

Effect of Some Substituted Anilines-Formaldehyde Polymers on Mild Steel Corrosion in Hydrochloric Acid Medium

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ABSTRACT: The influence of linear copolymer of amines and formaldehyde namely poly(aniline-formaldehyde) (Inh1), poly(*o*-toluidene-formaldehyde) (Inh2), and poly(*p*-chloroaniline-formaldehyde) (Inh3) on corrosion of mild steel in hydrochloric acid was evaluated by weight loss measurements, linear polarization, Tafel polarization, and electrochemical impedance spectroscopy. These polymers showed very high inhibition efficiency at very low concentrations. Results obtained showed that all inhibitors

are mixed inhibitors and participate in reaction probably in the form of metal inhibitor complex on metal surface. Atomic force microscopic studies reveal that the surface of metal is quite unaffected after use of inhibitor in hydrochloric acid solution. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5130–5137, 2012

Key words: adsorption; atomic force microscopy; copolymerization; mild steel; corrosion inhibition

INTRODUCTION

Acids are widely used in various industrial applications, for example, pickling, cleaning, descaling, and acidization of oil well. Inhibitors are used to reduce the rate of dissolution of metals in acidic solution. Organic compounds containing nitrogen, sulfur, and oxygen atoms and multiple bonds in their molecules act as efficient corrosion inhibitors for metals and alloys in acidic medium.^{1–7} The efficiency of an organic compound as an inhibitor mainly depends on its ability to get adsorbed on metal surface. Adsorption of these compounds is influenced by the electronic structure of inhibiting molecules, steric factor, aromaticity, and electron density at donor site, presence of functional group such as $-\text{CHO}$, $-\text{N}=\text{N}$, $\text{R}-\text{OH}$ and so on, molecular area, and molecular weight of the inhibitor molecule.^{8–11}

The use of polymers as corrosion inhibitors has drawn considerable attention due to their inherent stability and cost effectiveness.¹² They form complexes with metal ions, which occupy a large surface area thereby blanketing the surface and protecting

the metal. Both natural and synthetic polymers have been used as corrosion inhibitors.^{13–21} The insolubility of most of the polymers is the major limitation in corrosion inhibition application. Recently, some attempts have been made to increase solubility of polymers. The main approaches to make polymers more soluble are fictionalization and copolymerization of polymers.^{22–24} It is well known that compounds with high molecular weight and bulky structure may cover more area on the metal surface, which leads to high inhibition efficiency.

In continuation of our work on corrosion inhibition activity of soluble polymers,^{25,26} we report here inhibiting action of substituted anilines-formaldehyde linear copolymers namely poly(aniline-formaldehyde) (Inh1), poly(*o*-toluidene-formaldehyde) (Inh2), and poly(*p*-chloroaniline-formaldehyde) (Inh3) on mild steel corrosion in 1M HCl.

EXPERIMENTAL

Synthesis of linear copolymers

A solution of 5 mL of amine in dilute hydrochloric acid (3M) was taken in a 250-mL beaker. A total of 5 mL of formaldehyde solution (40%) was added slowly with stirring.²⁷ The mixture was then stirred for 15 min to form an orange-red solution was obtained. On the addition of aqueous sodium hydroxide solution (1%) solid polymer was precipitated. It was filtered, washed, and dried.

Formation of the polymers from the corresponding monomer amines were done by the UV-visible

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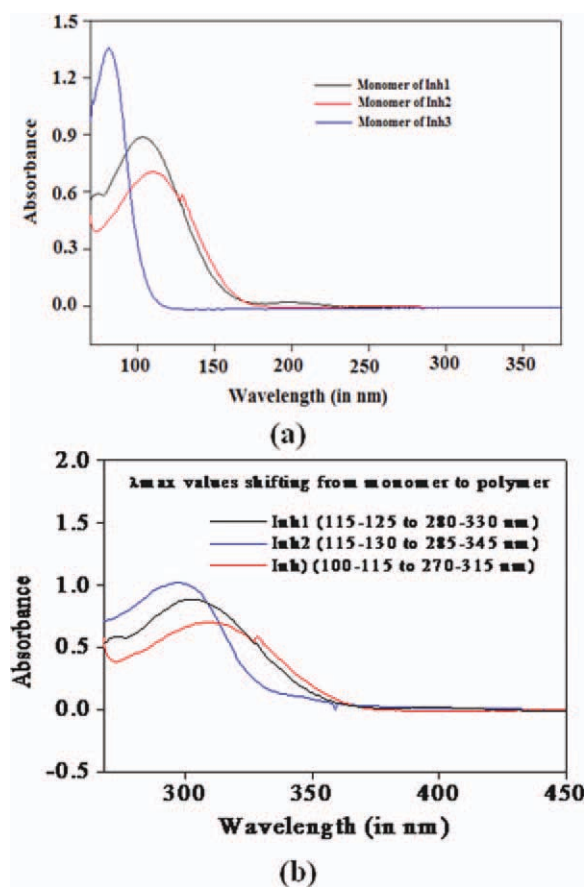
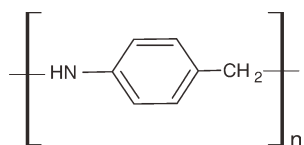


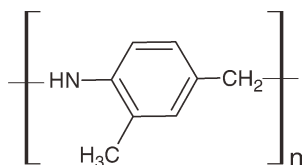
Figure 1 UV visible spectrum of (a) monomer amines and (b) synthesized polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spectral study. UV–vis study was done with Lambda 25 spectrophotometer of Perkin Elmer, Germany, to confirm the formation of polymer. In the UV–vis spectra [Fig. 1(a,b)] showed π – π^* transition at 275–345 nm range for different synthesized polymers from the amine monomers. In comparison with the spectra shown in Figure 1(a) of the monomer amines to the Figure 1(b) of the three different synthesized copolymers suggest the formation of the polymers.

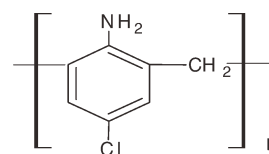
The structures of copolymers are given below:



Aniline-formaldehyde linear copolymer (Inh1)



o-Toluidene-formaldehyde linear copolymer (Inh2)



p-Chloroaniline-formaldehyde linear copolymer (Inh3)

Methodology

The mild steel strips having composition (wt %): C 0.14, Mn 0.035, Si 0.17, S 0.025, P 0.03, and remaining Fe were used for weight loss as well as electrochemical studies. The test solution of hydrochloric acid (AR grade) was used for all the corrosion testing. Double distilled water was used to prepare the acidic solutions of various concentrations.

All the concentrations of the inhibitors taken for weight loss and electrochemical study were taken in mg L^{-1} . The weight loss study was done on mild steel strips of $5.0 \times 2.0 \times 0.025 \text{ cm}^3$ sizes, in triplicate. The effect of immersion time, temperature, and acid concentration was studied without inhibitor and in presence of the optimum concentration of inhibitor. Percentage inhibition efficiency was calculated by following equation:

$$\eta_{\text{WL}}(\%) = \frac{W_o - W_i}{W_o} \times 100$$

where W_o and W_i are the weight loss values in absence and presence of inhibitor, respectively.

TABLE I
Corrosion Parameters for Mild Steel in Aqueous Solution of 1N HCl in Absence and Presence of Different Concentrations of Polymers from Weight Loss Measurements at 35°C for 3 h

Name of inhibitor	Inhibitor concentration (mg L^{-1})	Weight loss (mg cm^{-2})	IE (%)	CR (mm/y)
Blank	241.5	–	44.85	
Inh1	1.0	52.6	78.22	9.76
	2.5	41.4	82.86	7.68
	5.0	30.3	87.45	5.62
	7.5	19.8	91.80	3.67
	10.0	9.4	96.10	1.74
Inh2	15.0	6.7	97.23	1.24
	1.0	30.1	87.53	5.58
	2.5	18.9	92.17	3.51
	5.0	11.5	95.36	2.13
	7.5	8.1	96.60	1.50
Inh3	10.0	3.7	98.46	0.69
	15.0	3.7	98.46	0.69
	1.0	24.5	89.86	4.55
	2.5	15.9	93.41	2.95
	5.0	10.4	95.69	1.93
	7.5	6.9	97.14	1.28
	10.0	2.5	98.96	0.46
	15.0	2.5	98.96	0.46

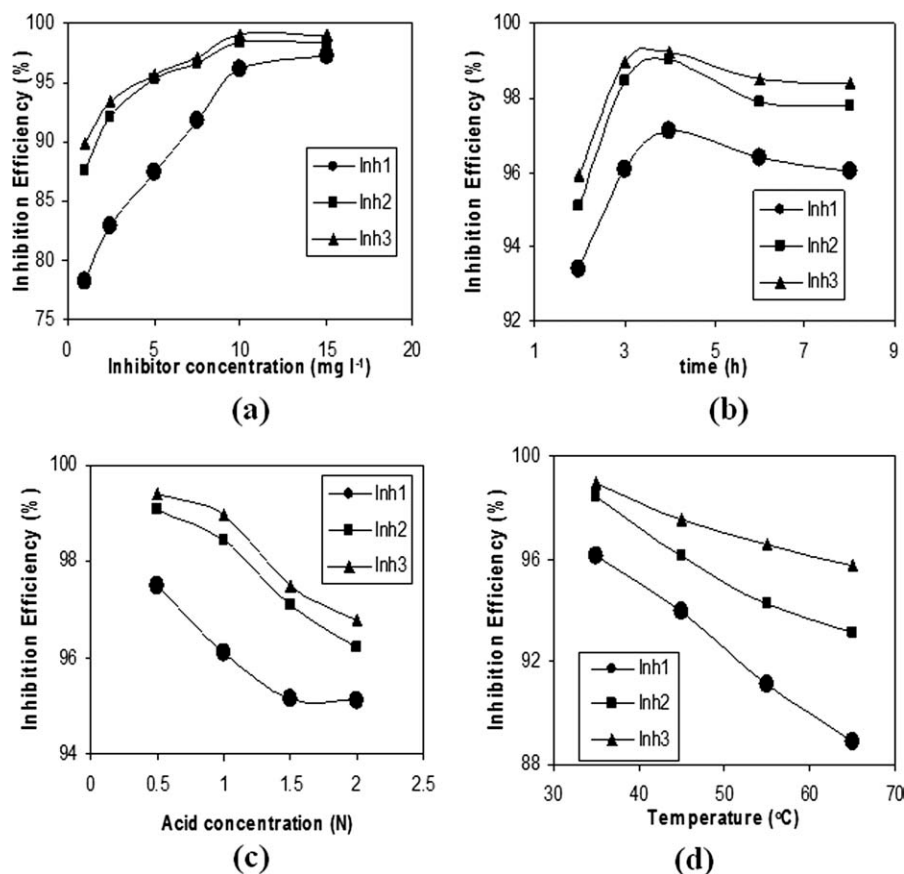


Figure 2 (a) Variation of inhibitor efficiency with concentration of all the polymers. (b) Variation of inhibitor efficiency with immersion time at 10 mg L⁻¹ concentration of all the polymers. (c) Variation of inhibitor efficiency with temp at 10 mg L⁻¹ concentration of all the polymers. (d) Variation of inhibitor efficiency with acid concentration at 10 mg L⁻¹ concentration of all the polymers.

The electrochemical studies were made using a three electrode cell assembly at room temperature. The working electrode was a mild steel of above composition of 1 cm² exposed area and the rest being covered by using commercially available lacquer. The working electrodes were polished with emery paper grade 600–1200, washed with water and degreased with acetone and mounted in the electrochemical cell through electrode holders and potentiostat was connected to the working electrode with crocodile clip. A platinum foil was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The polarization and impedance studies were carried out using Gamry Potentiostat/Galvanostat (model 300) with EIS software, Gamry-Instruments. The linear polarization study was carried out from cathodic potential of -0.02 V versus SCE to an anodic potential of +0.02 V versus SCE with respect to OCP at a sweep rate 0.125 mV s⁻¹ to study the polarization resistance (R_p). The Tafel polarization was carried out from cathodic potential of -0.25 V versus SCE to an anodic potential of +0.25 V versus SCE with respect to OCP at a sweep rate 0.5 mV s⁻¹ to study the electrochem-

ical nature of inhibitor on mild steel corrosion. The linear Tafel segment of anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (I_{corr}). The percentage corrosion inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$\eta_p(\%) = \frac{I_{corr}^0 - I_{corr}^i}{I_{corr}^0} \times 100$$

where I_{corr}^0 and I_{corr}^i are the corrosion current densities in absence and in presence of various concentrations of the inhibitor, respectively. The impedance studies were carried out using ac signals of 10 mV amplitude in the frequency spectrum from 100 kHz to 0.01 Hz after 30 min of immersion time to stabilize the system. The charge transfer resistance values were obtained from the diameter of the semicircles of the Nyquist plots. The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation

$$\eta_{R_t} = \frac{(1/R_t^0) - (1/R_t^i)}{(1/R_t^0)} \times 100$$

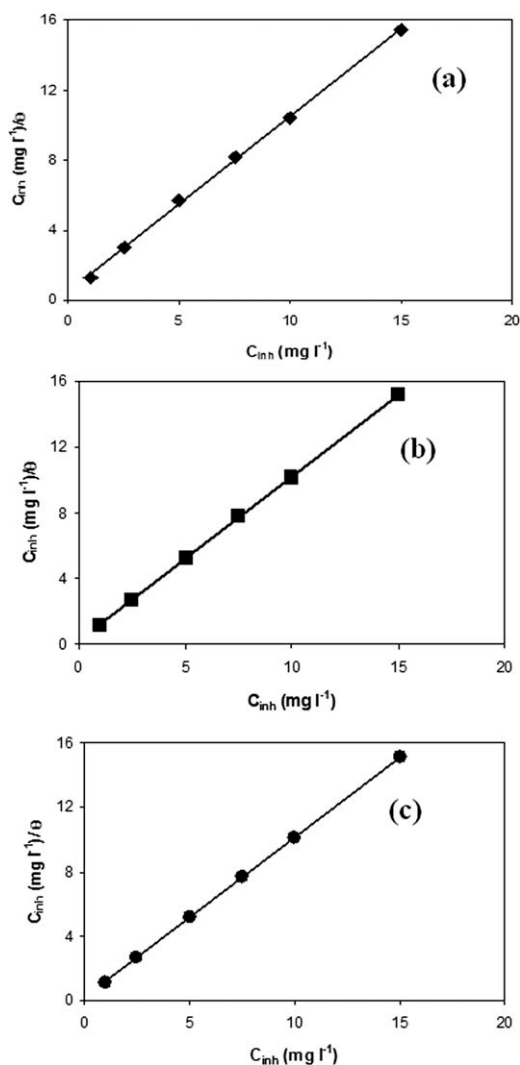


Figure 3 Langmuir adsorption isotherm plot for the adsorption of (a) Inh1 (b) Inh2 (c) Inh3, on the surface of mild steel in 1M HCl.

where R_t^0 and I_t^0 are the charge transfer resistances in absence and in presence of inhibitor, respectively. The interfacial double layer capacitance (C_{dl}) values

have been estimated from the impedance value using bode plot by the formula:

$$|Z| = \frac{1}{2\pi f C_{dl}}$$

where f is the frequency at which the imaginary component ($|Z|$) of impedance is maximum.

The surface characterization was performed using a NT-MDT multimode AFM (atomic force microscope) Russia, controlled by Solver Scanning probe microscope controller to know the surface morphology of the mild steel sample with and without optimum concentration of inhibitor.

RESULTS AND DISCUSSION

Weight loss study

The values of percentage inhibition efficiency (% IE) and corrosion rate (CR) obtained from weight loss method at different concentrations of inhibitors at 35°C are summarized in Table I. It has been found that polymers inhibit the corrosion of mild steel in hydrochloric acid solution, at all the concentrations ranging from 1–15 $mg\ L^{-1}$ used in this study. It is evident from Table I that the corrosion rate decreased from 44.85 to 9.76 mm/y, 5.58 mm/y, and 4.55 mm/y with the addition of 1.0 $mg\ L^{-1}$ of Inh1, Inh2, and Inh3, respectively. The maximum inhibition efficiency for Inh1 was obtained at 15 $mg\ L^{-1}$. The maximum inhibition efficiency for Inh2 and Inh3 was obtained at 10 $mg\ L^{-1}$. The variation of inhibition efficiency with increase in inhibitor concentrations is shown in Figure 2(a).

The effect of immersion time on inhibition efficiency from 2 to 8 h is shown in Figure 2(b). It was found that the inhibition efficiency first increases with increase in immersion time and after some time it becomes constant. This showed that the formation of inhibitor film takes some times.

TABLE II
Electrochemical Parameters for the Corrosion of Mild Steel in 1M HCl in Absence and Presence of Different Concentrations of Polymers

Name of inhibitors ($mg\ L^{-1}$)	Concentration of inhibitor ($\Omega\ cm^2$)	Polarization resistance				Tafel polarization					EIS		
		R_p (%)	IE (mm/y)	CR (mV vs. SCE)	$-E_{corr}$ (mV/dec)	b_a (mV/dec)	b_c ($\mu A\ cm^{-2}$)	I_{corr} (%)	IE (mm/y)	CR ($\Omega\ cm^2$)	R_t ($\mu F\ cm^{-2}$)	C_{dl} (%)	IE
Blank	13.99	–	14.41	470	65.5	107.1	1540.0	–	17.86	19.8	1555	–	
Inh1	5	145.3	90.4	1.39	478	79.9	153.9	119.0	92.3	1.38	162.4	192.3	87.8
	10	173.4	91.9	1.16	477	74.7	160.9	101.0	93.4	1.17	191.9	162.6	89.7
	15	221.0	93.7	0.91	474	75.1	187.1	93.2	93.9	1.08	291.0	103.2	93.2
Inh2	1	139.6	90.0	1.44	478	73.0	144.9	117.0	92.4	1.36	122.3	248.9	83.8
	5	199.9	93.0	1.01	473	82.9	182.4	91.0	94.0	1.06	361.7	86.2	94.5
	10	339.8	95.9	0.59	470	80.3	166.4	58.5	96.2	0.68	465.1	66.9	95.7
Inh3	1	222.5	93.7	0.91	477	68.0	148.2	87.0	94.4	1.01	284.9	107.6	93.1
	5	268.4	94.8	0.75	481	72.8	149.9	67.7	95.6	0.79	370.5	83.5	94.7
	10	349.4	96.0	0.58	495	81.6	146.1	53.3	96.5	0.62	477.6	63.8	95.9

The variation of inhibition efficiency with increase in acid concentration from 0.5 to 2.0M is shown in Figure 2(c). It is clear that change in acid concentration from 0.5 to 2.0M did not cause any significant change in inhibition efficiency values. The change in IE is less than 4%. This observation suggests that polymers are effective corrosion inhibitors in acid solution over the concentration range 0.5 to 2.0M.

The influence of solution temperature on inhibition efficiency is shown in Figure 2(d). It is observed that inhibition efficiency decreases with increase in temperature from 35 to 55°C. The decrease in inhibition efficiency with temperature may be attributed to desorption of the inhibitor molecules from metal surface at higher temperature.²⁸

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior.²⁹ The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated from weight loss data. Data were tested graphically by fitting to various isotherms. A straight line [Fig. 3(a-c)] was obtained on plotting C_{inh} versus C_{inh}/θ for all the polymers. From this plot, it is observed that all polymers obey Langmuir adsorption isotherm. The adsorption of all the polymers on to the metal surface occurs usually through the already adsorbed chloride ion.³⁰ The higher inhibitive properties of polymers are also due to the presence of π electrons, quaternary nitrogen atom, and the larger molecular size which, ensures greater coverage of the metallic surface.^{31,32}

Polarization resistance study

The polarization resistance (R_p) values of mild steel in 1M hydrochloric acid with different concentration of polymers are given in Table II. The R_p values of all the polymers are increase with increase in the inhibitor concentration. The increase in R_p values suggests that all inhibitors are very effective even at 1 mg L⁻¹.

Tafel polarization

The Tafel polarization curves for mild steel in 1.0M HCl with the addition of various concentrations of Inh1, Inh2, and Inh3 are shown in Figure 4(a-c). Electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel constants (b_a and b_c), percentage inhibition efficiency (% IE), and corrosion rate (CR) are calculated from the Tafel plots are given in Table II. It is evident from the results that all the polymers decrease I_{corr} values in the concentration range of 5–15 mg L⁻¹ for Inh1 and 1–10 mg L⁻¹ for Inh2 and Inh3. It is also observed that E_{corr} values did not change significantly with increase of concentration of inhibitors suggesting that all the polymers used in study are mixed type inhibitors. Jayaprabha et al.³³ have

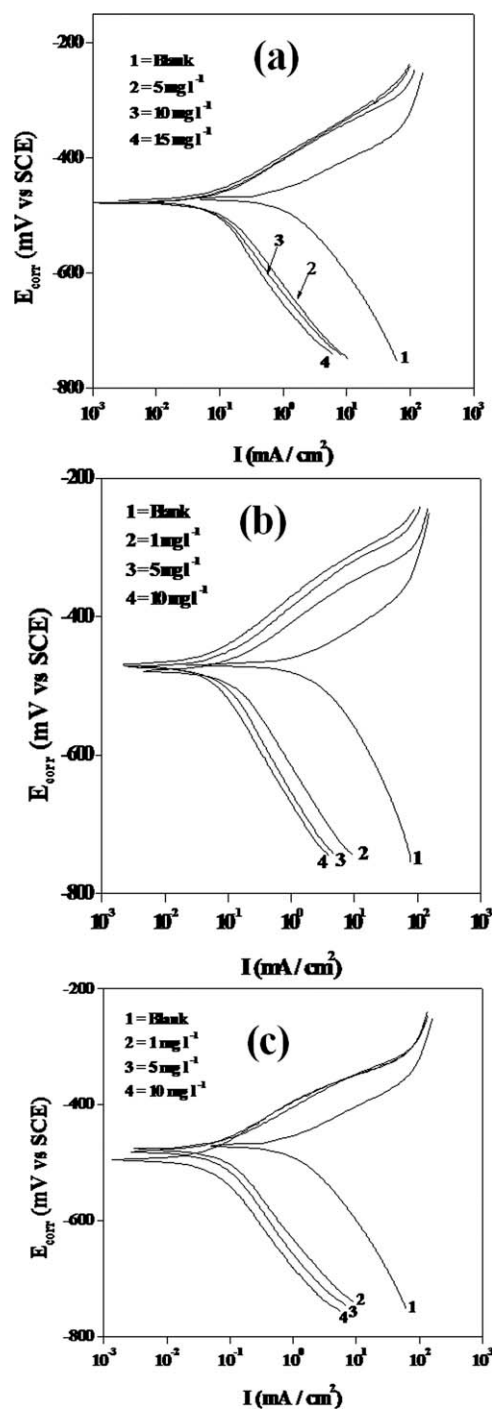


Figure 4 Potentiodynamic polarization behavior of mild steel in 1M HCl with the addition of various concentrations of inhibitors: (a) Inh1, (b) Inh2, and (c) Inh3.

reported that substituted polyanilines behave as mixed type of inhibitor in acid solution. The inhibition efficiency is seen to increase in the order: Inh3 > Inh2 > Inh1.

Electrochemical impedance studies

The impedance data were fitted in various circuits. Randle circuit was found to be best suited for the

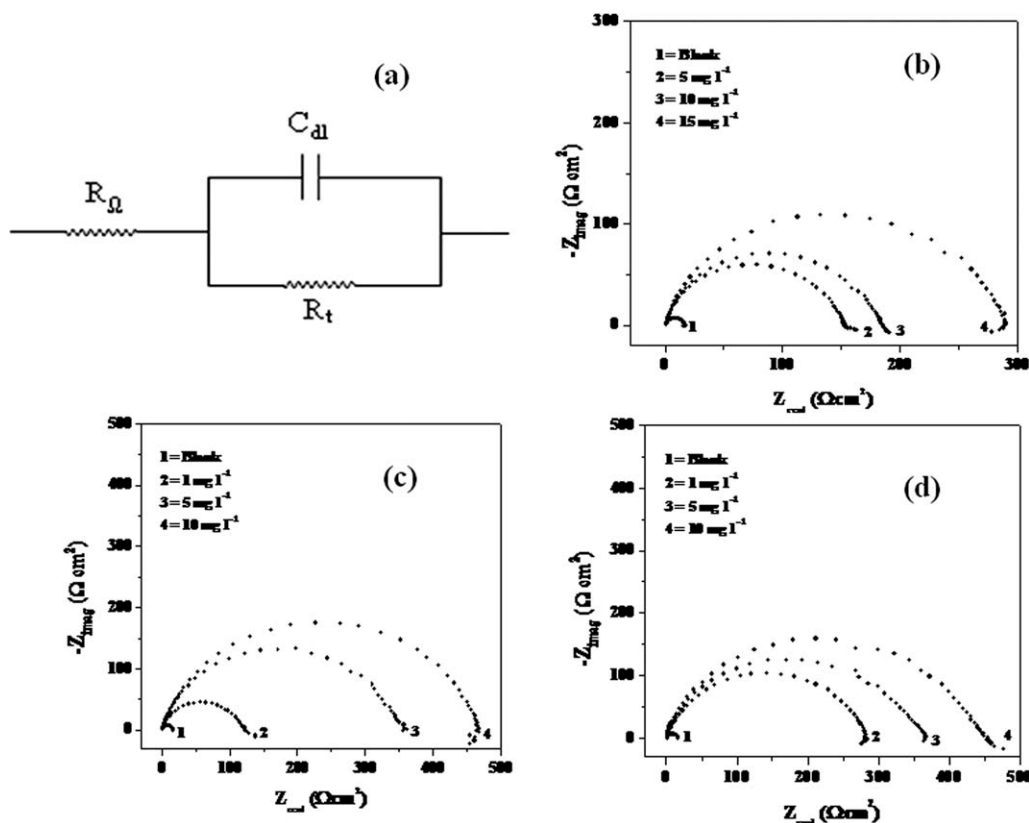


Figure 5 (a) Electrical equivalent circuit (R_{Ω} = uncompensated solution resistance, R_t = polarization resistance, C_{dl} = double layer capacitance). (b–d) Nyquist plot of mild steel in 1M HCl with the addition of different concentrations of inhibitors (b) Inh1, (c) Inh2, and (d) Inh3.

polymers. The Randle equivalent circuit was shown in Figure 5(a), where R_{Ω} represents the solution and corrosion product film; the parallel combination of resistor, R_t and capacitor C_{dl} represents the corroding interface. The Nyquist representation of the impedance behavior of mild steel in 1M HCl with and without addition of various concentrations of all the polymers are given in Figure 5(b–d). Various parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}), and percentage inhibition efficiency (% IE) have been calculated and listed in Table II.

Figure 5(b–d) shows the Nyquist plot for mild steel in 1M HCl in absence and presence of various concentration of polymers. The higher frequency capacitive loop is due to the adsorption of the polymer molecules.³⁴ The deviation from the perfect semi-circle shape, that is, depression is due to the frequency dispersion of interfacial impedance. This anomalous behavior is generally attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomenon.^{35–37} The smaller inductive loop is attributed to a process of relaxation of adsorbed compounds at lower frequency.³⁸

The decrease in C_{dl} is attributed to increase in thickness of electronic double layer.³⁹ The increase

in R_t value is attributed to the formation of protective film on the metal/solution interface.^{40,41}

Surface characterization: AFM study

Surface morphology of the polished mild steel and mild steel in 1M HCl in absence and presence of inhibitor was investigated through atomic force microscopy (AFM) technique. The result was shown in Figure 6(a–e). The average roughness of polished mild steel [Fig. 6(a)] and mild steel in 1M HCl without inhibitor [Fig. 6(b)] was calculated as 48 and 471 nm. It is clearly shown in Figure 6(b) that mild steel sample is rough due to the acid attack. However, in presence of optimum concentration of Inh1, Inh2, and Inh3, the average roughnesses [shown in Fig. 6(c–e)] were reduced to 87, 78, and 67 nm, respectively. The calculated roughness for the Inh3 is lowest among all the inhibitors thereby suggesting that Inh3 is the best inhibitor among the inhibitors studied.

Mechanism of inhibition

Corrosion inhibition of mild steel in hydrochloric acid solution by the polymers can be explained on the basis of molecular adsorption. The compounds

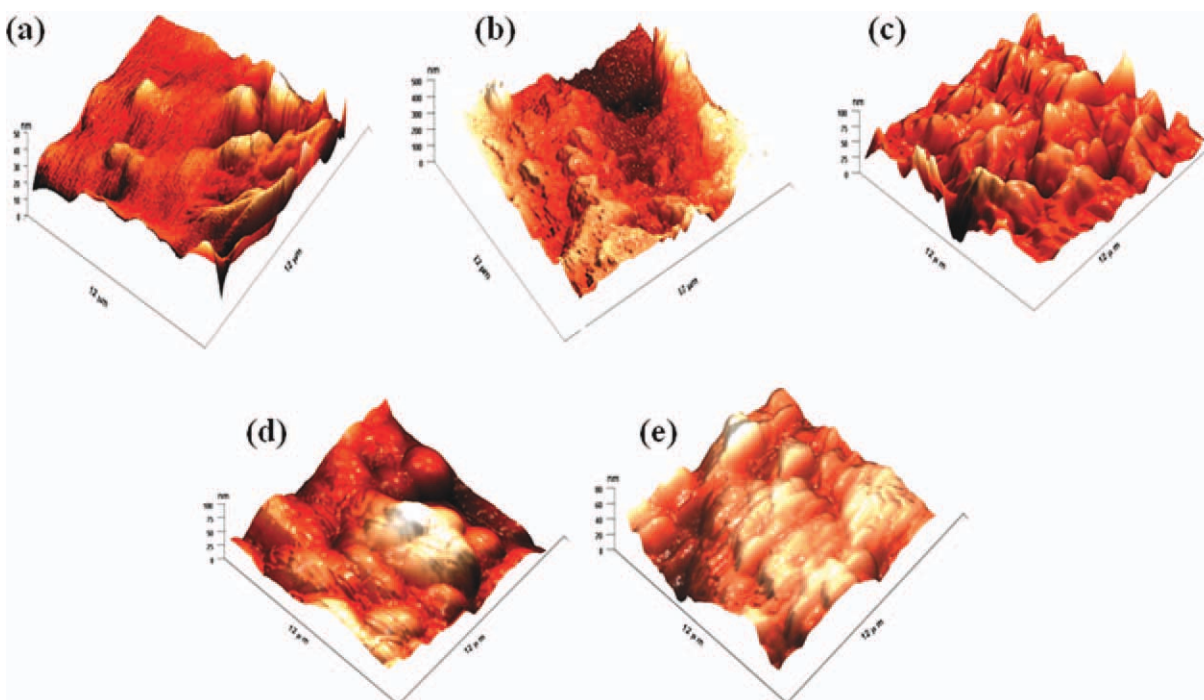
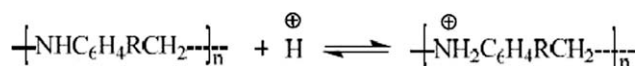


Figure 6 Surface morphology of mild steel surface (a). Polished mild steel surface (b) Mild steel surface in 1M HCl without inhibitor (c) Mild steel surface in 1M HCl with Inh1 (d) Mild steel surface in 1M HCl with Inh2 (e) Mild steel surface in 1M HCl with Inh3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

inhibit corrosion by controlling both the anodic and cathodic reactions. In acidic solution the polymers exist as protonated species.



These protonated species adsorb on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic sites occurs through π -electron of aromatic rings and lone pair of electrons of nitrogen atom, which decreases anodic dissolution of mild steel.⁴² Increase of both anodic and cathodic Tafel slopes indicate the polymers inhibit corrosion by affecting the mechanism of the reactions by formation of complexes. Similar explanation has been given by several investigators.^{43,44}

The high performance of the polymers is attributed to the presence of π -electrons, quaternary nitrogen atom, and the larger molecular size. The inhibition efficiency of the inhibitors at a common concentration of 10 mg L⁻¹ follows the order:

$$\text{Inh3} > \text{Inh2} > \text{Inh1}.$$

Among the compounds investigated in this study, Inh3 has been found to give the best performance, which attributed to the interaction of lone pair of electron of chlorine atom with metal surface. This facility is not available in other inhibitors. Gad-Allah et al.⁴⁵ have observed similar behavior of chloro-substituted

derivatives in case of chloro derivative of aminopyrazole. The better performance of Inh2 than Inh1 is due to the presence of electron releasing methyl group.

CONCLUSIONS

1. The inhibition efficiency of all the polymers increases with increase in the polymer concentration. Inh3 showed best performance as corrosion inhibitor giving >98% efficiency at 10 mg L⁻¹ concentration.
2. All the polymers show the decrease in the inhibition efficiency by increase in the temperature and no any significant change in the inhibition efficiency by the increase in acid concentration.
3. Langmuir adsorption isotherm and impedance studies showed that these polymers inhibits through adsorption mechanism.
4. Potentiodynamic polarization study showed that the polymers are mixed type of inhibitors.
5. AFM studies give the surface morphology of the protected mild steel sample by the polymers.

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