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Structural Effect in Ionic Liquids Is the Vital Role to Enhance the Corrosion Protection of Metals in Acid Cleaning Process

Perumal Kannan and Anitha Varghese

Abstract

Various kinds of methods have been developed and used to overcome different types of corrosion throughout the world. One possible and easy way to avert corrosion is use of an inhibitor. An inhibitor can be applicable to any type of metal irrespective of medium (acid, alkaline, and neutral). Still, several inhibitors are emerging day by day in the corrosion world and most of them are heterocyclic compounds. In this respect, ionic liquid is attracting the attention of the research community. Because of ionic liquid's salient feature of melting and boiling points, it is being employed as a solvent in various types of reaction. In recent years, synthesizing and functionalizing the structure of ionic liquids in such a way to attain the desire requirement have become significant key factors in the field. By altering the cationic part or anionic part (halogen group), the chemical property of ionic liquids will change considerably. Besides, it will enhance the tendency of the electron-donating nature of the cationic part. This behavior equips them to be employed in the field of corrosion. While it meets the metal surface in the aggressive medium it will be attracted, leads to better surface protection from metal dissolution.

Keywords: ionic liquids, inhibitor, electrochemical analysis, structure effect, surface protection

1. Introduction

Corrosion is defined as the destruction or deterioration of metal because of its reaction with the environment. The age of corrosion is as old as the earth. It is known that it had different names at different time. However, carbon steel is prone to corrosion in an acid environment, which causes material damage and increases downtime costs in industry. Hence, a periodical cleaning and descaling process is performed using inorganic acids to remove the corrosion products. Due to acid aggressiveness, inhibitors were used to reduce metal dissolution [1]. The study of corrosion inhibition and mechanistic processes is a key area of research [2]. A large number of organic compounds having nitrogen, oxygen, sulfur, and phosphorus were synthesized to reduce the corrosion of metal in aggressive medium. The literature also revealed that the organic compounds containing π -bonds, electron density on the heteroatom, planner structure, and aromaticity have supported the effects of adsorption inhibitor molecules on the metal surface.

Over the last few decades, several types of organic compounds have been synthesized and used as corrosion inhibitors to mitigate the corrosion process in different environments [3–5]. More recently, ionic liquids have been recognized as a better corrosion inhibitor for metal corrosion in an acid environment [6–9]. Due to their unique properties such as non-flammability, very low vapor pressure, and boiling and melting point, ionic liquids can be considered to be good corrosion inhibitors. Recently, the software development in the theoretical analysis of molecules to describe plausible corrosion mechanisms has increased considerably [10]. Ionic liquids are salts, a combination of (organic) cation and (organic/inorganic) anion as a liquid form at room temperature; in other words, they are called organic salts, which have melting points below room temperature. The electronic configuration of imidazolium (heterocyclic) depends on the heteroatom of the main carbon skeleton and furthermore causes the interaction between the metal surface and ionic liquid [11]. The significant features of its physical and chemical properties such as liquid state, low vapor pressure, viscosity, and inflammability place ionic liquids in the field of corrosion as inhibitors. The various kinds of cation and anion govern the possibility to have property that required. Many ionic liquids are used as solvents for batteries and organic reactions. The application of ionic liquids in the corrosion field was first reported in 1996. The ionic liquid dissociation pattern gave a clue to the adsorption mode on the metal surface. The adsorption combination of ionic liquids depends on the metal nature and temperature.

The literature shows that inhibition effect mainly depends on alkyl chain length substitution on the N_1/N_2 atoms. A heterocyclic compound containing a longer alkyl chain length would offer better corrosion protection [12]. However, many studies have implied that increasing the carbon chain length on N atoms does not necessarily increase the inhibition effect [13, 14]. Murulana [15] supported the above fact and described that not only does increasing alkyl chain length in the N atom increase protection efficiency but also other atoms close by will enhance the protection effect. The main reason for surface protection is the induction of alkyl substitution on the cationic part of the ionic liquid.

2. Structural impact of ionic liquid in various aspects

2.1 Implication of ionic liquid alkylation in electrochemical studies

Since ionic liquids possess cations and anions, they are adsorbed onto the metal surface anodes and cathodes, respectively. Because of this, metal dissolution considerably decreases. The adsorbing efficiency of the inhibitor purely depends on the electron-donating ability of the ionic liquid active site [16]. Likhanova et al. [17] explained in his research that the electrochemical parameter showed the alkylation of longer chain length on imidazolium and pyridinium and significantly improved charge transfer resistance. Additionally, inhibitor concentration also improved metal dissolution at the metal/solution interface. In the presence of ionic liquid, the anodic and cathodic reactions were affected. ImDC₁₈ Br and PyC₁₈ Br inhibit the anodic area more than the cathodic area, because of the adsorption between HSO₄⁻ and Br⁻, and consequently, the cathodic reaction is also arrested. The increased polarization resistance indicates the adsorption of ionic liquid on the metal surface to block the active area for the mitigation of corrosion. This efficiency has increased due to the presence of ethylbenzene at the N₃ atom of the imidazole ring. Delocalization of the electron is much favored in the 3-ethylbenzene form of imidazolium ionic liquid than in the acetyl imidazolium form [18]. On the other hand, the (pyridiazinium ionic liquid, S₁) 1-(6-ethoxy-6-oxohexyl) pyridazin-1-ium bromide bears a higher

charge transfer resistance value than the (S_2) 1-(2-bromoacetyl) pyridiazinium bromide, which is advocated for reasonable corrosion protection at elevated temperatures. The causes behind better corrosion protection were increased frequency of relaxation [19] as the concentration and temperature increased.

Long alkyl chain length improves the relaxation time at the interface of the metal/ solution interface. Some authors [20] have reported the influence of negative ions of ionic liquids in electrochemical studies. According to Martin et al., corrosion rate decreased with an ionic liquid with the same alkyl chain length but different counter ion (anionic). The surface coverage area obeys the following order: $PF_6^- > BF_4^- > Br^- > Cl^-$. Hence, the ionic radius of the anions is increased by the same amount. The larger anionic radius of PF_6^- turns out to have better protection than the others [14]. The negative ion contribution in the ionic liquid structure could be evaluated through its corrosion protection performance. Saleh et al. discussed the effect of Br^- and Cl^- ions with cetylpyridinium ions in sulfuric acid over mild steel [8, 21].

Corrosion current has decreased considerably compared to the blank medium. The bromide ion has a stronger effect on anodic dissolution than the chloride ion. The anionic radius of bromine atoms is better suited for the bonding and surface coverage area on the metal/solution interface. Likewise, the anionic effect of ethyl sulfate and acetate ions on ethylmethylimidazolium can be deduced by comparing its protection efficiency over mild steel. Among the ionic liquids, [EMIM] [EtSO₄] is better at mitigating the anodic curve current than the acetate ion. Most probably, the inhibition efficiency is higher than the acetate ion, and this is attributed to the increased number of electronegative (hetero) atoms in the ionic liquid. On the other hand, the [EMIM] [Ac] ionic liquid showed reduced contribution compared to the [BMIM] [Ac] ionic liquid because of its long alkyl chain length [22].

2.2 Improvement in electrochemical noise resistance due to structural modification of the inhibitor

Electrochemical noise is another technique to ensure corrosion protection of the metal surface offered by ionic liquids. When the metal is exposed to the acid medium, the electrochemical reaction commences as fast as it can. As a result, the current is measured in the form of current deviation (σI). For the blank medium, current noise appears with higher amplitude, vindicating the absence of passivation over the metal surface. Also, the current transient width and amplitude designate the available active surface area on the metal surface. Metal immersed in acid medium afforded the noise resistance value of $1.474 \times 10^4 \Omega \text{ cm}^2$. These active areas were reduced due to the adsorption of ionic liquid ($[BMMB]^+ Br^-$). Thus, the R_n value increased from 5.29 to $27.7 \times 10^4 \Omega \text{ cm}^2$, as the concentration increased from 150 to 250 ppm, respectively. On observing [23], the noise amplitude decreased at each concentration level of ionic liquid. This ionic liquid contributed to corrosion protection by governing its electron-rich center to form a bonding with the metal. On the other hand [24], $[BMEB]^+ BF_4^-$ ionic liquid influences the electrochemical noise to reduce gradually that of $[BMMB]^+ Br^-$, which is attributed to less electrochemical reaction taking place. As a result, current noise amplitude decreased and concurrently noise resistance increased.

On comparing the noise resistance value of both ionic liquids, it clearly indicates that ethyl-derived ionic liquid has a better tendency to protect the metal surface at the interface than $[BMMB]^+ Br^-$. $[BMEB]^+ BF_4^-$ possesses higher noise value at each concentration than $[BMMB]^+ Br^-$ at the same concentration. Ethyl and BF_4 groups were more susceptible to transferring electrons, which resulted in better corrosion protection in acid medium as shown in **Figure 1**.

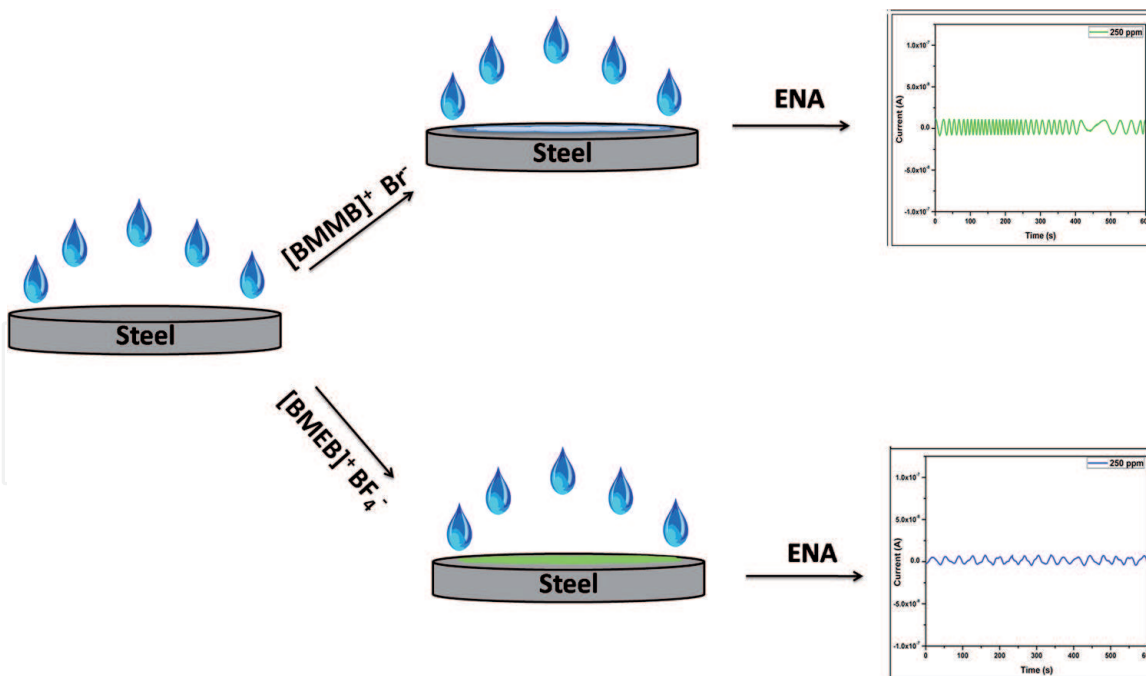


Figure 1.
Schematic representation of electrochemical noise analysis (ENA) of ionic liquids.

2.3 Significance of carbon chain length on surface protection of metal in acid medium

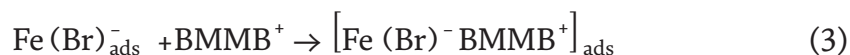
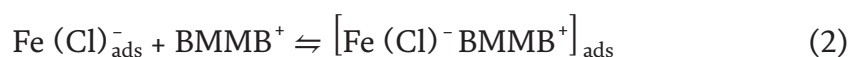
On comparing the surface protection effect of any ionic liquid with its alkylated and non-alkylated form, it would help to understand the structure effect of surface protection. Gabler et al. [25] reported that strong binding between metal surface and ionic liquid is key for corrosion reduction. In an electrochemical study of 2-hydroxy- and butylammonium sulfonyl imide, the C—F bond cleavage was reduced significantly in butyl form compared to the former. On the other hand, Kaczerewska et al. [26] studied the structural effect of inhibition efficiency on metal protection in acid medium. Interconnecting a gemini cation with a bridged oxygen atom showed better surface coverage to avert corrosive ion contact with metal surfaces. The 18-O-18 gemini cationic part of ionic liquid offered improved protection resistance against metal dissolution [27]. Vastag et al. suggested [12] that by increasing the alkyl chain number in N-substituted cations would favor the inhibitor action of organic compounds to isolate metal from further corrosion. Generally, the surface protection of ionic liquid on carbon steel was improved when the N₃ atom was alkylated with carbon chain lengths from n-7 to n-9. Infrared spectra also confirmed the shift in wave number [7]. Image examination of metal surfaces exposed to 1-ethyl [12] and 1-allyl [28] 3-butylimidazolium bromide ionic liquid expressed the inhibition effect of ionic liquid. The inductive effect of the allyl group offered increased electrons in its structure in the cation of ionic liquid. Hence, as resonance increased, the adsorption of ionic liquids over the metal surface also increased. Damage to the negative ions in the ionic liquids influenced corrosion protection [29]. HSO₄⁻ has greater tendency to render protection on metal surfaces than BF₄⁻. Sometimes, iminium compounds reduce surface heterogeneity, caused by adsorption of ionic liquid over the metal surface. Apparently, elemental analysis of the inhibited metal showed that the inhibitor's constituents were 15 wt% of carbon and 10 wt% of oxygen, and also corroborated that dodecyl iminium chloride is more favorably adsorbed than the non-alkylated form [30].

2.4 Study of hydrogen gas evolution over N₁ atom of ionic liquid acid

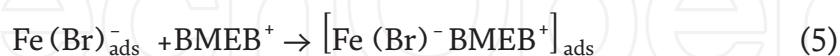
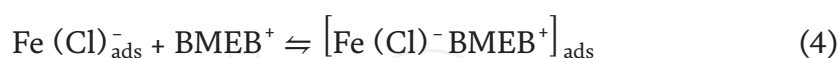
The hydrogen gas evolution method is one of the ways to determine the corrosion rate of metal in an aggressive medium. Hydrogen gas evolution is a result of a reduction (cathodic) reaction at the metal surface. The volume of hydrogen gas produced in the medium is gradually reduced in the presence of ionic liquid. The increment in alkyl chain length on N₁ atoms of the benzimidazolium cation offers maximum surface coverage on the active site. Thus, a lesser amount of hydrogen gas will be produced than the blank medium [24]. As seen, the volume of hydrogen gas is reduced for both methyl and ethyl benzimidazolium ionic liquid in concentration [23]. Furthermore, it can be understood that each concentration of ethyl benzimidazolium ([BMEB]⁺BF₄⁻) possesses a very low volume of H₂ gas compared to methyl benzimidazolium ([BMMB]⁺Br⁻).

From the above valid point, it is vindicated that the alkyl chain length offers maximum energy or electrons to adhere to the cathode area, which is also the route to sturdy passive film formation between the corrosive medium and the metal surface. The general corrosion mechanism for carbon steel in 1 N HCl acid is described below. As shown in the following equation the ionic liquid is adsorbed onto the anodic and cathodic areas of the carbon steel surface, respectively.

Anodic protection reaction of [BMMB]⁺Br⁻:

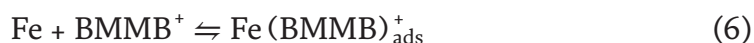


[BMEB]⁺BF₄⁻:

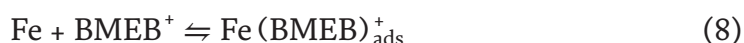


Likewise in the cathodic area, the reduction (hydrogen gas formation) reaction was considerably decreased due to the alkylation impact of ionic liquid on the adsorption effect instead of H⁺, and thus hydrogen gas evolution was reduced.

Cathodic protection reaction of [BMMB]⁺Br⁻:



[BMEB]⁺ BF₄⁻:





As seen in the above equations, the adsorption of the cationic part of ionic liquids is favored in both anodic and cathodic reactive sites. The most favored cationic part among the above three kinds of ionic liquids is $[\text{BMEB}]^+$. The $(\text{CH}_3 - \text{CH}_2^-)$ ethyl group, which effortlessly offered electrons to the metal surface, explains the reason for the occurrence of reduced volume of hydrogen gas in the acid medium. **Figure 2** shows the hydrogen gas evolution reaction in the blank and benzimidazolium ionic liquid.

2.5 Influence of alkyl chain length on quantum chemical parameters

Quantum chemical studies have been used as an efficient method to evaluate the corrosion inhibition performance of any kind of inhibitor. Since corrosion inhibition is adsorption related, dynamic and quantum studies are used to characterize the electronic properties that help to understand the adsorptive properties of the organic compound [31]. Many factors, including heteroatoms, π -electrons, aromatic rings, and carbon chain length, influence the adsorption properties of the inhibitor with metal surfaces [32]. The adsorption properties of ionic liquids will differ by their structural nature, particularly in HOMO and LUMO energy levels. The higher value of HOMO energy level contributes to the electron offering tendency to the acceptor molecule or lower energy state. Gad et al. [33] reported that increasing alkyl chain length increased HOMO energy level in pyridinium bromide ionic liquid. The maximum HOMO level was attained for (C_{12}) 4-mercapto-1-dodecyl-pyridinium bromide compared to C_8 and C_{10} .

Likewise, the LUMO energy level of an inhibitor also depends on the functional group present in the structure. The maximum LUMO value is acquired by (C_8) pyridinium bromide ionic liquid compared to the rest. A smaller alkyl chain length will decrease HOMO energy level and increase LUMO energy level. LUMO defines electron-accepting behavior of the molecule from the neighboring environments. Since (C_8) ionic liquid has a higher LUMO level, it can withdraw the electron from the metal, and even from feedback bonding, and result in strong adsorption with the metal surface. The change in energy gap is an important factor for measuring reactivity of ionic liquid to adsorb onto the metallic surface. The lower value of ΔE is the reason for the higher inhibition efficiency in metal corrosion. This is attributed to the

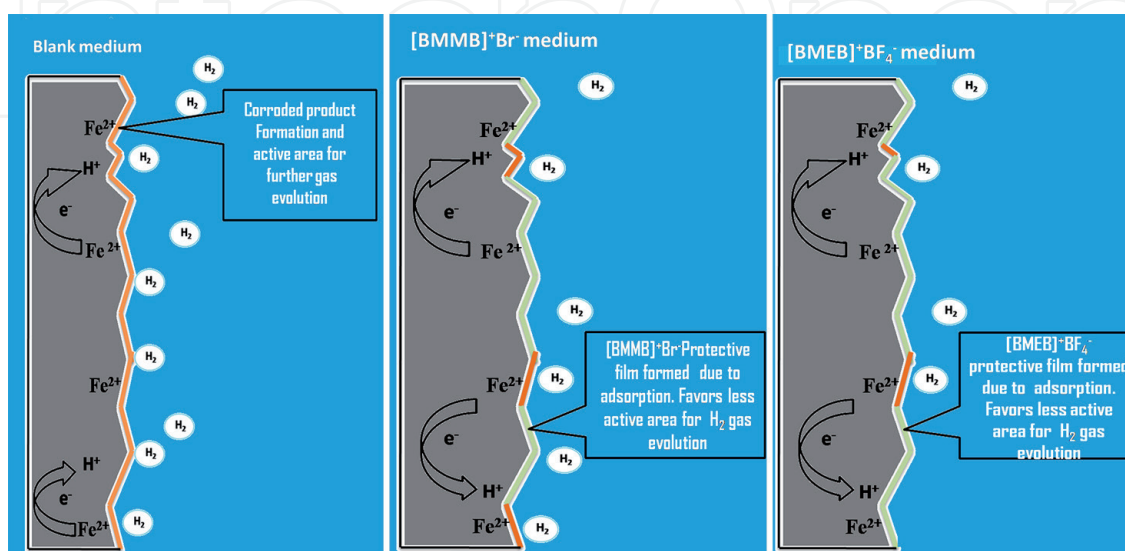


Figure 2. Pictorial representation of hydrogen gas evolution in the absence and presence of $[\text{BMMEB}]^+\text{Br}^-$ and $[\text{BMEB}]^+\text{BF}_4^-$ in 1 N HCl medium.

minimum amount of energy used to transfer the electron from the highest occupied orbital to the vacant “d” orbital of metal [34]. The ΔE value of the electrodeposition of polyaniline using tetrabutyl phosphonium bromide is less than that using ethyl tributyl phosphonium diethoxy phosphate. The above facts are the same as above in the phosphonium bromide molecule. The energy difference is much higher when substituting the 4-ethoxybenzyl group in the phosphonium [35] cationic part compared to butyl substitution [36]. Likewise, increasing the carbon chain length on the heterocyclic group also decreases the ΔE considerably [37]. The presence of methyl and ethyl groups in the benzimidazolium groups will maintain the minimum energy gap between the HOMO and LUMO groups as represented in **Figure 3**.

In addition, the binding energies of butyl and ethoxy-substituted phosphonium bromide were 2040.9 and 25505.6 kJ, respectively. Ethoxy-substituted phosphonium bromide possessed more negative than butyl-substituted phosphonium bromide. Hence, the ionic liquid is more stable and there is less chance of spitting in the medium because of better passive film on the metal surface. Still, many researchers are studying the structure impact on its corrosion performance. By introducing an alkyl functional group to imidazoline ionic liquid, the relationship between corrosion protection and structure can be discussed. Apparently, partial atomic charges of each atom in the compound describe structural influence using quantum chemical parameters on corrosion protection in the comparison study of [DMIM][BF₄] and [BMIM][BF₄] at corrosion inhibition efficiency; the partial atomic charges focus on cationic moiety rather than anionic moiety, because cations possess large molecular size. Finally, the carbon atom of the alkyl chain contains a negative charge. The C₅ carbon atom has a higher negative charge in [DMIM][BF₄] than in [BMIM][BF₄]. This makes DMIM ionic liquid effective in adsorption on the metal surface against corrosion [38].

In addition, Ibrahim et al. noted their point on structural effect in their research [18]. The adsorption of imidazolium ionic liquid took place through the nitrogen atom of the ring. The coordinate bond occurs between nitrogen and iron. On evaluating two ionic liquids (benzyl and ethyl acetate-substituted imidazolium ionic liquids), benzyl-substituted imidazolium ionic liquid has a higher rate of adsorption on the anodic curve area than ethyl acetate-substituted imidazolium ionic liquid, because the former has a higher rate of relaxation of adsorbed ionic liquid from the metal surface.

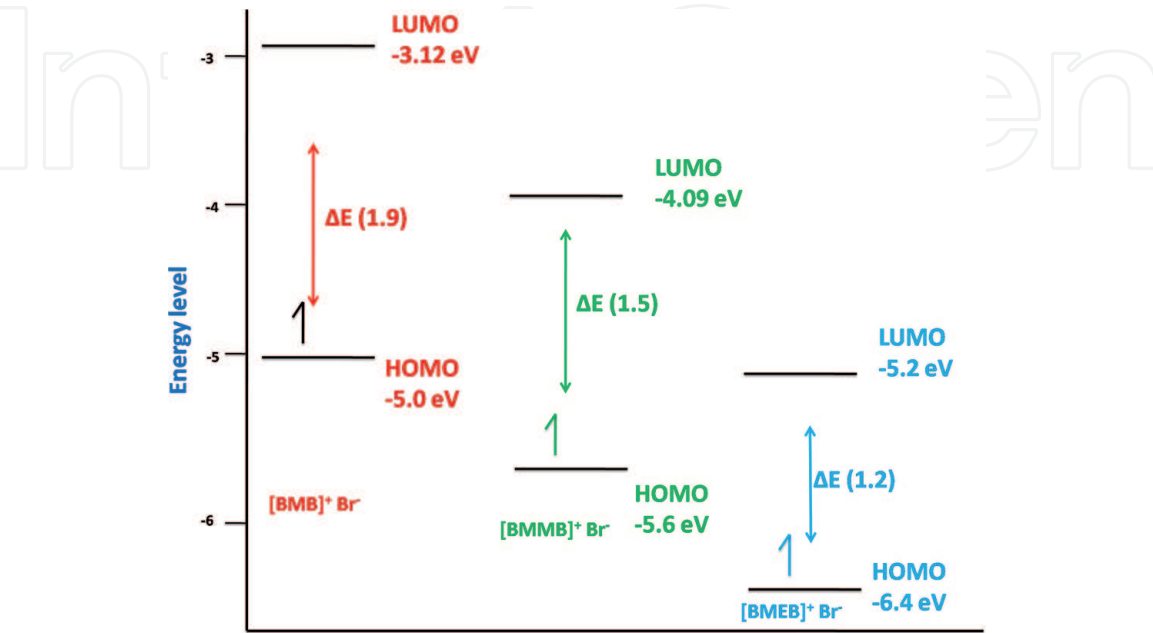


Figure 3.
Schematic representation of energy gap difference between various benzimidazolium ionic liquids.

3. Conclusion

On the basis of the above discussion of the alkylation effect on ionic liquids in various analyses, it can be concluded that structural effect is a considerable key factor in enhancing corrosion protection performance of metal in acid medium. Alkylation of the heterocyclic cation in the ionic liquid, particularly on N_1/N_2 of imidazolium, benzimidazolium, or N_1 of pyridinium or P_1 phosphonium, facilitates the physical/chemical properties of the ionic liquids compared to unalkylated ionic liquid. Not only had the physical/chemical properties changed but also electrochemical properties. This effect has been discussed with respect to various studies, such as electrochemical behavior, surface protection, electronic properties quantum chemical analysis (QCA), and hydrogen gas evolution. Adsorption of ionic liquid is favored mostly when it is being structurally modified as a result of passive film adsorption on the metal surface, which keeps the environment corrosion free. The reason for the extraordinary maturity of the alkylated ionic liquid could be described using theoretical study. This will support the alkylated or structurally modified ionic liquid electronic properties. The electron-donating nature of ionic liquid is being increased by alkylation. As a result, the resonance effect also increased, which contributes to the stability of the ionic liquid compared to the unalkylated form. The use of ionic liquid as a corrosion inhibitor is predominant and more efficient for structural modification.

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Conflict of interest

The author of this manuscript has no conflict of interest.

Notes/thanks/other declarations

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