

Application of Some Oligopolymers as Effective Corrosion Inhibitors for Mild Steel in 1M HCl: Gravimetric, Thermodynamic and Electrochemical Analysis

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Received: 23 March 2014 / Accepted: 5 May 2014 / Published: 16 July 2014

Three oligopolymers derived from α -Naphthol (N), formaldehyde (F) with aniline (TERP-1), para-aminobenzoic acid (TERP-2) and sulphanilic acid (TERP-3) were synthesized and their inhibitive action on corrosion of mild steel in 1M HCl was studied using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, linear polarization and gravimetric methods. The values of activation energy (E_a) and some thermodynamic parameters were calculated to describe the mechanism of adsorption. The inhibition efficiency of the all three inhibitors followed the order TERP-3 > TERP-2 > TERP-1. The potentiodynamic polarization studies reveal that investigated polymers are mixed type inhibitors. Out of three polymers, TERP-3 exhibited the best inhibition efficiency (95% at 50 ppm).

Keywords: Acid corrosion, mild steel, thermodynamic parameters, EIS, oligopolymers

1. INTRODUCTION

Hydrochloric acid is widely used in industries such as pickling, cleaning and descaling etc. corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. The use of inhibitors is one of the best options of protecting metals and alloys against corrosion. Many industrial divisions such as acid cleaning bath, water cooling system, various refinery units, pipelines, chemical operations, steam generators, ballast tanks, oil and gas production units are involved with inhibitors due to high corrosion rates in these parts [1-6]. A large number of polymers have been used as corrosion inhibition for mild steel [7-19], aluminum [20-26], iron [27-37]

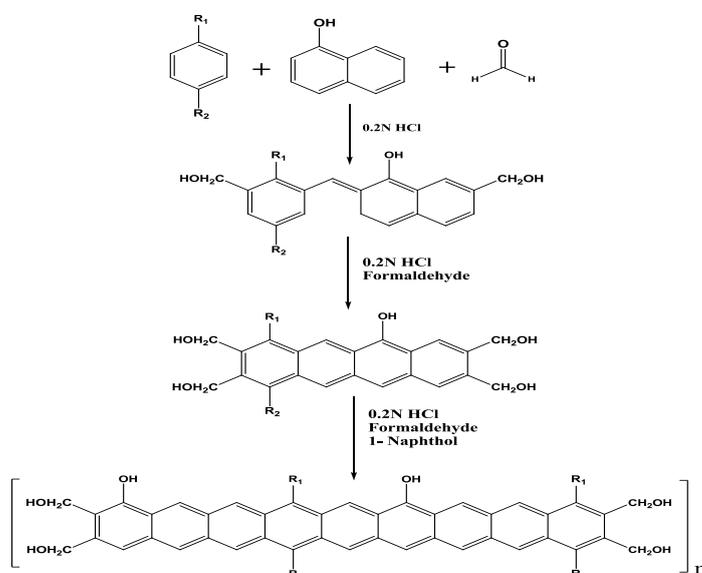
copper [38-40] and other metals [41, 42]. However most of the polymers have limited application due to their low solubility in study medium. In present study we have synthesized three oligomers and investigated their inhibition properties on corrosion of mild steel.

The choice of these polymers as corrosion inhibitor is based on the following considerations: these molecules (a) can be easily synthesized from relatively cheap Materials with very high yield, (b) contain $-\text{NH}_2$, $-\text{SO}_3\text{H}$ and $-\text{COOH}$ groups, electronegative oxygen/ Sulphur and aromatic ring as active centers and (c) have high solubility in acidic media. Oligomers find very useful applications as adhesives, high temperature flame resistant fibres, materials, semiconductors, catalysts, and ion-exchange resins [43-47]. Previously, some work has been done on oligomers as corrosion inhibitors for mild steel in acidic as well as in neutral media [48, 49].

2. EXPERIMENTAL

2.1. Inhibitors synthesis

The aniline derivatives (0.05 mol) added into 40% aqueous formaldehyde solution containing 10.14% methanol in order to prevent polymerization of formaldehyde. Carefully to this reactant mixture added α -naphthol (0.05 mol) and few drops of acid were added directly. The colour of the complex turned dark red. The solution was refluxed for 30 min on a water bath. The mixture was cooled at room temperature, and then placed mixture in an ice-bath for 30 min and collected the beautiful dark pink colored polymer was cold which becomes hard brittle on standing [50]. The simple procedure adopted for synthesis of oligomers from aniline derivatives, formaldehyde and α -naphthol is given in following scheme.



TERP-1 $R_1 = -\text{NH}_2$, $R_2 = -\text{H}$

TERP-2 $R_1 = -\text{NH}_2$, $R_2 = -\text{COOH}$

TERP-3 $R_1 = -\text{NH}_2$, $R_2 = -\text{SO}_3\text{H}$

Scheme 1. Synthetic scheme of oligomers

2.2. Materials

The mild steel specimens, with composition (wt %) Fe 99.30%, C 0.076%, Si 0.026%, Mn 0.192%, P 0.012%, Cr 0.050%, Ni 0.050%, Al 0.023%, and Cu 0.135%, were abraded successively with emery papers from 600 to 1200 mesh/in grade. Mild steel specimen washed with double distilled water, degreased with acetone and finally dried in hot air blower. The working electrode (WE) was a 7.0 cm long stem (isolated with epoxy resin) to provide an exposed surface area of 1.0 cm² for electrochemical measurements and dimension 2.5 × 2.0 × 0.025 cm³ were used in weight loss experiments. The test solution 1 M HCl prepared from analytical reagent grade reagent (37 % HCl) and double distilled water.

2.3 Weight loss method

The weight loss measurements were performed by immersing the mild steel coupons in 100 ml of 1 M HCl in conical flasks in absence and in presence of different concentration of inhibitors. After three hours (elapsed time), the mild steel specimen were taken out, washed, dried and weighed accurately. All the experiments were performed in triplicate in aerated 1M HCl and average values were taken. The corrosion inhibition efficiency (η %) and surface coverage (θ) is calculated by following equations:

$$\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \quad (1)$$

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \quad (2)$$

where C_R and $C_{R(i)}$ are the corrosion rate values in absence and presence of oligomers respectively. The corrosion rate (C_R) of mild steel in acidic medium was calculated by using following equation:

$$C_R = \frac{W}{At} \quad (3)$$

where, W is weight loss of mild steel specimens (mg), A is the area of the specimen (cm²) and t is the exposure time (h).

2.4. Electrochemical measurements

The electrochemical experiments were carried out using Potentiostat/Galvanostat having a Gamry framework system based on ESA400. The three-electrode cell consist of mild steel specimens of 1.0 cm² area exposed as working electrode, a high purity platinum foil as counter electrode and saturated calomel electrode (*SCE*) as a reference electrode respectively. The potentials were measured versus *SCE* (saturated calomel electrode). Gamry applications include software *EIS300* for electrochemical impedance, *DC105* for corrosion measurements. Echem Analyst version 5.50 software package was used for data fitting. It enables the fitting of the experimental results to a pure electronic

model for representing the electrochemical system under investigation. Prior to the electrochemical measurements the working electrode was immersed in 1 M HCl in absence and presence inhibitor for 30 minutes to stabilization of the OCP w.r.t. SCE . All the impedance measurements were performed under a potentiodynamic condition from 100,000 Hz to 0.01 Hz with amplitude of 10 mV peak-to-peak. The polarization measurements were performed by changing the electrode potential automatically from -250 to +250 mV vs. OCP at a scan rate of 1 $mV s^{-1}$. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion current densities (I_{corr}). The linear polarization study was carried out from cathodic potential of -20 mV vs. OCP to an anodic potential of +20 mV vs. OCP at a scan rate 0.125 $mV s^{-1}$ to study the polarization resistance (R_p).

3. RESULTS AND DISCUSSIONS

3.1 Weight loss studies

3.1.1 Effect of inhibitor concentration

The mild steel coupons were exposed to aerated 1 M HCl for 3 h immersion time. It has been found that inhibition efficiency of all the polymers increases with concentration. The maximum inhibition efficiency for each polymer was obtained at 50 ppm concentration and further increase in concentration did not cause any significant change in inhibition efficiency. The variation of inhibition efficiency with concentration from 10 ppm to 50 ppm is shown in Figure 1 (a). It is clear that inhibition efficiency of each polymer increases with concentration. The values of percentage inhibition efficiency (η %), corrosion rate (C_R) and surface coverage (θ) obtained from weight loss measurement at different concentrations of all the polymers at 308 K are summarized in Table 1.

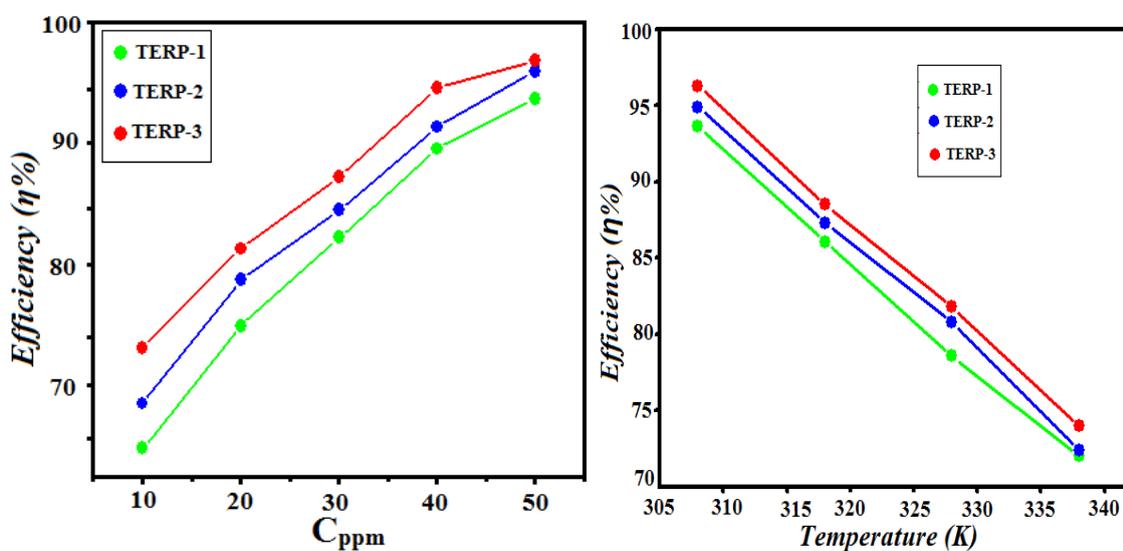


Figure 1. (a) Inhibition efficiency of oligomers at different concentration (b) Inhibition efficiency of oligomers at different temperature

3.1.2. Effect of temperature

Weight loss measurements were taken at various temperatures (308–338 K) in the absence and at optimum concentration of oligomers (50ppm) for 3 h of immersion in 1M HCl. The corrosion rate increases with the rise of temperature. The inhibition efficiencies are found to decrease with increasing the temperature from 308 to 338 K [Figure 1 (b)]. The decrease in inhibition efficiencies might be due the weakening of adsorbed inhibitors film on the mild steel surface [51].

Table 1. Corrosion rate (C_R), Surface coverage (θ) and corrosion inhibition ($\eta\%$) for mild steel in 1M HCl in absence and in presence of different concentrations of polymers from weight loss measurements at 308 K.

Inhibitor	Inhibitor conc ppm	Corrosion rate ($mg\ cm^{-2}\ h^{-3}$)	Surface coverage (θ)	$\eta\%$
Blank	0.0	85.33
TERP-1	10	28.56	0.6434	64.34
	20	20.40	0.7488	74.88
	30	14.47	0.8219	82.19
	40	8.53	0.8949	89.49
	50	5.19	0.936	93.6
	TERP-2	10	25.22	0.6849
20		18.18	0.787	78.7
30		12.61	0.8447	84.47
40		7.04	0.9132	91.32
50		3.33	0.9589	95.89
TERP-3		10	21.89	0.7305
	20	15.21	0.8127	81.27
	30	10.38	0.8721	87.21
	40	4.45	0.9452	94.52
	50	2.59	0.968	96.8

3.2.3 Thermodynamic parameters and adsorption isotherm:

Different isotherms were tested in order to gain information about interaction between the inhibitors molecules and mild steel surface. The Langmuir isotherm was found to be best fit according to which the solid surface contains a fixed number of adsorption centre and each centre holds one inhibitor [52]. Langmuir isotherm [Figure 2 (a)] give a straight line between $\log(\theta/1-\theta)$ and $\log C$ (M) having regression coefficient (R^2) 0.9889, 0.9975 and 0.9956 for TERP-1, TERP-2 and TERP-3 respectively.

The corrosion rate (C_R) depends upon temperature and this temperature dependence of corrosion rate for a chemical reaction can be expressed by following Arrhenius equation [53].

$$\log(C_R) = \frac{-E_a}{2.303RT} + \log \lambda \tag{4}$$

where E_a is activation energy for the corrosion of Mild Steel in 1 M HCl, λ Arrhenius pre-exponential factor, R is the gas constant and T is the absolute temperature. The Arrhenius plot [$\log C_R$ vs $1/T$, (Figure 2.b)] was give a straight line from which apparent activation energies (E_a) is calculated at optimum concentration and given in table2. From table it is clear that activation energy in presence of oligomers is greater than in absence of polymers. This increase in E_a is either due to physical adsorption in first stage [54-57] or due to decrease in the adsorption of inhibitor molecules on the mild steel surface with increase in temperature [58]. The higher values of E_a in the presence of inhibitor are due to increase thickness of the double layer which retards the corrosion process [59].

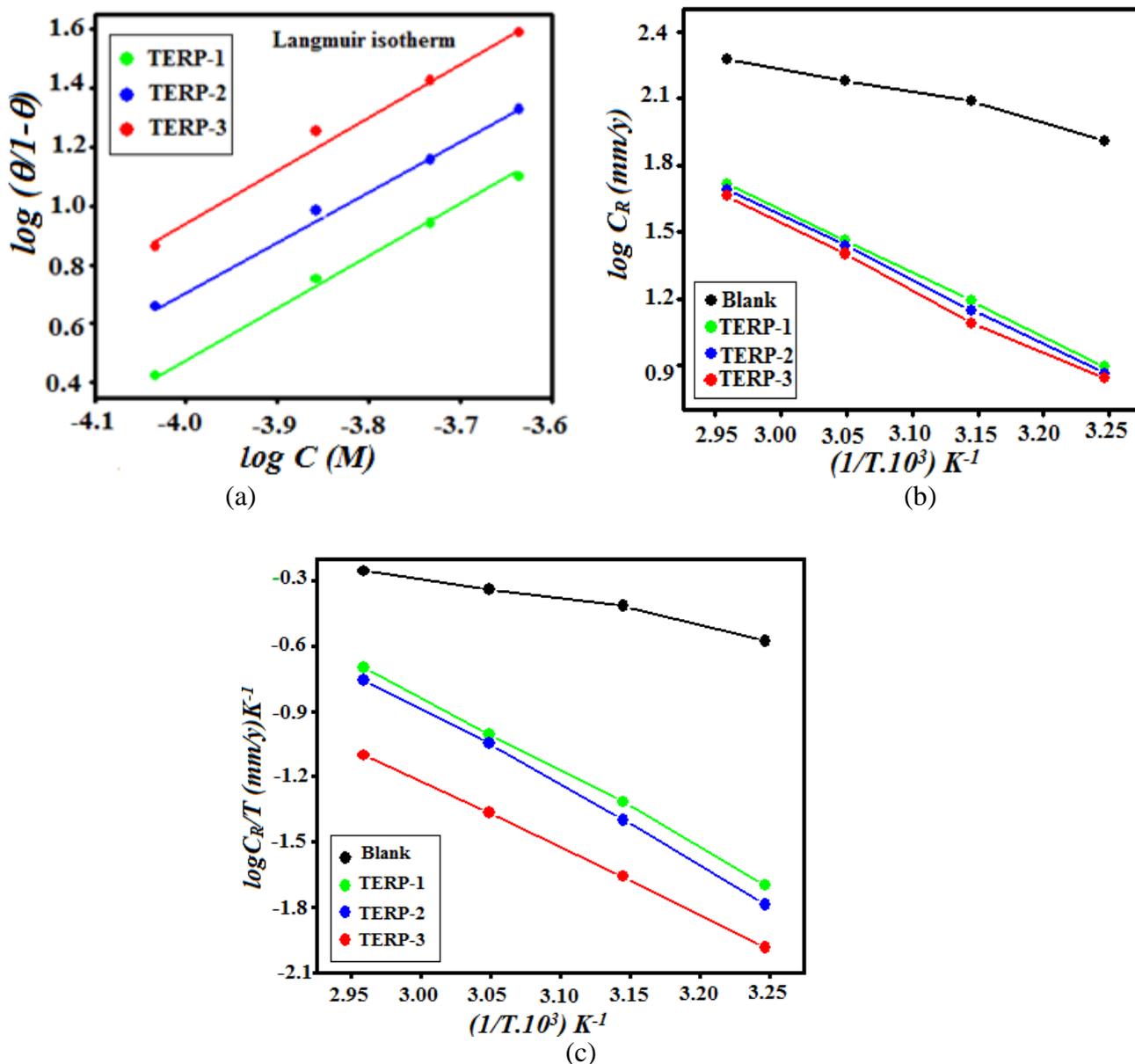


Figure 2. (a-c) (a) Langmuir adsorption isotherm (b) Arrhenius plot of $\log C_R$ Vs $1/T$ (c) Transition state plot of $\log C_R/T$ Vs $1/T$

The ΔH^* (enthalpy of activation) and ΔS^* (entropy of activation) can be calculated using following equation [60].

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{H_a}{RT}\right) \tag{5}$$

where h is Plank’s constant, N is Avogadro’s number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. Figure 2 (c), shows the plot between $\log CR/T$ vs. $1/T$. The plots obtained was straight lines and the values of ΔH^* are calculated from their gradient ($\Delta H^* = -\text{slope}/2.303R$) and ΔS^* from intercept [$\log(R/Nh) + (\Delta S^*/ 2.303R)$] and given in Table 2. From table it is clear that the ΔH^* values for dissolution of mild steel in 1M HCl in presence of inhibitors are higher (44.94– 90.51 kJ mol^{-1}) than that in absence of inhibitor (26.04 kJ mol^{-1}). The positive sign and higher value of ΔH^* reflected the endothermic nature of mild steel dissolution process, meaning that dissolution of mild steel is difficult in presence of inhibitors [61]. The shift towards positive value of entropies (ΔS^*) shows that the activated complex in the rate determining step represents dissociation rather than association, meaning that disordering increases on going from reactants to the activated complex [62].

To explain the mode and nature of adsorption, adsorption equilibrium constant (K_{ads}) and Gibbs free energy (ΔG_{ads}) also calculated at different temperature using following equations [63].

$$\frac{C_{(inh)}}{\theta} = \frac{1}{K_{(ads)}} + C_{(inh)} \tag{6}$$

$$\Delta G_{ads}^o = -RT \ln(55.5K_{ads}) \tag{7}$$

The negative values of ΔG_{ads} (Table 2) are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface. Generally, the energy values of -20 kJ mol^{-1} or less are associated with an electrostatic interaction between charged molecules and charged mild steel surface, (physisorption) those of -40 kJ mol^{-1} or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond (chemisorption) [64].

Table 2. Thermodynamic parameters for mild steel in 1M HCl in absence and presence of optimum concentration of investigate polymers.

Inhibitor	$E_a (\text{kJ mol}^{-1})$	$\Delta H (\text{kJ mol}^{-1})$	$\Delta S (\text{J K}^{-1} \text{mol}^{-1})$	$\Delta G (\text{kJ mol}^{-1})$
Blank	28.48	26.04	-148.9
TERP-1	51.37	66.62	-44.48	-34.25
TERP-2	58.54	58.82	-15.47	-34.85
TERP-3	72.32	84.82	40.41	-35.73

3.2 Electrochemical measurements

3.2.1. Electrochemical Impedance Spectroscopy

The corrosion behavior of mild steel in 1 M HCl in absence and presence of optimum concentration of oligomers were investigated by Electrochemical Impedance Spectroscopy after

immersion for 30 min at 303 ± 1 K. Both Nyquist and Bode plots in absence and presence of optimum concentration of polymers is given in figure 4(a,b). The Nyquist plots show a depressed capacitive loop in the high frequency (HF) range and an inductive loop in the lower frequency (LF) range. The HF capacitive loop can be attributed to the charge transfer reaction and time constant of the electric double layer and to the surface inhomogeneity of structural or interfacial origin, such as those found in adsorption processes [65]. The LF inductive loop may be attributed to the relaxation process obtained by adsorb species like Cl^-_{ads} and H^-_{ads} on the electrode surface [66–68]. It may also be attributed to the re-dissolution of the passivated surface at low frequencies [69]. It is obvious that addition of inhibitors resulted in an increase in diameter of the semicircular capacitive loop (Fig. 3a) and in the impedance of the double layer capacitance (Fig. 3b).

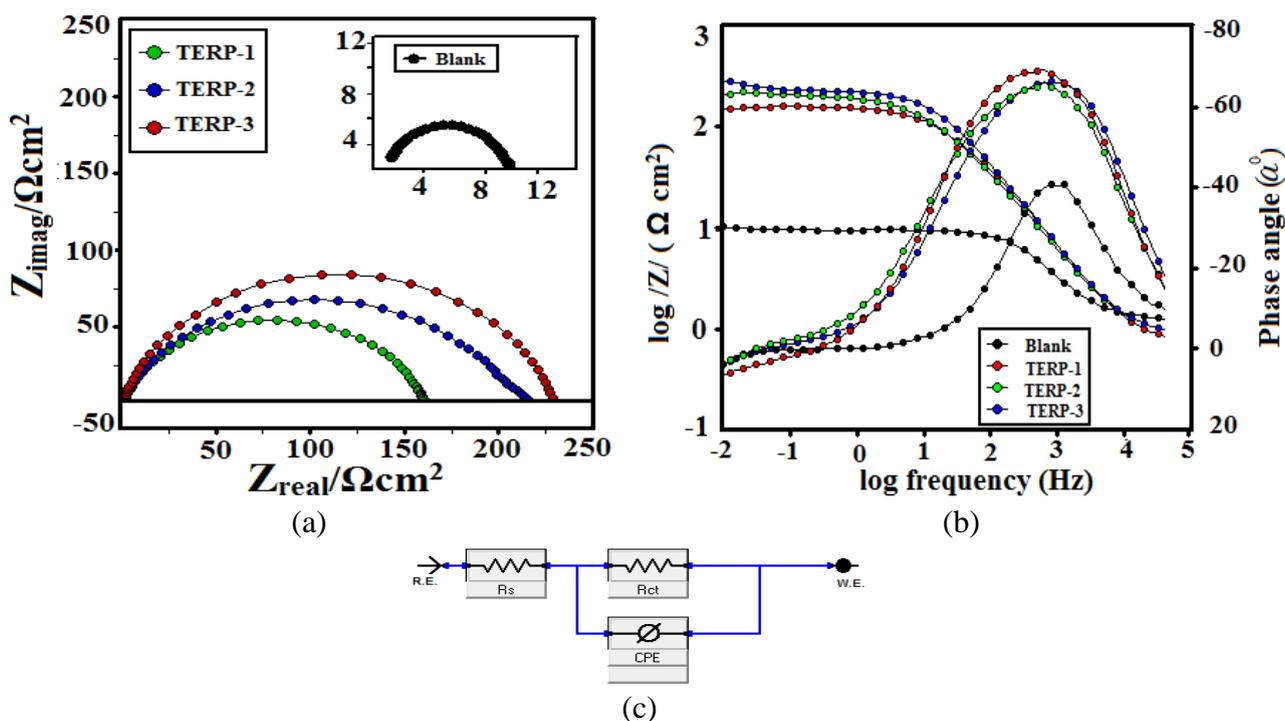


Figure 3. (a) Nyquist plot in absence and presence of optimum concentrations of polymers (b) Bode plot in absence and presence of optimum concentrations of polymers (c) Equivalent circuit used to fit the data

For corrosion reactions which are strictly charge transfer controlled, impedance behavior can be explained with the help of a simple and commonly used equivalent circuit [Figure 4 (b)] composed of a double layer capacitance, charge transfer resistance (R_{ct}) and solution resistance (R_s). The EIS parameters for polymers such as R_s , Y^0 , R_{ct} and C_{dl} were derived from the Nyquist plot are given in Table 3. It is clear from the result obtained from Nyquist plot [Figure-3 (a)] and table 3, that the value of R_{ct} increases from $11.8/ \Omega cm^2$ (Blank) to $155.10/ \Omega cm^2$, $204.17/ \Omega cm^2$ and $225.32 / \Omega cm^2$ for TERP-1, TERP-2 and TERP-3 respectively at 50 ppm concentration. It is also depicted from Table that the impedance of the inhibited system amplified with increase and the C_{dl} values decreased with

polymers concentration. The double layer capacitance (C_{dl}) was calculated by using following equation [70]:

$$C_{dl} = Y_0 (\omega_{max})^{n-1} \tag{8}$$

where, Y^0 is CPE coefficient, n is CPE exponent (phase shift), ω is the angular frequency. The ω_{max} represents the frequency at which the imaginary component reaches the maximum. This decrease in C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that polymers molecules inhibit the mild steel corrosion by adsorption at the metal/acid interface [71].

Table 3. The Electrochemical Impedance parameters and corresponding efficiencies of polymers in 1 M HCl at optimum concentration:

Inhibitor	Conc. (ppm)	R_s (Ω)	R_{ct} ($\Omega\text{ cm}^2$)	n	Y_0 ($\mu\text{F cm}^{-2}$)	C_{dl} ($\mu\text{F cm}^{-2}$)	\square	$\eta\%$
Blank	0.0	1.12	11.8	0.827	249.8	106.21
TERP-1	50	0.696	155.10	0.807	137.5	41.55	0.9210	92.10
TERP-2	50	0.823	204.17	0.786	116	35.89	0.9400	94.00
TERP-3	50	0.875	225.32	0.84	64.81	25.26	0.9456	94.56

3.2.2. Potentiodynamic polarization measurements

The polarization behavior of mild steel in 1 M HCl in the absence and presence of different concentrations of inhibitor under study is given in Figure 4. Various potentiodynamic polarization parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic Tafel slopes (β_a and β_c) obtained by extrapolation of Tafel lines and corrosion inhibition efficiency ($\eta\%$) were also calculated and are presented in Table 4.

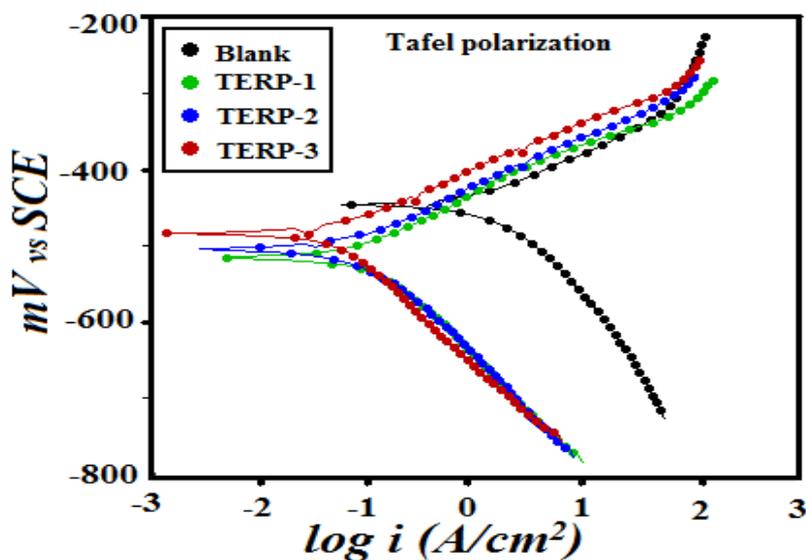


Figure 4. Tafel polarization curves for corrosion of mild steel in 1 M HCl in the absence and presence of optimum concentrations of polymers

The potentiodynamic polarization measurements shows that investigated polymers are good corrosion inhibitors for mild steel in 1M HCl. From table it is clear that I_{corr} values decreased considerably in presence of inhibitors than in absence of inhibitors while E_{corr} values do not show any significant change suggesting that studied polymers acts as a mixed-type inhibitors. This means the addition of oligomers modifies slightly anodic and cathodic slopes. The slopes of Tafel lines nearly remained the same indicating the inhibitive action to be the result of adsorption of inhibitor molecules on the mild steel surface and blockage of active sites [72].

Table 4. The Electrochemical Impedance and Linear polarization parameters and corresponding efficiencies of three polymers in 1 M HCl at optimum concentration

<i>Tafel data</i>								<i>Linear Polarization data</i>		
<i>Inhibitor</i>	<i>Conc ppm</i>	I_{corr} ($\mu A/cm^2$)	E_{corr} (mV/S CE)	β_a (mV/d ec)	β_c (mV/de c)	θ	$\eta\%$	R_p	θ	$\eta\%$
Blank	0.0	1150	-495	70.5	114.6	12.3
TERP-1	50	113.5	-514	94	139.3	0.9013	90.13	148	0.9168	91.68
TERP-2	50	78.7	-504	75.5	116	0.9332	93.32	131.1	0.9467	94.67
TERP-3	50	59.8	-482	47.7	131.5	0.9480	94.80	286.5	0.9570	95.70

3.2.3 Linear polarization

The inhibition efficiencies and polarization resistance (R_{ct}) parameters are presented in Table 4. The values calculated by Tafel polarization and *EIS* data shows good agreement with the results obtained from linear polarization resistance. The Linear polarization parameter also shows that on increasing concentration the inhibition efficiency also increases.

4. MECHANISM OF INHIBITION

Corrosion inhibition of mild steel in hydrochloric acid solution by polymers can be explained on the basis of molecular adsorption. In acidic solution, polymers exist as protonated species. The nitrogen atoms present in polymers can be easily protonated in acidic solution and convert into quaternary compounds. These protonated species adsorbed on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic site occurs through pi-electrons of aromatic ring and lone pair of electrons of nitrogen atoms which decrease the anodic dissolution of mild steel [73]. The high performances of polymers are attributed to the presence of pi-electrons, nitrogen atom and presence of polar group's larger molecular size and the planarity of compounds.

Thus polymers can adsorb on the mild steel surface by following ways:

- (a) Electrostatic interaction between the charged molecules and charged metal;
- (b) Interaction of π -electrons with the metal;
- (c) Interaction of unshared pair of electrons in the molecule with the metal; and
- (d) The combination of the all the effects [74-76].

The weight loss and electrochemical data reveal that inhibition efficiencies for all three polymers are in order:

$$\text{TERP-3} > \text{TERP-2} > \text{TERP-1}$$

This order of inhibition efficiency is best explained in term of presence of various substituents in the phenyl moiety. The TERP-2 show better inhibition performance than TERP-1 due to presence of $-\text{NH}_2$ and $-\text{COOH}$ groups. TERP-3 shows even better inhibition performance because it is adsorbed strongly by $-\text{NH}_2$ and SO_3H groups. The TERP-3 exhibited best inhibition efficiency this due to presence of d-orbital in S-atoms.

5. CONCLUSIONS

1. All the three polymers show good inhibition properties for the corrosion of mild steel in 1 M HCl solutions and the inhibition efficiency increases with increasing the concentration of the inhibitors. The increasing order of inhibiting performance of these polymers are in the order TERP-3 > TERP-2 > TERP-1.
2. Potentiodynamic polarization measurements show these polymers are mixed-type, types inhibitors.
3. The inhibiting efficiencies obtained by Tafel polarization, EIS, Linear polarization and weight loss measurements are in good agreement.
4. The adsorption of polymers on the mild steel/1 M HCl interface obeys the Langmuir adsorption isotherm.
5. The negative sign of the ΔG_{ads} and ΔH° indicates that the adsorption of polymers on the mild steel surface in 1 M HCl is spontaneous and exothermic.

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