

Corrosion Inhibition Studies of Poly (MPDMA C₁₆ -co-NCA) on Mild Steel in 0.05M H₂SO₄

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ABSTRACT

Copolymers of MPDMAC₁₆ and MPDMAC₁₈ with N-substituted acrylamide were synthesized in DMF solution using AIBN as initiator. Since MPDMA C₁₆ and MPDMA C₁₈ monomer was in the form of an aqueous solution (50 %) and the N-substituted acrylamide are in DMF solution was used for copolymerization. The synthesized copolymer MPDMA C₁₆ and MPDMA C₁₈ with NCA are characterized by ¹H-NMR, ¹³C-NMR, FTIR, and TGA analysis. The corrosion effect of copolymer on the mild steel in 0.05M H₂SO₄ solution was studied by potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) method. The % IE increases with increase in concentration fits the experimental data for the studied compound.

Keywords: Copolymer, Impedance, Inhibition Efficiency.

I. INTRODUCTION

Mild steel is one of the industrially important metals and is inevitable to expose its surface to the different industrial environments while in use. The steel undergoes corrosion to different extent depending on the aggressiveness of the medium or environment. Generally the service life of steel is enhanced by applying various corrosion control measures. Most of the available methods for controlling corrosion are based on modifying either the surface of the metal or local environment when the metal is exposed. In most of the industries like oil, refineries, nuclear power plants, fertilizer and chemical etc. the steel is used as containers, steam generators, liquid carrying pipes and so on. In such cases the corrosion of steel is effectively controlled by the application of suitable inhibitors. Most of the acid corrosion inhibitors are organic compounds, such as those containing N, S, O and aromatic ring. Sulphur and nitrogen containing compounds have been found to be effective corrosion inhibitors. Most of the organic inhibitors act by

adsorption on the metal surface. The adsorption of organic inhibitors at metal/solution interface can markedly change the corrosion resisting properties of metals. The protection of corroding surfaces prevents the waste of both resources and money during the industrial applications and it is vital for the extension of the life time of the equipment and limiting dissolution of toxic metals from components into environment. It has been reported that quaternary ammonium compounds are important as inhibitor additives in hydrochloric acid and sulphuric acids. The effect of concentrations, functional groups and halide ions of quaternary ammonium inhibitors on the corrosion of iron and steel have been studied extensively. The synergistic effect between the organic cations and the halide anions is considered to be an important factor in inhibiting action on metal corrosion [1,2]. As a representative type of these organic inhibitors, quaternary ammonium salts have been demonstrated to be highly cost-effective and used widely in various industrial processing for preventing corrosion of mild steel in acidic medium.

Literature revealed that long chain n -alkyl quaternary ammonium compounds act as good corrosion inhibitors. Meakins has reported that N-alkyl quaternary ammonium compounds inhibit the corrosion of mild steel in acids and the effectiveness of the inhibitor increases regularly with an increase in alkyl chain length. In the present work the inhibition of corrosion of mild steel in 0.05M H₂SO₄ in the presence of MPDMA C₁₆ and MPDMA C₁₈ with NCA has been evaluated at different concentrations of inhibitor using Tafel polarization and electrochemical impedance measurements. The synthesized copolymer MPDMA C₁₆ and MPDMA C₁₈ with NCA are characterized by ¹H-NMR, ¹³C-NMR, FTIR, TGA analysis. The relationship between these properties and the inhibitive efficiency of the corrosion inhibitor are discussed.

II. Experimental

2.1. Materials

2.2. Copolymerization

In a polymerization tube 50ml of DMF sol. consisting 2.0gm (0.016 mol) of N-cyclohexylacrylamide 0.33gm (0.0006 mol) of MPDMA - C₁₆ and MPDMA C₁₈ and 100 mg of AIBN was prepared. The solution was flushed with oxygen free dry nitrogen gas for 30 minutes the inlet and outlet of the polymerisation tube were closed by means of rubber tubing's and pinch cork. The polymerisation tube was then placed in a thermostatic water bath maintained at 60°C. The reaction was then allowed to proceed for 16 hours

2.3. NMR Spectroscopy

The ¹³C- NMR and ¹H- NMR spectra of copolymers were recorded on the JEOL GSX – 400 Bruker DPX 200 spectrometer operating at 400 MHz and 100 MHz respectively in CDCl₃ and DMSO respectively.

2.4. FT-IR Spectroscopy

Fourier transform infrared (FTIR) of monomers were recorded on Bruker IFS 66 FT-IR spectrometer using

Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% orthophosphoric acid solution in water to remove any basic impurities. Then the Acrylonitrile was washed with double distilled water and dried over anhydrous calcium chloride. The acrylonitrile was then distilled in an atmosphere of nitrogen under reduced pressure. The cyclohexanol were distilled before use. Methacrylamidopropyl – N, N – dimethylamine used as a commercial sample (Aldrich Co) is available as an aqueous solution (50% by weight). It was diluted with an equal amount of distilled water and decolorized with activated carbon prior to use. The initiator 2, 2' - azobisisobutyronitrile (AIBN) was recrystallized from methanol and chloroform. Methanol was refluxed along with quick lime (CaO) for 5 hrs and distilled for use. Benzene was dried overnight using anhydrous CaCl₂ and distilled before use. The monomer N-cyclohexylacrylamide (NCA) was prepared by a procedure described in literature [3].

after which the copolymer was precipitated from the solution by adding 0.1M NaI. The precipitated polymer was washed with benzene to remove the unreacted monomer, and the polymer was dried for 24 hours at 60°C under vacuum. The monomer feed was varied in order to prepare copolymers having different mol% of MPDMA C₁₆ and MPDMA C₁₈ with NCA as shown in Table 1 & 2. Copolymerization of MPDMA C₁₆ and MPDMA C₁₈ with N-substituted acrylamides as shown in Fig .1.

KBr pellets. A Perkin – Elmer thermal analyzer was used to study the thermal behavior of polymers.

2.5. TGA analysis

Thermogravimetric analysis (TGA) was carried out using TGA 7 at a heating rate of 20°C /min under nitrogen atmosphere. The amount of sample taken for each run was 5±0.2mg.

2.6. Solubility studies

Solubility of the MPDMAC₁₆ and MPDMA C₁₈ with N-Substituted acrylamides was tested in various polar and non-polar solvents. About 5-10 mg of the copolymer was added to about 2 ml of different solvents in a test tube and kept overnight with the test tube tightly closed. The solubility of the polymers was noted after 24 hr.

2.7. Potentiodynamic polarization (PDP)

The electrode of 1cm² area were cut from the mild steel sheet and one side of the electrode and stem was masked with epoxy resin. The electrode was polished with 400-1200 grit emery papers and degreased with acetone. 100 ml of the test solution was taken in a three electrode polarization cell and the electrode was introduced into the test solution in the polarization cell and allowed to attain a steady potential value for 20 min. A constant potential was applied and the resultant current was measured. The experiments were carried out ± 200 mV from corrosion potential. Polarization measurements were carried out using Electrochemical work station CHI 660 USA.

The potential of the working electrode was measured with respect to SCE and the platinum electrode was used as an auxiliary electrode. Then the applied potentials were plotted against resultant current density. The current density and Tafel slopes (β_a and β_c) values were obtained from the polarization curves by extrapolation of anodic and cathodic curves back to the corrosion potential. The experiments were performed with and without addition of inhibitors at different molar ratio. The inhibition efficiency of these systems was calculated by using the following equation [4].

$$IE\% = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \quad \text{---- (1)}$$

I_{corr} = Corrosion current density in the absence of inhibitor

$I_{corr(i)}$ = Corrosion current density in the presence of inhibitor.

2.8. Electrochemical Impedance Spectroscopy Studies

A well polished mild steel electrode was introduced into 100ml of test solution and allowed to attain a steady potential value. An A.C. signal of amplitude of 10mV was applied and the frequency was varied from 10 MHz to 10 KHz using electrochemical work station CHI 660USA. The real and imaginary parts of the impedance were plotted in the form of Nyquist plots. From the Nyquist plot, the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were calculated.

The charge transfer resistance values were obtained from the plots of Z' vs Z'' . The values of ($R_s + R_{ct}$) correspond to the point where the plots cuts Z' axis at low frequency and R_s corresponds to the point where the plot cuts Z' axis at high frequency. The difference between R_{ct} and R_s values give the charge transfer resistance (R_{ct}) values. The C_{dl} values were obtained from the relationship [5,6]

$$C_{dl} = \frac{1}{2\pi f_{max} \times R_{ct}} \quad \text{----- (2)}$$

Where C_{dl} = double layer capacitance
 R_{ct} = Charge transfer resistance
 f_{max} = frequency at Z'' value maximum.

The inhibition efficiencies were obtained from R_{ct} values as follows [7]

$$IE\% = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100 \quad \text{----- (3)}$$

where R_{ct} = Charge transfer resistance in the absence of inhibitor

$R_{ct(i)}$ = Charge transfer resistance in the presence of inhibitor

III. Results and Discussion

3.1. ¹³C-NMR study

The ¹³C NMR spectrum MPDMA C₁₆ and MPDMA C₁₈ with NCA copolymer is shown in Fig.2. The intense resonances at 29.44 -29.55 ppm is due to the long alkyl chain of MPDMA C₁₆ unit and the resonances at 25.73, 33.44 & 48.06 ppm are due to CH₂ carbon atoms of cyclohexyl group. The peak values confirm the occurrence of copolymerization.

3.2. ¹H-NMR study

The ¹H NMR spectrum showed the peaks at 1.2 and 0.80 ppm are methylene & methyl group. The resonance at 7.40 & 2.18 ppm are assigned to N-H & CH₂ - N in MPDMA-C₁₆ and MPDMA C₁₈ with NCA in Fig.3. The peak at 1.2 - 1.9, 3.84, 5.59-6.28 & 7.27 ppm are due to cyclohexylCH₂, Cyclohexyl methine, Vinyl protons & N-H protons in MPDMA C₁₆ and MPDMA C₁₈ with NCA.

3.3. FT-IR Spectroscopy

The IR spectra of the MPDMA C₁₆ and MPDMA C₁₈ with NCA show a band at 3309-3436 cm⁻¹ corresponding to the ν_s(N-H) stretching vibrations. The cyclohexyl ring in MPDMA C₁₆ with NCA shows bending vibrations band at 1200-1000cm⁻¹. FT-IR spectra of MPDMA C₁₆ and MPDMA C₁₈ with NCA are given in Fig. 4 respectively.

3.4. Solubility

The solubility of the newly prepared copolymers in various solvents was tested in room temperature. These copolymers were completely soluble in solvents like methanol chloroform and dimethylformamide and insoluble in water, acetone and benzene. The solubility test clearly shows that there is wide possibility for using different solvents for the copolymers to be used in coating applications. The solubility of the copolymers is given Table 3.

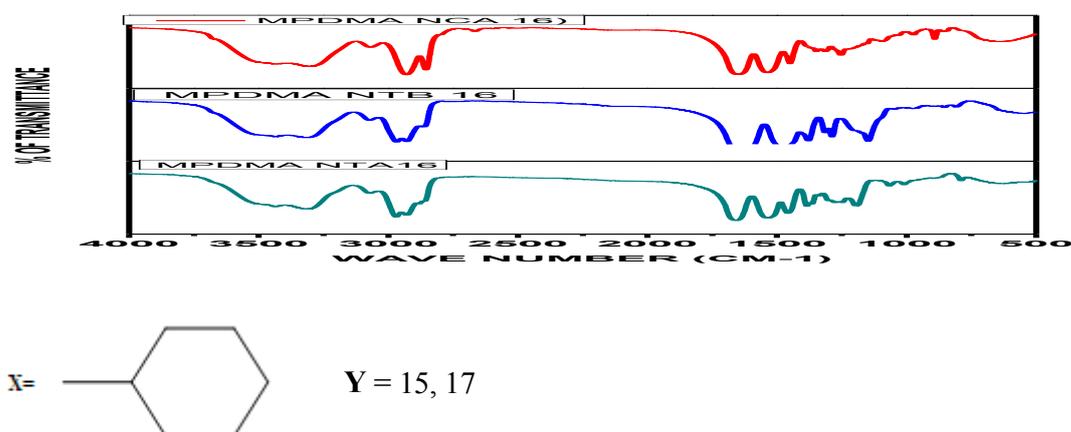


Fig. 1. Copolymerization of MDMAC₁₆ and MPDMA C₁₈ with NCA

Table 1. Copolymerization of MPDMA C₁₆ with NCA

A NCA (gm)	B MPDMA C ₁₆ (gm)	B/A (mol%)	Vol of DMF (ml)	Initiator AIBN (gm)	Temperature (°c)	Time (hr)	Yield (%)
2.0	0.27	4.0	50	0.100	60	16	90.9
2.0	0.68	10.0	50	0.100	60	16	70.2

Table 2. Copolymerization of MPDMA C₁₈ with NCA

A NCA (gm)	B MPDMA C ₁₈ (gm)	B/A (mol%)	Vol of DMF (ml)	Initiator AIBN (gm)	Temperature (°c)	Time (hr)	Yield (%)
2.0	0.27	4.0	50	0.100	60	16	90.9
2.0	0.68	10.0	50	0.100	60	16	70.2

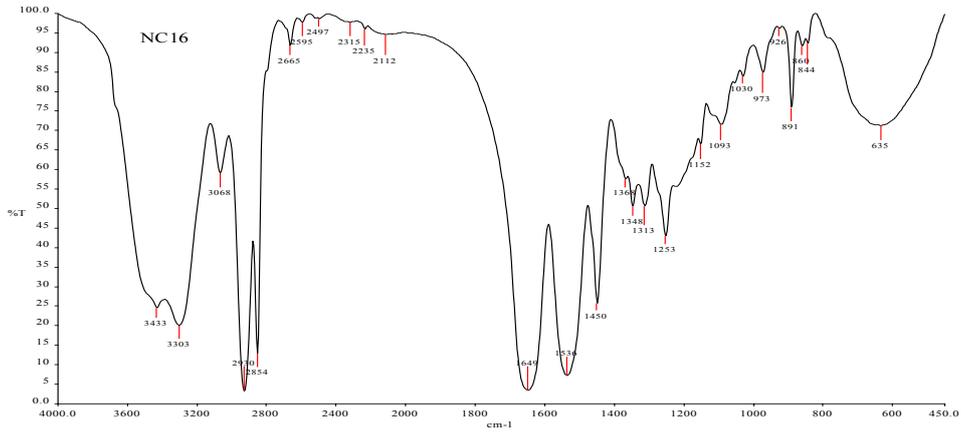


Fig. 4. FT-IR Spectrum of poly(MDMA C₁₆-co- NCA)

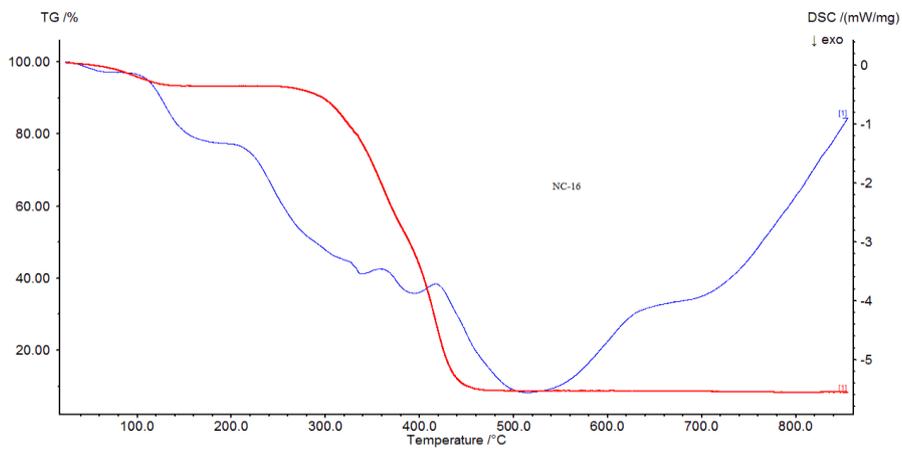


Fig. 5. TGA of poly(MDMA C₁₆-co- NCA)

Table 4 .Thermogravimetric analysis of copolymer

polymer	Mol% of quaternary ammonium (in feed)	Mol% of quaternary ammonium (in copolymer)	IDT (°C)	T ₁ (°C)	T ₂ (°C)	T _f (°C)
MPDMA C ₁₆ with NCA	10	-	160.3	300.1	360.4	458.1

IDT – Initial decomposition temperature ; T₁ – Decomposition temperature in stage 1

T₂ - Decomposition temperature in stage 2 ; T_f – Final decomposition temperature

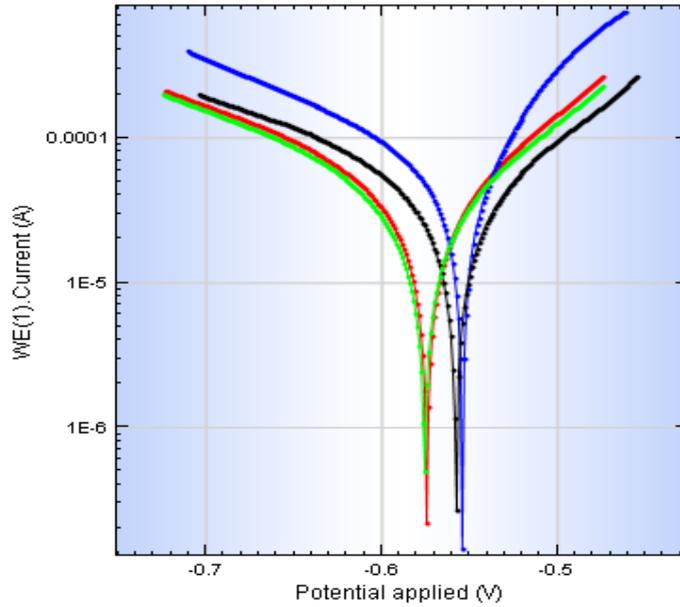


Fig. 6. Potentiodynamic Polarization curves of poly(MPDMA C₁₆-co-NCA)

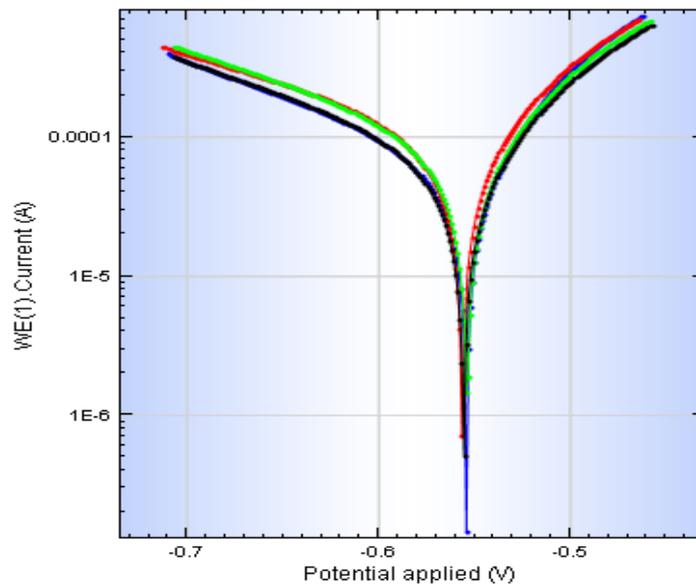


Fig. 7. Potentiodynamic Polarization curves of poly(MPDMA C₁₈-co-NCA)

Table 5. Potentiodynamic polarization parameters of poly(MPDMA C₁₆-co-NCA) for mild steel in 0.05M H₂SO₄ solution

Polymer Sample	ba (V/dec)	bc (V/dec)	E _{corr, Calc} (V)	E _{corr, Obs} (V)	Corrosion rate (mm/year)	Polarization resistance (Ω)	i _{corr} (A/cm ²)	Corrosion inhibition efficiency (%)
Uncoated	0.1190	0.0446	-0.4722	-0.48111	1.8849	86.91	0.000162	
200 ppm	0.3312	0.1979	-0.5414	-0.55776	0.8716	717.25	4.10E-05	74.69

400ppm	0.2468	0.1471	-0.5610	-0.5745	0.6283	740.38	2.90E-05	82.09
600ppm	0.2501	0.1623	-0.5617	-0.5759	0.6051	821.19	2.81E-05	82.71

Table 6. Potentiodynamic polarization parameters of poly(MPDMA C₁₈ –co- NCA) for mild steel in 0.05M H₂SO₄ solution

Polymer Sample	ba (V/dec)	bc (V/dec)	E _{corr} , Calc (V)	E _{corr} , Obs (V)	Corrosion rate (mm/year)	Polarization resistance (Ω)	i _{corr} (A/cm ²)	Corrosion inhibition efficiency (%)
Uncoated	0.1190	0.0446	-0.4722	-0.48111	1.8849	86.91	0.000162	
200 ppm	0.3104	0.1193	- 0.5580	- 0. 5564	1.5547	279.84	3.9E-05	75.92
400ppm	0.2646	0.1144	- 0.5553	- 0.5540	1.3192	305.58	2.86E-05	82.34
600ppm	0.2507	0.1093	- 0.5608	- 0.5557	1.0474	366.84	2.73E-05	83.14

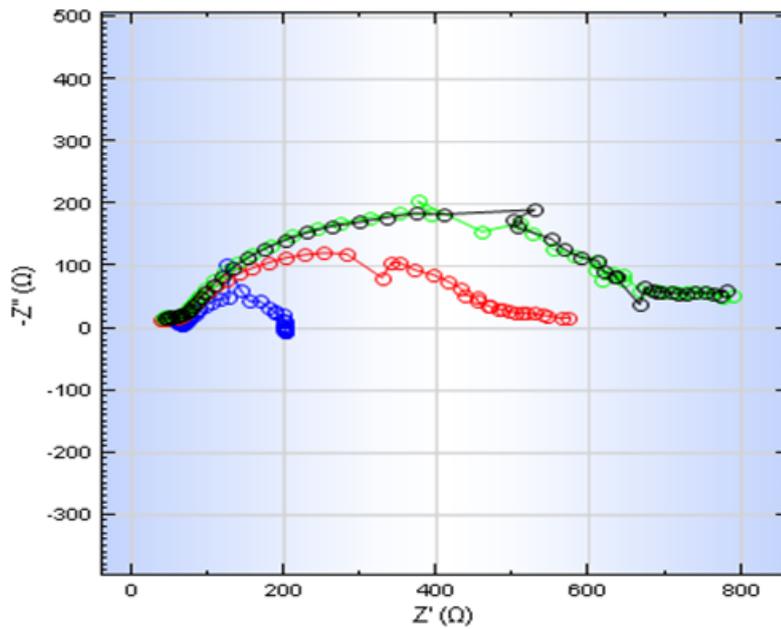


Figure 8. Nyquist plots of poly(MPDMA C₁₆ –co- NCA) mild steel in 0.05M H₂SO₄

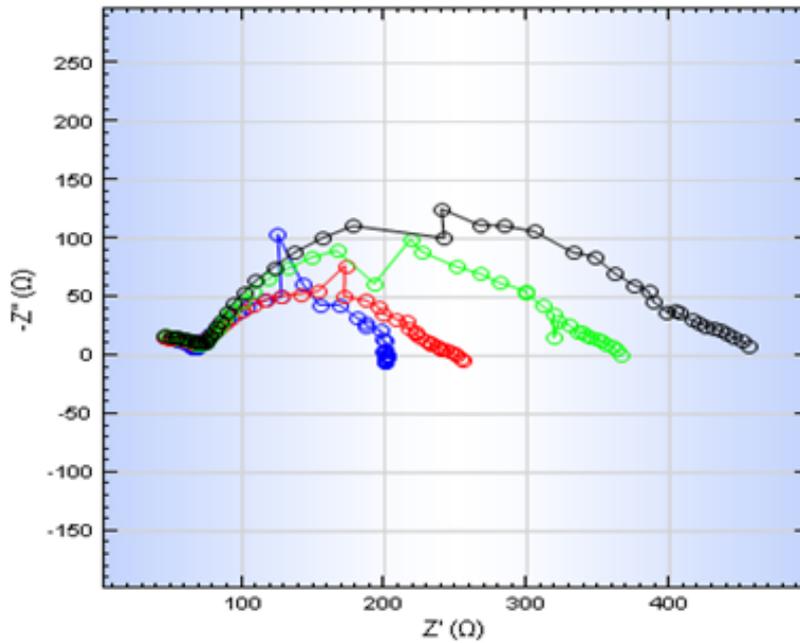


Fig. 9. Nyquist plots of poly(MPDMA C₁₈ –co- NCA) mild steel in 0.05M H₂SO₄

Table 7. Electrochemical impedance parameters of poly(MPDMA C₁₆ –co- NCA) for mild steel in 0.05M H₂SO₄ solution

Polymer Sample	R _{ct} (Ω)	C _{dl} (μ F cm ⁻²)x10 ⁻⁵	IE(%)
Uncoated	69.565	1.92	
200ppm	310.082	3.22E-06	77.56
400ppm	468.152	2.10E-06	85.14
600ppm	472.346	1.81E-06	85.27

Table 8. Electrochemical impedance parameters of poly(MPDMA C₁₈ –co- NCA) for mild steel in 0.05M H₂SO₄ solution

Polymer Sample	R _{ct} (Ω)	C _{dl} (μ F cm ⁻²)x10 ⁻⁵	IE(%)
Uncoated	69.565	1.92	
200ppm	312.551	0.108	77.74
400ppm	368.546	0.105	81.12
600ppm	401.358	0.102	82.66

3.5. Thermogravimetric Analysis

The TGA curves for MPDMA C₁₆ with NCA copolymers are depicted in Fig.5 and the thermo

gravimetric results are presented in the Table 4. There are two stages of decomposition observed in the TGA spectrum, in which the thermal stability of copolymer was assessed by comparing the initial decomposition

temperature (IDT). The decomposition temperature was observed for this copolymer due to the moisture absorbed by them. The first and second stages of decomposition were occurred around 347.1 °C and 360.4 °C respectively, further the final residue continued till 458.1 °C.

3.8. Potentiodynamic Polarization Studies

Polarization curves of mild steel in 0.05M H₂SO₄ with and without presence of copolymers are shown in fig. 6& 7. From the figure it is seen that the anodic and cathodic curves for mild steel in the presence of copolymers were shifted towards negative direction compared to the absence of copolymer immersed in 0.05M H₂SO₄. The polarization parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}) obtained by extrapolation of tafel lines are listed in Table 5 & 6. It is observed from the Table 5 & 6 that E_{corr} values increased significantly for mild steel in the presence of copolymers. The tafel plots of all the studied different concentration of (4%) MPDMA C₁₆ and MPDMA C₁₈ with NCA have good corrosion protective behavior. As can be seen, the corrosion current density in the presence of copolymer was lower than that of absence of copolymer in mild steel.

3.9. Electrochemical Impedance Spectroscopy (EIS)

EIS is a well known method for study of anticorrosive performance of org coatings [8-12]. The electrochemical impedance plots for in the presence and absence of various concentrations of (4%) MPDMA C₁₆ and MPDMA C₁₈ with NCA with mild steel shown in fig. 8&9. The Nyquist spectra showed semicircle, representing the corrosion process of the system. i.e., the charges transfer resistance due to the metal corrosion and the double layer capacitance of the liquid/metal interface.

However, the Nyquist spectra in presence of copolymer showed depressed semicircles. The depressed semicircles in the Nyquist plots were

probably due to the surface heterogeneity [13] or corrosion products of the metal surface heterogeneity [14] or corrosion products of the metal substrate developing the defects in the coatings [15]. The copolymer shows changes in both charge transfer resistance and capacitance. The charge transfer resistance increases much in consequence of the presence of copolymer film, it avoids the electrolyte. The film resistivity reduces the value of capacity of copolymer. As the (4%) MPDMA C₁₆ and MPDMA C₁₈ with NCA composition decreases, the adhesiveness of the copolymer on mild steel decreases, this in turn decreases the corrosion resistance.

The decrease in the C_{dl} resulting from a decrease in local dielectric constant and/or increase in the thickness of double layer, suggested that in the copolymer molecules function by strong adhesion at the metal/solution interface. [16]. Previous workers reported that the changes in C_{dl} values were caused by adhesion of organic molecules on the metal surface, decreasing the extent of dissolution reaction [17].

From the Table 7&8, (4%) MPDMA C₁₆ and MPDMA C₁₈ with NCA of high concentration exhibit high R_{ct} value. This shows high corrosion protection efficiency. Hence, all the concentration of this polymer showed good protection against corrosion. This behavior due to the uniform and adherent of copolymer on mild steel, which effectively prevent the penetration of corrosive ion. Both the potentiodynamic polarization and electrochemical impedance methods showed almost same corrosion resistance. This observation clearly indicated that the (4%) MPDMA C₁₆ and MPDMA C₁₈ with NCA system having anti-corrosive properties.

IV. CONCLUSION

Free radical copolymerization of (4%) MPDMA C₁₆ and MPDMA C₁₈ with NCA was carried out in DMF solution using AIBN as initiator. The synthesized copolymers were confirmed by ¹³C-NMR, ¹H-NMR and

FT-IR spectroscopy. TGA analysis indicates that copolymers undergo double stage of decomposition for this copolymer occurred around 292.1°C & 347.1°C and 300.1°C & 360.4°C respectively. In addition, the

thermal properties of these modified copolymers are influenced by the tertiary ammonium salts introduced onto polymer chains.

V. REFERENCES

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