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New corrosion inhibitor acrylamide methyl ether for mild steel in 1 M HCl

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ABSTRACT

Pursuit of good inhibition performance has been a persistent objective for advanced inhibitor industry. Here we demonstrate the experimental realization of a new corrosion inhibitor acrylamide methyl ether (AAME) from *N*-Methylol acrylamide (N-MAM) for mild steel in 1 M HCl. The resultant adsorption films have inhibition efficiency as high as 96.2%. Moreover, a theoretical investigation is also launched to demonstrate the potential mechanism behind the promising corrosion behaviors. This work represents a significant step forward, as it demonstrates how to make scalable AAME inhibitors as well as to enhance inhibition performances for high-efficiency and cost-effective corrosion inhibition platforms.

1. Introduction

Steel and corresponding alloys have been a mainstay in nowadays social forward due to their merits on cost-effectiveness, facile fabrication, and excellent mechanical strength [1]. Application-specific requirements for advanced steel species include persistent stability in ambient environment such as acidic solution for gas distribution networks and oil pipelines [2], allowing for an inevitable topics on corrosion [3]. By addressing this issue, many methods such as electrochemical protection and brushing coatings have been created to enhance corrosion resistance. Among diversiform strategies, utilization of corrosion inhibitors in corrosion coatings is attracting considerable attentions in elevating attack from acid species [4–6]. As a crucial placeholder, organic inhibitors [7–9], having nitrogen, oxygen, sulfur, unsaturated bond, or aromatic rings [10] can adsorb onto the outward steel surface by electrostatic interactions between the inhibitor and metal (physical adsorption) or by coordinate covalent bonds (chemical adsorption), creating an aggressive media for steel protection [11]. Previous studies have demonstrated that the adsorption behavior of inhibitors is of highly dependent on the structure of organic compounds including adsorption active center, charge density, and functional groups [12]. Amides and derivatives like urea, thioureaor thioacetamide display satisfactory performances as inhibitors for mild steel in acid solutions [12,13]. A remaining problem is that some avenues of synthesizing organic compounds always create toxic byproducts and sometimes the organic inhibitors are also toxic toward environment. In this fashion, a prerequisite of expanding applications of corrosion inhibitors is to develop cost-effective and nontoxic organic inhibitors [14], aiming at reducing environmental damage and resource consumption.

In the current work, we launch an experimental realization of new inhibitor AAME by a facile and green strategy using *N*-methylol acrylamide (N-MAM) as raw material. The corrosion resistances of resultant adsorption films on mild steel are thoroughly investigated with gravimetric and electrochemical characterizations when suffer HCl attack. Moreover, quantum chemical calculation is employed to study the dependence of corrosion performances on molecular structure.

2. Experimental

2.1. Material and medium

Q235 mild steel with compositions of C = 0.18 wt%, Si = 0.02 wt%, Mn = 0.45 wt%, S = 0.02 wt%, P = 0.01 wt%, and Fe = 99.32 wt% was

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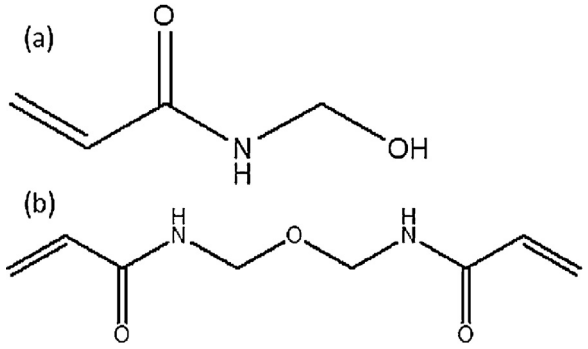

Fig. 1. Structure of (a) N-MAM (b)AAME.

used as protecting target. Before use, the steel rods were polished by SiC abrasive paper (600, 800, 1000, 1200 mesh), subsequently rinsed by acetone and ethanol, and stored in a desiccator for drying. The working electrodes with an area of 1 cm^2 were covered by Teflon and sealed by epoxy resin. Except the investigation of the temperature effect for AAME, all the experiments were carried out at 25 °C.

2.2. Synthesis and characterizationof the corrosion inhibitor

The feasibility of synthesizing AAME was confirmed by following procedures: 50.55 g of N-MAM was dissolved into 200 mL of acetone under vigorous agitation. Subsequently, a mixture containing 8 g of $AlCl_3$ and 50 mL of acetone was added dropwise at 35 °C. After reaction for 4 h, the as-synthesized species were filtered, rinsed, recrystallized by ethyl acetate and dried [15] .The solubility of N-MAM and AAME are 0.0882 g and 0.052 g in water at 25 °C. IR, ^{1}H NMR, ^{13}C NMR, mass spectrum along with elemental analysis were used to characterize the product. The results were shown below:

IR(KBr)γ_{max} = 3267.64(N—H), 3070.1(=CH), 2987.88(—CH), 1677.1 (C=O), 1118.03(—O—) cm^{-1}

^{1}H NMR (500 MHz. DMSO) δ: 8.862(t,2H,N—H), 6.18(m,4H,C—H), 5.69(Q,2H,=CH), 4.64(d, 4H,—CH_2)

^{13}C NMR(500 MHz, ethanol) δ: 57.985,127.071,131.846,165.725.

MASS (M^+): The base peak appeared at 185 which due to protonated molecular ion peak $(M+H)^+$ confirm the formula $C_8H_{12}N_2O_3$

Elemental analysis: N, 15.05 (15.06, 15.07); C, 52.11(52.06, 52); H, 5.833(5.78, 5.618)

All of these confirm the structure shown in Fig. 1b

2.3. Gravimetric experiment

The weight loss test was performed by immersing the steel rods (50mm × 10 mm with a 6 mm diameter hole) which had been weighed accurately into the 1 M HCl within and without a series of concentrations inhibitors at different temperatures (25–65 °C) for 24 h. The specimens were taken out after erosion, washed out corrosion products, rinsed with distilled water, dried and weighed accurately. The corrosion efficiency (IE) and the surface coverage θ were calculated by using the following equation [16]:

$$\theta = \frac{V_0 - V}{V_0} \quad (1)$$

$$V = \frac{W_1 - W_2}{St} \quad (2)$$

$$IE(\%) = \left(\frac{V_0 - V}{V_0}\right) \times 100 \quad (3)$$

where W_1 (mg) and W_2 (mg) were the mean weight of specimens, V_0 (mg cm^{-2} h^{-1}) and V (mg cm^{-2} h^{-1}) are corrosion rate without and with inhibitor, S(cm^2) is the area of the specimens, t(h) is the time of corrosion.

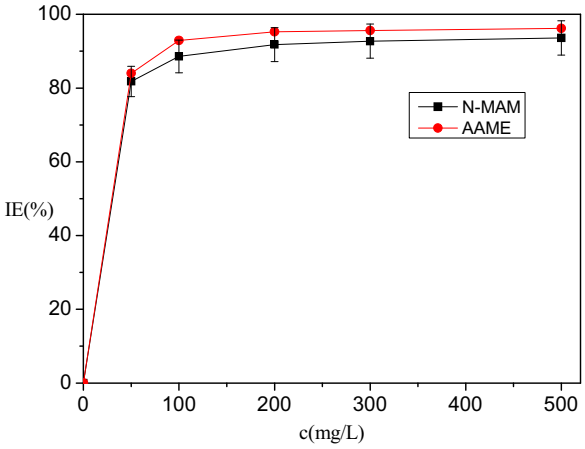

Fig. 2. Relationship between inhibition efficiency (IE) and concentration (c) of inhibitor in 1 M HCl at 25 °C acquired from gravimetric experiment.

2.4. Electrochemical experiment

The electrochemical test was performedin a conventional three electrode cell consisting a mild steel working electrode(WE, 1 cm^2), a saturated calomel reference electrode(SCE) and a platinum foil electrode(CE) at 25 °C. The electrochemical measurements were performed onMetrohmautolab electrochemical instrument, PGSTAT302N. Data were analyzed using NOVA 1.8 software.

The potential of potentiodynamic polarization tests was started from −250 mV to +250 mV vs SCE at open circuit potential(OCP) with a scan rate 1 mV/s. Corrosion current density was fitted by Tafel extrapolation method.

The electrochemical impedance spectroscopy(EIS) tests were carried out at OCP in the 100 kHz to 10mHz frequency range with a signal amplitude of 10 mV using alternating current.

3. Quantum chemical calculation

The quantum chemical calculations were performed by using Gauss View molecular Visualization program and Gaussian-03 software package [17]. The geometric optimization of the molecular structure was carried out by density function theory(DFT) B3LYP method with 6–31G(d, p) [18,19]. Theoretical parameters such as the energies of the lowest unoccupied molecular orbitals (E_{LUMO}), the energies of the highest occupied orbital (E_{HOMO}), energy gap (△E) were calculated.

4. Result and discussion

4.1. Gravimetric experiment

The inhibition performance of N-MAM and AAME at different molality in 1 M HCl under 25 °C for 24 h was studied by using gravimetric experiment. We also use a conventional inhibitor hexamethylenetetramine (HMTA) as control group. The corrosion rate (v), surface coverage(θ) and inhibition efficiency(IE) were listed in Table 1. It can be seenthat corrosion ratesof N-MAM and AAME are both 4.7 mg cm^{-2} h^{-1} without inhibitor,while in presence of 500 mg/L inhibitor, the rates decrease to 0.305 and 0.182 mg cm^{-2} h^{-1}, respectively. The relationship between concentration and inhibition efficiency were shown in Fig. 2. The IE increases with the inhibitor concentration increasing (Fig. 2) due to the increase of adsorption and the size or structure of molecule.