Chapter 6

Ionic Liquids as Green Corrosion Inhibitors for Industrial Metals and Alloys

Chandrabhan Verma, Eno E. Ebenso and Mumtaz Ahmad Quraishi

Additional information is available at the end of the chapter

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Abstract

Present chapter describes recent advances in the field of development of ionic liquids as green and sustainable corrosion inhibitors for metals and alloys. The present chapter has been divided into several sections and subsections. Recently, development of the green and sustainable technologies for the corrosion prevention is highly desirable due to increasing ecological awareness and strict environmental regulations. In the last two decades, corrosion inhibition using ionic liquids has attracted considerable attention due to its interesting properties such as low volatility, non-inflammability, non-toxic nature, high thermal and chemical stability and high adorability. Several types of ionic liquids have been developed as "green corrosion inhibitors" for different metals and alloys such as mild steel, aluminum, copper, zinc, and magnesium in several electrolytic media. The ionic liquids are promising, noble, green and sustainable candidates to replace the traditional volatile corrosion inhibitors.

Keywords: ionic liquids, corrosion, adsorption, green corrosion inhibitors, designer solvents, ferrous and non-ferrous metals

1. Introduction

1.1. Corrosion and its economic impact

Corrosion is an irreversible and spontaneous deterioration of metal or alloy through chemical or electrochemical reaction with the environment [1, 2]. Corrosion causes enormous wastes of metallic materials which lead to enormous economic losses all over the world. Therefore, corrosion has drawn considerable academic and industrial attention [1–4]. According to highly cited study carried out by the National Association of Corrosion Engineers (NACE), in 1998,

the total annual direct cost (estimated) of corrosion in U.S.A. was US $276 billion, equating approximately around 3.1% Gross Domestic Product (GDP; NACE 2002) [5]. In 2011, the total cost of corrosion in U.S.A. became more than US $2.2 trillion. As for as the corrosion cost in India is concern, it was around Rs. 2 lackscrores (US $45 billion) as proposed by 1st Global Corrosion Summit held in New Delhi, India in 2011 [6]. However, these estimated data are outdated and recently closer investigation of the NACE on the cost of corrosion is available according to which the annual global cost of corrosion is approximately US $2.5 trillion, equating 3.4% of the global GDP [7, 8]. In India, the annual corrosion cost is more than US $100 billion, while in South Africa, the direct corrosion cost is estimated to be around R130 billion (i.e. about US $ 9.6 billion) [7, 8]. There are several methods of corrosion protection have been developed such as coating, anodic and cathodic protections, alloying and de-alloying and use of synthetic corrosion inhibitors by suitably applying them we can reduce this cost of corrosion from 15% (US $375 billion) to 35% (US $ 875 billion).

1.2. Causes of corrosion

Pure metals are chemically unstable and undergo chemical and/or electrochemical reactions with their environments to form more stable oxides. The chemical reactivity of pure metals is related to their natural tendency of oxidation (except gold, silver and platinum), as they have tendency to return their natural state by chemical reactions with the constituents of environment [9–12]. Since corrosion is a spontaneous process, relative rate of corrosion among a given series of metals is related to the change in standard Gibb's free energy (ΔG^o). As more negative value of ΔG^o as high spontaneity of reaction and consequently higher corrosion rate [9–12]. When metals and alloys exposed to environment and particularly in acid solution during several industrial processes like acid pickling, acid descaling, etc., corrosion will undergo forming stable oxides [13–15]. Therefore, these processes required some additives known as corrosion inhibitors that form protective covering over the metallic surface and isolate metals from the environment and thereby inhibit the corrosive degradation [13–17]. The corrosion products such as rust and scale can also act as corrosion inhibitors by accumulation on the surface and act as physical protective barrier. The natural tendency of metallic corrosion can be affected by several factors, however, the relative rate of corrosion of any particular metal is depending upon the Pilling—Bedworth ratio which is defined as Md/nmD, where m and d are the atomic weight and density of the metal, respectively and M and D are the molecular weight and density of scale (corrosion product) accumulated on the metallic surface, and n denotes the number of metallic atoms in the molecular formula of corrosion product (rust or scale); for example for Fe_2O_3 and Al_2O_3, n = 2 [18, 19]. The magnitude of Pilling – Bedworth ratio can be used to explain where the surface film will be protective or not. The volume of corrosion product will be small than the volume of metal from which it was formed for $Md/nmD < 1$, in this situation it is expected that surface film of corrosion product contains pores and cracks that would be relatively non-protective. On the other hand, volume of corrosion product will be larger than the volume of metal for $Md/nmD > 1$, in that situation it is expected that surface film of corrosion product is relatively more compressed and compact and consequently the metal would be relatively more protected.

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1.3. Corrosion prevention methods and corrosion inhibitors

There are several methods of corrosion protection have been developed among which, synthetic corrosion inhibitors are one of the best methods due to its advantages such as cost effectiveness and ease of application in industry [20–23]. The flow diagram of the available corrosion protection measures is shown in **Figure 1**. The passivating inhibitors are also known as anodic inhibitors because they general inhibit the metallic corrosion by forming the surface oxide (passive) film and causes the large anodic shift corrosion potential (E_{corr}) [24]. The passivating inhibitors can be further classified into oxidizing anions that passivate the metallic surface in the absence of oxygen such as chromate, nitrite and nitrate and non-oxidizing anions that can passivate the metallic surface only in the presence of oxygen such as phosphate, tungstate and molybdate. The cathodic inhibitors either decrease the rate of cathodic reactions or precipitate on the cathodic areas to increase the surface impedance that decrease the diffusion of reducible species to these areas [24]. The cathodic inhibitors act by three different mechanisms namely, cathodic poisons, cathodic precipitates and oxygen scavengers. Generally, arsenic and antimony make the association of hydrogen more difficult and act as cathodic poisons, calcium, zinc and magnesium precipitates in their oxide forms and act as cathodic precipitates and sodium sulfite and hydrazine react with surrounding oxygen and act as oxygen scavengers [25–28].

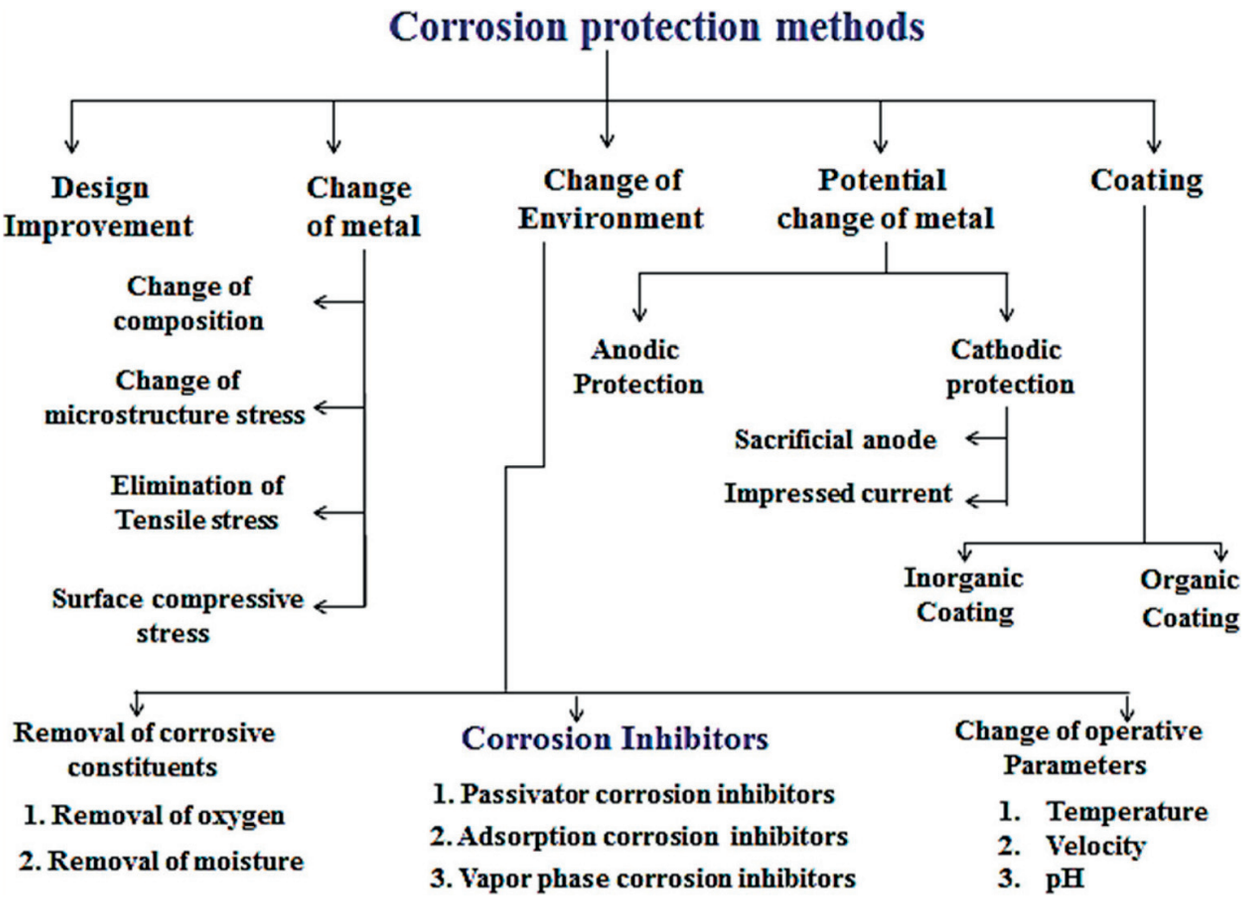

Figure 1. Available methods of metallic corrosion protection.

Organic compounds are also known as filming inhibitors; generally inhibit metallic corrosion by forming the protective surface film that isolates the metal form the surrounding (corrosive) environments. Most of the well know organic inhibitors are heterocyclic compounds containing polar functional groups such as -NO_2, -OH, -OCH_3, -CH_3, -NH_2, -$COOC_2H_5$, -$CONH_2$, -COOH, etc. [29–31]. These polar functional groups and conjugated π-electrons of multiple bonds (double and triple) act as adsorption centers during metal-inhibitor interactions. This type of adsorption results into blocking of anodic and cathodic reactions indirectly. The adsorption of these inhibitors is affected by several factors such as nature and magnitude of charge present on metal, nature of electrolyte, electronic structure of inhibitor molecules, nature of substituents, solution temperature, exposure time etc. [29–34].

1.4. Ionic liquids as green corrosion inhibitors

"Green chemistry" which is a relatively new and rapidly growing area of chemistry that involves designing of products and processes that reduce the use and production of toxic substances [35–38]. Recently, worldwide growing ecological awareness and strict environmental protocols do not permit the synthesis and utilization of hazardous traditional volatile corrosion inhibitors. Therefore, there is vital need for improvement in the synthetic and engineering chemistry either by environmental friendly starting materials or proper designing for synthesis using non-classical energy sources such as ultrasound and microwave heating. In this regard use of multi component reactions (MCRs) in combination with ultrasonic (sonochemical) and microwave irradiation is one of the best alternative synthetic strategies toward "green synthesis." Recently, scientists are trying to develop plant extracts and drugs as green corrosion inhibitors due to their natural and/or biological origins and non-toxic nature [39–41]. However, extraction and purification of plant extracts is very tedious, laborious, extremely expensive, time consuming and requires large amount of organic solvents [42, 43]. Therefore, there is need to develop "green inhibitors" by proper designing of the synthesis that can be achieved either by using cheap and environmental friendly starting materials or by synthesizing them from one step MCR reactions.

Toward, "green chemistry," utilization of ionic liquids has immersed as new strategy due to its several fascinating properties such as low melting point (lower that 100°C), high polarity, low toxicity, low vapor pressure, very high thermal and chemical stability, less hazardous influence on environment and living being [44–48]. By definition, ionic liquids are materials that mainly composed of ions with melting point below than 100°C. The properties of ionic liquids could be modified according to the need by proper selection of cations and anions, which is the greatest advantage for designing ionic liquids of specific properties [49–51]. Due to this reason ionic liquids are also known as "designer chemicals" that have potential to consume as solvent or catalysis for various chemical transformations [44–51]. The rapid utilization of ionic liquids in almost all fields of chemistry and chemical engineering is resulted to their above mentioned fascinating properties which enable them as "green and sustainable chemicals" having tendency to dissolve wide range of inorganic and organic compounds. The ionic liquids follow the principals of "green chemistry" proposed by Paul Anastas and John Warner [52–54].

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1.4.1. Properties and applications of ionic liquids

The ionic liquids have several fascinating properties such as low volatility (low vapour pressure), very high stability over wide range of pH and temperature, capability to dissolve a wide range of organic and inorganic compounds as they generally exist in their ionic forms through which they easily dissolve in polar solvents like H_2O, HCl, etc., moreover, their cationic counterparts generally contain large organic moieties through which they are capable to dissolve non-polar organic compounds, capability to solubilize gases like H_2, CO, CO_2 etc., dependency of solubility on the nature of cations and anions, acceleration of reaction rate for chemical transformation under microwave heating, long time stability without decomposition and their high selectivity [55–62]. These fascinating properties of ionic liquids make them good candidature to replace conventional organic volatile solvents with non-conventional ionic liquids that have been employed in variety of chemical transformations such as solvents for synthesis of nanomaterials and nanostructure, biochemical transformations, nucleophilic substitution reactions, electrodeposition of metals and semiconductors and solvent extraction, separation of petrochemical relevance mobile phase converter in HPLC, catalyst in various chemical and biochemical transformations, dye sensitizer for solar cells, oil shale processing, etc. (**Figure 2**) [55–62].

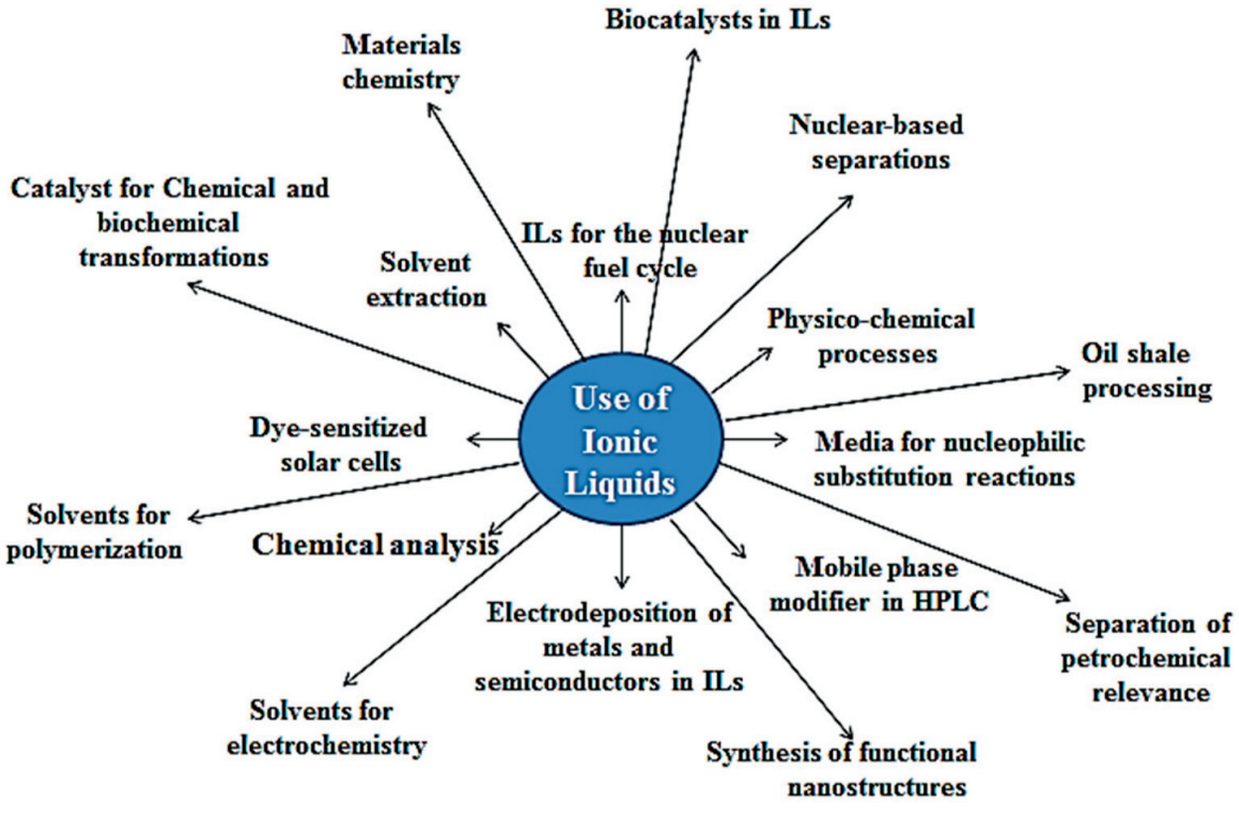


Figure 2. Applications of ionic liquids.

1.4.2. Classification of ionic liquids

The ionic liquids can be classified into several categories based on various bases. Hajipour and Refiee [63] have classified the ionic liquids into eleven classes namely, neutral ionic liquids, acid ionic liquids, basic ionic liquids, ionic liquids with amphoteric anions, functionalized ionic liquids, protic ionic liquids, chiral ionic liquids, supported ionic liquids, bio-ionic liquids, poly-ionic liquids, and energetic ionic liquids and also have described common features and properties of these ionic liquids. However, Suresh and Sandhu [62, 63] classified ionic liquids into only two classes namely, cationic and anionic ionic liquids. They were further subdivided anionic ionic liquids into several subclasses namely, borates, dicyanamide (DCN), Halide, Bis(trifluoromethylsulfonyl)imide (NTF), nonaflate (NON), phosphate, sulfate, sulfonate, thiocyanate (SCN), tricyanomethide (TCC) based anionic liquids. Some common classes of ionic liquids with examples and their salient features are described in **Table 1**.

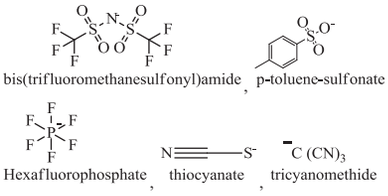
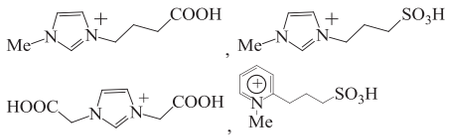
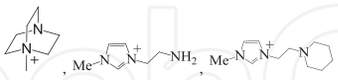
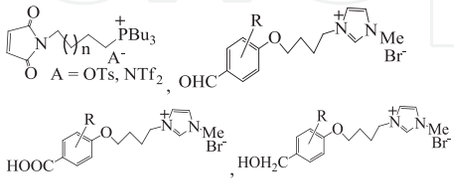
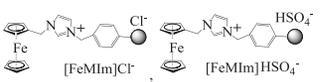
SN	Types of ionic liquids (classes)	Some typical examples	Remark
1	Neutral ionic liquids	 bis(trifluoromethanesulfonyl)amide, p-toluene-sulfonate, Hexafluorophosphate, thiocyanate, tricyanomethide	Anions are associated with cations with weal electrostatic interaction, low melting point, low viscosity, used as inert solvent, good thermal and electrochemical stability
2	Acidic ionic liquids	 $Me_3\overset{+}{N}\text{-}CH_2COOH$ Anions= (HSO_4^-, $H_2PO_4^-$, $M_3Cl_7^-$; Zn, Fe, Al)	Ionic liquids with acidic cations or acidic anion, enhanced solubility in water, possess good catalytic efficiency
3	Basic ionic liquids	 Common anions: Cl^-, CH_3OO^-, oxalate ion, etc.	These ionic liquids are basic in nature due to presence of one or more amine group (1^o, 2^o or 3^o amine)
4	Functionalized ionic liquids	 A = OTs, NTf_2	Ionic liquids that has a covalently bound functional group on the cation and/or anion
5	Supported ionic liquids	 [FeMIm]Cl^-, [FeMIm]HSO_4^-	

Table 1. Classification of ionic liquids and their common features.

1.5. Comparison between organic inhibitors and ionic liquids

Over past two decades corrosion inhibition using ionic liquids (ILs) has experienced an outstanding growth and abundant examples on corrosion inhibitions are available that have been effectively carried out in different corrosive media. Although, traditional volatile compounds have been most extensively used as corrosion inhibitors in several industries. However, most of them are toxic for living being and environment [64–66]. In view of this, ionic liquids (ILs) have been used extensively in recent years. Ionic liquids have several advantageous physiochemical properties including non-toxic, high conductivity, non-flammability, as well as high thermal and chemical stability [35–63]. One of the most significant characteristics of ionic liquids is their environmental friendly and non-hazardous nature due to their non-negligible vapour pressure. Unlike to traditional volatile corrosion inhibitors, due to their extremely low vapour pressure these compounds will not evaporate and will not contaminate the surrounding environment [67, 68]. Additionally, sometimes the use of organic inhibitors particularly polymeric and high molecular weighted organic compounds is limited due to their extremely low solubility in the polar corrosive media [69–72]. However, ionic liquids are highly soluble in the polar corrosive environments due to their ionic nature [73]. Furthermore, there is limit less prospect of suitably modifying the structure of the anion and cation of any given ionic liquids delivers an unlimited amount of potential derivatives having numerous physiochemical properties, while this type of modification is not possible with volatile corrosion inhibitors. In summary, the use of ionic liquids as corrosion inhibitors is preferred as compared to traditional volatile (toxic) corrosion inhibitors due to their several advantageous physiochemical properties including their high solubility, non-toxic, high conductivity, non-flammability, less volatility as well as high chemical stability and more importantly due to their "green and sustainable" nature.

2. Applications of ionic liquids as corrosion inhibitors

Several fascinating properties of the ionic liquids make them ideal candidates to replace the traditional corrosion inhibitors that have several adverse effects on environment and living beings. Recently, a large number of works have been reported describing the use of ionic liquids as corrosion inhibitors.

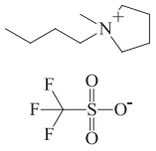
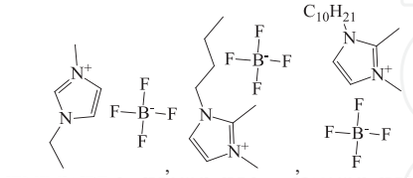
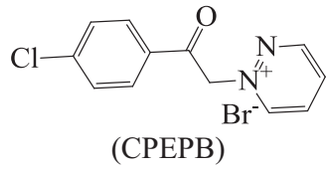
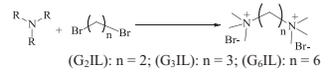
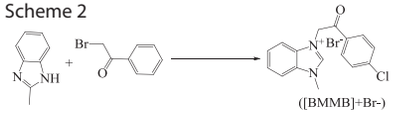
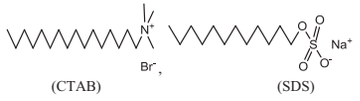
2.1. Ionic liquids as corrosion inhibitors for mild steel

Mild steel is most frequently used as constructional material for several industries due to its high mechanical strength and low cost [74, 75]. However, these materials are highly reactive and undergo corrosive degradation during various industrial processes like acid cleaning, acid descaling, acid etching, and acid pickling processes that require use of additives in order to increase the lifespan of metal/alloy has used [76]. The use of organic compounds containing heterocyclic rings and polar fictional groups such as amino, hydroxyl, methyl, methoxy, nitro, nitrile, etc., as additive is one of the most important alterative to protect metals and alloys from these unsolicited reactions [74, 75]. These compounds inhibit corrosion by adsorbing over the metallic surface [74–77]. However, the use of these highly volatile traditional toxic corrosion

inhibitors is limited due to increasing ecological awareness and strict environmental regulations. In this regards consumption of "ionic liquids" as corrosion inhibitors has become an important green alternative methods of corrosion protection. Literature survey reveals that several synthetic ionic liquids have been used as effective corrosion inhibitors for mild steel (or carbon steel) in various electrolytic media. Likhanova et al. [78] synthesized two ionic liquids namely, 1,3-dioctadecylimidazolium bromide ($ImDC_{18}Br$) and N-Octadecylpyridiniumbromide ($PyC_{18}Br$) using conventional and microwave heating methods, respectively and investigated their inhibition performance on mild steel corrosion in 1M H_2SO_4 using several experimental techniques. They were observed that studied ionic liquids acted as good corrosion inhibitors for mild steel in aqueous acid solution. The adsorption on metallic surface takes place via chemisorption mechanism which obeyed the Langmuir adsorption isotherm. Potentiodynamic polarization results revealed that applied ionic liquids behaved as mixed type inhibitors. These authors were proposed a mechanism of corrosion inhibition on the basis of results obtained from SEM-EDX, XRD and Mossbauer analyses. The inhibition performance of the 1-ethyl-3-methylimidazolium dicyanamide (EMID) on mild steel corrosion in 0.1M H_2SO_4 using several experimental techniques [79] has been tested. Results showed that EMID inhabits metallic corrosion by adsorption on the metallic surface which was confirmed by decreased values of C_{dl} and increased surface coverage in presence of the inhibitor. The adsorption of the EMID over metallic surface obeyed the Langmuir adsorption isotherm. The inhibition performance of two ionic liquids namely 1-butyl-3-methylimidazolium chlorides (BMIC) and 1-butyl-3-methylimidazolium hydrogen sulfate ($[BMIM]HSO_4$) on mild steel corrosion in 1M HCl have been studied by Zhang and Hua [80] using electrochemical and weight loss experiments. Results showed that the inhibition efficiency of both ionic liquids obeyed the order: ($[BMIM]HSO_4$) > (BMIC). They were found that adsorption of these compounds on mild steel surface obeyed the Langmuir adsorption isotherm. Potentiodynamic study suggested that both ionic liquids acted as mixed type inhibitors. The effect of temperature (303–333 K) was also investigated on both the ionic liquids. Finally, several activation and thermodynamic parameters such as energy of activation (E_a), enthalpy of activation (ΔH), entropy of activation (ΔS), adsorption constant (K_{ads}) and Gibb's standard free energy (ΔG^{o}) were calculated in order to explain the mechanism of adsorption and corrosion inhibition of both the ionic liquids.

The inhibition performance of 1-octyl-3-methylimidazolium bromide ([OMIM]Br) and 1-allyl-3-octylimidazolium bromide ([AOIM]Br) on mild steel corrosion in 0.5 M H_2SO_4 using weight loss, electrochemical, scanning electron microscopy (SEM) and Quantum chemical calculations techniques showed that both the ionic liquids acted as good corrosion inhibitors and their adsorption on the metallic surface obeyed the El-Awady thermodynamic–kinetic model and acted as slightly cathodic type inhibitors [81].

Table 2 represents the corrosion inhibition properties of several other ionic liquids that have been employed as inhibitors for mild steel corrosion in electrolytic media [82–116]. The chitosan-based ionic liquid was synthesized using oleic acid and p-toluene sulfonic acid and its corrosion inhibition efficiency was determined using several electrochemical measurements [117]. Results of the investigated study revealed that presence of the ionic liquid in the chloride containing corrosive medium decreased the rate of metallic dissolution as well as hydrogen evolution. Adsorption of the ionic liquid followed the Langmuir adsorption

Synthetic scheme and/or chemical structure of ionic liquids	Techniques	Nature of adsorption	Electrolytic media	Ref.
	Electrochemical and scanning electron microscopy	Langmuir adsorption isotherm, mixed type	3.5% NaCl	[82]
 [EMIM]+[BF$_4$]–, [BDMIM]+[BF$_4$] –, [C10MIM]+[BF$_4$]–	Experimental, quantum chemical, Monte Carlo simulation	Langmuir adsorption isotherm, mixed type	1M HCl	[83, 84]
 (CPEPB)	Gravimetric, electrochemical, quantum chemical calculations	Langmuir adsorption isotherm, mixed type	1M HCl	[85]
Scheme 1  (G_2IL): n = 2; (G_3IL): n = 3; (G_6IL): n = 6	Gravimetric, electrochemical	Langmuir adsorption isotherm, mixed type	1M HCl	[86]
Scheme 2  ([BMMB]+Br-)	Electrochemical, Quantum chemical calculations (DFT)	Langmuir adsorption isotherm, mixed type	1M HCl	[87]
 (CTAB) (SDS)	Electrochemical, Scanning electron microscopy	Flory–Huggins adsorption isotherm, mixed type	3.5% NaCl	[88]

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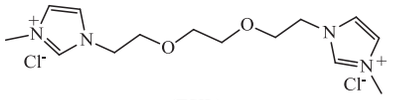
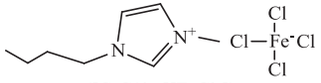
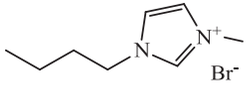
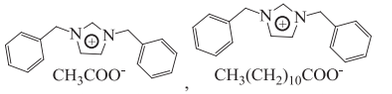
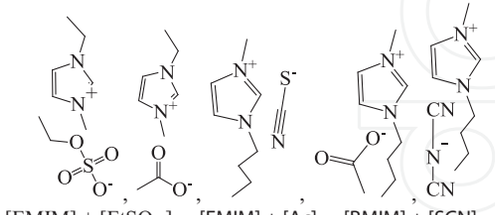
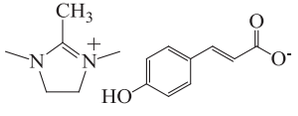
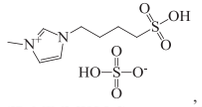
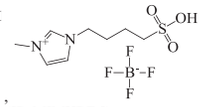
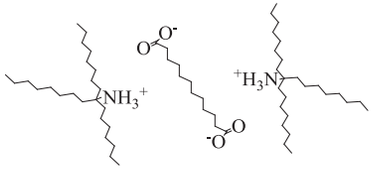
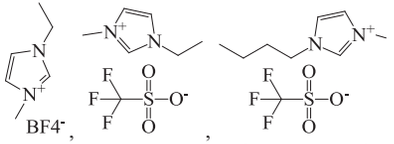
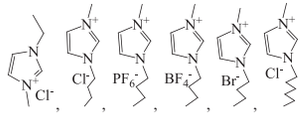
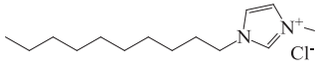
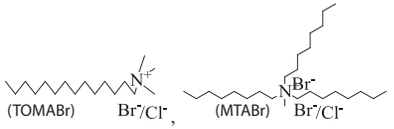
Synthetic scheme and/or chemical structure of ionic liquids	Techniques	Nature of adsorption	Electrolytic media	Ref.
 (TSIL)	Weight loss, electrochemical, SEM, AFM, contact angle method	Langmuir adsorption isotherm, mixed type	1M HCl	[89]
 ([C_4C1im][$FeCl_4$])	Weight loss, electrochemical, SEM, DFT methods	–	Open and controlled environments	[90]
 [BMIM]Br	Weight loss, electrochemical	Langmuir adsorption isotherm, mixed type	1M HCl	[91, 92]
 (DBImL) , (DBImA)	Electrochemical, SEM	Langmuir adsorption isotherm, mixed type	1M HCl, 1M H_2SO_4	[93]
 [EMIM] + [$EtSO_4$] - , [EMIM] + [Ac] –, [BMIM] + [SCN] –, [BMIM] + [Ac] –, [BMIM] + [DCA] –	Electrochemical, spectroscopic, SEM, DFT, QSAR and Monte Carlo simulation	Langmuir adsorption isotherm, mixed type	1M HCl,	[94]
	Electrochemical, Immersion, SEM	–	0.01M NaCl	[95]

Synthetic scheme and/or chemical structure of ionic liquids	Techniques	Nature of adsorption	Electrolytic media	Ref.
 ([BsMIM]-[HSO_4]) ,  ([BsMIM][BF_4]),	Gravimetric, electrochemical, SEM	Langmuir adsorption isotherm	1M H_2SO_4	[96]
	Weight loss and polarization techniques	Langmuir adsorption isotherm, mixed	Production water	[97]
 [EMIM][BF_4], [BMIM][Otf], [EMIM][Otf]	Electrochemical techniques	–	CO_2	[98]
 (EMIm Cl), (BMIm Cl), (BMIm PF_6), (BMIm BF_4), (BMIm Br), (HMIm Cl)	Electrochemical), AFM, dynamic light scattering (DLS), FT-IR and DFT	Langmuir adsorption isotherm, mixed type	2 M HCl	[99]
 (DMICL)	Electrochemical, surface analysis techniques	–	NaCl (pH 3.8 and pH 6.8)	[100]
 (TOMABr) Br^-/Cl^-, (MTABr) Br^-/Cl^-	Electrochemical measurements	Flory-Huggins adsorption isotherm, mixed type	2M H_2SO_4	[101]

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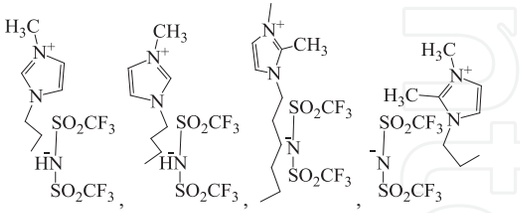
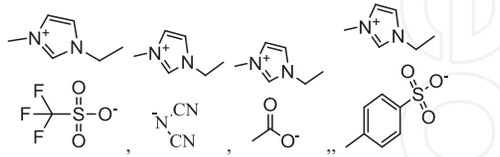
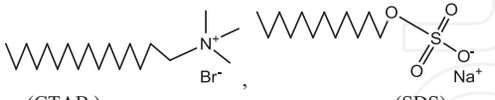
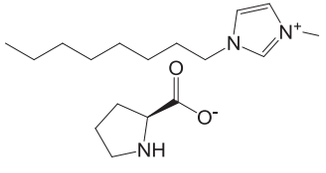
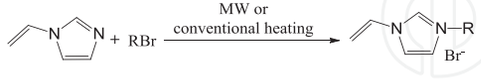
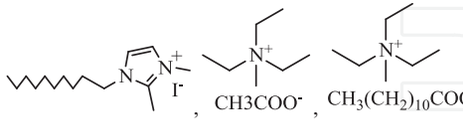
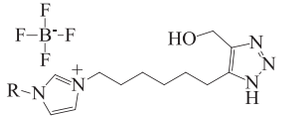
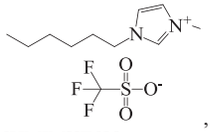
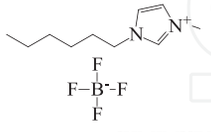
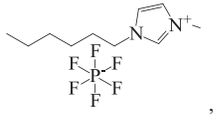
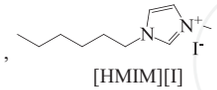
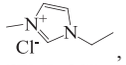
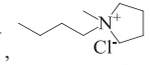
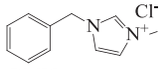
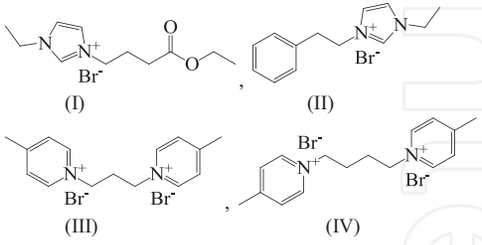
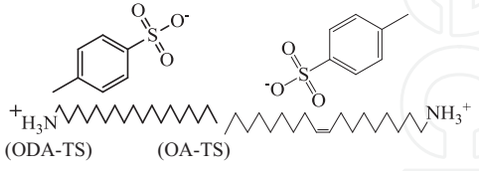
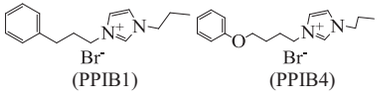
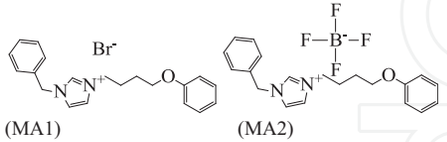
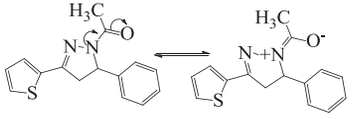
Synthetic scheme and/or chemical structure of ionic liquids	Techniques	Nature of adsorption	Electrolytic media	Ref.
	Weight loss, electrochemical measurements, QSAR, quantum chemical calculations	Langmuir adsorption isotherm, mixed type	1M HCl	[102]
 [emim]-[Otf], [emim][tosylate]) [emim]-[DCA], [emim][acetate],	Electrochemical	–	CO_2 capture system	[103]
 (CTAB) (SDS)	Electrochemical and surface analysis	Flory – Hugginsadsortion isotherm, mixed type	2 M HCl	[104]
	Weight loss, electrochemical, SEM, and quantum chemical calculation	Flory – Huggins isotherm, mixed type	0.5 M H_2SO_4	[105]
Scheme 5  R= IL1:C_4H_9; IL2:C_8H_{17}; IL3:$C_{12}H_{25}$; IL4:$C_{18}H_{37}$; IL5: $C_{22}H_{45}$	Weight loss, electrochemical, SEM, AFm	Langmuir isotherm, mixed type but IL3 behave as cathodic type	1M H_2SO_4	[106]

Synthetic scheme and/or chemical structure of ionic liquids	Techniques	Nature of adsorption	Electrolytic media	Ref.
 (DDI), (TMA) (TML)	Weight loss, electrochemical, SEM	Langmuir isotherm, mixed type	1M H_2SO_4	[107]
 R= -CH_3 (I); -C_4H_8 (II); -C_8H_9 (III)	Electrochemical polarization test, SEM	–	Ethanol solution	[108]
 [HMIM][TfO]  [HMIM][BF_4],  [HMIM][PF_6]  [HMIM][I]	Electrochemical, spectroscopic analyses, quantum chemical calculations	Langmuir isotherm, mixed type	1M HCl	[109]
 ([EMIm]Cl)  ([Py1,4]Cl)	Weight loss, electrochemical	–	Arabian Gulf Sea-water	[110]
 (BMIC)	Weight loss, electrochemical	Langmuir adsorption isotherm, mixed type	2M H_2SO_4 and 3.5% NaCl	[111]

Synthetic scheme and/or chemical structure of ionic liquids	Techniques	Nature of adsorption	Electrolytic media	Ref.
 (I), (II), (III), (IV)	Potentiodynamic polarization, linear polarization and weight loss	Langmuir adsorption isotherm, mixed type	1M HCl	[112]
 (ODA-TS) (OA-TS)	Electrochemical, SEM, EDX, contact angle measurement	Langmuir adsorption isotherm, mixed type	1M HCl	[113]
 (PPIB1) (PPIB4)	Weight loss and electrochemical methods	Langmuir adsorption isotherm, mixed type	1M HCl	[114]
 (MA1) (MA2)	Weight loss and DFT studies	Langmuir adsorption isotherm	1M HCl	[115]
	Weight loss and electrochemical methods	Langmuir adsorption isotherm, mixed type	1M HCl/1M H_2SO_4	[116]

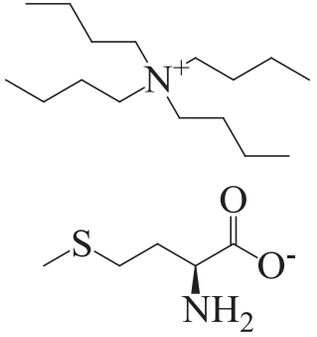
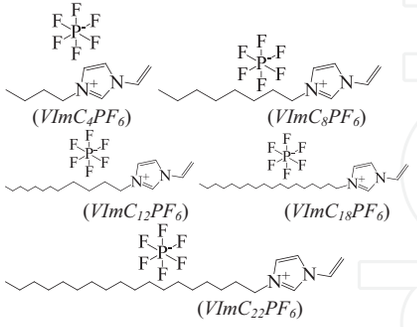
Synthetic scheme and/or chemical structure of ionic liquids	Techniques	Nature of adsorption	Electrolytic media	Ref.
	Electrochemical, Quantum, surface analysis methods	Mixed type	1M HCl	[121]
 (EOPC)	Weight loss, electrochemical methods	Langmuir adsorption isotherm, mixed type	0.5M H_2SO_4	[122]
 ($VImC_4PF_6$) ($VImC_8PF_6$) ($VImC_{12}PF_6$) ($VImC_{18}PF_6$) ($VImC_{22}PF_6$)	Weight loss and electrochemical polarization methods	Langmuir adsorption isotherm, mixed type	1M H_2SO_4	[123]

Table 2. Ionic liquids as corrosion inhibitors for mild steel in different electrolytic media, their mode of adsorption and techniques used for evaluation of the inhibition performance.

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isotherm. Polarization study suggested that investigated ionic liquid acted as mixed type inhibitor. Tseng and coworkers [118] investigated the corrosion characteristics of carbon steel, 304 stainless steel (304 SS) and pure titanium (Ti) in aluminum chloride–1-ethyl-3-methylimidazolium chloride ionic liquid for the first time. These authors reported the active-to-passive transition behavior for CS sample. Among the tested materials 304 SS exhibited the maximum stability in the high chloride environment. The most peculiar finding was that Ti was severally corroded in the ionic liquid because it does not undergo passivation. The ionic liquid in non-aqueous, low-oxygen and high halogen containing showed different corrosion behavior and mechanism. Similar observation has been reported by other authors for different metals including copper, nickel and stainless steel [119]. Recently, the inhibition behavior of 1,4-di [1-methylene-3-methyl imidazolium bromide]- benzene on mild steel corrosion in 1M H_2SO_4 have been studied using electrochemical and surface analysis methods [120]. The ionic liquid under taken in the study inhibits metallic corrosion by adsorbing on the surface which mechanism obeyed the Langmuir adsorption isotherm. The adsorption mechanism was supported by SEM, EDX and AFM analyses. Polarization study reveals that studied ionic liquid acted as mixed type inhibitor. The ongoing discussion reveals that although, several classes of ionic liquids have been used as effective inhibitors for mild steel corrosion in various aggressive media, however, imidazole based ionic liquids have been used most extensively [78–84, 89–96, 98–112, 114–116, 123].

2.2. Ionic liquids as corrosion inhibitors for aluminum

Aluminum is the second most commonly used metal due to its several fascinating properties like its low atomic mass and negligible standard electrode potential. Several traditional organic and inorganic compounds have been used previously in order to protect dissolution of protective surface oxide film and ultimately decrease the corrosion rate. However, employment of the ionic liquids as corrosion inhibitors is limited as literature survey reveals that only few works are available describing the corrosion inhibition performance of ionic liquids. The inhibition performance of 1-butyl-3-methylimidazoliumchlorides (BMIC), 1-hexyl-3-methylimidazolium chlorides (HMIC) and 1-octyl-3-methylimidazoliumchlorides (OMIC) on aluminum corrosion in 1M HCl using electrochemical and weight loss methods showed that inhibition efficiencies of these ionic liquids increase with increasing their concentration and obeyed the order: OMIC > HMIC > BMIC [124]. Potentiodynamic study revealed that all ionic liquids acted as mixed type inhibitors and their adsorption on aluminum surface followed the Langmuir adsorption isotherm. The inhibition efficiency of an ecofriendly ionic liquid, 1,3-bis (2-oxo-2-phenylethyl)-1H-imidazol-3-ium bromide (OPEIB) on 6061 Al-15 alloy in 0.1 M H_2SO_4 solution using electrochemical impedance spectroscopy and potentiodynamic polarization, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopic methods revealed that it is a good corrosion inhibitor and its adsorption on aluminum surface obeyed the Temkin adsorption isotherm [125]. The three synthesized ILs, namely poly(ionic liquid)s (PILs), namely (poly(1-vinyl-3-dodecyl-imidazolium) (PImC12), poly(1-vinyl-3-octylimidazolium) (PImC8) and poly(1-vinyl-3-butylimidazolium) (PImC4) hexafluorophosphate) tested as inhibitor for aluminum alloy AA6061 in 0.1-1.0 M H_2SO_4 solution [126]. Results showed that they act as mixed type inhibitor and their inhibition efficiencies obeyed

the order: (PImC12 > PImC8 > PImC4). Adsorption of these ionic liquids followed the Langmuir adsorption isotherm. Four newly synthesized quaternary ammonium based surfactants in the series of hexanediyl-1,6-bis-(diethyl alkyl ammonium bromide), designated as $C_mC_6C_m(Et)\cdot 2Br$ (m = 10, 12, 14, 16), were synthesized and evaluated as inhibitors for aluminum corrosion in 1M HCl solution [127]. Results showed that all investigated surfactants act as good inhibitors and inhibit corrosion by becoming adsorbate at metal/electrolyte interfaces and their adsorption on metallic surface obeyed the Langmuir adsorption isotherm. Trombetta et al. [128] studied the stability of the aluminum in 1-butyl-3methylimidazolium tetrafluroborate ionic liquid and ethylene glycol mixtures using electrochemical impedance spectroscope (EIS). These authors observed decrease in polarization resistance and increase in the capacitance related with the passive oxide dielectric properties on increasing the ethylene glycol and/or water content in the mixtures. Presence of salts namely $Na_2B_4O_7.7H_2O$ and NaH_2PO_4 in the mixtures, stabilize the oxide payer form over the metallic surface and thereby reduce the changes of metallic corrosion. The inhibition behavior of 1,3-bis(2-oxo-2-phenylethyl)-1H-imidazol-3-ium bromide (OPEIB) on 6061 Al-15 vol. pct. SiC(p) composite in 0.1M H_2SO_4 solution was studied by Shetty and Shetty [125] using electrochemical (EIS and PDP), SEM and EDX methods. The investigated ionic liquid exhibits the maximum efficiencies of 96.7 and 94% using PDP and EIS methods, respectively. Potentiodynamic polarization study further reveals that studied ionic liquid behaves as cathodic type inhibitor and its adsorption on the composite surface followed the Temkin adsorption. Li et al. [129] study the inhibition behavior of tetradecylpyridinium bromide (TDPB) on aluminum corrosion in 1M HCl solution using weight loss and electrochemical methods. Results of the investigation showed that TDPB inhibits the aluminum corrosion by adsorbing on the metallic surface. The adsorption of the TDPB followed the Langmuir adsorption isotherm. Polarization study suggested that TDPB acts as cathodic type inhibitor for acidic aluminum corrosion. Bermudez and coworkers [130] investigated the surface interactions of seven alkylimidazolium ionic liquids with aluminum alloy Al 2011 using immersion test. The immersion experiments for aluminum corrosion was carried out in 1 and 5 wt.% of 1-ethyl,3-methylimidazolium tetrafluoroborate (IL1) in water. Results showed that neat solution of ionic liquids did not cause any corrosion. The inhibition behavior was discussed on the basis of SEM, EDX, XPS and XRD techniques.

2.3. Ionic liquids as corrosion inhibitors for copper and zinc

Copper and its alloys have been extensively employed in industries for various applications such as building construction, electricity, electronics, coinages, ornamental and formation of industrial equipment due to their relatively good thermal, electrical, mechanical and corrosion resistance properties [131]. However, in presence of aggressive anions like chloride, sulphate and nitrate these materials undergo sever attack resulting into loss of these materials due to corrosion occurs [132, 133]. Similar to the aluminum the use of ionic liquids as corrosion inhibitors for copper and zinc is also limited as literature survey revealed that only few ionic liquids have been used as corrosion inhibitors for these materials. Qi-Bo and Yi-Xin [134] newly synthesized three ionic liquids namely 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO_4), 1-hexyl-3-methylimidazolium hydrogen sulfate ([HMIM]HSO_4), and 1-octyl-3-methylimidazolium

hydrogen sulfate ([OMIM]HSO_4) and studied their inhibition efficiency on copper corrosion in 0.5 M H_2SO_4 using electrochemical impedance spectroscopy and potentiodynamic polarization techniques. The inhibition efficiency of the ionic liquids follows the order: [OMIM]HSO_4 > [HMIM]HSO_4 > [BMIM]HSO_4. Results obtained by these authors showed that adsorption of the studied ionic liquids followed the Langmuir adsorption isotherm. Polarization study revealed that these ionic liquids behaved as mixed type inhibitors. Gabler et al. [135] studied the inhibition performance of two ionic liquids namely (2-hydroxyethyl)-trimethyl-ammonium (IL1) and Butyl-trimethyl-ammonium (IL2) with identical anions; bis(trifluoromethyl-sulfonyl)imide on $CuSn_8P$ and steel $100Cr_6$, purchased from Metal Supermarkets (Brunn am Gebirge, Austria) using inductively coupled plasma optical emission spectrometry (ICP-OES), scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) and X-ray photoelectron spectroscopy (XPS) in water in the absence and presence of 1.5% of the ionic liquids. Manamela et al. [136] studied the inhibition performance of two ionic liquids; 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4^-] and 1-decyl-3-methylimidazolium tetrafluoroborate [DMIM][BF_4^-] on corrosion of zinc in 1M HCl using gravimetric analysis and theoretical Density Functional Theory (DFT) approach, using the B3LYP functional. Results showed that both the ionic liquids acted as good corrosion inhibitors and their inhibition efficiencies increase with increasing their concentrations. The inhibition efficiencies of the ionic liquids obeyed the order: [DMIM][BF_4^-] > [BMIM][BF_4^-]. Values of activation energy (E_a) and enthalpy of activation (ΔH) suggested that both the ionic liquids adsorbed over the surface through physisorption mechanism. Adsorption of these ionic liquids on metallic surface followed the Langmuir adsorption isotherm.

2.4. Ionic liquids as corrosion inhibitors for magnesium

Unlike active light metals such as aluminum and titanium, magnesium based alloys do not form protective passivating film. Moreover, these alloys easily react with the components of environment to from hydroxides, oxides, carbonates films that are highly porous, inhomogeneous and poorly bonded that cannot provide satisfactory protection to the metals against corrosion. Among the available methods of corrosion protection, organic coating is one of the best methods. Huanga et al. [137] has presented an early review on the corrosion protection of magnesium by some ionic liquids. However, present chapter is describing the few recent advances in the utilization of ionic liquids as corrosion inhibitors. Suna et al. [138] have investigated the inhibition effect of six phosphonium cation based ionic liquids (ILs) namely, tetradecyltrihexylphosphonium diphenylphosphate (1), tetradecyltrihexylphosphoniumdibutylphosphate (2), tetradecyltrihexylphosphonium bis(2-ethylhexyl) phosphate (3), tetradecyltrihexyl phosphonium diisobutyldithiophosphinate (4), tetradecyltrihexylphosphoniumbis(2,4,4-trimethyl pentyl) phosphonate (5), and tetradecyltrihexyl phosphonium O,O-diethyl dithiophosphate on magnesium alloys using electrochemical and surface investigation methods.

3. Ionic liquids as corrosion inhibitors: DFT study

Nowadays, several computational methods particularly, DFT (Density Functional Theory) based quantum chemical calculations have been emerged as potential tools for studying the

interactions between inhibitors and metallic surface. The DFT calculations provide several important parameters such as energies of highest occupied molecular orbital (E_{HOMO}), lowest unoccupied molecular orbital (E_{LUMO}), energy band gap ($E_{LUMO} - E_{HOMO} = \Delta E$), global electronegativity (χ), global hardness (η) and softness (σ), fraction of electron transfer (ΔN) and dipole moment (μ). In general, value of E_{HOMO} is related with electron donating ability, while the value of E_{LUMO} related with the electron accepting ability of the inhibitor molecules [74–77]. A higher value of E_{HOMO} and lower value of E_{LUMO} associated with high inhibition performance. The inhibition efficiency of inhibitor increases with decreasing the energy band gap (ΔE). A high value of global electronegativity (χ) is related with lower electron donating ability and therefore, the value of electronegativity (χ) inversely related with the inhibition efficiency order [74–77]. Inhibition efficiency of the inhibitor molecules decreases with increasing the hardness (η) and decreasing the softness (σ). Generally, inhibition performance of the inhibitor molecules increases with increasing their dipole moment (μ), however, negative trends of the inhibition efficiency is also reported by several authors [74–77]. Lastly, the value of electron transfer gives direct information about the relative extent of metal-inhibitor interactions. A high value of ΔN is associated with high charge transfer and therefore high inhibition efficiency [74–77, 102].

The DFT based quantum chemical calculations have also been employed to describe the adsorption behavior of some ionic liquids on the metallic surface. Our research group [102] studied the adsorption behavior of four imidazolium-based ionic liquids, namely 1-propyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide ([PMIM][NTf2), 1-butyl-3-methylimidazoliumbis(trifluoromethyl-sulfonyl) imide ([BMIM][NTf2), 1-hexyl-3-methylimidazolium bis (trifluoromethyl-sulfonyl) imide([HMIM][NTf2]), and 1-propyl-2,3-methylimidazolium bis (trifluoromethyl-sulfonyl) imide ([PDMIM][NTf2]) on mild steel corrosion in 1M HCl using experimental and quantum chemical calculations. The inhibition efficiencies of these ionic liquids follow the experimental trend: [PDMIM][NTf2] > [HMIM][NTf2] > [BMIM][NTf2] > [PMIM][NTf2]. The values of E_{HOMO} and E_{LUMO} are well satisfied the experimental order of inhibition efficiency. Results showed that [PDMIM][NTf2] exhibited the lowest value of ΔE and therefore related with the highest chemical reactivity and inhibition efficiency. The values of dipole moment (μ) and the molecular volume (MV) did not show any regular trends. However, the values of global softness (σ) again show that the [PDMIM][NTf2] is most soft molecule among the tested compounds thereby associated with highest chemical reactivity and inhibition efficiency. The quantum chemical calculations provide good insight about the inhibition mechanism and well supported the experimental order of inhibition efficiency. Similar observations were reported for few other metals and alloys in several corrosive media [82, 139–143].

4. Mechanism of corrosion inhibition

Similar to most of the organic corrosion inhibitors, ionic liquids (ILs) inhibit metallic corrosion by blocking the anodic and cathodic sites present over the metallic surface [78, 144, 145]. Therefore, inhibition of metallic corrosion in presence of ionic liquids involves blocking of anodic oxidative metallic dissolution as well as cathodic hydrogen evolution reactions [78, 144]. The mechanism of metallic (M) corrosion inhibition by ionic liquids in

sulphuric acid has been described below. The inhibition mechanism of metallic corrosion by ionic liquids in other protic acidic solutions such as in HCl and HNO_3 will be similar because of their similar nature. The only difference in their nature is that they possess different counter ions (Cl^-, NO_3^-) rather than sulphate ion of sulphuric acid. According to Likhanova et al. [78], anodic dissolution of metals (M) in aqueous acidic solution (e.g. H_2SO_4) can be represented as follows [78]:

$$M + nH_2O \longleftrightarrow M(H_2O)n_{ads} \tag{1}$$

$$M(H_2O)n_{ads} + {SO_4}^{2-} \longleftrightarrow M\left[(H_2O)_n SO_4^{2-}\right]_{ads} \tag{2}$$

$$M\left[(H_2O)_n SO_4^{2-}\right]_{ads} \longrightarrow M\left[(H_2O)_n SO_4\right]_{ads} + 2e^- \tag{3}$$

$$M\left[(H_2O)_n SO_4\right]_{ads} \longrightarrow M^{2+} + OH^- + SO_4^{2-} + H^+ \tag{4}$$

However, in presence of ionic liquids, anodic reactions can be represented as follows:

$$M + nH_2O \longleftrightarrow M(H_2O)n_{ads} \tag{5}$$

$$M(H_2O)n_{ads} + {SO_4}^{2-} \longleftrightarrow M\left[(H_2O)_n SO_4^{2-}\right]_{ads} \tag{6}$$

$$M(H_2O)_n SO_4^{2-}]_{ads} + ILsC^+ \longrightarrow M(H_2O)_n SO_4 ILsC]^-_{ads} \tag{7}$$

$$M(H_2O)_n SO_4 ILsC]^-_{ads} + ILsC^+ + SO_4^{2-} \longrightarrow \left(M(H_2O)_n SO_4 ILsC\right]^-{}_{ads} ILsC^+ SO_4^{2-}/ILsC^+ \tag{8}$$

$$M + X^- \longleftrightarrow (MX^-)_{ads} \tag{9}$$

$$(MX^-)_{ads} + ILsC^+ \longleftrightarrow \left(MX^- ILsC^+\right)_{ads} \tag{10}$$

where, $ILsC^+$ and X^- represent the cationic counter part of the ionic liquids (mostly organic) and anionic counter part of the ionic liquid, respectively. It is important to mention that the concentration of sulphate ions is much higher as comared to the concentration of anionic counter part of the ionic liquids (X^-) that results into formation of $[M(H_2O)\ SO^{2-}{}_4]_{ads}$ in larger proporsion than $[MX^-]_{ads}$. Nevertheless, these both anionic charged species attracted positively charged cationic counter part of the ionic liquids ($ILsC^+$) by electrostatic force of attraction (physisoprtion) and forms monomolecular layer as an insoluble complex on the metallic surface [78, 145]. The adsortion of the $ILsC^+$ on metallic surface causes change in the surface polarity which induces the adsorption of the sulphate and X^- ions again which results into multimolecular layer [78, 146]. The multimolecular layers are stabilized by Vanderwaal's cohesion force acting beteween organic moeity of the ionic liquids which causes a more closely adsorbed film at metal/electrolyte interfaces. Generally, the cationic part ($ILsC^+$) interacts with the metallic surface and forms the multimolecular layers while rest of the part of the ionic liquids form hydrophobic hemi-micelles, ad-micelles and/or surface aggregation [78, 147]. The adsorbed multimolecular layers of the ILs isolate the metal (M) from corrosive enviroment and protect from corrosive dissolution.

The cathodic hydrogen evolution reaction (HER) can be represented by following simple stoichimmetry equation [148]:

$$H_2O + 2e^- \longleftrightarrow H_{2(g)} + 2OH^- \tag{11}$$

Generally, the hydrogen evolution reaction (HER) follows two very common mechanisms that is, Volmer-Heyrovsky mechanism represented by Eqs. (12) and (13) or according to the Tafel hydrogen evolution mechanism represented by Eq. (14). In acidic medium, the Volmer-Heyrovsky and Volmer-Tafel hydrogen evolution mechanisms have been shown below [148–150]:

$$M + H_3O^+ + e^- \longleftrightarrow MH_{ads} + H_2O \quad (\text{Volmer, V}) \tag{12}$$

$$MH_{ads} + H_3O^+ + e^- \longleftrightarrow H_2 + M + H_2O \quad (\text{Heyrovsky, H}) \tag{13}$$

$$MH_{ads} + MH_{ads} \longleftrightarrow H_2 + 2M \quad (\text{Tafel, T}) \tag{14}$$

During the first step of cathodic reactions hydrogen ions (or hydronium ions) first adsorbed on the metallic surface by Volmer mechanism followed by discharge of hydrogen gas by Heyrovsky and Tafel mechanism represented by Eqs. (13-14). All these reactions do not occur with the same rate. Generally, a slow reaction step is followed by a fast reaction step [151]. If the Volmer reaction is fast, then Heyrovsky and/or Tafel reactions occur with slower rate and vice versa. Presence of the organic corrosion inhibitors (ILs) in the corrosive solution may retards or slow down the formation of MH_{ads} or retards the electron transfer to the hydronium ions and suppresses the Heyrovsky reactions (13). In general, in corrosive medium, the adsorbed hydrogen on metallic surface recombined and evolved as the bubbles of hydrogen gas. The formation of bubble and its evolution is the second step in the HER. The formation of hydrogen gas either occurs through hydrogen atom-atom combination as denoted by Volmer-Tafel Eq. (14) or may results through hydrogen atom-hydrogen ion combination as represented by Volmer-Heyrovsky Eq. (13) [151].

In the presence of inhibitors (ILs), cathodic can be represented as follows:

$$M + ILsC^+ + e^- \longleftrightarrow M(ILsC)_{ads} \tag{15}$$

Initially, adsorption of hydronium ions and evolution of hydrogen gas occur at cathodic sites, simultaneously. At cathode, the cationic part of ionic liquids ($ILsC^+$) starts competing with hydrogen ions for electrons [78, 152]. In general, $ILsC^+$ has large molecular size and therefore replaces greater number of water molecules from the metallic surface. After their adsorption, cationic part of the ILs accepts electrons from the metal (M) which results into the formation of electrically neutral ionic liquids (inhibitors). The neutral species transfer (donation) their non-bonding (of heteroatoms) and π-electrons into the d-orbitals of the surface metallic atoms resulting into the formation of co-ordinate bonds between metal and ILs (chemisorption) as reported for several organic conventional inhibitors [78, 146, 153–156]. However, metals are already electron rich species; this type of donation causes inter electronic repulsion which interns resulted into transfer of electrons from d-orbitals of the surface metallic atoms to antibonding molecular orbitals of the ILs (retro-donation). Both donation and retro-donation strengthen each other through synergism [153–160].

5. Conclusions and future perspectives

On the basis of ongoing discussion it can be concluded that ionic liquids are green and sustainable inhibitors for corrosion of metals and alloys. The superiority of the use of ionic liquids as corrosion inhibitors compared to traditional volatile (toxic) corrosion inhibitors is based on the fact that they possess several fascinating properties such lower volatility, non-inflammability, non-toxic nature, chemical stability, high solubility in the polar solvents and their ability to easily adsorb on the metallic surface. Adsorption of the ionic liquids over the metallic surface results into formation of protective film which isolates the metals (alloys) from the corrosive environment and thereby inhibits corrosion. Among several available ionic liquids, imidazole based ionic liquids have been most extensively used. Some reports described the adsorption behavior of ionic liquids on metallic surface using DFT based quantum chemical calculations. However, the use of this technique should be further explored owing to its green nature to understand the mechanistic aspects of corrosion inhibition. The use of ionic liquids as corrosion inhibitors is preferred comparing with traditional inhibitors due to several physiochemical properties advantageous including their high solubility, non-toxic, high conductivity, and non-flammability, less volatility as well as high chemical stability and more importantly due to their "green and sustainable" nature.

Author details

Chandrabhan Verma[1,2], Eno E. Ebenso[2] and Mumtaz Ahmad Quraishi[1,3]*

*Address all correspondence to: maquraishi.apc@itbhu.ac.in

1 Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi, India

2 Material Science Innovation and Modelling (MaSIM) Research Focus Area, Department of Chemistry, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag, Mmabatho, South Africa

3 Center of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

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