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Electrochemical Investigation of Substituted Aniline, Melamine and Formaldehyde Based Terpolymers as Effective Corrosion Inhibitors for Mild Steel in 1M Hydrochloric Acid Solution

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Three Terpolymers TERP-1, TERP-2 and TERP-3 were synthesized using melamine, formaldehyde and substituted aniline and their inhibitive action on corrosion of mid steel in 1M HCl was studied using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, linear polarization and gravimetric and weight loss methods. The inhibition efficiency of these inhibitors followed the order TERP-3 > TERP-2 > TERP-1. Among the studied polymers, TERP-3 exhibited the best inhibition efficiency (98%) at 50 ppm).Tafel polarization studied reveals that investigated polymers are mixed type inhibitors. EIS plot indicates that the addition of inhibitor increases the charge-transfer resistance (R_{ct}) and decreases the double-layer capacitance (C_{dl}) of the corrosion process, These observation reveal that investigated polymers inhibits mild steel corrosion by adsorption mechanism. Various thermo dynamical parameters were also calculated to substantiate the mechanism of adsorption.

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

1. INTRODUCTION

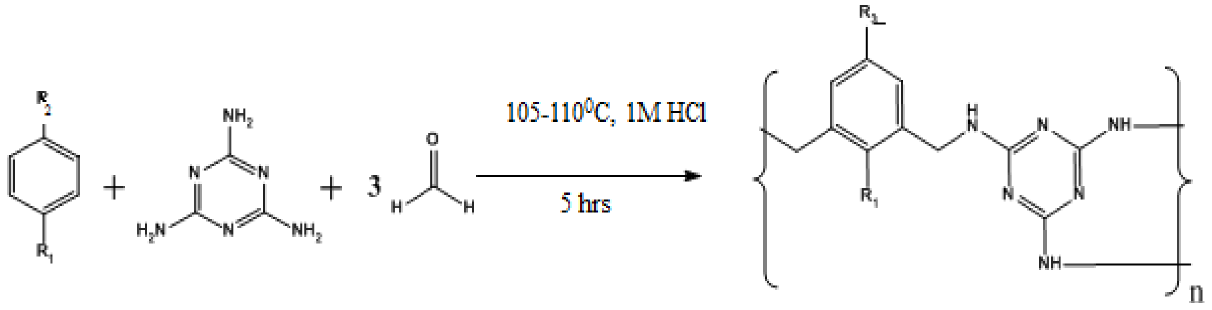
Corrosion control of metals is an important issue of technical, economical, environmental and aesthetical importance. The use of inhibitors is one of the best options for controlling corrosion of metals in various industrial processes [1-7]. A large number of polymers have been used as corrosion inhibition for mild steel [8-13], aluminum [14-19], iron [20-25] copper [26-28] and other metals [29-

30]. Terpolymers finds wide applications in industries as adhesives, high temperature flame resistant fibres, materials, semiconductors, catalysts, and ion-exchange resins [31-35].The literature survey reveals that there are only few reports on terpolymers as corrosion inhibitors [36, 37]. The choice of these polymers as corrosion inhibitors is based on following considerations: (a) they can be easily synthesized from relatively cheap materials in high yield, (b) presence of $–NH_2$,$-SO_3H$ and –COOH groups as active centers facilitates their adsorption on metal surface (c) they soluble in test solution. In view of these observations, we have synthesized three terpolymers namely TERP-1, TERP-2 and TERP-3 and investigate their inhibition properties on corrosion of mild steel.

2. EXPERIMENTAL

2.1. Inhibitors synthesis:

Three terpolymers, TERP-1, TERP-2 and TERP-3 were synthesized by condensing melamine and formaldehyde with aniline, p-amino benzoic acid and sulphanilic acid according to the procedure given in literature [38] as per scheme-1 which is given below:



TERP-1 R_1= $-NH_2$, R_2= -H TERP-2 R_1= $-NH_2$, R_2= -COOH

TERP-3 R_1= $-NH_2$, R_2= $-SO_3H$

Scheme 1. Synthetic scheme of terpolymers

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 cm^2 for electrochemical measurements and dimension 2.5 × 2.0 × 0.025 cm^3 were used in weight loss experiments. The test solution 1 M HCl was prepared from analytical grade reagent (37 % HCl) and double distilled water.

2.3. Test Solution

Stock solutions of polymers was made by dissolving them in 1 M HCl solution was diluted with double distilled water to prepare inhibitor solution of different concentration.

2.3 Weight loss method:

The weight loss measurements were carried out by standard method as described earlier [39].The inhibition efficiency (η %) and surface coverage (□) was calculated by using the following equations:

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

$$\theta = \frac{C_{\mathrm{R}} - C_{\mathrm{R(i)}}}{C_{\mathrm{R}}} \qquad (2)$$

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

$$C_{\mathrm{R}} = \frac{W}{At} \qquad (3)$$

where, W is weight loss of mild steel specimens (mg), A is the area of the specimen (cm^2) and t is the exposure time (h).

2.4. Electrochemical measurements:

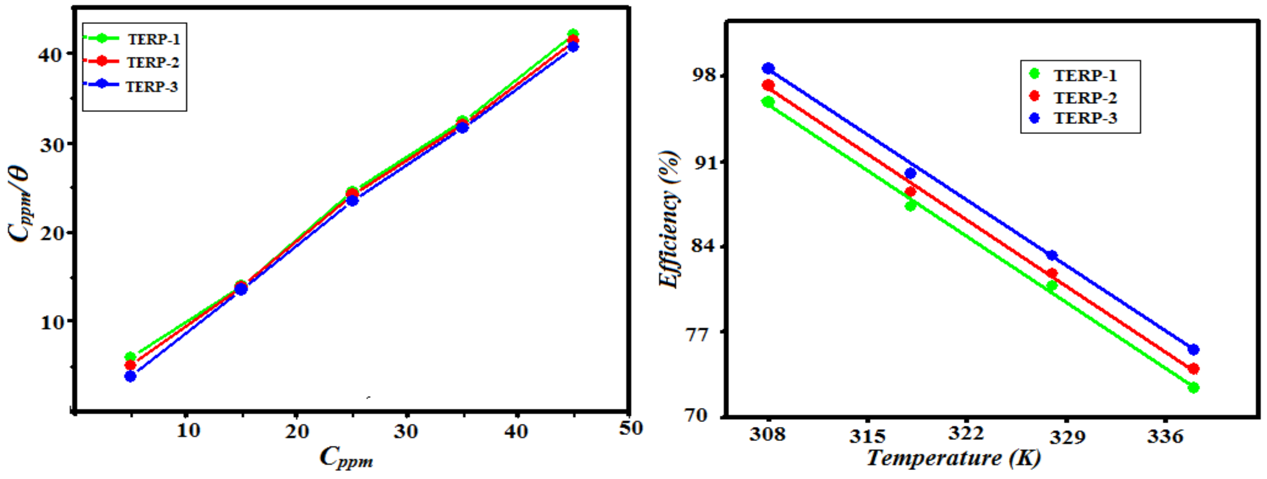
The weight loss measurements were carried out by standard method as described earlier [39].

3. RESULTS AND DISCUSSIONS

3.1 Weight loss studies:

3.1.1 Effect of inhibitor concentration:

The inhibition efficiencies (η %) and corrosion rates (C_R) obtained from weight loss measurements for three polymers at different concentrations in 1 M HCl are given in Table 1. From figure 1(a), it is found that inhibition efficiencies increases and corrosion rate decreases with increasing inhibitors concentration. The TERP-3 gave the maximum inhibition efficiency (98.7%) at 50ppm concentration. These results show that polymers are good inhibitors exhibiting more than 95% inhibition efficiency at 50 ppm concentration.



(a) (b)

Figure 1. (a) Surface coverage of polymers at different concentration (b) Inhibition efficiency of polymers at different temperature

3.1.2. Effect of temperature

Weight loss measurements were taken at various temperatures (308–338 K) in the absence and presence of polymers (50 ppm) for 3 h of immersion in 1 M HCl. The effect of temperature on inhibition property of polymers is shown in figure 1(b). The inhibition efficiencies are found to decrease with increasing the solution temperature from 308 to 338 K. The decrease in inhibition efficiencies might be due desorption of inhibitor film on the mild steel surface [41].

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)*	*η%*
Blank	0.0	85.3	……	….
TERP-1	10	32.6	0.6213	62.13
	20	23.3	0.7849	78.49
	30	13.3	0.8695	86.95
	40	9.6	0.9434	94.34
	50	6.6	0.9608	96.08
TERP-2	10	26.7	0.6608	66.08
	20	19.6	0.8347	83.47
	30	11.5	0.8782	87.82
	40	6.6	0.9521	95.21
	50	4.4	0.9739	97.39
TERP-3	10	24.11	0.7173	71.73
	20	12.98	0.8478	84.78
	30	8.90	0.8956	89.56
	40	3.33	0.9608	96.08
	50	1.11	0.9869	98.69

3.1.3 Thermodynamic parameters and adsorption isotherm

Basic information of the interaction between inhibitor molecules and the metal surface could be provided from the adsorption isotherms [figure 2(a)]. The adsorption depends on the molecule's chemical composition, the temperature and the electrochemical potential at the metal/solution interface. Several adsorption isotherms were applied to fit the surface coverage (θ) values at different concentrations of inhibitors however best fit was obtained by Langmuir isotherms which is given by following formula.

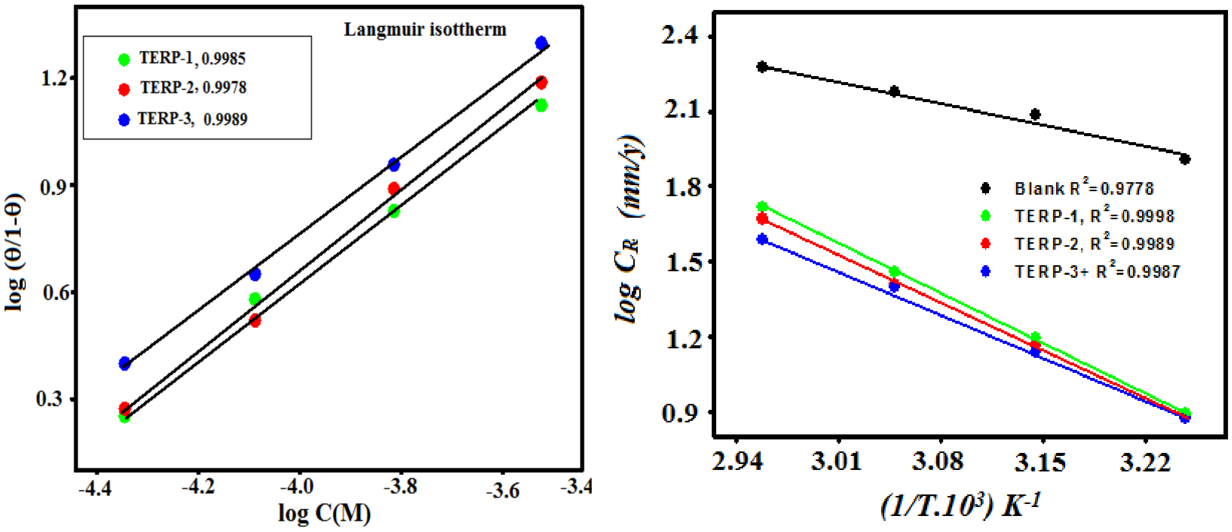
$$\frac{C_{(\mathrm{inh})}}{\theta} = \frac{1}{K_{(\mathrm{ads})}} + C_{(\mathrm{inh})} \tag{4}$$

where K_{ads} is the equilibrium constant of the adsorption–desorption process, θ is the degree of surface coverage and C_{inh} is molar concentration of polymers in the bulk solution. The values of regression coefficient are close to unity (R^2 = 0.9985 for the compound TERP-1, R^2 = 0.9978 for TERP-2 and R^2 = 0.9989 for TERP-3) which confirm the validity of this approach. Deviation of slope from unity (for ideal Langmuir isotherm) can be attributed to the molecular interaction among the adsorbed polymers species, a factor which was not taken into consideration during the derivation of the Langmuir equation [42]. Langmuir isotherm assumes that:

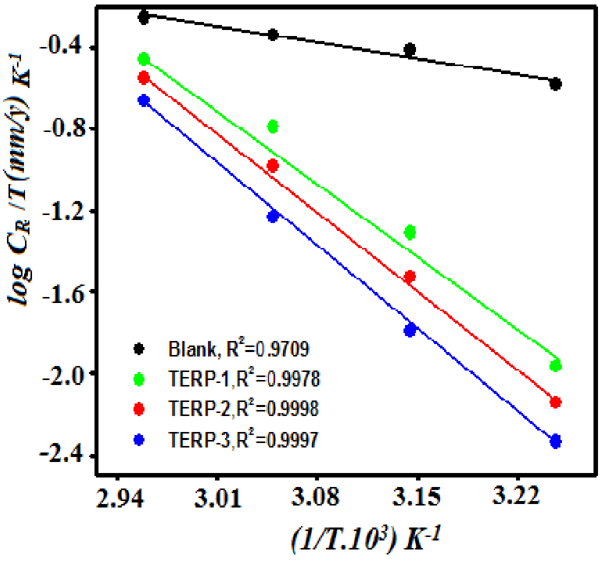
(i) The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate.

(ii) $\Delta G^o_{\mathrm{ads}}$ is the same for all sites and it is independent of h.

(iii) The adsorbates do not interact with one another, i.e. there is no effect of lateral interaction of the adsorbates on ΔG^o_{ads} [43].



(a) (b)



(c)

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

Gibbs free energy of adsorption ΔG^o_{ads} calculated from the equation:

$$\Delta G^{o}_{\mathrm{ads}} = -RT\ln(55.5K_{\mathrm{ads}}) \quad (5)$$

where R is the universal gas constant, T the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution [44]. Gibbs free energy were calculated and given in table 2. Generally, the ΔG^o_{ads} values of -20 *kJ mol*$^{-1}$ or less negative are associated with an electrostatic interaction between charged molecules and charged metal 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 i.e. chemisorption [45]. In present study, Gibbs free energy is in between -34.78 to -35.91 *KJmol*$^{-1}$, this is attributed to the mixed mode of adsorption.

The dependence of corrosion rate at temperature can be expressed by Arrhenius equation and transition state equation:

$$\log(C_{\mathrm{R}}) = \frac{-E_{\mathrm{a}}}{2.303RT} + \log\lambda \quad (6)$$

$$C_{\mathrm{R}} = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \quad (7)$$

where, E_a apparent activation energy, λ is the pre-exponential factor, ΔH^* is the apparent enthalpy of activation, ΔS^* the apparent entropy of activation, h is Planck's constant and N is the Avogadro number. A linear plot between log (CR) vs. *1/T* and log(*CR/T*) vs. 1/*T* (Figure 2 b-c), with a slope of ($-\Delta H^*/2.303R$) and an intercept of [$\log(R/Nh)$ + ($\Delta S^*/2.303R$)], from which the values of ΔS^* and ΔH^* were calculated and listed in Table 2. From table it is clear that ΔS^* in presence of inhibitor is greater than in absence of inhibitors this shows the spontaneous nature of adsorption [46, 47]. The negative sign of Δ *H** shows that the adsorption of inhibitor is an exothermic process [48].

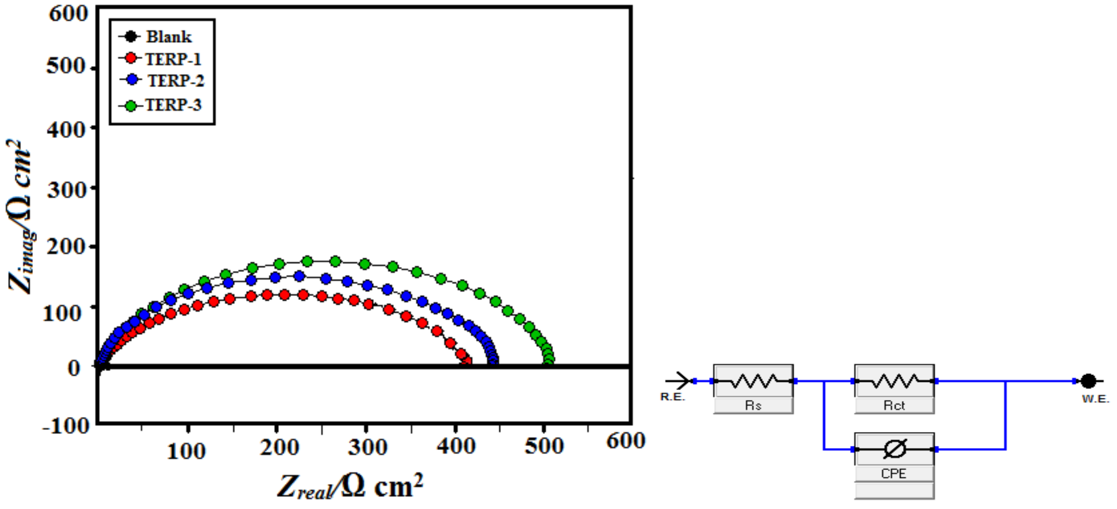
Table 2. Thermodynamic parameters for mild steel in 1M HCl in absence and presence of optimum concentration of investigate polymers.

Inhibitor	*E_a (kJ mol^{-1})*	*ΔH (kJ mol^{-1})*	*ΔS (J K^{-1} mol^{-1})*	*ΔG(kJ mol^{-1})*
Blank	28.48	26.04	-148.9	………
TERP-1	54.61	106.15	106.47	-34.78
TERP-2	52.77	113.89	134.81	-35.22
TERP-3	48.04	117.70	137.88	-35.91

3.2 Electrochemical measurements

3.2.1. Electrochemical Impedance Spectroscopy

The impedance measurements of mild steel coupons were carried out after immersion of mild steel coupons in 1 M HCl solutions for 30 minutes in absence and presence of 50 ppm concentration of polymers. Figure 3(a) shows typical Nyquist plot for mild steel in 1 M HCl in the absence and presence of studied polymers at 50 ppm concentration. The Nyquist plot 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 [49]. The impedance parameters such as *Rct*, *Rs*, Y^0, *n* and C_{dl} calculated from Nyquist plot using equivalent circuit [3 (c)] are given in table.3. From Nyquist plot it is clear that impedance increases with increasing concentration which shows the effectiveness of inhibitors [50].



(a) (b)

(b)

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

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 419.34/ Ω $cm^{2,}$ 441.58/ $\Omega\ cm^2$ and 488.41/ $\Omega\ cm^2$ for TERP-1, TERP-2 and TERP-3 respectively at 50 ppm concentration. The value of C_{dl} in presence of inhibitors is lower than in absence of inhibitor. The decrease in capacitance (C_{dl}) on addition of inhibitor may be due to increase in local dielectric constant and/or may be due to increase in the thickness of the double layer, showing that investigated polymers inhibit mild steel corrosion by adsorbing at the metal/acid interface [51].

The amplitudes of *CPE* were calculated by using following equation:

$$Z_{\mathrm{CPE}} = Q^{-1}(j\omega)^{-n} \qquad (8)$$

where, Y^0 is magnitude of *CPE* and j is an imaginary constant. The value of n (phase shift) gives information about degree of inhomogeneities.

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} ($\Omega\ cm^2$)	*n*	Y_0 ($\mu F\ cm^{-2}$)	C_{dl} ($\mu F cm^{-2}$)	θ	$\eta\%$
Blank	0.0	1.12	11.8	0.827	249.8	106.21	….	….
TERP-1	50	0.86	419.34	0.857	14.13	6.36	0.9708	97.08
TERP-2	50	0.619	441.581	0.769	43.54	12.33	0.9722	97.22
TERP-3	50	0.987	488.413	0.839	62.7	25.65	0.9749	97.49

3.2.2 Linear Polarization resistance study

The linear polarization resistance values of mild steel in 1 N HCl at optimum concentration of 50 ppm for TERP-1–TERP-3 are given in Table 4. The Rp values of different polymers at 50 ppm concentration are 391.7 (TERP-1), 501.9 (TERP-2) and 688.9 $\Omega\ cm^2$ (TERP-3) respectively. The increase in the R_p value further suggests that effectiveness of polymer even at 50ppm only. All the polymers are effective inhibitors at 50 ppm and they inhibit corrosion by blocking the active sites of mild steel.

3.2.3. Potentiodynamic polarization measurements

Electrochemical corrosion kinetics parameters, i.e. corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_a, β_c) and corrosion current density (I_{corr}) obtained from the extrapolation of the polarization curves, are given in Table 4. From table, it is found that Icorr values decreased considerably in presence of inhibitor and decreased with increasing inhibitor concentration. The maximum decrease in I_{corr} was obtained at 50 ppm concentration.

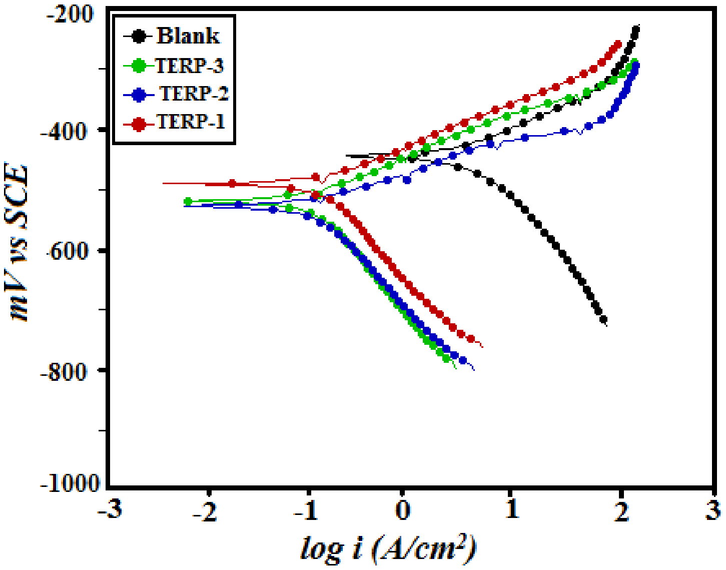


Figure 4. Tafel polarization curves for corrosion of mild steel in 1 M HCl in the absence and presence of different concentrations of polymers.

From the Figure 4 , it is clear that both the cathodic and anodic reactions are inhibited and the inhibition efficiency increased as the inhibitor concentration increased in 1M HCl , but the cathode is more polarized ($\beta_c > \beta_a$). From the Table 4, it is clear that there was no definite trend in the shift of Ecorr values, in the presence of various concentrations of polymers in 1 M HCl solution. This result indicated that polymers can be classified as mixed type of inhibitor which predominantly showed cathodic behavior in 1 M HCl [52].

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

Tafel data								***Linear Polarization data***		
Inhibitor	*Conc ppm*	I_{corr} (µA/cm^2)	E_{corr} (mV/SCE)	β_a (mV/dec)	β_c (mV/dec)	θ	$\eta\%$	*Rp*	θ	$\eta\%$
Blank	0.0	1150	-495	70.5	114.6	….	…..	12.3	….	….
TERP-1	50	38.8	-490	71.8	214.7	0.9662	96.62	391.7	0.9453	96.85
TERP-2	50	28.4	-520	66.5	198.7	0.9753	97.53	501.9	0.9488	97.54
TERP-3	50	25.9	-528	52.3	164.6	0.9774	97.74	688.9	0.9552	98.21

4. MECHANISM OF INHIBITION

The adsorption mechanism is influenced by nature, charge on mild steel surface and chemical structure of inhibitors. Since it is well known that the mild steel surface bears positive charge in acid solution [53], so it is difficult for the protonated polymer to approach the positively charged mild steel surface (H_3O^+/metal interface) due to the electrostatic repulsion.

The terpolymers can adsorb on mild steel/ acid solution interface by:

(i) electrostatic interaction of protonated polymers with previously adsorbed chloride ions (physisorption)

(ii) donor–acceptor interactions between the π-electrons of aromatic ring and vacant d orbital of surface iron atoms (chemisorption)

(iii) interaction between d-electrons of surface atoms to the vacant orbitals of the inhibitor molecules (retro-donation)

In aqueous HCl solution, terpolymer molecules may adsorb through protonated heteroatom's (N) and through Cl^- which is previously adsorbed on mild steel surface. Initially, the protonated form of polymers in acid medium start competing with H^+ ions for electron on mild steel surface. However after release of hydrogen gas (H_2), the cationic form of the polymers return to the neutral form and adsorption occur between lone pair of neutral polymers and d-orbital of surface iron atoms (chemisorption). Due to presence of extra charge, the electrons from the d-orbitals of iron might be transfer to the vacant π- (antibonding) orbitals of the polymer molecules and hence enhances the adsorption of polymers. The weight loss and electrochemical data reveal that inhibition efficiencies for all three polymers are in order:

TERP-3 > TERP-2 > 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 $-NH_2$ and –COOH groups.TERP-3 shows even better inhibition performance because it is adsorbed strongly by $-NH_2$ and SO_3H groups.

The schematic illustration of different modes of adsorption of polymers on metal/acid interface is shown in Figure 5.

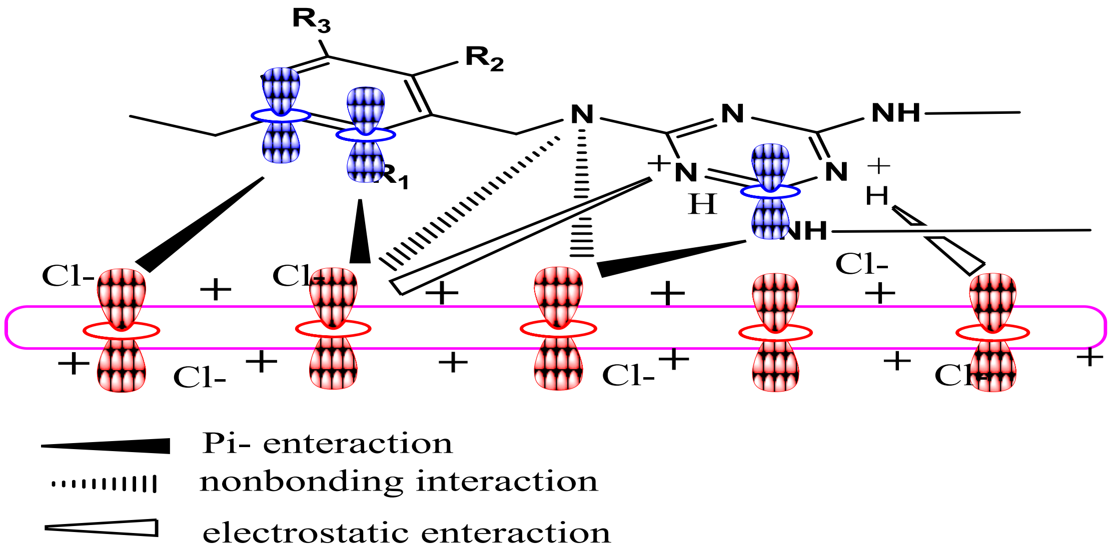


Figure 5. The schematic illustration of different modes of adsorption by polymers on mild surface in 1M HCl solution.

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. Tafel polarization measurements show these polymers are mixed-type, predominantly cathodic types inhibitors.
3. The inhibiting efficiencies obtained by polarization, EIS 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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