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Methyl Acrylate Derivatives as Corrosion Inhibitors for X-65 Type Carbon Steel in 1 M HCl

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Inhibition efficiency of prepared Methyl acrylate derivatives 2named Methacryloyloxyethyloctadecyldimethylammonium Bromide (MEODAB), poly(2-Methacryloyloxyethyloctadecyldimethylammonium Bromide) (PMEODAB) for X-65 type carbon steel in 1 M HCl has been investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The prepared acrylate derivatives act as mixed-type inhibitors, which suppresses both cathodic and anodic processes by its adsorption on the electrode surface according to Langmuir adsorption isotherm, together with a slight positive shift in corrosion potential (E_{corr}). The inhibition efficiency IE% reached 89.3% for compound (MEODAB) and 88.1 % for compound (PMEODAB) at 150 ppm. The data obtained from electrochemical impedance spectroscopy (EIS) was analyzed to model the corrosion inhibition process through equivalent circuit. The nature of the protecting film formed on carbon steel was investigated by SEM and EDX techniques.

Keywords: Methyl acrylate derivatives, Impedance spectroscopy, Corrosion, SEM.

1. INTRODUCTION

Carbon steel is utilized as an integral part of marine construction applications, petroleum facilities and refining, process systems for chemical and petrochemical industries [1]. Depending on the process and operations conditions, the carbon steel is commonly exposed to corrosive media which impacts its integrity and lifetime as well.

Poly(methyl methacrylate) (PMMA) is an acrylate derivative and it is considered as one of the most interesting industrial thermoplastic polymers. It has a clear appearance and excellent optical transparency from ultraviolet to near infrared regions [2-4]. It is resistant to weather, and nontoxic, so it

has many applications. PMMA can be modified by blending with other polymers, or by the addition of nano- or micro-inorganic fillers, and this leads to enhancing the thermal properties [5-8]. It has been reported that its chemical structure can be modified by cationic surfactants having short and long alkyl chains [9-13]

The aim of the work is to prepare polymer with dielectric properties, then assess their efficiency as corrosion inhibitors for X-65 type carbon steel in 1 m HCl using different techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements.

2. EXPERIMENTAL

2.1. Chemical composition of X-65 type carbon steel alloy

X-65 type carbon steel specimens used in this investigation were cut from unused petroleum pipeline. The chemical composition (weight%) of carbon steel is C 0.09, Si 0.22, Mn 1.52, P 0.01, S 0.05, Ni 0.04, Cr 0.02, Mo 0.004, V 0.002, Cu 0.02, Al 0.04 and reset is Fe.

2.2. Solution

The testing solution employed in this study is 1M HCl, which prepared using bi-distilled water through a dilution process of AR class 37% HCl.

2.3. Synthesis of the inhibitors

Synthesis of poly(2-methacryloyloxyethyloctadecyldimethylammonium Bromide) (2)

2-Methacryloyloxyethyloctadecyldimethylammonium bromide (MEODAB) (1) was prepared and characterized in a recently published work [2]. Briefly, 0.01 mole of N,Ndimethylaminoethylmethacrylate was reacted with 0.01 mole of 1-bromooctadecane in acetonitril at 40 °C for 24 hrs in presence of 3000 ppm of hydroquinone inhibitor. A white precipitate was formed, filtered, and dried. Poly(2-methacryloyloxyethyloctadecyldimethylammonium Bromide) (2), abbreviated as PMEODAB, was prepared by conventional free radical polymerization of ammonium salt (1) with ammonium persulfate (APS) in distilled water at 80 °C for 6 hrs as shown in scheme 1. Water was evaporated and solid pale yellow powder was obtained. The compound polymer (PMEODAB) was characterized by ¹HNMR spectroscopy in figure 1.



Figure 1. ¹H-NMR spectroscopy of the synthesized PMEODAB inhibitor



Scheme 1. Synthesis of Methyl acrylate derivatives (1) MEODAB, (2) PMEODAB

2.4. Potentiodynamic polarization measurement

Electrochemical measurements were carried out using Autolab PGSTAT 30. Electrochemical tests were conducted by using three-electrode corrosion cell made from Perspex glass, platinum anode was utilized as auxiliary electrode. All electrochemical measurements were recorded against saturated calomel electrode (SCE) as reference electrode. All measurements were conducted in air-soaked system and at surrounding temperature of (298 K). Polarization measurements were conducted at a consistent scan rate of 1mVs⁻¹. The measured current densities were investigated utilizing Tafel extrapolation technique.

2.5. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements were conducted utilizing Autolab PGSTAT 30 using electrochemical cell as described in section 2.5. AC signal with 10 mV abundancy top to top was utilized to annoy the framework. EIS graphs are given in Nyquist plots. The impedance measurements were carried out at the open circuit potential (E_{ocp}). EIS outlines are given in Nyquist plot in the recurrence run from 100 kHz and 10 mHz utilizing 10 stages for every recurrence decade after 4 h drenching time. Air conditioning signal with 10 mV plentifulness top to top was utilized to irritate the framework.

2.6. Surface Investigation

Scanning electron microscope (SEM) is used to investigate the shape of the carbon steel surface, Zeiss Smart EDX, Egyptian Petroleum Research Institute, Egypt.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization measurements

The working electrode was first immersed in the test solution for 1 h to build up a consistent state open circuit potential (E_{ocp}). After assurance of the open circuit potential, potentiodynamic polarization measurements were conducted with a scan rate of 1mVs–1 in both cathodic and anodic directions. Figures 2, 3 show the cathodic and anodic polarization measurements of carbon steel immersed in 1M HCl in the absence and presence of the prepared MEODAB and PMEODAB inhibitors. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel inclines (b_c and b_a) were recorded [14-20].



Figure 2. Potentiodynamic polarization curves of carbon steel in absence and presence of different concentrations of compound I (MEODAB) in 1 M HCl at room temperature.



Figure 3. Potentiodynamic polarization curves of carbon steel in absence and presence of different concentrations of compound II (PMEODAB) in 1 M HCl at room temperature.

From the obtained polarization measurements, the corrosion current densities (i_{corr}) were minimized with increasing the concentration of MEODAB and PMEODAB molecules compared to the inhibitor free solution. The degree of surface coverage (θ) and the inhibition efficiency (η %) were determined utilizing the following equations:

$$\theta = 1 - \frac{\iota}{i_o}$$
(1)

$$\eta \% = \left[1 - \frac{i}{i_o}\right] \times 100$$
(2)

where i_0 and i are the corrosion current densities in the absence and presence of the inhibitor, respectively.

A cautious investigation of the Potentiodynamic polarization measurements demonstrated that the obtained curves are moved to more negative and more positive values for the anodic and cathodic polarizations, compared to the blank solution. This indicates that the prepared inhibitors act as mixed type inhibitors, i.e., increase the polarization resistance of both anodic and cathodic directions. Additionally, the slopes of the cathodic and anodic Tafel lines are roughly constant and autonomous on the inhibitor concentration. This confirms that the investigated inhibitors have no impact on the metal disintegration system. Complete information obtained from polarization measurements are summarized in tables 1, 3. The outcomes show that the inhibition efficiency (η %) of compound PMEODAB is more prominent than that of compound MEODAB. This could be attributed to the solvency which advances more grounded adsorption film and subsequently more defensive layer and higher protection efficiency.

Table 1. Potentiodynamic polarization values for the corrosion of carbon steel in absence and presence of different concentrations of compound I (MEODAB) in 1 M HCl at room temperature.

Conc.	I _{corr} x 10 ⁻⁵ (A/cm ²)	r (mm/year)	$egin{array}{c} \mathbf{R}_{\mathrm{p}} \ (\mathbf{\Omega}) \end{array}$	E _{corr} (V)	ba (V/dec)	bc (V/dec)	θ	%
Blank	54.60	6.34	49.5	-0.452	0.114	0.152	-	-
5	10.80	1.26	300.8	-0.451	0.124	0.197	0.80	80.2
15	8.80	1.02	327.9	-0.460	0.112	0.176	0.83	83.9
25	7.55	0.88	415.5	-0.450	0.123	0.194	0.86	86.2
50	7.09	0.82	445.9	-0.453	0.124	0.194	0.87	87.0
100	6.16	0.72	554.9	-0.494	0.145	0.180	0.88	88.7
150	5.82	0.68	540.2	-0.477	0.121	0.187	0.89	89.3

Table 2. Electrochemical impedance parameters for carbon steel in absence and presence of different concentrations of compound I (MEODAB) in 1 M HCl at room temperature.

Conc.	R _{ct} (Ω)	Rs (Ω)	CPE.N	CPE.Y0 (F) x 10 ⁻³	Θ	%
blank	49.0	1.45	0.83	0.099	-	-

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5	306.0	2.59	0.67	0.227	0.83	84.0
15	321.9	9.06	0.74	0.129	0.84	84. 8
25	341.8	11.33	0.74	0.131	0.85	85.7
50	384.1	9.96	0.71	0.114	0.87	87.2
100	450.5	7.23	0.63	0.148	0.89	89.1
150	453.1	9.62	0.68	0.201	0.89	89.2

Table 3. Potentiodynamic polarization values for the corrosion of carbon steel in absence and presenceof different concentrations of compound II (PMEODAB) in 1 M HCl at room temperature.

Conc.	Icorr x 10 ⁻⁵ (A/cm ²)	r (mm/year)	R _p (Ω)	Ecorr (V)	ba (V/dec)	bc (V/dec)	Θ	%
Blank	54.6	6.34	49.5	-0.45	0.12	0.15	-	-
5	18.1	2.10	133.5	-0.44	0.09	0.15	0.66	66.9
15	9.0	1.05	251.5	-0.46	0.09	0.13	0.83	83.5
25	8.8	1.03	342.3	-0.45	0.10	0.24	0.83	83.8
50	8.1	0.95	350.7	-0.46	0.12	0.15	0.85	85.1
100	6.5	0.75	435.5	-0.45	0.10	0.19	0.88	88.2
150	5.8	0.68	520.7	-0.46	0.12	0.17	0.89	89.3

3.2. Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of carbon steel in 1 M HCl solution in the absence a presence of different concentrations of the prepared MEODAB, PMEODAB inhibitors were examined by EIS procedure. Nyquist plot is showed in figures 4, 5.

It is obvious from plots that the impedance reaction of carbon steel in the corrosive media was essentially changed after the addition of the inhibitor molecules. Impedance parameters, for example, the charge transfer resistance R_t , layer capacitance CPE and inhibition efficiency η % were determined and recorded in tables 2, 4.

Table 4. Electrochemical impedance parameters for carbon steel in absence and presence of different concentrations of compound II (PMEODAB) in 1 M HCl at room temperature.

Conc.	R _{ct} (Ω)	Rs (Ω)	CPE.N	CPE.Y0 (F) x 10 ⁻³	θ	%
blank	49.0	1.45	0.83	0.099	-	-
5	101.2	1.21	0.76	0.083	0.51	51.6
15	223.0	3.43	0.77	0.117	0.78	78.0
25	277.1	4.35	0.75	0.103	0.82	82.3
50	355.6	3.06	0.62	0.044	0.86	86.2
100	398.0	3.87	0.64	0.066	0.87	87.7
150	413.6	7.01	0.70	0.087	0.88	88.2

The values of R_t were given by subtracting the high frequency impedance from the low frequency one as follows [21].

 $R_{t} = Z_{re}^{} (at low frequency) - Z_{re}^{} (at high frequency)$ (3)

The values of C_{dl} were obtained at the frequency f_{max} ,

at which the imaginary component of the impedance is maximal $-Z_{max}$ using the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max}} \frac{1}{R_t} \tag{4}$$

and percentage inhibition efficiency $\eta\%$ were calculated from the values of R_t using the following equation:

$$\eta\% = \left[1 - \frac{R_t}{R_{t(inh)}}\right] \times 100\tag{5}$$

where R_t and $R_{t(inh)}$ are the charge transfer resistance in the absence and presence of inhibitor, individually. Increasing the values of (R_t) and decreasing the values of (CPE) by increasing inhibitor concentration demonstrate that the polymeric molecules inhibit corrosion rate of carbon steel in HCl by adsorption mechanism.



Figure 4. Nyquist plots of carbon steel in absence and presence of different concentrations of compound I (MEODAB) in 1 M HCl at room temperature.



Figure 5. Nyquist plots of carbon steel in absence and presence of different concentrations of compound II (PMEODAB) in 1 M HCl at room temperature.

For investigation of the obtained impedance spectra, the equivalent circuit (EC) was modeled utilizing Boukamp program as showed in figure 6, where R_S is the arrangement opposition , R_t is the charge transfer resistance, CPE is the electrochemical twofold layer capacitance , R_f is the film resistance and C_f is the film capacitance[22-24]. From EIS information it was confirmed that the inhibition efficiency of compound MEODAB is more prominent than that of compound PMEODAB. Along these lines, concurring with previously mentioned outcomes potentiodynamic polarization measurements.



Figure 6. Equivalent circuit used to model impedance data of for X-65 type carbon steel in 1 M HCl

3.3. Surface investigations

The morphological changes that happened on the carbon steel surface were investigated in various cases, treated with and without inhibitor [25, 26], and are showed in figure 7(a, b).



Figure 7. SEM micrographs of carbon steel samples with and without 150 ppm of MEODAB after the immersion in 1 M HCl solution at 298 K

The carbon steel surface had all the earmarks of being attacked and loaded with pits after immersion in 1 M HCl without being treated with (MEODAB) compound for 7 h (figure 7a), which showed the string attack of corrosion species, for instance, H^+ and Cl^- . In any case, within the addition of 150 ppm of (MEODAB) (figure 7b), a smooth carbon steel surface indicates the formation of strong protective layer. This shows the good inhibition efficiency of the tested inhibitor. On the same time, the EDX spectrum shows the synthetic structure of the uncovered metal surface wherein the oxygen signal

shows up because of the presentation to 1.0 M HCl corrosive (figure 8a). Nonetheless, by including 150 ppm of (MEODAB) to the medium, the Fe top is significantly stifled compared to the inhibitor free sample (figure 8b), notwithstanding the presence of the N top that affirm the development of the defensive inhibitor film. The obtained surface investigation results are matching with the results of electrochemical techniques discussed earlier.



Figure 8. EDX for carbon steel surface: (a) sample immersed in 1.0 M HCl acid solution without inhibitor, (b) sample immersed in 1 M HCl acid solution with 150 ppm of MEODAB inhibitor.

3.4. Mechanism of Inhibition

The hindrance execution for the corrosion inhibition of carbon steel in 1 M HCl was evaluated using the prepared inhibitors MEODAB and PMEODAB. The hindrance cycle depends on numerous elements, for example, fixation, the quantity of dynamic destinations and their charge densities, and atomic mass and their strength in their surroundings [27]. As a matter of fact, the heterogeneity of mixes

with incredible nucleophilicity, electrons and charge of heteroatoms (N, O, and S iotas) tend to restrain the erosion of the metal surface. The hindrance relies upon the adsorption of the surfactants on the carbon steel, obstructing the dynamic habitats of the carbon steel surface. The structure of the considered mixes contains heads and tails. The head gatherings of the mixes (polar part) were in rich electronically dynamic utilitarian gatherings, which share in the adsorption cycle with unfilled d-orbitals of the carbon steel (coordination obligation of chemisorption), through the removal of adsorbed water particles from the carbon steel by hetero-molecules that can give the electron chemisorption holding [28]. The hydrophobicity chain (tail) of the compound causes the migration of the acrylate from the arrangement mass to interface, and, besides, these hydrophobic tails fill in as an obstruction film to shield the metal from responding with its condition. The adsorption cycle relies on the inclination of the carbon steel toward electron densities that encourage better surface inclusion [29].



Figure 9. Suggested model of adsorption of the PMEODAB inhibitor on carbon steel surface in 1 M HCl.

4. CONCLUSIONS

The prepared MEODAB and PMEODAB compounds can be considered as good corrosion inhibitors for carbon steel surface immersed in 1 HCl aqueous solution. The electrochemical techniques investigations of the tested inhibitors showed that it acts as a mixed type inhibitor. The charge transfer resistance, R_{ct}, decreased steadily as a result of the adsorbed inhibitor layers on the carbon steel surface within adding MEODAB and PMEODAB molecules. The surface investigation results are in a good agreement with the electrochemical investigation technique results and confirms the good inhibition efficiency of the prepared inhibitors.

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