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Experimental and theoretical investigations of 1,3,5-tris(4-aminophenoxy)benzene as an effective corrosion inhibitor for mild steel in 1 M HCl

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ABSTRACT

The amine derivative 1,3,5-tris(4-aminophenoxy) benzene (TAPOB) was newly synthesized, characterized and evaluated for the first time by weight loss, electrochemical methods and quantum chemical calculation. The inhibition efficiency of TAPOB was as high as 95% according to gravitational method. Information based on potentiodynamic polarization indicated that TAPOB was a mixed-type inhibitor. Electrochemical impedance spectroscopy study proved that TAPOB could adsorb on mild steel surface and impart high charge-transfer resistance. The thermodynamic results demonstrated that the adsorption process of TAPOB on mild steel surface obeyed to Langmuir adsorption isotherm and involved both physical and chemical adsorption. The surface analysis of mild steel further suggested that TAPOB existed on the metal surface to form a protective film by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) technique. The relationship between the inhibition efficiency and molecular structure was discussed via theoretical calculation, which was in a good agreement with the experiment results. All these evidence revealed that TAPOB was an effective and potential amine-typed corrosion inhibitor.

1. Introduction

The hydrochloric acid (HCl) solutions have been extensively used in industry for ore production, acid pickling of metals, chemical cleaning, descaling and acidizing, where the surrounding environment are often corrosive, which can result in severe corrosion problems encountered in industrial processes [1–7]. To solve the thorny issue, the acid corrosion inhibitors are adopted to retard metal loss during contact with various acid in industry [8–10]. Generally, organic compounds containing heteroatoms (N, O, S or P), π bond and aromatic rings act as effective corrosion inhibitors [11–19]. These organic molecules can impede the corrosion rate by adsorbing on the metal surface and forming a protective film by adsorption (physical and/or chemical adsorption). The adsorbed film blocks the active sites on the metallic surface, thereby isolating the metal from corrosive attack [20,21]. Recently, great effort has been devoted to developing novel and efficient corrosion inhibitors, and various inhibitors such as azoles derivatives [22], quaternary ammonium salt derivatives [23] and amine derivatives [24] have been investigated as efficient inhibitors for different metals in acidic media.

Among these corrosion inhibitors, some amine derivatives (except Schiff base derivatives) have been successfully used as corrosion inhibitors in many practical applications due to be easily synthesized, high solubility in acid media and good inhibition efficiency [25,26]. For example, Obot et al. reported the synergistic inhibitive effect of 2,3-naphthalenediamine and iodide ions in 1 M HCl for aluminium corrosion [27]. Bentiss and coworkers demonstrated two new diamine derivatives DAME and DAMP as efficient corrosion inhibitors of mild steel in HCl with efficiency of 91.7% [28]. These encouraging results urge us to develop new amine derivatives as corrosion inhibitors applied for mild steel in acidic media.

In this work, the amine derivative, i.e., 1,3,5-tris(4-aminophenoxy) benzene (TAPOB) was newly synthesized to be investigated about the effect on the corrosion behavior of mild steel in HCl solution. To the best of our knowledge, TAPOB has not been treated as a corrosion inhibitor. TAPOB is selected as corrosion inhibitor mainly based on the following factors: 1) to be easily synthesized and inexpensive; 2) to contain multiple N and O as active centers and aromatic rings system; 3) to have high solubility in acid media; 4) to have bulky steric hindrance. Here, the inhibition effect of TAPOB on mild steel in 1 M HCl solutions was studied by some sophisticated methods including weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS). Meanwhile, the thermodynamic parameters were summarized and discussed for providing better insight into the activated and adsorbent processes. The scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were

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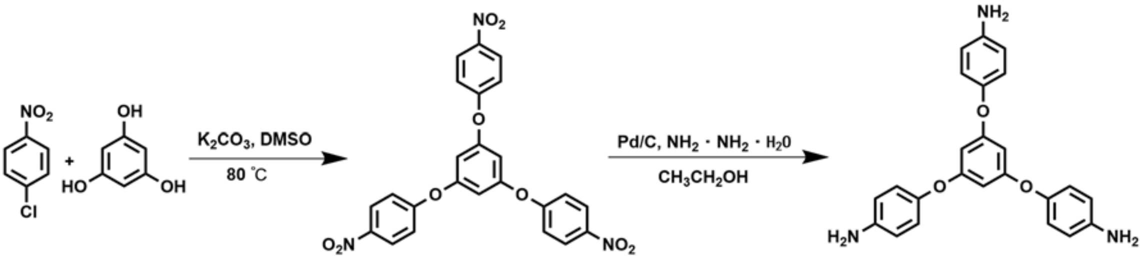

Fig. 1. The synthesized routes of the investigated TAPOB inhibitor.

conducted to observe the surface of mild steels. Furthermore, theoretical calculations using the Density Functional Theory (DFT) method were employed on TAPOB to further clarify the effect of the organic molecule's structure on inhibition efficiency.

2. Experimental

2.1. Material preparation

The chemical composition (wt%) of mild steel used for corrosion measurements was shown as the following: Fe-98.96, C-0.2, Si-0.2, Mn-0.5, P-0.02, Cu-0.02, Cr-0.02, Ni-0.02. The mild steel sheets were abraded with a series of SiC paper, then cleaned successively in deionized water and ethanol. The corrosive tested medium 1 M HCl was prepared by analytical grade HCl (37 wt%) with deionized water.

2.2. The inhibitor

The new inhibitor based on the amine derivative (TAPOB) was synthesized according to the routes in Fig. 1 [29]. M.p.: 147.5–148.7 °C. IR (KBr, cm^{-1}): 3450-3346, 3207, 1620, 1502, 1446, 1201, 866-823. ^1H NMR ($CDCl_3$, ppm): δ: 6.85-6.84 (m, 6H), 6.65-6.63 (m, 6H), 6.16 (s, 3H), 3.57 (s, 6H).

2.3. Weight loss tests

Due to the simplicity and reliability of the weight loss method, it is popularly used to evaluate the inhibition performance of TAPOB. Weight loss experiments were consistent with the standardized method [30]. After attaining immersion time, the samples were fetched out, then cleaned in deionized water and ethanol, dried and finally weighed accurately.

The corrosion rate (C_w), the degree of surface coverage (θ), the efficiency of inhibitor (IE_w) obtained from gravitational testes were determined by the following equations:

$$C_w = \frac{\Delta W}{S \times t} \quad (1)$$

$$\theta = \frac{m - m_{inh}}{m} \quad (2)$$

$$IE_w = \frac{(m - m_{inh})}{m} \times 100 \quad (3)$$

where S and t represented the surface area of specimens and immersion time, respectively; m and m_{inh} were the weight loss values of the samples for the blank and the test solution.

2.4. Electrochemical measurements

Electrochemical experiments were performed using a conventional three-electrode electrochemical cell, in which a saturated calomel electrode (SCE) was used as reference electrode, a platinum foil as a counter electrode, and the treated mild steel with an exposed area of 1.0 cm^2 as working electrode, respectively. Before all electrochemical tests, the working electrode was inserted into test fluid for 45 min to establish a steady state open circuit potential (OCP). The electrochemical data were acquired with a Switzerland Auto lab electrochemical workstation.

The EIS experiments were carried out at OCP on mild steel specimens in the frequency range of 100 kHz to 0.1 Hz using a 10 mV peak-to-peak voltage excitation. The charge-transfer resistance was obtained from Nyquist plot and used to calculate the corrosion inhibition efficiency by the following equation:

$$IE_r = \frac{R_{pi} - R_p}{R_{pi}} \times 100 \quad (4)$$

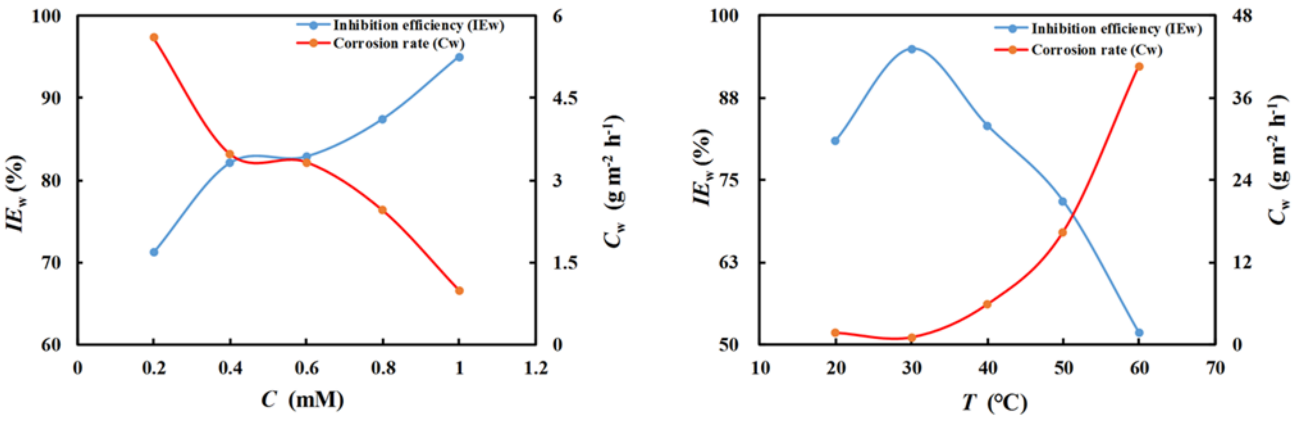

Fig. 2. Variation of the inhibition efficiency and corrosion rate as a function of different concentration of TAPOB (a) and temperature (b).