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The enhancing of 2-pyrazinecarboxamide inhibition effect on the acid corrosion of carbon steel in presence of iodide ions

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ABSTRACT

The inhibition effect of 2-pyrazinecarboxamide (PCA), KI and their synergistic effect on the corrosion of carbon steel in 0.5 M H_2SO_4 solution was studied by electrochemical techniques. Scanning electron microscopy (SEM) was used to characterize the steel surface. The inhibition efficiency increases with the concentration of PCA and KI and increase further in the presence of PCA/KI mixture. The open circuit potential and polarization measurements suggested that PCA and its mixture with KI act as mixed-type inhibitor; while, KI only acts as mixed-type inhibitor with a predominant anodic inhibitor. The adsorption of PCA and KI on the metal surface in 0.5 M H_2SO_4 solution obeys the Langmuir adsorption isotherm. The thermodynamic parameters K_{ads} and ΔG°_{ads} are calculated and discussed. The probable inhibitory mechanism is proposed from the viewpoint of adsorption theory. The synergism parameter suggests that there is a cooperative mechanism between the iodide anion and PCA cations.

1. Introduction

Carbon steel is used in mass amounts in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment [1–4], despite it has a relatively high cost. These applications usually induce serious corrosive effects on equipment's, tubes and pipelines made of iron and its alloys [5–7]. The use of corrosion inhibitors is one of the most effective measures for protecting metal surfaces against corrosion in acidic environments [8].

Some organic compounds are found to be effective corrosion inhibitors for many metals and alloys. A literature survey shows that most of the organic inhibitors will act upon adsorption onto the metal surface. The adsorption of inhibitors takes place through hetero-atoms such as nitrogen, oxygen, phosphorus, and sulfur, as well as through triple bounds or aromatic rings. The inhibition efficiency is reported to increase in the order $O < N < S < P$ [9].

Synergistic inhibition is an effective means to improve the inhibiting force of the inhibitor, to decrease the amount of usage and to diversify the application of the inhibitor in acidic media. It is necessary for corrosion scientists to discover, explore and use synergism in the complicated corrosive media. It is generally observed that the addition of halide ions to the corrosive media increases the adsorption ability of organic cations by forming interconnecting bridges between negatively charged metal surface and inhibitor cations. The order of synergism of halide ions is $I^- > Br^- > Cl^-$ [10]. Since it has a larger size and ease polarizability, I^- ions are adsorbed on metal surface and provide better synergistic effect [11].

Many investigations in regard to synergistic inhibition have been carried out and are being investigated. Abdel Rehim et al. [12] have studied the synergistic inhibition between adenine and iodide ions for low carbon steel corrosion in sulfuric solutions. They have found that the inhibition efficiency of adenine is greatly enhanced in the presence of KI because of synergism. They have also reported that the inhibition mechanism involves the electrostatic adsorption of protonated adenine molecules on the low carbon steel surface charged with a negative layer of chemisorbed I^- ions. Umoren et al. [13] have studied the synergistic inhibition effect of iodide ions and polyacrylamide (PA) on the corrosion of pure iron in 0.5 M H_2SO_4 solution. They have reported that the inhibition efficiency of PA was enhanced by the addition of iodide ions because of synergistic effects. The synergistic effect of iodide ions and PA is due to the co-adsorption of iodide ions and PA molecules, which is synergistic in nature.

To our surprise, neither the inhibiting ability of 2-pyrazinecarboxamide (PCA) (Fig. 1) nor the synergistic effects with iodide

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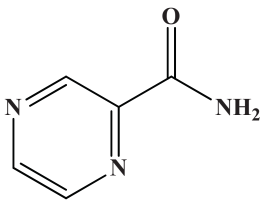

Fig. 1. The chemical structure of the PCA.

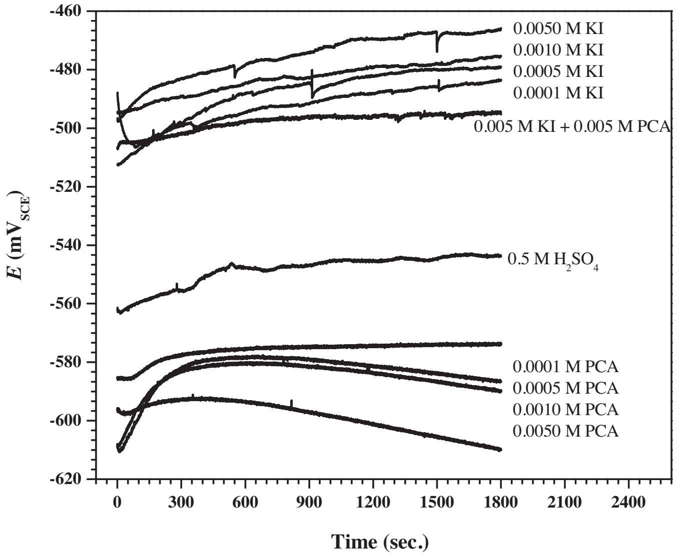

Fig. 2. Variation of potential of carbon steel vs. immersion time in 0.5 M H_2SO_4 solutions in the absence and presence of the investigated inhibitors at 298 K.

ions toward the acid corrosion of carbon steel have been previously studied. In the present a new corrosion inhibitor, 2-pyrazinecarboxamide (PCA) and KI, have been investigated their inhibition effect on the corrosion of carbon steel in 0.5 M H_2SO_4 solutions by open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Then, we attempted to enhance inhibition efficiency synergistically further by the addition of KI to PCA molecules containing corrosive solution.

The selection of PCA ($C_5H_5N_3O$) as a corrosion inhibitor is based on: (a) non-toxicity (b) contain electronegative oxygen and three nitrogen's and aromatic ring as active centers through which they can easily adsorb on the metal surface.

2. Experimental

2.1. Materials

Tests were performed on a carbon steel of the following composition (wt.%): 0.07% C, 0.24% Si, 1.35% Mn, 0.017% P, 0.005% S, 0.16% Cr, 0.18% Ni, 0.12% Mo, 0.01% Cu and the remainder Fe.

2.2. Solutions

The inhibitor solutions of PCA were prepared in 0.5 M H_2SO_4. The corrosion tests were performed in 0.5 M H_2SO_4 solution in the absence and presence of various concentrations of PCA and/or KI. 0.5 M H_2SO_4 solution was prepared by dilution of 98% H_2SO_4 with distilled water. For each experiment, a freshly prepared solution was used under air atmosphere without stirring at 298 K.

2.3. Electrochemical measurements

The electrochemical measurements were carried out using Volta lab 40 (Tacussel-Radiometer PGZ301) potentiostate and controlled by Tacussel corrosion analysis software model (Voltamaster 4) under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode. Carbon steel coupons having the area of 1 cm^2 were used as a working electrode.

The working electrode was immersed in test solutions for 30 min to a establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp}, the electrochemical measurements were performed. The EIS experiments were conducted in a frequency range with high limit of 10^5 Hz and different low limit 10^{-2} Hz with an amplitude of 10 mV peak-to-peak using ac signals at open circuit potential. The polarization curves were obtained in the potential range from −900 to −200 mV (SCE) with 1 mV s^{-1} scan rate. To achieve a reproducibility three parallel experiments were performed for each test.

2.4. Surface morphology

The surface morphology of polished carbon steel specimens before and after exposure to 0.5 M H_2SO_4 solution in the absence and presence of PCA and PCA/KI mixture solutions for 24 h were examined by JEOL 5410 scanning electron microscope SEM (Japan) instrument.

3. Results and discussion

3.1. Open circuit potential (OCP) versus time measurements

Fig. 2 shows the variation of potential of carbon steel (vs. SCE) as a function of time in aerated 0.5 M H_2SO_4 solutions in the absence and presence of various concentrations of PCA, KI and PCA/KI mixture at 298 K. In inhibitor-free sulfuric acid solution, the OCP changed quickly toward negative values, indicating the initial dissolution process of the pre-immersion, air formed oxide film and the attack on the bare metal [14]. A steady potential (vs. SCE) was readily attained, corresponding to the free E_{corr} (vs. SCE) of the carbon steel [15]. In inhibited sulfuric acid solution the steady state E_{corr} drifts to positive values (anodic direction) in case of KI and PCA/KI mixture. While in case of PCA the steady state E_{corr} drifts to negative values (cathodic direction).

According to Riggs [16], the classification of a compound as an anodic or cathodic type inhibitor is feasible when the OCP displacement ($E_{ocp\ (uninhibited)} - E_{ocp\ (inhibited)}$) is at least 85 mV. Inspection of Table 1 reveals that the values of OCP displacement were about (−59.9 to −77.8 mV) in the presence of individual KI, and (−48.4 mV) in the presence of PCA/KI mixture. While, the

Table 1
Open circuit potentials for carbon steel in 0.5 M H_2SO_4 solution in the absence and presence of the investigated inhibitors at 298 K.

Inhibitors	*C* (M)	$-E_{ocp}$ (mV_{SCE})	$E_{ocp\ (uninhibited)} - E_{ocp\ (inhibited)}$ (mV_{SCE})
Blank	0.0000	543.7	–
PCA	0.0001	573.8	30.1
	0.0005	586.7	43.0
	0.0010	589.5	45.8
	0.0050	609.9	66.2
KI	0.0001	483.8	−59.9
	0.0005	479.1	−64.6
	0.0010	475.3	−68.4
	0.0050	465.9	−77.8
PCA + KI	0.005 + 0.005	495.3	−48.4