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ORIGINAL ARTICLE

Electrochemical investigation of corrosion and corrosion inhibition of iron in hydrochloric acid solutions

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Abstract The inhibition effect of 1-methyl pyrazole (MPA) on the acidic corrosion of iron in 1.0 M HCl was studied at different concentrations (10^{-3}–10^{-2} M) by potentiodynamic polarization and electrochemical impedance spectroscopy, and EIS measurements. It is found from the polarization studies that methyl pyrazole (MPA) behaves mainly as anodic inhibitor in HCl. Values of polarization resistance (R_p) and double layer capacitance (C_{dl}) in the absence and presence of MPA in 1.0 M HCl are determined. The adsorption of MPA on iron surface from HCl is found to obey Temkin adsorption isotherm.

1. Introduction

In practice, numerous chemical compounds are used for the prevention and long-term control of corrosion, inhibiting the aggressive action of the medium in contact with metallic constructions (Subramania et al., 2004; Larabi et al., 2004; Rajendran et al., 2005; Ashassi et al., 2009; Bibicu et al., 2004; Samide et al., 2004, 2008; Okafor et al., 2010; Khaled, 2009b). The inhibition importance is greater in hydrochloric acid solutions since iron and its alloys are the most exposed materials both in industrial and other media, these metallic materials being more susceptible to an attack in acid pH medium rather than in alkaline one. The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the layer formed on the metal surface under particular experimental conditions (Samide et al., 2009, 2005; Bentiss et al., 2000; Samide and Bibicu, 2008; Maaya and Al-Rawashdeh, 2004). The available results show that most inhibitors act by adsorption on the metal surface (Solmaz et al., 2008; Moretti et al., 2004). The strength of adsorption and hence, the inhibition extent are dependent on the organic compounds nature, the metal nature and the corrosive media.

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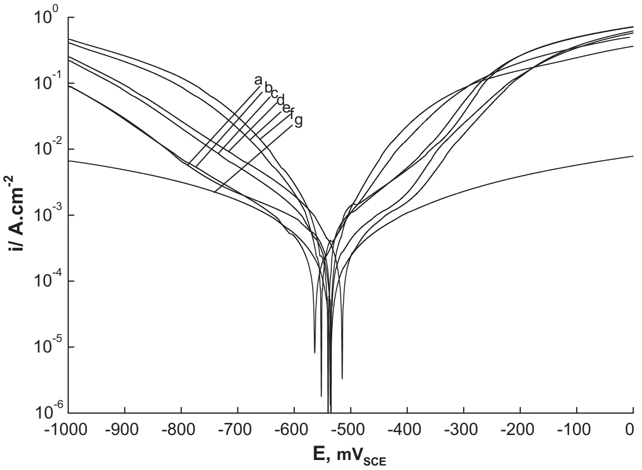

Figure 1 Potentiodynamic polarization curves of iron immersed in 1.0 M HCl and different concentrations of 1-methyl pyrazole (MPA): (a) Blank, (b) 1×10^{-3}, (c) 3×10^{-3}, (d) 5×10^{-3}, (e) 7×10^{-3}, (f) 9×10^{-3}, (g) 10×10^{-3}.

Table 1 Electrochemical parameters for iron in 1.0 M HCl with different concentrations of 1-methyl pyrazole at 25 °C.

Conc. (M)	i_{corr} (μA cm^{-2})	$-E_{corr}$ (V)	$-b_c$ (V dec^{-1})	$-b_a$ (V dec^{-1})	CR$_{mpy}$	ψ%
Blank	965.2	0.535	0.131	0.091	882.5	–
1×10^{-3}	826.6	0.520	0.119	0.107	755.8	14.35
3×10^{-3}	726.4	0.522	0.120	0.097	664.2	24.73
5×10^{-3}	544.1	0.502	0.133	0.100	497.5	43.62
7×10^{-3}	433.1	0.499	0.142	0.099	396.0	55.127
9×10^{-3}	393.2	0.487	0.146	0.095	359.5	59.26
10×10^{-3}	368.8	0.479	0.138	0.107	337.2	61.79

Acidizing is the stimulation technique used to make water-insoluble salts into water-soluble salts. It includes the use of solvents and surfactants to dissolve and disperse organics. Hydrochloric acid is the major acidizing agent and is probably the most corrosive medium that oil and gas well tabular and down hole tools ever come into contact with. An acid corrosion inhibitor is generally included with the acid when treating a formation. The inhibition characteristics of some inhibitors have already been reported (Abdel-Rehim et al., 2006; Khaled, 2008a,b,c,d,e,f, 2009a; Khaled and Amin, 2008; Abdel Rehim et al.,2001). The aim of this work is to study the corrosion inhibition characteristics of iron in the absence and presence of 1-methyl pyrazole (MPA) in acid chloride media.

2. Experimental details

Iron specimens from Johnson Mattey (Puratronic, 99.995%) were mounted in Teflon. An epoxy resin was used to fill the space between Teflon and iron electrode in order to prevent crevice corrosion. The electrochemical measurements were performed in a typical three-compartment glass cell; the iron specimen was the working electrode. Pt gauze was used as an auxiliary electrode and a saturated calomel electrode (SCE) was used as a reference electrode. The auxiliary electrode was separated from the working electrode compartment by fritted glass. The reference electrode was connected to Luggin capillary to minimize IR drop and chloride contamination.

Solutions were prepared from deionized water of resistivity equal to 13 M Ω cm. The specimens were abraded with emery papers, washed with double-distilled water, etched in 12.0 M HCl for 10 min, and rinsed with double distilled water and then with acetone before immersion in the solutions. This procedure was used to ensure a reproducible starting surface state. The electrode potential was allowed to stabilize 30 min before starting the measurements. All experiments were conducted at 25 °C. The solutions were prepared by mixing HCl (Fisher Scientific) with 1-methyl pyrazole (MPA) from Aldrich and were dissolved in HCl without any pretreatment. The measurements were performed by means of EG&G Princeton Applied Research Potentiosate/Galvanostat (PAR model 273) in com-

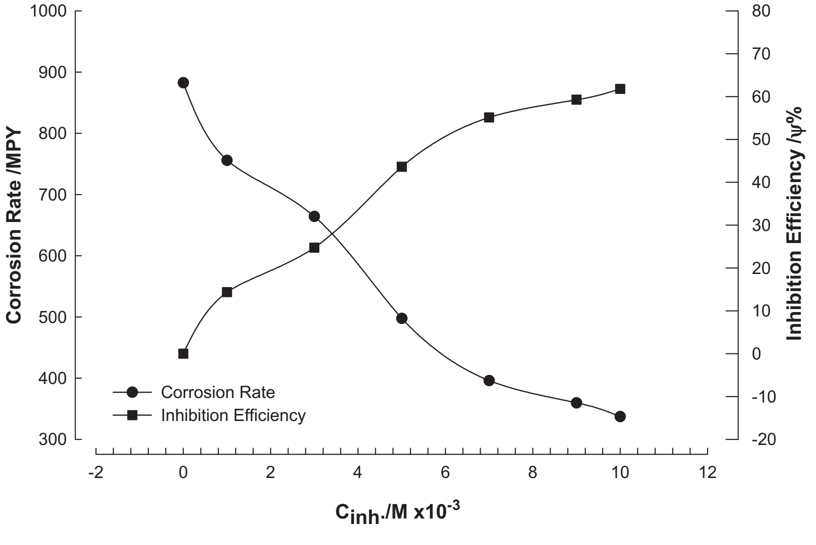

Figure 2 The corrosion rate/mpy and the inhibition efficiency ψ% for iron in 1.0 M HCl containing different concentrations of 1-methyl pyrazole (MPA) (from potentiodynamic data).

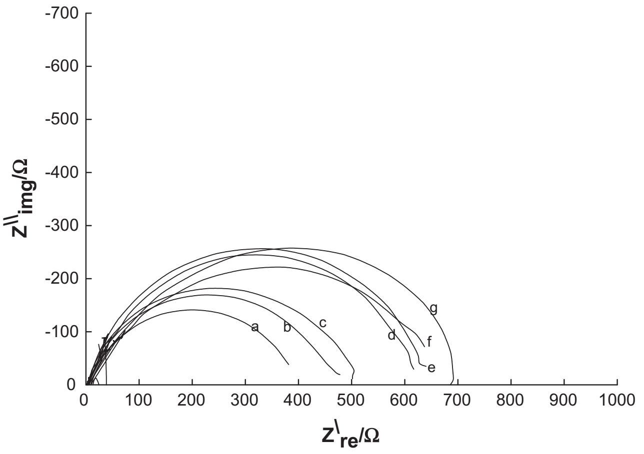

Figure 3 Nyquist plots of iron in 1.0 M HCl in the presence of different concentrations of 1-methyl pyrazole (MPA) at 25 °C, (a) Blank, (b) 1×10^{-3} M, (c) 3×10^{-3} M, (d) 5×10^{-3} M, (e) 7×10^{-3} M, (f) 9×10^{-3} M, (g) 10×10^{-3} M.

Table 2 Impedance data of iron in 1.0 M HCl solution containing different concentrations of 1-methyl pyrazole at 25 °C.

Conc. (M)	R_{ct} (Ω cm^2)	$1/R_{ct}$ (Ω^{-1} cm^{-2})	C_{dl} (μA cm^{-2})	δ%
Blank	427.4	2.339 E−3	93.5	–
1×10^{-3}	471.9	2.119 E−3	84.7	9.43
3×10^{-3}	528.5	1.892 E−3	75.6	19.13
5×10^{-3}	624.12	1.602 E−3	64.1	31.52
7×10^{-3}	660.59	1.513 E−3	60.5	35.30
9×10^{-3}	738.17	1.354 E−3	54.2	42.10
10×10^{-3}	817.68	1.223 E−3	48.8	47.73

bination with a Solarton 1250 frequency response analyzer which was used for polarization and capacitance measurements. The system is attached to a PC for collecting data. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -1000 to 0.000 $\mathrm{mV_{SCE}}$ with a scan rate of 1.0 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 10 KHz to 10 mHz using an amplitude of 5 mV peak to peak using a.c. signal at open circuit potential. The softwares used in this study are electrochemical impedance software (Model 398), corrosion software (Model 352–252, Version 2.23), and equivalent circuit software (EQUIVCRT.PAS).

3. Results and discussion

The potentiodynamic curves of iron electrode in 1.0 M HCl, recorded in the absence and the presence of different concentrations of 1-methyl pyrazole, (MPA) are shown in Fig. 1. Fig. 1 shows that the addition of MPA to the acid solution shifts the anodic polarization to more positive and the cathodic polarization to more negative values. The effect of MPA is more pronounced on anodic polarization than on cathodic polarization. Values of the electrochemical parameters and the percentage inhibition efficiency are given in Table 1. The inhibition efficiency ψ% is given from the Eq. (1) Abdel Rehim et al., 2001:

$$\psi\% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \tag{1}$$

where i^0_{corr} and i_{corr} are the corrosion current densities of iron in 1.0 M HCl without and with MPA, respectively, which determined by extrapolation of Tafel lines. The values of i_{corr} decrease with increasing concentration, the decrease in i_{corr} values are associated with a shift in E_{corr} to less negative values. These results suggest that MPA behaves mainly as an

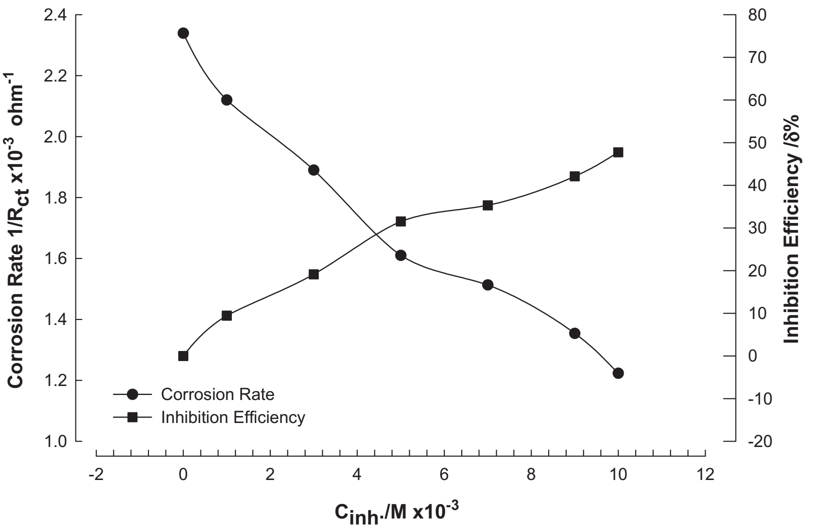

Figure 4 The inverse charge transfer resistance $1/R_{ct}$ and the inhibition efficiency δ% for iron in 1.0 M HCl containing different concentrations of 1-methyl pyrazole (MPA) (from impedance data).

anodic inhibitor. The approximately constant values of the Tafel slopes (near 0.09 V dec^{-1} for b_a and 0.13 V dec^{-1} for b_c suggest that the inhibition mechanism for MPA involves a single reaction site blocking (Khaled, 2008f, 2009a; Abdel Rehim et al., 2001).

Fig. 2 shows the effect of MPA on the corrosion rate of iron in 1.0 M HCl at 25 °C. The corrosion rate decreases with an increase in the concentration of MPA, presumably because of adsorption on the iron surface. Fig. 2 also shows that the inhibition efficiency $\psi\%$ increases with increasing the concentration of MPA.

Fig. 3 shows the Nyquist plots of iron in 1.0 M HCl without and with various concentrations of MPA (10^{-3}–10^{-2} M) at 25 °C.

This indicates that iron impedance increases with increasing the inhibitor concentration and consequently the inhibition efficiency increases. It is also apparent from these plots that Nyquist curves (Fig. 3) are consisted of one capacitive loop (one phase angle maximum in Bode format).

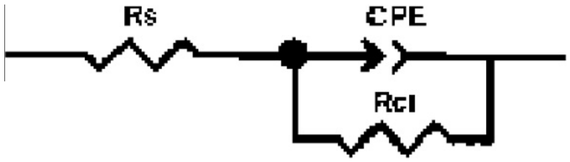

Figure 5 Equivalent circuit model for iron/1.0 M HCl interface.

Furthermore, the impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion (Mansfeld et al., 1982). The charge transfer resistance R_{ct} is calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. (1978). To obtain the double layer capacitance C_{dl}, the frequency at which the imaginary component of the impedance is maximum $(-Z''_{img})$ is found and C_{dl} values are obtained from the Eq. (2) Ross Macdonald, 1987.

$$f(-Z''_{max}) = \frac{1}{2\pi C_{dl} R_{ct}} \tag{2}$$

EIS results show that C_{dl} decreases and R_{ct} increases suggesting that the amount of the inhibitor molecules adsorbed increases.

The decrease in C_{dl} values could be attributed to local dielectric constant decrease and/or an increase in the thickness of the electrical double layer, signifying that MPA acts by adsorption at the metal/solution interface (Khaled, 2003). The MPA molecules adsorption also produces important modifications in the double electric layer structure. Electrode/electrolyte interfaces demonstrate a capacitance whose magnitude reflects the ions distribution on the solution side of the interface. The electrolyte double layer is composed of the Helmholtz layer consisting of ions and solvent in physical contact with the electrode and the diffuse layer, which contains iron ions near the electrode whose concentrations deviate from bulk concentrations (Samide et al., 2009).

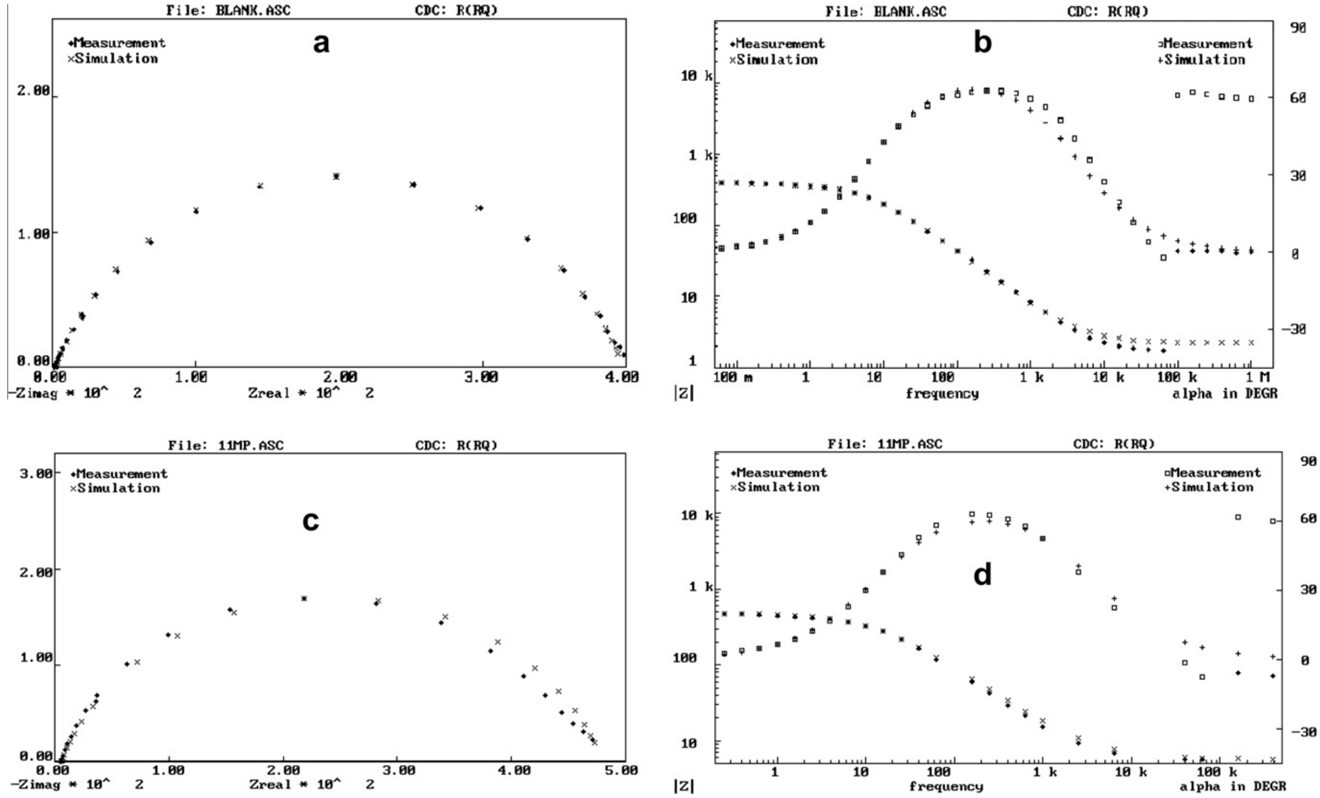

Figure 6 Impedance data for corroding iron at corrosion potential in 1.0 M HCl at 25 °C. Plot (a, c) shows the complex plan representation; each data point corresponds to a different frequency; Plot (b, d) shows the magnitude and phase angle of the impedance as a function of frequency. Plot (a, b) for blank, and (c, d) for 10^{-3} M 1-methyl pyrazole (MPA)/1.0 M HCl. (+) curves are the nonlinear regreation to the data, open symbols are experimental data.

According to these affirmations, the change in R_s, R_{ct} and C_{dl} values was caused by the gradual replacement of water molecules through MPA molecules adsorption on the metal surface (Muralidharan et al., 1995).

From the charge transfer resistance we can calculate the inhibition efficiency of the corrosion of iron, as in Eq. (3) Khaled, 2009a.

$$\delta\% = \left(1 - \frac{R^0_{ct}}{R_{ct}}\right) \times 100 \tag{3}$$

where R^0_{ct} and R_{ct} are the charge transfer resistance values without and with inhibitor, respectively. The impedance parameters derived from this investigation are given in Table 2. Fig. 4 shows that by increasing the concentration of MPA, corrosion rate ($1/R_{ct}$) decreases and the inhibition efficiency $\delta\%$ increases. The equivalent circuit model used to fit the experimental results is suggested in Fig. 5, the suggested model is used to generate the simulated data, which are fitted well with the experimental data as shown in examples Fig. 6a–d. The charge transfer resistance R_{ct} and the double layer capacitance were calculated and given in Table 2. The fitted parameters calculated using equivalent circuit in Fig. 5 are presented in Tables 3 and 4. It is clear that by increasing the concentration of the inhibitor MPA the corrosion rate $1/R_{ct}$ decreases and in the same time the inhibition efficiency $\delta\%$ increases.

Table 3 Circuit element R_s, R_{ct}, and CPE values and their error percent for circuit in Fig. 5 for iron in 1.0 M HCl.

Conc. (M)	Element	Value	Error	Error (%)
Blank	RS	1.6	0.05	3.1
	CPE-T	1.4 E−4	6.5 E−6	4.71
	CPE-P	0.78	6.3 E−3	0.79
	Rp	395.8	7.22	1.83

Table 4 Circuit element R_s, R_{ct}, and CPE values and their error percent for iron in 1.0 M HCl + 1-methyl pyrazole.

1-Methy pyrazole	Element	Value	Error	Error (%)
0.001.0 M	RS	5.57	0.14	2.56
	CPE-T	4.4E−5	3.53 E−6	6.53
	CPE-P	0.832	0.01	1.06
	Rp	427.1	8.08	1.89
0.003 M	RS	3.063	0.11	3.36
	CPE-T	4.66 E−5	3.25 E−6	6.98
	CPE-P	0.84	0.01	1.06
	Rp	493.2	10.9	2.22
0.005 M	RS	2.82	0.67	24.1
	CPE-T	7.9 E−5	1.2 E−5	16.2
	CPE-P	0.77	0.023	2.92
	Rp	545.7	11.21	2.05
0.007 M	RS	2.9	0.09	3.17
	CPE-T	4.5 E−5	1.2 E−6	2.54
	CPE-P	0.84	0.003	0.41
	Rp	581	4.9	0.84
0.009 M	RS	9.3	0.19	2.2
	CPE-T	5.2 E−5	3.1 E−6	5.9
	CPE-P	0.7	0.008	1.1
	Rp	688.6	7.9	1.2
0.01.0 M	RS	3.99	0.21	5.22
	CPE-T	7.6 E−5	5.9 E−6	7.7
	CPE-P	0.75	0.02	1.42
	Rp	756	20.24	2.67

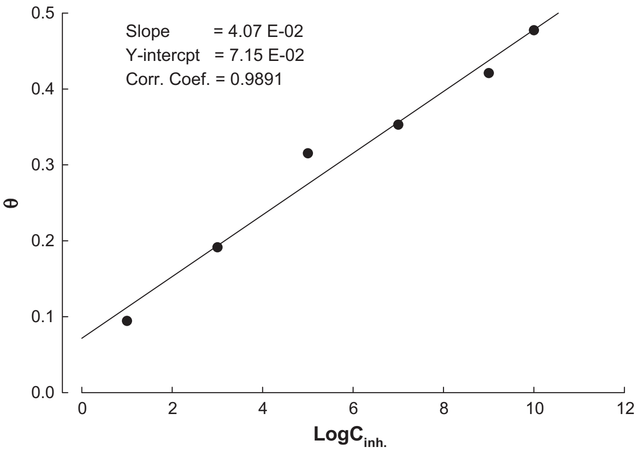

Figure 7 Temkin adsorption plots for iron in 1.0 M HCl containing different concentrations of 1-methyl pyrazole.

The adsorption of inhibitor molecules on the metal surface is a substitute process, during which the adsorbed water molecules on the metal surface are replaced by inhibitor molecules. In order to better understand the adsorption mechanism, the degree of surface coverage θ for different concentrations in HCl has been evaluated from electrochemical measurements, using the following Eq. (4) Khaled, 2009a:

$$\theta = 1 - \frac{R^0_{ct}}{R_{ct}} \tag{4}$$

The Plot of θ versus Log C_{inh} yields a straight line, Fig. 7, proving that the adsorption of MPA from HCl solutions on the iron surface obeys Temkin adsorption isotherm.

This isotherm clearly reveals that the adsorption of MPA on the carbon steel surface obeys the Temkin adsorption isotherms, and the inhibitor molecules are adsorbed on iron surface forming a film, which prevents the iron from corrosion induced by the medium.

The adsorption of MPA on the metal surface can occur either directly on the basis of donor-acceptor interactions between the π-electrons of the heterocyclic compound and the vacant d-orbitals of iron surface atoms or by the interaction of MPA with already adsorbed chloride ions (Hackerman et al., 1966). The performance of 1-methylpyrazole as an inhibitor in 1.0 M HCl can be explained in the following way. In aqueous acidic solutions, the 1-methylpyrazole compound exists either as neutral molecules or in the form of cations. Amines may be adsorbed on the metal surface in the form of neutral molecules, involving the displacement of water molecules from the metal surface and sharing of electrons between the nitrogen atoms and the metal surface (Khaled, 2008f). Amines and heterocyclic nitrogen compounds may also adsorb through electrostatic interactions between the positively charged nitrogen atom and the negatively charged metal surface (Khaled et al., 2009). The presence of lone pairs and π-electrons of the 1-methypyrazole compound enhanced the inhibitory effect of this compound.

4. Conclusion

It can be concluded that MPA inhibits the corrosion of iron in HCl solutions. MPA behaves mainly as an anodic inhibitor. The adsorption of MPA from HCl obeys Temkin adsorption isotherm.

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