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Synthesis and Characterization of an Innovative Polymer Surfactant as a Corrosion Inhibitor for Mild Steel in Hydrochloric Acid

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Abstract: The co-polymer surfactant, 2-(4-(Methoxy carbonyl)-2,4-dimethyl hexanamido)-2-methyl propane-1-su lfonic acid (M1) at diffident concentrations (250,500,750 & 1000) ppm, was produced and studied structurally by Fourier-transform infrared (FTIR) spectroscopy, 1H NMR, 13C NMR, and elemental analysis. The corrosio n inhibition efficacy of M1 on mild steel in 1 M HCl solution was assessed via Potentiodynamic polarization. The results indicated a notable reduction in corrosion rates with different concentrations of M1 at 25°C. M1 att ained a corrosion inhibition efficacy of 77.528% at an optimal concentration of 1000 ppm. Tafel polarization i nvestigations indicated that M1 functions as a mixed-type inhibitor, inhibiting both cathodic and anodic process es. The adsorption characteristics of M1 on the mild steel surface were optimally represented by the Langmuir adsorption isotherm, signifying a blend of physical and chemical adsorption mechanisms.

Keywords: anionic surfactant, polarization, corrosion inhibitor and mild steel

1. Introduction

Investigating corrosion inhibition is essential for two primary reasons: it reduces material degradation, thereby averting abrupt failures of pipelines and structures, and it contributes to the conservation of finite metal resources while diminishing water and energy usage linked to metal structure production(Asfour et al. 2023). Mild steel is extensively utilized in the oil and natural gas processing sector owing to its strength, ductility, cost-effectiveness, accessibility, and advantageous mechanical qualities. Hydrochloric acid (HCl) is a commonly utilized mineral acid employed in well acidizing, water treatment, chemical cleaning, and acid pickling(Erramli, Assouag, and Elharfi 2020; El-haddad et al. 2019). Selecting economical materials that can endure hydrochloric acid contact necessitates meticulous planning and thorough engineering. Impurities such as ferric salts, cupric salts, and chlorine, in conjunction with elevated aeration levels, enhance the oxidizing potency of hydrochloric acid, leading to expedited corrosion damage. In the petroleum and gas sector, materials are predominantly subjected to acidic environments rather than neutral or alkaline conditions (Karthikaiselvi and Subhashini 2018). This requires the formulation of efficient techniques to prevent and manage the corrosion of different steel varieties, which represent a substantial proportion of metallic materials subjected to acidic conditions. Synthetic corrosion inhibitors have become one of the most dependable and effective methods for safeguarding mild steel in these environments. Their popularity arises from efficient synthesis methods, configurable characteristics, and cost-effectiveness (Azzam et al. 2018; Joseph and Joseph 2016; Matjaž Finšgar 2014).

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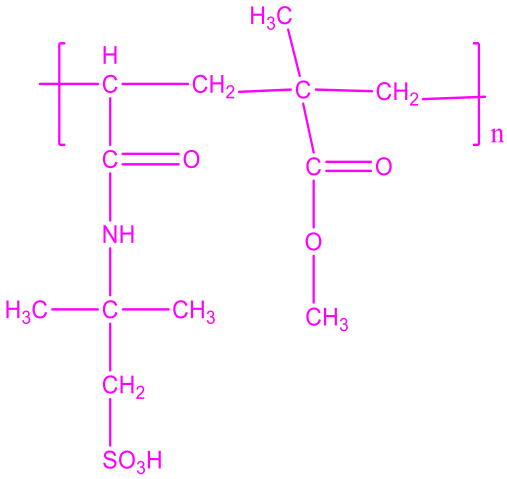
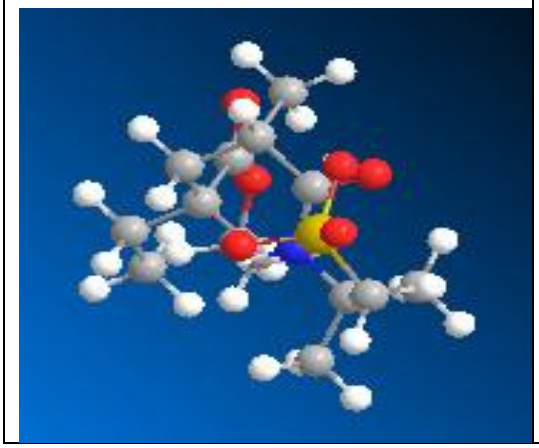
Recently, polymers including heteroatoms like nitrogen (N), oxygen (O), sulfur (S), or phosphorus (P) have attracted significant interest as corrosion inhibitors. Their attractiveness is attributed to their accessibility, economic efficiency, stability, and the existence of numerous attachment sites within the polymer backbone or pendant groups (Hamilton-amachree and Iroha 2019; S. Andreani, M. Znini, J. Paolini, L. Majidi, B. Hammouti, J. Costa 2016; Al-nami 2021). The numerous anchoring sites offered by atoms and functional groups in the polymer chain provide straightforward adhesion and adsorption onto metal surfaces, so efficiently protecting them from corrosive conditions. Furthermore, polymers generally demonstrate reduced toxicity and enhanced adsorption relative to their monomer equivalents (Atta and Al-lohedan 2013; Umoren and Solomon 2014). Polymers are expected to be superior corrosion inhibitors for metal protection compared to their respective low molecular weight organic chemicals or monomers (Chamovska, Cvetkovska, and Grchev 2007; Dwivedi 2021). Polyethyleneglycol bisphenol A epichlorohydrin copolymer (PEG-BEC) effectively inhibits mild steel corrosion in 1 M HCl, achieving 97.6% inhibition efficiency at 10 ppm and 25°C, primarily through adsorption and protective film formation on the steel surface (AlGhamdi, J. M., Haladu, S. A., Mu'azu, N. D., Alqahtani, H. A., Zubair, M., Manzar, M. S., Alkhowildi, F. A., Kuban, R. Z. M., & AlSubaie, N. F. (2024).

This polymer (M1) was prepared for the first time by addition polymerization, due to the presence of a double bond which represents the active group in the monomers. These monomers also contain active atoms such as oxygen, nitrogen, and sulfur, which have lone electron pairs that enhance the interaction between the prepared polymer and the metal surface.

The presence of these active atoms (S, O, N) increases the adhesion capability due to electrostatic interactions between the polymer and the metal surface, leading to effective corrosion inhibition. Therefore, this polymer is considered a highly active inhibitor owing to the lone electron pairs present in sulfur, oxygen, and nitrogen atoms.

This work seeks to evaluate the efficacy of a newly synthesized polymer surfactant (M1) as an innovative corrosion inhibitor for mild steel in a highly corrosive 1 M HCl solution, employing potentiodynamic polarization techniques. The adsorption characteristics of the inhibitor on mild steel surfaces were examined utilizing the Langmuir adsorption isotherm. The synthesized polymer's structure was studied using FTIR spectroscopy, 1H NMR, and 13C NMR, with molecular structures, weights, and formulas presented in Table 1. This study demonstrates the potential utility of the newly synthesized anionic polymer surfactant in reducing corrosive damage inflicted by hydrochloric acid on mild steel, a material commonly utilized in oil field operations.

Table 1. Formula and Chemical Structure of M1.

Chemical structure	Code name	Mol. Formula and Mol. Wt.	IUPAC Name
 	**M1**	$C_{14}H_{27}NO_6S$ 335.49	(2-(4-(Methoxy carbonyl)-2, 4- dimethyl hexanamido)-2-methyl propane-1-sulfonic acid)

2.Experimental Work

2.1. Materials Preparation

Elemental analysis was conducted to ascertain the elemental composition of mild steel, with the percentage composition detailed in Table 2. Mild steel specimens were fabricated as coupons measuring 3.6 × 1.7 × 0.02 cm for electrochemical investigations. The specimens underwent mechanical polishing, edge smoothing with fine-grade emery paper, degreasing with acetone, and air-drying at ambient temperature before testing. A 1 M HCl solution was prepared using double-distilled water, and the inhibitor was evaluated at concentrations between 250 and 1000 ppm.

Table 2. The elemental composition of mild steel

Element	%wt
C	0.3
Mn	1.2
S	0.06
P	0.05
Fe	98.39

2.2. Polymer Synthesis

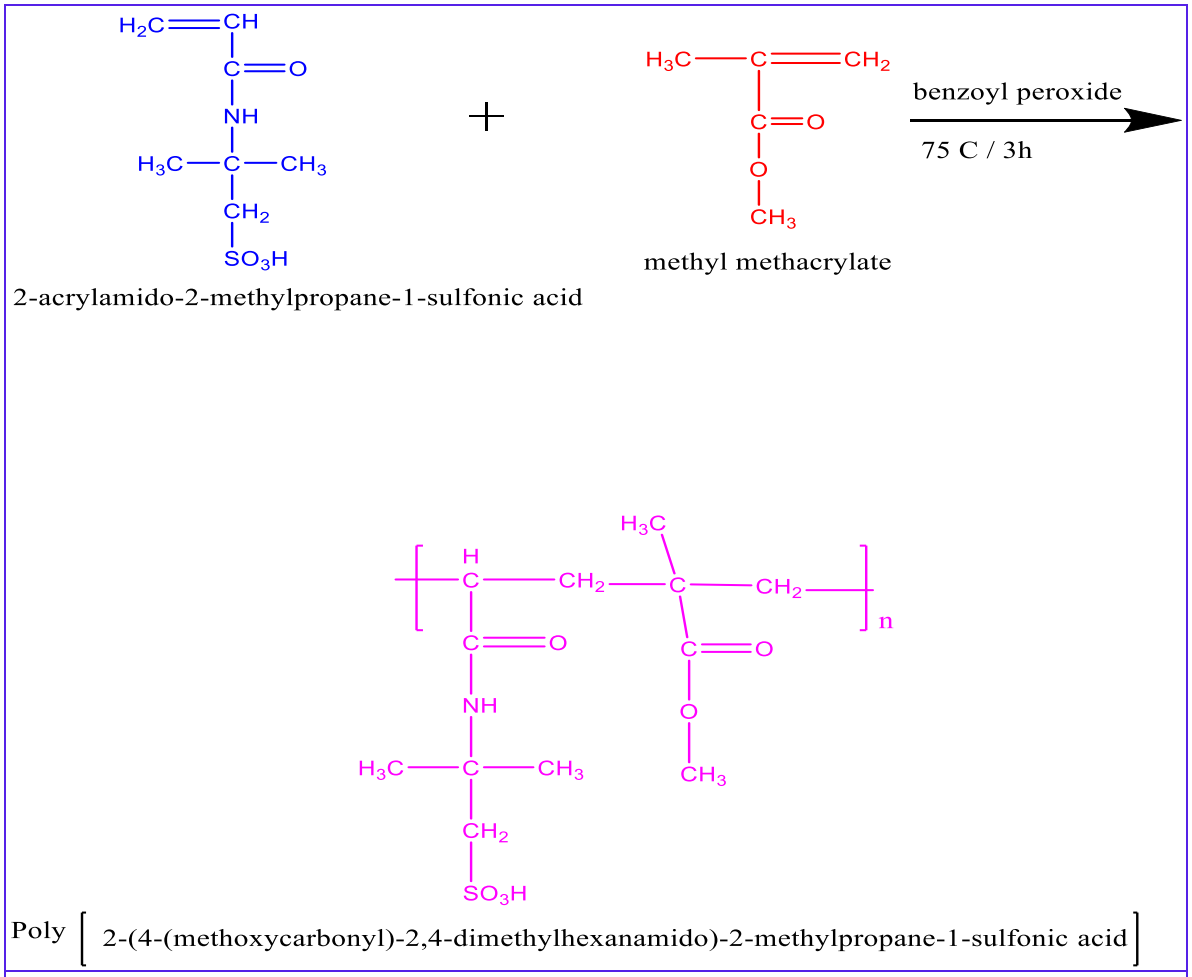
The polymer surfactant was synthesized according to Butler's cyclopolymerization technique. The polymer was synthesized by combining 2g (0.01mol) of acrylamide-2-methyl propane sulfonic acid, dissolved in 10ml of DMF, with 1.28g (0.01mol) of methyl methacrylate (M.W. = 100.12g) in a 250ml round flask. The reaction was conducted at 75°C under a nitrogen atmosphere for 3 hours, by using magnetic stirrer hotplate with the addition of a small quantity of benzoyl peroxide as a polymerization initiator, while continuously stirring for three hours. Subsequently, the product was allowed to cool, followed by the addition of a mixture of acetone and diethyl ether for washing, drying, and removal of excess solvent, yielding an 80% result. As seen in Scheme 1, it delineates the stages of surfactant polymer synthesis.

2.3. Linear Polarization Method

The polymer surfactant acts as a corrosion inhibitor for mild steel in test solutions, and its impact on the corrosion rate can be assessed by many methods, with the Tafel polarization technique being among the most commonly employed. Linear voltammograms (LVs) were recorded at a scan rate of 1 mV/s, covering a potential range from -250 mV (cathodic) to +250 mV (anodic) relative to the open circuit potential (OCP) at 25°C. The studies were conducted in both the absence and presence of different concentrations of zwitterionic polymers in the 1 M HCl solution. To prevent secondary reactions on the electrode surface, dissolved oxygen was removed from the solution before recording the LVs, and a 60-minute conditioning time at OCP was implemented to achieve a quasi-equilibrium state at the electrode/electrolyte interface. Thereafter, icorr was utilized to determine inhibition efficiency and surface coverage (Θ) as follows (Atta and Al-lohedan 2013):

$$IE\% = \Theta \times 100 = \left[1 - \frac{icorr}{i°corr}\right] \times 100 \quad (1)$$

Where; $i°_{corr}$ and i_{corr} represent the corrosion current densities in the absence and presence of the inhibitor, respectively. Analysis of Variance (ANOVA) from Origin Lab 2024 was used to forecast errors for each experiment, which was carried out in triplicates.



Scheme 1. Synthesis route of the investigated (M1).

3. Results and Discussions

3.1. Infrared spectrum of the polymeric surfactant (M1)

The polymer surfactant, (M1), was produced using Butler's cyclopolymerization technique. The polymer was found to be very soluble in deionized water. The produced polymeric surfactant was analyzed using FT-IR spectroscopy, as shown in Fig.1.

The infrared spectra of the polymeric surfactant M1 displayed a broad peak between 3360 and 3280 cm^{-1}, signifying the presence of the (-NH) amide bond, which appeared broad due to hydrogen bonding interactions; peaks corresponding to the -OH group were also detected. The sulfonic group was identified in the range of 3020 to 3470 cm-1, whereas the carbonyl (C=O) group was noted at 1726 cm^{-1}. The $-CH_2$ group displayed symmetric and asymmetric stretching between 2810 and 2960 cm^{-1}. The (C = O) group was detected at (1660) cm^{-1}, the ($-CH_2$) bending vibration was recorded between (2810-2970) cm^{-1}, the (S = O) bands were observed at (1388 cm^{-1}), the amplitude oscillation of (CO) was identified in the range of (1120 cm^{-1}), and the bands at (1050 cm^{-1}) were associated with the polymeric surfactant.

The interaction between M1 (which contains functional groups like -OH, $-NH_2$, -SH, =O, etc.) and the mild steel surface mainly occurs through adsorption. This process forms a protective layer that prevents

corrosion. The mechanism of adsorption can be explained by both physical and chemical interactions.

M1 likely contains atoms like nitrogen (N), oxygen (O), or sulfur (S).These atoms have lone pairs of electrons. Mild steel surfaces (mostly iron) have vacant d-orbitals.

The lone pairs from N, O, or S in M1 coordinate with the vacant orbitals of Fe atoms on the steel surface. This form coordinate covalent bonds (chemisorption) a strong and stable interaction that anchors M1 onto the surface.

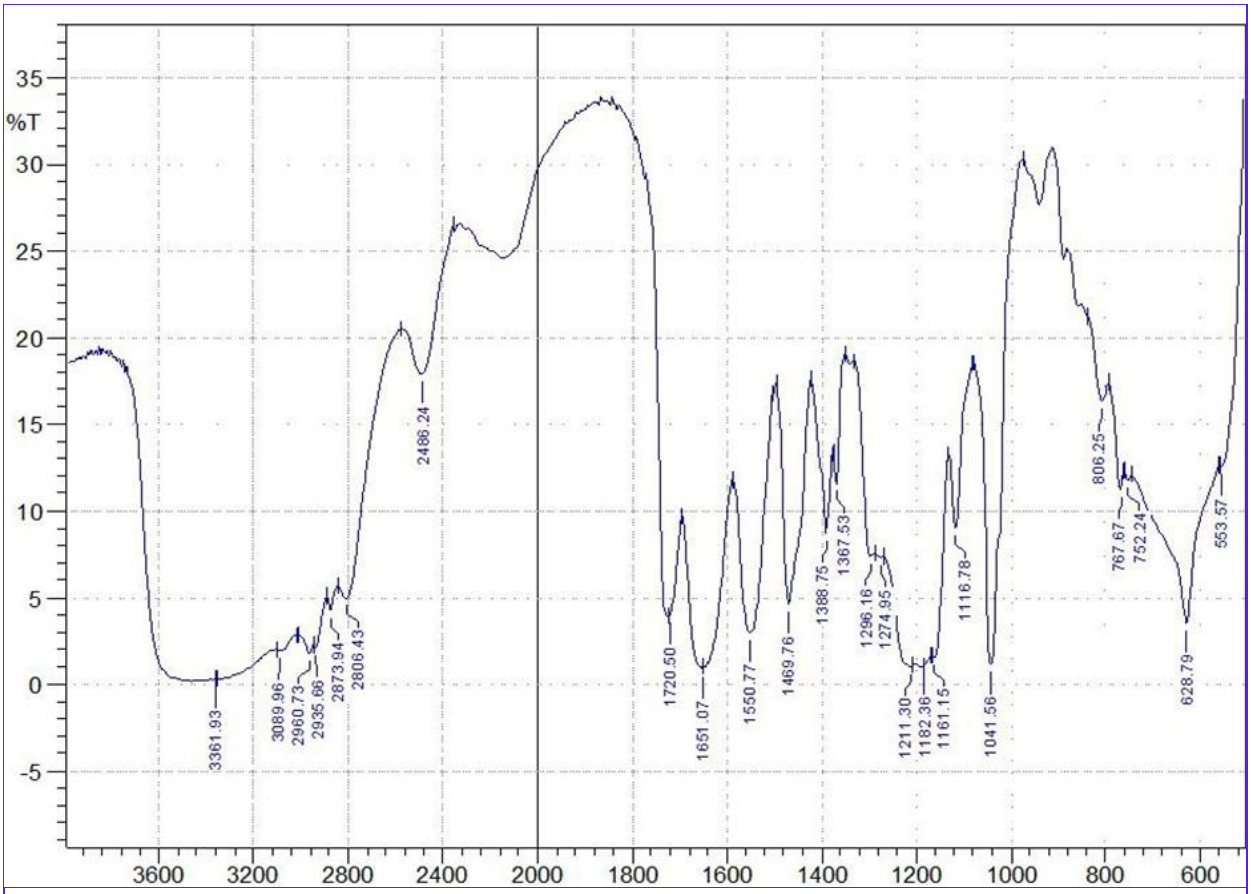


Fig. 1. Infrared spectrum of the polymeric surfactant (M1)

3.2. ^{1}H NMR spectrum of surfactant

The NMR spectrometer for the produced polymer in the diluted solvent DMSO yields two signals at 2.60 and 2.56 ppm, attributed to the protons of DMSO. Spectra exhibited signals at 3.42 ppm corresponding to water protons in the solvent. The polymer spectra exhibit a singlet signal at 8.33 ppm corresponding to OH in -O2S-OH, and at 8.12 ppm indicating a singlet signal for NH in the amide group (HN-C=O)[1].

The HNMR spectra of the synthesized polymer exhibit two singlet signals at 3.00 and 2.91 ppm, corresponding to the protons of the methyl group in the ester linkage (CH3-COO) and the methylene group associated with the sulfonic acid (CH2-SO3H), respectively. The methylene proton at the heart of the polymer's repeating unit exhibited a doublet signal at 2.41 ppm, whereas the protons of the methyl groups displayed singlet signals at 1.32 and 0.81 ppm, as illustrated in Fig. 2. The purity of the polymer

was determined using NMR measurements, which showed clear signals with no undesirable values, indicating the polymer's high purity.

3.3. ^{13}C-NMR carbon magnetic resonance spectra of polymeric surfactant

The HNMR spectra of the synthesized polymer exhibit two signals at 35.86 ppm and 63.76 ppm, corresponding to the methyl group in the ester linkage (CH3-COO) and the methylene group associated with the sulfonic acid (CH2-SO3H), respectively. The methylene group in the central location of the polymer's repeating unit exhibited a signal at 30.86 ppm, whereas the methyl groups displayed signals at 18.66 ppm and 13.05 ppm (Asfour et al. 2023).

The two-tetra carbon atom in the repeating unit exhibited two signals at 51.76 and 34.54 ppm. Additionally, two signals at (30.16, 26.3 ppm) correspond to the two carbon atoms of the repeating unit (CH and CH_2), as illustrated in Fig.3.

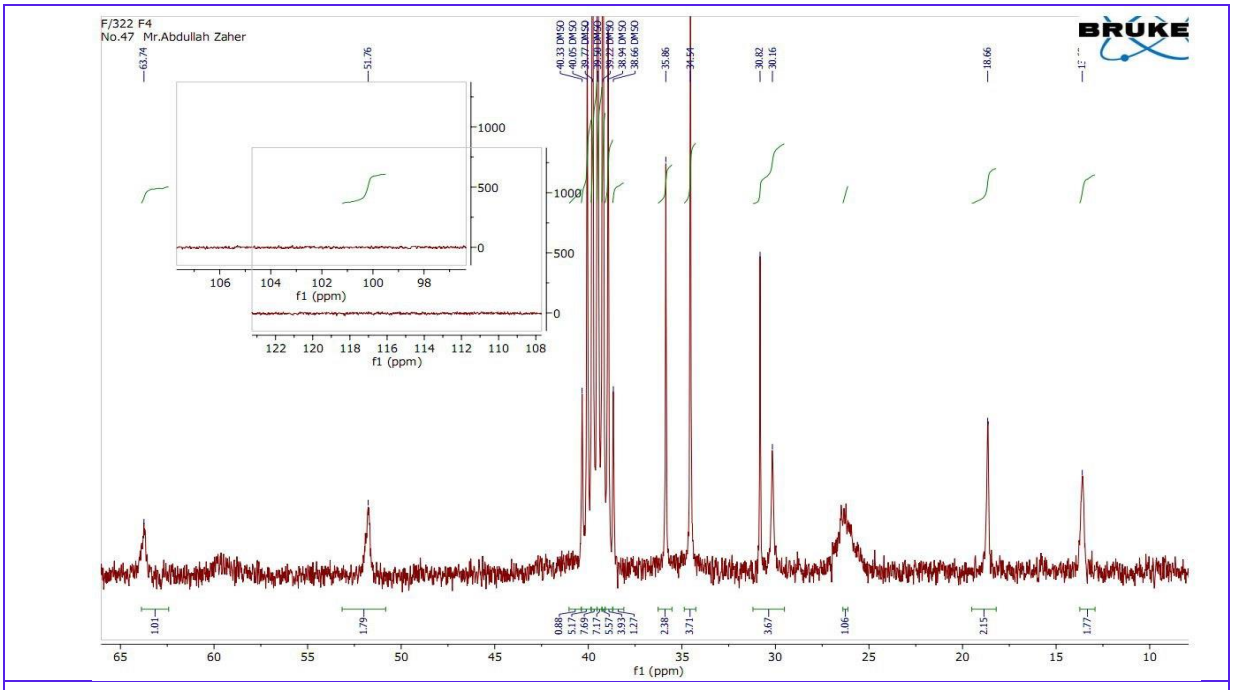


Fig. 2. ^{1}H NMR spectrum of surfactant

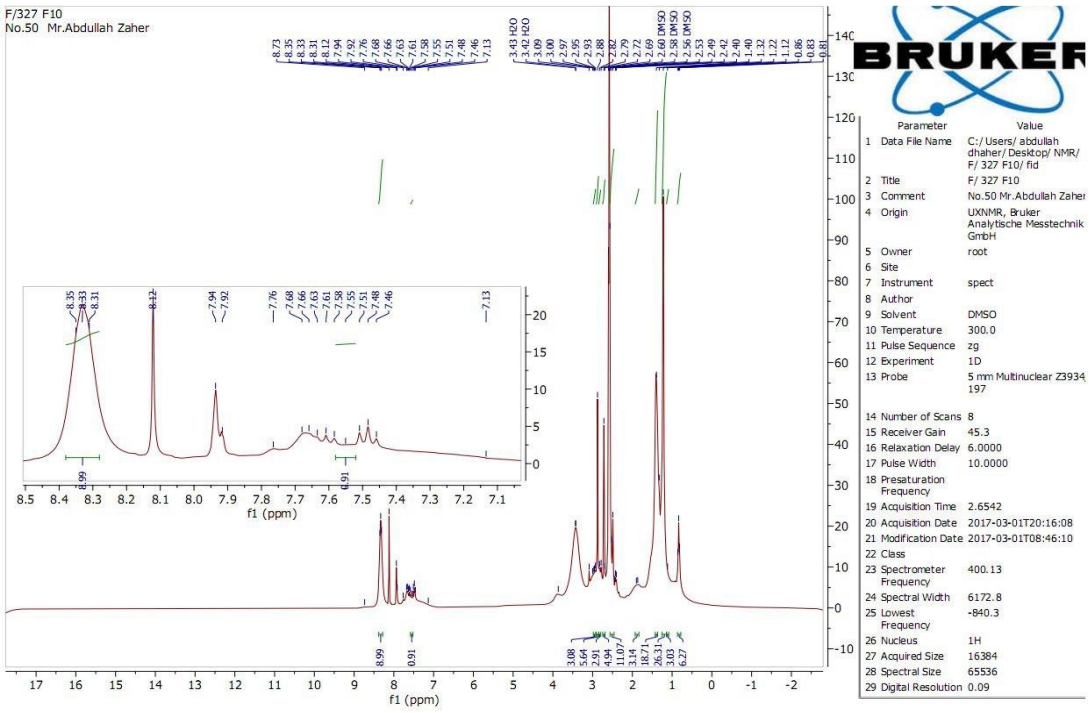


Fig. 3 .^{13}C- NMR carbon spectrum of surfactant (M1)

3.4. Linear Polarization study

The polarization curves for mild steel in 1 M HCl are shown in Fig. 4, which contrasts conditions with and without different inhibitor concentrations at 25°C. Table 3 provides a summary of the primary corrosion characteristics. At the ideal inhibitor dose of 1000 ppm, the inhibition efficiency dramatically rose to 77.528%. By decreasing corrosion current (Icorr), an increase in inhibitor concentration improves inhibition efficiency.

The results of the anodic slope (ba) show a significant decline, suggesting that the polymer prevents mild steel from dissolving anodically. Whether the polymer was present or not had no effect on the cathodic slope (bc) results. By effectively blocking the metal surface's active spots, the inhibitor seems to obstruct the anodic process. The cathodic slope (bc) readings remain unchanged with or without the inhibitor, and the addition of the inhibitor has no discernible effect on the Ecorr data. This suggests that, as shown in Fig. 4, M1 acts as a mixed-type inhibitor in 1 M HCl. The hydrogen evolution reaction is activation-controlled, as seen by the cathodic polarization curves, which show a gradual step. The mechanism of this reaction remains unaffected by the addition of M1(El-monem et al. 2020; Doaa. R. Mohammedali, Hamida. I. Salman, Mohammed. N. Bahjat 2022).

Table 3. Polarization parameters for mild steel in 1 M HCl, both with and without different concentrations of M1.

Solution	Conc. (ppm)	I_{corr} (µA/cm^2)	E_{corr} (mVvs.SCE)	% IE	Θ
blank	0	28.97± 0.03	219.49±0.1	-	-
M1	250	8.37±0.02	228.79±0.4	71.108±0.1	0.7110
	500	7.27±0.01	240.30±0.6	74.905±0.3	0.7490
	750	6.83±0.008	240.66±0.8	76.423±0.4	0.7642
	1000	6.51±0.007	307.08±0.9	77.528±0.6	0.7752

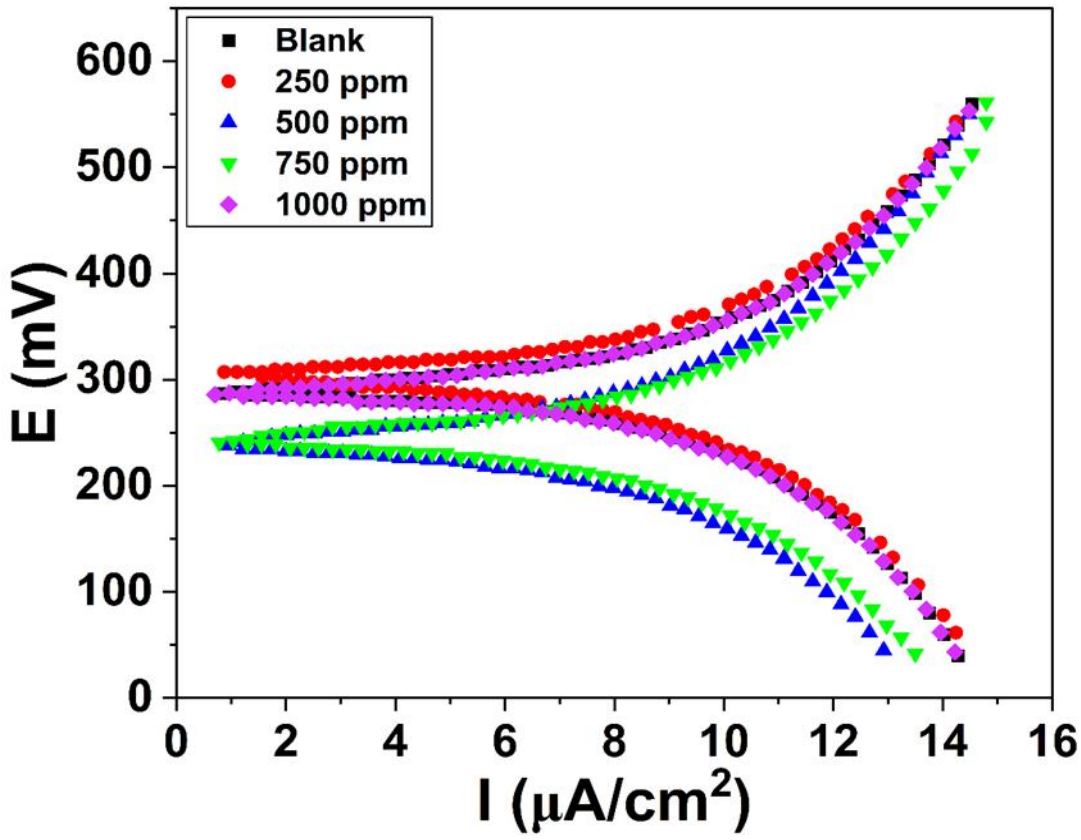


Fig. 4. Tafel curves for mild steel in 1 M HCl with and without altered doses of M1 at 25℃, which explain the relation between potential (E) mV and current density I(µA/cm^2).

3.5. Adsorption Isotherm

The interaction between the inhibitor and the mild steel surface is clarified by the adsorption isotherm. As seen in Eq. (2), we used the Langmuir adsorption isotherm.(Asfour et al. 2023):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (2)$$

In this case, Θ stands for surface coverage, Kads for adsorption equilibrium constant, and C for inhibitor concentration. Through computational approaches, surface coverage values were used to

calculate linear regressions between C/θ and C. The link between C/θ and C is shown in Fig.5. The findings show that, with slopes roughly equal to 1, all linear correlation coefficients (R^2) approach 1.

With an adsorptive equilibrium constant of 0.0247 (L mg^{-1}), this suggests that the inhibitor's adsorption on the mild steel surface follows the Langmuir adsorption isotherm (Basiony et al. 2021). The adsorption mechanism is central to understanding an inhibitor's behavior under different environmental conditions. An inhibitor like M1, which likely relies on chemisorption via heteroatoms (N, O, S), offers greater stability due to stronger interactions with the steel surface. However, elevated temperatures, prolonged exposure, and aggressive media can still challenge its stability. Therefore, understanding and optimizing the adsorption strength and mode is crucial to ensuring long-term and temperature-resilient corrosion inhibition.

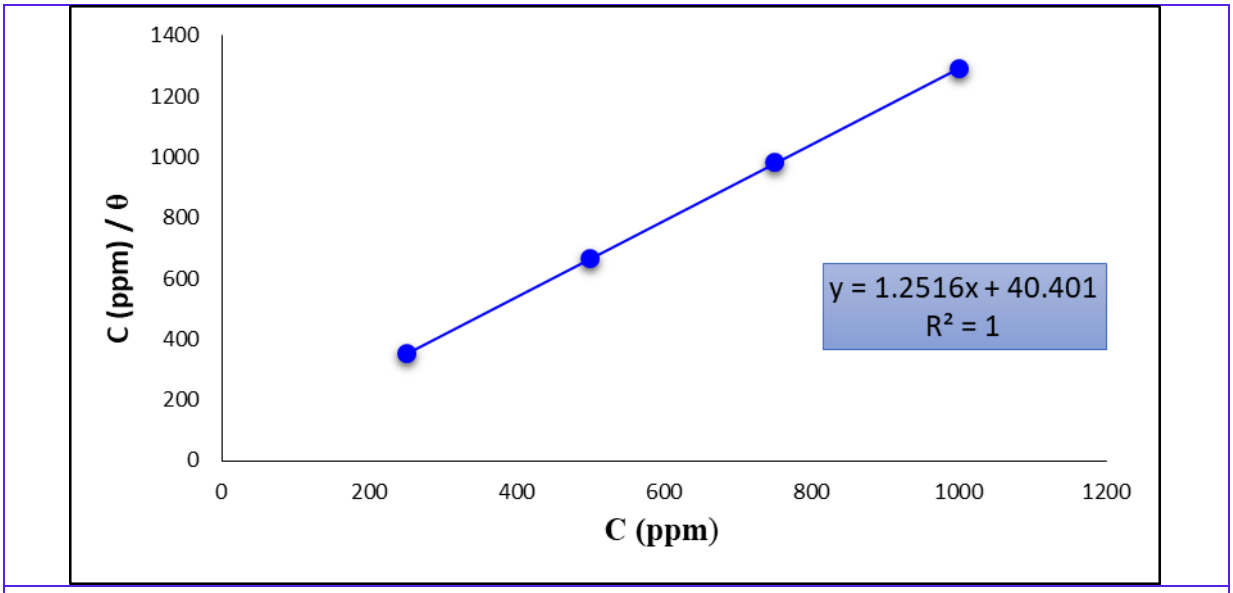


Fig. 5. Langmuir adsorption isotherm model for the adsorption of M1 in 1M HCl on to the mild steel at 25 ℃.

4. Conclusion

At a dosage of 1000 ppm, the polymer surfactant demonstrated a 77.528% inhibitory efficiency for mild steel in 1 M HCl. By adhering to the mild steel surface in 1 M HCl and using Langmuir's adsorption isotherm, it successfully decreased corrosion. The polymer surfactant functions as a mixed-type inhibitor in 1 M HCl, according to electrochemical studies. This work has provided a platform for the development of a novel polymer for the improvement corrosion resistance of mild steel . It is interest to further study the effectiveness of polymer at different pH value, immersion time and temperature.

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Funding: This study received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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