43.87
800	3.9989	3.5192	0.4797	219.74	0.54694	54.69
1000	4.2569	3.9306	0.3263	153.25	0.69182	69.18

Table 4.4: Effect of different concentration of [BuEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 333 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.3256	2.7018	1.6238	753.13	---	---
200	3.9865	2.7754	1.2111	561.71	0.25415	25.41
400	4.0258	2.8898	1.136	533.53	0.30004	30.04
600	3.9658	2.9825	0.9833	456.06	0.39444	39.44
800	4.1236	3.2346	0.889	408.25	0.45251	45.25
1000	4.2158	3.6092	0.6066	283.46	0.62643	62.64

Table 4.5: Effect of different concentration of [PEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 303 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.3093	3.9686	0.3407	160.01	---	---
200	4.2349	4.0297	0.2052	95.17	0.3977	39.77
400	4.3098	4.1449	0.1649	76.48	0.5159	51.59
600	4.2274	4.1155	0.1119	52.16	0.6715	67.15
800	4.3323	4.2791	0.0532	24.98	0.8438	84.38
1000	4.2262	4.2007	0.0255	11.82	0.9251	92.51

Table 4.6: Effect of different concentration of [PEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 313 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.2338	3.5896	0.6442	301.038	---	---
200	4.179	3.7476	0.4314	203.642	0.3303	33.03
400	4.2112	3.8494	0.3618	167.806	0.4383	43.83
600	4.1282	3.8439	0.2843	131.861	0.5586	55.86
800	4.4912	4.2829	0.2083	97.831	0.6766	67.66
1000	4.0454	3.9595	0.0859	39.841	0.8666	86.66

Table 4.7: Effect of different concentration of [PEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 323 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.3556	3.2898	1.0658	494.32	---	---
200	4.1847	3.443	0.7417	344.00	0.3040	30.40
400	4.2764	3.6265	0.6499	301.42	0.3902	39.02
600	4.3212	3.7813	0.5399	253.57	0.4934	49.34
800	4.319	3.8741	0.4449	210.01	0.5825	58.25
1000	4.1623	3.8665	0.2958	137.19	0.7224	72.24

Table 4.8: Effect of different concentration of [PEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 333 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	3.7087	2.1019	1.6068	750.865	---	---
200	3.9916	2.7992	1.1924	557.214	0.2579	25.79
400	3.9342	2.8382	1.096	508.334	0.3178	31.78
600	3.9641	3.0365	0.9276	430.229	0.4227	42.27
800	3.9777	3.2173	0.7604	358.946	0.5267	52.67
1000	4.0711	3.5013	0.5698	261.668	0.6453	64.53

4.1.4 Results and discussion of gravimetric study

(A) Effect of concentration

At a particular temperature considerable results were obtained with the change in concentration of inhibitor in weight loss study. The analysis of weight loss data clearly indicated that the effectiveness of all investigated corrosion inhibitors was increased as the concentration of inhibitors were increased. The reason behind the increments in inhibition efficiency and decrements in corrosion rate parameter is that the increasing concentration leads the greater adsorption of inhibitor on metal surface and also the greater surface coverage area of metal. The concentration at which, inhibitor show maximum adsorption and maximum surface coverage is known as optimum concentration of inhibitor [4]. For such of investigated inhibitors optimum concentration was found 1000 ppm at all experimental temperatures. After that there were no significant changes obtained in the corrosion parameters. The % inhibition efficiency at optimum concentration was 88.71% % 92.51% for [BuEImBr] & [PEImBr] respectively at 303 K.

The summary of inhibition efficiency and corrosion rate are tabulated in Table 4.9 and 4.10 respectively. As the carbon chain length was increase the inhibition behaviour of inhibitor also increase [7]. It is also concluded that cation structure effect more significantly than the anion because the difference in inhibition efficiency at different concentration of ImILs of similar anion [8]. **Figure 4.3 and 4.4** reveals the increasing trend of inhibition efficiency with the increasing concentration for [BuEImBr] & [PEImBr] respectively at all experimental temperatures.

Table 4.9: Variation in the inhibition efficiency (%IE) at different temperature and different concentration of ImILs for mild steel in 0.5 M H_2SO_4 for 3-hour immersion time

Name of ionic liquids	Temp. / Conc.	303 K	313 K	323 K	333 K
[BuEImBr]	Blank	---	---	---	---
	200	36.90	32.84	29.11	25.41
	400	45.96	41.04	35.55	30.04
	600	60.40	53.20	43.87	39.44
	800	75.58	65.05	54.69	45.25
	1000	88.71	81.02	69.18	62.64
[PEImBr]	Blank	---	---	---	---
	200	39.77	33.03	30.40	25.79
	400	51.59	43.83	39.02	31.78
	600	67.15	55.86	49.34	42.27
	800	84.38	67.66	58.25	52.67
	1000	92.51	86.66	72.24	64.53

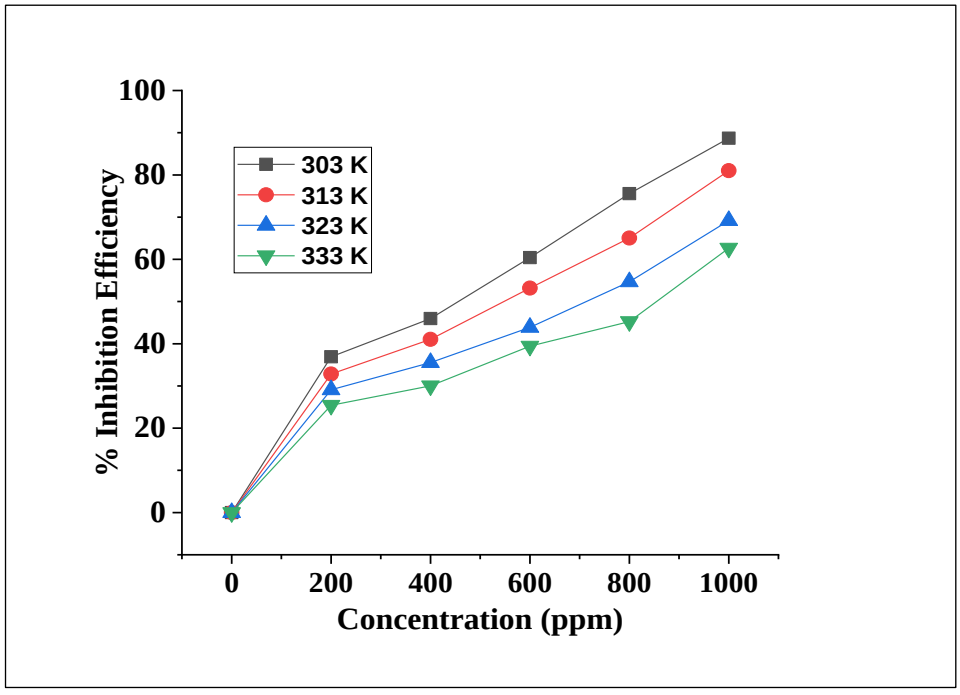


Figure 4.3: Variation of % IE with concentration of [BuEImBr] at different temperature

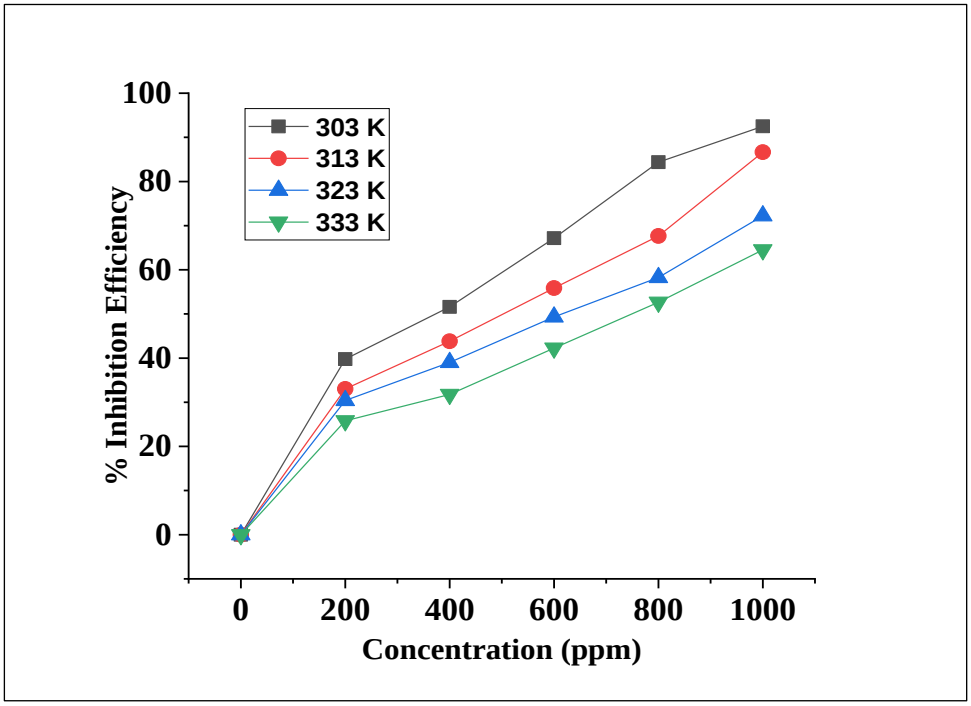


Figure 4.4: Variation of % IE with concentration of [PEImBr] at different temperature

(B) Effect of temperature

Temperature plays an important role in adsorption phenomenon. Corrosion rate was increases as temperature rises because the desorption process proceeds simultaneously with adsorption of inhibitor on mild steel or we can say that there will be an equilibrium exists between adsorption and desorption process which is shifted towards desorption on increasing the temperature. Desorption of inhibitor molecules causes the decrement in surface coverage on mild steel which is indicating enhancement in corrosion rate and decrement in inhibition efficiency of inhibitor [9-10]. In additionally increment in corrosion rate at high temperature was due to increase the mobility of ions in corrosive solution which provide the chance of aggressive ions on attacking the oxide film of metal surface [11-12]. The summarised data of corrosion rate for both studied corrosion inhibitors are tabulated in Table 4.10 at 303 K, 313 K, 323 K, and 333 K in presence and absence of inhibitors. **Figure: 4.5 and 4.6** indicated the decreasing trends of corrosion rate with increasing concentration for both inhibitors [BuEImBr] and [PEImBr] respectively at all experimental temperatures.

Table 4.10: Variation in the corrosion rate (C_R) at different temperature and different concentration of ImILs for mild steel in 0.5 M H_2SO_4 for 3-hour immersion time

Name of ionic liquids	Temp. / Conc.	303 K	313 K	323 K	333 K
[BuEImBr]	**Blank**	158.62	300.22	491.08	753.13
	200	102.65	201.61	352.48	561.71
	400	85.49	177.87	315.66	533.53
	600	63.11	142.98	275.59	456.06
	800	38.72	104.91	219.74	408.25
	1000	18.22	57.38	153.25	283.46
[PEImBr]	**Blank**	160.01	301.03	494.32	750.86
	200	95.17	203.64	344.00	557.21
	400	76.48	167.80	301.42	508.33
	600	52.16	131.86	253.57	430.22
	800	24.98	97.83	210.01	358.94
	1000	11.82	39.84	137.19	261.66

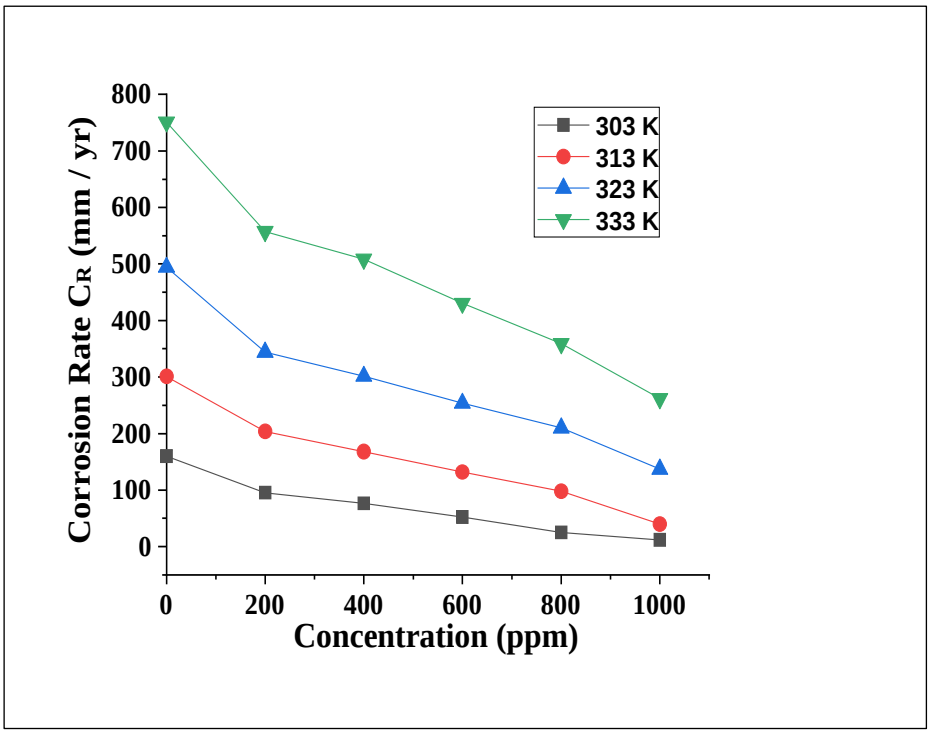


Figure 4.5: Variation of corrosion rate (C_R) with concentration of [BuEImBr] at different temperature

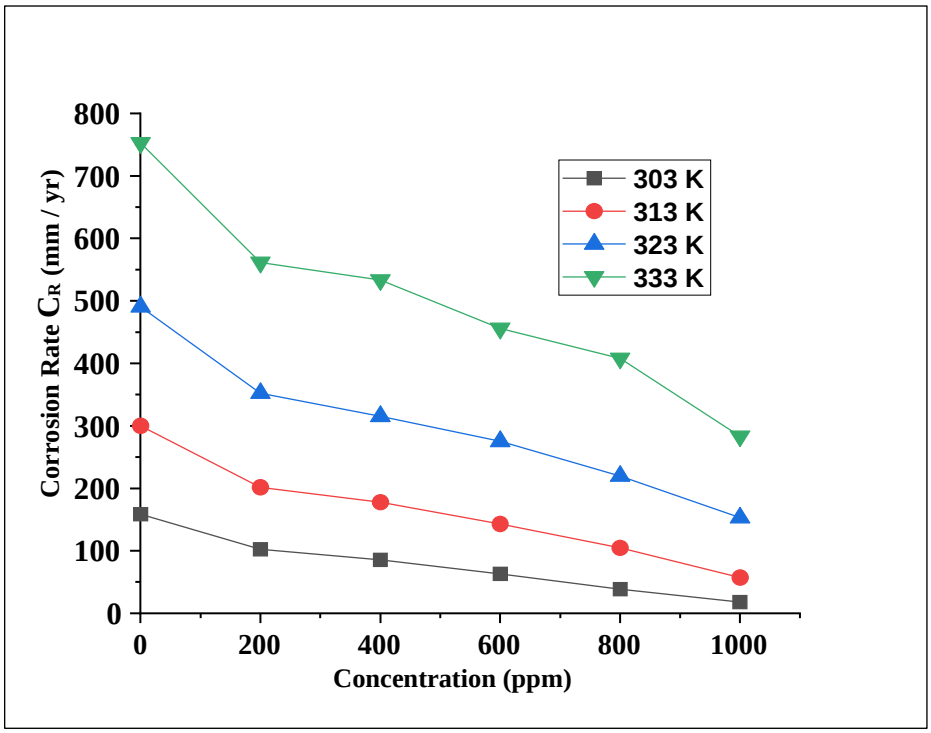


Figure: 4.6 Variation of corrosion rate (C_R) with concentration of [PEImBr] at different temperature

(C) Effect of immersion time

At a particular temperature, immersion time affect the all calculating parameters of corrosion testing. To determining effects of immersion time of mild steel in different inhibitor solutions of 0.5 M H_2SO_4 at 303 K, mild steel coupons were immersed for 12h, 24h, 36h and 48h time in blank solution of 0.5 M H_2SO_4 and 1000 ppm concentration solution of experimental inhibitors (BuEImBr & PEImBr).

The finding results illustrated in Table 4.11, reveals that in absence of inhibitor the weight loss due to the corrosion was increased with immersion time period. While in presence of inhibitor with maximum concentration of 1000 ppm the inhibition efficiency order was followed the constant nature up to the 24h after that inhibition efficiency was partially decreased.

Table 4.11: Effect of immersion time on the corrosion inhibition of the mild steel in 0.5 M H_2SO_4 in absence & presence of optimum concentration of ImILs at 303 K

Immersion time	Weight-loss in absence of inhibitor	% IE in presence of [BuEImBr]	% IE in presence of [PEImBr]
12 h	0.4292	88.69	92.57
24 h	0.5778	89.16	92.78
36 h	0.8582	73.53	77.02
48 h	1.1453	67.49	73.80

4.2 Potentiodynamic polarization (PDP) technique

Polarization is an advance technique of corrosion testing. It provides a rapid, reasonable, and quantitative prediction of electrochemical corrosion. This technique specially used to assess localized corrosion such as pitting and stress corrosion [13]. It was performed by the help of Potentiostat-Galvanostat instrument. Potentiostat used to control potential (or voltage) difference across the two electrodes and measures the resulting current. It helps in the grading of material-environment combination.

4.2.1 Basic principle & experimental setup of PDP technique

The Potentiostat instrument consist three electrode system in which corroded metal coupon used as a working electrode, silver/silver chloride in 3M KCl as reference electrode and graphite electrode as counter electrode [14]. Potentiostat control the voltage between the working electrode and reference electrode by supplying current through counter electrode [15].

Polarization study used to simply determine the corrosion behaviour of any metal or alloys in electrolytic solution. It involves to applied the potential on working electrode (metal or alloys) at a constant scan rate and measuring the resulting current.

Polarization experiments are majorly conducted into following manner [16-17].

Potentiostatic polarization – In this type of experiments the applied potential is constant on working electrode for a specific time period and current is measured which is plotted with time (t).

Potentiodynamic polarization – In this type of experiments applied potential is increased with time t and current is monitor continuously which is plotted with applied potential.

The polarization curves are required to produce for electrochemical study of mild steel in corrosive solution. These curves have diverse physical significance. The effect of critical parameters such that scan rate, solution resistivity, dissolution gas, pH, immersion period, point of scan reversal, aggressive ions, temperature, roughness of surface etc can be discussed by the help of PDP method [18]. In the phenomenon of electrochemical corrosion there is a net flow of electrons or current in corrosion reaction. Once the flow of electrons is balanced for each of reaction there are no net flow of electrons and these two reactions reach equilibrium. The process of deviation from equilibrium induced by electrode reaction due to flow of electrical current through the electrochemical cell causing a change in the potential in working electrode referred as polarization. This deviation in equilibrium is the reason of electrical potential difference between the polarised and unpolarised electrode potential. This electrical potential difference is known as overpotential [19].

In order to understood the behaviour of polarized mild steel electrode in electrolytic solution in presence and absence of inhibitor taffel diagram is plotted with the help of Potentiostat. **Figure 4.7** shows the taffel diagram with the kinetic parameters [20].

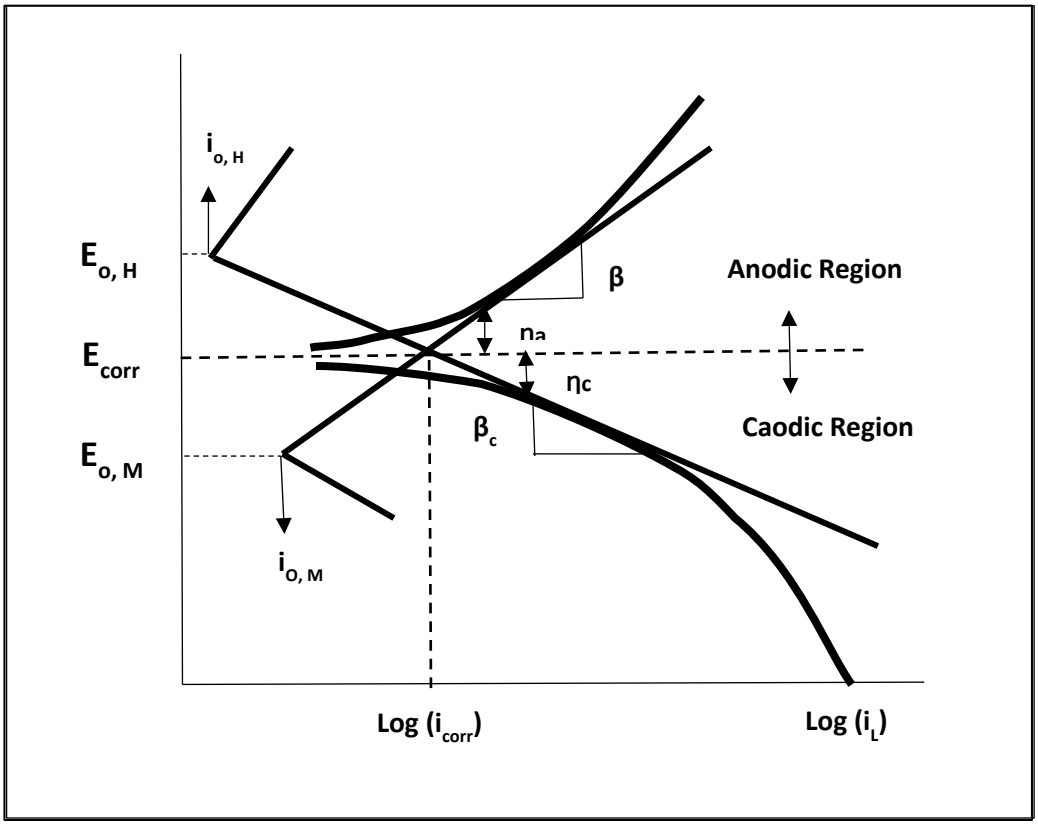


Figure 4.7: Taffel diagram with kinetic parameters

$E_{O,M}$ - Open circuit potential of mild steel, $E_{O,H}$ - Open circuit potential of hydrogen, $i_{O,M}$ - exchange current density of mild steel, $i_{O,H}$ - exchange current density of hydrogen, Ηa anodic over potential, Ηc cathodic overpotential, 'βa' taffel anodic slope, 'βc' taffel cathodic slope. There are two ways to determine the corrosion current from the polarization parameters [21-22].

1. Taffel extrapolation method – This method is based on activation controlled electrochemical reactions. In this method the linear portion of either cathodic or anodic taffel curves are extrapolated and the intersection point is noted as $i_{corr.}$ For better accuracy the linear region must be minimum an order of magnitude of current.
2. Linear polarization method – Stern and Geary described that the LPR method exploit the linearity of the corrosion potential which is appears in 5 to 10 mV. In this method the Icorr determine by the following equation (4.5)

$$i_{corr} = [\frac{\beta a \; X \; \beta c}{2.3(\beta a + \beta c)}] X [\frac{1}{Rp}] \qquad (4.5)$$

where i_{corr} is current density, βa and βc are anodic and cathodic slope, Rp is polarization resistance.

In anodic polarization the metal surface is positively charged and the anodic overpotential is greater than zero i.e., En^0 is positive to E_{op}. while in case of cathodic polarization the electrons supply to the metal at negative overpotential i.e., Ep^0 is negative to E_{op} [23]. There are four major parts illustrated in **Figure 4.8** for anodic polarization curve [24-25].

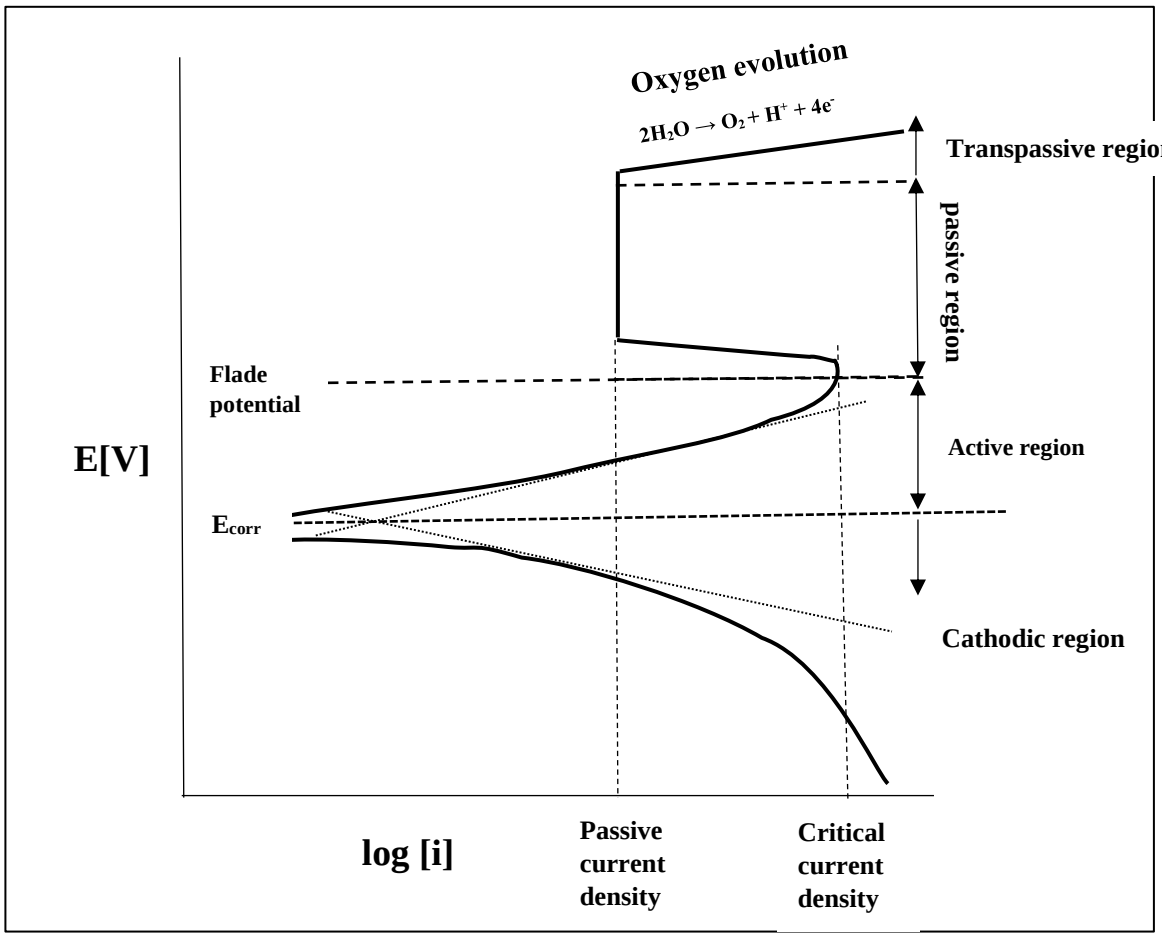


Figure 4.8: Schematic representation of anodic polarization curve

a. Cathodic region is the region of negative potential
b. Active region with positive potential where metal corrodes at higher rate
    - **Flade potential** the specific positive potential at which the current density is rapidly decrease is known as Flade potential (Epp) and the current density at Flade potential is referred as critical current density for passivation (Icc). The reason behind the decrement in current density is the deposition of passive film on mild steel surface. This region known as active/passive transition region [26].

c. Passive region where the corrosion rate is decrease due to alteration in the chemical reactivity on metal surface.
    - **Passivation** the phenomenon in which the metal surface convert into the inert one by the formation of oxide passive film on metal surface known as passivation [27].
d. Transpassive region, at high electrode potential current density rises rapidly due to rapid dissolution of metal or evolution of oxygen by the breakdown of water molecules in electrolytic solution rather than metallic corrosion [28].

To perform all the PDP experiments working electrode (mild steel coupon) was polished and degreased by different grades emery papers and acetone. The dry mild steel coupon was kept in a static test solution of 0.5 M H_2SO_4 for 30 minutes at an ambient temperature. After the establishment of constant or stable open circuit potential polarization parameters were measured in presence and absence of inhibitor at a constant scan rate 0.01 $Vsec^{-1}$.

4.2.2 Open Circuit Potential (OCP)

Open circuit potential (OCP) used to determine corrosion potential at which corrosion will being to start. In this mode only resting potential is measured between the working electrode (mild steel surface) and electrolytic solution with respect to reference electrode. OCP is only one of the techniques to informed that electrochemical system is thermodynamically stable enough to perform the experiment. It is used to allow the stabilization of system for short time period before applying another electrochemical technique [29]. The variation in the OCP with the time gives the important valuable information about the inhibition process [30]. OCP described the domination of electrochemical inhibition reaction in presence of inhibitor. The movement of OCP towards the more negative side in presence of inhibitor compare to the blank solution indicate the domination of cathodic inhibition reaction while the more positive movement revealed the domination of anodic inhibition reaction [31-33].

The evolution of OCP with time frame for [BuEImBr] and [PEImBr] was shown in **Figure 4.9 and 4.10** respectively.

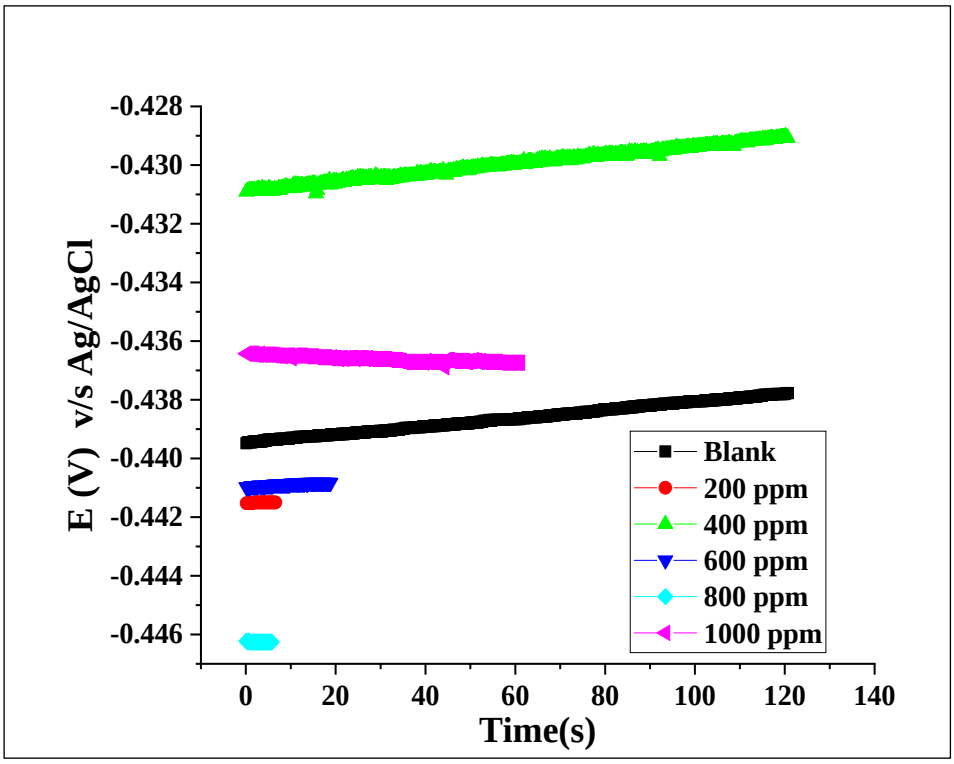


Figure 4.9: Variation of E_{ocp} of mild steel in absence and presence of different concentration of [BuEImBr]

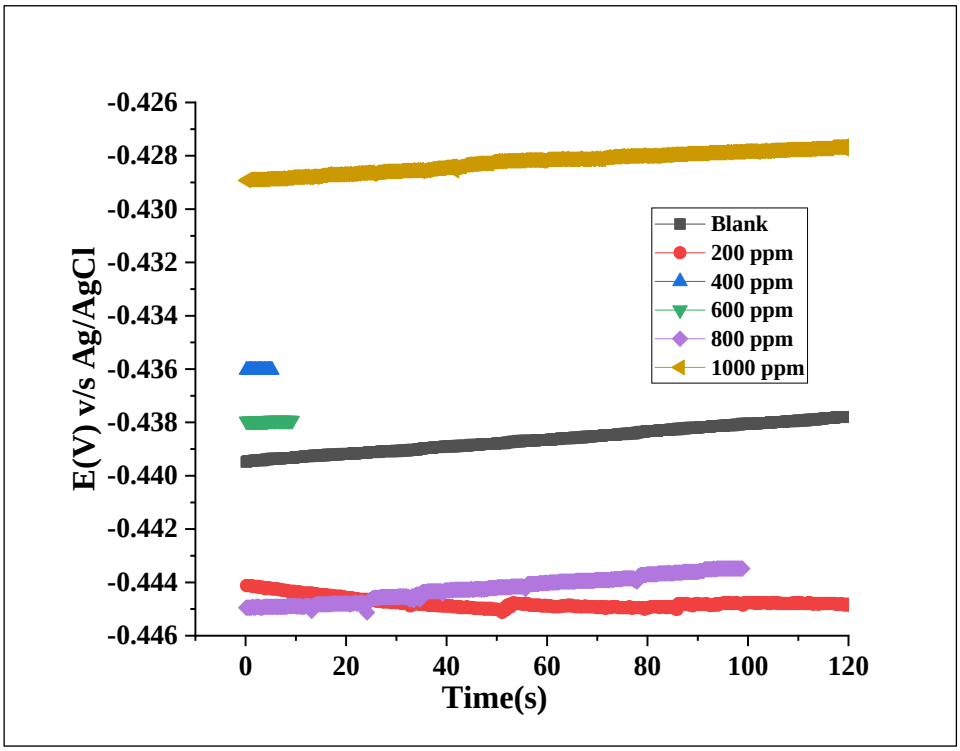


Figure 4.10: Variation of E_{ocp} of mild steel in absence and presence of different concentration of [PEImBr]

The obtained data of OCP in absence of inhibitor is (-0.440V) and for different concentration the obtained OCP values indicated that both corrosion inhibitor acted as mixed type of inhibitor because OCP of different concentration are higher and lower with respect to blank concentration.

4.2.3 Polarization Resistance (PR)

Polarization technique is based on an electrochemical theory. According to this there is approximately linear relation between the applied potential and logarithm of measured current density if the weak polarization is done near the E_{corr} within a small region. In this technique polarization resistance is determine on metal surface in corrosive medium in presence and absence of inhibitor by equation (4.6) [34]. It is very helpful technique for selection of material in various industries and infrastructure like aerospace, automotive, oil and gas where corrosion resistance is major concern [35].

$$R_P = (\Delta E/\Delta i)_{\Delta E \to 0} \quad (4.6)$$

R_P = Polarization resistance

i_{corr} is determine with the help of polarization resistance according to Stern-Geary equation (4.7)

$$i_{corr} = \left[\frac{B}{Rp}\right] \quad (4.7)$$

Where B = $\left[\frac{\beta a \ X \ \beta c}{2.3(ba+bc)}\right]$

Following equation (4.8) and (4.9) are used to calculate inhibition efficiency of inhibitor with the help of current density and polarization resistance respectively [36].

$$\%IE = \frac{i_{corr_{unInhibited}} - i_{corr_{Inhibited}}}{i_{corr_{UnInhibited}}} \ X \ 100 \quad (4.8)$$

$$\%IE = \frac{R_{P_{unInhibited}} - R_{P_{Inhibited}}}{R_{P_{UnInhibited}}} \ X \ 100 \quad (4.9)$$

4.2.4 Evaluation and interpretation of PDP parameters

The polarization curves for mild steel in 0.5 M H_2SO_4 corrosive solution in absence and presence of inhibitor with different concentration were generated in potential range of -800 mV to -200 mV at 0.01 $Vsec^{-1}$ scan rate **Figure 4.11 and 4.12** All polarization parameters such that corrosion potential (E_{corr}), Corrosion current density (i_{corr}),

Polarization resistance (R_p), anodic taffel slope (β_a) and Cathodic taffel slope (β_c) were obtained by extrapolation of the linear region of polarization curves. Nova (1.10) software version was used to generate polarization curves. The summarized data of PDP study are tabulated in the Table 4.12.

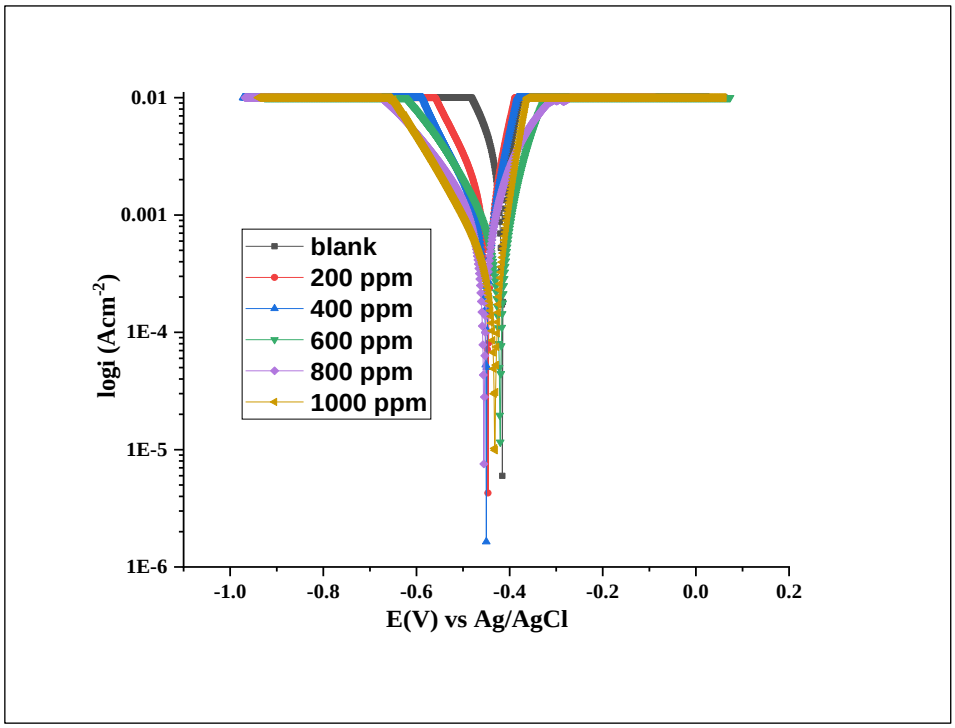


Figure 4.11: Polarization curves for mild steel in absence and presence of different concentration of [BuEImBr]

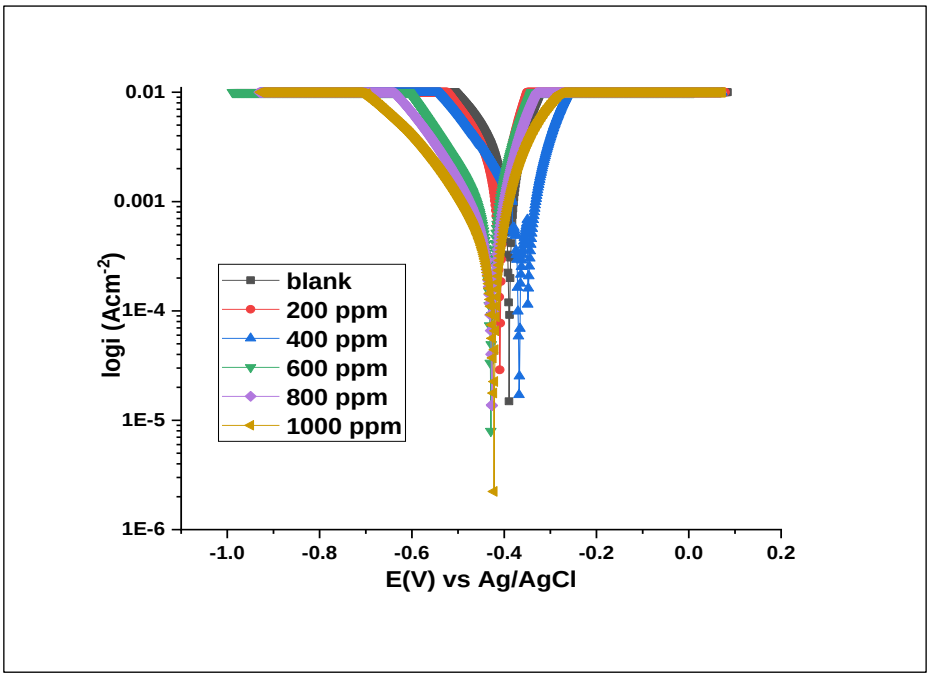


Figure 4.12: Polarization curves for mild steel in absence and presence of different concentration of [PEImBr]

Table 4.12: Polarization parameters for mild steel in 0.5 M H_2SO_4 solution in absence and presence of varying concentration of [BuEImBr] & [PEImBr]

Name of ImILs	Conc. (ppm)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	$E_{corr.}$ (mV)	$i_{corr.}$ ($\mu A/cm^2$)	R_p (Ω)	C_R (mmpy)	%IE
[BuEImBr]	**Blank**	182.26	66.28	-413.84	822.63	25.66	9.55	---
	200	254.58	65.17	-424.47	716.87	31.43	8.33	12.85
	400	224.47	60.35	-428.24	638.64	32.34	7.42	22.36
	600	142.46	37.18	-384.87	426.39	30.03	4.95	48.16
	800	163.57	54.94	-431.91	243.99	73.2	2.83	70.34
	1000	222.21	54.28	-418.16	198.44	95.48	2.3	75.87
[PEImBr]	**Blank**	182.26	66.28	-413.84	822.63	25.66	9.55	---
	200	226.3	68.23	-444.6	338.4	59.85	4.42	58.86
	400	237.1	59.44	-439.45	285.52	72.29	3.31	65.29
	600	343.37	59.34	-418.57	276.91	79.36	3.21	66.33
	800	188.19	45.36	-425.56	128.56	123.48	1.49	84.37
	1000	42.33	105.15	-433.99	92.29	142.03	1.07	88.78

The literature of PDP study for investigated corrosion inhibitors revealed that the change in the value of E_{corr} less than 85 mV denoted as mixed type of inhibitor while inhibitor is referred as cathodic or anodic inhibitor if the change in E_{corr} value is greater than 85 mV. The change in the value of anodic and cathodic taffel slope with increasing concentration of inhibitors also favour this statement [37-38]. In case of [PEImBr] inhibitor the maximum changes in E_{corr} values are 30.76 mV so that it acted as mixed type of inhibitor by deteriorating both metal dissolution and hydrogen evolution reactions but on increasing the concentration of this inhibitor only more negative shifts are obtained in the E_{corr} value suggested it as predominant cathodic inhibitor. A more positive and more negative shift in the E_{corr} value for (BuEImBr) indicate mixed type of inhibition with the maximum change in the E_{corr} value 28.97 mV. The values of corrosion current density i_{corr} and polarization resistance R_p are regularly decrease and increase respectively with the increasing concentration of inhibitors due to the effectively adsorption of inhibitor molecules and blocking the exposed active sites of mild steel surface. The maximum inhibition efficiency obtained for [BuEImBr] and [PEImBr] ILs were 75.87 % & 88.78 % respectively which were show good agreement with the results obtained by the gravimetric experiments.

4.3 Electrochemical impedance spectroscopy (EIS)

In PDP method direct current (DC) is used to perturbed the equilibrium while in EIS study a low amplitude sinusoidal signal (5-10 mV) as a function of frequency (Typically 100 KHz to 10 mHz rang) used to perturbed electrochemical system from equilibrium. Over 20 years AC impedance measurement used to investigate the electrical properties of conductive material and their surface. External electrical impulse work as driving force in EIS study [39-40]. The advantages of EIS study are discussed as follows [41].

- EIS uses a small excitation amplitude to perturbed the electrochemical system in compare to the polarization curves to minimize the destruction in corrosion potential.
- It provides a real time measurement of corrosion rate in situ over long time immersion.
- EIS study allows to determine the much lower corrosion rate that cannot be measurable by conventional weight loss method.

- EIS technique has the ability to study the coating and lining, high impedance system and corrosion study in low conductive solutions.

For interpretation and analyse, first collect the data of EIS study and after it fitted to a mathematical model known as equivalent circuit (EEC) consisting of resistors (R), capacitors (C) or constant phase elements (CPE), inductors (L) and Warburg impedance (W) connected either in series or in parallel manner [39].

4.3.1 Basic principle of EIS technique

A small amplitude of AC voltage applied on the working electrode as a function of frequency by using potentiostate consist of three electrode system electrochemical cell. The current response is a sinusoidal signal of the same frequency but with a different phase and amplitude with respect to perturbation [42].

The basic measuring parameter of EIS study is impedance (Z) that is equal to the polarization resistance of PDP technique. Impedance is reflecting the resistance to flow the electrons in AC circuit due to the presence of Resistor, capacitor and inductors.

To understood the theory of EIS study two periodic wave are consider, one is signal wave of potential (E) and another is related to the signal wave of current (I). Both wave oscillating with same frequency and intensity but there is a constant time shift at certain angle, this is called phase angle shift (ϕ) that is vary from 0^0 to 90^0 [43]. The excitation signal of potential as function of time (t) is represented as

$$E_r = E_0 \, \mathrm{Sin} \, (\omega t) \qquad (4.10)$$

E_0 = amplitude of potential

$\omega = (2\pi f)$ angular frequency

The function of response current

$$i_r = i_0 \, \mathrm{Sin} \, (\omega t + \phi) \qquad (4.11)$$

I_0 = amplitude of current

ϕ = shifted phase angle

According to ohm's formula impedance (Z) is calculated as complex ratio of applied potential sine wave and current response.

$$Z = E_r / i_r \qquad (4.12)$$

$$Z = \frac{E_0 \text{ Sin } (\omega t)}{i_0 \text{ Sin } (\omega t + \phi)} = Z_0 \frac{\text{Sin } (\omega t)}{\text{Sin } (\omega t + \phi)} \qquad (4.13)$$

Where $Z_0 = \frac{E_0}{I_0}$

The complex representation of impedance Z and phase angle tan ϕ is as-

$$Z = Z_0 \, e^{(i\Phi)} \qquad (4.14)$$

This equation can be simplified by using Euler's formula-

$$e^{(i\Phi)} = [\cos (\Phi) + i \sin (\Phi)] \qquad (4.15)$$

Now the equation-

$$Z (\omega) = Z_0 \cos (\phi) + Z_0 \, i \sin (\phi) \qquad (4.16)$$

Compare with (Z (ω) = Z' + iZ")

Real part (Z') = Z_0 cos (Φ)

Imaginary part (Z") = Z_0 i sin (Φ)

$$|Z| = \sqrt{(Z')^2 + (Z'')^2}$$

Phase angle

$$\tan (\Phi) = \text{Imaginary part (Z")} / \text{Real part (Z')} \qquad (4.17)$$

The complex representation of the impedance and it's phase angle as the vector is illustrated in **Figure 4.13** [39].

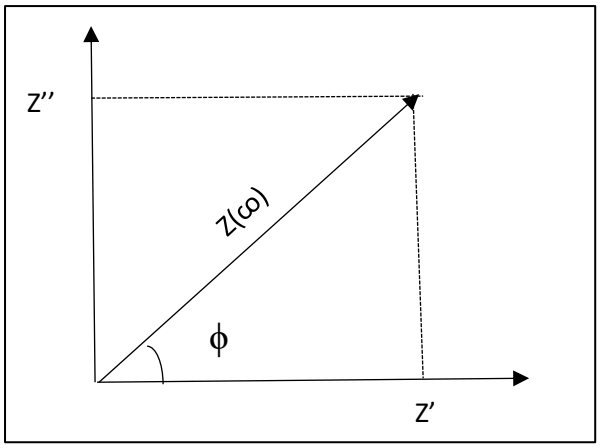


Figure 4.13: Schematic representation of impedance in vector form

Equivalent circuit models are frequently used to described the behaviour of active electrochemical system. These circuits were made up by the various combination of electrical and electronic components. Even some particular equivalent circuits are selected for EIS analysis for investigation of specific electrochemical system. For example, the parallel combination of resistance-capacitor or RC network produced a perfect semicircle in Nyquist plot **Figure 4.14** [46].

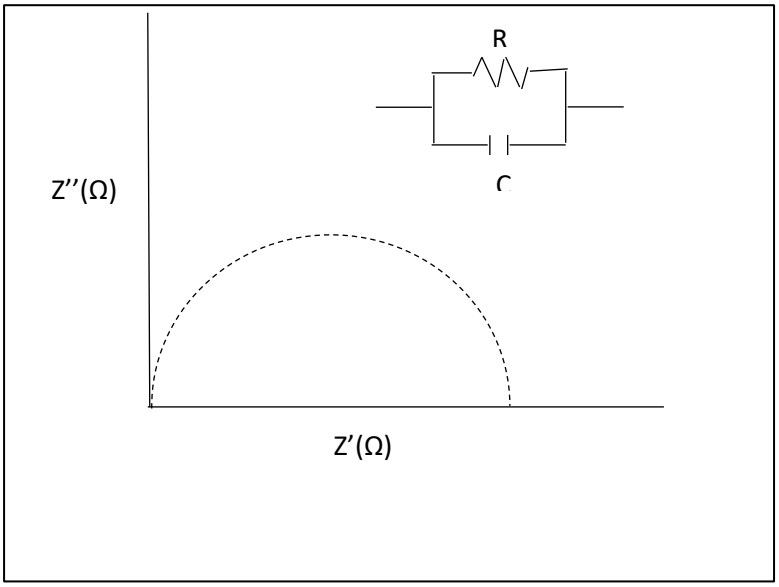


Figure 4.14: Nyquist plot semi-circle for RC equivalent circuit

British electrochemist A.J. Randles employed an equivalent circuit model to characterised the impedance behaviour of an electrochemical system in which the electrode rection occurs in electrolytic solution. A simple corroding system can be assumed as solution resistance (Rs), in series with combination of a resistor and a

capacitor, represent polarization resistance and double layer capacitance respectively. This simple representation is known as Randles circuit. One of these elements related to real impedance (Z') and another is related to imaginary impedance (Z") [44].

$$Z(\omega) = R + \frac{1}{i\omega C} \qquad (4.18)$$

where $Z' = R$ and $-Z'' = \frac{1}{i\omega C}$

The EIS parameters obtained from Randles circuit are described as-

1. Solution resistance (R_s) – Solution resistance is representing the resistance of electrolytic solution it is take into the consideration as the resistance of ionic conductivity and cell connection. It is obtained by the intersection of Nyquist plot to the Real-axis (Z') at high frequency.
2. Charge transfer resistance (R_{ct}) – It is denoted as the resistance of the charge transfer process at metal-electrolyte interface. At high to medium frequency range, it is appearing as the semi-circle arc. High value of R_{ct} suggest that the inhibitor effectively hindered the charge transfer process.
3. Double layer capacitance (C_{dl}) – It is representing the capacity of electrical double layer to store the electrical charge formed at the metal electrolytic interface. It is depending on the surface area of the metal, electrolyte composition and applied potential. Larger the semicircle diameter associate with the larger values of capacitance [45].
4. Maximum Frequency (f_{max}) -This parameter denotes the frequency at which the phase angle reaches its maximum value. A higher f_{max} is indicative of a slower charge transfer process. In the presence of inhibitors, f_{max} is noticeably reduced.

The graphical representation of EIS data can be easily represented by Nyquist and Bode plots [46].

(A) **Nyquist Plot**: Nyquist plot is graphical representation used in study of corrosion control. The real part of complex form of impedance (Z') present on x-axis while the imaginary part of impedance (Z") present on y-axis. A semi-circle Nyquist plot is obtained. Each point of Nyquist point reflects the complex value of impedance at one frequency. On Nyquist plot the impedance (Z) is represented as a vector of length |Z| and the angle at which vector form from x-axis denoted as phase angle. The left most end of Nyquist plot (semicircle) displayed at higher frequency the

impedance of the Randle's cell is entirely produced by ohmic resistance R(Ω) while the right most end of semicircle displayed at lower frequency produced by sum of solution resistance and polarization resistance (R_Ω + Rp). It is helpful to predict the possible mechanism in an equivalent circuit model. The similar shape of the Nyquist plot in presence of inhibitors indicated that the charge transfer play important role in inhibition and the increment in the Nyquist plot size with inhibitor concentration denote the charge transfer is mainly controlled by the inhibitor adsorption [47-49].

(B) **Bode Plot**: The another most popular graphical representation to analysed the EIS study data is bode plots in which absolute impedance and phase shifts are plotted as a function of frequency in two different graphs-

(a) **Bode modulus**: This graph plotted between the impedance and log of frequency (*log* f). It informs the strong dependence of impedance on frequency.

(b) **Bode phase**: Bode phase graph plotted phase angle versus log of frequency. The phase angle starts from zero, reach 90^0 and end with zero. The phase angle reaches zero at highest and lowest frequency limit with purely resistive nature while at intermediate frequencies phase angle increases with increasing imaginary impedance component and shows only capacitive nature at 90^0 phase angles [49].

4.3.2 Evaluation and interpretation of EIS parameters

All EIS experiments were carried out at OCP by applying an AC signal of ±10 mV amplitude in the frequency range 100 KHz to 0.1 Hz. All impedance parameter such as solution resistance (Rs), Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were obtained by fitting the experimental data to the equivalent Randles circuit in absence and presence of various concentration of inhibitors. f_{max} is the frequency at which the imaginary impedance (Z") has maximum value [50]. Double layer capacitance (C_{dl}) was calculated by the help of Charge transfer resistance (Rct) and maximum frequency $f_{max.}$ [51].

$$C_{dl} = [\frac{1}{2\pi f_{max} R_{ct}}] \qquad (4.19)$$

The inhibition efficiency was calculated by using the formula-

$$\% IE = \left[\frac{\left[R_{ct_{Inhibited}} - R_{ct_{unInhibited}}\right]}{R_{ct_{Inhibited}}}\right] X\ 100 \qquad (4.20)$$

$R_{ct_{unInhibited}}$ is the resistance to charge transfer in an unconstrained solution and $R_{ct_{Inhibited}}$ is the resistance to charge transfer in an inhibited solution.

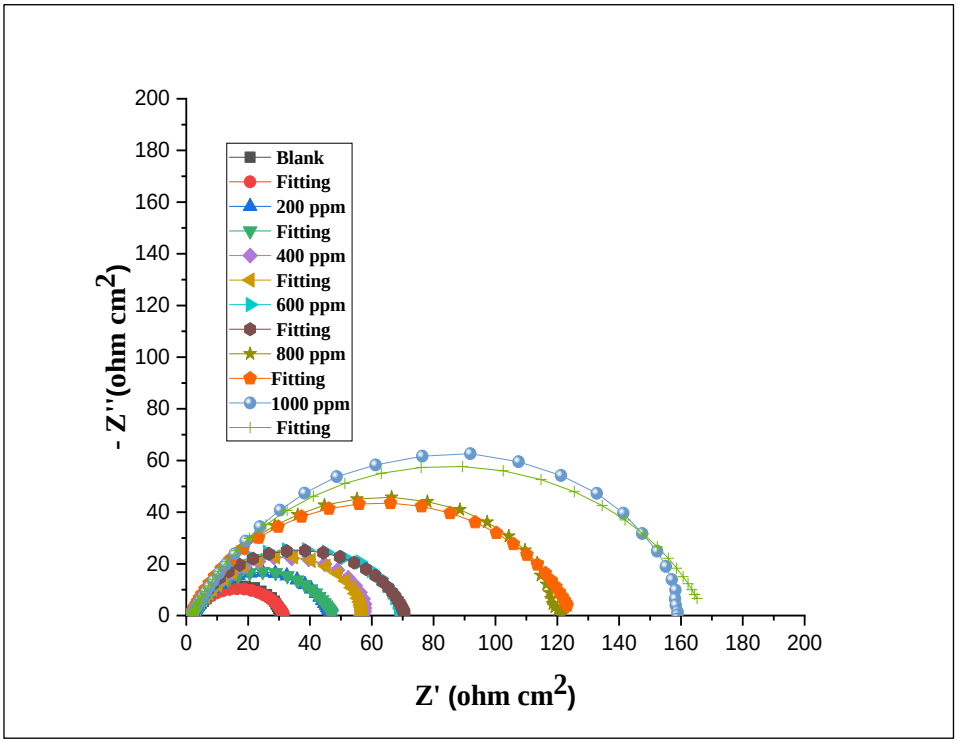


Figure 4.15: Nyquist plots for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BuEImBr]

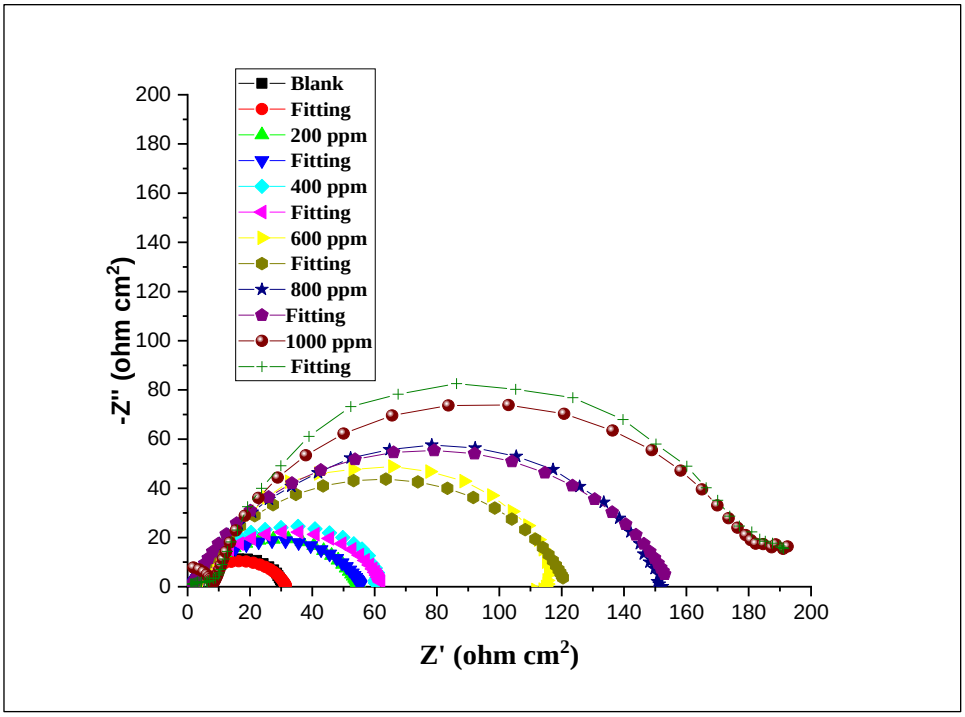


Figure 4.16: Nyquist plots for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [PEImBr]

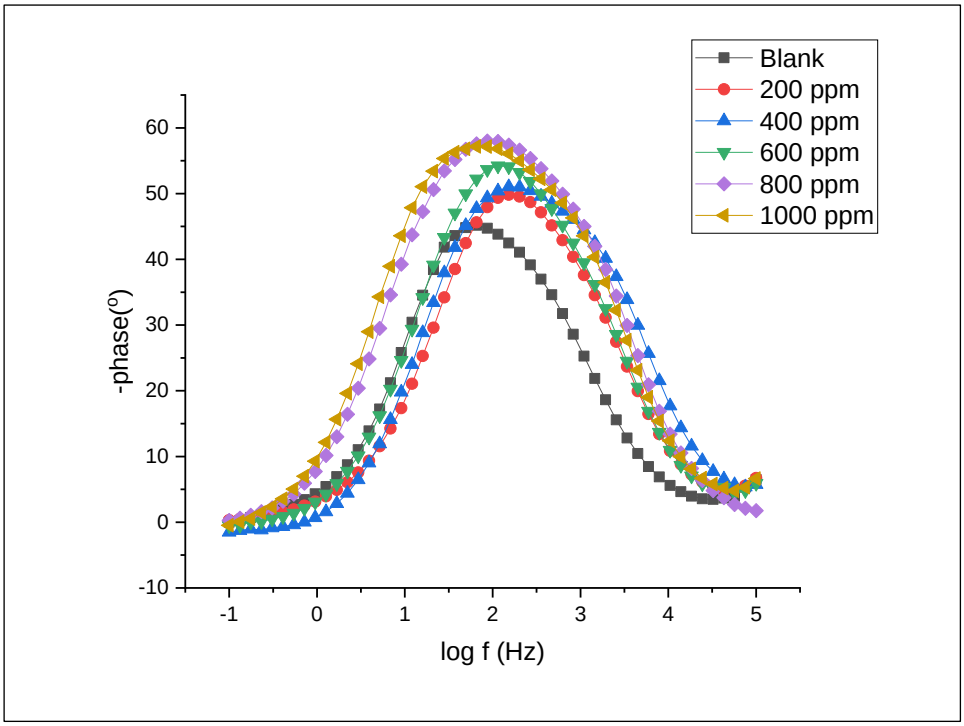


Figure 4.17: Bode phase angle plots (Phase angle vs. log f) for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BuEImBr]

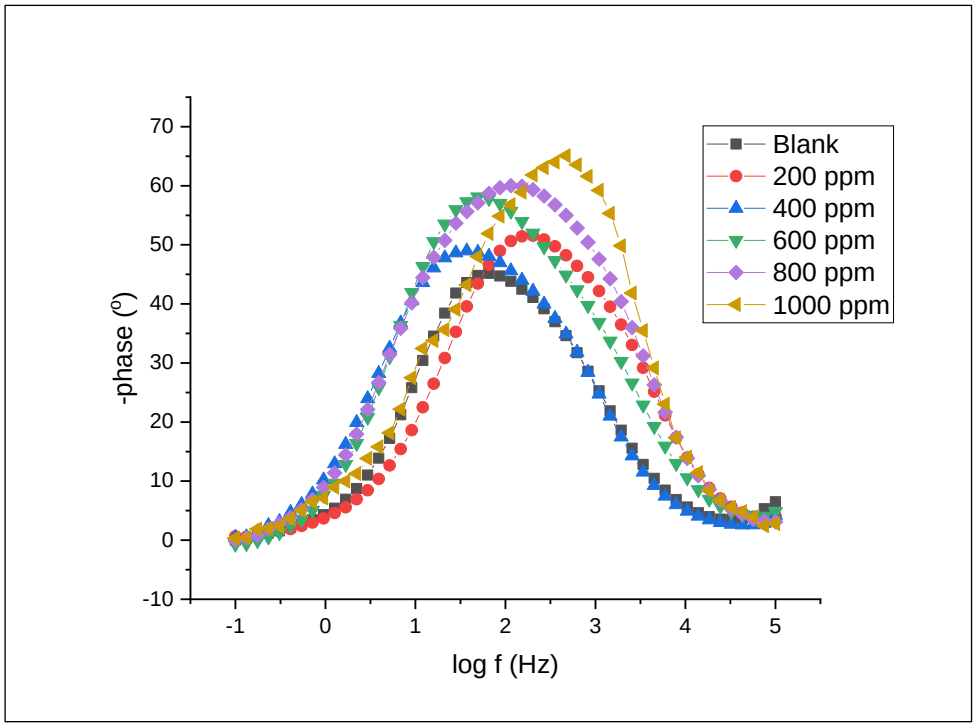


Figure 4.18: Bode phase angle plots (Phase angle vs. log f) for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [PEImBr]

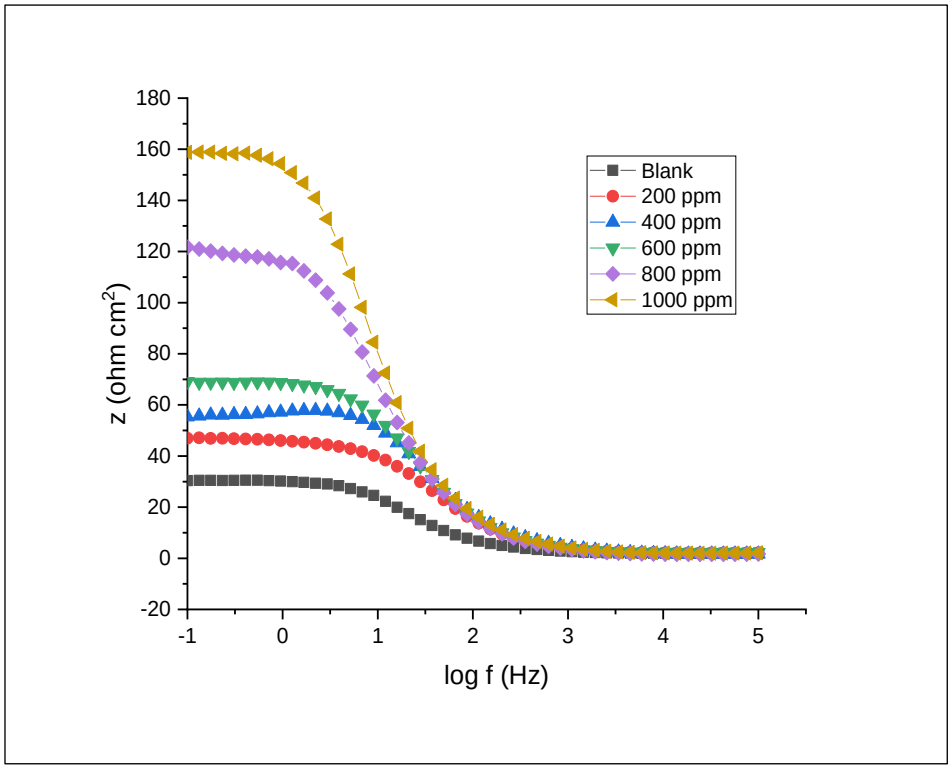


Figure 4.19: Bode modulus plots (Z vs. log f) for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BuEImBr]

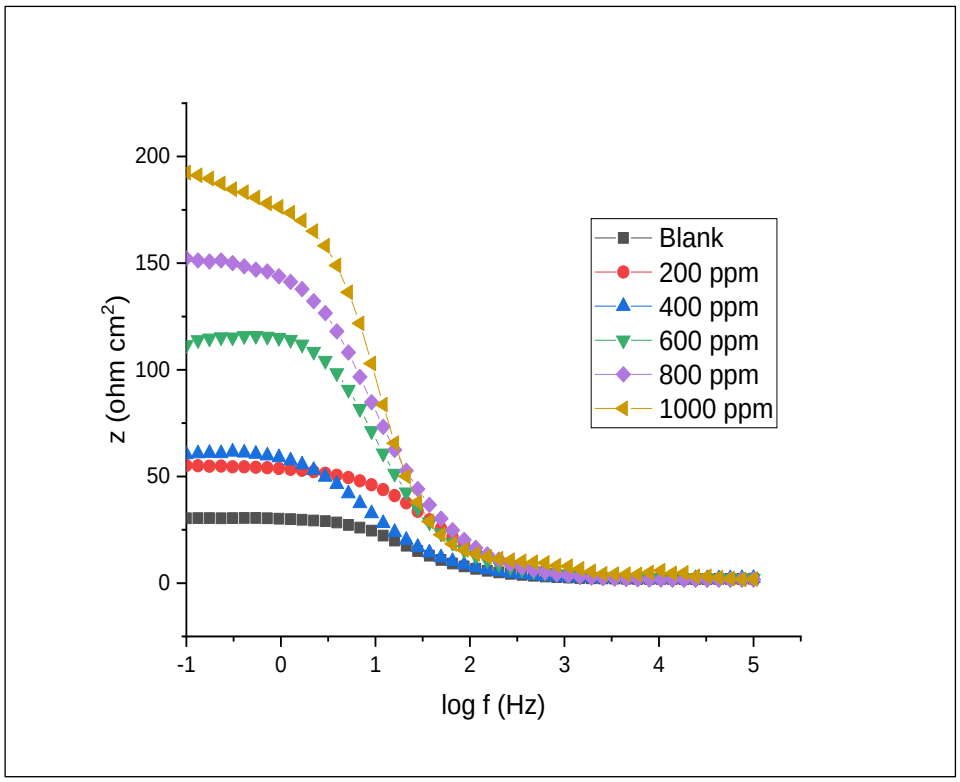


Figure 4.20: Bode modulus plots (Z vs. log f) for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [PEImBr]

Portrays the arrangement of the equivalent model circuit used to describe the observed Nyquist plots (figure 4.21). This circuit model is crucial for interpreting and understanding the impedance behavior of the system.

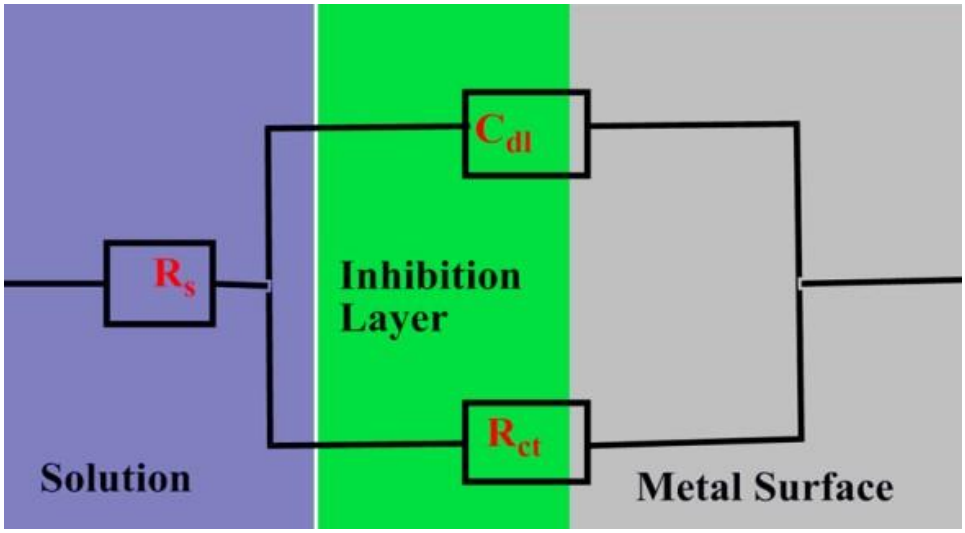


Figure 4.21: Equivalent model circuit of the Nyquist plots

Table 4.13: EIS parameters for mild steel corrosion in 0.5 M H_2SO_4 solution in absence and presence of varying different concentration of [BuEImBr] and [PEImBr]

Name of ImILs	Conc. (ppm)	R_s (Ω Cm^2)	R_{ct} (Ω cm^2)	f_{max} (Hz)	C_{dl} (μFcm^{-2})	IE (%)	χ^2
[BuEImBr]	**Blank**	1.9	30.39	37.27	140.58	---	0.079151
	200	2.0	46.96	28.11	120.62	35.28	0.021787
	400	1.6	55.29	28.11	102.45	45.04	0.035563
	600	2.2	69.11	28.11	81.95	56.02	0.075303
	800	1.6	121.72	15.99	81.80	75.03	0.08065
	1000	2.1	158.77	15.99	62.72	80.86	0.079151
[PEImBr]	**Blank**	1.9	30.39	37.27	140.58	---	0.079151
	200	1.8	55.14	21.21	136.14	44.89	0.066291
	400	2.3	60.29	21.21	124.52	49.59	0.024113
	600	2.1	111.67	12.06	118.23	72.78	0.079151
	800	1.6	152.30	9.1	114.89	80.04	0.021787
	1000	1.8	192.45	9.1	90.92	84.20	0.035563

All analysed data of EIS study in absence and present of both inhibitors are tabulated in the Table 4.13 by using equivalent Randle circuit. The graphical analysis of EIS is given by the help of Nyquist and bode plots depicted in **Figure 4.14, 4.16, 4.18 and 4.15, 4.17, 4.19** for [BuEImBr] and [PEImBr] respectively. All Nyquist plots in absence and presence of inhibitors exhibit as a semicircle or a single depressed capacitive with increments in the diameters with increasing concentration for over the applied frequency range which is strongly supported that mild steel dissolution in 0.5 M H_2SO_4 solution is mainly controlled by charge transfer mechanism and bode plots also favour this mechanism by having a onetime constant or single maxima observed in **Figure 4.16 & 4.17** for both inhibitors [BuEImBr] & [PEImBr] respectively.

The increments in the phase angle value with increasing concentration of inhibitor compare to the 0.5 M H_2SO_4 blank solution indication of smooth surface of mild steel due to the presence of protective film of inhibitor. Bode modulus shows the strong dependence of impedance on the frequency. At low frequency the absolute impedance is increase with increasing concentration revealed the enhancement of corrosion protection.

According to the electrical double layer concepts the value of C_{dl} strongly related to the thickness of the double layer and local dielectric constant [52]. At 1000 ppm concentration the value of C_{dl} was 62.72 μFcm^{-2} and 90.92 μFcm^{-2} for both inhibitors which was lowest in compare to the blank 0.5 M H_2SO_4 solution suggesting that on increasing concentration C_{dl} value is decrease by leading the thickness of electrical double layer and retardation in local dielectric constant. The reduction in the corrosion process or effectiveness of inhibitor is determine by the help of inhibition efficiency which is based on the value of charge transfer resistance R_{ct}. As the concentration of inhibitor increase the charge transfer resistance R_{ct} increase and reached at 158.77 Ω cm^2 and 192.45 Ω cm^2 at 1000 ppm concentration for [BuEImBr] and [PEImBr] respectively. All EIS parameters strongly favour that [PEImBr] acted as better corrosion inhibitor compare to the [BuEImBr].

4.4 Adsorption study of ILs on mild steel surface

Adsorption is mainly depended on the charge of ILs and nature of metal surface. A protective film formation at the metal electrolyte interface is the general accepted theory of corrosion inhibition by ionic liquids in electrolytic solution. The molecules of ILs

replaced the initially adsorbed water molecules on metal surface due to having more favourable energy interaction than the water molecules [53]. On the basis of interaction energy, the adsorption of inhibitor on metal surface classified as physisorption, chemisorption and mixed type. Physisorption referred for the weak type of electrostatic interaction and low activation energy due to the not directly physical contact between the adsorbed ions and metal. If the charge on metal surface known as potential difference is negative than cationic adsorption is governed and if potential difference is positive, anionic adsorption is governed [54]. Chemisorption defines as the strong electrostatic interaction with high activation energy through the charge transfer process involve between the non-bonding electrons present on the heteroatoms or π- electrons of the imidazole rings of ionic liquids and vacant d-orbitals of the metal. Now the mechanism of interaction between the inhibitor and metal interface can be investigated by using adsorption process and suitable adsorption isotherm model.

4.4.1 Adsorption isotherms

Adsorption isotherm is a tool to predict the correlation between the degree of adsorbate coverage on metal surface with changes in certain critical factors such that concentration, pressure and time at a constant temperature [55]. Temperature investigation allows to describe different adsorption process and inhibition mechanisms through the determination of kinetic and thermodynamic parameters. There are some basic approaches discussed used to classified different adsorption isotherms such that potential theory of adsorption isotherms. Kinetic approach is based on the dynamic equilibrium exists between the adsorption and desorption rates. The thermodynamic approach is based on energy criteria as a driving force of adsorption. The best fitted adsorption isotherms are taken into the account which show high equilibrium constant values (K_{ads}.) with appropriate correlation coefficient value equal to unity or close to 1 in the isotherm plots between the surface coverage and the concentration of corrosion inhibitors [56].

There are some adsorption isotherm models which are favourable for corrosion inhibitor adsorption on metal surface are discussed as:

4.4.1.1 Freundlich adsorption isotherm

Freundlich isotherm described the nonideal and reversible adsorption process. It is able to interpreted multilayer adsorption [57]. Freundlich suggested a mathematical expression for explain the surface heterogeneity and the exponential distribution of

active sites and their energies [58]. The linear form of Freundlich adsorption isotherm which related to the concentration of adsorbate present in the experimental solution and amount of adsorbate present on the adsorbent surface is given by equation (4.21).

$$\theta = K_{ads}\, C_{inh}^{1/n} \qquad (4.21)$$

To simplify the equation on taking logarithm on both site of equation the modified equation is represented as-

$$log\ \theta = log\ K_{ads} + (1/n)\ log\ C_{inh} \qquad (4.22)$$

where ($0 < n < 1$); n is the empirical constant, θ is degree of surface coverage, C_{inh} is concentration of inhibitors, K_{ads} is the adsorption equilibrium constant. [59].

A linear plot between *log* θ versus *log* C_{inh} with correlation coefficient close to unity obey the Freundlich model of adsorption isotherm.

4.4.1.2 Langmuir adsorption isotherm

In 1916 Irving Langmuir American scientist proposed a most feasible adsorption isotherm model for monolayer adsorption. It is based on some assumptions such that all adsorption sites are equivalent and particle binding occurs independently. A dynamic equilibrium exists between the adsorbate molecules and surface of adsorbent. In case of Langmuir adsorption isotherm, the relation between the surface coverage θ and inhibitor concentration is given by the equation 4.23 [60-61].

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \qquad (4.23)$$

K_{ads} – adsorption equilibrium constant, θ – degree of surface coverage, C_{inh} – concentration of inhibitor. An isotherm curve obtained by plotting C_{inh}/ θ against the concentration.

A linear plot between C_{inh}/ θ versus C_{inh} with correlation coefficient close to unity obey the Langmuir model of adsorption isotherm.

4.4.1.3 Temkin adsorption isotherm

Temkin adsorption isotherm show by the equation (4.24). It is only valid for the intermediate range of concentration. Temkin adsorption isotherm described the indirect interaction between the adsorbate in the adsorption process specially when the heat of

adsorption of all molecules in the layer are inversely proportional to surface coverage [62-63].

$$-2a\theta = ln\ K_{ads} + ln\ C_{inh} \qquad (4.24)$$

θ is degree of surface coverage, C_{inh} concentration of inhibitor, K_{ads} is the adsorption equilibrium constant, 'a' is the molecular interaction parameter

A linear plot is obtained on by plotting a graph on taking surface coverage (θ) at y-axis and logarithm of concentration (log C) at x-axis. The negative value of interaction parameter 'a' indicate the repulsive nature of inhibitor molecules on the metal surface [64].

Some of other adsorption isotherm models are also discussed by various authors to explain the adsorption mechanism for different electrolytic solution and different adsorbent surface. For examples Flory-Huggins adsorption isotherm, Frumkin, Parsons, El-Awady isotherm etc.

4.4.2 Results and discussion of ILs adsorption on mild steel surface in 0.5 M H_2SO_4 solution

To understood the adsorption behaviour of ILs on mild steel surface in 0.5 M H_2SO_4 solution, all weight loss experiments were conducted at four different temperatures with the help of thermostat. All obtained data were analysed and plotted according to different adsorption isotherms equations. The most fitted model is adopted on the basis of correlation coefficient values close to unity. The summarized data of weight loss study at different temperature are tabulated in the Table 4.14 and illustrated in **Figure 4.22 and 4.23** for [BuEImBr] & [PEImBr] respectively.

Table 4.14: Surface coverage (θ) calculated by gravimetric measurements for corrosion inhibition of mild steel in presence of different concentration of ImILs at different temperatures

Name of ImILs	Temp. / Conc. (ppm)	303 K	313 K	323 K	333 K
[BuEImBr]	200	0.36900	0.32844	0.29117	0.25415
	400	0.45964	0.41047	0.35559	0.30004
	600	0.60409	0.53205	0.43879	0.39444
	800	0.75584	0.65054	0.54694	0.45251
	1000	0.88713	0.81028	0.69182	0.62643
[PEImBr]	200	0.3977	0.3303	0.3040	0.2579
	400	0.5159	0.4383	0.3902	0.3178
	600	0.6715	0.5586	0.4934	0.4227
	800	0.8438	0.6766	0.5825	0.5267
	1000	0.9251	0.8666	0.7224	0.6453

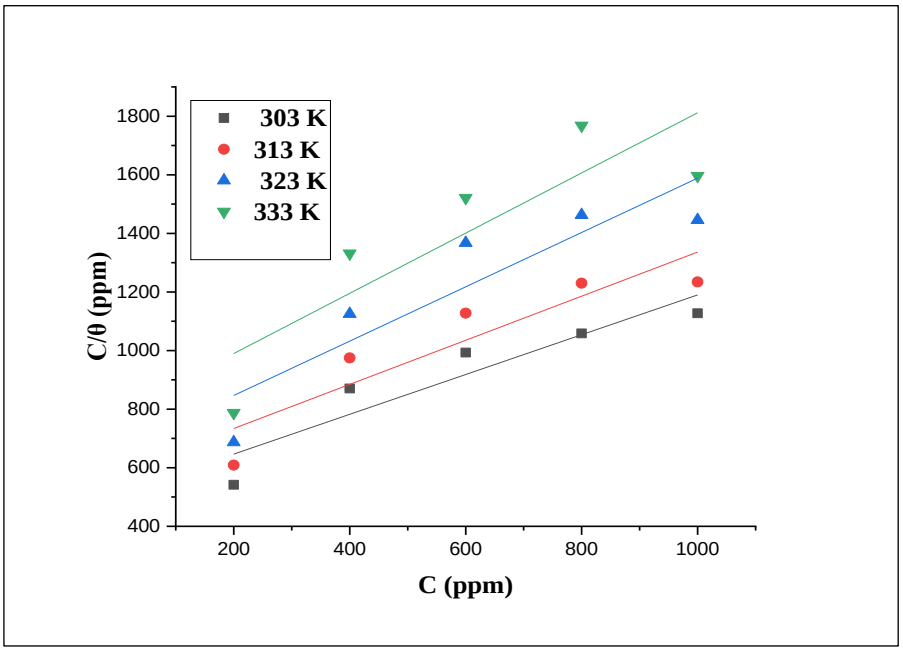


Figure 4.22: Langmuir adsorption isotherm plots in absence and presence of [BuEImBr] at different temperature

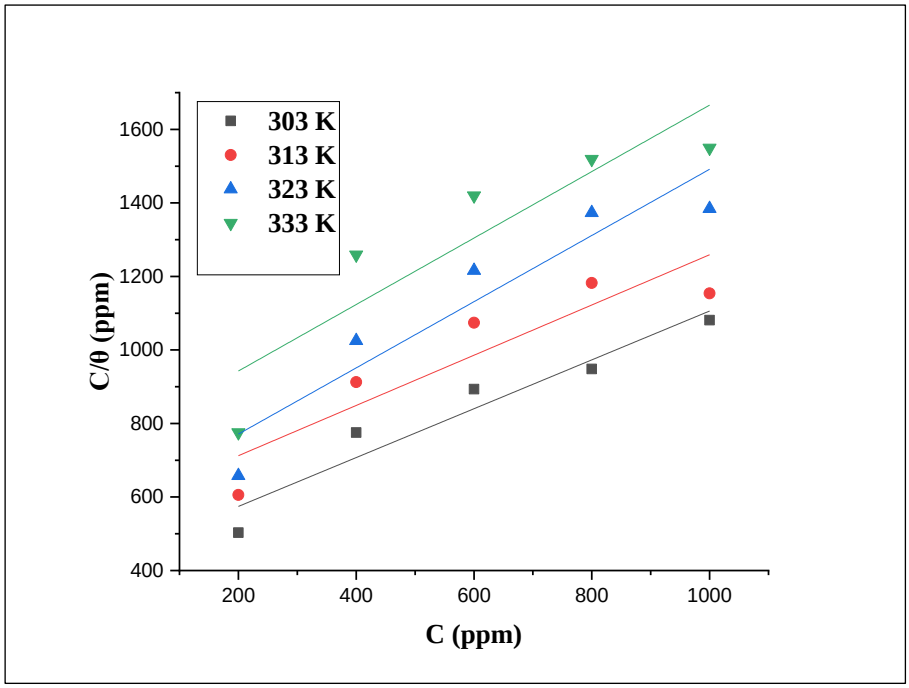


Figure 4.23: Langmuir adsorption isotherm plots in absence and presence of [PEImBr] at different temperature

For both ILs best fitted adsorption isotherms graph obtained on plotting C/θ against the concentration of corrosion inhibitor for which the equilibrium constant seems to decrease with increasing the temperature with correlation coefficient (R^2) close to 1. Hence Langmuir model of adsorption isotherm followed by the both ILs of having the different cationic part.

4.5 Kinetics and Thermodynamic parameters

The thermodynamic and kinetical study of corrosion inhibition process is an important part to verify the good interaction between the inhibitor and metal surface. Thermodynamic and kinetic study of corrosion inhibition process deals with various type of energies such that Gibbs free energy of adsorption (ΔG^0_{ads}), Activation energy (E_a), Enthalpy of adsorption (ΔH_a) and Entropy of adsorption (ΔS_a). Best fitted adsorption isotherm and Arrhenius equation were used in order to calculate kinetics and thermodynamic parameters.

4.5.1 Activation energy of adsorption (E_a)

Arrhenius attempts to predict the effect of temperature on the kinetics of chemical reactions. The corrosion rate and inhibition efficiency parameters of electrochemical

corrosion inhibition process is significantly influenced by temperature. In case of metal corrosion in acidic medium the corrosion rate is exponentially increase as the temperature increase due to the hydrogen evolution overpotential is decrease. This system can be estimated by Arrhenius plot equation (4.25) [65-66].

$$ln\ C_R = ln\ A - \frac{E_a}{RT} \quad (4.25)$$

C_R = Corrosion rate, E_a = Activation energy in kJ/mol, A = Preexponential factor, T = Absolute Temperature, R = Universal gas constant (8.314 J/Kmol)

As literature reported that the increasing activation value create a physical barrier to charge transfer at adsorbent surface which leading to reduction in corrosion rate [67]. The activation energy parameter also suggested that if the value of activation energy in both absence and presence of inhibitor is greater than 20 KJ/mol then the inhibition process is mainly controlled by surface reaction [68-69].

To obtained the activation energy for [BuEImBr] and [PEImBr] inhibitor gravimetric experiments were performed at different concentration and different temperature. The graphs plotted on taking *log* C_R data at y-axis and 1/T on x-axis (**Figure 4.24 & 4.25**). The slope of the graph used to calculate activation energy parameter. The analysed data are tabulated in Table 4.15.

Table 4.15: Corrosion rate (C_R) for different concentration of ImILs at different temperatures

Name of ILs	Temp. (K)	Blank	200 ppm	400 ppm	600 ppm	800 ppm	1000 ppm
[BuEImBr]	**303 K**	158.62	102.65	85.49	63.11	38.72	18.22
	313 K	300.22	201.61	177.87	142.98	104.91	57.38
	323 K	491.08	352.48	315.66	275.59	219.74	153.25
	333 K	753.13	561.71	533.53	456.06	408.25	283.46
[PEImBr]	**303 K**	160.01	95.17	76.48	52.16	24.98	11.82
	313 K	301.03	203.64	167.80	131.86	97.83	39.84
	323 K	494.32	344.00	301.42	253.57	210.01	137.19
	333 K	750.86	557.21	508.33	430.22	358.94	261.66

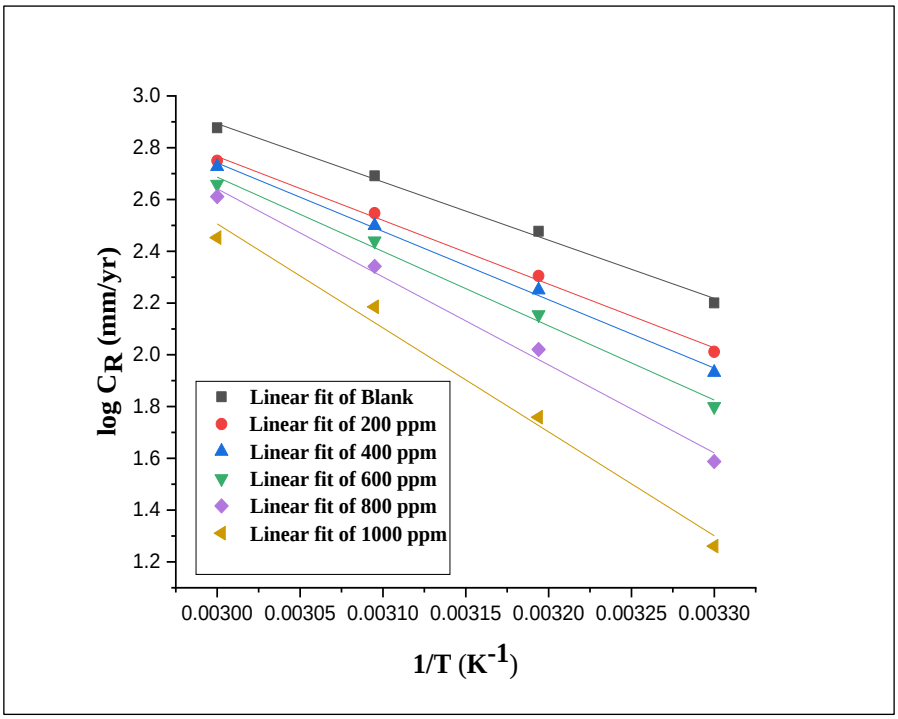


Figure 4.24: Arrhenius plots for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BuEImBr]

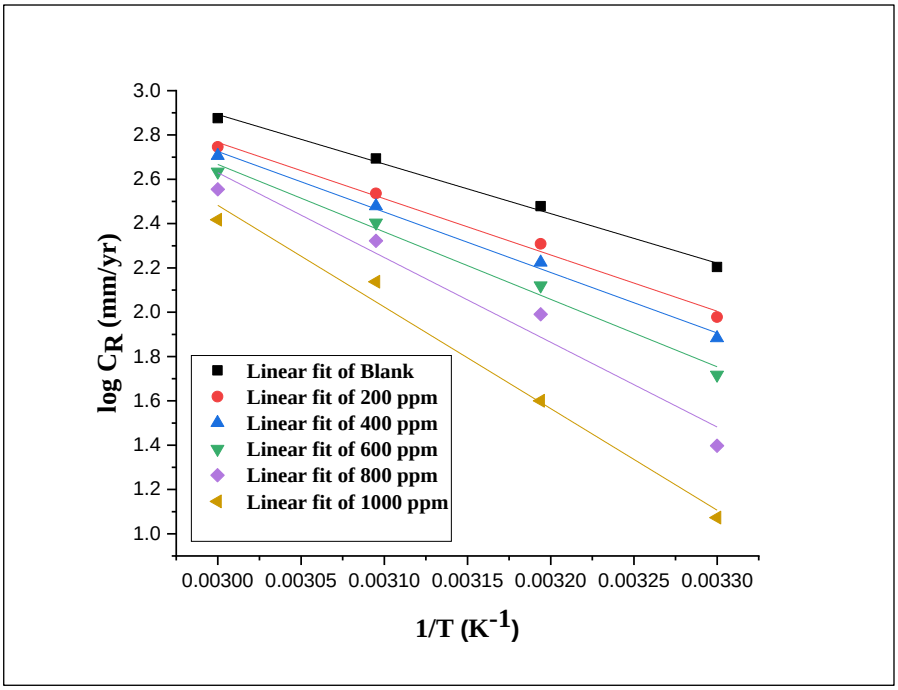


Figure 4.25: Arrhenius plots for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [PEImBr]

Table 4.16: Activation energy parameter for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of ImILs

Name of ImILs	Concentration (ppm)	Slope	R^2	E_a (kJ mol^{-1})
[BuEImBr]	**Blank**	-2249.23	0.99773	43.06
	200	-2463.07	0.99833	47.16
	400	-2640.86	0.99854	50.56
	600	-2870.31	0.99667	54.95
	800	-3400.32	0.99645	65.10
	1000	-4016.41	0.99431	76.90
[PEImBr]	**Blank**	-2235.68	0.99763	42.80
	200	-2538.09	0.99620	48.59
	400	-2729.66	0.99745	52.26
	600	-3043.95	0.99460	58.28
	800	-3825.53	0.98240	73.24
	1000	-4586.17	0.99359	87.81

On the basis of tabulated results in Table 4.16 for both ILs [BuEImBr] and [PEImBr], the activation parameter E_a value is greater than 20 kJ/mol in absence and presence of inhibitors and also the values of E_a in presence of inhibitors found to be greater than compare to the blank solution revealed that the corrosion inhibition process was controlled by surface reactions and more energy required for metal dissolution in presence of inhibitors due to the inhibitor molecules adsorption on the mild steel surface through the physisorption or electrostatic attraction respectively.

4.5.2 Enthalpy of adsorption (ΔH_{ads}) & Entropy of adsorption (ΔS_{ads})

The two thermodynamic parameter enthalpy of adsorption and entropy of adsorption can be determined by using transition state equation (4.26) [70].

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta Sa}{R}\right) \exp -\left(\frac{\Delta Ha}{RT}\right) \qquad (4.26)$$

R = Universal gas constant, T = Absolute temperature, N = Avogadro's number, h = Plank's constant

Equation (4.26) can be plotted as log C_R/T against 1/T. The slopes are equal to ΔH_a / 2.303 R and the intercept is equal to log (R/N*h*) + (ΔS_a / 2.303R).

The positive values of enthalpy indicated that the metal dissolution is an endothermic process. As temperature rise the corrosion rate increase due to decrease in the energy barrier of metal dissolution process. More positive values of enthalpy as concentration of inhibitor rise indication of needed more energy for metal dissolution [71].

The entropy of adsorption may be positive or e negative as literature reported. Change in the entropy is the algebraic sum of adsorption of inhibitor molecules and desorption of water molecules. The inhibition process involves substitution of water molecules by inhibitor molecules. Usually, the negative value of entropy changes with increasing concentration obtained because the restriction of free translation motion of adsorbate molecules or activated complex is rate determining step represents an association process rather than dissociation [72-73]. A moderate positive value of ΔS_{ads} is attribute to the increase of randomness due to the displacement of adsorbed water molecules from the metal surface or the adsorption of inhibitor molecules in a disorder fashion. [74]. Both the parameters ΔH_{ads} and ΔS_{ads} find out by plotting graph between the log C_R/T versus 1/T. the slope of the graph helps to provide the value of ΔH_{ads} while the intercept gives the values of ΔS_{ads}. (**Figure 4.26 & 4.27**)

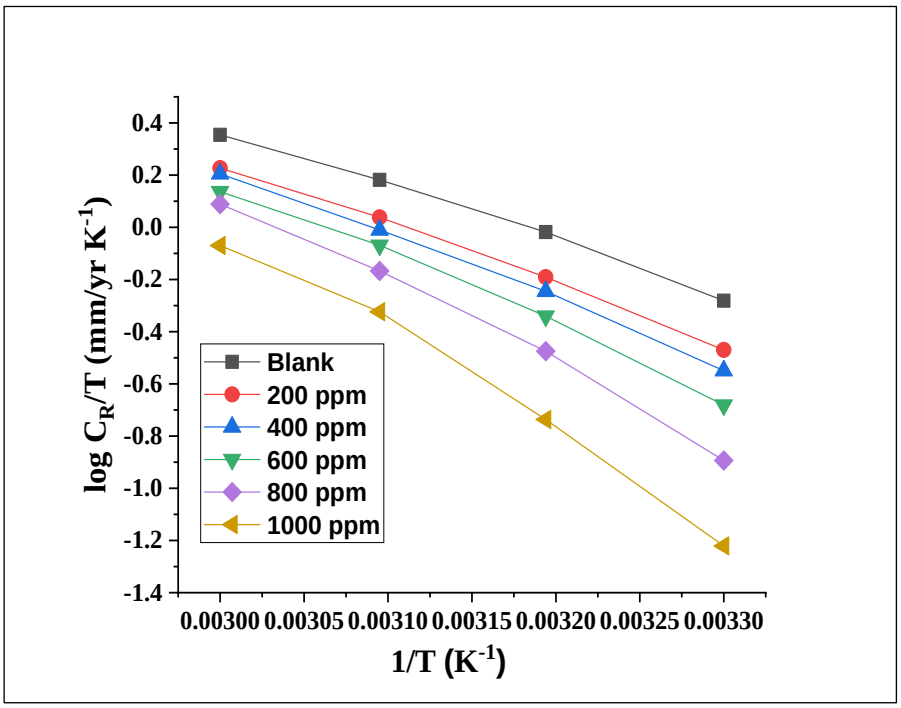


Figure 4.26: Plots of log (C_R/T) versus (1/T) for mild steel in in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BuEImBr]

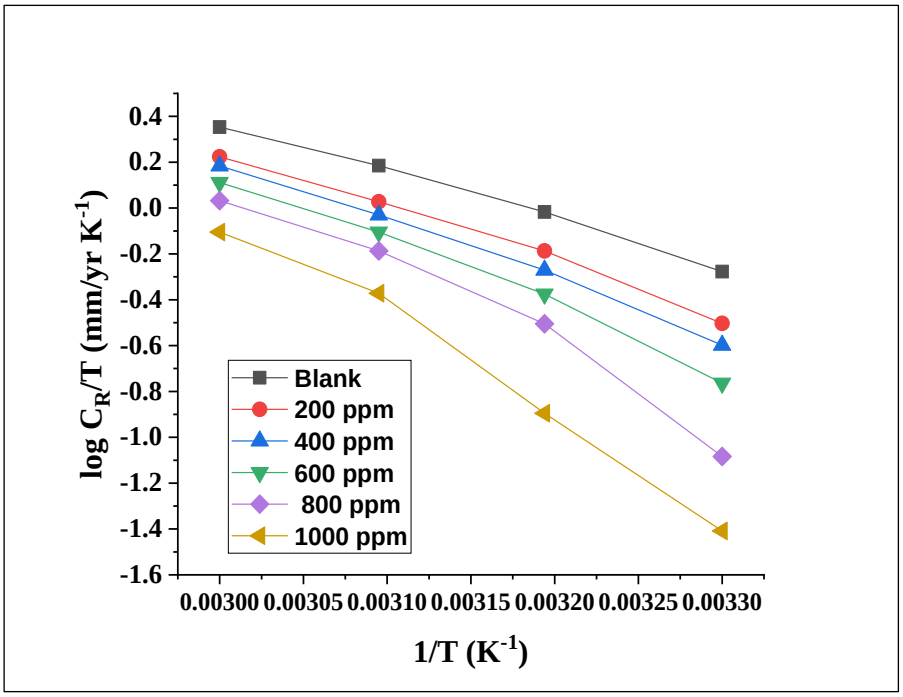


Figure 4.27: Plots of log (C_R/T) versus (1/T) for mild steel in in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [PEImBr]

Table 4.17: Thermodynamic parameters for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BuEImBr] and [PEImBr]

Name of ImILs	Concentration (ppm)	Slope	Intercept	ΔH_a (kJ mol^{-1})	$\Delta Sa(JK^{-1}$ $mol^{-1})$
[BuEImBr]	**Blank**	-2112.49	6.707826	40.45	-68.8222
	200	-2326.3	7.222441	44.54	-58.9725
	400	-2504.09	7.730969	47.95	-49.2393
	600	-2733.55	8.364672	52.34	-37.1102
	800	-3263.55	9.909492	62.49	-7.54233
	1000	-3879.64	11.62237	74.28	25.2422
[PEImBr]	**Blank**	-2098.92	6.66675	40.19	-69.6084
	200	-2401.33	7.447908	45.98	-54.657
	400	-2592.9	7.98176	49.65	-44.4391
	600	-2907.18	8.866282	55.66	-27.5094
	800	-3688.77	11.17368	70.63	16.65414
	1000	-4449.4	13.3083	85.19	57.51077

The obtained results indicated that the values of ΔH_a and ΔS_a were gradually increased with increasing concentration and strongly favored as literature reported. Greater value of ΔH_a also attributed the more inhibition nature of [PEImBr] compare to the [BuEImBr].

4.5.3 Gibb's free energy of adsorption (ΔG_{ads})

The value of Gibb's free energy for adsorption can be determine with the help of best fitted adsorption isotherm for inhibition process. The following equation (4.27) can be used to determine the Gibb's free energy [75].

$$\Delta G_{ads} = -RT\ ln(55.5K_{ads}) \qquad (4.27)$$

ΔG_{ads} = Gibb's free energy of adsorption, R = Universal gas constant, 55.5 = Molar concentration of water, T = Absolute temperature, K_{ads} = Adsorption equilibrium constant

Negative values of ΔG_{ads} revealed the spontaneity of the adsorption process and positive and increasing large value of K_{ads} indicated the strong attraction between the inhibitor molecule and metal surface. As literature reported that the Gibb's free energy around

to -40kJ/mol or higher associated with the chemisorption adsorption mechanism through the charge transfer process and around to -20 kJ/mol or smaller implied an electrostatic attraction through physisorption. The value between the -20 kJ/mol to -40KJ/ mol indicated the mixed type of adsorption [76-77].

Table: 4.18 Adsorption parameters in the presence of ImILs on mild steel surface.

Name of ILs	**Temp. (K)**	**K_{ads}**	**R^2**	**Slope**	**ΔG^0_{ads} ($kJmol^{-1}$)**
[BuEImBr]	**303 K**	1958.33	0.93133	0.67931	-29.21
	313 K	1714.04	0.91398	0.752832	-29.83
	323 K	1512.1	0.89999	0.92726	-30.45
	333 K	1274.94	0.86150	1.02753	-30.92
[PEImBr]	**303 K**	2265.03	0.96298	0.66444	-29.58
	313 K	1736.93	0.91170	0.68330	-29.86
	323 K	1691.94	0.94247	0.90051	-30.75
	333 K	1312.58	0.90290	0.90429	-31.00

As the analyzed results tabulated in the Table 4.18 the gradually decrement in the adsorption equilibrium constant with increasing temperature revealed that the distortion of adsorbing inhibitor is started as the temperature raised. The negative value of Gibbs free energy strongly favors the spontaneity of the adsorption of inhibitor on mild steel surface in 0.5 M H_2SO_4 solution. For both ILs the value of Gibbs free energy exists between the -20kJ/mol to -40kJ/mol that is the indication of mixed type of adsorption inhibition mechanism.

4.6 Surface morphological study of mild steel by Scanning electron microscopy (SEM)

Corrosion inhibition of metal by using inhibitor is a surface adsorption phenomenon hence surface analysis is a major work to describe the inhibition mechanism and other Important information regarding the inhibition process. There are several advance tools and techniques are available for surface morphology analysis of metal such that scanning electron microscopy (SEM), electron dispersive x-ray spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS) etc. SEM is an advanced imaging technique that is provide high quality picture of metal surface by using electron beam of high energy. SEM can be used in combination with different methods such that x-ray spectroscopy in order to assessments of corrosion product, kind of corrosion and origin of corrosion etc. [78].

4.6.1 Basic principle of SEM and EDS techniques

The SEM technique provide a flexible tool which examines and analyses the microstructure properties of solid samples through emissive electron samples interaction [79]. An electron beam of energy range 0.1 to 50 KeV emitted from tungsten filament accelerated by the positive electrode potential towards the sample. Electron column having the series of electromagnetic lens used to focused electron beam onto the sample surface. The electron beam interacts with the atoms of sample surface, back scattered and secondary electrons are produced which are used to generate a signal with the help of detector. Vacuum environment used to avoid the electron interaction with the gas molecules of environment. signal contains information about the sample surface such that chemical composition and other properties. The signal provides an image of material surface with excellent resolution [80].

Energy dispersive x-ray spectroscopy is a technique used for element analysis of solid material by monitoring x-rays emitted by the material surface [81]. These x-rays provide a peak of characterise energy signal of elements. This technique provides not only the information about the elements but also inform about their concentration. Basically, x-rays contain small current which are converted into the voltage pulse depends on the x-ray energy. Element analysis can be done on basis of this energy spectrum [82-83].

4.6.2 Results and discussion of surface morphological study

For study the surface morphology of mild steel coupon in 0.5 M H_2SO_4 solution in presence and absence of inhibitor. Mild steel coupons of specific dimensions 1.0 cm x 1.0 cm x 1.0 mm (length x width x thickness) were firstly abraded and digressed with the help of emery papers of different grades and acetone than immersed into the 100 ml solution of 0.5 M H_2SO_4 in absence of inhibitor and presence of 1000 ppm concentrated solution of both experimental inhibitors separately for 24-hour immersion time at 303 K. After 24-hour coupons are taken out from the solutions washed with double distilled water and acetone than dried in desiccator. These coupons were used for SEM & EDS study.

It is observed from the surface morphological study obtained by the SEM images that the mild steel surface was well furnished and smooth before immersion as **Figure 4.28 (a)**. After immersion in 0.5 M H_2SO_4 solution without any inhibitor mild steel surface is rough, damaged and pits developed with porous cavities due to the oxidation of metal as **Figure 4.28 (b)**. However, in presence of 1000 ppm concentration of both experimental inhibitor the surface is smoother compare to the blank solution. **Figure 4.28 (c)** obtained by [BuEImBr] while the **Figure 4.28 (d)** obtained by [PEImBr]. On comparing **Figure 4.28 (c) & (d)**, it is observed that **Figure 4.28 (d)** is predicted much smoother compare to **Figure 4.28 (c)**. It confirms the better protective layer formation of [PEImBr] inhibitor compare to the [BuEImBr].

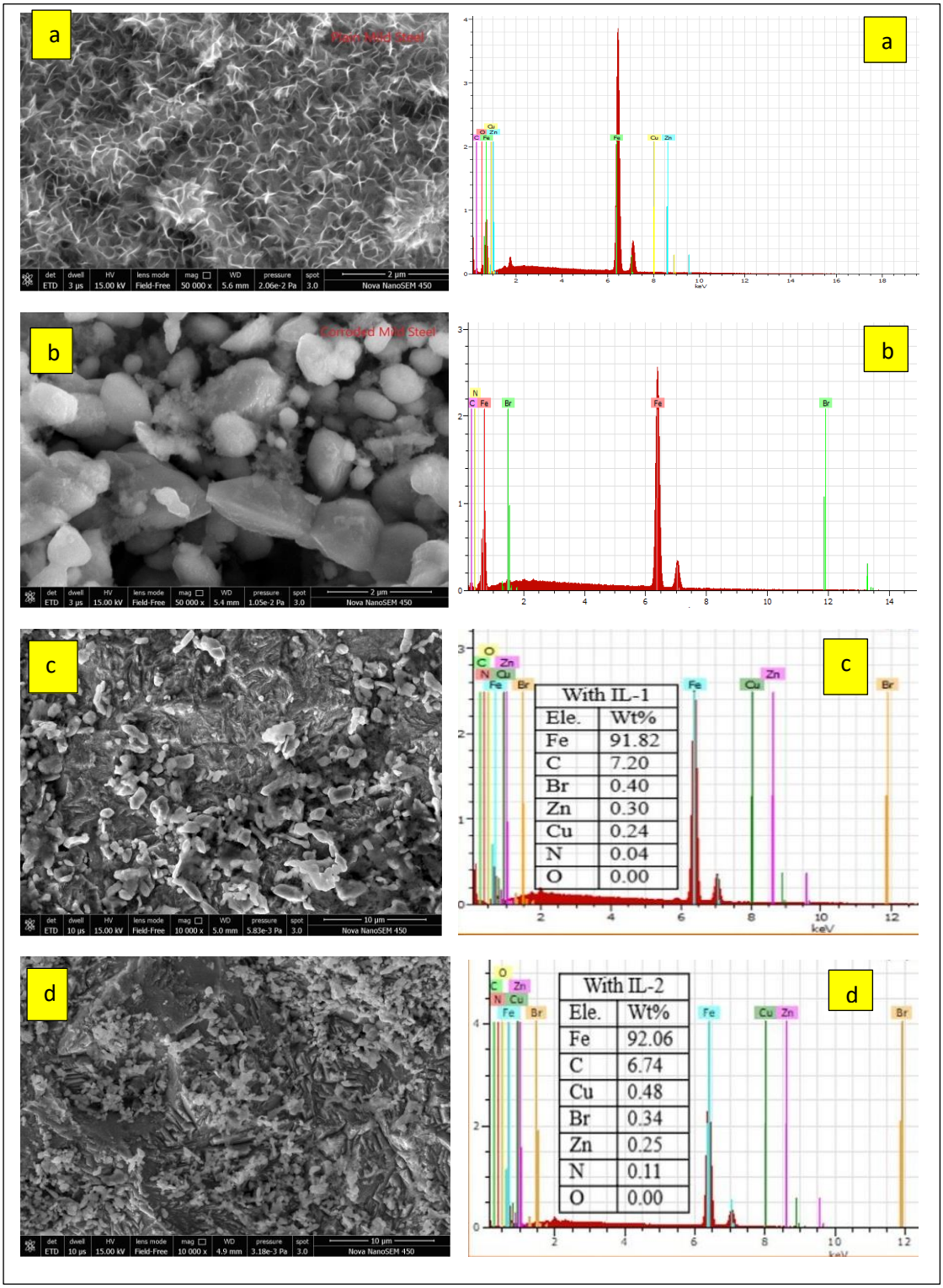


Figure 4.28: SEM-EDS micrographs (a) Fresh mild steel coupon before immersion (b) Corroded mild steel coupon in 0.5 M H_2SO_4 (c) Mild steel coupon after immersion in 1000 ppm [BuEImBr] concentrated solution of 0.5 M H_2SO_4 for 24 hours at 303 K (d) Mild steel coupon after immersion in 1000 ppm [PEImBr] concentrated solution of 0.5 M H_2SO_4 for 24 hours at 303 K

The weight percentage of elements present in plain mild steel, corroded and inhibited mild steel coupons were obtained by the EDS. The summarized results are listed in Table 4.19. The obtained results reveals that the weight percentage of Fe is highest in plain mild steel sample compare to other while lowest in corroded sample of blank solution without inhibitor. In other hand the weight percentage of Fe in mild steel sample of corroded with inhibitor [BuEImBr] is lower than the corroded sample of mild steel with inhibitor [PEImBr]. And also, the weight percentage of carbon is increase in presence of both inhibitors. All obtained results of EDS revealed that on increasing the length of side carbon chain the inhibition efficiency of inhibitor is increase due to better adsorption of inhibitor on mild steel surface.

Table 4.19: Percentage elemental composition of mild steel coupon before immersion and in absence and present of optimum concentration (1000 ppm) of ImILs inhibitors in 100 ml of 0.5 M H_2SO_4 solution for 24 hour of immersion time at 303 K

Elements	**Plain mild steel before immersion**	**Corroded mild steel in 0.5 M H_2SO_4**	**Inhibited mild steel in presence of [BuEImBr]**	**Inhibited mild steel in presence of [PEImBr]**
Fe	94.64	90.89	91.82	92.06
C	3.77	3.74	7.20	6.74

4.7 Proposed corrosion inhibition mechanism of mild steel in absence and presence of imidazolium based ionic liquids in 0.5 M H_2SO_4 solution.

4.7.1 Proposed corrosion mechanism of mild steel in 0.5 M H_2SO_4 solution

The electrochemical corrosion process is the sum of two complementary electrode reactions. In which oxidation reaction occurs at anode through the metal dissolution while reduction reaction occurs at cathode in form of hydrogen evolution by consuming electrons of oxidation. The role of so_4^{2-} anion and other components in the mild steel corrosion in sulphuric acid solution is the matter of interest. The corrosion on mild steel

in sulphuric acid solution can be explained according to the electron exchange by metal dissolution and hydrogen evolution or anodic reaction and cathodic reaction. [83-84]. In the presence of so_4^{2-} ion several following reactions are assumed at anode-

<u>At anodic site-</u>

$Fe + nH_2O \leftrightarrow Fe(H_2O)n_{ads}$ adsorption of water molecules on mild steel surface

$Fe(H_2O)n_{ads} + so_4^{2-} \leftrightarrow [Fe(H_2O)_n\, so_4^{2-}]_{ads}$ formation of sulphate complex

$[Fe(H_2O)_n\, so_4^{2-}]_{ads} \leftrightarrow [Fe(H_2O)_n\, SO_4]_{ads} + 2e^-$ oxidation of mild steel

$[Fe(H_2O)_n\, so_4^{2-}]_{ads} \leftrightarrow Fe^{+2} + OH^- + so_4^{2-} + 2e^-$ desorption of sulphate ions

<u>At cathodic site-</u>

The cathodic hydrogen evolution reaction might be described as follows-

$Fe + H_3O^+ \leftrightarrow Fe(H_3O^+)_{ads}$ adsorption of hydronium ion on mild steel surface

$Fe(H_3O^+)_{ads} + e^- \leftrightarrow Fe(H_3O)_{ads}$ reduction of hydronium ion or principle discharge stage.

$Fe(H_3O)_{ads} + 2H^+ + 2e^- \leftrightarrow Fe + H_2 + H_2O$ evolution of hydrogen gas.

Evaluated hydrogen gas raised in form of bubbled in mild steel surface.

4.7.2 Proposed corrosion inhibition mechanism of mild steel in 0.5 M H_2SO_4 solution by imidazolium based ILs

The adsorption mechanism of inhibitor depends on chemical structure & physical qualities of the inhibitor. The imidazolium based ionic liquids with various carbon chain length provide a better option of corrosion prevention on mild steel surface in acidic medium. The aromatic ring is acted as bonding site between the ionic liquids and metal surface while the carbon chain aids in protection by providing a hydrophobic dense protecting film on mild steel. Longer the alkyl chain facilitates more compact film formation [85].

As literature reported that there are two types of interactions, physisorption and chemisorption involve in the corrosion inhibition mechanism of mild steel surface in presence of imidazolium based ionic liquids solution of 0.5 M H_2SO_4. Inhibitor

molecules block the anodic as well as the cathodic sites of mild steel by forming protective layer in corrosive solution [86]. The inhibition reaction involve in anodic sites are discussed as follow.

In presence of imidazolium based ionic liquids the anionic part and the sulphate ions initially adsorbed on the mild steel surface. Now the anionic charged mild steel surface attract the imidazolium cation by electrostatic force of attraction [87-88]. It is a substitution reaction in which water molecules are replaced by anions and cations of imidazolium ILs by forming a protective film. The presence of bromide ions within these inhibitors' molecular structure reduces their direct interaction with the metal surface significantly. Additionally, the nitrogen atoms in the imidazole cation play a crucial role by forming coordination bonds and donating lone pairs of electrons to the mild steel surface. This action effectively suppresses the corrosion process by hindering the electrochemical reactions responsible for metal dissolution.

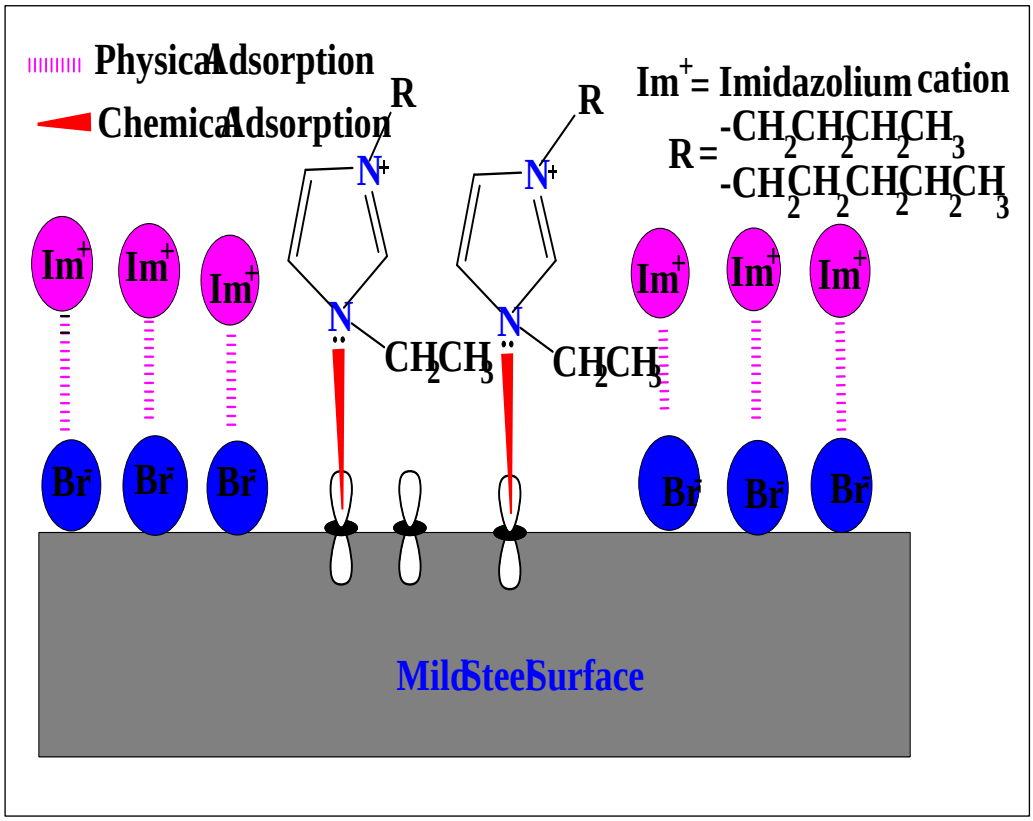
<u>At anodic site</u>

$Fe + nH_2O \leftrightarrow Fe(H_2O)n_{ads}$ adsorption of water molecules on mild steel surface

$Fe(H_2O)n_{ads} + so_4^{2-} \leftrightarrow [Fe(H_2O)_n so_4^{2-}]_{ads}$ formation of sulphate complex

$Fe(H_2O)n_{ads} + Br^- \leftrightarrow [Fe(H_2O)_n Br^-]_{ads}$ adsorption of anion of ILs

$[Fe(H_2O)_n so_4^{2-}]_{ads} + Im^+ \leftrightarrow Fe[(H_2O)_n so_4^{2-} Im^+]_{ads}$ formation of salt



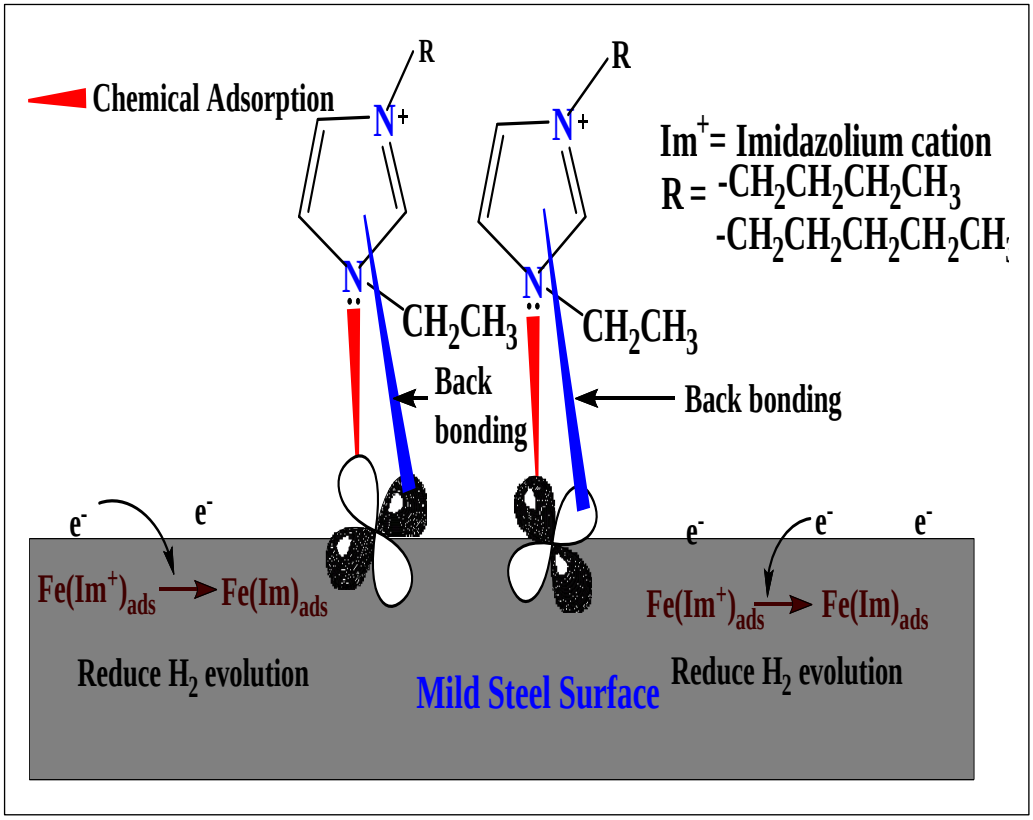
Scheme 4.1 (a) : Mechanism of corrosion inhibition at anode of mild steel in 0.5 M H_2SO_4 with ImILs

<u>At cathodic site</u>

The adsorbed Imidazolium cation accept the electrons from the metallic surface & gain electro-neutrality and reduce the evolution of hydrogen gas.

$$Fe + Im^+ \leftrightarrow Fe(Im^+)_{ads}$$ adsorption of imidazolium cation

$$Fe(Im^+)_{ads} + e^- \leftrightarrow Fe(Im)_{ads}$$ adsorbed Im^+ gain electrons



Scheme 4.1 (b): Mechanism of corrosion inhibition at cathode of mild steel in 0.5 M H_2SO_4 with ImILs.

The high inhibitory efficiency observed in these ionic liquid inhibitors is attributed to electron-donating groups, commonly referred to as +I group, within the imidazolium base. These groups enhance the electron density on the nitrogen atom of the -C=N- group, reinforcing the inhibitory action. Moreover, the unoccupied d orbitals of the metal interact with the electrons from the imidazole aromatic rings, further hindering the dissolution of the metal by creating electronic barriers. When mild steel comes into contact with the solution, an ionic liquid with a longer alkyl chain denoted as [PEImBr], forms a more compact protective layer, leading to higher surface coverage and enhanced corrosion prevention. This superior inhibitory effect of [PEImBr], compared to [BuEImBr], is evident in **Figure: 4.28 (c) & (d)**. The protective effects of these ionic liquid inhibitors, especially in the context of sulfuric acid corrosion, stem from their ability to form robust protective layers on the metal surface.

The specific structural features of these inhibitors, notably the alkyl chain length, play a pivotal role in determining the extent of their inhibitory effectiveness in sulfuric acid, providing valuable insights into tailoring corrosion inhibitors for specific environments [89-90].

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Chapter – 5

IMIDAZOLIUM-BASED IONIC LIQUIDS OF DIFFERENT ANION AS GREEN CORROSION INHIBITOR

Abstract

This chapter deals with the corrosion inhibition properties of imidazolium based ionic liquids containing different anion [BzEImBr] and [BzEImCl]. Chapter provide the strong evidences for the metal inhibitor interaction. Various advanced methods such that weight loss, electrochemical measurements used for determine corrosion parameters. Surface morphology of mild steel surface studied by the use of SEM (scanning electron microscopy) in absence and presence of inhibitor in 0.5 M sulphuric acid solution. Kinetical and thermodynamic parameters help to describe inhibition mechanism and determining temperature effects.

5.1 Gravimetric measurements

The conventional gravimetric measurement is easiest, simplest to handle and least expensive methods among the all corrosion testing methods. It is based on the weight-loss of the metal specimens over a time in which metal is exposed in the corrosive solution. An average value of corrosion rate for over the period can determined by converting the weight loss into the uniform corrosion rate [1]. It is not possible to analyse the short-term deviation in uniform corrosion rate and change in corrosion mechanism [2]. The change in the corrosion rate with changing the temperature, concentration and immersion period can be easily determine by gravimetric analysis.

5.1.1 Experimental setup & Evaluation of gravimetric measurement Parameters

For getting the weight loss data in the gravimetric measurements. A rectangular shaped mild steel coupons with following dimensions [3.6 x 2.3 x 0.3 (length x width x thickness)] were subjected to immersed in the 100 ml corrosive solution in absence and presence of different concentration of inhibitors with the help of glass hooks. Mild steel coupons were abraded and degreased with different grades (80, 220, 320, 400, 600, 800 and 1000) emery papers and acetone before immersion. After immersion washed with double distilled water and acetone than dried in desiccator. The weight of mild steel coupons measures with the help of digital balance than calculate the weight loss by the equation (5.1).

$$\Delta W = W_1 - W_2 \qquad (5.1)$$

W_1 = weight of coupon before immersion, W_2 – weight of coupon after immersion

The other parameters corrosion rate and inhibition efficiency was determined by using equation number (5.2) & (5.3) respectively.

$$C_R = [\frac{87.6\ X\ \Delta W}{AtD}] \qquad (5.2)$$

C_R = Corrosion rate in mmpy, ΔW = Weight loss of material in gram, A = Exposure surface area of coupon in cm^2, t = Exposure time in hour, D = Density of mild steel coupon (7.86 g cm^{-3})

$$\%IE = [\frac{[(W0 - Wi)}{W0}]X100 \qquad (5.3)$$

W_0 = Weight losses without inhibitor, W_i = Weight losses with inhibitor

The evaluation of parameters obtained from weight-loss study for both ionic liquids at four different temperatures was summarized in the Tables from 5.1 to 5.8 for 3-hour.

Table 5.1: Effect of different concentration of [BzEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 303 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.3480	4.0000	0.3480	154.10	---	---
200	4.2955	4.0700	0.2255	99.85	0.3520	35.20
400	4.3980	4.1909	0.2071	91.70	0.4048	40.48
600	4.0717	3.9082	0.1635	72.40	0.5301	53.01
800	4.2778	4.1536	0.1242	54.99	0.6431	64.31
1000	4.3868	4.3000	0.0868	38.43	0.7505	75.05

Table 5.2: Effect of different concentration of [BzEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 313 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.3900	3.7368	0.6532	301.83	---	---
200	4.3490	3.8256	0.5234	231.77	0.1987	19.87
400	4.4004	3.9389	0.4615	213.24	0.2934	29.34
600	4.5248	4.1217	0.4031	186.26	0.3828	38.28
800	4.4177	4.1556	0.2631	121.11	0.5987	59.87
1000	4.3771	4.1232	0.2539	112.43	0.6112	61.12

Table 5.3: Effect of different concentration of [BzEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 323 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.4132	3.3222	1.0910	483.12	---	---
200	4.3755	3.4228	0.9527	421.88	0.1267	12.67
400	4.4382	3.5819	0.8563	379.19	0.2151	21.51
600	4.0065	3.2867	0.7198	338.06	0.3402	34.02
800	4.1616	3.5059	0.6557	307.95	0.3989	39.89
1000	4.2199	3.7562	0.4637	211.37	0.5749	57.49

Table 5.4: Effect of different concentration of [BzEImBr] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 333 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.4397	2.7585	1.6812	744.48	---	---
200	4.0098	2.5339	1.4759	653.56	0.1221	12.21
400	4.3550	3.0323	1.3227	585.72	0.2132	21.32
600	4.2919	3.0715	1.2204	540.42	0.2740	27.40
800	4.2084	3.0008	1.2076	534.75	0.2817	28.17
1000	4.2944	3.2327	1.0617	470.14	0.3684	36.84

Table 5.5: Effect of different concentration of [BzEImCl] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 303 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.4197	4.0633	0.3564	157.5	---	---
200	4.2309	4.0320	0.1989	88.07	0.4419	44.19
400	4.3307	4.1929	0.1378	61.02	0.6133	61.33
600	4.3299	4.2226	0.1073	47.51	0.6989	69.89
800	4.2809	4.2275	0.0534	23.46	0.8501	85.01
1000	4.3934	4.3640	0.0294	13.01	0.9175	91.75

Table 5.6: Effect of different concentration of [BzEImCl] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 313 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.3242	3.6750	0.6492	299.98	---	---
200	4.3226	3.8910	0.4316	191.12	0.3351	33.51
400	4.4209	4.0930	0.3279	145.20	0.4949	49.49
600	4.2246	3.9724	0.2522	111.68	0.6115	61.15
800	4.5395	4.3231	0.2164	95.82	0.6666	66.66
1000	4.2465	4.1047	0.1418	62.79	0.7815	78.15

Table 5.7: Effect of different concentration of [BzEImCl] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 323 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	3.9216	2.8715	1.0501	485.83	----	---
200	3.9082	3.0928	0.8154	361.08	0.2235	22.35
400	4.1736	3.4956	0.6780	313.29	0.3543	35.43
600	3.9433	3.4336	0.5097	225.70	0.5146	51.46
800	3.8856	3.4880	0.3976	176.06	0.6216	62.16
1000	4.0392	3.6849	0.3543	156.89	0.6626	66.26

Table 5.8: Effect of different concentration of [BzEImCl] on the corrosion inhibition parameters of mild steel for 3-hour immersion time in 0.5 M H_2SO_4 at 303 K

Conc. (ppm)	Weight of MS before Immersion W_1 (g)	Weight of MS after Immersion W_2 (g)	Weight Loss ΔW (g)	Corrosion rate (C_R) (mmpy)	Surface coverage (θ)	Inhibition efficiency (% IE)
Blank	4.3006	2.6275	1.6731	740.89	----	----
200	4.3121	3.9849	1.3272	587.71	0.2067	20.67
400	4.3086	3.1482	1.1604	513.29	0.3067	30.67
600	4.3312	3.3550	0.9762	432.28	0.4165	41.65
800	4.3687	3.5280	0.8407	372.28	0.4975	49.75
1000	4.2304	3.5125	0.7179	317.90	0.5709	57.09

5.1.2 Results and discussion

The results of weight-loss analysis are very help full to describe the effects of concentration, immersion time and temperature on corrosion rate & inhibition efficiency.

(A) Effect of concentration

The concentration of inhibitor is an important factor in case of industrial application of corrosion inhibitor to achieve maximum inhibition efficiency with effective concentration. The optimum concentration is the concentration at which the corrosion rate is lowest and the surface coverage of mild steel surface is maximum [3]. As the concentration of inhibitor was increase in the corrosive solution of 0.5 M H_2SO_4 solution the inhibition efficiency and surface coverage were increase. In our study, 1000 ppm was observed as optimum concentration of imidazolium based ionic liquids. The effect of concentration on the corrosion parameters for both inhibitors at four different temperatures were tabulated in the Tables 5.9. **Figure 5.1 and 5.2** represent the increasing % inhibition efficiency with inhibitor concentration for [BzEImBr] and [BzEImCl] respectively.

Table 5.9: Variation in the inhibition efficiency (%IE) at different temperature and different concentration of ImILs for mild steel in 0.5 M H_2SO_4 for 3-hour immersion time

Name of ionic liquids	Temp / Conc.	303 K	313 K	323 K	333 K
[BzEImBr]	**Blank**	---	---	---	---
	200	35.20	19.87	12.67	12.21
	400	40.48	29.34	21.51	21.32
	600	53.01	38.28	34.02	27.40
	800	64.31	59.87	39.89	28.17
	1000	75.05	61.12	57.49	36.84
[BzEImCl]	**Blank**	---	---	---	----
	200	44.19	33.51	22.35	20.67
	400	61.33	49.49	35.43	30.67
	600	69.89	61.15	51.46	41.65
	800	85.01	66.66	62.16	49.75
	1000	91.75	78.15	66.26	57.09

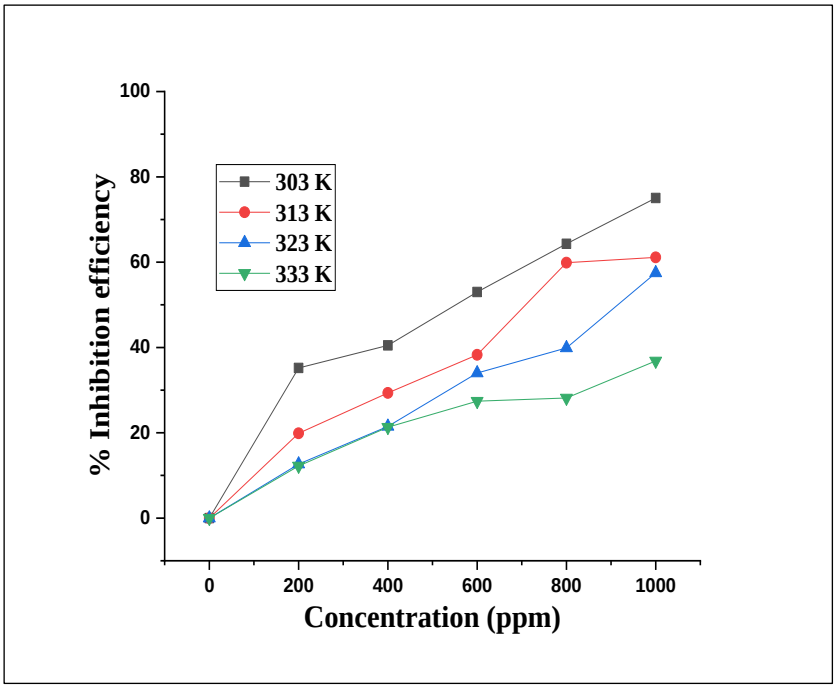


Figure 5.1: Variation of % IE with concentration of [BzEImBr] at different temperature

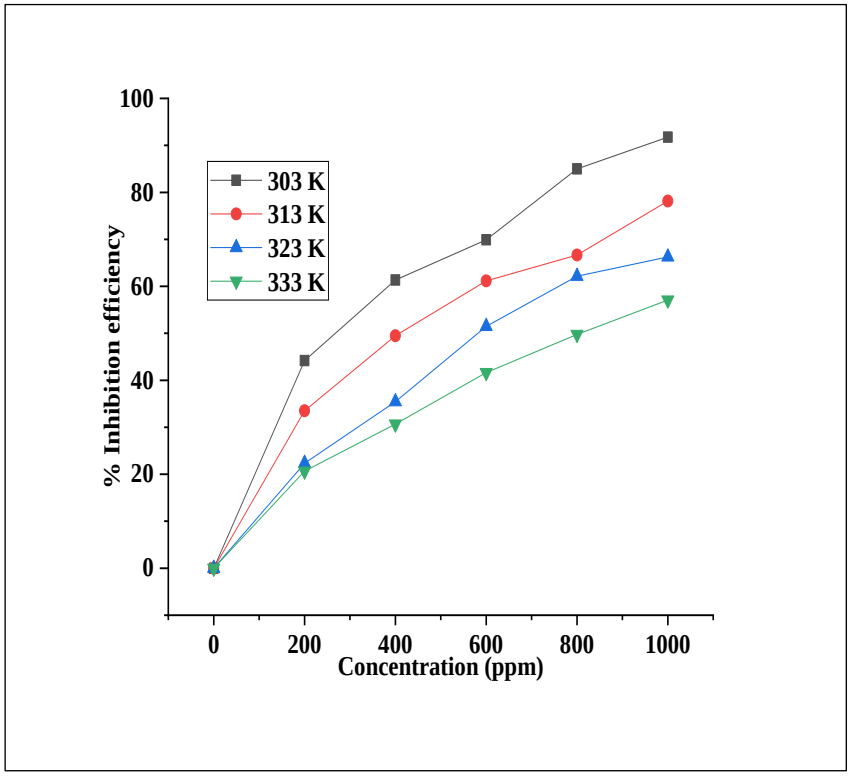


Figure 5.2: Variation of % IE with concentration of [BzEImCl] at different temperature

As the results obtained from the gravimetric analysis for [BzEImBr] and [BzEImCl] inhibitors the maximum inhibition efficiency obtained 75.05% & 91.75% at 1000 ppm concentration at 303 K. respectively. At 1000 ppm concentration both inhibitors have maximum surface coverage of mild steel surface with lowest corrosion rate. The inhibition efficiency at all four temperature was maximum at 1000 ppm individually compare to other concentration hence 1000 ppm is noted as optimum inhibition concentration for both inhibitors [BzEImBr] and [BzEImCl].

(B) Effect of temperature

It is well understood that adsorption phenomenon is involve in the corrosion inhibition process which is affected by temperature. It is considered that increasing temperature stimulated the surface kinetic energy which is adverse effect of the adsorption of inhibitor molecules on mild steel surface. As temperature rises the equilibrium is shifted towards desorption of inhibitor molecules on mild steel surface [4]. On increasing temperature from the 303 K the surface coverage area decreases and show deviation from unity confirm the desorption of inhibitor molecules [5]. The summarized results

for [BzEImBr] and [BzEImCl] inhibitors are listed in the Table 5.10 and illustrated in **Figure 5.3 & 5.4** for different temperatures.

Table 5.10: Variation in the corrosion rate & surface coverage area at different temperature and different concentration of ImILs for mild steel in 0.5 M H_2SO_4 for 3-hour immersion time

Name of ionic liquids	Temp. / Conc.	303 K		313 K		323 K		333 K	
		θ	**C_R**	**θ**	**C_R**	**θ**	**C_R**	**Θ**	**C_R**
[BzEImBr]	**Blank**	---	154.10	---	301.83	---	483.12	---	744.48
	200	0.3520	99.85	0.1987	231.77	0.1267	421.88	0.1221	653.56
	400	0.4048	91.70	0.2934	213.24	0.2151	379.19	0.2132	585.72
	600	0.5301	72.40	0.3828	186.26	0.3402	338.06	0.2740	540.42
	800	0.6431	54.99	0.5987	121.11	0.3989	307.95	0.2817	534.75
	1000	0.7505	38.43	0.6112	112.43	0.5749	211.37	0.3684	470.14
[BzEImCl]	**Blank**	---	157.5	---	299.98	---	485.83	----	740.89
	200	0.4419	88.07	0.3351	191.12	0.2235	361.08	0.2067	587.71
	400	0.6133	61.02	0.4949	145.20	0.3543	313.29	0.3067	513.29
	600	0.6989	47.51	0.6115	111.68	0.5146	225.70	0.4165	432.28
	800	0.8501	23.46	0.6666	95.82	0.6216	176.06	0.4975	372.28
	1000	0.9175	13.01	0.7815	62.79	0.6626	156.89	0.5709	317.90

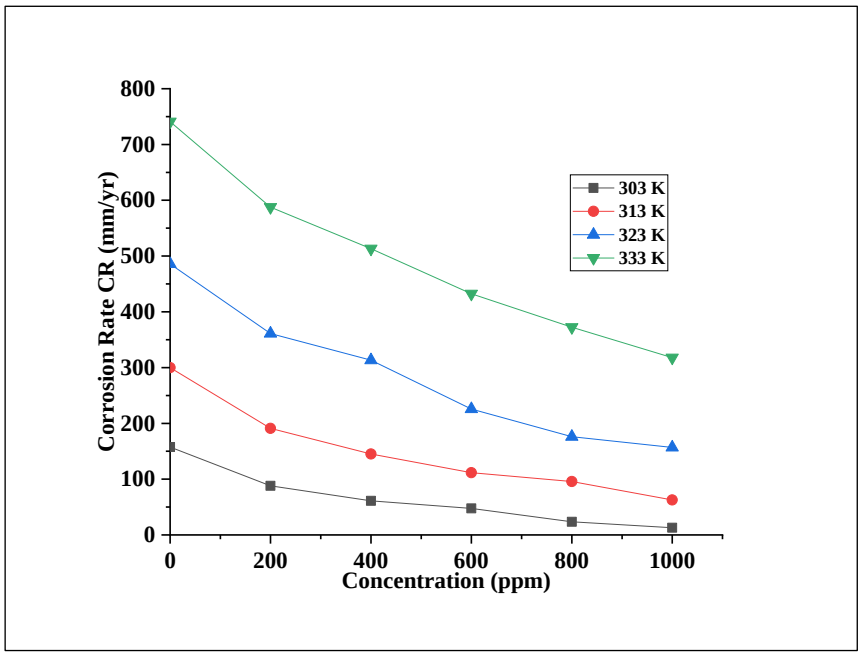


Figure 5.3: Variation of corrosion rate (C_R) with concentration of [BzEImBr] at different temperature

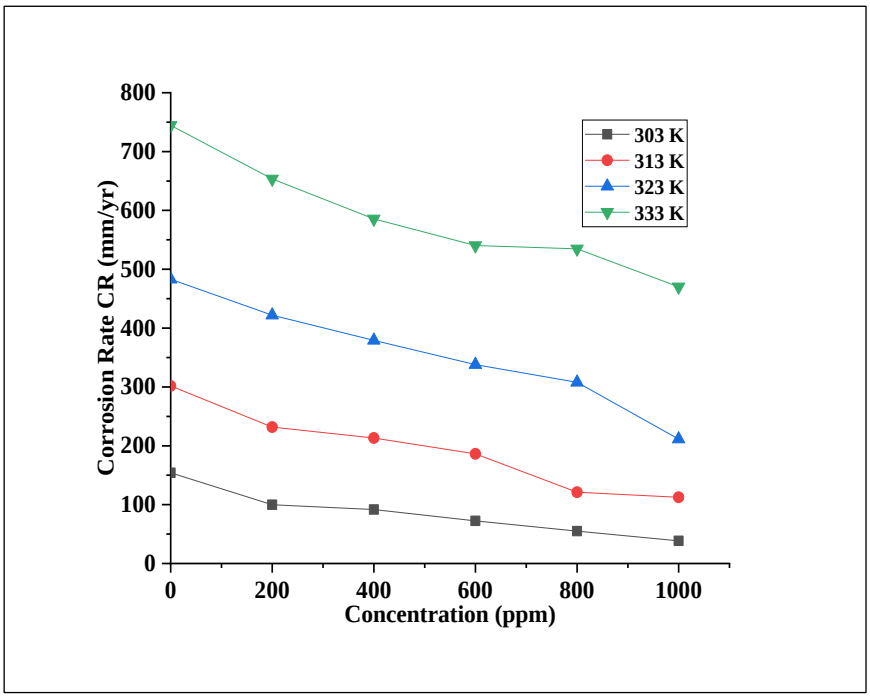


Figure 5.4: Variation of corrosion rate (C_R) with concentration of [BzEImCl] at different temperature

As the results obtained from the gravimetric measurements the highest surface coverage 0.7505 and 0.9175 obtained at 303 K which is continuously decrease on increasing

temperature due to the shifting of equilibrium towards the desorption. Similarly, the increment in the corrosion rate from 54.99 to 470.14 & 23.45 to 317.90 with increasing temperature also suggesting the physisorption type of adsorption for both the inhibitor [BzEImBr] and [BzEImCl] respectively.

(C) Effect of immersion time

The time of immersion is also a considerable parameter in case of industrial corrosion testing where the corrosive electrolytic solution is used as a material of cleaning agent. As the literature reported that the electrostatic force of attraction is involve between the inhibitor and mild steel surface. Which is week type of attraction force. Hence on increasing the immersion time the weight loss is continuously increase and corrosion rate is continuously increase in absence of inhibitor while in presence of inhibitor the inhibition efficiency firstly increases than decrease after a specific immersion time.

The extracted data of weight loss measurements in absence and presence of both inhibitor for different immersion time are listed in Table 5.11.

Table 5.11: Effect of immersion time on the corrosion inhibition of the mild steel in 0.5 M H_2SO_4 in absence & presence of optimum concentration of ImILs at 303 K

Immersion time in hours	**Weight-loss in absence of inhibitor**	**% IE in presence of [BzEImBr]**	**% IE in presence of [BzEImCl]**
12 h	0.9320	74.78	91.28
24 h	1.6857	75.58	92.21
36 h	2.4361	66.77	80.71
48 h	3.4902	51.15	76.92

On the basis of obtained data the maximum surface coverage attends at 24-hour immersion time at which the both inhibitor shows maximum inhibition efficiency after 24-hour the adsorption surface coverage is decreased regularly.

5.2 Electrochemical measurements

The electrochemical performance of green corrosion inhibitors for mild steel in 0.5 M H_2SO_4 were evaluated by potentiodynamic curves. All electrochemical experiments are performed by using Potentiate/Galvanostat instrument consisting three electrode system [6]. Mild steel coupons with 1 cm^2 surface area immersed in electrolytic solution in absence and presence of inhibitor consider as a working electrode. Silver/silver chloride in 3 M KCl used as reference electrode connected through the Luggin's capillary and graphite rod used as counter electrode. The mild steel coupon immersed in the test solution for 30 minutes until the system is thermodynamically stable enough to perform polarization experiments [7-8].

5.2.1 Open circuit potential (OCP)

The potential different between the mild steel coupons and electrolytic solution at this state known as open circuit potential. OCP of the system recorded as a function of time. To achieved a steady-state or quasi-stationary value a time is necessary so mild steel coupon immersed into the test solution for 30 minutes. It indicates the thermodynamic stability of the system [9-10]. The parallel graph of OCP versus time indicating the removal of accumulated oxide layer on mild surface and adsorption of inhibitor molecules. The positive shifting of OCP at some selected concentration of inhibitor compare to the blank or uninhibited condition revealed the anodic type of inhibition or inhibition by alter the metal dissolution reaction while the negative shifting of OCP at some selected concentration indicate that the inhibitor acted as cathodic inhibitor or inhibition by opposing the hydrogen evolution reaction on cathode. The corrosion inhibitor which shows both type of OCP shifting assumed as mixed type of inhibitor with predominance of some specific concentration [11-13].

The OCP versus time plots are presented in **Figure 5.5 & 5.6** for mild steel in 0.5 M H_2SO_4 in absence and presence of [BzEImBr] and [BzEImCl] respectively.

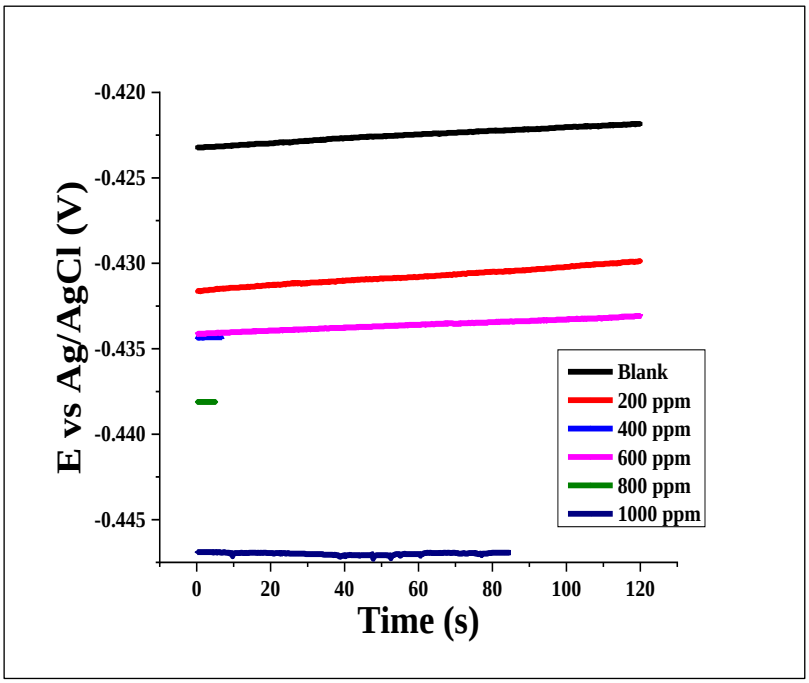


Figure 5.5: Variation of E_{ocp} of mild steel in absence and presence of different concentration of [BzEImBr]

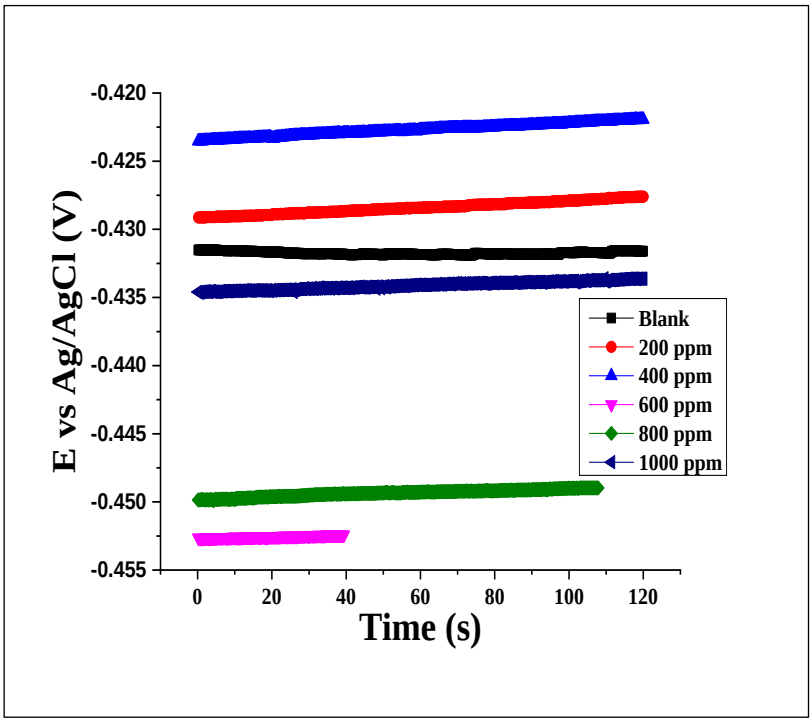


Figure 5.6: Variation of E_{ocp} of mild steel in absence and presence of different concentration of [BzEImCl]

It is clear from the OCP plots that in presence of [BzEImBr] inhibitor the OCP shifted to the negative values with the increasing concentration compare to the blank or absence of inhibitor while in case of [BzEImCl] inhibitor OCP shifted at both positive and

negative values compare to the blank. It indicated that [BzEImBr] inhibitor acted as mixed type of inhibitor with dominance of reduction of cathodic hydrogen evolution reaction and [BzEImCl] inhibitor acted as mixed type of inhibitor.

5.2.2 Potentiodynamic polarization measurements

Potentiodynamic Tafel curves plotted after 30 minutes of immersion mild steel coupons in absence and presence of inhibitors. The change in the E_{corr} < 85 and Taffel slopes (βa & βc) signify the mixed type of inhibition [14]. The corrosion current density calculated by the help of Stern-Geary equation (5.3) to evaluate % inhibition efficiency [15].

$$\%IE = \frac{i_{corr_{unInhibited}} - i_{corr_{Inhibited}}}{i_{corr_{UnInhibited}}} X\ 100 \qquad (5.3)$$

The polarization curves for both inhibitor [BzEImBr] and [BzEImCl] in 0.5 M H_2SO_4 in absence and presence of various concentration of inhibitors obtained in potential region (-800) mV to (-200) mV at 0.01 $Vsec^{-1}$ scan rate. All the polarization parameters calculated by extrapolation of Taffel curves. The extract data of polarization curves for both inhibitors listed in Table 5.12 and the polarization curves represented in **Figure 5.7 & 5.8.**

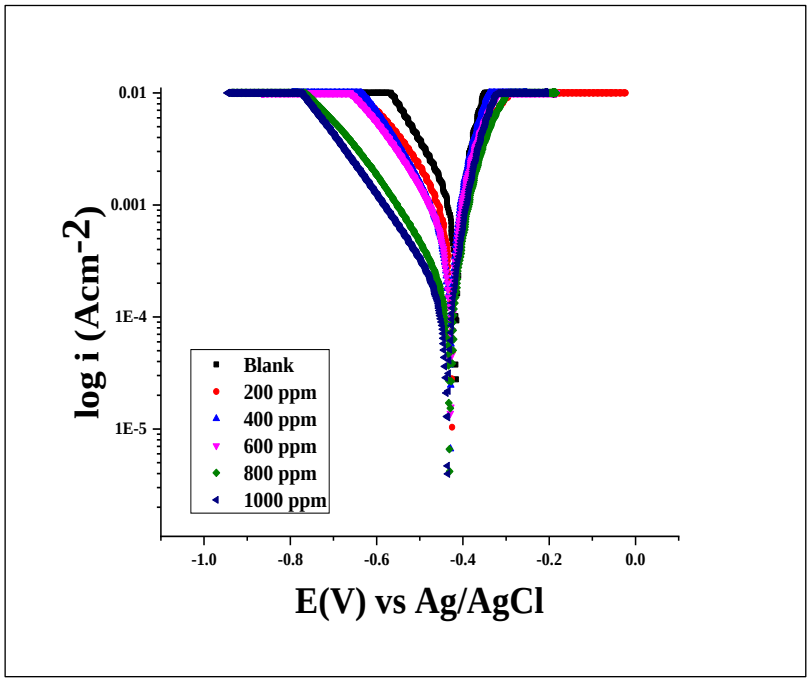


Figure 5.7: Polarization curves for mild steel in absence and presence of different concentration of [BzEImBr]

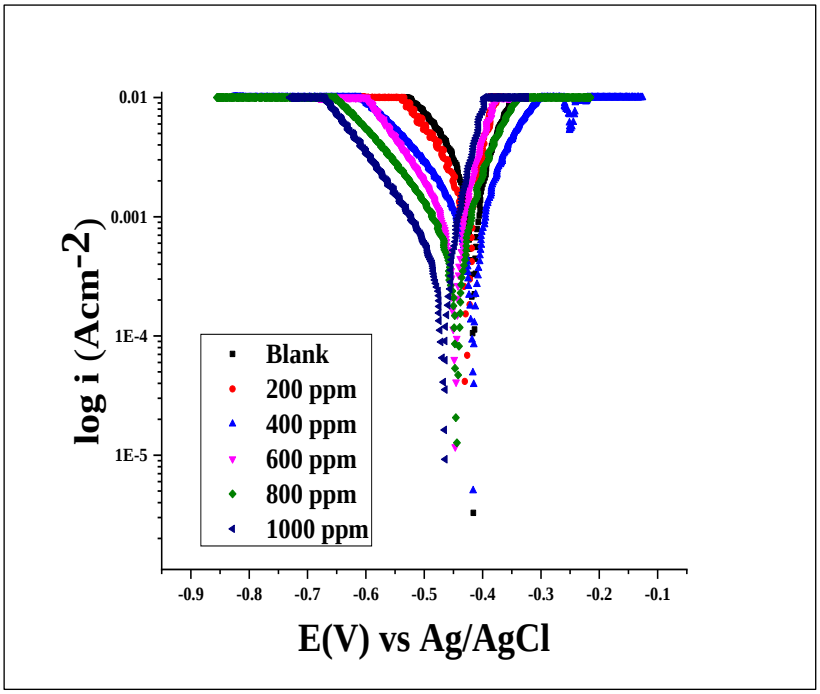


Figure 5.8: Polarization curves for mild steel in absence and presence of different concentration of [BzEImCl]

Table 5.12: Polarization parameters for mild steel in 0.5 M H_2SO_4 solution in absence and presence of varying concentration of [BzEImBr] & [BzEImCl]

ImILs	Conc. (ppm)	β_a (mV/dec)	$-\beta_c$ (mv/dec)	$E_{corr.}$ (mV)	$i_{corr.}$ ($\mu A/cm^2$)	R_p (Ω)	C_R (mmpy)	%IE
[BzEImBr]	**Blank**	253.02	141.99	-417.82	4041.20	9.45	46.95	-----
	200	175.46	68.14	-427.00	2255.00	9.77	26.20	44.02
	400	204.83	106.56	-417.66	1251.10	24.33	14.53	69.04
	600	166.96	69.10	-448.07	1038.50	20.43	12.06	74.30
	800	194.93	92.58	-445.20	899.13	24.82	10.45	77.73
	1000	176.37	72.61	-429.71	878.53	31.03	10.20	78.26
[BzEImCl]	**Blank**	164.96	61.54	-416.10	1160.50	16.68	13.55	---
	200	206.41	98.40	-426.01	1026.10	28.20	11.92	11.58
	400	159.54	66.12	-430.99	618.38	32.85	7.18	46.71
	600	175.10	70.78	-429.49	584.51	37.43	6.79	49.63
	800	158.60	53.26	-431.17	174.58	99.18	2.02	84.96
	1000	182.83	53.83	-437.34	158.42	114.01	1.84	86.35

As the results obtained from the polarization Taffel plots the current density values deduced as concentration of inhibitor increase for both [BzEImBr] and [BzEImCl] inhibitor. It indicates the good protective layer formation on mild steel surface and excellent inhibition efficiency of inhibitors. The more cathodic shifting of E_{corr} values with less than changes of 85 mV reveal mixed type of inhibition with pronounced the cathodic inhibition. The maximum inhibition efficiency is 78.26 % & 86.35% for [BzEImBr] and [BzEImCl] inhibitor respectively. All the results of polarization study show good agreements with gravimetric measurements.

5.2.3 Electrochemical impedance measurements

The electrochemical impedance measurements were carried out by low amplitude (±10 mV) AC signal as a function of frequency (100 KHz to 10 mHz). The electrochemical impedance measurements used to study the electrical properties of conductive material and their interface by applying external electrical impulse in form of voltage (V) as a driving force. (15) Impedance test provide the information of surface resistance, capacitance, inhibitory potential of an inhibitor and the nature of the inhibition process. All the impedance experiments perform at OCP and parameters such as solution resistance (Rs), charge transfer resistance (Rct), double layer capacitance (C_{dl}) in absence and presence of studied inhibitors in 0.5 M H_2SO_4 solution calculated by fitting the experimental data to the Randless equivalent circuit.

The EIS results are represented in the form of Nyquist plots in **Figure 5.9 & 5.10** in absence and presence of various concentration of bothy inhibitor [BzEImBr] and [BzEImCl] respectively. A perfect semicircle represents a single time constant. The deviation in the shape of semicircle attributed to the interfacial frequency dispersion associated with the heterogeneity, roughness and adsorption of inhibitor on metal surface. The diameter of semicircle or value of Rct is increases as the concentration of both inhibitor increases revealed that charge transfer mechanism oversees in most corrosion responses at metal electrolyte interface [16]. Decrease in C_{dl} values in the presence of ionic liquids, caused by a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the water molecules are replaced by ionic liquids molecules [17]. The charge transfer mechanism also supported by the bode phase angle plots with single maxima in the mid frequency region depicted in **Figure 5.11 & 5.12**. In case of ideal capacitor, the phase angle is 90^0 in bode plots. Smaller the phase angle than the 90^0 indicate the depression in Nyquist semi-

circle plots and confirming the mentioned equivalent circuit. Furthermore, the increment in the phase angle with the increasing concentration of both studied inhibitors is directly correlated with the adsorption of inhibitor molecules and protective layer formation [18]. The values of phase angle and impedance (Z) become zero at high frequency also indicate the resistive behaviour of solution [19].

The EIS data calculated by the simulation of equivalent circuit fitting method are tabulated in the Table 5.13.

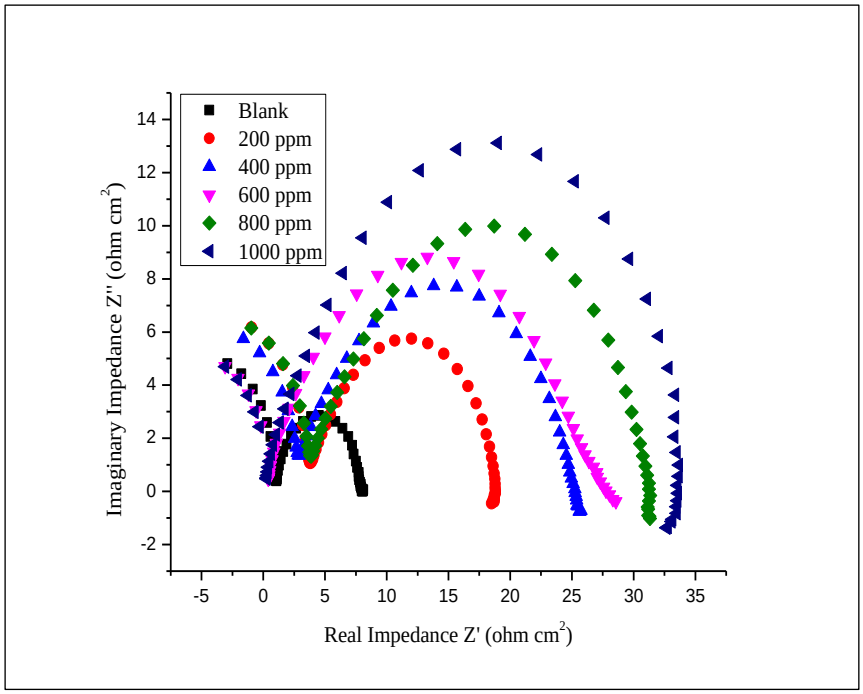


Figure 5.9: Nyquist plots for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImBr]

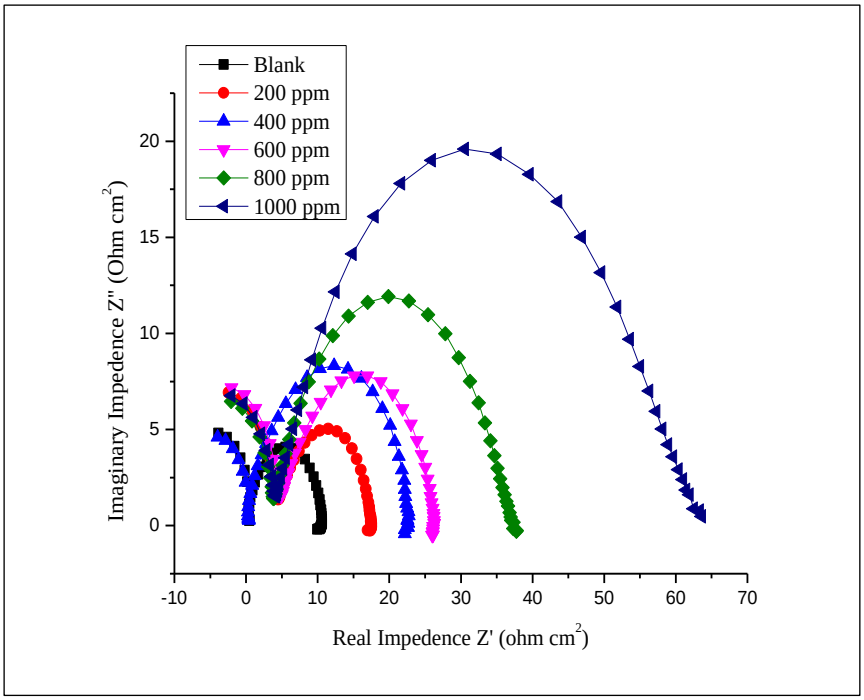


Figure 5.10: Nyquist plots for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImCl]

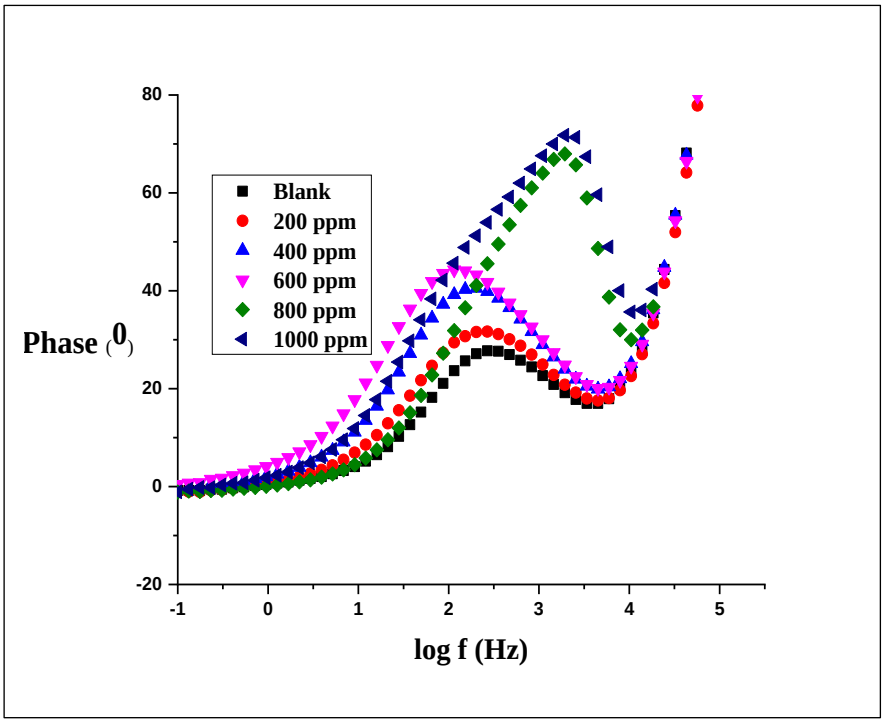


Figure 5.11: Bode phase angle plots (Phase angle vs. log f) for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImBr]

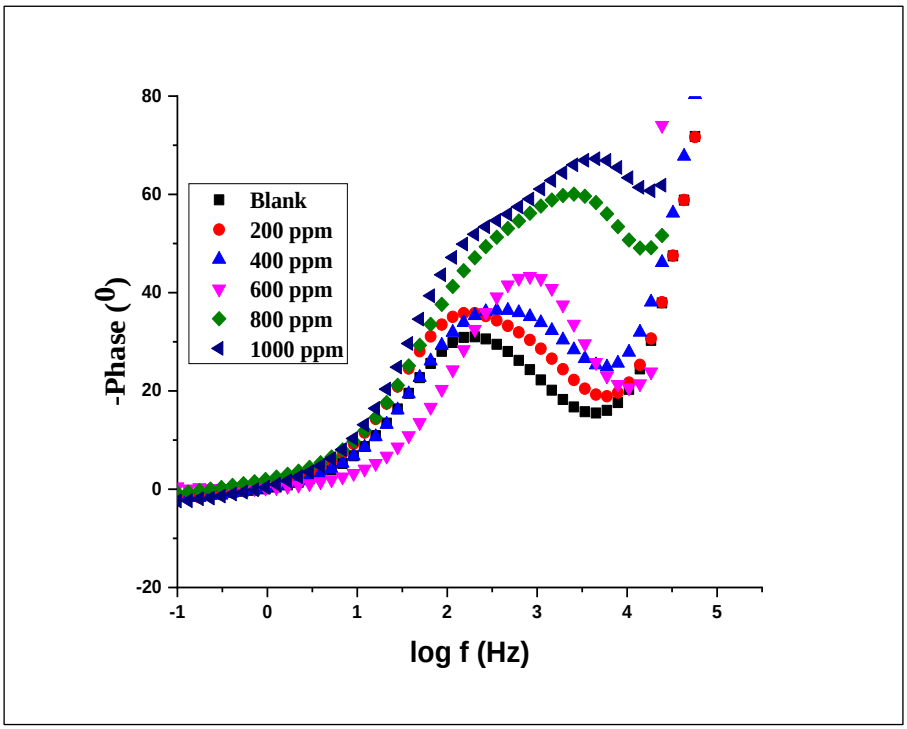


Figure 5.12: Bode phase angle plots (Phase angle vs. log f) for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImCl]

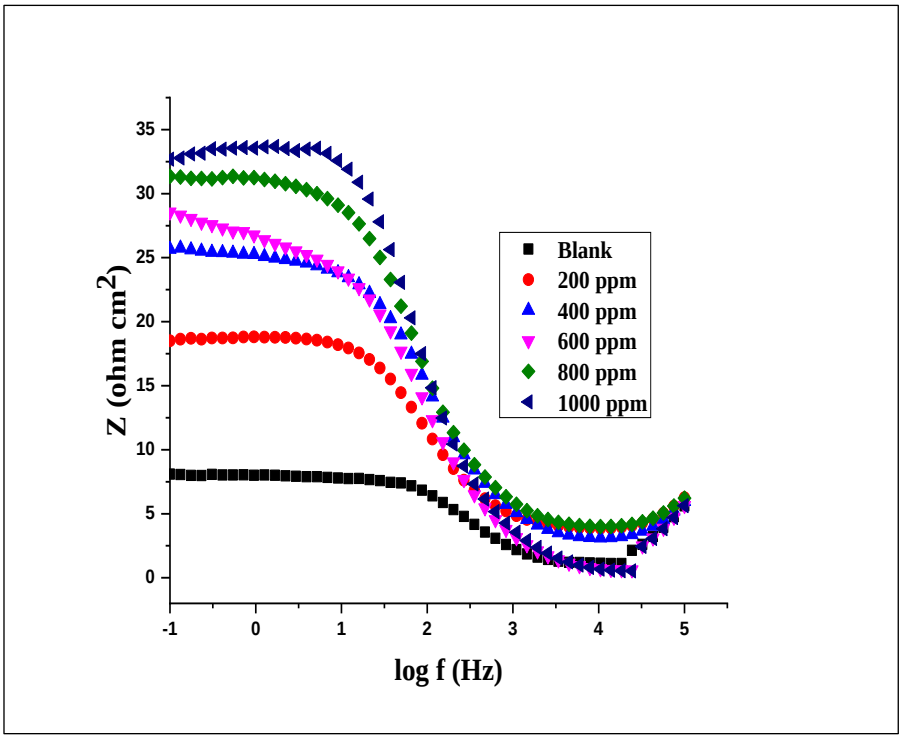


Figure 5.13: Bode modulus plots (Z vs. log f) for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImBr]

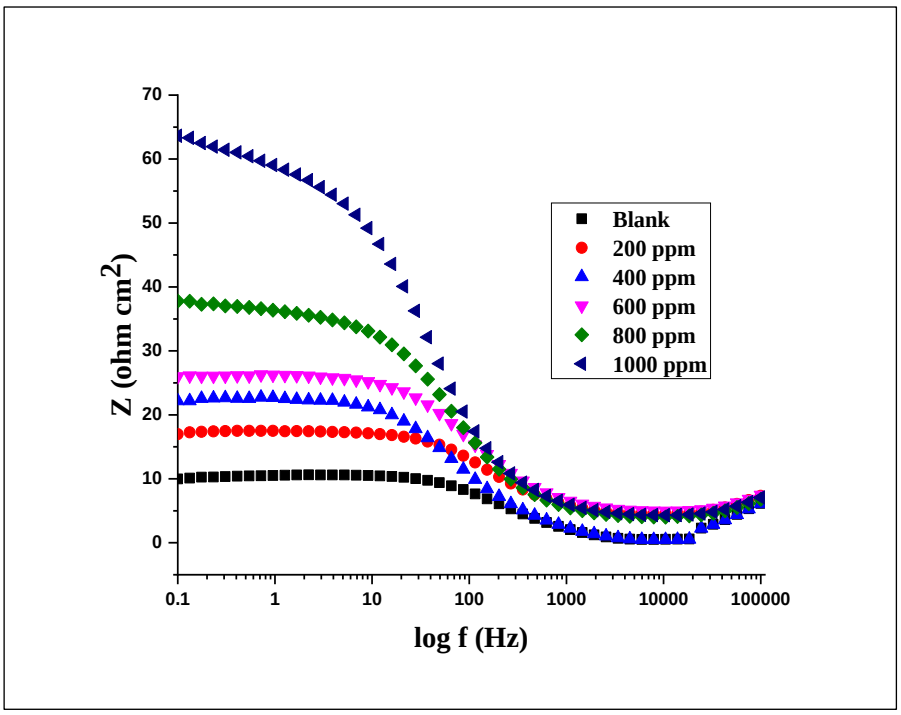


Figure 5.14: Bode modulus plots (Z vs. log f) for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImCl]

Table 5.13: EIS parameters for mild steel corrosion in 0.5 M H_2SO_4 solution in absence and presence of varying different concentration of [BzEImBr] & [BzEImCl]

Inhibitors	Conc. (in ppm)	R_s (Ω Cm^2)	R_{ct}(Ω cm^2)	f_{max} (Hz)	C_{dl} (µFcm^{-2})	IE (%)
[BzEImBr]	**Blank**	0.29	7.81	202	100.93	---
	200	0.44	18.06	115	76.66	56.75
	400	0.76	24.94	86.9	73.47	68.68
	600	0.38	28.22	86.9	64.93	72.32
	800	0.45	30.84	81.2	63.58	74.67
	1000	0.25	32.55	78.41	62.39	76.00
[BzEImCl]	**Blank**	0.19	9.77	153	106.52	-----
	200	0.86	16.14	115	85.79	39.46
	400	0.41	21.79	86.9	84.09	55.16
	600	1.32	24.78	86.9	73.94	60.57
	800	0.85	36.95	65.5	65.79	73.55
	1000	1.02	62.58	49.4	51.50	84.38

In the present work the R_{ct} values are continually increase in compare to the blank solution while the double layer capacitance which is inversely related to the thickness of the protective layer formed on the mild steel surface is decrease gradually. Both the parameters strongly support the inhibition of mild steel corrosion in presence of [BzEImBr] & [BzEImCl] inhibitor. The maximum inhibition efficiency was obtained 76.00% in case of [BzEImBr] inhibitor at 1000 ppm concentration while the 84.38% for [BzEImCl] inhibitor at 1000 ppm. The single time maxima at mid frequency region and zero tends of phase angle and impedance (Z) at high frequency region in the bode plots obtained for both studied inhibitor support strongly the protective layer formation and excellent inhibition tendency of both inhibitors.

5.3 Kinetic and thermodynamic parameters

The thermodynamic investigation & kinetic activation model are important techniques to study the corrosion inhibition mechanism and explain the features of protective action of both studied inhibitors at different temperatures [20]. The activation energy parameter determined by employed the Arrhenius equation (5.4).

$$\ln C_R = \ln A - \frac{E_a}{RT} \qquad (5.4)$$

Where, (CR) represents the corrosion rate, (E_a) is the energy of activation, (R) is the gas constant, and (A) is the pre-exponential factor. Another formulation of transition state equation (5.5) used to determine enthalpy of adsorption ΔH_{ads} and entropy of adsorption ΔS_{ads}.

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta Sa}{R}\right) \exp - \left(\frac{\Delta Ha}{RT}\right) \qquad (5.5)$$

The terms of the equation are, Plank's constant (h), Avogadro's number (N), the activation entropy (ΔS_a), and the activation enthalpy (ΔH_a) [21].

The activation energy term is defined as the minimum energy required to convert reactant to product such as rust in the corrosion phenomenon. The low activation energy associate with the high metal dissolution while the high activation energy reveals the high energy barrier for metal dissolution in electrolytic solution [22]. The more than 20kJ per mol activation energy suggest that the corrosion inhibition process is mainly controlled by the surface reactions [23]. Activation energy parameter also helpful to described the adsorption inhibition mechanism such as physical adsorption or chemisorption [24]. The positive values of enthalpy indicate endothermic nature of metal dissolution while the negative values of entropy indicate the active complex in rate determining step represents association rather than dissociation which signify the decrement in the stochastic conversion from reactants to activating complexes [25].

The arrhinias plots of the relations between *ln* (CR) and 1/T are depicted in **Figure 5.15 & 5.16.** As seen, a linear relation is obtained and the slopes of the straight lines is ($-E_a/R$) hence, the values of the activation energy (E_a) in the presence and absence of various concentrations of [BzEImBr] & [BzEImCl] were determined. The plots of *ln* C_R/T versus 1/T for the studied ionic liquids are presented in **Figure 5.17 & 5.18**. The slope of the obtained straight lines equals ($-\Delta H^*/R$) and the intercept is

(lnR/Nh + ΔS^*/R), hence the values of ΔH_{ads} and ΔS_{ads} can be estimated. At definite concentration ranges of the ionic liquids the activation parameters for mild steel in 0.5 M H_2SO_4 medium were gathered and listed in Table 5.14. The results reveal that with the existence of both inhibitors the activation energy rises and obtained 68.41 kJ & 88.50 kJ, the increasing value of enthalpy with increasing concentration revealed the more energy required for metal dissolution process. The negative value of entropy signifies the rate determining step is active complex association while the increment in the entropy with increasing concentration for both studied inhibitor due to the water molecule desorption [26].

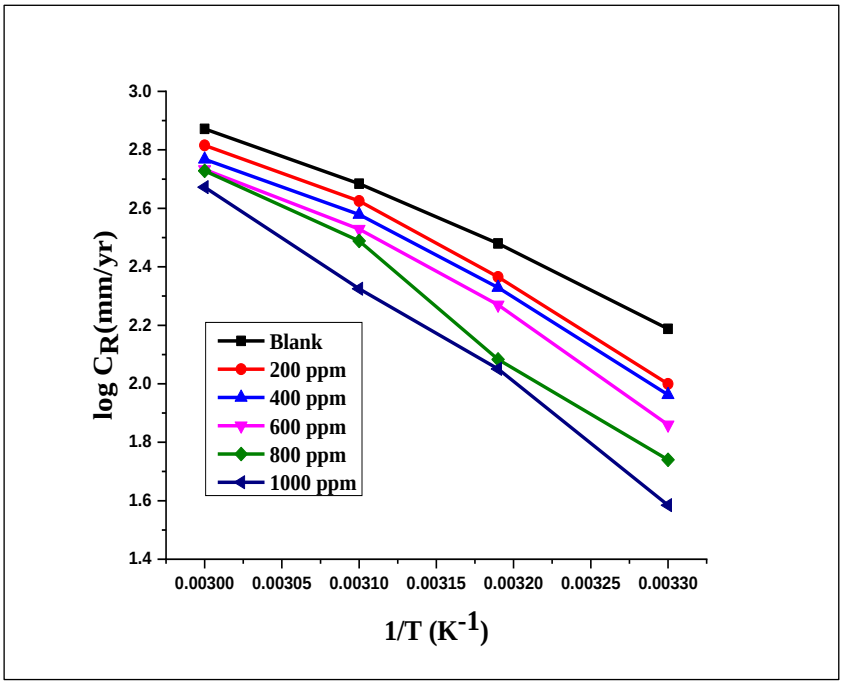


Figure 5.15: Arrhenius plots for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImBr]

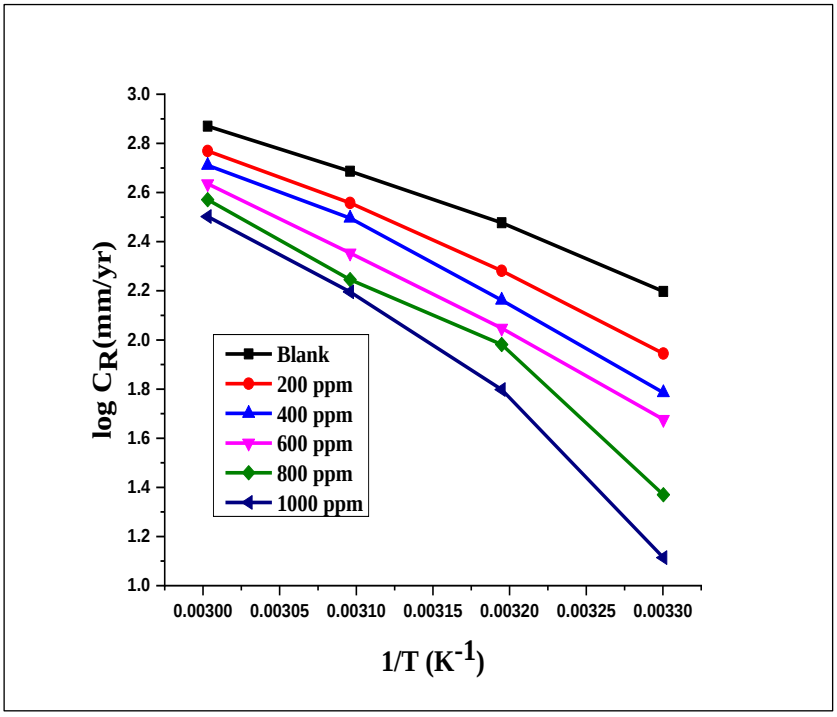


Figure 5.16: Arrhenius plots for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImCl]

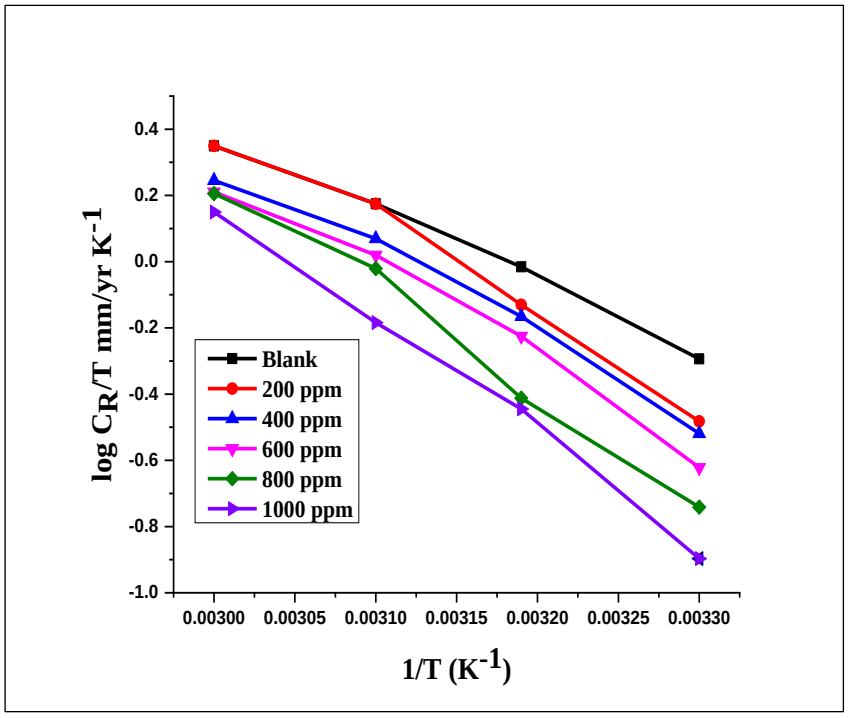


Figure 5.17: Plots of log (C_R/T) versus (1/T) for mild steel in in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImBr]

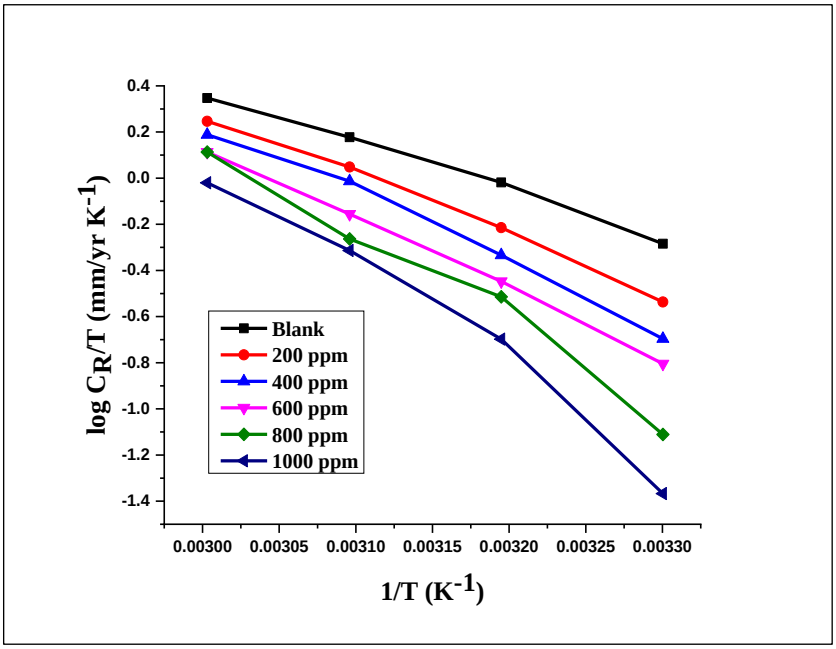


Figure 5.18: Plots of log (C_R/T) versus (1/T) for mild steel in in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImCl]

Table 5.14: Activation energy and Thermodynamic parameters for mild steel in 0.5 M H_2SO_4 solution in absence and presence of different concentration of [BzEImBr] & [BzEImCl]

Inhibitors	Concentration (ppm)	E_a (kJmol^{-1})	ΔH_a (kJmol^{-1})	ΔS_a (JK^{-1}mol^{-1})
[BzEImBr]	Blank	43.67	41.03	-66.96
	200	51.67	49.01	-44.66
	400	52.47	54.25	-32.79
	600	55.79	53.15	-26.81
	800	65.14	62.50	-5.04
	1000	68.41	65.77	3.29
[BzEImCl]	Blank	43.09	40.45	-68.76
	200	53.21	50.57	-40.14
	400	60.22	57.58	-19.79
	600	61.53	58.89	-17.97
	800	74.96	76.01	33.60
	1000	88.50	85.86	61.66

5.3.1 Adsorption isotherms study

The nature of interaction between the studied ionic liquids and mild steel surface can be explore by performing adsorption isotherm studies. Several types of adsorption isotherm models are existed to describe the relation between the surface coverage and various concentration range of studied ionic liquids at a particular temperature such that Langmuir, Freundlich, Temkin etc. The best fitted adsorption isotherm provides a straight-line graph with a correlation coefficient of unity. The adsorption equilibrium constant K_{ads} also calculated with the help of slope of the graph. The K_{ads} values employed in the equation number (5.6) to determine the value of $\Delta G_{ads.}$

$$\Delta G_{ads} = -RT\ ln\ (55.5K_{ads}) \qquad (5.6)$$

The various significant information such that spontaneity of adsorption process, type of adsorption easily explained on the basis of $\Delta G_{ads.}$ as the literature reported that the negative values of Gibbs free energy associated with the spontaneity of the adsorption process. The Gibbs free energy up to the -20kJ/mol revealed the electrostatic interaction of physisorption, higher than the -40kJ/mol signify the charge transfer between the adsorbate and adsorbent or chemisorption [27-28].

In the present work of the study of corrosion inhibition effect of ionic liquids of different anions on mild steel surface. The Freundlich model found to be best suitable for [BzEImBr] ionic liquid adsorption on mild steel surface while the Langmuir model fitted with [BzEImCl] ionic liquids. The K_{ads} decrease with increasing temperature due to desorption of ionic liquids at high temperature. The Freundlich adsorption isotherm plot for [BzEImBr] obtained in **Figure 5.19** on plotting log(θ) against log (C_{inh}) by following equation (5.7).

$$log(\theta) = \log(Kads) + \left(\frac{1}{n}\right)\log(C_{Inh}) \qquad (5.7)$$

Where C_{inh} = Concentration of investigated inhibitors and K_{ads} = Adsorptive equilibrium constant, θ =Surface coverage, n is the empirical constant (0<n<1)

The Langmuir adsorption isotherm plots for [BzEImCl] obtained in **Figure 5.20** on plotting (C_{inh}/θ) versus C_{inh} by following the equation nu. (5.8) [29].

$$\frac{Cinh}{\theta} = \frac{1}{K_{ads}} + C_{Inh} \qquad (5.8)$$

Where C_{inh} = Concentration of investigated inhibitors and K_{ads} = Adsorptive equilibrium constant.

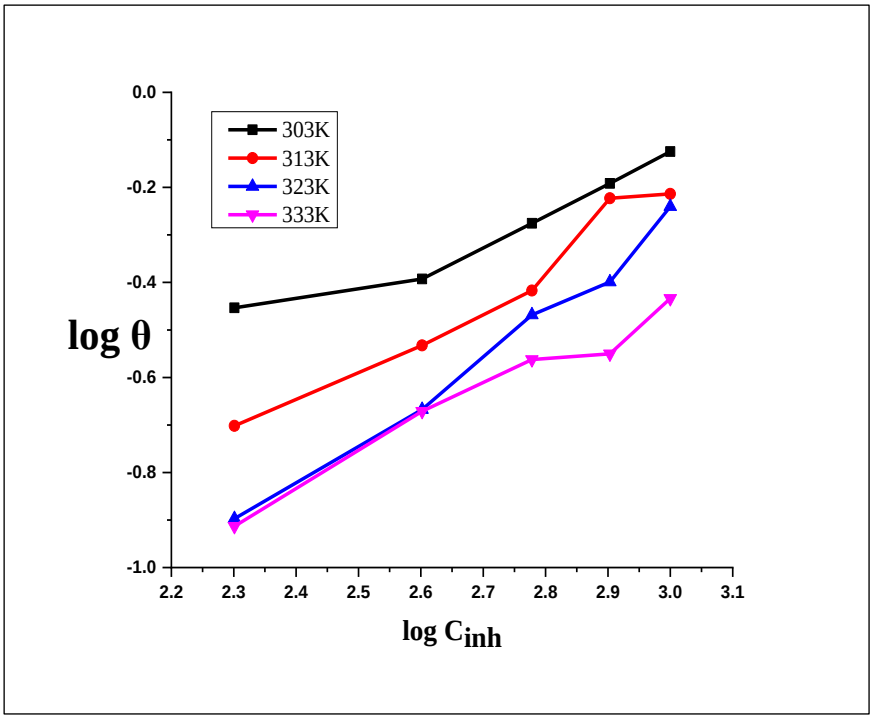


Figure 5.19: Freundlich adsorption isotherm plots in absence and presence of [BzEImBr] at different temperature

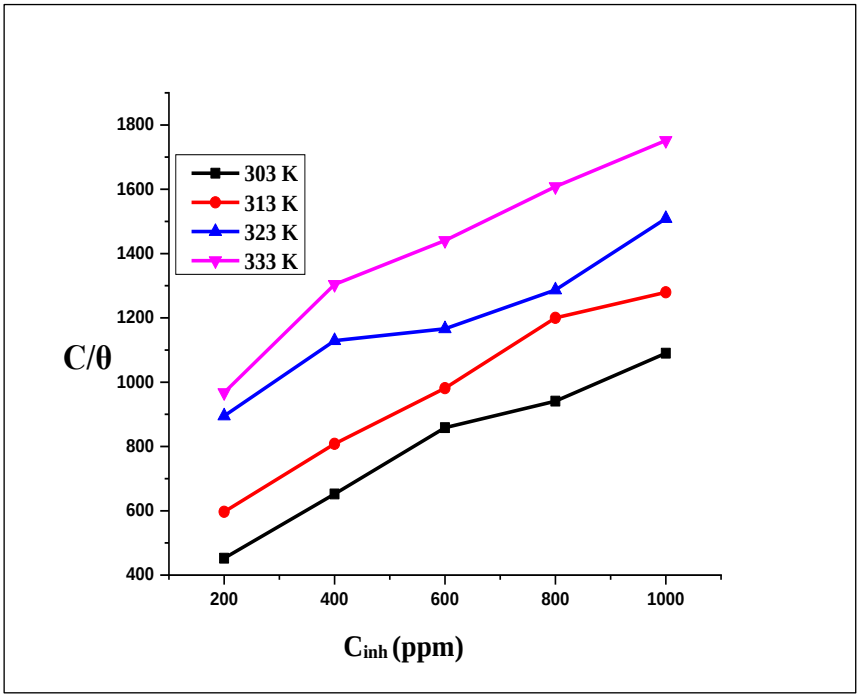


Figure 5.20: Langmuir adsorption isotherm plots in absence and presence of [BzEImBr] at different temperature

The Table 5.15 illustrated the adsorption isotherm study results for both ionic liquids in 0.5 M H_2SO_4 medium for mild steel.

Table 5.15: Adsorption parameters in the presence of ImILs on mild steel surface

Inhibitors	Temperature (K)	K_{ads}	R^2	Slope	ΔG^0_{ads}(kJmol^{-1})
[BzEImBr]	**303**	25859.49	0.91545	0.47839	-35.73
	313	3738.69	0.9482	0.73971	-31.85
	323	957.61	0.98481	0.91441	-29.21
	333	414.22	0.96103	0.64695	-27.80
[BzEImCl]	**303**	3032.14	0.97095	0.7811	-30.31
	313	2242.25	0.97687	0.8786	-30.52
	323	1280.11	0.93312	0.6933	-29.99
	333	1172.56	0.95312	0.9359	-30.68

For the present study the $\Delta G_{ads.}$ values obtained for [BzEImBr] (-35.73kJmol^{-1}, -31.85kJmol^{-1}, -29.21kJmol^{-1}, -34.15kJmol^{-1}) and for [BzEImCl] (-30.31kJmol^{-1}, -30.52kJmol^{-1}, -29.99kJmol^{-1}, -30.68kJmol^{-1}) which reveals the mixed type of interaction between the both ionic liquids and mild steel surface.

5.4 Surface morphology study

Surface morphological study is an important method which is confirm the protective layer formation. There are several tools available for exploring the morphology of metallic surface at the nano and micro scale such that scanning electron microscopy (SEM), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS) etc. [30].

5.4.1 Scanning electron microscopy (SEM)

Scanning electron microscopy is provide a high-quality surface image by employed high energy electron beam. SEM-EDS tool provide a flexibility to be used with combination of other methods. SEM examine the microstructural properties of solid surface [31-32].

In order to prepare the sample for SEM-EDS study mild steel coupons of dimensions 1.0 cm x 1.0 cm x 0.10 cm (length x width x thickness) were abraded and digressed with the help of emery papers of different grades and acetone before immersed into the 100 ml solution of 0.5 M H_2SO_4 in absence of inhibitor and presence of 1000 ppm concentrated solution of both studied inhibitors separately for 24-hour immersion time at 303 K. After 24-hour coupons are taken out from the solutions washed with double distilled water and acetone than dried in desiccator. **Figure 5.21 (a, b, c and d)** show the SEM-EDS image obtained for fresh mild steel coupon, mild steel coupon immersed in blank solution of 0.5 M H_2SO_4, mild steel coupon immersed in solution of 1000 ppm concentration of BzEImBr and mild steel coupon immersed in solution of 1000 ppm concentration of [BzEImCl] respectively.

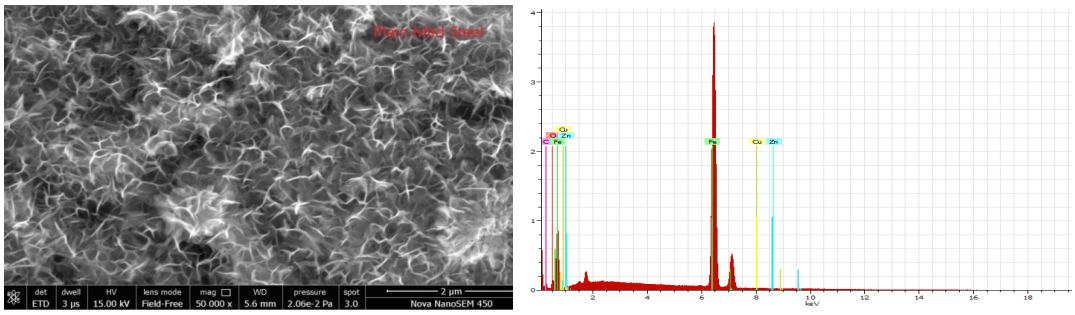


Figure: 5.21 (a)

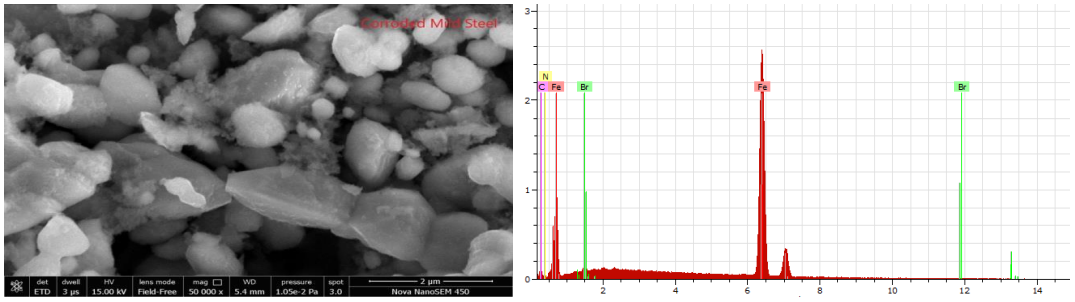


Figure: 5.21 (b)

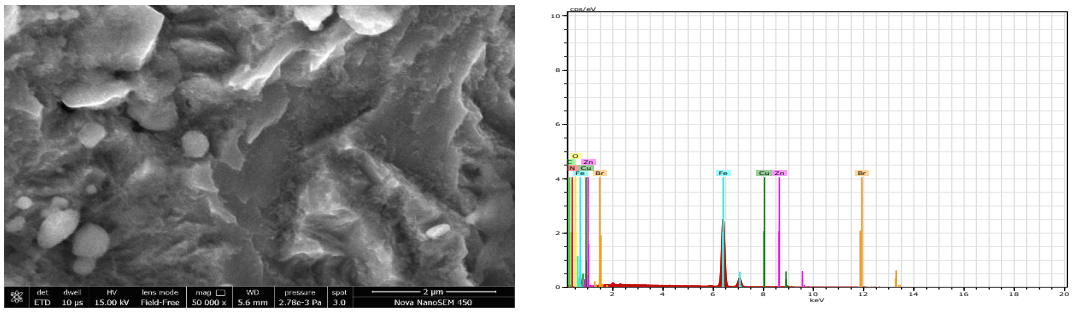


Figure: 5.21 (c)

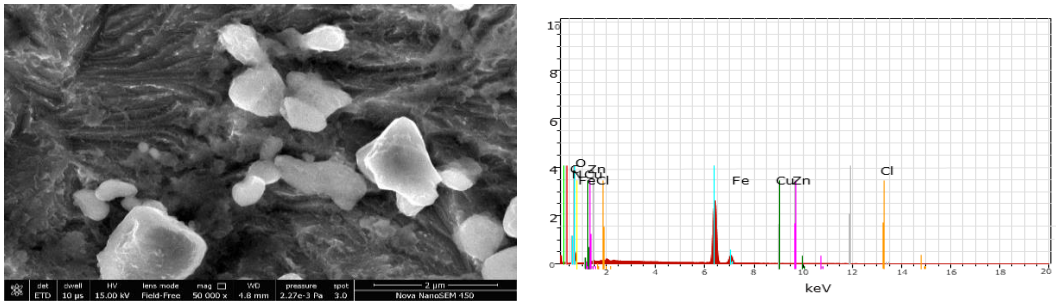


Figure: 5.21 (d)

Figure 5.21: SEM-EDS micrographs (a) Fresh mild steel coupon before immersion (b) Corroded mild steel coupon in 0.5 M H_2SO_4 (c) Mild steel coupon after immersion in 1000 ppm [BzEImBr] concentrated solution of 0.5 M H_2SO_4 for 24 hours at 303K (d) Mild steel coupon after immersion in 1000 ppm [BzEImCl] concentrated solution of 0.5 M H_2SO_4. for 24 hours at 303 K.

It is found that the surface of fresh mild steel coupon was smoothest, pour less and SEM-EDS graphs show the high amount of Fe percentage in it as illustrated in **Figure 5.21(a)** while the mild steel surface of **Figure 5.21(b)** is highly damaged rough with cavity and pits revealed the high oxidation in blank solution without inhibitor. On compare the **Figure: 5.21 (c) & 5.21 (d)** it is clear that the **Figure 5.21 (d)** is smoother than the **Figure 5.21 (c).** EDS graphs also reported that the percentage of Fe is obtained more for [BzEImCl] than the [BzEImBr] and Cl peak for [BzEImCl] & Br peak for [BzEImBr].

5.5 Proposed corrosion inhibition mechanism in presence of imidazolium based ionic liquids of different anions in 0.5 M sulphuric acid.

As the literature reported that the most probable mechanism is the blocking of anodic and cathodic reaction by adsorption of ionic liquids on mild steel surface. It is a substitution reaction in which inhibitor molecules substitute the already adsorbed water molecules on mild steel surface [33-34]. This substitution reaction represented as.

$$M + nH_2O \rightarrow M(H_2O)_n$$

$$IL(sol.) + nH_2O\ (adsorbed) \rightarrow IL(adsorbed) + nH_2O\ (sol.)$$

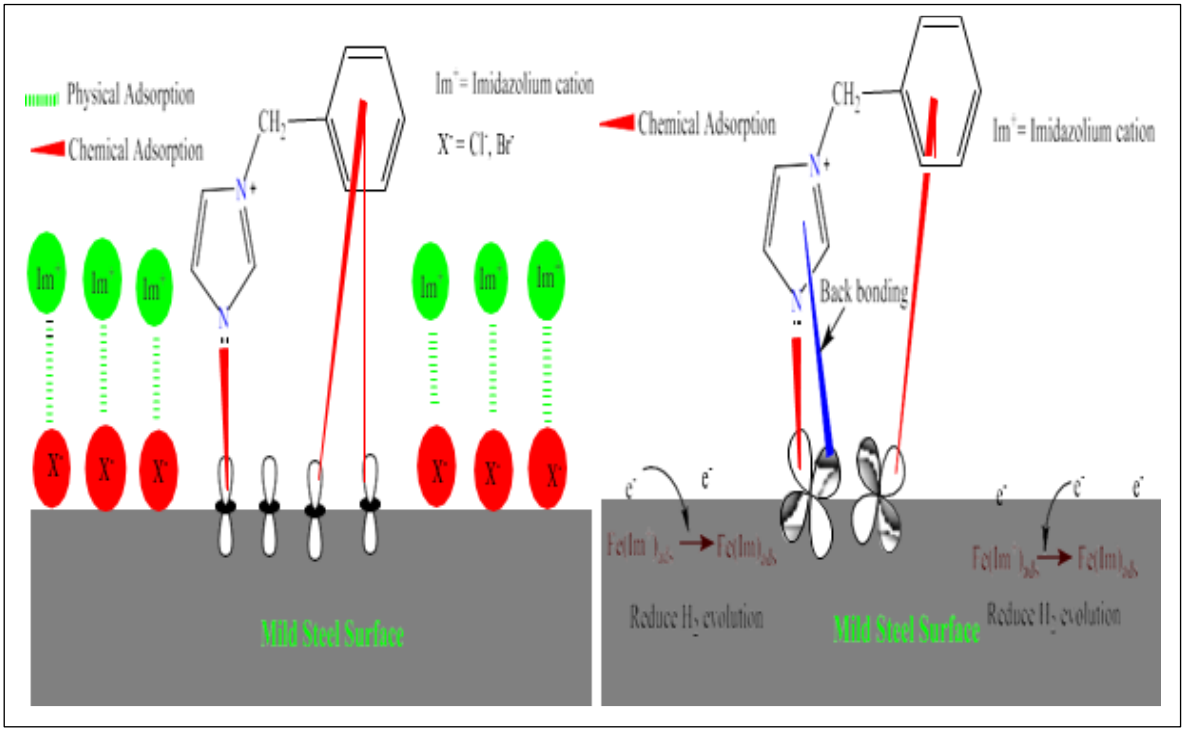
5.5.1 Reaction at anode

Firstly, the anionic part (Br^-, Cl^-) of the imidazolium based ionic liquid adsorbed on mild steel surface than the negatively charged mild steel surface attracts the positively charged imidazolium cation (Im^+) by electrostatic force of attraction. It is a substitution reaction in which water molecules substituted by the molecules of ionic liquids [35]. This effect forms a protective film on mild steel surface which is effectively alter the electrochemical reaction responsible for metal dissolution.

5.5.2 Reaction at cathode

The bulky Imidazolium cations substituted several numbers of water molecules from the mild steel surface. The electron of the mild steel surface adsorbed by imidazolium cation (Im^+) to maintain electro-neutrality and reduction in evolution of hydrogen gas from cathode. The donor- acceptor complex form between adsorbed ionic liquid inhibitor and mild steel surface by the donation of lone pair of nitrogen atoms and pi electrons of the benzyl ring to the empty d-orbitals of the mild steel surface. The

combined mutual donation and back bonding reinforce each other and block the mild steel surface [36].



Scheme 5.1: Mechanism of corrosion inhibition of mild steel in 0.5 M H_2SO_4 with ImILs.

The magnitude of the decrease in corrosion rate and increase in the inhibition efficiency decides the efficiency of the inhibitor. In the present study, the high electronegativity of chlorine anion enhances inter ionic interactions with the metallic surface and improves the inhibition efficiency of [BzEImCl] imidazolium-based ionic liquid inhibitor [37].

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Conclusion

Metallic materials are showing great importance in the industrial and infrastructure developments. Corrosion is realized a major issue for developing nations as it results high economical and social losses. Corrosion can lead to severe failures in automotive devices, bridges, tanks, containers, turbines, buildings and many other parts of machines.

In metallic materials mild steel (MS) is widely used due to low carbon content and many other specific characteristics such that low cost, high tensile strength, easily weldable, good malleability etc. In industries mild steel is used to design tanks, pipes, reaction vessels etc. Sulphuric acid solution is used as cleaning agent in descaling and pickling process due to cost effectiveness, low fumes and non-corrosive nature of sulphate ions.

The use of inhibitor is most popular technique of corrosion control or prevention. Past of decades corrosion scientists focuses to develop "green inhibitor" which is cost-effective, non-toxic and eco-friendly in nature. The utilization of ionic liquids as green corrosion inhibitor is the result of this study. Ionic liquids show great importance in the field of corrosion inhibition due to having several fascinating properties such as low melting point, low toxicity, negligible vapour pressure, high thermal and chemical stability, non-flammability, high ionic conductivity etc. Their synthesis and designing also follows the principles of green chemistry.

In the present work four imidazolium based ionic liquids namely: 1-Ethyl-3-ButylImidazolium Bromide [BuEImBr], 1-Ethyl-3-PentylImidazolium Bromide [PEImBr], 1-Ethyl-3-BenzylImidazolium Bromide [BzEImBr], 1-Ethyl-3-BenzylImidazolium Chloride [BzEImCl] have been synthesized by microwave irradiation method and characterized by various spectroscopic technics such that ^{1}H NMR, ^{13}C NMR, IR and Mass Spectrometry, to study the corrosion inhibition performance on mild steel in 0.5 M sulphuric acid medium.

The following techniques used for study:

1. Weight Loss Measurements (WL)
2. Potentiodynamic Polarization (PDP)
3. Electrochemical Impedance Spectroscopy (EIS)
4. Thermodynamic and Kinetic Parameters
5. FE-SEM with EDS

The following concluding remarks can be derived from the above studies.

- Gravimetric or weight loss measurement clearly revealed that the weight loss of mild steel coupon is decreased with an increase in concentration of imidazolium based ionic liquids at all investigated temperatures. This is because a protective film form on mild steel surface as the concentration of ionic liquids increased. The corrosion parameters such as corrosion rate and inhibition efficiency were decreased and increased respectively with increasing concentration of all four ionic liquids. The order of inhibition efficiency of all investigated four ionic liquids was as followed: [BzEImBr] < [BuEImBr] < [BzEImCl] < [PEImBr].
- The effect of temperature on corrosion parameters clearly indicated that the equilibrium between adsorption and desorption process shifted towards the desorption site as the temperature raised. The results of temperature study revealed that the corrosion rate and inhibition efficiency increased and decreased respectively with an increase in temperature. This is because the decrease in the surface coverage of inhibitor molecules on mild steel surface.
- The optimum concentration of inhibitor was found at which no significant change in the inhibition efficiency observed with immersion time. This is because sufficiently adsorption of inhibitor molecules through electrostatic force of attraction. In the present study the highest inhibition efficiency of [BuEImBr], [PEImBr], [BzEImBr] and [BzEImCl] are 89.16%, 92.78%, 75.58% and 92.21% respectively was observed over a long exposure period 3 hour which confirmed the stability of protective film of inhibitor molecules on mild steel surface in 0.5 M H_2SO_4 medium at 303 K.
- The PDP results indicated that all investigated ionic liquids reduced the both anodic and cathodic Tafel reactions and follow mixed type of inhibition. The decreasing values of corrosion current density in presence of inhibitors suggests the effective blocking of active sites of mild steel surface.
- The increasing value of charge transfer resistance R_{ct} and decreasing value of double layer capacitance C_{dl} with increasing concentration of ionic liquids suggest that the inhibition process is mainly controlled by a charge transfer process.
- The negative values of Gibb's free energy of adsorption (ΔG_{ads}) indicated an efficient and spontaneous adsorption process and stability of adsorbed protective film on the mild steel surface.

- The adsorption isotherm study showed that the Langmuir model of adsorption isotherm was best fitted for [BuEImBr], [PEImBr] and [BzEImCl] while [BzEImBr] followed the Freundlich model of adsorption isotherm.
- The thermodynamic parameters $E_{a,}$ and ΔH_{ads} indicated that the metal dissolution process is endothermic in nature and mainly controlled by surface reactions. The increasing values of ΔH_{ads} support the protective film formation on mild steel surface.
- In the presence of investigated ionic liquids entropy of adsorption is increases with respect to blank. The negative value of entropy indicated the decrement in the translation motion of inhibitor molecules. The increasing value of entropy suggested that the activation complex in rate determining step represent association rather than dissociation step. The moderate positive value of entropy at optimum concentration indicated the adsorption of inhibitor molecules in a disordered fashion.
- The SEM micrographs showed smooth images of mild steel surface in presence of ImILs compare to the image in presence of blank solution of 0.5 M H_2SO_4 medium. These results indicated the formation of inhibitor film on mild steel surface in presence of ImILs.
- The EDS spectra clearly showed the N, Br and Cl peak in presence of ImILs while these peaks were absent in blank solution which indicated the ImILs adsorption on mild steel surface.
- All obtained results are showed good agreement to each other and support the good corrosion inhibition performance of all investigated ImILs.

On the basis of all collective results, it can be concluded that all investigated imidazolium based ionic liquids act as efficient corrosion inhibitor in 0.5 M H_2SO_4 medium. However, the results obtained from the various techniques revealed that the Ionic liquids which have greater alkyl chain show better inhibition efficiency compare to the IL having small alkyl chain, similarly the ImIL with chloride anion show better inhibition tendency compare to the ImIL with bromide anion. Due to the more surface coverage and more electrostatic attraction between the ImILs and mild steel surface. These results also suggest the inhibition mechanism which involves physical adsorption as well as chemical adsorption.

Summary

The infrastructure and industrial developments are important consideration for a developing and developed nation. Mild steel is an engineering material used world wild to reduce the cost of maintenance and production. Mild steel material has great importance in the field of oil and petrochemical industries, automobile industries etc. due to easily availability, cost effectiveness, good malleability, high ductility, high tensile strength and many other properties. Acids such that hydrochloric acid, sulphuric acid, nitric acid are used as a cleaning agents in acid descaling and acid pickling process. The corrosion of mild steel is a dangerous phenomenon which is affect the growth of the nation as well as the health of humans. Some of major incidents such that Bhopal chemical plant explosion, Gokhale bridge collapsed in Andheri etc. are the examples of corrosion failure in India. Many corrosion scientists and researchers also concluded the economic impact of the corrosion in their research. The NACE (National Association of Corrosion Engineers) study shows the estimated annual global cost of corrosion as approximately US $ 2.5 trillion equating to 3.4% of the global GDP of 2013. It is not possible to completely removed or escaped the corrosion so the prevention methods gain more attention. Some of important prevention techniques such that selection of material, proper designing, protective coating, cathodic and anodic protection, use of inhibitors etc. are used to protect the material. In acidic medium the use of corrosion inhibitor shows considerable practical importance as one of the most effective prevention methods because of having both metallic prevention and corrosive environment reduction nature. A small concentration of corrosion inhibitor is enough to retard or block the anodic and cathodic corrosion reaction on metallic surface. The adsorption phenomenon physisorption or chemisorption or both are the part of inhibition process. The present research work explored the synthesis and anticorrosive application of imidazolium based ionic liquids (ImILs) with different alkyl chain of cation and different anions on mild steel in 0.5 M H_2SO_4 medium. The methodology used for synthesis is based on the principle of the green chemistry and anticorrosive study was carried out by advance corrosion testing methods. The observations and results are presented in tabular and graphical forms. All the observations and obtained results are given in the thesis which are divided into the five chapters. The summary of these five chapters has been depicted below.

Chapter 1 provide the detail description about the concept of corrosion, historical background of corrosion study, cause of corrosion, classification of corrosion process, various form of corrosion, corrosion rate and factor affecting the corrosion rate, electrochemical theory of corrosion, economic and social impact of corrosion, corrosion prevention methods, corrosion inhibitors and criteria for selection of corrosion inhibitor. Ionic liquids are also discussed with their structural specification. Most of effective ionic liquids are comprised by novel anion and cation which contains hetero atoms N, O, P, S etc. with polar functional group such as such as $-NO_2$, -OH, $-COOC_2H_5$, $-NH_2$, -COOH, $-CONH_2$ etc. These polar functional groups and conjugated π electrons of multiple bonds (double and triple) act as adsorption centers during metal-inhibitor interactions. Ionic liquids are promising corrosion inhibitor towards corrosion of mild steel in acidic medium due to their remarkable physio-chemical properties such as low vapor pressure, low critical micelle concentration (CMC), excellent thermal and chemical stability, water dissolving capacity, ionic conductivity, non-flammability as well as excellent inhibition efficiency in different electrolytic media. The literature review part included research of last ten years of the corrosion inhibition by imidazolium based ionic liquids on mild steel in acidic medium at different temperatures. The literature described the previous work, instrumentation, reagents and mechanism of corrosion inhibition.

Chapter 2 deals with the materials, methods and methodology adopted for experimental work. It is described the details about the experimental setup and experimental procedure to fulfil the aims and objective of the present studies. A brief knowledge of some conventional and advanced tools and techniques employed to investigate the corrosion inhibition performance of ImILs are also illustrated in this chapter.

Chapter 3 deals with the procedure adopted for the synthesis of ImILs. Chapter also provide the detail information about the quality of the chemicals used in the entire research work. The imidazolium based ionic liquids namely 1-Ethyl-3-ButylImidazolium Bromide [BuEImBr], 1-Ethyl-3-PentylImidazolium Bromide [PEImBr], 1-Ethyl-3-BenzylImidazolium Bromide [BzEImBr], 1-Ethyl-3-BenzylImidazolium chloride [BzEImCl] have been synthesized by microwave

irradiation method and characterized by various spectroscopic technics such that ^{1}H NMR, ^{13}C NMR, IR and Mass Spectrometry.

Chapter 4, In the past decades the use of ionic liquids as corrosion inhibitor is the topic of interest of research in the field of material science. Various chemical variants of ionic liquids are synthesized among of these Imidazole based ionic liquids reported as excellent corrosion inhibitor on mild steel material in acidic medium. This chapter deals with the effect of side alkyl chain of cation on the corrosion inhibition parameters. This chapter also included results and graphs of various techniques to find out the relevance of the work. The finding results of various techniques of corrosion inhibition of ionic liquids with different alkyl chain was showed good agreement to each other which are discussed below.

1.1 Weight Loss Measurements:

The weight loss (ΔW) and Corrosion rate (C_R) was calculated using Equations. (1) and (2) respectively.

$$\Delta W = W_1 - W_2 \qquad (1)$$

W_1 = Weight of coupon before immersion in mg

W_2 = Weight of coupon after immersion in mg

$$C_R = \frac{87.6 * \Delta W}{AtD} \qquad (2)$$

C_R is the corrosion rate (mmpy), ΔW is weight loss of metal (mg), A is the area of the coupon (cm^2), t is the exposure time (hours) and D is the density of mild steel sample (7.85 g cm^{-3}). The percentage inhibition efficiency (% IE) was calculated using Equations. (3) and (4).

$$\% IE = \frac{C_{R_o} - C_{R_i}}{C_{R_o}} X100 \qquad (3)$$

C_{Ro} and C_{Ri} are corrosion rates in absence and presence of inhibitors.

$$\% IE = \frac{W_0 - W_i}{W_0} X100 \qquad (4)$$

W_o and W_i are weight losses in absence and presence of inhibitor.

The value of surface coverage (θ) was determined by Equations. (5)

$$\theta = \frac{\%IE}{100} \qquad (5)$$

The obtained results of weight loss study are described below in the following points.

- The [PEImBr] found to be more effective corrosion inhibitor compare to the [BuEImBr]. The maximum inhibition efficiency at optimum concentration (1000 ppm) for [BuEImBr] and [PEImBr] are 88.71% and 92.51% respectively at 303 K.
- As the concentration of inhibitor increase the corrosion rate is decrease for both inhibitor due to the formation of protective film on mild steel surface.
- As the temperature increase the corrosion rate is increase and inhibition efficiency is decrease gradually due to the desorption of adsorbed molecules of ionic liquids on mild steel surface. The high corrosion rate at higher temperature favors the physical interaction between the ionic liquid molecules and mild steel surface.
- All thermodynamic and kinetical parameters support the spontaneous and mixed type of adsorption mechanism for both ionic liquids.

4.2 Potentiodynamic Polarization Measurements (PDP)

The polarization study results were obtained in the form of polarization parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_c and β_a) and polarization resistance (R_p). The inhibition efficiency was calculated with the help of these parameters by using the equation (6).

$$\%IE = \frac{i^\circ corr - i^\circ inh}{i^\circ corr} X100 \qquad (6)$$

Where i°_{corr} and i^o_{inh} represent the corrosion current densities without and with corrosion inhibitor respectively.

Following points are described the results of potentiodynamic polarization study.

- The values of corrosion current density i_{corr} and polarization resistance R_p are regularly decrease and increase respectively with the increasing concentration of inhibitors due to the effectively adsorption of inhibitor molecules and blocking the exposed active sites of mild steel surface.
- The maximum change in corrosion potential (E_{corr}) is less than 85 mV for both inhibitor which suggest the mixed type of inhibition. The change in the value of anodic and cathodic taffel slope with increasing concentration of inhibitors also favors this statement.
- The results of PDP study suggest the following order of inhibition efficiency.

  [PEImBr] > [BuEImBr]

4.3 Electrochemical Impedance Spectroscopy (EIS)

The kinetics of electrode process and surface properties of the corrosion inhibition system was investigated with the help of Electrochemical Impedance Spectroscopy (EIS). The results of EIS study were obtained in semi-circle Nyquist plot form in absence and present of various concentrations of both ionic liquids on mild steel surface in 0.5 M H_2SO_4 solution. Furthermore, the diameter of the capacitive loop increases with increasing the concentrations of both inhibitors [PEImBr] and [BuEImBr]. It suggested that the corrosion of mild steel in 0.5 M H_2SO_4 solution is mainly controlled by a charge transfer process. The important parameters of EIS study Inhibition efficiency and double layer capacitance (C_{dl}) were calculated from Eq. (7) and (8) respectively.

$$\% IE = \frac{R_{ct}^{inh} - R_{ct}^{\circ}}{R_{ct}^{inh}} X100 \qquad (7)$$

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \qquad (8)$$

Where, R_{ct}^{inh} and R_{ct}° are the charge transfer resistance's with and without inhibitor. The results found from EIS are described below.

- EIS study revealed that on increasing the concentrations of [PEImBr] and [BuEImBr] in 0.5 M H_2SO_4 solution the values of R_{ct} increases and C_{dl} decreases which suggested the adsorption of inhibitor on mild steel surface.

- Bode plots also favors charge transfer mechanism due to having a one-time constant or single maximum.
- Bode modulus shows the strong dependence of impedance on the frequency. At low frequency the absolute impedance was increase with increasing concentration of imidazolium based ionic liquids revealed the enhancement of corrosion protection.

4.4 Adsorption Isotherms

The corrosion inhibition process is mainly depended on the nature of interaction between the ionic liquid molecules and mild steel surface. At a particular temperature this interaction can be explained by using various adsorption isotherm models such that Freundlich adsorption isotherm, Langmuir adsorption isotherm, Temkin adsorption isotherm etc. The model was chosen as best fitted model which was showed best agreement with the data of surface coverage. For both ILs best fitted adsorption isotherms graph obtained on plotting C/θ against the concentration (C) of corrosion inhibitor for which the equilibrium constant seems to decrease with increasing the temperature with correlation coefficient (R^2) close to 1. Hence Langmuir model of adsorption isotherm followed by the both ILs [PEImBr] and [BuEImBr]. The value of K_{ads} obtained from the linear plot from any of the best fit adsorption isotherm a used to find the Gibb's Free Energy of adsorption via the Equation (9).

$$\Delta G_{ads} = -RTln(55.5K_{ads}) \qquad (9)$$

Where, ΔG_{ads} is the Gibb's free energy of adsorption, the value of 55.5 is the molar concentration of water in the solution expressed in $molL^{-1}$, R is the universal gas constant, T is the thermodynamic temperature. A high value of K_{ads} and negative numerical value of ΔG_{ads} indicates an efficient and spontaneous adsorption process and stability of adsorbed protective film on the mild steel surface.

4.5 FE-SEM EDS with Elemental mapping

For better observation of protective film on mild steel surface in presence of ImILs in 0.5 M H_2SO_4 solution, Field-Emission-Scanning electron (FE-SEM) micrographs were recorded for the mild steel surface before exposure, after exposure for immersion time of 24 hours without and with 1000 ppm concentration of studied

ImILs. The observed results indicated that the FE-SEM images of before immersion, the mild steel surface appeared smooth. However, after immersion in 0.5 M H_2SO_4 without inhibitor severely damaged, rough, porous, cavity and pits developed on the mild steel surface. However, in the presence of inhibitor the mild steel images predict much smoother and homogeneous due to the formation of protective film of ImILs. The presence of nitrogen peak in EDS spectra in presence of [BuEImBr] and [PEImBr] confirms the adsorption of inhibitors on mild steel surface.

Chapter 5: Imidazolium-based Ionic liquids of different anion as Green Corrosion Inhibitor, This chapter deals with the corrosion inhibition properties of imidazolium based ionic liquids with different anions [BzEImBr] and [BzEImCl] on mild steel in 0.5 M H_2SO_4 solution. To determine the effect of anions on the corrosion parameters various techniques such as weigh loss method, potentiodynamic polarization (PDP), electrochemical impedance study (EIS), Field-Emission-Scanning electron (FE-SEM) were used. The results obtained from above techniques were in good agreement with each other. Chapter provided the strong evidences for the metal inhibitor interaction which is helpful to predict the preferable inhibition mechanism. The detail discussions of results are described below.

5.1 Weight Loss Measurements

The weight loss (ΔW), Corrosion rate (C_R) and percentage inhibition efficiency (% IE) was calculated using Eq. (1), (2), (3) and (4) respectively.

Following points are represent the results of weight loss study.

- The [BzEImCl] found to be more effective corrosion inhibitor compare to the [BzEImBr]. The maximum inhibition efficiency at optimum concentration (1000 ppm) for [BzEImCl] and [BzEImBr] are 91.75% and 75.05% respectively at 303 K.
- [BzEImCl] acted as more effective corrosion inhibitor due to the more effective adsorption of (Cl^-) anion on mild steel surface compare to the adsorption of (Br^-) anion.

- As the temperature increase from 303 K the corrosion rate increase and inhibition efficiency are decrease due to the desorption process at high temperature. This is also favoring the physical type of adsorption nature of both type of inhibitors [BzEImBr] and [BzEImCl].
- The kinetic and thermodynamic parameters reveal that the corrosion inhibition process mainly controlled by surface reactions, metal dissolution process is endothermic in nature and spontaneity of the adsorption process.

5.2 Potentiodynamic Polarization Measurements (PDP)

Polarization parameters namely corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_c and β_a) and polarization resistance (R_p) were obtained from the PDP study. % IE calculated from the Eq. (6).

- The decrease in corrosion current density on increasing the concentration of both imidazolium-based ionic liquids (inhibitors) is indication of formation of a protective layer on the mild steel surface.
- The more cathodic shifting of E_{corr} values with less than changes of 85 mV reveal mixed type of inhibition with pronounced the cathodic inhibition for [BzEImBr].
- The maximum inhibition efficiency was observed 78.26 % & 86.35% for [BzEImBr] and [BzEImCl] inhibitor respectively at optimum concentration 1000 ppm.

5.3 Electrochemical Impedance Spectroscopy (EIS)

- EIS study suggests that the presence of [BzEImBr] and [BzEImCl] in the corrosive medium increases the values of charge transfer resistance and decreases the values of C_{dl}. This observation indicates that both inhibitors become effective by adsorbing at the metal-electrolyte interfaces.
- The electrochemical analyses were performed to support the gravimetric study and good agreement was observed.

5.4 Adsorption Isotherms

The nature of interaction between the corrosion inhibitor molecules and mild steel surface can be explore by performing adsorption isotherm studies. For the present

study the Freundlich model found to be best suitable for [BzEImBr] ionic liquid adsorption on mild steel surface while the Langmuir model fitted with [BzEImCl] ionic liquids.

5.5 FE-SEM EDS with Elemental mapping

- The micrograph images of mild steel surface in presence both ionic liquids were much smoother than the images of mild steel in absence of ionic liquids in 0.5 M H_2SO_4 solution.
- The nitrogen, bromine and chlorine peaks in EDS (Energy Dispersive X-Ray Spectroscopy) spectra indicated the effective adsorption of ionic liquids on mild steel surface.

Future Outlook

The present study exhibited to the corrosion inhibition properties and adsorption characteristics of imidazolium based ionic liquids on mild steel in 0.5 M H_2SO_4 solution. This study also recommended the use of more advance techniques such as XPS (x-ray photoelectron spectroscopy) for interaction between ionic liquids and mild steel surface especially in corrosion inhibition studies. Utilization of ionic liquids as corrosion inhibitor in other electrolytic solutions such as NaCl, HCl, HNO_3 should be explored. In future corrosion inhibition study of ionic liquid may be studied on different metal like aluminium, cupper etc.

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List of publication

1. Rathore, A., Sharma, S., Sharma, A., & Sharma, S. K. (2024). Evaluation of structure-reactivity correlation of efficient corrosion inhibitor ionic liquids for mild steel in acidic medium. Journal of Dispersion Science and Technology, 45(6), 1107-1119.https://doi.org/10.1080/01932691.2023.2197996

2. Sharma, S., Rathore, A., Thakur, A., Gurjar, S., Sharma, A., Kumar, A., & Sharma, S. K. (2024). An electrochemical and theoretical approach towards the efficient microwave synthesis of imidazolium-based ionic liquids for unprecedented mild steel corrosion inhibition in 0.5 M H2SO4 solution. Results in Surfaces and Interfaces, 17, 100295. https://doi.org/10.1016/j.rsurfi.2024.100295

3. Sharma, S., Rathore, A., Sharma, S., Sharma, A., & Sharma, S. K. (2024). "Heterocyclic Compounds as Corrosion-Inhibiting Agents for different metals in acidic media- A review", Journal of Heterocyclic Chemistry (Communicated).

4. Rathore, A., Sharma, S., Sharma, S., Sharma, A., Tahkur A. & Sharma, S. K. (2024). "Gravimetric, Electrochemical and Computational investigation of Thalidomide drug in a 1.0 M HCl solution as an effective mild steel corrosion inhibitor", Journal of Dispersion Science and Technology (Communicated).

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An electrochemical and theoretical approach towards the efficient microwave synthesis of imidazolium-based ionic liquids for unprecedented mild steel corrosion inhibition in 0.5 M H_2SO_4 solution

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ABSTRACT

The inhibition potential of newly synthesized imidazolium-based ionic liquids (IL-1 and IL-2) on mild steel corrosion in a 0.5 M H_2SO_4 solution has been comprehensively investigated using gravimetric analysis, potentiodynamic polarization, and electrochemical impedance spectroscopy across various temperatures. Gravimetric analysis indicated that the adsorption of these inhibitors adhered to the Langmuir adsorption isotherm. Significantly, IL-2, featuring a longer alkyl chain, demonstrated superior inhibition efficiency (92.51 % at 303 K) compared to IL-1 (88.71 % at 303 K). Potentiodynamic polarization studies revealed a mixed-type inhibitory behavior, impacting both anodic and cathodic reactions. Surface morphological analyses via SEM and EDX confirmed the formation of a protective film on the mild steel surfaces, substantiating the corrosion inhibition capabilities of IL-1 and IL-2. The novelty of this research lies in the application of density functional theory (DFT) using the B3LYP method, which elucidated that the alkyl chain length at the N-3 position in imidazolium cation-based ionic liquids significantly enhances their inhibition potential. This mechanistic insight suggests that these ionic liquids effectively obstruct both anodic and cathodic sites, providing robust corrosion protection in a 0.5 M H_2SO_4 solution.

1. Introduction

In the current era of accelerated industrialization and urbanization, the need for metal-based materials with superior mechanical properties has become increasingly critical. As industries expand and urban infrastructures grow, there is a heightened demand for metals that can withstand the rigorous requirements of construction, manufacturing, and technological advancements. This demand underscores the importance of developing materials that not only meet high-performance standards but also offer durability and reliability in a variety of applications (Mrani et al., 2022; Al-Rashed and Nazeer, 2022). These materials are used in various applications, from construction to manufacturing, due to their strength, durability, and versatility. Mild steel holds a special place among these materials due to its cost-effectiveness (Verma et al., 2023a; Thakur et al., 2022; Kumar and Thakur, 2020; Arifa Farzana et al., 2023). Its affordability makes it a popular choice in industries where budgets are of concern. However, this affordability comes at a cost, where mild steel is susceptible to corrosion, particularly in acidic environments. Acids are commonly used in industrial pickling, cleaning, and descaling(Nardelli et al., 2022; Abdel-Karim and El-Shamy, 2022). These acids create a corrosive environment that can lead to the deterioration of mild steel and other metals. This corrosion can result in economic losses, structural damage, and even safety hazards. To combat the adverse effects of corrosion, various techniques are employed. One of the most straightforward and practical approaches to corrosion control is corrosion inhibitors.

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Evaluation of structure-reactivity correlation of efficient corrosion inhibitor ionic liquids for mild steel in acidic medium

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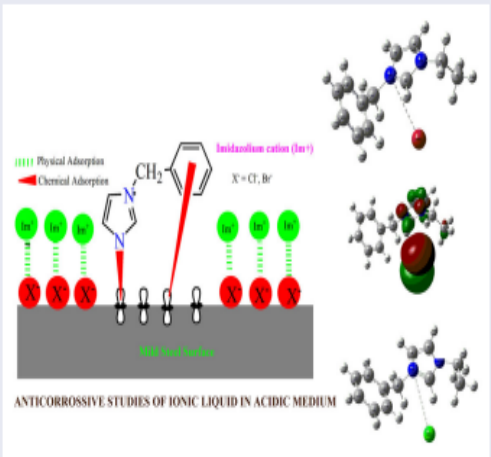
ABSTRACT

The synthesis and characterization of Imidazolium cation-based ionic liquids having different anions were reported in the present article. The physicochemical and spectral analyses were used to characterized these ionic liquids. The theoretical studies using the B_3LYP method provide optimized structure, HOMO–LUMO plots, thermodynamic parameters, and quantum descriptors. The anti-corrosive property of Imidazolium cation-based ionic liquids was observed in 0.5 M H_2SO_4 corrosive medium at 303, 313, 323, and 333 K temperatures by various strategies like gravimetric studies, electrochemical impedance spectroscopy, potentiodynamic polarization studies, and scanning electron microscopy (SEM). The interesting feature of this article is that both ionic liquids follow different adsorption isotherms. IL-1 ionic liquid shows physisorption adsorption behavior, and IL-2 exhibits mixed adsorption (chemisorptions and physiorption). The electrochemical strategies and E_{gap} value obtained from DFT reveal the maximum inhibition efficiency of IL-2 for the corrosion process in an acidic medium on mild steel. Potentiodynamic polarization studies reveal the mixed type behavior for ionic liquid inhibitors. EIS results indicate that the inhibition efficiency improved by enhancing ionic liquids concentration. The protective layer formation or adsorption of ionic liquid on metallic surface was confirmed by SEM. In the present article, the proposed mechanism shows the blockage of anodic and cathodic sites by ionic liquids to inhibit the corrosion process on mild steel in an acidic medium.

GRAPHICAL ABSTRACT



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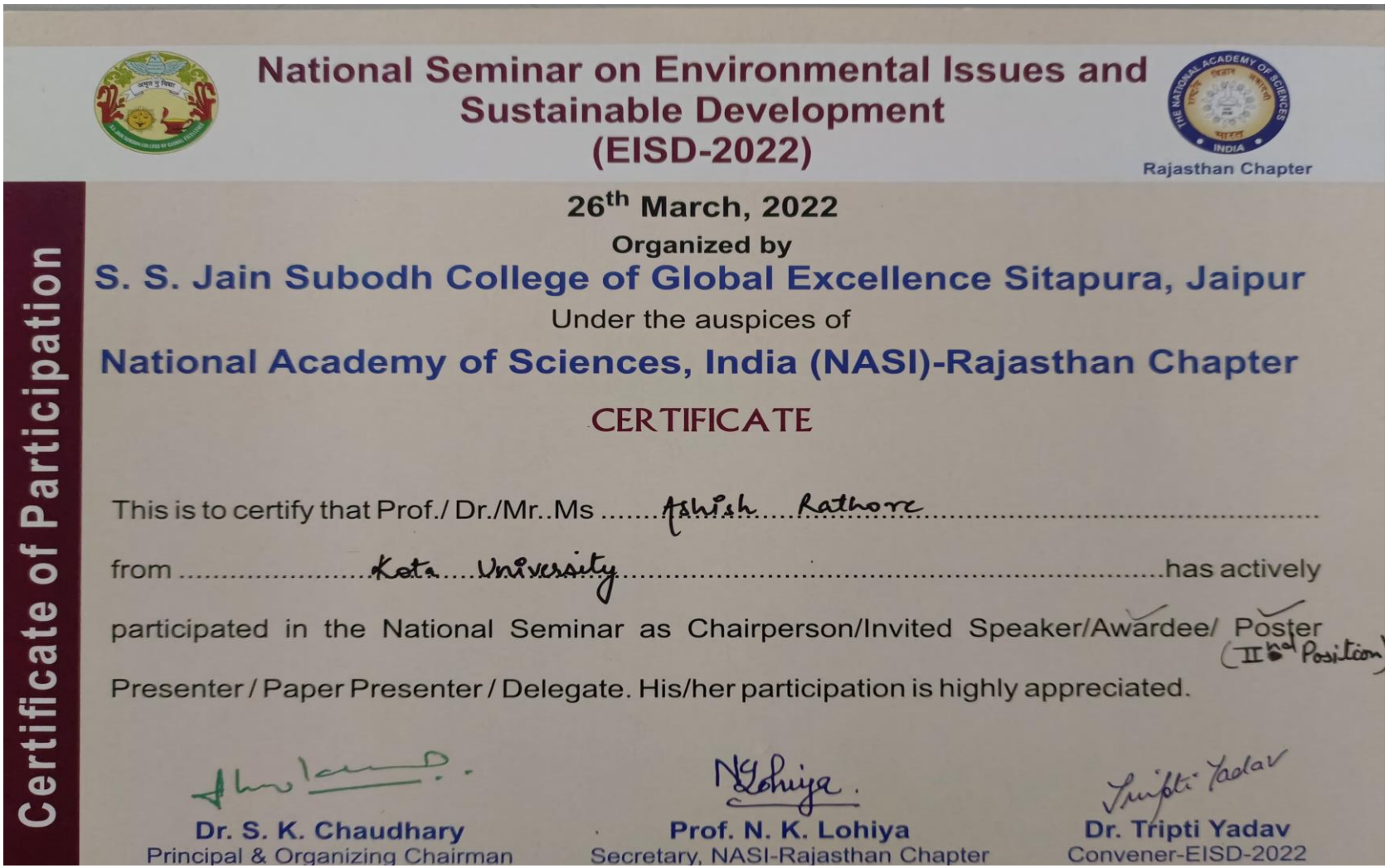
Ionic liquids; gravimetric method; quantum descriptors; electrochemical study; adsorption isotherm

1. Introduction

Industrialization and urbanization continuously increase the demand for metal-based materials with outstanding mechanical properties.[1] Compared with other metals, mild steel is descaling in industries.[3,4] The electrochemical reactions in the environment lead to the irreversible deterioration of metal based-materials, known as corrosion. Corrosion is a surface phenomenon that transforms metal and alloy by oxi-

List of presentations

1. Poster Presentation on “Microwave-Assisted Green Synthesis, Characterization and Corrosion Inhibition Potential of 1-Benzylpyridazinium bromide: Gravimetric, Electrochemical and Computational Studies” in the National Seminar on Environmental Issues and Sustainable Development (EISD-2022) Organized by S.S. Jain Subodh College of Global Excellence, Sitapura, Jaipur on 26 March, 2022.
2. Poster Presentation on “Imidazolium-based Ionic liquids with different anions use as corrosion inhibitor for mild steel in acidic medium: Experimental and Theoretical studies” in the National Conference on Recent Advances in Science and Technology organized by Department of Chemistry, Govt. College, Kota on 6-7 October, 2023.
3. Poster Presentation on “Microwave-Assisted Synthesis, Characterization and AntiCorrosion Study of Imidazolium based Ionic Liquid” in the 42th Indian Council of Chemists Organized by Department of Pure and Applied Chemistry, University of Kota, Kota on 20-22 December,2023.



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This is to certify that Prof / Dr. / Mr. / Ms. ASHISH RATHORE from U.O.K., KOTA. has participated / presented a paper / poster entitled Imidazolium-Based Theoritical Studies in the two day National Conference, organised by Department of Chemistry, Government College Kota(Raj) on 6th & 7th October 2023.

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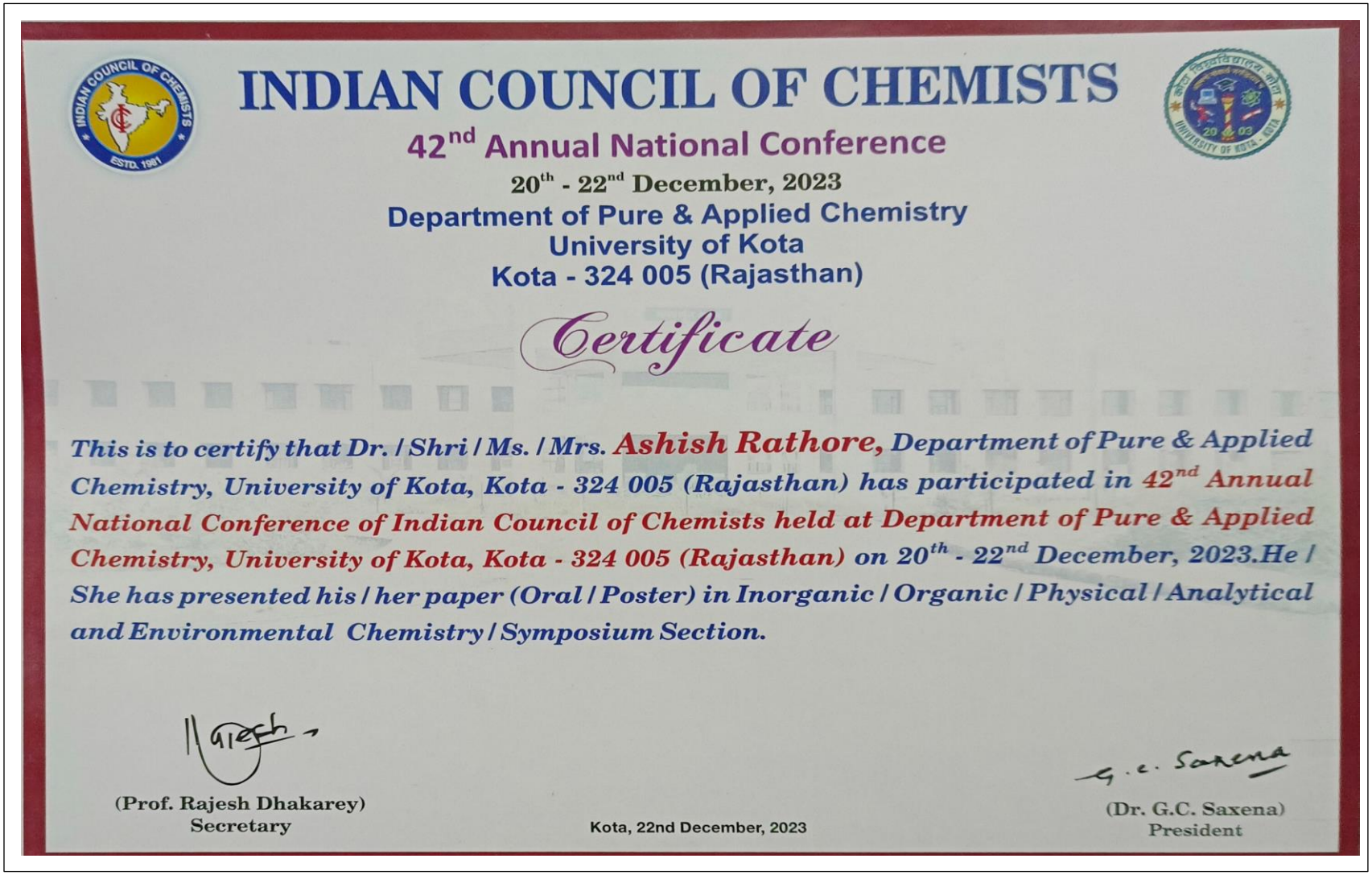

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This is to certify that Dr. / Shri / Ms. / Mrs. ***Ashish Rathore,*** *Department of Pure & Applied Chemistry, University of Kota, Kota - 324 005 (Rajasthan) has participated in 42nd Annual National Conference of Indian Council of Chemists held at Department of Pure & Applied Chemistry, University of Kota, Kota - 324 005 (Rajasthan) on 20th - 22nd December, 2023.He / She has presented his / her paper (Oral / Poster) in Inorganic / Organic / Physical / Analytical and Environmental Chemistry / Symposium Section.*

(Prof. Rajesh Dhakarey)
Secretary

Kota, 22nd December, 2023

(Dr. G.C. Saxena)
President

Conferences/Workshops/Short Term Course Attended

1. One day International Symposium (Chemtalk-2021) on "Organometallic Chemistry and Its Opportunities" Organised by Department of Chemistry, **Agrawal PG College, Jaipur** on 1 May 2021.
2. Four days online faculty development programme on "Recent Trends in Teaching and Research in Applied Science" Organised by **Poddar International College** from 20 to 24 January 2022.
3. International Webinar Series on "Advanced Chemical Techniques" Organised by Department of Pure and Applied Chemistry, **University of Kota, MBS Road, Kota (India)**, on 19 June to 3 July 2021.