

Electrochemical and Thermodynamic Investigation of Some Soluble Terpolymers as effective corrosion inhibitors for Mild Steel in 1M hydrochloric acid solution

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Three Terpolymers derived from resorcinol (R) and formaldehyde (F) and diaminoethane (TER-1), urea (TER-2) and thiourea (TER-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 and weight loss methods. The values of activation energy (E_a) various thermodynamic parameters were calculated to describe the mechanism of adsorption. The inhibition efficiency of the synthesized inhibitors followed the order TER-3 > TER-2 > TER-1. Among the studied terpolymers, TER-3 exhibited the best inhibition efficiency (95% at 50 ppm). Potentiodynamic polarizations studies suggest that all terpolymers are mixed type inhibitors.

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

1. INTRODUCTION

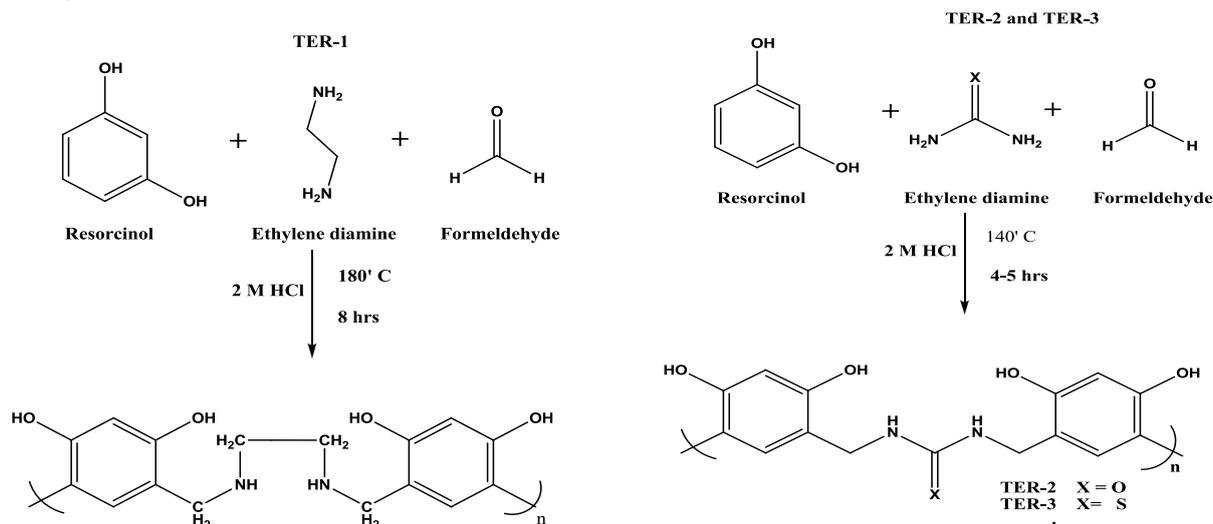
The investigation of the inhibition of corrosion of steel is a subject of high theoretical as well as practical interest. Mineral acids particularly hydrochloric acid are frequently used in industrial processes during acid cleaning, acid pickling, acid descaling, and oil well acidizing [1–3]. A large number of polymers have been used as corrosion inhibition for mild steel [4-16], aluminum [17-23], iron [24-34] copper [35-37] and other metals [38, 39]. However most of the polymers have limited application due to their low solubility in acidic solutions. In present study we have synthesized three terpolymers 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 $-\text{NH}-\text{CO}(\text{S})-\text{NH}-$ group, electronegative oxygen/ Sulphur and aromatic ring as active centers and (c) have high solubility in acidic media. Terpolymers find very useful applications as adhesives, high temperature flame resistant fibres, materials, semiconductors, catalysts, and ion-exchange resins [40-44]. In our present work, we have synthesized Terpolymers of resorcinol, formaldehyde with Ethylene diamine, Urea and Thiourea by polycondensation technique. Previously, some work has been done on Terpolymers as corrosion inhibitors for mild steel in acidic as well as in neutral media [45-46].

2. EXPERIMENTAL

2.1. Inhibitors synthesis

The TER-1 resin was synthesized by the polycondensation of resorcinol and ethylene diamine with formaldehyde in 1:1:2 mole ratio in presence of 2M HCl catalyst at $180 \pm 2^\circ\text{C}$ in an oil bath for 8 h. The separated product was then cooled, poured into crushed ice with constant stirring and left overnight. The brick red colored resin obtained was separated and washed with warm water, ethanol, ether and air dried [47-49]. Where as TER-2 and TER-3 were synthesized by polycondensation reaction of Resorcinol, formaldehyde and Urea (for TER-2) and Thiourea (for TER-3) using 2M H_2SO_4 as the reaction medium and refluxed with occasional shaking at $140 \pm 2^\circ\text{C}$ for 4 h. The reaction mixture was then cooled, poured into crushed ice with constant stirring and left [50-57]. The synthetic scheme is given in Scheme 1.



Scheme 1. Synthetic scheme of TER-1, TER-2 and TER-3.

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 carried out by standard method as described earlier [58,59]. The inhibition efficiency ($\eta\%$) and surface coverage (θ) were calculated by using the 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 terpolymers 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 weight loss measurements were carried out by standard method as described earlier [58,59].

3. RESULTS AND DISCUSSIONS

3.1 Weight loss studies

3.1.1 Effect of inhibitor concentration

The values of percentage inhibition efficiency ($\eta\%$) and corrosion rate (C_R) obtained from weight loss method at different concentrations of each Terpolymer at 35⁰C are given in Table 1. It has been found that inhibition efficiency of all of these terpolymers increases with increase in

concentration. The maximum inhibition efficiency for each compound was obtained at 50 ppm and further increase in concentration did not cause any appreciable change in the inhibition performance. As the concentration of the terpolymers increases, corrosion rate values decreases and inhibition efficiency increases. The variation of inhibition efficiency with concentrations is shown in Figure 1(a).

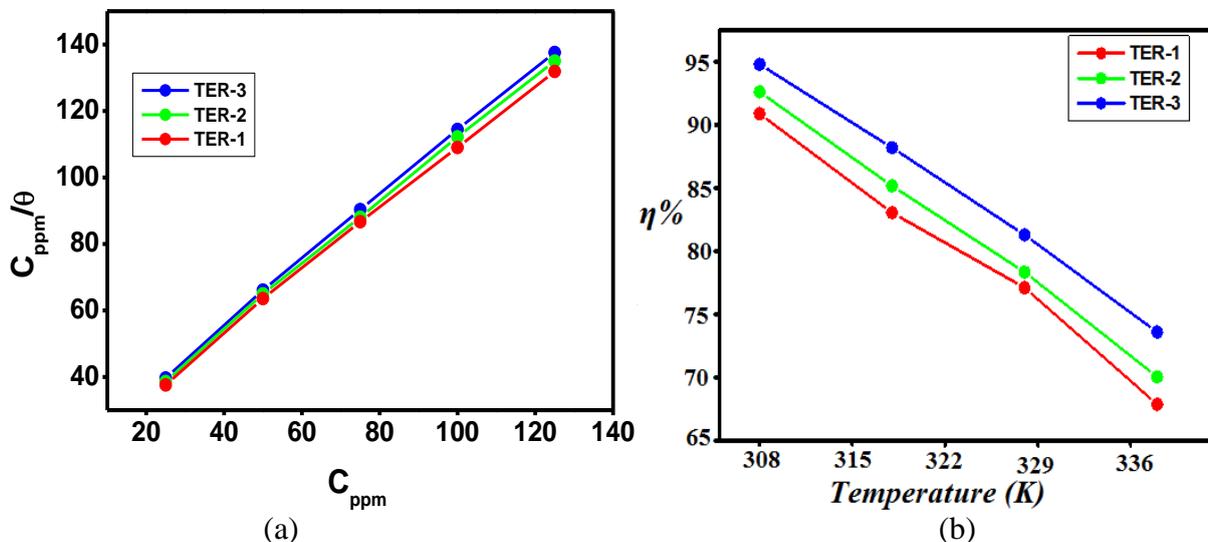


Figure 1. (a) Inhibition efficiency of terpolymers at different concentration (b) Inhibition efficiency of terpolymers at different temperature

3.1.2. Effect of temperature

Table1. 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 terpolymers 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
TER-1	10	31.53	0.6304	63.04
	20	20.77	0.7565	75.65
	30	14.47	0.8304	83.04
	40	10.75	0.8739	87.39
	50	7.79	0.9086	90.86
TER-2	10	30.05	0.6478	64.78
	20	19.66	0.7695	76.95
	30	12.61	0.8521	85.21
	40	9.27	0.8913	89.13
	50	6.30	0.9260	92.60
TER-3	10	28.56	0.6652	66.52
	20	18.18	0.7869	78.69
	30	11.50	0.8652	86.52
	40	7.04	0.9173	91.73
	50	4.45	0.9478	94.78

Weight loss measurements were taken at various temperatures (308–338 K) in the absence and presence of terpolymers (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 solution temperature from 308 to 338 K (Figure 1(b)). The decrease in inhibition efficiencies might be due the weakening of adsorbed inhibitor film on the mild steel surface [60].

3.1.3 Thermodynamic parameters and adsorption isotherm

The adsorption isotherm experiments were performed to have more insights into the mechanism of corrosion inhibition, since it describes the molecular interaction of the inhibitors molecules with the active sites on the mild steel surface [61]. Various isotherms were also tested to show the mechanism of adsorption, however Langmuir isotherm found to be best fitted. The Langmuir isotherm is given by following formula:

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

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 terpolymers in the bulk solution. Though the Langmuir adsorption isotherm is linear [Figure 2 (a), correlation > 0.9], deviation of slope from unity (for ideal Langmuir isotherm) can be attributed to the molecular interaction among the adsorbed terpolymers species, a factor which was not taken into consideration during the derivation of the Langmuir equation [62]. Langmuir isotherm assumes that:

- (i) The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate.
- (ii) ΔG°_{ads} is the same for all sites and it is independent of θ .
- (iii) The adsorbates do not interact with one another, i.e. there is no effect of lateral interaction of the adsorbates on ΔG°_{ads} [63].

To evaluate the adsorption and thermodynamic parameters of corrosion processes of mild steel in acidic media, weight loss measurements were carried out in the temperature range 308–338 K in absence and presence of terpolymers in 1M HCl, after 3 h of immersion time. The apparent activation energy (E_a) for the corrosion process of mild steel was calculated from Arrhenius type plot using the following equation:

$$\log(C_R) = \frac{-E_a}{2.303RT} + \log \lambda \quad (5)$$

where C_R is the corrosion rate (obtained from weight loss measurements), R is the universal gas constant, T is the absolute temperature and λ is Arrhenius pre-exponential constant. Arrhenius plots (a plot of $\log C_R$ vs. $1/T$) are given in Figure 2(b) from which value of E_a calculated and given in table2. . The data shows that thermodynamic activation functions (E_a) of the corrosion in mild steel in 1 N HCl solution in the presence of the terpolymers is higher than those in free acid solution indicating that all the terpolymers lowers the inhibition efficiency at higher temperature [64-66].

An alternative formulation of Arrhenius equation is [67].

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{H_a}{RT}\right) \tag{6}$$

where, h is Plank’s constant, N is Avogadro’s Number, ΔS_a the entropy of activation, and ΔH_a the enthalpy of activation. A plot of $\log C_R/T$ versus $1/T$ gave a straight line (Figure. 2c) with a slope of $\Delta H_a/2.303 R$ and an intercept of $\log R/Nh + \Delta S_a/2.303 R$, from which the values of ΔS_a and ΔH_a were calculated and listed in Table 2. In all the cases, the positive signs of enthalpies (ΔH_a) reflect the endothermic nature of dissolution process. The shift towards positive value of entropies (ΔS_a) imply 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.

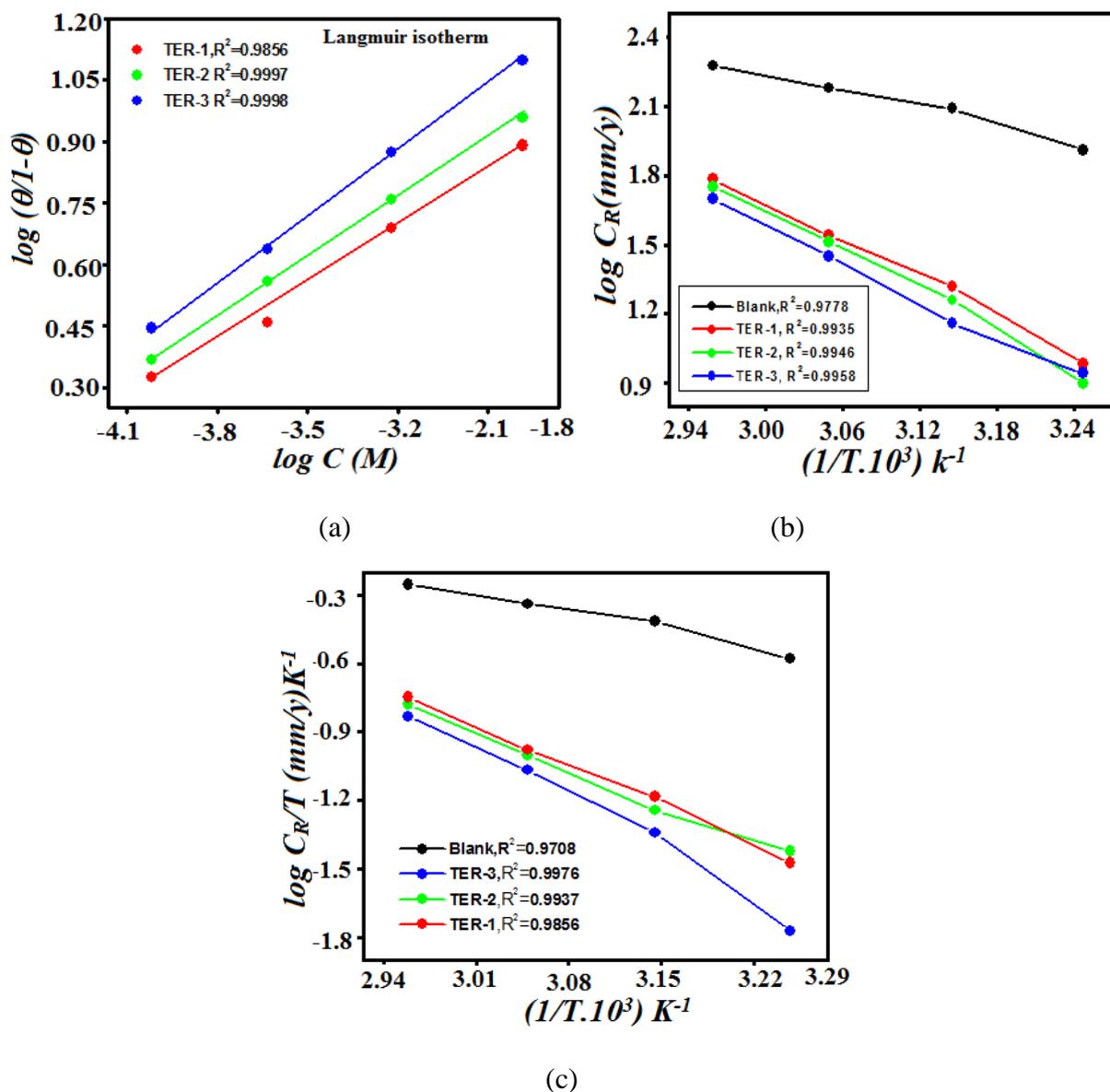


Figure 2.(a-c) (a) Langmuir adsorption isotherm (b) Arrhenius plot of $\log C_R$ Vs $1/T$ (c) Arrhenius plot of $\log C_R/T$ Vs $1/T$

The value 55.5 in this case is the concentration (M) of water in solution [68]. The negative values of ΔG°_{ads} ensure the spontaneity of adsorption process and stability of the adsorbed layer on the mild steel surface. Generally, the values of around -20 kJ mol^{-1} or lower are consistent with physisorption, while those around -40 kJ mol^{-1} or higher involve chemisorptions [69]. In present case value of ΔG°_{ads} are around -36 kJ mol^{-1} this shows that terpolymers have strong adsorption efficiency on mild steel surface in 1M HCl solution.

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

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
TER-1	43.19	43.22	-139.2	-35.26
TER-2	50.00	47.58	-127.5	-35.85
TER-3	56.25	61.98	-119.3	-36.11

3.2 Electrochemical measurements

3.2.1 Electrochemical Impedance Spectroscopy

Electrochemical impedance measurements were carried over the frequency range from 100 to 0.01 Hz at open circuit potential. The simple equivalent circuit for studies has shown in Figure 3(c), where R_s represents the solution resistance, R_{ct} the charge transfer resistance and C_{dl} the double layer capacitance. Nyquist and Bode plots of mild steel at optimum concentrations of terpolymers in 1M HCl solution are given in Figure 3 (a) and (b), respectively. Inhibition efficiency can be calculated from Nyquist plot as follows; [70].

$$\eta\% = \frac{R_{ct}^i - R_{ct}^0}{R_{ct}^i} \times 100 \tag{7}$$

where, R_{ct}^i and R_{ct}^0 are the charge transfer resistance of mild steel with and without terpolymers molecules, respectively. Inhibition efficiencies and other calculated impedance parameters are given in Table 3. It is clear from Table, the R_{ct}^i values increased with increasing the concentration of the terpolymers indicating a charge– transfer process mainly controlling the corrosion of steel. The deviations of perfect circular shape are often known as frequency dispersion of interfacial impedance and are due to the inhomogeneity the metal surface arising from surface roughness or interfacial phenomena [71–73].

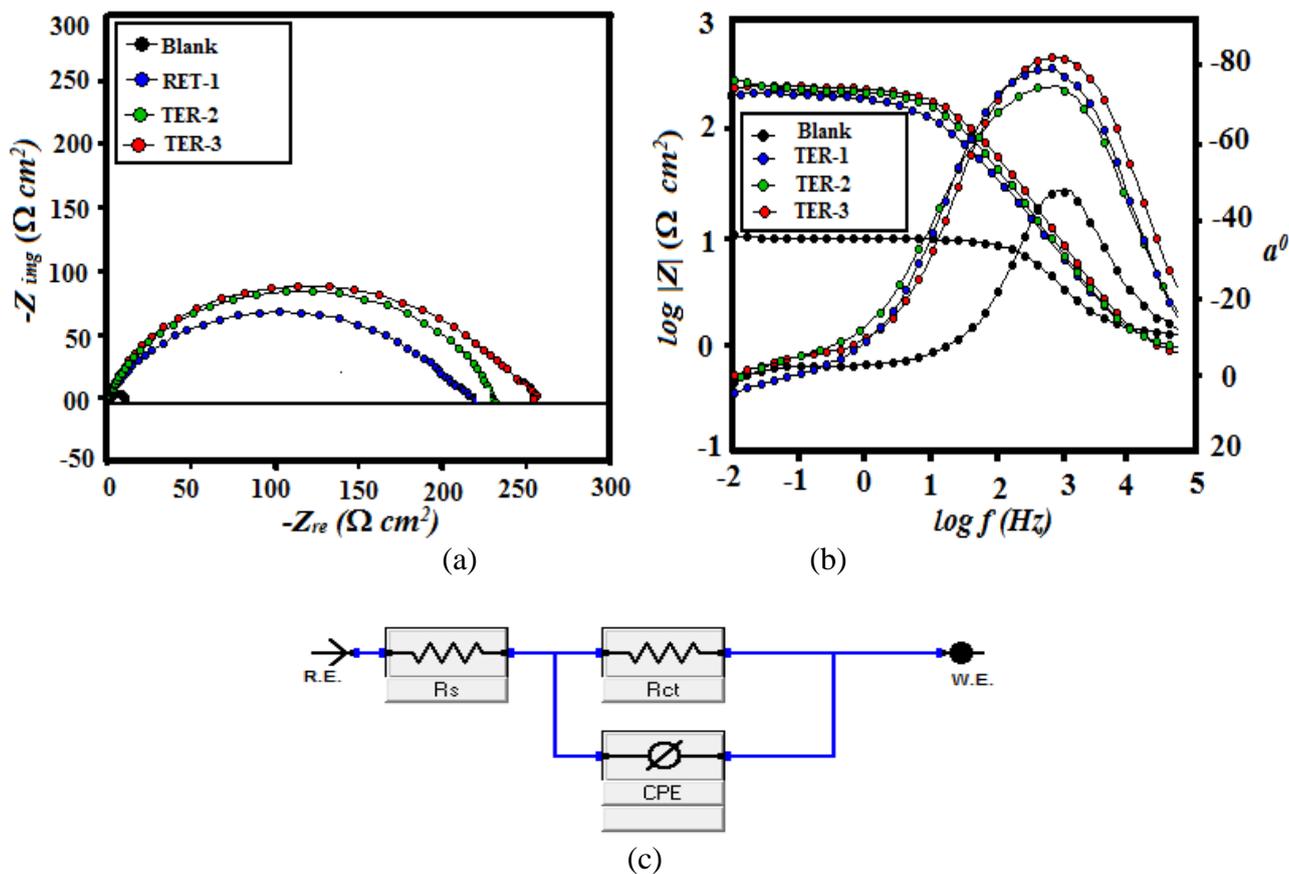


Figure 3. (a) Nyquist plot in absence and presence of optimum concentrations of terpolymers (b) Bode plot in absence and presence of optimum concentrations of terpolymers (c) Equivalent circuit used to fit the data

The Nyquist plots show a depressed capacitive loop shifted along the real impedance (Z_{re} axis) axis in the high frequency (HF) range and an inductive loop in the lower frequency (LF) range (in Bode plot). The HF capacitive loop can be attributed to the charge transfer reaction and time constant of the electric double layer and to the surface non-homogeneity of structural or interfacial origin, such as those found in adsorption processes [74].

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

Inhibitor	Conc. (ppm)	R _s (Ω)	R _{ct} (Ω cm ²)	n	Y ₀ (μF cm ⁻²)	C _{dl} (μF cm ⁻²)	θ	η%
Blank	0.0	1.12	11.8	0.827	249.8	106.21
TER-1	50	0.824	205.0	0.852	180.7	21.74	0.9400	94.00
TER-2	50	0.875	226.7	0.840	100.3	20.39	0.9457	94.57
TER-3	50	0.724	241.3	0.786	71.74	15.33	0.9491	94.91

3.2.2 Polarization resistance study

The polarization resistance values of mild steel in 1 N HCl at optimum concentration (50 ppm) of TER-1–TER-3 are given in Table 4. The R_p values of different terpolymers at 50 ppm concentration are 225.1 (TER-1), 240.7 (TER-2) and 274.9 $\Omega \text{ cm}^2$ (TER-3). The increase in the R_p values suggests that the inhibition efficiency increases with the increase in the terpolymer concentrations. All the terpolymers are effective inhibitors at 50 ppm and they inhibit corrosion by blocking the active sites of metal.

3.2.3. Potentiodynamic polarization measurements

The polarization behavior of mild steel in 1.0 M HCl and 0.5 M H₂SO₄ in the absence and presence of optimum concentration of inhibitors under study is given in Figure 4. Various electrochemical corrosion 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 calculated $\eta\%$ are presented in Table 4.

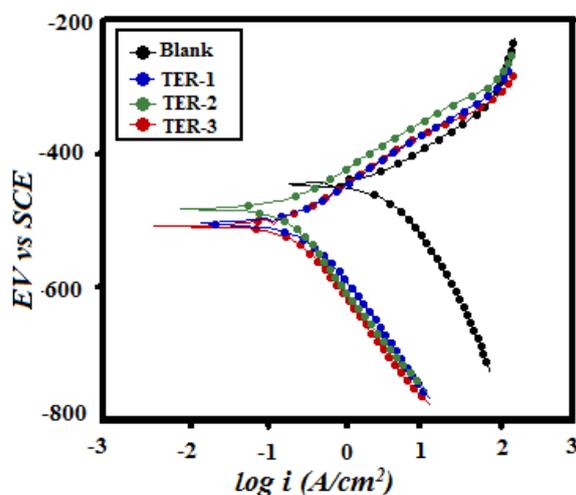


Figure 4. Tafel polarization curves for corrosion of mild steel in 1 M HCl in the absence and presence of optimum concentrations of terpolymers.

It can be seen from the result that maximum reduction of I_{corr} for each inhibitor is obtained at 50 ppm. It is also observed that E_{corr} values did not change significantly in presence of terpolymers suggesting that all the Terpolymers are mixed type inhibitors [75], but as it can also be seen from Table 4, that β_a values are almost same with and without terpolymers whereas the value of β_c is slightly increased in the presence of terpolymers indicating that it is a mixed type predominantly cathodic inhibitors. The slopes of Tafel lines nearly remained the same indicating the inhibitive action

to be the result of adsorption of terpolymers molecules on the mild steel surface and blockage of active sites [47].

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

Tafel data								Linear Polarization data		
Inhibitor	Conc ppm	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV/SC E)	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
TER-1	50	76.10	-504	75.0	115.2	0.9338	93.38	225.1	0.9453	94.53
TER-2	50	69.70	-508	77.60	142.2	0.9393	93.93	240.7	0.9488	94.88
TER-3	50	62.80	-482	69.90	161.8	0.9453	94.53	274.9	0.9552	95.52

4. MECHANISM OF INHIBITION

Corrosion inhibition of mild steel in 1M HCl by terpolymers can be explained on the basis of molecular adsorption on to the mild steel surface. It is generally considered that the first step in the corrosion inhibition of a metal is the adsorption of the terpolymers at metal / solution interface [78].

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

- Electrostatic interaction between the charged molecules and charged metal;
- Interaction of π -electrons with the metal;
- Interaction of unshared pair of electrons in the molecule with the metal; and
- The combination of the all the effects [79-81].

The inhibition efficiency of the inhibitors at a optimum concentration of 50 ppm follows the order:

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

Among the compounds investigated in the present study TER-3 has been found to give the best performance which is attributed to its high dipole moment than other inhibitors. The protonated terpolymers may adsorb on surface through synergistic effect with Cl^- in hydrochloric acid solution [52]. It is well known fact that the inhibitors which not only offer d-electrons but also have unoccupied orbitals, so exhibit a tendency to accept electrons from d-orbital of metal to form stable chelates which are considered as excellent inhibitor (TER-3) [53].

5. CONCLUSIONS

From above study it is concluded that:

1. Terpolymers are good corrosion inhibitors for corrosion of mild steel in 1M HCl solution. The maximum efficiency was found to be 95% at 50 ppm concentration.
2. The adsorption of terpolymers on mild steel surface obeyed the Langmuir isotherm.
3. The Potentiodynamic studies reveal that terpolymers are mixed type inhibitors i.e. it affected both cathodic and anodic reactions predominantly cathodic type.
4. The negative values of ΔG shows that adsorption of inhibitors on mild steel is a spontaneous process.
5. The results obtained from weight loss and electrochemical methods are in good agreement.

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