J Mater Sci (2006) 41:5033–5035
DOI 10.1007/s10853-006-0104-x

LETTER

AFM and electrochemical study of the effect of dodecylamine on carbon steel corrosion

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Received: 30 April 2005 / Accepted: 13 December 2005 / Published online: 16 May 2006

The adsorption-type inhibitors play an important role in preventing corrosion of metals in acidic solutions, so the study of the relations between the adsorption and corrosion inhibition is of great importance. Dodecylamine is considered as adsorption-type inhibitor for carbon steel in acidic solutions [1]. Polarization curve measurement is commonly employed in inhibitor research. For example, the modes of inhibition effect of interface inhibitors can be classified by polarization curve [2], corrosion current densities or inhibition efficiencies are often estimated by extrapolation of polarization curves to corrosion potentials. In some cases, equations of adsorption isotherms of interface inhibitors are obtained from plots of the inhibition efficiencies vs concentrations of the inhibitors studied [3–6].

Atomic force microscopy (AFM) is receiving considerable attention in the field of surface science and engineering, it has also been successfully applied to the investigation of corrosion processes and proofed to be an excellent tool [7, 8], however since the roughness of the surface is much higher compared with adsorption film, especially when the film is monolayer, it is very difficult to evaluate the adsorption behavior of inhibitors through imaging surface topography, but the conductivity of the surface will be changed after the adsorption of inhibitor, and the force curves will also exhibit different characters after the adsorption of inhibitor. The application of AFM current image and force curves will be new ways to investigate the adsorption behavior of inhibitor.

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The aim of this study is to present new methods to evaluate the inhibitor adsorption behavior. Firstly, the polarization curves were applied to study the adsorption behavior of dodecylamine on carbon steel, then the current image and force curves of carbon steel surface after immersion in test solution containing inhibitor were measured.

All the tests were performed on carbon steel of the following composition (wt.%): C, 0.24; Mn, 1.19; P, 0.013; S, 0.004; Cr, 0.036; Mo, 0.021; Ni, 0.028; Fe, Remainder. The base solution was HCl solution, and the inhibitor is dodecylamine. All the solutions were prepared from analytical grade reagents and distilled water.

The electrochemical measurements were conducted through a three-electrode cell connected to a Zahner IM6e electrochemical workstation. A platinum electrode and a saturated calomel electrode (SCE) were used as reference electrode and counter electrode respectively. Polarization curves were obtained by sweeping the potential from a value of −200 to 200 mV vs. E_{corr} with a potential scan rate of 0.5 mV s^{-1}. The working electrode for electrochemical tests was embedded in PTFE ring leaving an area of 1 cm^2 exposed to solution. Before tests, the samples were wet ground through 1200 grit SiC paper, rinsed with distilled water and ethanol, dried at room temperature.

The topography of the sample surface was measured with a commercial AFM system (SPI3800, Seiko Instruments Inc.) operated in contact mode, and the current image was simultaneously measured by applying a bias voltage of 0.5 V between the sample and the Au-coated conductive tip. Specimens for AFM measurement were wet ground through 1200 grit SiC paper, and then polished to 0.5 μm with diamond paste using a polishing cloth. After being rinsed with distilled water and treated with supersonic cleaning in ethyl alcohol, the samples were stored in air.

Potentiodynamic polarization characteristics for N80 steel in 0.3 M HCl containing various concentrations of dodecylamine are shown in Fig. 1.

The open circuit potential E_{OCP}, the corrosion current density i_{corr}, the anodic and cathodic tafel slopes b_a and b_c are listed in Table 1.

It can be observed from Table 1 that the inhibitor addition negligibly changes the open circuit potential, anodic and cathodic tafel slopes, which indicates that the carbon steel corrosion inhibition is due to geometric blocking effect of the dodecylamine [2]. In this case, as proposed by Vračar and Dražić [9, 10], the surface coverage θ may be calculated using the following equation

$$\theta(C_{\text{inh}}) = 1 - \frac{(i_{\text{cor}})_{C_{\text{inh}}}}{(i_{\text{cor}})_{C_{\text{inh}=0}}} = \eta$$

Where $(i_{\text{cor}})_{C_{\text{inh}}}$ and $(i_{\text{cor}})_{C_{\text{inh}=0}}$ are corrosion current density with and without dodecylamine. Surface coverage data are quite useful in determining inhibitor adsorption characteristics. Such data are applied in construction of adsorption isotherms, which give detailed information on adsorption mechanisms. The adsorption of dodecylamine on carbon steel surface was found to follow the Flory–Huggins isotherm given by [11, 12].

$$\log\left[\frac{\theta}{C}\right] = \log K + x\log(1-\theta)$$

Where x is the size parameter and measured by the number of adsorbed water molecules substituted by a given inhibitor molecule. Curve fitting of data to the Flory-Huggins isotherm is given in Fig. 2, value of x calculated from Fig. 2 is 2.32, meaning that [13] dodecylamine forms a monolayer film on the carbon steel surface, and each dodecylamine molecule averagely replaces 2.32 water molecules. Theoretical calculations show that the diameter of a water molecule and a dodecylamine molecule are

Table 1 Potentiodynamic polarization parameters for the corrosion of carbon steel at different dodecylamine concentrations at 30 °C

Concentration (ppm)	E_{ocp} (mV)	b_a (mV)	b_c (mV)	i_{cor} (mA/cm^2)	η (%)
0	−519	55	64	0.7643	–
15	−519	56	62	0.3245	0.58
30	−526	51	69	0.1564	0.80
60	−521	52	69	0.1098	0.86
90	−520	55	64	0.08696	0.89
120	−523	53	68	0.05973	0.92
150	−519	51	68	0.05686	0.93

2.8×10^{-10}m and 3.2×10^{-10}m, respectively, the length of a dodecylamine molecule is 14.9×10^{-10}m. The diameter and length of a dodecylamine molecule are about 1.1 and 5.3 times of the diameter of a water molecule, respectively, but a dodecylamine molecule only replaces 2.32 water molecules, which indicates that dodecylamine molecules are lying obliquely to the surface. What's more, there is a synergistic effect between dodecylamine and chloride [14]. Since the adsorption of chloride ions, the metal surface becomes more negatively charged, which made the dodecylamine molecule be adsorbed on the iron surface more easily [15].

After being immersed in 0.3 M HCl solution containing 15 ppm dodecylamine for 15 min, the sample was taken out of the solutions and rinsed with distilled water. The topographic and current images were measured simultaneously by AFM applying a bias voltage of 0.5 V between the sample and the Au-coated conductive tip. The images are shown in Fig. 3.

Since the roughness of the surfaces is much higher comparing with a molecular monolayer, it is difficult to identify the adsorbed monolayer film of dodecylamine on the metal surfaces from the topographic image. But obvious difference can be observed from the current image.

Then the force curves were measured on the sample surfaces. In order to minimize error brought by uncertain

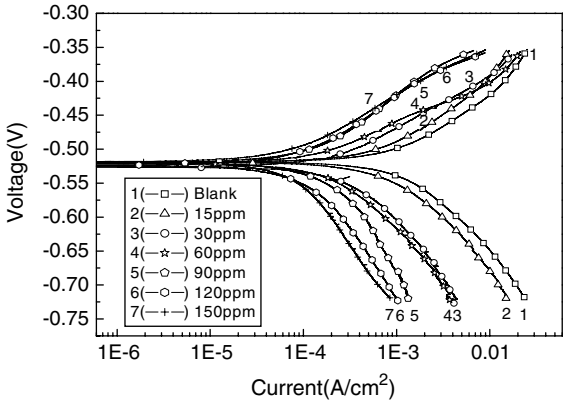

Fig. 1 Polarization curves at different dodecylamine concentrations for carbon steel at 30 °C

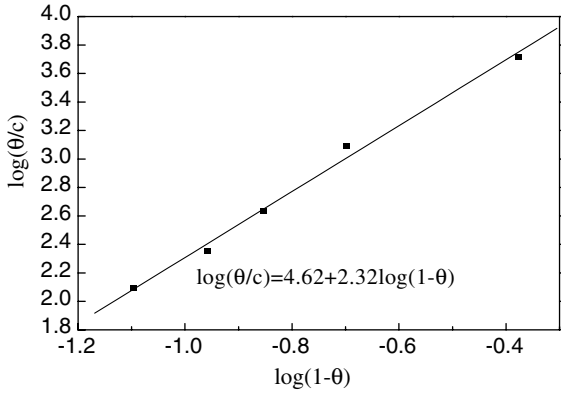

Fig. 2 Flory–Huggins isotherm for dodecylamine on carbon steel in 0.3 M HCl at 30 °C

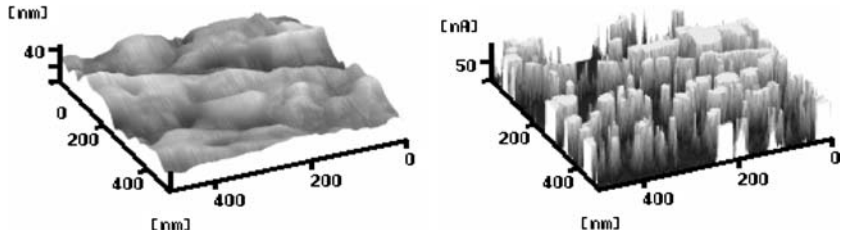

Fig. 3 AFM image of carbon steel surface after 15 min immersion in 0.3 MHCl+ 15 ppm dodecylamine. (**a**) topography (**b**) current image

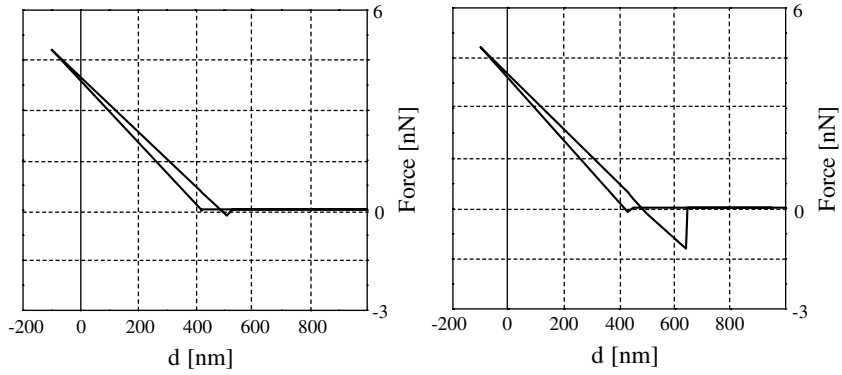

Fig. 4 Traces of force curves measured at. (**a**) high conductivity area (**b**) low conductivity area

factors, repeated experiments were done at difference areas. The representative curves were picked out and the average adhesive forces were calculated. Figure 4 (a) and (b) showed the representative force curves at high and low conductivity area respectively.

It can be observed from Fig. 4 that the curves recorded at high conductivity area exhibited no obvious adhesive forces. However adhesive force features appeared in low conductivity area and the average adhesive force is calculated to −1.3 nN. Dodecylamine molecules in solution formed a hydrophobic film on the metal surface, when we detached the tip from the hydrophobic surface, a long-range, strong attractive forces would appear which was in consistent with the hydrophobic interaction reported in some published literatures [16, 17].

In summary, the inhibition of dodecylamine on carbon steel corrosion is due to geometric blocking effect, and each dodecylamine molecule averagely replaces 2.32 water molecules on the metal surface thus formed a monolayer on carbon steel surface. AFM current image reveals that the adsorption of dodecylamine molecules greatly decreased the conductivity of the carbon steel surface, and the force curves exhibited adhesive force features at the dodecylamine adsorption areas.

Acknowledgments This project was supported by the Chinese National Science Fund 50 471 062.

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