



Experimental and theoretical studies on some selected ionic liquids with different cations/anions as corrosion inhibitors for mild steel in acidic medium



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ARTICLE INFO

Article history:

Received 6 November 2015

Revised 4 March 2016

Accepted 6 April 2016

Available online 12 May 2016

Keywords:

Ionic liquids

Mild steel

Corrosion inhibition

QSAR

Monte Carlo simulations

ABSTRACT

Inhibition of mild steel corrosion in 1 M HCl solution by some alkylimidazolium-based ionic liquids (ILs) namely 1-ethyl-3-methylimidazolium ethylsulfate [EMIM]⁺[EtSO₄]⁻, 1-ethyl-3-methylimidazolium acetate [EMIM]⁺[Ac]⁻, 1-butyl-3-methylimidazolium thiocyanate [BMIM]⁺[SCN]⁻, 1-butyl-3-methylimidazolium acetate [BMIM]⁺[Ac]⁻ and 1-butyl-3-methylimidazolium dicyanamide [BMIM]⁺[DCA]⁻ was investigated using electrochemical, spectroscopic, surface morphology, quantum chemical calculations, quantitative structure activity relationship (QSAR) and Monte Carlo simulation methods. The studied ILs showed appreciable inhibition efficiencies within the range of concentrations considered. Polarization measurements showed that the studied ILs are mixed-type inhibitors, that is, they inhibit both the anodic mild steel dissolution and cathodic hydrogen evolution reactions. The adsorption of the ILs on mild steel affords competitive physisorption and chemisorption processes and obeyed the Langmuir adsorption isotherm. Spectroscopic studies confirmed chemical interactions between the ILs and mild steel, while the scanning electron microscopy (SEM) images revealed the formation of protective film of the inhibitors on mild steel surface. Theoretical quantum chemical calculations, QSAR analyses and Monte Carlo simulations studies were used to correlate experimental results. The best fit QSAR equations are functions of molecular weight, fraction of electrons transferred from the inhibitor to the metal and dipole moment of the ILs.

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1. Introduction

The use of corrosion inhibitors to reduce the unwanted metal dissolution process associated with various industrial practices such as cooling water recirculation, acid pickling, acid descaling, oil-well acidizing etc. has been widely studied [1,2]. The use of corrosion inhibitors is one of the most practical and economical methods of protecting metals against corrosion and the initial mechanism involved in any corrosion inhibition process is the adsorption of the inhibitor on the surface of the metal [3–6]. Corrosion inhibitors are often synthesized from relatively cheap and readily available raw materials such as carbonyl compounds,

amines, alcohols etc. Most of these compounds contain π -electrons and functional groups such as $-C=C-$, $-OR$, $-OH$, $-NR_2$, $-NH_2$ and $-SR$, and heteroatoms such as S, O and N [7].

Ionic liquids (ILs) are among the compounds that have been gaining increasing popularity in corrosion inhibition studies in the recent times. Ionic liquids (ILs) are salts with low melting points, frequently below room temperature [8]. The most common ILs are based on imidazolium, pyridinium, quaternary ammonium and quaternary phosphonium cations, but there is growing interest in some other classes of salts. They usually exhibit diverse chemical and physical properties, as well as phase behavior with other compounds. ILs can be designed for a particular application by selectively choosing the cation, anion and functional groups. Most ILs exhibit extremely low volatility over normal operating temperatures. In addition, they show good thermal stability (473–673 K before noticeable decomposition) and thus, exists as liquids over a rather wide temperature range. This affords the possibility of

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using ILs under many different processing conditions without fear of vapor emissions [9]. A huge number of different ILs can be generated due to the large number of possible permutations of cations and anions as well as variation of the side chain length, nature of ring substituents and/or substituents position on the ring [10,11]. Despite the large number of ILs known, the 1-alkyl-3-methylimidazolium based ILs constitute the most commonly used family of ILs in industrial applications [10]. This may be partly due to the availability of quite a number of spectroscopic and physico-chemical data on these compounds as compared to other families of ILs [12]. The corrosion inhibition activities of a few number of imidazolium ILs have been documented in the literature [13–16].

The comparative studies on corrosion inhibition properties of IL systems often reported in the literature typically comprise two compounds with the same cations but different anions or vice versa [17–20]. Reports on the effects of alkyl chain length on the inhibition efficiency of ILs are also more common than those on the effects of anions [18,21,22]. Experimental and theoretical investigations on comparative inhibition activities of more than three IL systems are fragmentary. This may be due to the rather complex nature of interactions that exist in IL solutions. Another possible reason is the difficulties in carrying out reliable experimental studies, which is associated with the hygroscopicity of many ILs and presence of impurities [10].

This has motivated us to carry out the present study on the corrosion inhibition properties of five IL systems namely: 1-ethyl-3-methylimidazolium ethylsulfate $[\text{EMIM}]^+[\text{EtSO}_4]^-$, 1-ethyl-3-methylimidazolium acetate $[\text{EMIM}]^+[\text{Ac}]^-$, 1-butyl-3-methylimidazolium thiocyanate $[\text{BMIM}]^+[\text{SCN}]^-$, 1-butyl-3-methylimidazolium acetate $[\text{BMIM}]^+[\text{Ac}]^-$ and 1-butyl-3-methylimidazolium dicyanamide $[\text{BMIM}]^+[\text{DCA}]^-$ using electrochemical measurements, spectroscopic techniques, quantum chemical calculations coupled with quantitative structural activities relationship (QSAR) and Monte Carlo simulations approach. The set of ILs considered in the present work comprises those with the same cations but different anions, those with the same anions but different cations and those with different cations and different anions. This kind of composite system will provide undissipated information about the effects of cations, anions and chain length on the corrosion inhibition properties of the ILs. More so, the QSAR analysis generated from such composite systems is expected to be more robust as it takes more factors into consideration. The test material in the present study is mild steel in 1 M HCl solution. To the best of our knowledge, the kind of study reported on the set of ILs considered in this work has not been documented in the literature. The schematic representation of the structures of the studied ILs are presented in Fig. 1.

2. Experimental

2.1. Mild steel specimens

All experimental procedures were carried out using mild steel specimens of composition (wt%) of C=0.17, Mn=0.46, Si=0.26, S=0.017, P=0.019, and balance Fe. These specimens were carefully prepared prior to each experiment. They were abraded using various grades of emery papers, washed with doubly distilled water, degreased with acetone, air-dried and finally stored in the desiccators. Each mild steel specimen with prepared shining surface is used for respective experimental measurements within 1 h.

2.2. Inhibitors

The ILs $[\text{EMIM}]^+[\text{EtSO}_4]^-$, $[\text{EMIM}]^+[\text{Ac}]^-$, $[\text{BMIM}]^+[\text{SCN}]^-$, $[\text{BMIM}]^+[\text{Ac}]^-$ and $[\text{BMIM}]^+[\text{DCA}]^-$ were purchased from Sigma Aldrich with mass fraction purity $\geq 0.97\%$ and were used without

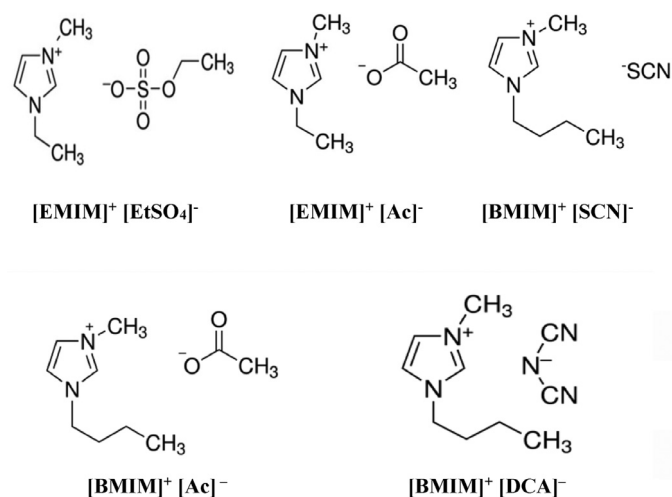


Fig. 1. Schematic representation of the structures of 1-Ethyl-3-methylimidazolium ethyl sulfate $[\text{EMIM}]^+[\text{EtSO}_4]^-$, 1-Ethyl-3-methylimidazolium acetate $[\text{EMIM}]^+[\text{Ac}]^-$, 1-Butyl-3-methylimidazolium thiocyanate $[\text{BMIM}]^+[\text{SCN}]^-$, 1-Butyl-3-methylimidazolium acetate $[\text{BMIM}]^+[\text{Ac}]^-$, 1-Butyl-3-methylimidazolium dicyanamide $[\text{BMIM}]^+[\text{DCA}]^-$.

any further purification. All the chemicals were stored over 0.4 nm molecular sieves to remove moisture.

2.3. Acid and inhibitor solutions

Aggressive solution of 1 M HCl was prepared by diluting the 37% AR grade HCl solution with distilled water. The stock solutions of ILs were diluted to 100, 300 and 500 ppm and used for the experiments.

2.4. Electrochemical measurements

All electrochemical measurements were carried out on Autolab PGSTAT 302N purchased from Metrohm and controlled by the general-purpose electrochemical software (GPES). A three-electrode electrochemical setup was used with mild steel as working electrode (WE), platinum rod as counter electrode (CE) and Ag/AgCl in 3 M KCl as reference electrode (RE). All the experiments were performed under atmospheric condition without stirring. Prior to the all electrochemical measurements, a stabilization period of 30 min was allowed for the system to attain a relatively stable value of open circuit potential (OCP). The potentiodynamic polarization curves were recorded in the potential range from -250 to $+250$ mV (vs Ag/AgCl, 3 M KCl) at a scan rate of 1 mV s^{-1} . The electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range from 100 kHz to 1 Hz with amplitude of 10 mV peak-to-peak using the AC signal at the OCP.

2.5. UV-visible spectroscopic studies

Mild steel samples with pretreated surfaces as described in Section 2.1 were immersed in acidic solutions of 500 ppm IL solutions for 24 h. The UV-vis spectra of the IL solutions before and after mild steel immersion were recorded on the UViLine 9400 obtained from Schott instruments.

2.6. FTIR spectroscopic studies

Mild steel samples with pretreated surfaces as described in Section 2.1 were immersed in acidic solutions of 500 ppm IL solutions for 24 h. The FTIR spectra for the pure ILs and the resulting

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