Journal of Molecular Liquids 268 (2018) 425–437

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Designing and fabricating of time-depend self-strengthening inhibitor film: Synergistic inhibition of sodium dodecyl sulfate and 4-mercaptopyridine for mild steel

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ARTICLE INFO

Article history:
Received 14 March 2018
Received in revised form 11 July 2018
Accepted 20 July 2018
Available online 23 July 2018

Keywords:
Surfactant
EIS
Weight loss
Synergistic effect
Acid inhibition

ABSTRACT

12-Sodium alkyl sulfate (SDS) was used as supporting frame for the adsorption of 4-mercaptopyridine (4MP) molecules, and the synergistic effect of 4MP and SDS (MP-SDS) was studied. Long time immersion tests showed that MP-SDS inhibitor film changed from monolayer to bilayer structure with time. Owning to the occurrence of the inhibitor bilayer, the corrosion inhibition loss induced by the de-adsorption of first inhibitor layer after long period of immersion was recuperated. MP-SDS shows good synergistic inhibition performance toward the corrosion of the steel in 0.5 M HCl solution. The relative synergistic mechanism was finally discussed.

1. Introduction

Organic compounds containing heteroatoms (N、O、S、P), multiple bonds or aromatic rings are reported effective inhibitors [1–3], these inhibitors were usually used in industries, such as acid pickling, chemical cleaning, oil transportation and etc. [4, 5].

Mercaptopyridines are organic compounds containing nitrogen atoms and sulfur atoms in the molecule [6, 7]. They can interact with metal surface through nitrogen and sulfur atoms and show good film-forming properties. Among these compounds, 4-mercaptopyridine (4MP) has been proved to have good self-assembling performance on gold surface in acid medium [8]. Wan et al. [9] found that 4MP molecules can adsorb on gold surface mainly through nitrogen atoms and sulfur atoms at pH range from 1 to 5, and film can be formed on gold surface at pH 10 through the adsorption of deprotonated 4MP molecules, 4MP molecules show good adsorption ability in a broad pH range. On the basis that the inhibition performance of the organic compounds is related to the structure and the performances of the film formed on the metal surface [10, 11], Hassan et al. [12] studied the corrosion inhibition performance of 4-mercaptopyridine (4MP) in NaCl solution, results showed that the inhibition performance of 4MP toward the corrosion of gold is poor. Up-to-date, no attempts have been made to apply 4MP as inhibitor in acid medium.

Synergistic effect study is an effective method to improve the performances of the inhibitor film, such as the inhibition performance, the adsorption uniformity and the stability [13–15]. Yousefi et al. [16] and Javadian et al. [17] found that the aggregate state of the properly mixed inhibitor is helpful for the enhancement of the inhibition performance. Fuchs [18] demonstrated that this phenomenon attributes to the second state of aggregation for surfactant mixtures appeared. Due to the good migration resistance of the inhibitor film, Zhao et al. [19] found that the nature formation of the inhibitor film on the metal surface can improve the inhibition performance of the single component to a large degree. Han et al. [20] believed that an inhibitor pair having distinct electron-accepting and electron-donating ability can show the synergistic effect, where the adsorption of the inhibitor mixture is improved in comparison to these when are adding single component inhibitors. Though the significant advances of the synergistic inhibition performances of mixed inhibitors, the preparation of an inhibitor mixture with both fantastic inhibition performance and favorable durability remains of a challenge.

Earlier results showed that organic compounds containing alkyl chains can be used as template for the synthesizing of mesoporous materials [21]. These compounds can adsorb on surfaces orderly and the alkyl chains in organic molecules work as a framework for the growing of the target substance [22]. From this perspective, our aim is to use the 12 sodium alkyl sulfate (SDS) as a framework for the adsorption of 4MP

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https://doi.org/10.1016/j.molliq.2018.07.087
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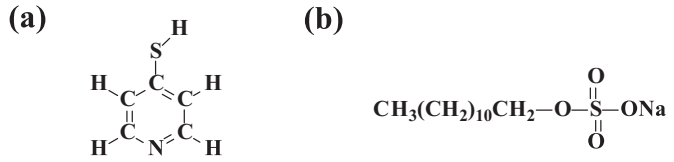

Fig. 1. Chemical structure of (a) 4MP and (b) SDS.

molecules, the enhanced inhibition performance of 4MP and SDS (MP-SDS) is expected.

Based on the aforementioned insights, SDS and 4MP were selected as the studying compounds, the synergistic effect of SDS and 4MP was studied using electrochemical method (Tafel and electrochemical impedance spectroscopy) and weight loss technique. The corroded surfaces were examined by scanning electron microscopy (SEM). The synergistic inhibition mechanism was also discussed according to the results obtained from theoretical calculations.

2. Experimental and theoretical calculation details

2.1. Material preparation

The structure of 4MP and SDS are shown in Fig. 1. 4MP (96%) was purchased from Mackline Co. Ltd. SDS (97%) and hydrochloric acid (38%) were purchased from Adamas-beta. All chemicals were used as received.

Air hardening tool steel (A_3) with chemical composition (wt%) C (0.20%), Si (0.35%), Mn (1.40%), P (0.040%), S (0.040%), and Fe (balance) was used. Samples (50 mm × 15 mm × 1.5 mm) and columned samples (ø 3 × 15 mm) were cut from A_3 steel stock for weight loss measurements and electrochemical measurements, respectively. Before each experiment, the working electrode was mechanically abraded with emery paper beginning from 400 # to 3000 #, then rinsed with double distilled water and finally dried in air.

2.2. Electrochemical tests

Electrochemical measurements were performed in a conventional three-electrode cell, using CHI660-E electrochemical workstation. A_3 steel, Pt sheet and saturated calomel electrode (SCE) with Luggin capillary salt bridge were used as the working electrode (WE), counter electrode and the reference electrode, respectively. 0.5 M HCl solution was used as the test solution. Before each test, 50 mg L^{-1}, 100 mg L^{-1} or 200 mg L^{-1} inhibitor (SDS, 4MP or MP-SDS) was added into the test solution. The open circuit potential (OCP) was recorded for 30 min until a stable state reached (OCP fluctuation less than ±5 mV vs. SCE). Potentiodynamic polarization tests were performed by polarization from −0.8 to −0.2 V vs. SCE with a scan rate of 1 mV s^{-1}. All potentials reported here are referenced to SCE. The corrosion current density was obtained by extrapolating the linear Tafel segments of the cathodic curves to the corrosion potential [23, 24]. The inhibition efficiency obtained from potentiodynamic polarization test was obtained according to the following equation,

$$\eta\% = \frac{i^0_{corr.} - i_{corr.}}{i^0_{corr.}} \times 100\% \quad (1)$$

where $i^0_{corr.}$ is the corrosion current density of A_3 steel without inhibitor, $i_{corr.}$ is the corrosion current density of A_3 steel in the test solution in the presence of inhibitor.

EIS measurements were carried out at the OCP. The ac frequency range extended from 100 kHz to 10 mHz with a 10 mV peak-to-peak sine wave as the excitation signal. Then the impedance data were analyzed and fitted. The inhibition efficiency (IE%) obtained from EIS measurement was calculated according to the following equation,

$$IE\% = \frac{R^0_{ct} - R_{ct}}{R^0_{ct}} \times 100\% \quad (2)$$

where the R_{ct} is the charge-transfer resistance of A_3 steel in the test solution without inhibitor, R^0_{ct} is the charge-transfer resistance of A_3 steel in the test solution in the presence of inhibitor.

2.3. Weight loss tests

Weight loss measurements were performed in wide mouthed jars at 25 °C. 0.5 M HCl solution was used as the test solution. Before each experiment, the weights of the prepared samples were recorded (be accurate to 0.00001 g). Three specimens were immersed for each experimental condition in the test solution without inhibitor and with the addition of 100 mg L^{-1} selected inhibitors for 8 h. Then samples were carefully scrubbed with a bristle brush in 0.1 M HCl solution containing 5 wt% Methenamine until all rust and corrosion scale were removed. Methenamine was used to make sure that the sample surfaces were well protect from corrosion during the rust removal procedure. Then samples were rinsed with double distilled water, dried in air and

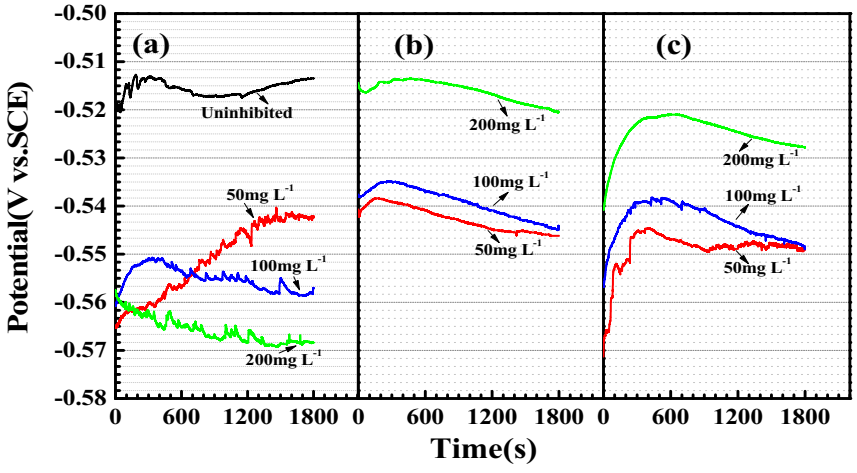

Fig. 2. Open circuit potential of A_3 steel in the 0.5 M HCl solution without inhibitor and with the addition of various concentrations (50 mg L^{-1}, 100 mg L^{-1} and 200 mg L^{-1}) of (a) SDS inhibitor, (b) 4MP inhibitor and (c) MP-SDS inhibitor at 25 °C.