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Corrosion inhibition properties of two imidazolium ionic liquids with hydrophilic tetrafluoroborate and hydrophobic hexafluorophosphate anions in acid medium

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ABSTRACT

The ionic liquids, 1-vinyl-3-aminopropylimidazolium hexafluorophosphate ([VAIM][PF_6]) and 1-vinyl-3-aminopropylimidazolium tetrafluoroborate ([VAIM][BF_4]) acted as the corrosion inhibitors. Weight loss measurements showed the corrosion inhibition efficiencies of [VAIM][PF_6] and [VAIM][BF_4] were 90.53% and 54.01% at 45 °C, respectively. The ILs were mix-type inhibitors. Raising the temperature can have a decreased inhibition efficiency of [VAIM][BF_4], while [VAIM][PF_6] presented an opposite trend. In addition, [VAIM][PF_6] obeyed Langmuir monolayer adsorption isotherm, while [VAIM][BF_4] obeyed EI-Awady kinetic-thermodynamic adsorption for blocking active sites. Moreover, Molecular Dynamic Simulations showed that [VAIM][PF_6] owned a higher adsorption energy, which may be responsible for the more adsorption groups of [VAIM][PF_6].

Introduction

Corrosion inhibition has always been the focus of metal protection in aggressive environment. Corrosion inhibitor addition was the most convenient and common way to improve the corrosion phenomenon [1,2]. Generally speaking, organic compounds which containing nitrogen, oxygen, sulfur atoms and multiple bonds can be functioned as corrosion inhibitors [3–6]. It was noticeable that imidazoline and its derivatives had a wide application due to the advantages of high corrosion inhibition efficiency and easy degradation [7]. Meanwhile, ionic liquids (ILs), a kind of molten salt composed of organic cations and various anions, were seen as a kind of green solvent due to its physical advantages, such as high ionic conductivity, non-flammability, great thermal stability and low volatility over normal operating temperature [8–10]. Zhang and Hua [1] studied the corrosion inhibition of alkylimidazolium ionic liquids for its potential as green solvent. The mechanism of such inhibitors had been interpreted as the adsorption process benefiting from the free electron pairs, the π-orbital character of free electrons and the electron density around the nitrogen atoms.

Because more and more attention was paid to environmental and sustainable development, many organic inhibitors have been restricted to use as the corrosion inhibitors for their high toxicity. As describe above, ILs was introduced into corrosion inhibition field for the concept of "green chemistry" [8]. A survey of literature revealed that the ILs had huge potential application as corrosion inhibitors in acid solution on copper alloys [11], aluminum [12], and steel [13]. For example, Qiang et al. [11] studied four allylimidazolium-based ionic liquids, 1-allyl-3-ethylimidazolium bromide ([AEIM][Br]), 1-allyl-3-butylimidazolium bromide ([ABIM][Br]), 1-allyl-3-hexylimidazolium bromide ([AHIM][Br]), 1-allyl-3-octylimidazolium bromide ([AOIM][Br]), on the corrosion of copper in 0.5 M H_2SO_4 solution. And it was found that the inhibition efficiencies increased with incremental concentration and longer alkyl chain attached to the imidazolium ring. Trombetta et al. [12] studied The aluminium corrosion susceptibility in the mixtures solution of ethylene glycol, which was composed of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMI][BF_4]), $Na_2B_2O_7{\cdot}10H_2O$ and NaH_2PO_4 at a concentration of 0.1 mol L^{-1}. The results attested to the stability of dielectric oxide in a pure [BMI][BF_4] medium. Likhanova et al. [14] studied 1,3-dioctadecylimidazolium bromide and *N*-Octadecylpyridinium

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bromide as corrosion inhibitors on mild steel in acid solution and 1,3-Dioctadecylimidazolium bromide provided a better inhibition efficiency than *N*-Octadecylpyridinium bromide. In addition to the metal materials, the ILs corrosion inhibition studies were mainly in the following directions [3,14–17]: the effects of the cation kind, the length of the hydrophobic chain, and the novel ILs (poly ILs, Gemini-cationic ILs etc.). Sasikumar et al. [3] had a comparison of some imidazolium ionic liquids containing tetrafluoroborate anion as corrosion inhibitors on mild steel in acidic medium. It was found that the corrosion inhibition efficiency followed the sequence 1-decyl-3-methylimidazolium tetrafluoroborate [C_{10}MIM][BF_4] > 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [BDMIM][BF_4] > 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4]. Hanza et al. [17] studied the corrosion inhibition effectiveness of 1,4-di[1-methylene-3-methyl imidazolium bromide]-benzene on mild steel in 1 M H_2SO_4. The corrosion inhibition mechanism might be the formation of a layer on the metal surface which blocked the active sites. Kowsari et al. [8] synthesized tetra-n-butyl ammonium l-methioninate [TBA][L-Met] which acted as corrosion inhibitor of carbon steel in acid solution. The IL was a mixed-type inhibitor with dominant anodic inhibition. Shetty and Shetty [9] studied ionic liquid, 1.3-bis[2-(4-methoxyphenyl)-2-oxoethyl]-1H-benzimidazol-3-ium bromide (MOBB), as corrosion inhibitor on 6061 Al-15 vol % $SiC_{(P)}$ composite in 0.1 M HCl and 0.1 M H_2SO_4. The adsorption of MOBB on the composite was predominantly through chemisorptions and obeyed Langmuir adsorption isotherm. Chong et al. [10] synthesized a family of ionic liquids and organic salts based on the imidazolinium cation. These materials were found to have interesting physical properties such as facile ion transport, as well as demonstrating synergistic corrosion inhibition on mild steel. 2-methylimidazolinium 4-hydroxycinnamate was found to show strong anodic corrosion inhibition on mild steel. Despite this, there was much unknown space for ILs resulting from its structural diversity because it can be designed into different cations, anions, as well as type and position of substituent.

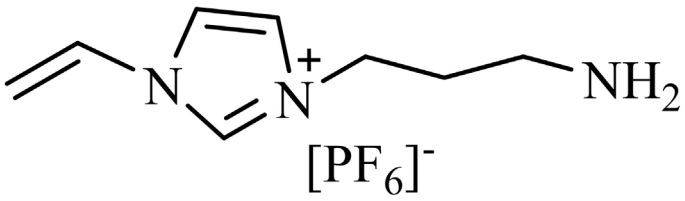
As far as the author knew, no reports referred to the influence of hydrophilic and hydrophobic anions on the corrosion inhibition were reported. Therefore, the present work was to study the corrosion inhibition of two synthesised ILs, 1-vinyl-3-aminopropylimidazolium hexafluorophosphate ([VAIM][PF_6]) and 1-vinyl-3-aminopropylimidazolium tetrafluoroborate ([VAIM][BF_4]) (Fig. 1), on the carbon steel in 1.0 M HCl solution for the purpose of comparing the inhibition effect of $[BF_4]^-$ and $[PF_6]^-$ anions with the same cation. The difference of the anions was that the $[PF_6]^-$ was a hydrophobic group, while the $[BF_4]^-$ was a hydrophilic group. For the part of $[VAIM]^+$, it contained not only hydrophobic groups (multiple bonds) but also hydrophilic groups (–NH_2, quaternary ammonium salt). Owing to the inherent amphiphilicity properties, the studied ILs were placed in the class of ionic surfactant [18,19]. We obtained the value of critical micelle concentration (CMC) which was set as the maximum inhibitor concentration aiming at promising the homogeneous solution because the formation of micelles may affect the corrosion inhibition efficiency. Conductivity measurements and the theory of ionic surfactant verified that ILs existed in the form of ions and ion pairs below the CMC. In addition, weight loss and electrochemical measurements were conducted along with several other surface analyses. Then, molecular dynamic simulation calculation was used to study the adsorption model of ILs in the vacuum and aqueous solution, respectively. Some reports have compared the physics and chemistry properties of ILs based on different anions [20,21], such as water solubility, solubility of H_2S in ILs and so on. Combining with the former study achievements on the interaction between water molecules and ILs by the computational chemistry and IR-spectroscopy methods, we provided a mechanism to explain the corrosion inhibition efficiency gap between the two investigated green ILs, which has not been raised in ILs corrosion inhibition field nowadays. In addition, the theory may be introduced into the corrosion inhibition process of ionic surfactants.

Experimental

Chemical and sample preparation

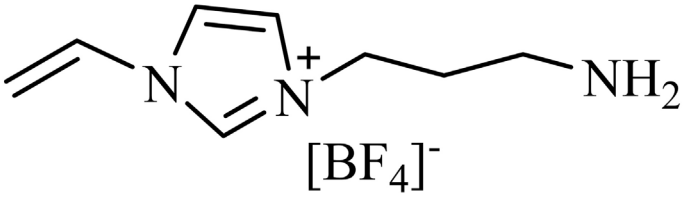
All the chemicals were analytical grade (>98% pure). The used samples were Q235 carbon steels containing 0.17% C, 0.37% Mn,

(a)



1-vinyl-3-aminopropylimidazolium hexafluorophosphate ([VAIM][PF_6])

(b)



1-vinyl-3-aminopropylimidazolium tetrafluoroborate ([VAIM][BF_4])

Fig. 1. The chemical structure of the synthesized inhibitors.

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