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Electrochimica Acta 53 (2007) 1722–1730
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Inhibition of mild steel corrosion in hydrochloric acid solution by triazole derivatives
Part II: Time and temperature effects and thermodynamic treatments

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Received 11 May 2007; received in revised form 8 August 2007; accepted 10 August 2007

Abstract

The corrosion behaviour of mild steel in 0.1 M HCl solution without and with 5-amino-1,2,4-triazole (5-ATA), 5-amino-3-mercapto-1,2,4-triazole (5-AMT), 5-amino-3-methylthio-1,2,4-triazole (5-AMeTT) or 1-amino-3-methylthio-1,2,4-triazole (1-AMeTT) was studied as a function of the immersion time and the solution temperature. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques were used in this study. Results obtained showed that the inhibition efficiency (IE%) increases with increasing the immersion time reaching its maximum value after 1 h, IE% slightly decreased and subsisted at reasonable values at least during the studied 20 h. The adsorptive behaviour of the investigated inhibitors on the steel surface followed Langmiur-type isotherm. Increasing temperature was found to greatly enhance IE% till arriving plateau at about 80% for 5-ATA and more than 90% for the other compounds between 323 and 348 °K. The polarization and impedance measurements were in good agreement. These results indicate the suitability of the use of the investigated inhibitors in the cooling systems. The plots of $\ln K$ versus $1/T$ for the four studied inhibitors showed non-linear behaviour. The standard enthalpy, ΔH^{o}_{ads}, entropy, ΔS^{o}_{ads} and free energy changes of adsorption ΔG^{o}_{ads} were evaluated using a proposed quadratic equation based on an inverse square dependence of the heat capacity on temperature. The calculated values of ΔG^{o}_{ads} were negative while those for ΔH^{o}_{ads} and ΔS^{o}_{ads} were positive. The values of the three thermodynamic functions of adsorption for the four investigated inhibitors were decreased with increasing the solution temperature. All the above results are suggestive of chemisorption of inhibitor molecules on the steel surface.

Keywords: Mild steel; Triazoles; Non-linear van’t Hoff relation; EIS; Positive heat of adsorption

1. Introduction

The inhibition of steel in acid solutions by different types of organic inhibitors has been extensively studied. Among these compounds, the use of environmentally acceptable inhibitors such as the triazoles, molybdates and *o*-phosphates/polyphosphates is favoured. Many substituted triazole compounds have been still studied in considerable details as effective corrosion inhibitors for steel in acidic media [1].

In part I of this study, we compared the performances of 5-amino-1,2,4-triazole (5-ATA), 5-amino-3-mercapto-1,2,4-triazole (5-AMT), 5-amino-3-methylthio-1,2,4-triazole (5-AMeTT) and 1-amino-3-methylthio-1,2,4-triazole (1-AMeTT) as inhibitors for the corrosion of mild steel in 0.1 M HCl solution at 20 °C [1]. Steady-state open circuit potential (OCP) values were obtained after 1 h of immersing the electrode in 0.1 M HCl solutions without and with different concentrations of the studied inhibitors. At the same concentration, the inhibition efficiency (IE%) of the four tested inhibitors decreases in the order: 5-AMT > 5-AMeTT > 1-AMeTT > 5-ATA. The highest inhibition efficiency of 96% was obtained after 1 h of immersing the electrode in 0.1 M HCl + 10^{-3} M 5-AMT solution at room temperature. A great limitation of the inhibitor applications in cooling systems is the fall down of their efficiencies with time

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0013-4686/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2007.08.021

and at high temperatures. In order to demonstrate the validity of these inhibitors at longer times and higher temperatures, we will be concerned, in the present study, with the variation of IE% with the immersion time and the solution temperature.

The effect of temperature on the inhibited acid–metal reaction is highly complex because many changes occur on the metal surface, such as rapid etching and desorption of the inhibitor and the inhibitor itself, in some cases, may undergo decomposition and/or rearrangement [2]. However, it provides the ability of calculating many thermodynamic functions for the inhibition and/or the adsorption processes which contribute in determining the type of adsorption of the studied inhibitors. Many authors performed thermodynamic calculations based on the van't Hoff Eq. (1) [2–10]:

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^{\mathrm{o}}_{\mathrm{ads}}}{\mathrm{R}T}\right), \quad \ln K = -\frac{\Delta G^{\mathrm{o}}_{\mathrm{ads}}}{\mathrm{R}T} + \ln\frac{1}{55.5} \tag{1}$$

where K is the adsorption–desorption equilibrium constant, $\Delta G^{\mathrm{o}}_{\mathrm{ads}}$ is standard free energy of adsorption, 55.5 is the molarity of water in the solution and R is the universal gas constant. The contribution of the standard enthalpy, $\Delta H^{\mathrm{o}}_{\mathrm{ads}}$, and entropy changes, $\Delta S^{\mathrm{o}}_{\mathrm{ads}}$, to the standard free energy of the adsorption process, $\Delta G^{\mathrm{o}}_{\mathrm{ads}}$, can be quantitatively evaluated from the well known Gibbs–Helmholtz Eq. (2):

$$\Delta G^{\mathrm{o}}_{\mathrm{ads}} = \Delta H^{\mathrm{o}}_{\mathrm{ads}} - T\Delta S^{\mathrm{o}}_{\mathrm{ads}} \tag{2}$$

Combining Eq. (2) with the logarithmic form of Eq. (1), the dependence of ln$K$ on temperature is obtained as:

$$\ln K = -\frac{\Delta H^{\mathrm{o}}_{\mathrm{ads}}}{\mathrm{R}T} + \frac{\Delta S^{\mathrm{o}}_{\mathrm{ads}}}{\mathrm{R}} + \ln\frac{1}{55.5} \tag{3}$$

These classical linear forms of van't Hoff Eqs. (1 and 3) are traditionally used to calculate $\Delta G^{\mathrm{o}}_{\mathrm{ads}}$, $\Delta H^{\mathrm{o}}_{\mathrm{ads}}$ and $\Delta S^{\mathrm{o}}_{\mathrm{ads}}$ assuming their independence on temperature. A linear plot of ln$K$ versus $1/T$ is mandatory for application of these equations. We didn't find in the literature concerning the corrosion inhibition studies any attempt to calculate the thermodynamic functions of adsorption when a non-linear van't Hoff relation was obtained. However, during the study of the retention thermodynamics in hydrophobic interaction chromatography (HIC) [11–16], many authors were concerned with this subject. The non-linearity of the van't Hoff relation was attributed to a large negative heat capacity change associated with adsorption. It is explained in terms of the dependence of $\Delta H^{\mathrm{o}}_{\mathrm{ads}}$ and $\Delta S^{\mathrm{o}}_{\mathrm{ads}}$ on temperature, as a result of the variation of heat capacitance change, $\Delta C^{\mathrm{o}}_{\mathrm{p}}$, with temperature according to Kirchoff's law:

$$\Delta H^{\mathrm{o}}_{\mathrm{ads}} = \int \Delta C^{\mathrm{o}}_{\mathrm{p}}\mathrm{d}T \tag{4}$$

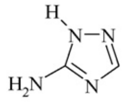
$$\Delta S^{\mathrm{o}}_{\mathrm{ads}} = \int \left(\frac{\Delta C^{\mathrm{o}}_{\mathrm{p}}}{T}\right)\mathrm{d}T \tag{5}$$

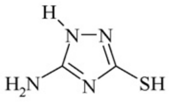
$$\Delta C^{\mathrm{o}}_{\mathrm{p}} = \frac{2\delta\mathrm{R}}{T}, \tag{6}$$

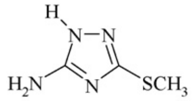
where δ is constant (vide infra). This approach and the previously obtained equations will be adopted in the present work in order to perform thermodynamic analysis where the van't Hoff relations are not valid.

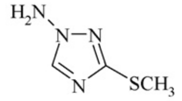
2. Experimental

In order to study the time and temperature effects on the performance of the investigated azole inhibitors towards the corrosion of steel in acidic solution, experiments were carried out in 0.1 M HCl without or with different inhibitors at different times of immersion and at a variety of solution temperatures (293–348 °K). The chemical structure of the investigated compounds is given below:


5-amino-1,2,4-triazole
(5-ATA)


5-amino-3-mercapto-1,2,4-triazole
(5-AMT)


5-amino-3-methylthio-1,2,4-triazole
(5-AMeTT)


1-amino-3-methylthio-1,2,4-triazole
(1-AMeTT)

All solutions were prepared from analytical-grade chemicals and doubly distilled water. The working electrode was a mild steel rod containing: C = 0.390%; Si = 0.70%; Mn = 0.56%; S = 0.24%; P = 0.06%; Cu = 0.078%; Ni = 0.038%; Cr = 0.045%; V = 0.013%. The apparent exposed surface area of the working electrode was 0.5 cm^2. The counter electrode was a platinum wire. The working electrode potentials were recorded versus a silver–silver chloride electrode (Ag/AgCl). Prior to each experiment, the working electrode was successively polished with finest-grade emery papers, degreased with acetone and washed with running doubly distilled water and finally dried with filter paper. The electrode was then immediately immersed in the test solution without or with the desired concentration of the investigated inhibitors.

Electrochemical impedance spectroscopy (EIS) measurements were carried out as described before [17], using AC signals of amplitude 5 mV peak to peak at different conditions in the frequency range of 10 kHz–50 mHz. When Tafel plots were studied with the EIS, they were performed after the EIS without removing the electrodes from the corrosion cell. The potentiodynamic Tafel measurements were started from the cathodic to the anodic direction, $E = E_{\mathrm{corr}} \pm 200$ mV, with a scan rate of 1.0 mV s^{-1}. An Autolab Potentiostat/Galvanostat (PGSTAT30) with FRA2 module for impedance measurements and a personal computer were used with GPES and FRA (ver. 4.9) software provided by Autolab.

3. Results and discussion

Part I of this study demonstrated that the inhibitor concentrations that gave the highest inhibition efficiency, IE%, when added to 0.1 M HCl at 20 °C after 1 h of immersion at the OCP conditions were found to be 10^{-3} M for 5-AMT and 10^{-2} M