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Experimental and theoretical studies of two imidazolium-based ionic liquids as inhibitors for mild steel in sulfuric acid solution

Xingwen Zheng [a,b,c], Shengtao Zhang [a,*], Wenpo Li [a], Min Gong [c], Linliang Yin [a]

[a] *College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China*
[b] *School of Chemical and Pharmaceutical Engineering, Sichuan University of Science & Engineering, Zigong 643000, China*
[c] *Key Laboratory of Material Corrosion and Protection of Sichuan Province, Zigong 643000, China*

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ABSTRACT

The inhibition performance and mechanism of 1-octyl-3-methylimidazolium bromide ([OMIM]Br) and 1-allyl-3-octylimidazolium bromide ([AOIM]Br) for the corrosion of mild steel in 0.5 M H_2SO_4 were investigated using weight loss method, electrochemical measurements, scanning electron microscope (SEM) and quantum chemical calculation. The results revealed that [OMIM]Br and [AOIM]Br acted as modest cathodic inhibitors, and due to the electron-donating effect of allyl group, [AOIM]Br showed better inhibitive performance. The adsorption of both inhibitors on steel surface obeyed El-Awady thermodynamic–kinetic model, thus the thermodynamic and kinetic parameters were calculated and discussed. Moreover, theoretical calculation was used to investigate inhibition mechanism of studied inhibitors.

1. Introduction

Ionic liquids are one of the most promising alternative chemicals in the future [1]. Their peculiar properties appeal to diverse technological areas such as synthetic chemistry, electrochemistry, analytical chemistry, separation and extraction, and other engineering and biological applications [2]. Ionic liquid is composed of entirely ions, usually an inorganic anion and an organic cation. Generally, the cation part is a bulky organic cation, such as N-alkylimidazolium, alkylammonium, alkylpyridinium or alkylphosphonium. Previous studies have demonstrated that imidazole [3–6], ammonium [7–9], pyridine [10–12] and phosphonium [13,14] have good inhibitory effect on the corrosion behavior of metal in aggressive media. Moreover, there may be a synergistic effect between anion and cation in ionic liquid. Meanwhile, the amount of ionic liquid is tremendous in theory, therefore, ionic liquid is of great potential to be explored as a novel green corrosion inhibitor.

Recently, some ionic liquids have been investigated as inhibitors for carbon steel [15–21] and aluminum [22,23]. However, to the authors' best efforts, few reports have been found to focus on the substituent in the imidazole ring is how to influence the inhibitive performance of imidazolium-based ionic liquid. The research on the pyrimidine compound as inhibitor has been found that its inhibition efficiency mainly depends on the substitution group in the pyrimidine ring [24]. Accordingly, there is a great need to investigate the influence of substituent on the inhibitive performance of ionic liquid. Besides, ionic liquids containing long chain length may exhibit stronger corrosion inhibiting ability because of their good hydrophobicity, but the long alkyl chain also induced poor water-solubility and strong foaming-ability for the ionic liquids, which is detrimental when they used as corrosion inhibitors. Thus, in this paper, we evaluate the inhibition effectiveness of two imidazolium-based ionic liquid, 1-octyl-3-methylimidazolium bromide ([OMIM]Br) and 1-allyl-3-octylimidazolium bromide ([AOIM]Br), on the corrosion of mild steel in 0.5 M H_2SO_4 solution. These two molecules contain short alkyl chain (8 carbon atoms) and are only minor difference on the substitute groups. The results could help us to understand the effect of substituent on the inhibition performance of imidazolium-based ionic liquid, and provide guidance or direction to design and develop new containing short chain imidazolium-based ionic liquids as inhibitor.

2. Experimental

2.1. Preparation of solutions and samples

The corrosive solution 0.5 M H_2SO_4 was prepared using analytical grade sulfuric acid and distilled water. The test inhibitors [OMIM]Br and [AOIM]Br, whose molecular formulas were shown

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* Corresponding author. Tel.: +86 23 65112134.
E-mail addresses: stzhang@cqu.edu.cn, stzhangcqu@126.com (S. Zhang).

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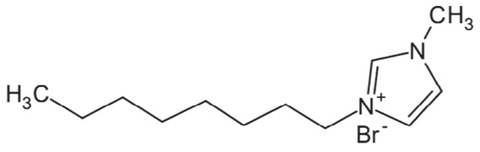
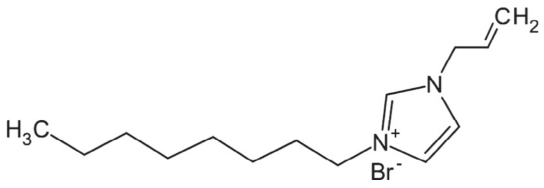


(a) [OMIM]Br



(b) [AOIM]Br

Fig. 1. Molecular structures of the investigated inhibitors: [OMIM]Br (a) and [AOIM]Br (b).

in Fig. 1, were purchased from Lanzhou Greenchem ILS, LICP. CAS. China with the purity of 99% and were not purified further before use. The concentration range of the inhibitors employed was 0.5–10 mM, and the solution in the absence of inhibitors was taken as blank for comparison.

In all experiments, the samples were cutted from a mild steel plate with a chemical composition (in wt%) as follows: C (0.16%), Si (0.18%), Mn (0.29%), P (0.014%), S (0.013%) and Fe for balance. Prior to all measurements, the samples were mechanically abraded with emery paper up to 1000 grit, then rinsed with distilled water, degreased in acetone and dried at room temperature. During the weight loss and electrochemical measurements, the temperature of solution was controlled by a water thermostat with an accuracy of 1 K, and all experiments were open to the air and carried out under static conditions.

2.2. Weight loss experiment

Square specimens with dimensions 50 mm × 25 mm × 5 mm were used for weight loss measurements. The specimens in triplicate for each inhibitor concentration were accurately weighted and then immersed in 0.5 M H_2SO_4 solution for 4 h at 298, 308, 318 and 328 K, respectively. After that, the specimens were withdrawn, scrubbed with bristle brush, cleaned by distilled water and acetone, then dried and weighed. The corrosion rate (v), inhibition efficiency (η) and surface coverage (θ) were calculated from the following equations:

$$v = \frac{W}{St} \tag{1}$$

$$\eta(\%) = \frac{v_0 - v}{v_0} \times 100 \tag{2}$$

$$\theta = \frac{v_0 - v}{v_0} \tag{3}$$

where W is the weight loss of the mild steel sample, S is the total surface area of the sample, t is the immersion time, v_0 and v are the corrosion rates of the mild steel sample without and with inhibitor, respectively.

2.3. Electrochemical experiment

A traditional three-electrode cell assembly with mild steel working electrode, saturated calomel electrode (SCE) and platinum electrode was used for electrochemical measurements using PARSTAT 2273 advanced electrochemical system. The working electrode had an exposed surface area of 0.785 cm^2 and was embedded in epoxy resin. All potential data reported were referred to SCE reference electrode. First, the working electrode was immersed into test solution for 30 min at open circuit potential (OCP) to reach a steady state, correspondingly, the OCP–time curves are depicted in Fig. 2, it could be seen that the OCP reached a steady state value after 30 min immersion. Then electrochemical impedance spectroscopy (EIS) measurement was performed in frequency range of 10^{-2}–10^5 Hz using a sinusoidal AC perturbation with amplitude of 5 mV peak-to-peak at OCP. At last, the potentiodynamic polarization curve was obtained in potential range of −250 mV to +250 mV versus OCP with a scan rate of 0.5 mV/s. The EIS and Polarization data were analyzed by ZSimpWin software and PowerSuite ver.2.58 electrochemical software, respectively. The inhibitive efficiency (η%) was respectively calculated from potentiodynamic polarization curves and EIS as follows:

$$\eta = \left(1 - \frac{I_{corr}}{I_{corr,0}}\right) \times 100 \tag{4}$$

where $I_{corr,0}$ and I_{corr} are the corrosion current densities without and with inhibitor, respectively.

$$\eta = \frac{R_{ct} - R_{ct,0}}{R_{ct}} \times 100 \tag{5}$$

where $R_{ct,0}$ and R_{ct} are the charge transfer resistances without and with inhibitor, respectively.

2.4. Surface analysis

The surface morphology analysis of mild steel specimens with dimensions 15 mm × 10 mm × 5 mm before and after immersion in 0.5 M H_2SO_4 solution without and with 10 mM inhibitor for 10 h were performed on a Tescan Vega3 SEM instrument at high vacuum.

2.5. Quantum chemical study

Quantum chemical calculations were made by using Gaussian 03W software. All molecules were fully optimized by density functional theory (DFT) using B3LYP functional with 6-311++G(d,p) basis set in gas phase [25]. Quantum chemical parameters including the energy of highest occupied molecular orbital (E_{HOMO}), the energy lowest unoccupied molecular orbital (E_{LUMO}), energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), dipole moment ($\mu$), the fraction of electrons transferred (ΔN) and Mulliken charge were calculated.

3. Results and discussion

3.1. Weight loss measurements

The weight loss results of mild steel in 0.5 M H_2SO_4 solution without (blank) and with different concentrations of [OMIM]Br/[AOIM]Br for 4 h at different temperatures (298–328 K) are provided in Table 1. It obviously shows that the corrosion rate decreases with the increase of inhibitor concentration at 298 and 308 K, consequently, the inhibitive efficiency increases with the presence of higher concentrations inhibitors. And the maximum inhibitive efficiencies are respectively about 90% and 95% at 10 mM for [OMIM]Br and [AOIM]Br, which suggest the two imidazolium-based ionic liquids effectively inhibited the corrosion of mild steel in acidic solution. It is also noted that the inhibitory effect for both inhibitor is very weak at low concentrations and the effective concentrations of the two inhibitors are certainly