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Thermodynamic study of metal corrosion and inhibitor adsorption processes in mild steel/1-methyl-4[4′(-X)-styryl pyridinium iodides/hydrochloric acid systems

Ehteram A. Noor*, Aisha H. Al-Moubaraki

King Abd El-Aziz University, Girls' College of Education, Department of Chemistry, Jeddah-9470, Saudi Arabia

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Abstract

The corrosion and inhibitor adsorption processes in mild steel/1-methyl-4[4′(-X)-styryl] pyridinium iodides (X: $-$H, $-CH_3$ and $-OCH_3$)/hydrochloric acid systems was studied at different temperatures (25–60 °C) by means of hydrogen evolution (HE) and weight loss (WL) measurements. It was found that the studied compounds exhibit a very good performance as inhibitors for mild steel corrosion in 1.5 M HCl. Results show that the inhibition efficiency increases with decreasing temperature and increasing concentration of inhibitors. Good agreement between the results obtained from hydrogen evolution and weight loss measurements was appeared. It has been determined that the adsorption for the studied inhibitors on mild steel complies with the Langmuir adsorption isotherm at all studied temperatures. The kinetic and thermodynamic parameters for mild steel corrosion and inhibitor adsorption, respectively, were determined and discussed. On the bases of thermodynamic adsorption parameters, comprehensive adsorption (physisorption and chemisorption) for the studied inhibitors on mild steel surface was suggested. A good correlation between the substituent type and the inhibition efficiency of inhibitors through the application of Hammet relationship was obtained. Results show that with increasing the donor property of the substituent, the inhibition efficiency of the inhibitor is increased in the order: I-H < II-CH_3 < III-OCH_3.

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1. Introduction

To remove undesirable scales (e.g., mill scale, rust) the particular piece of metal is immersed in a suitable acid solution, called an acid pickling bath. The acid solution attacks and dissolves the scale. Once the scale is dissolved, the acid is then free for further attack upon the metal. In order to reduce the metal dissolution and the consumption of acid, corrosion inhibitors are added to the pickling solution. As known, Hydrochloric acid (HCl) is the most important pickling acid. It is used with concentrations from 5 to 15 mass % at temperature up to 80 °C [1]. These required inhibitors that remain effective even under such severe conditions. Accordingly, the method of acid corrosion inhibition must be evaluated according to the parameters of the particular corrosion system. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, temperature, the presence of dissolved inorganic and/or organic substances even in minor amounts and, of course, on the type of metallic material exposed to the action of acidic solution [1].

Generally speaking, corrosion inhibitors are found to protect steel corrosion in acid solutions by adsorbing themselves on steel surface. Adsorption is a separation process involving two phases between which certain components can become differentially distributed. Adsorption can be described by two main types of interaction [2]:

- *Physisorption*, involves electrostatic forces between ionic charges or dipoles on the adsorbed species and the electric charge at the metal/solution interface. The heat of adsorption is low and therefore this type of adsorption is stable only at relatively low temperatures.
- *Chemisorption*, involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type bond. In fact, electron transfer is typically for transition metals having vacant low-energy electron

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* Corresponding author. Tel.: +966 26939746.
E-mail address: m7o7o7n@hotmail.com (E.A. Noor).

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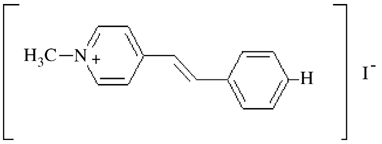
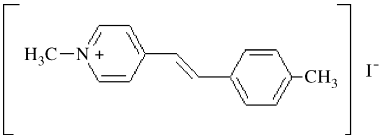
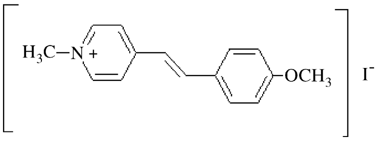
Table 1
Names, structures and abbreviations of the studied inhibitors

Inhibitor	Structure	Abbreviation
1-Methyl-4[4′(-H)-styryl] pyridinium iodide		I-H
1-Methyl-4[4′(-CH_3)-styryl] pyridinium iodide		II-CH_3
1-Methyl-4[4′(-OCH_3)-styryl] pyridinium iodide		III-OCH_3

> orbital. Chemisorption is typified by a much stronger adsorption energy than physical adsorption. Such a bond is therefore more stable at higher temperatures.

Thermodynamic adsorption parameters and kinetic corrosion parameters are a useful tool for clarifying the adsorption behaviour of an inhibitor. Earlier work for Riggs and Hurd [3] revealed that from a comparison of activation energies of uninhibited and inhibited corrosion reaction, heats of inhibitor adsorption may obtained. However, It was found that while positive heat of adsorption, $\Delta H_{\mathrm{ads.}} > 0$ (endothermic process) is attributed unequivocally to *chemisorption* [4,5], a negative heat of adsorption, $\Delta H_{\mathrm{ads.}} < 0$ (exothermic process) may involve either *physisorption* [6] or *chemisorption* [7,8] or mixture of both processes (*comprehensive adsorption*) [9–11].

It is well known that the effect of temperature on the inhibited acid–metal reaction is highly complex, because many change occur on the metal surface such as rapid etching and desorption of inhibitor and the inhibitor itself may undergo decomposition and/or rearrangement. It was found that few inhibitors with acid–metal systems have specific reactions which are effective at high temperature as (or more) they are at low temperature [12–14].

The object of the present work is to evaluate the corrosion kinetic parameters of mild steel and the adsorption thermodynamic parameters of three selected inhibitors (Table 1) in mild steel/inhibitor/1.5 M HCl system. The choice of these compounds is based on molecular structure considerations, i.e., these are organic compounds having the same adsorption centers but they only differ in the substituent type at the para position of phenyl group and hence if a difference in the protective properties is observed, it should be predominately attributed to a difference in the electronic effect of the substituent type. Two chemical methods were employed to carry out the measurements, these are hydrogen evolution (HE) and weight loss (WL) methods.

2. Experimental details

2.1. Materials preparation

1-Methyl-4[4′(-X)-styryl] pyridinium iodides (Table 1) were synthesized as previously reported in the literature [15]. The purity of the studied compounds was checked by chemical analysis, melting point determination and spectral data. Prior all measurements, the steel samples (P: 0.02%, Mn: 0.370%, S: 0.030%, Mo: 0.010%, Ni: 0.039%, C: 0.210%, Si: 0.170 and the remainder is iron) are abraded with a series of emery papers from 400 to 1200 grade. The specimens are washed thoroughly with bidistilled water, degreased with acetone and dried with air. The aggressive solution (1.5 M HCl) is prepared by dilution of analytical grade 37% HCl with bidistilled water in absence and presence of the studied inhibitors in the concentration range from 5×10^{-5} to 5×10^{-4} M.

2.2. Methods

2.2.1. Hydrogen evolution measurements (HE)

50 ml of tested solution were placed in flask of Mylius type [16] and a degreased and weighed mild steel sample was introduced into the solution. The time was recorded and H_2 evolved was collected in the calibrated tube by the downward displacement of water over time interval of 90 min. A plot of H_2 evolved per unit area against time in absence and presence of different concentrations of the studied inhibitors produced a straight lines. The slope of this lines gave the rate of H_2 evolved (ρ_{HE}, ml cm^{-2} min^{-1}). Inhibition efficiency is calculated using the following equation:

$$\mathrm{IE}_{\mathrm{HE}}(\%) = \left(\frac{\rho^{\mathrm{o}}_{\mathrm{HE}} - \rho_{\mathrm{HE}}}{\rho^{\mathrm{o}}_{\mathrm{HE}}}\right) \times 100 \qquad (1)$$

where $\rho^{\mathrm{o}}_{\mathrm{HE}}$ and ρ_{HE} are the corrosion rates in absence and presence of a certain concentration of inhibitor, respectively.

2.3. Weight loss measurements (WL)

At the end of each experiment of HE, the sample was withdrawn from the tested solution, washed thoroughly with bidistilled water followed by acetone and dried with air, then weighed again. The rate of mass loss was calculated (ρ_{WL}, g cm^{-2} min^{-1}) as follows:

$$\rho_{\mathrm{WL}} = \frac{W_{\mathrm{b}} - W_{\mathrm{a}}}{S \cdot t_{\infty}} \qquad (2)$$

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