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Inhibition effect of polyacrylic acid and its mixture with potassium iodide on mild steel corrosion in acid solution

I. Dehri*, G. Sigircik, A. Sari, M. Erbil

Çukurova University, Faculty of Science and Letter, Chemistry Department, Adana, Turkey

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The synergistic inhibition effect of polyacrylic acid and iodide ions was studied against mild steel corrosion in 0.5 M HCl solution. Potentiodynamic and electrochemical impedance spectroscopy measurements were realized in order to examine the corrosion process. In addition, the effect of long exposure period on inhibition efficiency was investigated. Surface morphology of steel was investigated by scanning electron microscopy technique. The obtained consequences revealed that mixture of polyacrylic acid and potassium iodide exhibited enhanced inhibition efficiency for mild steel corrosion because of synergistic effect.

Keywords: Synergistic effect, acid solution, corrosion inhibitor

INTRODUCTION

Mild steel and its alloys are widely used in industrial applications for lots of purposes such as construction materials, storage tanks and pipelines, etc. These metallic substances are in general exposed to hydrochloric and sulphuric acid solutions for pickling, cleaning and descaling processes in industries [1-5]. Various efforts have been made to better protect metals against corrosion in industrial processes. Organic corrosion inhibitors are some of the most suitable agents for prevention metals from corrosive species due to their strong adsorptive interaction with the metal surface. The molecular structure of inhibitor molecules plays a decisive role on their adsorption ability. In particular, heteroatoms like sulphur, nitrogen, phosphorus and oxygen, π-electrons and electronegative functional groups display high adsorption capacity for organic molecules [6-10]. A protective adsorption layer is formed since inhibitor molecules adhere to the metal surface. Besides, some properties of organic corrosion inhibitors such as low cost, environmental friendliness and good inhibition efficiency in aqueous corrosive solution are generally expected [11,12]. Synergistic effect offers a successful way to enhance inhibition efficiency on metal against corrosion. It is well known that inhibition efficiency could be increased with the addition of halide ions. The synergistic inhibition effect of halide ions is in the order: $I^- > Br^- > Cl^-$. The high synergistic effect of the iodide ion is related to its low electronegativity, large ionic radius and high hydrophobicity [13-16].

The aim of this study is to investigate the inhibition efficiency of polyacrylic acid with potassium iodide for mild steel corrosion in 0.5 M HCl solution. Electrochemical impedance spectroscopy and potentiodynamic measurements were utilized. The change of inhibition efficiency with immersion time was also studied *via* electrochemical impedance spectroscopy measurements. The surface was examined by scanning electron microscopy. The results show that the inhibition efficiency increased in the presence of iodide ions.

EXPERIMENTAL

Mild steel cylindrical rods with 0.5 cm^2 immersed surface area were used. The working surface area was abraded mechanically with SiC paper to 1200 grit finish, then degreased with 1:1 ethanol/water mixture and washed with distilled water. Finally, mild steel electrodes were dried at room temperature. Polyacrylic acid (PA) was used within the range of 3%, 5% and 10% without and with addition of 1.0 mM KI in 0.5 M HCl acid solution. The corrosive aqueous solution was obtained by dilution of analytical grade 37% HCl with distilled water. The molecular structure of polyacrylic acid is given in Fig. 1.

Electrochemical measurements were performed in a conventional three-electrode system. A mild steel working electrode was used. The auxiliary electrode was a platinum sheet and Ag/AgCl (3 M KCl) electrode was used as the reference. The electrochemical impedance spectroscopy (EIS) measurements were carried out at instantaneous open circuit potential, in the frequency range of 10 mHz - 100 kHz and amplitude was 5 mV. The potentiodynamic polarization measurements were performed for cathodic (from open circuit potential (E_{ocp}) to -1.0 V) and anodic (from open circuit

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* To whom all correspondence should be sent:
E-mail: idehri@cu.edu.tr

potential (E_{ocp}) to 0.0 V) current with a scan rate of 1 mV/s. The surface morphology of the mild steel samples in HCl solution without and with 10% PA (in the absence and presence of 1.0 mM KI) were examined by scanning electron microscopy (SEM) after 5 days immersion period.

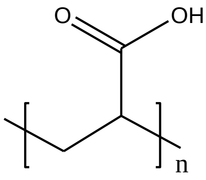

Figure 1. The molecular structure of polyacrylic acid.

RESULTS AND DISCUSSION

Potentiodynamic polarization measurements

Potentiodynamic polarization measurements were applied in order to study the corrosion inhibition process. The potentiodynamic measurement results of mild steel in 0.5 M HCl solution in the absence and presence of PA at different concentrations are given in Fig. 2. It is seen from the figure that cathodic current values were lower for PA-containing acid solution. Besides, the cathodic current values decreased regularly with the increase of inhibitor concentration. This situation was related to the good interaction between metal surface and inhibitor molecules. Thus, in cathodic side, the rate of hydrogen evolution reaction decreased due to adsorption of PA molecules on the metal surface. Addition of PA molecules to the corrosive solution led to a significant decrease of the anodic current values, too. Thus, anodic current values were even much lower for 3% PA-containing acid solution. This situation could be attributed to the significant adsorption property of PA with electronegative oxygen atoms and –OH groups. Aliphatic chain also offers a hydrophobicity characteristic against the attack of corrosive solution by forming a protective film on the metal surface.

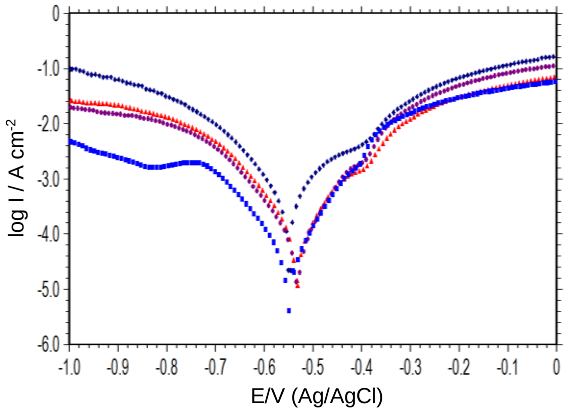

Figure 2. The potentiodynamic polarization curves of mild steel in 0.5 M HCl solution (♦) and containing 3% (▲), 5% (●), 10% (■) PA.

Electrochemical impedance spectroscopy measurements

EIS measurements were carried out to investigate the inhibitor effect of PA in 0.5 M HCl solution in the absence and presence of KI on mild steel corrosion. In Fig. 3, Nyquist and Bode plots are given. Single capacitive loop was observed for all Nyquist plots. This shows that the corrosion of mild steel is mostly controlled by the rate of charge transfer process in 0.5 M HCl solution [17]. The Nyquist plot is applied to determine polarization resistance (R_p) value which includes charge transfer resistance (R_{ct}) and diffuse layer resistance (R_d). As can be clearly seen from the Nyquist plots, the R_p values increased with increasing inhibitor concentration. As a result, the corrosion rate of mild steel decreased. It is also seen that only one time constant is observed in the Bode plots of mild steel in 0.5 M HCl solution without and with different PA concentration.

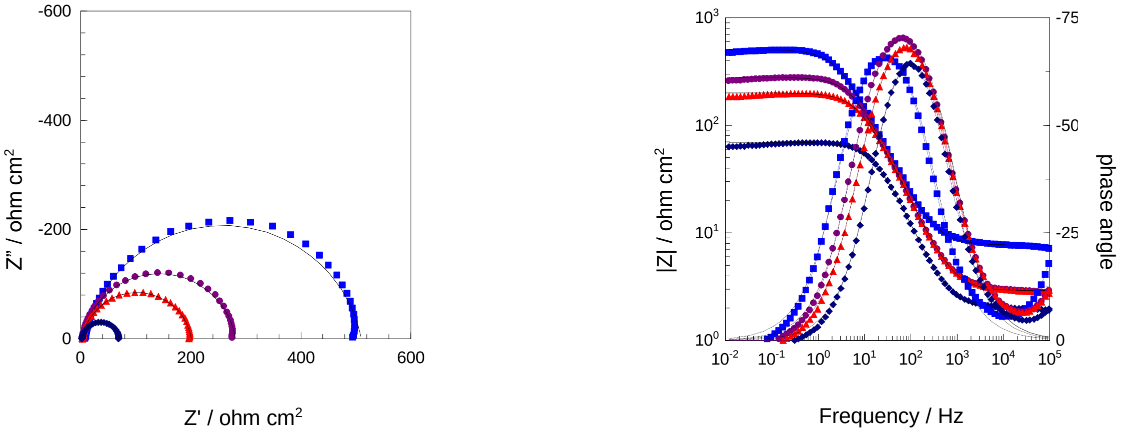

Figure 3. The EIS results of mild steel in 0.5 M HCl solution (♦) and containing 3% (▲), 5% (●), 10% (■) PA. (solid lines show fitted results)

In Fig. 4a, the electrical equivalent circuit applied to model the mild steel/solution interface is depicted. The used equivalent contains CPE, R_s and R_p. In here, CPE is the constant phase element, R_s and R_p are solution and polarization resistance, respectively.

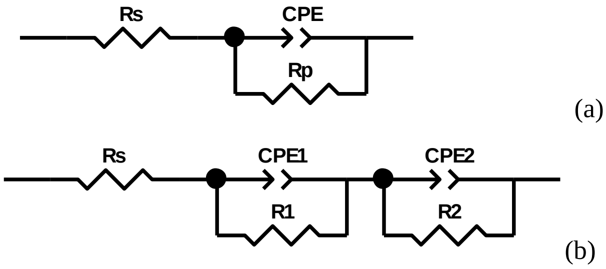

Figure 4. The equivalent circuit used to fit the EIS results without and with PA (a), after 48h and more immersion time with PA in presence of KI (b).

The impedance of the CPE is explained by equation (1), where Y_o is a proportionality coefficient, $j^2 = -1$ is the imaginary number, w is the angular frequency and n is the phase shift. The n value is related to the deviation from ideal capacitance behaviour. Thus, CPE does not have the equal unit with the capacitance (F cm^{-2} or s Ω^{-1} cm^{-2}). Dimension of CPE is given with s^n Ω^{-1} cm^{-2}, so the unit correction was utilized as defined by Mansfeld and Hsu [18].

$$Z_{CPE} = [Y_o(jw)^n]^{-1} \quad (1)$$

The inhibition efficiency (η) was determined from the polarization resistance by the help of the equation (2) where R_p and R_p' are the polarization resistances in the absence and presence of inhibitor molecules, respectively. The parameters calculated from EIS results are listed in Table 1.

$$\eta\% = \left(\frac{R_p' - R_p}{R_p'}\right) x100 \quad (2)$$

The polarization resistance value was determined as 67.5 Ω cm^2 for the condition without inhibitor. These R_p values increased with the addition of inhibitor molecules in the HCl solution. This is a result of the protective adsorption layer formed between PA molecules and steel surface. It is seen from Table 1 that the obtained R_p values of mild steel have increased with increasing inhibitor concentration. The polarization resistance value was determined as 502.0 Ω cm^2 and inhibition efficiency was calculated as 86.6% for 10% PA. Besides, the CPE values which are related to open surface area decreased with addition of PA. It follows from these results that the corrosion rate has gradually decreased because of adsorption capacity of PA molecules on steel surface.

Effect of KI addition

Inhibitor molecules are responsible for reducing the corrosion rate by forming an adsorption layer on the metal surface. This situation is strongly related to their interaction capability with the metal surface. Adsorption ability of an inhibitor molecule has crucial importance on inhibition efficiency. The protective adsorption layer is formed as long as inhibitor molecules take place on the metal surface. Synergistic effect offers a successful way to enhance inhibition efficiency on the metal against corrosion. Adsorption of organic molecules could be improved with halide ions *via* forming intermediate bridges between positively charged inhibitor molecules and metal surface. Thus, inhibition efficiency could be increased with the addition of halide ions, especially iodide ions, to the acidic medium [15,19].

EIS method was used to study the synergistic effect of iodide ions on inhibition efficiency in 0.5 M HCl solution. Both Nyquist and Bode plots are given in Fig. 5. Nyquist plots have the similar appearance with iodide-free condition. However, the diameter of the capacitive loop increased gradually with increasing concentration of PA in the presence of iodide ions. Therefore, the iodide ions enhanced the inhibition efficiency of PA at all concentrations. Such occurrences have been observed in lots of studies in the literature [20,21]. The parameters calculated from EIS results for 1.0 mM KI containing various concentrations of PA in 0.5 M HCl solution are listed in Table 1, too. The polarization resistance value was determined as 750.0 Ω cm^2 and inhibition efficiency was calculated as 91.0% for 10% PA in the presence of 1.0 mM KI. Furthermore, smaller CPE values were obtained compared with those in the absence of iodide. This result is an evidence for a synergism between the iodide ions and PA molecules. As a result, the corrosion current has significantly decreased due to the strong adsorption behaviour of PA and KI molecules on the steel surface.

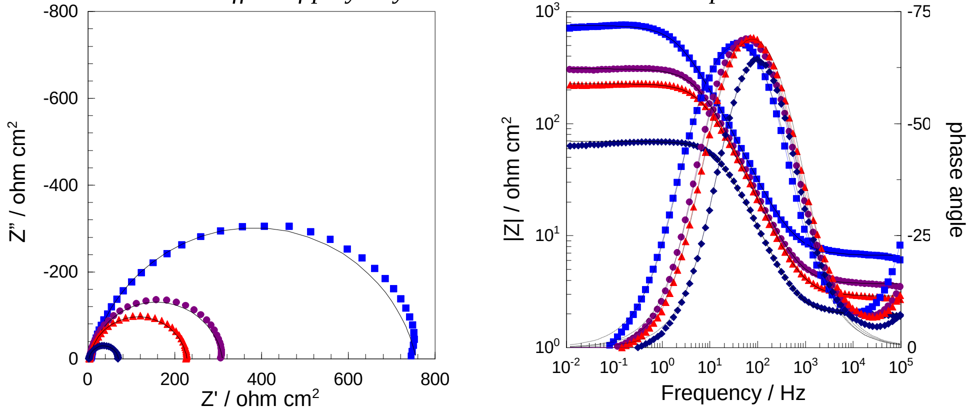

Figure 5. The EIS results of mild steel in 0.5 M HCl solution (♦) and containing 3% (▲), 5% (●), 10% (■) PA in the presence of 1.0 mM KI. (solid lines show fitted results)

Table 1. Electrochemical parameters obtained from EIS results.

	C_{inh} (%)	R_p (Ω cm^2)	CPE Y_o (x10^6 s^n Ω^{-1} cm^{-2})	n	C_{dl} (x10^6 s Ω^{-1} cm^{-2})	η%
Blank	-	67.5	225.4	0.92	157.2	-
PA	3	198.0	155.3	0.90	104.9	65.9
	5	278.0	150.1	0.90	105.4	75.7
	10	502.0	164.7	0.88	118.1	86.6
PA+ 1.0 mM KI	3	224.9	145.6	0.90	100.3	70.0
	5	305.9	134.9	0.90	94.7	77.9
	10	750.0	131.1	0.86	91.3	91.0

Effect of immersion time

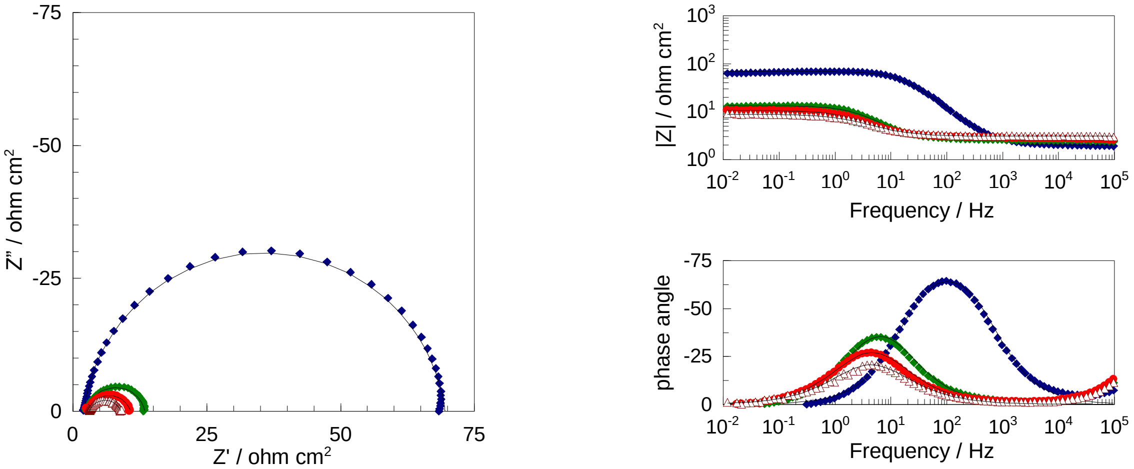

Figure 6. The EIS results of mild steel in 0.5 M HCl solution at different immersion time: 1h (♦), 48h (♦), 72h (●), 96h (Δ).

The effect of exposure time on the inhibition efficiency was also investigated by EIS. The Nyquist and Bode plots of mild steel in 0.5 M HCl at different immersion times are shown in Fig. 6. One capacitive loop was observed for all Nyquist plots at different exposure times. After 48h immersion time, polarization resistance value significantly decreased. This case could be explained with the fact that there is no opportunity for the formation of a protective layer on the metal surface in this acidic medium. The polarization resistance value was determined as 10.9 Ω cm^2 after 48h. Moreover, due to this reason, the polarization resistance values tend to gradually decrease with further increasing of the immersion period. The EIS measurement results of mild steel in 0.5 M HCl solution containing 10% PA in the absence and presence of 1.0 mM KI at different immersion times are given in Figs. 7 and 8, respectively. As it is seen from Fig. 7, the polarization resistance values are still high enough due to the adsorption of PA on the metal surface at a long exposure time. These R_p values decreased because of the stronger dissolution of metal compared with the first hour of immersion. However, high inhibition efficiency (98.4%) was calculated after 96h. Together Nyquist and Bode plots for mild steel in 0.5 M HCl solution containing 10% PA with 1.0 mM KI at different exposure period are depicted in Fig. 8. As it is expected from these Nyquist plots the obtained diameters of the capacitive loops were higher than iodide free form for all concentrations. Besides, the polarization resistances of mild steel remain almost stable with the further immersion time. This situation is attributed to improved adsorption ability of inhibitor molecules via iodide ions which offer synergistic effect [22]. As a result, electrified interface altered since steel surface was covered strongly by PA molecules and iodide ions. The used electrical equivalent circuit was shown in Fig. 4b. In this equivalent circuit, CPE1 and CPE2 represent the film capacitance and double layer capacitance. R_p value is the sum of R1 and R2 which are related to every capacitive loop.

The obtained R_p and inhibition efficiency values at different exposure time were given in Table 2. The polarization resistance values were determined as 367.1 Ω cm^2 and 676.8 Ω cm^2 without and with iodide ions after 96h. The inhibition efficiencies were calculated as 98.4% and 99.1% in the absence and presence of iodide ions, respectively after 96h immersion time.

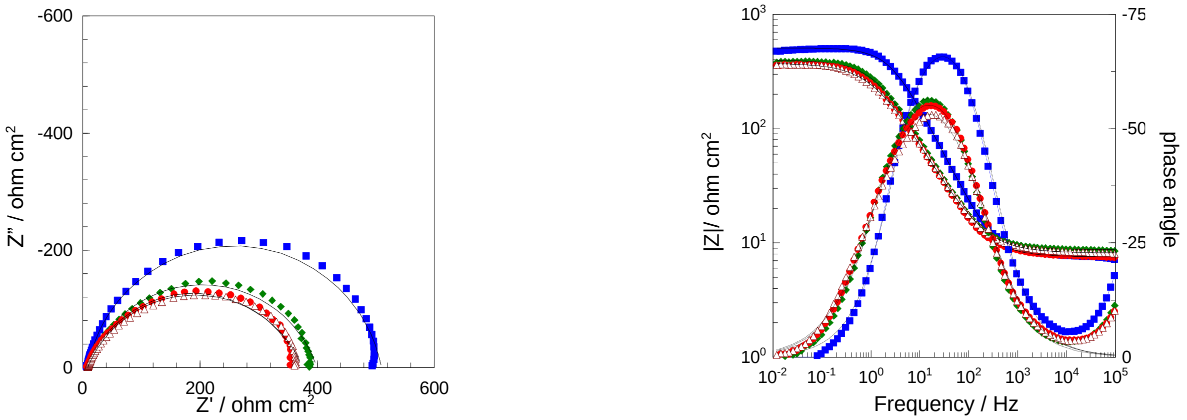

Figure 7. The EIS results of mild steel in 0.5 M HCl solution containing 10% PA at different immersion time: 1h (■), 48h (♦), 72h (●), 96h (Δ).

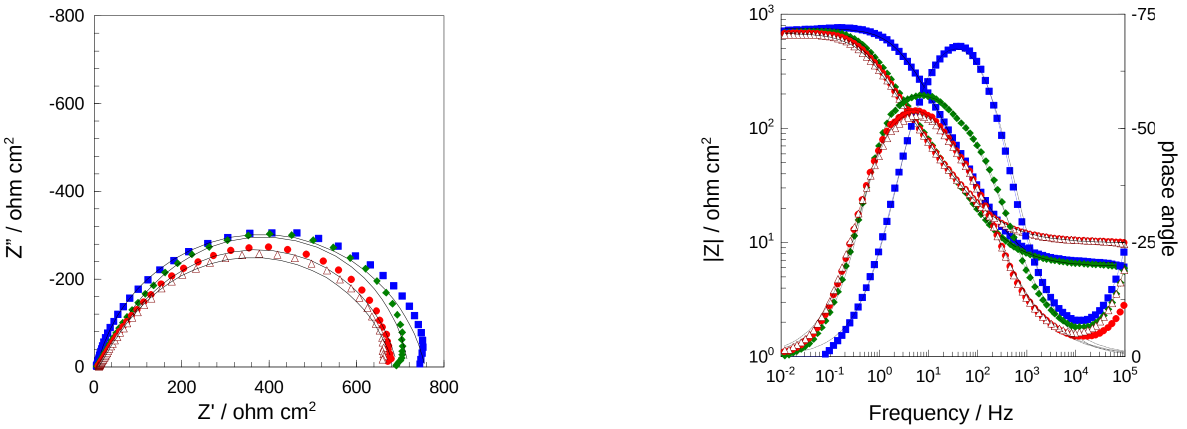

Figure 8. The EIS results of mild steel in 0.5 M HCl solution containing 10% PA in presence of 1.0 mM KI at different immersion time: 1h (■), 48h (♦), 72h (●), 96h (Δ).

Table 2. R_p values obtained from EIS results and calculated η% at different exposure time.

Immersion time	R_p (Ω cm^2)		η%	R_p (Ω cm^2)	η%
	blank	10% PA		10% PA+ 1.0 mM KI	
1h	67.5	502.0	86.6	750.0	91.0
48h	10.9	390.9	97.2	713.1	98.5
72h	7.9	363.9	97.8	684.8	98.8
96h	5.8	367.1	98.4	676.8	99.1

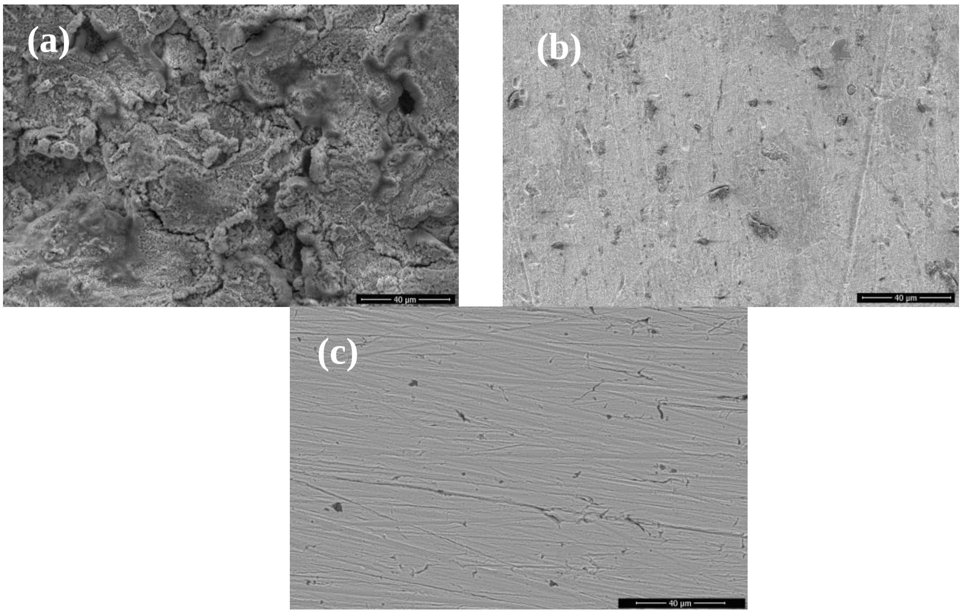

Figure 9. The SEM images of mild steel in 0.5 M HCl solution (a), with 10% PA (b) and with 10% PA in the presence of 1.0 mM KI (c) after 5 days immersion time.

Scanning electron microscopy studies

To observe the appearance of the metal surface is a practical way to have information about the role of inhibitor molecules on the corrosion process. The SEM images of mild steel in 0.5 M HCl solution after 5 days of exposure are given in Fig. 9a. The metal surface is strongly damaged and contains holes and porous structures. This is an expected result for bare metal in acidic environment because of the open surface area for corrosive species. The SEM images of mild steel in 0.5 M HCl solution containing 10% PA without and with 1.0 mM KI after 5 days immersion time are depicted in Figs. 9b and c. Steel surface is more homogeneous with less damage in the presence of PA. Smoother and much less damaged surface was obtained in the presence of iodide. These results also support the synergistic effect of iodide ions added to the inhibitor on corrosion process.

CONCLUSIONS

The potentiodynamic polarization measurement results showed that both anodic and cathodic current values which are related with metal dissolution and hydrogen evolution reactions were reduced in the presence of PA. EIS measurement results revealed that polarization resistance values increased with increasing inhibitor concentration in the absence and presence of iodide ions. Moreover, inhibition efficiencies increased for all PA concentrations in the presence of 1.0 mM KI through synergism. Thus, the corrosion rate decreased due to enhanced adsorption of inhibitor *via* iodide ions on the steel surface. Immersion time results revealed that polyacrylic acid with potassium iodide exhibited better inhibition efficiency even for a long exposure period. Thus, iodide ions provided strong interaction between mild steel and inhibitor molecules. Furthermore, SEM images showed that the addition of iodide ions synergistically improved the formation of adsorptive layer on the steel surface. Mild steel surface has smoother appearance even after 5 days exposure time.

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ИНХИБИРАЩ ЕФЕКТ НА ПОЛИАКРИЛОВА КИСЕЛИНА И СМЕСТА Й С КАЛИЕВ ЙОДИД ВЪРХУ КОРОЗИЯТА НА МЕКА СТОМАНА В КИСЕЛ РАЗТВОР

И. Дехри*, Г. Сигирчик, А. Сари, М. Ербил

Университет Чукурова, Научен факултет, Департамент по химия, Адана, Турция

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(Резюме)

Изследван е синергичният инхибиращ ефект на полиакрилова киселина и йодидни йони върху корозията на мека стомана в разтвор на 0.5 M HCl. Корозионният процес е изследван с помощта на потенциодинамични и електрохимично импедансни спектроскопски измервания. Изследвано е и влиянието на дълъг период на експозиция върху ефективността на инхибицията. Повърхностната морфология на стоманата е шзследвана чрез сканираща електронна микроскопия. От получените резултати следва, че сместа от полиакрилова киселина и калиев йодид проявява повишена инхибиционна ефективност върху корозията на мека стомана поради синергичен ефект.