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A study of differential polarization curves and thermodynamic properties for mild steel in acidic solution with nitrophenyltriazole derivative

Z. Tao [a,*,1], W. He [a,*], S. Wang [a], S. Zhang [b], G. Zhou [a]

[a] State Key Lab of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, China
[b] College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

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ABSTRACT

The nitrophenyltriazole derivative, namely 2-[1,2,4]-triazole-methyl-4-acetyl-5-nitrophenyl-[1,3,4]-oxadiazole (TMANO) was synthesized and its inhibiting action on the corrosion of mild steel in 0.5 M H_2SO_4 solution was investigated by weight loss test, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and scanning electron microscopy (SEM). The selective desorption of TMANO from mild steel surface was also studied by the differential polarization curves. Both thermodynamic and kinetic parameters were calculated and discussed. The results showed that the adsorption of TMANO on steel surface obeys the Langmuir adsorption isotherm. The calculated values of ΔH^0_{ads} and ΔS^0_{ads} indicated that the adsorption process of TMANO on steel surface was exothermic and accompanied by a decrease in entropy.

1. Introduction

Mild steel is widely used in various industrial processes such as acid pickling, industrial cleaning, acid descaling, oil-well acidizing, shipbuilding and petrochemical processes [1–3]. However, mild steel is very susceptible to corrosion in aqueous solution, especially in acidic media. The use of corrosion inhibitor is an effective and practical method to reduce the corrosive attack on metal materials [4–5]. Unfortunately, most of these inhibitor compounds are not only expensive but also toxic to living beings. Therefore, investigating new environmentally friendly inhibitors for steel corrosion in acid media is important. Generally, the inhibiting effect mainly depends on some physicochemical and electronic properties of the organic compound molecule which related to its functional groups (–C=O, –C=N, –C=S etc.), the steric effects, π orbital character of donating electrons and electronic density of donor atoms [6–8]. Due to the predominance in their molecule structures and properties, some triazole derivatives were reported as good corrosion inhibitors for many metals in various aggressive media [9–12], and they are also environment friendly[13–15]. Although various experimental techniques and theoretical methods have been developed to study the relation between the inhibition efficiency and temperature, structural properties of triazole derivatives, the understanding of the relationship between the stability and the desorption potential is still limited [16]. Therefore, investigation of the basic adsorption mechanism of nitrophenyltriazole derivatives has great significance for selection as well as application of the most suitable inhibitors in various corrosive environments.

In this work, the corrosion behavior of mild steel in 0.5 M H_2SO_4 solution with addition of newly synthesized compound of TMANO as inhibitor was investigated by weight loss test, EIS, potentiodynamic polarization and SEM technique, the variation of desorption potentials with inhibitor concentration was observed, where the desorption potential was determined by the differential polarization curves. The more efforts were focused on the adsorption mechanism of TMANO and their inhibiting effects.

2. Experimental

2.1. Materials and test solution

Mild steel containing 0.17 wt.% C, 0.26 wt.% Si, 0.46 wt.% Mn, 0.0047 wt.% P, 0.017 wt.% S, 0.019 wt.% Cu and balance Fe were used for weight loss and electrochemical measurement. The mild steel specimens for weight loss were mechanically machined with a dimension of 3.0 × 1.5 × 1.5 cm. For electrochemical tests, the specimens were embedded in epoxy resin with an exposed working surface area of 1 cm^2.

The aggressive solution of 0.5 M H_2SO_4 was prepared by dilution of analytical reagent grade 98% sulfuric acid with double distilled water.

The compound 2-[1,2,4]-triazole-methyl-4-acetyl-5-nitrophenyl-[1,3,4]-oxadiazole (TMANO) was synthesized in our laboratory,

* Corresponding authors.
E-mail addresses: tzh3595@126.com (Z. Tao), hewei999@vip.sina.com (W. He).
[1] State Key Lab of Electronic Thin Films and Integrated Devices, UESTC, Chengdu 610054, China. Tel.: +86 28 83203218; fax: +86 28 83203218.

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which was purified and characterized by ^{1}HNMR, IR and MS. TMANO is yellow solid, yield 75.0%; m.p. 164–166 °C, ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 9.16 (s, 1H, Tr–H), 8.19 (s, 1H, Tr–H), 8.03 (s, 1H, CH), 7.42–7.27 (m, 4H, Ph-H), 5.56 (s, 2H, CH_2), 2.60 (s, 3H, CH_3); IR (KBr) ν: 1676 (C=O), 1293 (=C–O–C), 1524 (C=N), 1073 (N–N) cm^{-1}; MS (ESI) m/z: 207, 161, 149, 148, 135; 120, 105, 92, 77,64,59,51. Anal. Calcd for $C_{13}H_{12}N_6O_4$: C 50.19, H 3.92, O 26.85; found C 49.37, H 3.82, O 26.57. The synthetic route and molecular structures are shown in Fig. 1. The concentration of TMANO was ranged from 1×10^{-5} to 1×10^{-3} M in 0.5 M H_2SO_4 solution.

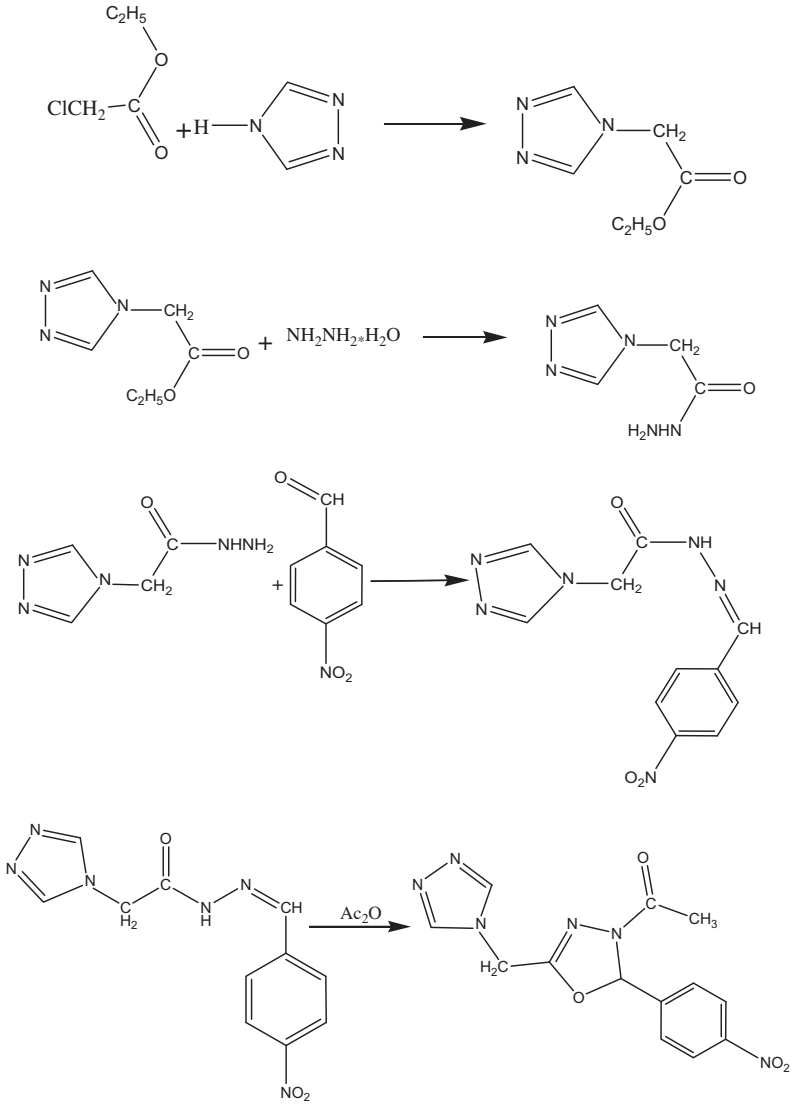
2.2. Electrochemical measurements

The electrochemical measurements were conducted through PARSTAT 2273 Potentiostat/Galvanostat equipped with a conventional three-electrode glass cell with capacity of 500 ml. A mild steel specimen and a platinum electrode with a dimension of 1.5 cm × 1.5 cm were used as working electrode and counter electrode, respectively. A saturated calomel electrode (SCE) with a Luggin capillary is used as reference electrode. All the potentials reported are with reference to SCE. Prior to measurement, the exposed surface of working electrode was polished subsequently with silicon carbide abrasive paper from #400 to #1200 grade, rinsed with distilled water, degreased ultrasonically in acetone and ethanol, then rinsed in distilled water and dried in warm air.

Prior to measurement, the open-circuit potential (OCP) was monitored in test solution at 298 K (±1 K) for 60 min until a steady-state was reached. EIS measurement was carried out in the frequency range of 100 kHz–10 mHz with a 10 mV peak-to-peak sine wave as the excitation signal at steady OCP. The impedance data was analyzed and fitted by using commercial software. The inhibitor efficiency obtained from EIS measurements was calculated by the charge transfer resistance as follows [17]:

$$I_{EZ}\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (1)$$

Where R_{ct}^0 and R_{ct} are the charge transfer resistance in the absence and presence of various concentrations of inhibitor in 0.5 M H_2SO_4 solution, respectively.



2-[1,2,4] triazole-methyl-4-acetyl-5-nitrophenyl -[1,3,4]-oxadiazole (TMANO)

Fig. 1. The synthetic route and molecular structure of the studied compound of TMANO.