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Experimental, quantum chemical and Monte Carlo simulation studies on the corrosion inhibition of some alkyl imidazolium ionic liquids containing tetrafluoroborate anion on mild steel in acidic medium

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ABSTRACT

The inhibition of mild steel corrosion in 1 M HCl solution by some imidazolium-based ionic liquids (ILs), namely 1-ethyl-3-methylimidazolium tetrafluoroborate $[EMIM]^+[BF_4]^-$, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate $[BDMIM]^+[BF_4]^-$ and 1-decyl-3-methylimidazolium tetrafluoroborate $[C_{10}MIM]^+[BF_4]^-$ was investigated using experimental and theoretical techniques. All the studied ILs showed appreciable inhibition efficiencies. Polarization measurements showed that the studied compounds are mixed-type inhibitors and the results obeyed Langmuir adsorption isotherm. Spectroscopic studies confirmed chemical interactions between mild steel and the ILs. Scanning electron microscopy images revealed that the inhibitors formed protective film on mild steel surface. The results of quantum chemical calculations and Monte Carlo simulations agree with experimental observations.

1. Introduction

Mild steel is widely used as construction material in many industries due to its exceptional mechanical properties and low cost. But, during some industrial processes such as acid cleaning, etching, etc. this metal corrodes easily, implying that the use of an inhibitor is necessary if the life of this valuable metal is to be protected [1–3]. The use of inhibitors is one of the most practical methods of protecting metals against corrosion [4–6]. It has been established that the initial mechanism involved in any corrosion inhibition process is adsorption of the inhibitor on the surface of the metal [7,8]. The inhibitors influence the kinetics of the electrochemical reactions which constitute the corrosion process and there by modify the metal dissolution in acids. They change the structure of the electrical double layer by adsorption on the metal surface. The adsorption of the inhibitor on the metal surface is a complex mechanism involving a number of factors such as the nature of the metal, the environment, the electrochemical potential at the metal/solution interface and nature of the inhibitor [9]. Corrosion inhibitors are often synthesized from cheap raw materials and include compounds that have π-electrons and functional groups such as —C═C—, —OR, —OH, $—NR_2$, $—NH_2$ and —SR. These functional groups facilitate the adsorption of the inhibitor on the metal surface [7,8,10]. However, many organic inhibitors are not environmentally benign. The increasing campaign towards the use of "green" compounds in industrial processes has shifted the attention of researchers to the study of ionic liquids (ILs) as environmental friendly corrosion inhibitors in the past few years [11–13].

Ionic liquids (ILs) are molten salts composed of organic cations and various anions. The organic cation usually has a π system and/or a heteroatom, such as nitrogen, sulfur or phosphorus as the central atoms for interaction with the metal surface. They possess a large number of physicochemical properties [14–17] such as good electrical conductivity, solvent transport and a relatively wide electrochemical window, making them highly efficient for both physisorption and chemisorption processes. ILs have been reported to have good corrosion inhibition properties for metals in acidic medium [12,18]. As a result, these compounds are reportedly used in oil field to minimize carbon dioxide induced corrosion [19,20]. Similarly, ILs have successfully mitigated the corrosion of carbon steel in hydrogen sulfide environment [21,22] and their inhibitive effects in aqueous HCl and H_2SO_4 media have also been reported [23,24]. ILs can be tailored to specific applications by fine-tuning the functional groups of the weakly coordinating organic cation and the inorganic/organic anion [25]. It is known that the alkyl chain length of the cation influences both the physical and chemical properties of room temperature ionic liquids (RTILs). A longer cation side chain is commonly accompanied by

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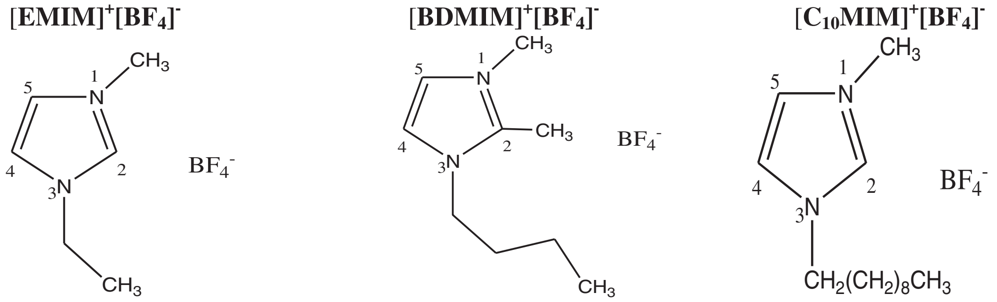

Fig. 1. Schematic representation of the structures of ionic liquids $[EMIM]^+[BF_4]^-$, $[BDMIM]^+[BF_4]^-$, and $[C_{10}MIM]^+[BF_4]^-$.

lower density, lower solubility, slower diffusion, and higher viscosity [26–28]. Imidazolium-based ILs, one of the most studied RTILs to date, have been reported to exhibit aggregation behavior as a function of alkyl chain length by atomistic/coarse grained molecular dynamic simulation [29–32]. The effect of cation asymmetry on structural heterogeneity and several physicochemical properties has also been recently reported [33,34]. Small-angle neutron scattering has been used to show that the increased heterogeneity stems primarily from the increasing asymmetry of the cation as the chain length is increased [35–37].

The objective of this work is to investigate the corrosion inhibition properties of three methylimidazolium based ILs, namely 1-ethyl-3-methylimidazolium tetrafluoroborate $[EMIM]^+[BF_4]^-$, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate $[BDMIM]^+[BF_4]^-$, and 1-decyl-3-methylimidazolium tetrafluoroborate $[C_{10}MIM]^+[BF_4]^-$ on mild steel in 1 M HCl using electrochemical techniques, spectroscopic methods, quantum chemical calculations and Monte Carlo simulations. The schematic representation of the structures and the atom numbering relevant for the discussion is presented in Fig. 1.

2. Experimental

2.1. Materials

Mild Steel (MS) having composition (wt.%) of C = 0.17, Mn = 0.46, Si = 0.26, S = 0.017,P = 0.019, and balance Fe were used for electrochemical studies. An aggressive solution of hydrochloric acid (AR grade) of 1 M concentration was used for all the experiments.

2.2. Inhibitors

The ILs $[EMIM]^+[BF_4]^-$, $[BDMIM]^+[BF_4]^-$ and $[C_{10}MIM]^+[BF_4]^-$ were purchased from Sigma Aldrich with mass fraction purity $\geq 0.97\%$

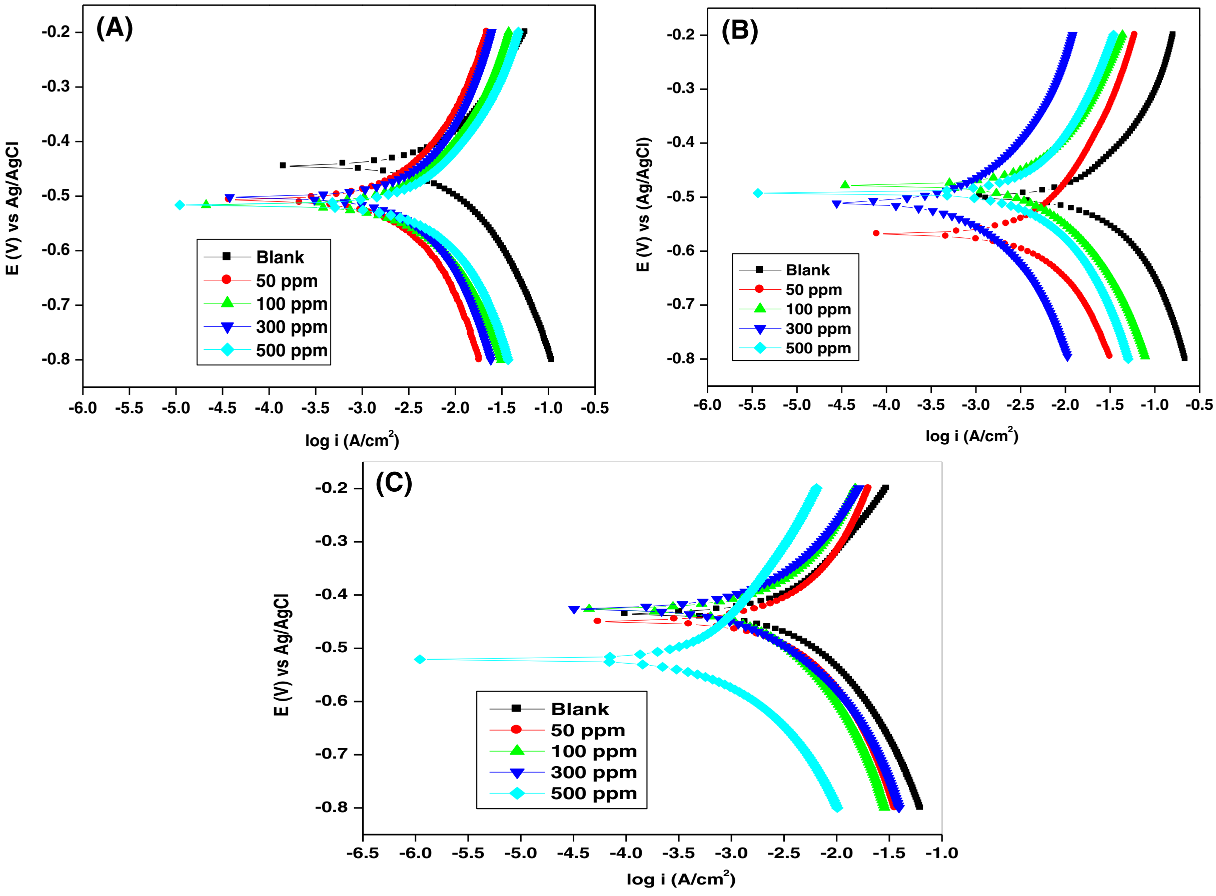

Fig. 2. Potentiodynamic polarization curves of mild steel in 1 M HCl without and with various concentrations of (A) $[EMIM]^+[BF_4]^-$, (B) $[BDMIM]^+ [BF_4]^-$, and (C) $[C_{10}MIM]^+[BF_4]^-$.