دراسة خصائص الإمتزاز وتثبيط تآكل الفولاذ الطري في وسط من حامض الهيدروكلوريك وذلك باستعمال البوليمر المؤلف قابل الذوبان في الماء "بولي فينيل الكحول- ميثوكسي أنيلين" (PVAMOA)

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الستخلص:

تمت دراسة كفاءة البوليمر المؤلف قابل الذوبان في الماء بولي فينيل الكحول- ميثوكسي أنيلين (PVAMOA) في تثبيط تآكل الفولاذ الطري الموجود في وسط حامض الهيدروكلوريك بتركيز 1 مولاري. لقد تم استقصاء تثبيط التآكل باستخدام دراسة فقدان الوزن وديناميكا جهد الاستقطاب والممانعة الكهروكيميائية. لقد تم تعيين ومناقشة معاملات الحركية والديناميكيا الحرارية للفولاذ الطري في حالتي التآكل والتثبيط بواسطة الامتزاز. ولقد لوحظ بأن امتزاز البوليمر المؤلف PVAMOA على سطح الفولاذ الطري يخضع لمنحنيات لانجمير والتي تتبع خط ثابت حراري امتزاز العوادي. وجدير بالاشاره إن عملية امتزاز البوليمر المؤلف PVAMOA تم التثبت منها باستخدام المجهر الالكتروني الماسح SEM.

ORIGINAL ARTICLE

Study of adsorption properties and inhibition of mild steel corrosion in hydrochloric acid media by water soluble composite poly (vinyl alcohol-*o*-methoxy aniline)

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Abstract   The efficiency of new water soluble composite namely, poly (vinyl alcohol-*o*-methoxy aniline) PVAMOA has been studied for corrosion inhibition of mild steel in 1 M hydrochloric acid (HCl). Corrosion inhibition was investigated using weight loss, potentiodynamic polarization and electrochemical impedance studies. The kinetic and thermodynamic parameters for mild steel corrosion and inhibitor adsorption respectively, were determined and discussed. The adsorption of PVAMOA on the mild steel surface obeyed Langmuir followed by El-Awady adsorption isotherm. The adsorption of the composite was established by scanning electron microscope (SEM).

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1. Introduction

Mild steel finds wide application in a broad field of industry and machinery. However its tendency to corrode makes it unsuitable for exposure to acids. For example, the scale formation in mild steel steam boilers is a quite common problem in industries which has to be removed. Hydrochloric acid is used for removing scales from the boiler surface. To minimize the metal loss during this process, corrosion inhibition programs are required. The corrosion inhibition is achieved by the addition of inhibitor to the system that prevents corrosion of the metal surface. The influence of the inhibitor upon metal corrosion is often associated with physical or chemical adsorption. This phenomenon is related to the presence of hetero atoms (N, O, and S) as well as multiple bonds or aromatic rings in the inhibitor (Azhar et al., 2002).

The use of polymers as corrosion inhibitors has considerable attention recently. Polymers are used as corrosion inhibitors because, through their functional groups they form complexes with metal ions and on the metal surface these complexes occupy a large surface area, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution.

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The corrosion inhibitive properties of polyvinyl alcohol have been identified by Strawhecker and Manias (2000). Manickavasagam et al. (2002) examined poly (styrene sulfonic acid) – doped polyaniline influence on the inhibition of corrosion of mild steel in 1 M HCl. The effect of polyvinyl alcohol and other polymers on the corrosion of cadmium in a 0.5 M hydrochloric acid solution was studied by Khairou and El-Sayed (2003). The corrosion behavior of mild steel in HCl and its inhibition by 4-actamidoaniline were studied by Okafor et al. (2003). The corrosion protection of mild steel by paint containing polyaniline – hydrochloride was investigated by Samui et al. (2003). The effect of poly (4-vinylpyridine isopentyl bromide) in 3° of quaternization (6%, 18% and 79%) on the corrosion of pure iron was investigated by Chetouani et al. (2003). Selvaraj et al. (2004) studied the inhibition efficiency of polyvinyl pyrrolidone in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of Zn^{2+} using weight loss method. Rajendran et al. (2005) investigated the corrosion behavior of carbon steel using polyvinyl alcohol in neutral aqueous solution containing 60 ppm of Cl^- in the absence and presence of Zn^{2+} ions using weight loss method. Manivel and Venkatachari (2006) examined the corrosion behavior of iron exposed to 1 M HCl solution and its inhibition using poly (p-amino benzoic acid) compared with p-amino benzoic acid. Polyethylene glycol, polyvinyl alcohol and polyacrylamide exhibited the best inhibiting performance toward the corrosion of mild steel in hydrochloric acid (Umoren et al., 2006; Umoren and Obot, 2008). Poly (aniline-formaldehyde) was used as an inhibitor on mild steel corrosion (Quraishi and Shukla, 2009).

The compound such as polyvinyl alcohol – sulfanilic acid has been used as corrosion inhibitor for mild steel in various aqueous environments (Srimathi et al., 2010). Inhibitive action of polyvinyl alcohol – Zn (II) system in corrosion inhibition of carbon steel in ground water was examined by Manimaran et al (2012). Conducting polyaniline as corrosion inhibitor for mild steel in hydrochloric acid was studied by Feng et al. (2013). Thus many research papers have reported the use of polymers as corrosion inhibitors.

Substituted polyaniline such as poly (o-methoxy aniline) inhibits metal corrosion efficiently and further its stability and solubility are improved using polyvinyl alcohol (PVA) as a supporting polymer. Water soluble PVA is nontoxic, acts as steric stabilizer and prevents the precipitation of polymer-ized o-methoxy aniline and makes it finely dispersed in solution. The safety of PVA is shown in the literature study as (i) The acute oral toxicity of PVA is very low, (ii) The orally administrated PVA is very poorly absorbed from the gastrointestinal tract. (iii) PVA dos not accumulate in the body when administrated orally. (iv) PVA is not mutagenic (De merlis and schoneker, 2003). PVA was used as a steric stabilizer for the dispersion polymerization of cross-linked poly (N-isopropylacrylamide) in water (Lee et al., 2011).

In the present work, water soluble composite poly (vinyl alcohol-o-methoxy aniline) has been synthesized and tested as corrosion inhibitor for mild steel in 1 M HCl.

2. Experimental

2.1. Polymer synthesis

20 mL of PVA (10% w/w) was mixed with 20 mL of o-methoxy aniline in oxalic acid (1 mL in 100 mL) using a magnetic stirrer. The system was then cooled below $-5\,°C$ and followed by the addition of 20 mL of aqueous acidic (oxalic acid) solution of ammoniumpersulfate (APS). APS mole ratio was maintained as 1:1. Polymerization was allowed to proceed for 3 h and the composite was formed as bright green stable solution (Gangopadhyay et al., 2001). The proposed structure of PVAMOA is shown in Fig. 1.

The structural characteristic of PVAMOA (Fig. 2) was investigated by FTIR spectroscopy in the range of 2000–400 cm^{-1}. The predominant OH stretching of PVA appearing at 3285 cm^{-1} and characteristic NH stretching vibration (3400–3250) were displaced toward the lower wave number 3188 cm^{-1}. This shifting of peak might be due to the hydrogen bonding between PVA and PMOA. A new peak observed at 3188 cm^{-1} was associated with peaks at 1699 cm^{-1} and 1297 cm^{-1} which was an indication of the presence of C–N=C and C–NH –C in the composite (Sazou and Georgolios, 1997). The characteristic CH stretching vibrational peak of PVA at 2912 cm^{-1} was shifted to 2850 cm^{-1}. A band at 2967 cm^{-1} could be assigned to the aromatic C–H stretching. The composite showed a band at about 1097 cm^{-1} that corresponds to C–O stretching of the PVA. The peak at 1584 cm^{-1} was due to the C=C double bond of the quinonoid ring, where
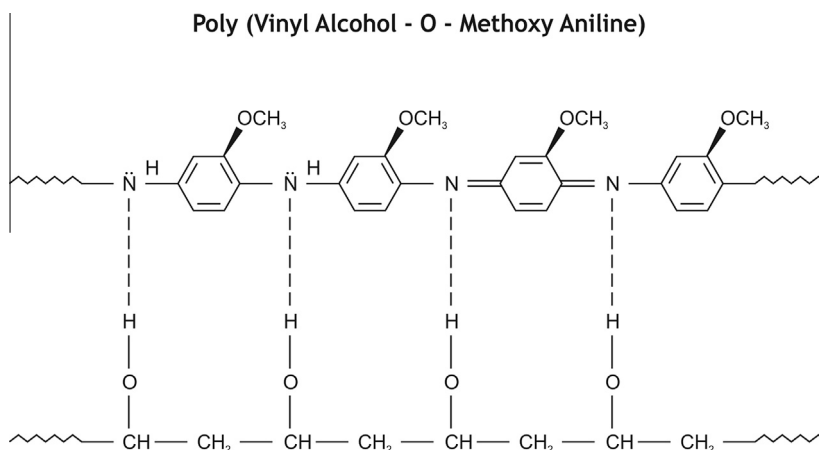

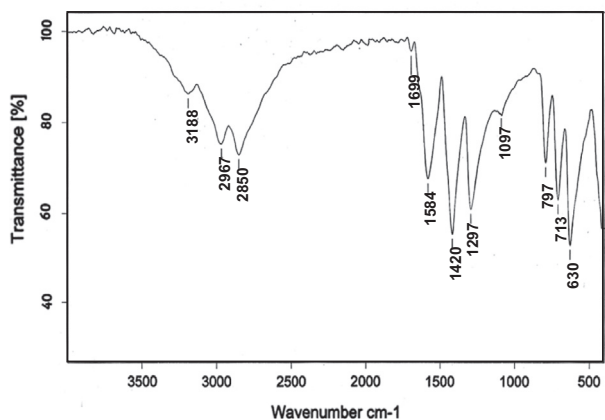**Figure 1**   The proposed structure of synthesized PVAMOA.

Figure 2 FTIR spectra for PVAMOA.

as the peak at 1420 cm^{-1} arises due to vibration of the C=C bond associated with the benzenoid ring (Zheng et al., 1996). 1, 2 and 1, 4 di substitution were indicated by the peaks appearing at 797 cm^{-1} and 713 cm^{-1} (Coates, 2000). Appearance of several peaks between 900 and 630 cm^{-1} represented the aromatic H out of plane bending.

2.2. Material preparation

Elemental analysis was carried out to determine the percentage of elements present in the mild steel. Corrosion tests were performed on the mild steel of the following percentage composition: carbon 0.126%, manganese 0.181%, silicon 0.058%, phosphorous 0.033%, sulfur 0.029%, chromium 0.012%, molybdenum 0.012%, nickel 0.002% and iron 99.547%. Mild steel specimens were cut into 5 cm × 1 cm coupons for gravimetric measurements and were lacquered so as to expose an area of 1 cm^2 for all electrochemical studies. The specimens were mechanically polished, their edges were abraded with fine grade emery paper, degreasing in acetone, and dried at room temperature before use. Molar acid solution was prepared by using double-distilled water. The concentration range of inhibitor employed was 100–2000 ppm in 1 M HCl.

2.3. Weight loss measurements

Gravimetric experiments were carried out in a double walled glass cell. The solution volume was 100 cm^3; the temperature of the solution was controlled thermostatically. Weight loss measurements were carried out in triplicate in the absence and presence of various concentrations of PVAMOA solution in 1 M HCl at 303–343 K temperature.

2.4. Electrochemical measurements

Electrochemical measurements were done by means of solartron electrochemical analyzer model (1280B) interfaced with an IBM computer and Z plot and corrware software were used for data acquisition and analysis.

2.4.1. Potentiodynamic polarization curves

Polarization experiments were carried out in a conventional three-electrode glass cell with a platinum counter electrode

and a saturated calomel electrode (SCE) as reference with a luggin capillary bridge. The cathodic plot was always determined first; the open-circuit potential was then re-established and the anodic plot was determined. The anodic and cathodic polarization curves were recorded at a constant scan rate of 2 mV s^{-1}. Inhibition efficiencies were determined from corrosion currents calculated by the tafel extrapolation method.

2.4.2. Electrochemical impedance spectroscopy

Impedance spectra were obtained in the frequency range of 20 kHz to 0.1 Hz. A sine wave with 10 mV amplitude was used to perturb the system (Mehdi et al., 2003; Bentiss et al., 2005). SCE was used as reference and a platinum plate was used as counter electrode. All potentials were reported versus SCE. The charge transfer resistance (R_{ct}) values were obtained from the diameter of the semi circles of the Nyquist plots. The inhibition efficiency (IE) of the inhibitor was calculated from R_{ct} values using the following equation:

$$IE\,(\%) = (R_{ct}(I) - R_{ct})/(R_{ct}I) \times 100 \qquad (1)$$

2.4.3. Surface analysis

The surface morphology of mild steel specimens was examined before and after exposure to HCl for 12 h with and without inhibitor using Jeol JSM 6390 scanning electron microscope. The energy of the acceleration beam employed was 20 keV.

3. Results and discussion

3.1. Effect of immersion time

The weight loss study results indicated the increase in IE with increase in time of immersion till 3 h. At 3 h, efficiency was maximum 97.21 and then decreased to 92.02 at 24 h. The best performance of the PVAMOA has been perceived at 3 and 6 h of immersion period with the entire concentration of the inhibitor. The variation of inhibition performance of PVAMOA with immersion time at various concentrations is shown in Fig. 3.
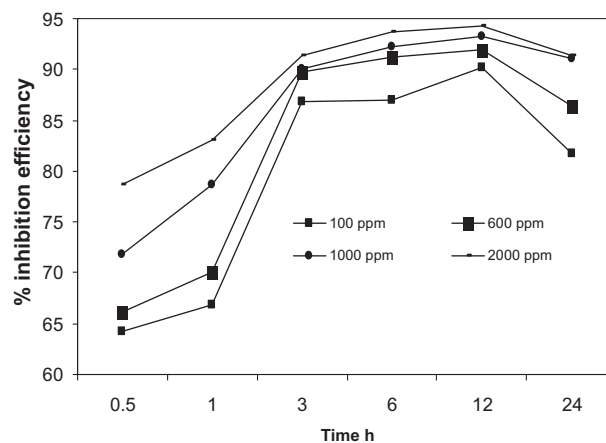

Figure 3 Variation of inhibition efficiency with different immersion times of PVAMOA in 1 M HCl on the mild steel surface.

3.2. Effect of temperature

The effect of temperature on the inhibited acid–metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition (Bentiss et al., 2005). The change of the corrosion rate (CR) at selected concentrations of PVAMOA during 1/2 h of immersion at different temperatures (303–343 K) was studied in 1 M HCl, both in the absence and presence of PVAMOA and CR was calculated using the following expression:

$$CR\,(mpy) = 534\,W/DAT \tag{2}$$

where, W is the weight loss in g, D is the density of mild steel in g/cm2, A is the area of the specimen in cm2, and T is the exposure time in hours.

In general IE increases with the inhibitor concentration (Li et al., 2009). But in acidic media, corrosion of metal is accompanied with evolution of H_2 gas, rise in temperature accelerates CR which results in a higher dissolution rate of metal. It has been observed from Table 1 that IE increased with increase in temperature up to 323 K and beyond this decrease in efficiency was noted. The decrease in IE with temperature might be attributed to desorption of the inhibitor molecule from the metal surface at higher temperatures (Shukla and Quraishi, 2010). When temperature increased, CR increased which was due to desorption of PVAMOA from the metal surface and exposure of more area of the metal surface to acidic medium. The decreased in the adsorption at higher temperature indicated that physical adsorption of inhibitor (Maayata and Al-Rawashdeh, 2004).

To calculate activation and thermodynamic parameters of the corrosion process, Arrhenius Eq. (1) and transition state Eq. (2) were used

$$\log CR = \log \lambda - (E_a/2.303RT) \tag{3}$$

$$CR = RT/Nh \exp(\Delta S/R)\exp(-\Delta H/RT) \tag{4}$$

where, E_a is the apparent activation energy, R is the molar gas constant, λ is the frequency factor, h is Planck's constant, N is the Avogadro's number, ΔS is entropy of activation and ΔH is enthalpy of activation. Values of apparent activation energy of corrosion (E_a) for mild steel in 1 M HCl with the absence and presence of various concentrations of PVAMOA were determined from the slope of log (CR) versus $1/T$ plots and λ obtained from the intercept (log λ) are shown in Table 2.

Table 2 showed that the values of E_a for inhibited solution were higher than those for uninhibited solution. The higher values of E_a indicated that the dissolution of mild steel was slow in the presence of PVAMOA. Rise in activation energy in the presence of inhibitor was explained in different ways in the literature. The decrease in apparent activation energy at higher levels of inhibition arises from a shift of the net corrosion reaction, from uncovered surface to directly involving the adsorbed sites. The increase in activation energy could be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature (Szauer and Brand, 1981). Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of mild steel comes in contact with aggressive environment, resulting in an increase of corrosion rates with temperature (Herrag et al., 2010).

The values of λ were higher for inhibited solution than those for uninhibited solution. It was clear from Eq. 3 that

Table 1 Corrosion rate of mild steel and inhibition efficiency of PVAMOA for mild steel corrosion at various temperatures.

Conc. (ppm)	303 K		313 K		323 K		333 K		343 K	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	1250.72		4246.69		6954.84		10823.88		15675	
100	459.64	63.25	1269.33	70.11	1646.90	76.32	3905.25	63.92	8182.35	47.8
200	442.63	64.61	1159.77	72.69	1450.78	79.14	3664.96	66.14	7563.19	51.75
400	429.12	65.69	1176.33	72.30	1349.24	80.60	3160.57	70.80	7368.82	52.99
600	422.99	66.18	1137.26	73.22	1322.11	80.99	2783.90	74.28	7006.72	55.30
800	356.83	71.47	1096.07	74.19	1204.57	82.68	2647.52	75.54	6085.03	61.18
1000	288.16	76.96	948.28	77.67	1169.80	83.18	1893.09	82.51	5395.33	65.58
2000	268.53	78.53	607.27	85.70	910.38	86.91	1688.52	84.40	4233.81	72.99

Table 2 Activation and thermodynamic parameters of mild steel in 1 M HCl without and with PVAMOA.

| Conc. (ppm)	E_a (kJ/mol)	$\lambda \times 10^9$ (mg /cm^2)	DG (kJ/ppm)					ΔH (kJ/ppm)	ΔS (kJ /K/ppm)
Blank	52	1.89	382.52	393.51	404.50	415.49	426.48	49.55	−1098.93
100	59	9.59	389.51	400.49	411.47	422.46	433.44	56.75	−1098.22
200	58	7.28	389.02	400.01	410.99	421.97	432.96	56.22	−1098.34
400	57	4.16	387.74	398.72	409.71	420.70	431.68	54.87	−1098.59
600	56	2.31	386.37	397.36	408.35	419.34	430.33	53.42	−1098.84
800	56	2.51	386.84	397.83	408.82	419.81	430.79	53.90	−1098.81
1000	56	2.12	386.87	397.86	408.85	419.84	430.83	53.91	−1098.88
2000	56	1.55	386.68	397.67	408.66	419.65	430.64	53.68	−1099.01
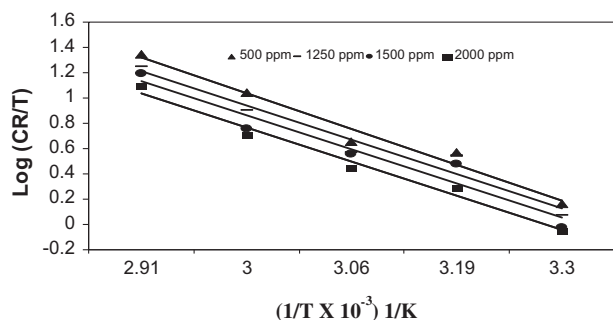
Figure 4 Transition state plot for mild steel corrosion in 1 M HCl and at different concentrations of PVAMOA.

the higher E_a and the lower λ lead to the lower CR. When the concentration of inhibitor was relatively higher, the decrease in mild steel CR was mostly linked to pre exponential factor. In general, the effect of E_a on mild steel corrosion was larger than that of λ. However, if the change in λ was larger than that in E_a, λ value might be a dominating factor to determine the corrosion of mild steel. In the present study, values of E_a and λ vary in a similar manner and therefore, the combined effect of E_a and λ resulted in the increase of CR with temperature (Ahamad et al., 2010).

A plot of log (CR/T) versus $1/T$ was shown in Fig. 4. Straight lines were obtained with slope $(-\Delta H/2.303\ R)$ and intercept of [log $(R/$Nh$) + (\Delta S/2.303\ R)$] from which ΔH and ΔS were calculated and are listed in Table 2. Inspection of these data revealed that the thermodynamic parameter (ΔH) for dissolution reaction of mild steel in 1 M HCl in the presence of inhibitor concentration was higher (53.6–56.7 kJ ppm^{-1}) than that in the absence of inhibitor (49.5 kJ ppm^{-1}). The positive sign of ΔH reflected the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel was slow (Guan et al., 2004) in the presence of inhibitor. It was noticed that E_a and ΔH values vary in the same way (Table 2). This result permitted to verify the known thermodynamic relation between E_a and ΔH as shown in Table 2.

$$\Delta H = E_a - \text{RT} \tag{5}$$

Large and negative values of entropies (ΔS) implied that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complex (Martinez and Stern, 2002).

The change in activation free energy (ΔG) of the corrosion process can be calculated at each temperature by applying the equation

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

The calculated ΔG values are presented in Table 2. The values of ΔG were positive and showed almost no change with increasing temperatures, indicating that the activated complex was not stable and the probability of its formation decreased somewhat with rise in temperature. However ΔG values for the inhibited system revealed that in the course of inhibitor addition, the activated corrosion complex becomes less stable as compared to its absence.

3.3. Adsorption isotherm and adsorption parameters

In order to gain more information about the mode of adsorption of the composite on the mild steel surface, the experimental data have been tested with several adsorption isotherms. The weight loss temperature results were used to calculate the adsorption isotherm parameters. The most frequently used isotherms are Langmuir, Frumkin, Temkin, Flory-Huggins and thermodynamic/kinetic model of El-Awady isotherm. Inhibitor molecules were adsorbed on the metal surface if the interaction between molecule and metal surface was higher than that of the water molecule and the metal surface. Many adsorption isotherms were plotted and Langmuir adsorption isotherm was found to be the best description of the adsorption behavior. Langmuir adsorption isotherm is given by the following equation:

$$\log(C/\theta) = \log C - \log K \tag{7}$$

The values of regression coefficients (R^2) confirmed the validity of this approach.

Though the linearity of the Langmuir plot (Fig. 5) may be taken to suggest that the adsorption of inhibitor follows the Langmuir isotherm, the considerable deviation of the slope from unity indicated that the isotherm could not be strictly applied (Table 3). It has been postulated in the derivation of Langmuir isotherm equation that adsorbed molecules did not interact with one another, but this was not true in the case of large polymer molecules having polar atoms or groups which could be adsorbed on the metal surface. Such adsorbed species interact by mutual repulsion or attraction and would affect the slope. The deviation of the slope could also be interpreted due to the changes in adsorption heat with increasing surface coverage which has also been ignored in the derivation of Langmuir isotherm (Oguzie et al., 2004).

The experimental data have been then fitted into the modified form of Langmuir isotherm known as El-Awady isotherm which can appropriately represent the adsorption behavior of the inhibitor onto the iron surface.

El-Awady isotherm is given by (El-Awady et al., 1992)

$$\log(\theta/1 - \theta) = \log \text{K} + y \log \text{C} \tag{8}$$

where, y is number of inhibitor molecules occupying one active site. θ (IE/100) is the surface coverage. C is the concentration, K is the constant related to the equilibrium constant of adsorption process. $K_{ads} = K^{1/y}$ and y represent the number of inhibitor molecules occupying a given site. The values of $1/y$ calculated from El-Awady model is given in Table 3. The
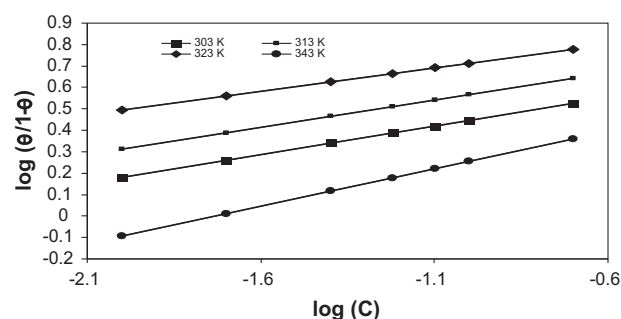

Figure 5 Langmuir isotherm plots for adsorption of PVAMOA on the mild steel surface in 1 M HCl solution.

Table 3 Adsorption parameters calculated from Langmuir adsorption isotherm.

Temperature (K)	K_{ads}/ppm	$1/y$	R^2	Slope	ΔG_{ads} (kJ/ppm)
303	4.73×10^4	3.7603	0.7771	0.2659	−25.64
313	1.68×10^5	3.9282	0.6630	0.2545	−29.78
323	1.91×10^6	4.6013	0.9282	0.2173	−37.26
333	3.07×10^4	2.5293	0.9056	0.3953	−26.98
343	5.39×10^3	2.8750	0.8687	0.3478	−22.83
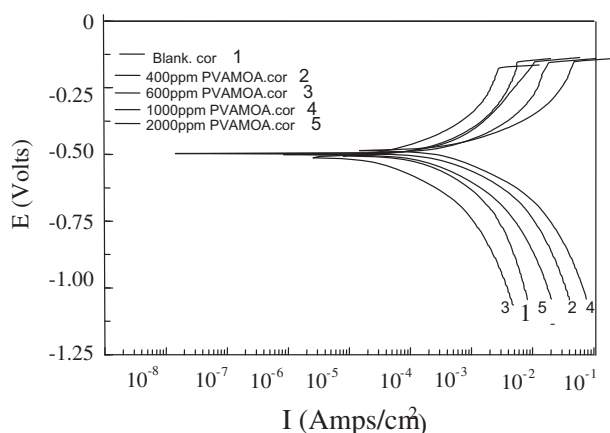
Figure 6 Potentiodynamic polarization behavior of mild steel in 1 M HCl with the addition of PVAMOA.

values of $1/y$ less than one imply multilayer adsorption. In the current work the values of $1/y$ obtained were more than unity which indicates that each molecule of PVAMOA involved in the adsorption process was attached to more than one active site on the metal surface. K_{ads} represents the strength between adsorbate and adsorbent. Larger values of the K_{ads} implied more efficient adsorption and hence better IE. With increase in the temperature, K_{ads} value decreased in the presence of PVAMOA indicating that the adsorption of composite on the mild steel surface was unfavorable at higher temperatures.

The equilibrium constant for the adsorption process was related to the standard free energy of adsorption by the expression

$$\Delta G_{ads} = -2.303\,RT \log(55.5\,K_{ads}) \tag{9}$$

where ΔG_{ads} is Gibbs free energy of adsorption, T is the temperature in Kelvin and 55.5 is the molar concentration of water in solution. The negative values of ΔG_{ads} ensure the spontaneity of adsorption process and stability of the adsorbed layer on

the metal surface (Bentiss et al. 2005). Generally, values of (ΔG_{ads}) up to −20 kJ ppm−1 are consistent with the electrostatic interactions between the charged molecules and the charged metal (physisorption) while those around −40 kJ ppm−1 or higher are associated with chemisorption as a result of sharing or transfer of electrons from polymer molecules to the metal surface to form a coordinate type of bond (chemisorption) (Hosseini et al., 2003). The values of ΔGads listed in Table 3 indicate the chemisorption of PVAMOA on the mild steel surface. Inspection of Table 3 revealed that ΔGads value decreases from −26 to −22 kJ ppm−1 with increasing temperature from 333 to 343 K. These results showed that inhibition efficiency decreased with increase in temperature (Ahamad and Quraish, 2010).

3.4. Electro chemical measurements
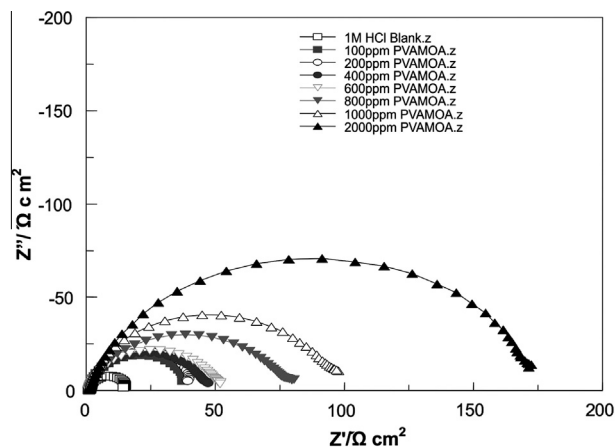
3.4.1. Tafel polarization

The Tafel polarization curves for mild steel in hydrochloric acid with the addition of various concentrations of PVAMOA are shown in Fig. 6. Electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel constants (b_a and b_c), IE and CR were calculated from the Tafel plots and are given in Table 4. It was evident from the Table 4 that the corrosion current value (I_{corr}) was decreased from 59.81 mAcm^{-2} of the blank to 32.22 mAcm^{-2} with the addition of 100 ppm inhibitor and it gets further reduced gradually with increasing concentrations of inhibitor. No definite trend was observed in the shift of E_{corr} values. Both anodic and cathodic reactions of mild steel electrode corrosion were inhibited with the increase of PVAMOA concentration and the addition of PVAMOA in 1 M HCl solution modified slightly the cathodic and anodic slopes (Fig. 6 and Table 4). This result showed that the addition of PVAMOA reduced the anodic dissolution and also retards the hydrogen evolution reaction, indicating that this inhibitor exhibited both cathodic and anodic inhibition effects (Olivares et al. 2006). Therefore, PVAMOA can be classified as inhibitor of relatively mixed effect (anodic/cathodic inhibi-

Table 4 Electrochemical parameters for the corrosion of mild steel in 1 M HCl containing PVAMOA.

Conc. (ppm)	E_{corr} (mV(SCE))	I_{corr} 10^{-4} (mA /cm^2)	b_a (mV/dec)	b_c (mV/dec)	IE (%)	R_P (Ohm cm^2)	IE (%)
Control	−481.11	59.81	153.48	124.9		4.85	
100	−454.29	32.22	132.6	114.61	46.13	7.53	35.59
200	−447.93	23.73	124.87	103.18	60.32	12.09	59.88
400	−451.6	23.34	145.11	122.48	60.98	12.44	61.01
600	−445.94	21.7	140.62	105.6	63.72	12.5	61.20
1000	−443.37	17.52	134.37	98.69	70.71	13.3	63.53
2000	−459.04	14.91	149.22	137.79	75.07	16.47	70.55

Table 5 Parameters derived from Nyquist plot of mild steel in 1 M HCl containing PVAMOA.

Concen. (ppm)	R_{ct} (Ohm cm^2)	IE (%)	C_{dl} (μF/cm^2)	θ
Control	14.59		39.04	
100	38.5	62.10	16.63	0.57
200	40.35	63.84	15.86	0.59
400	45.52	67.95	14.06	0.64
600	50.05	70.85	12.79	0.67
800	76.33	80.89	8.39	0.79
1000	94.99	84.64	6.74	0.83
2000	173.73	91.60	3.68	0.91

3.4.3. Electro chemical impedance studies

The impedance parameters deduced from the analysis of Nyquist diagram and values of IE are given in Table 5. As it can be seen, the impedance response of mild steel in uninhibited solution has significantly changed after the addition of PVAMOA. Nyquist plots (Fig. 7) were depressed into the real axis and not perfect semi-circles as a result of the roughness and other in homogeneities of the metal surface (Lebrini et al., 2007). Double layer capacitance values (C_{dl}) and charge-transfer resistance values (R_{ct}) were obtained from impedance measurements. By increasing the inhibitor concentration, R_{ct} value increased. A large R_{ct} has associated with a slower corroding system. Furthermore, better protection provided by an inhibitor could be associated with a decrease in capacitance of the metal. The decrease in C_{dl}, which could result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that PVAMOA molecules function by adsorption at the metal solution/interface. Increase in surface coverage value from 0.57 to 0.91 has been found due to reduction in C_{dl} value in the presence of inhibitor.

3.5. Scanning electron microscope

The micrograph of mild steel specimen without polymer composite showed a large number of pits and cracks due to the attack of aggressive corrosive medium (Fig. 8a). SEM micrographs of mild steel specimen in the presence of polymer composite illustrated a uniform layer formation on the metal surface (Fig. 8b). This showed that PVA incorporated polymethoxyaniline has more surface adhesion and close packing nature. (Athawal and Bhagwat, 2003). As shown in the SEM image, each unit has many polymer granules. This might be due to the multiple nucleation of polymer preferentially on the same site of the substrate. In some of the micrographs, it was possible to see a compact granular structure with few pores between the grains. This observation was similar to the report of polyaniline metal bilayer coating (Ananda Kumar et al., 2008). The resulting micrograph revealed that the surface was strongly damaged owing to corrosion in the absence of the inhibitor, but in the presence of the inhibitor there was much less damage on the surface. This was attributed to the formation of a good protective film on the mild steel surface (Migaheda et al., 2011).

Figure 7 Nyquist plot of mild steel in 1 M HCl with different concentrations of PVAMOA.

tion) in 1 M HCl. It was also observed that the values of b_a and b_c did not show any significant change indicating that the studied inhibitor is a mixed type inhibitor.

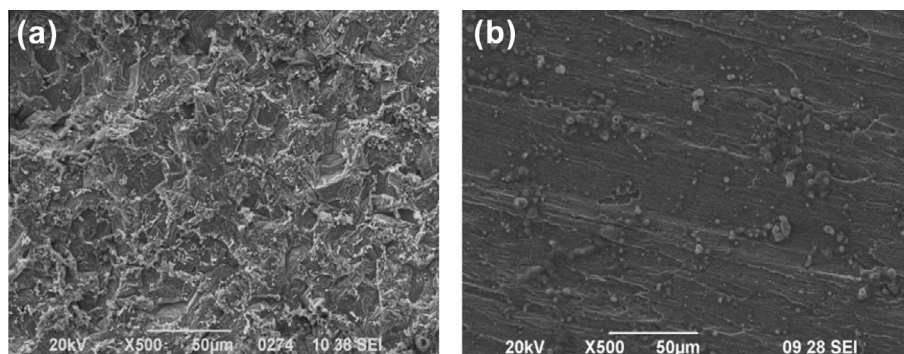### 3.4.2. Polarization resistance study

The polarization resistance (R_p) values of mild steel in hydrochloric acid increased from 4.85 Ohm cm^2 that of the blank to 16.47 Ohm cm^2 with 2000 ppm concentration of inhibitor (Table 4). The increase in R_p value showed that IE increases with increase in the inhibitor concentration.

Figure 8 (a) Scanning electron micrographs of mild steel immersed in 1 M HCl at 500 magnification. (b) Scanning electron micrograph of PVAMOA deposited on the mild steel surface.

3.6. Mechanism of inhibition

The inhibition of active dissolution of the metal was due to the adsorption of the inhibitor molecules on the metal surface forming a protective film. Poly methoxy aniline might adsorb on the iron surface as (i) by sharing of electrons between the nitrogen atom and iron. (ii) through π electron interactions between the benzene ring of the molecule and the metal surface. (iii) through the cationic form with positively charged part of the molecule oriented toward the negatively charged iron surface. As chloride ions were adsorbed on the iron surface, the cationic form of methoxy aniline molecule can adsorb on the iron surface. The adsorption of polymer composite on anodic sites occurs through the π electrons of the aromatic rings and lone pair electrons of nitrogen and oxygen atoms which may decrease the anodic dissolution of mild steel. The adsorption mechanism may take place by electrostatic attraction between the charged molecules and charged metallic ions. As the electron density around nitrogen of the amino group formed coordination bonds with Fe atoms a protective layer on the metal surface evolves to shield steel from the aggressive environment (Azhar et al., 2002).

4. Conclusion

The results obtained from weight loss, EIS and polarization measurements showed that the adsorption of PVAMOA composite at the metal/acid solution interface occurs which inhibited corrosion of mild steel in 1 M HCl solution. The inhibition efficiencies determined by weight loss and electrochemical measurements were in reasonable agreement. The inhibition efficiency of PVAMOA was found to decrease with increasing temperatures. The corrosion process was inhibited by the adsorption of PVAMOA on the mild steel surface fits Langmuir isotherm followed by El Awady adsorption model. The kinetic parameter obtained from the study indicated that the presence of inhibitor increased the activation energy and the negative value of ΔG showed the spontaneous adsorption of the inhibitor on the surface of mild steel. SEM analysis has given the inference of the surface morphology that was smoothly covered by composite film.

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