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THE EFFECT OF TEMPERATURE ON MILD STEEL CORROSION IN 1 M HCl BY SCHIFF BASES

(Kesan Suhu Terhadap Kakisan Keluli Lembut Dalam 1 M HCl oleh Ligan Bes Schiff)

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Abstract

The temperature effects in the range of 25 to 55°C on the inhibition efficiency of three Schiff bases which were (*E*)-*N*^{1}-benzylidene-*N*^{4}-phenylbenzene-1,4-diamine (K1), *N*-[(*E*)-4-chlorobenzylidene-*N*`-phenylbenzene-1,4-diamine (K2), and *N*-[(*E*)-4-methoxybenzylidene-*N*`-phenylbenzene-1,4-diamine (K3) against mild steel in 1 M hydrochloric acid (HCl) solution were studied using polarization method. Thermodynamic adsorption parameter suggests that the inhibitors under study were mixed type inhibitors dominated by anodic reaction and it was found that from all of the three inhibitors, K2 having the highest corrosion inhibition efficiency.

Keywords: 1 M HCl, mild steel, Schiff base, temperature, corrosion

Abstrak

Kesan suhu dalam lingkungan 25 hingga 55°C kepada kecekapan pengekangan tiga ligan bes Schiff iaitu (*E*)-*N*^{1}-benzylidene-*N*^{4}-phenylbenzene-1,4-diamine (K1), *N*-[(*E*)-4-chlorobenzylidene-*N*`-phenylbenzene-1,4-diamine (K2), dan *N*-[(*E*)-4-methoxybenzylidene-*N*`-phenylbenzene-1,4-diamine (K3) terhadap keluli lembut dalam 1 M asid hidroklorik (HCl) telah dikaji dengan menggunakan kaedah polarisasi. Parameter penjerapan termodinamik mencadangkan bahawa perencat di bawah kajian ialah perencat jenis bercampur dikuasai oleh reaksi anodik dan didapati bahawa dari ketiga-tiga perencat, K2 mempunyai tertinggi kecekapan kakisan pengekangan.

Kata kunci: 1 M HCl, keluli lembut, bes Schiff, suhu, kakisan

Introduction

In industrial applications such as acid pickling, the metals are immersed in an appropriate acid media to eliminate unwanted rust and mill scale. After the scales are removed, the surface of the metal is exposed for dissolution of metal due to the attack of the aggressive media. To overcome this problem organic inhibitors are added into the acid pickling bath generally hydrochloric acid solution at elevated temperature to inhibit the corrosion of metal [1]. The acid inhibitors available are mostly organic compounds containing heteroatoms of N, O and S which effectively retarding the dissolution of metal in an acid solution by adsorption on the surface of metal [2]. Schiff base known as a nitrogen bearer (C=N bond) inhibitor was chosen due to the planarity and lone pair of electrons in its molecular structure therefore increase the adsorption on the active sites of metal surface as reported to by several authors [3,4]. These inhibitors have to be chemically stable and provide high protection to the metal from the corrosive media even under high temperature condition. The aim of this work is to study the temperature effect of studied Schiff bases (Table 1) as organic inhibitor in retarding the corrosion of mild steel in 1 M HCl. The investigated Schiff bases are selected based on the analogous molecular area and any distinction in the inhibiting properties attributed mainly due to effect of substituent in the molecular structure of the organic compound.

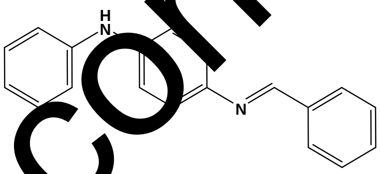
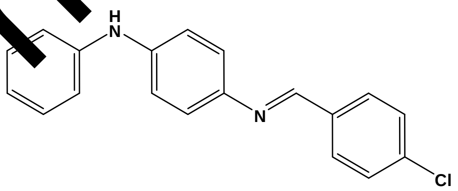
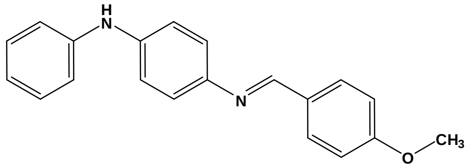
Materials and Methods

Schiff bases as in Table 1 were synthesized using the established method [5] and structure confirmation was done by elemental analysis, infrared spectroscopy (IR), and nuclear magnetic resonance spectroscopy (NMR). Electrode for polarization measurement was square shaped mild steel specimen embedded in an epoxy resin having exposed surface area of 0.049 cm^2. The specimen was mechanically polished using different grades of silica carbide paper then polished to mirror finish using diamond paste. It was degreased with ethanol and cleaned using distilled water and lastly dried before introducing it to the acidic solution. The test was carried out at stagnant open air condition in a 100 ml volume cell using a thermostat controlled waterbath and experiment was conducted at 25, 35, 45 and 55^oC. In the conventional three electrode cell system, platinum rod as counter electrode, Gamry instruments silver-silver chloride ($Ag|AgCl|Cl^-$) as reference electrode and mild steel as working electrode were employed. The measurement was done using Gamry 600^{TM} potentiostat/galvanostat potential connected to a personal computer. For polarization method, the working electrode was immersed completely in the acid solution at open circuit potential (E_{ocp}) in 30 min. The curves were obtained in the potential sweeping rate of 1 mV/sec from the corrosion potential (E_{corr}) in the cathodic followed by anodic direction. Inhibition efficiency (η_{pol}%) were calculated using equation (1) [6].

$$\eta_{pol}\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} x100 \qquad (1)$$

where i_{corr} and i'_{corr} are the corrosion current densities without and with addition of inhibitors, respectively.

Table 1: Schiff base under investigation

Inhibitor	Structure	Abbreviation	Molar mass (g/mol)
(*E*)-N^1-benzylidene-N^4-phenylbenzene-1,4-diamine		K1	272.34
N-[(*E*)-4-chlorobenzylidene]-*N*'-phenylbenzene-1,4-diamine		K2	306.79
N-[(*E*)-4-methoxybenzylidene]-*N*'-phenylbenzene-1,4-diamine		K3	302.37

Results and Discussion

The change in the corrosion rate of mild steel in 1 M HCl at different temperatures was investigated in the presence of 2.0 mM inhibitor and absence of inhibitor. The corrosion parameters extracted from polarization measurements at different temperatures are shown as in Table 2 while the polarization curves are demonstrated in Figure 1. In Figure 1, it is apparent that by increasing the temperature of the solution, the values of i_{corr} in the absence and presence of corrosion inhibitors are increased (Table 2). The increases in i_{corr} indicate increase in hydrogen gas evolution (cathodic reaction) and also iron corrosion (anodic reaction) in the corrosive solution [7]. Furthermore, the corrosion potential (E_{corr}) in the inhibited solution shifted to anodic region at higher temperature in comparison to the 1 M HCl. This finding suggests inhibitors are mixed type predominantly anodic.

From Table 2, most of the studied compounds demonstrated decreased in the inhibition efficiency (η_{pol}%) at higher temperature apart from K2. The results for η_{pol}% differ slightly at certain temperature for each inhibitor, but sustain the efficiency to protect mild steel from corroded in the acid solution at highest temperature studied compared to the blank of 1 M HCl. At 25°C, the highest η_{pol}% is as follows: K2 > K1 > K3. The K1 inhibitor η_{pol}% at 25°C is 95.1 %, but the value slightly increased at 35°C and starting to decrease again until 84.3% at 55°C. For K2, the η_{pol} % slightly increases up to 97.2% at the highest temperature examined. As for K3, η_{pol}% illustrate decrease in value but sudden slight increase at 95.0% during 45°C then starting to decrease until 81.8% at the highest temperature tested. Thus at 55°C only K2 have high η_{pol}%, and the order for inhibition efficiency at the temperature is as follows: K2 > K1 > K3. The reason is that the effect of temperature in the presence of inhibitor at the metal interface reaction is highly complex since modification at the mild steel surface example as etching at higher rate, inhibitors desorption process at the surface and decomposition at elevated temperature [8].

Table 2: Corrosion parameter values from polarization measurements for mild steel in 1 M HCl at inhibitors optimum concentration (2.0 mM) in different temperatures

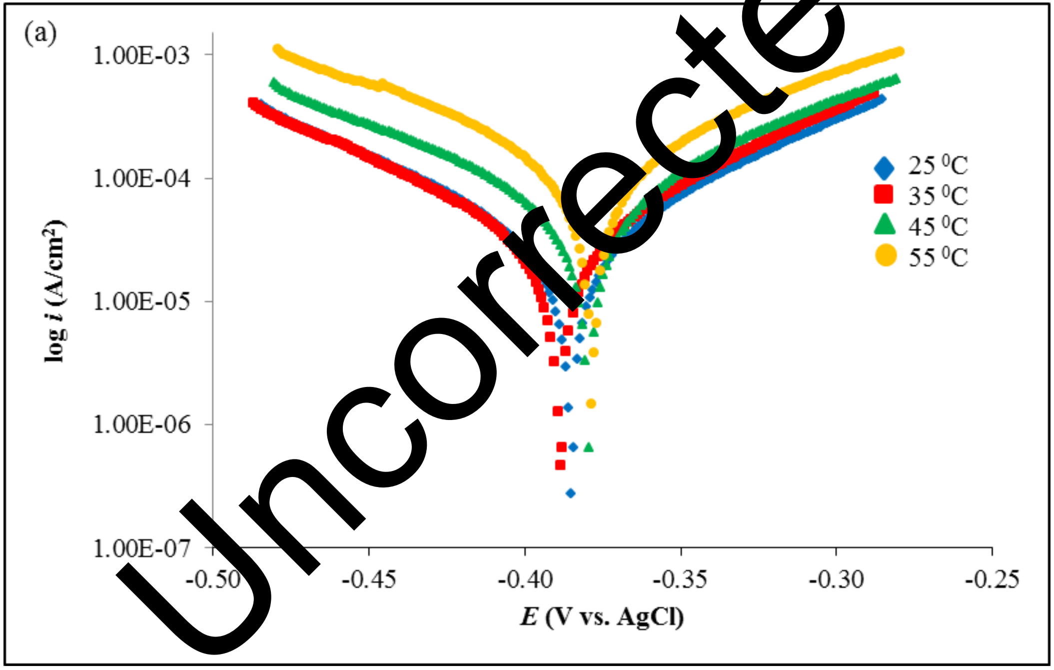
Compound	**Temperature (°C)**	**i_{corr} (μA/cm^2)**	**E_{corr} (-mV)**	**η_{pol} %**
1 M HCl	25	706.1	385	-
	35	767.3	389	-
	45	1359	380	-
	55	1724	378	-
2.0 mM K1	25	34.63	373	95.1
	35	38.78	343	95.0
	45	122.9	359	91.0
	55	271.4	367	84.3
2.0 mM K2	25	20.86	354	96.0
	35	22.14	343	97.1
	45	41.80	341	96.9
	55	48.71	357	97.2
2.0 mM K3	25	42.61	354	94.0
	35	45.71	387	94.0
	45	67.55	356	95.0
	55	314.3	374	81.8

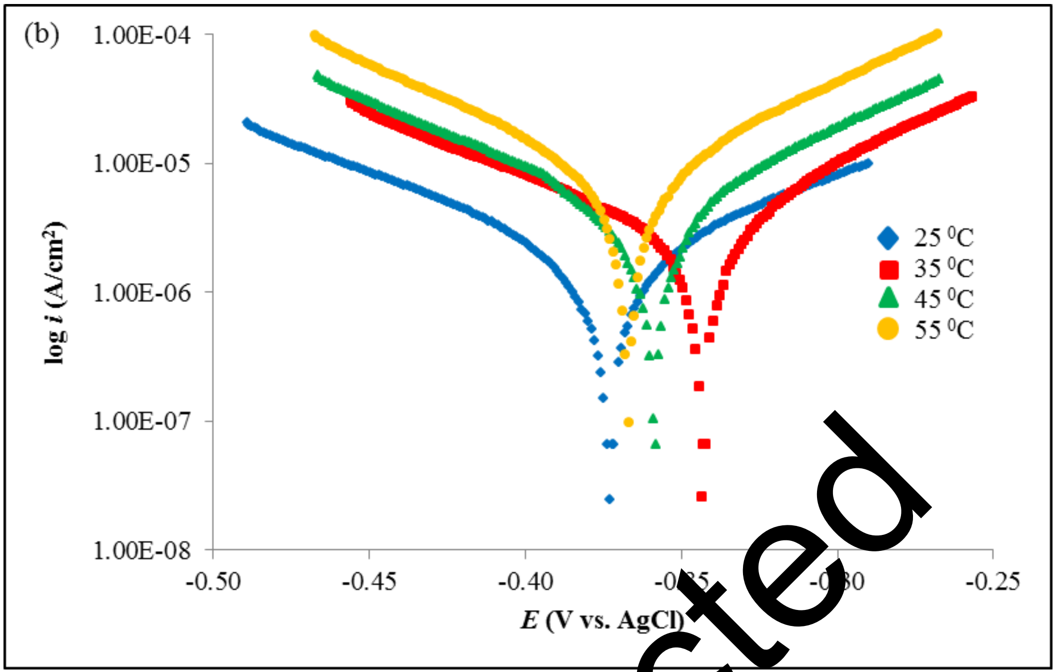
According to the Arrhenius equation to express the activation energy (E_a) of corrosion process of mild steel in the blank solution of 1 M HCl and presence of 2.0 mM inhibitors, the calculation involve is as following equation (2) [8]:

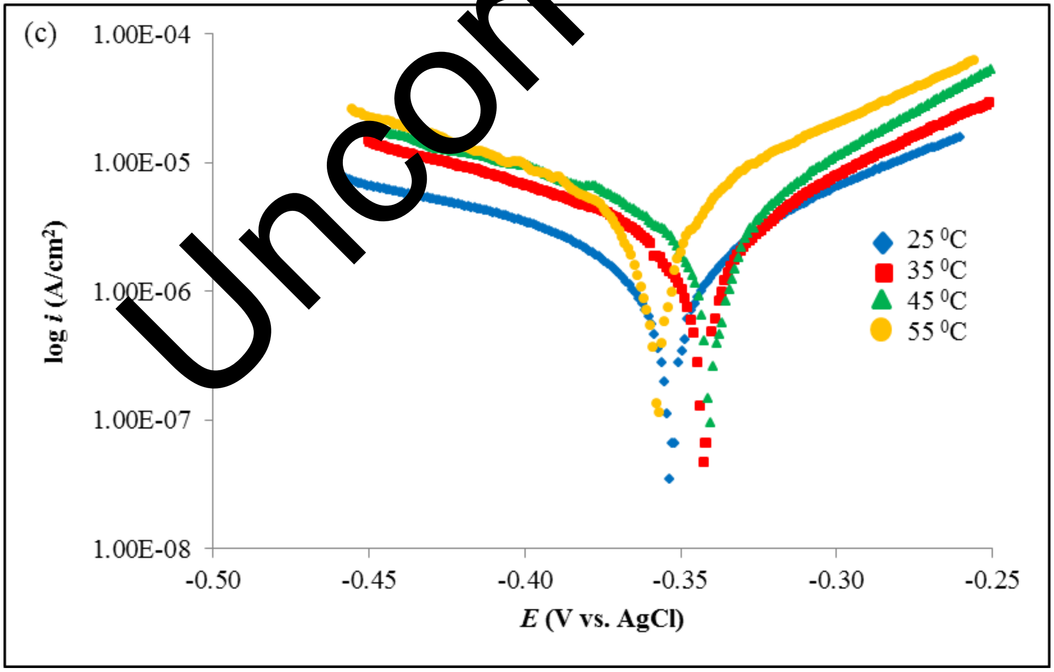
$$i_{corr} = k \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where E_a is the activation energy in the corrosion of iron reaction in kJ mol^{-1}, k is the pre-exponential constant, R is the gas constant and T is the temperature in Kelvin (K). using the logarithm form equation (3) [9]:

$$\log i_{corr} = \log k - \frac{E_a}{RT} \tag{3}$$




(b)
1.00E-04
1.00E-05
1.00E-06
1.00E-07
1.00E-08
log i (A/cm^2)
-0.50
-0.45
-0.40
-0.35
-0.30
-0.25
E (V vs. AgCl)
25 ^{0}C
35 ^{0}C
45 ^{0}C
55 ^{0}C


(c)
1.00E-04
1.00E-05
1.00E-06
1.00E-07
1.00E-08
log i (A/cm^2)
-0.50
-0.45
-0.40
-0.35
-0.30
-0.25
E (V vs. AgCl)
25 ^{0}C
35 ^{0}C
45 ^{0}C
55 ^{0}C

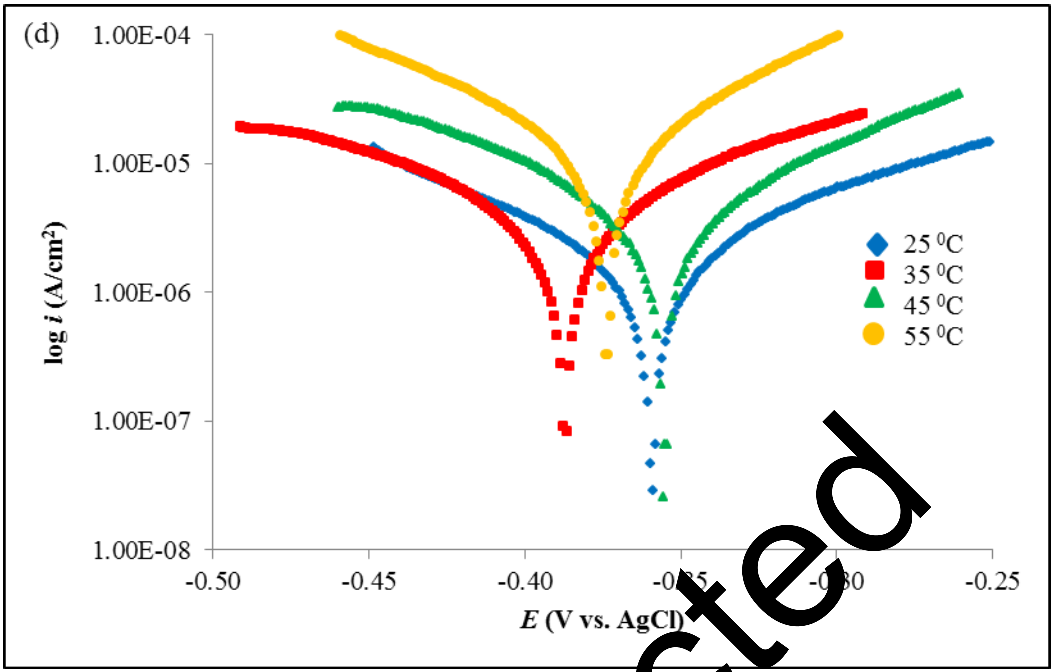


Figure 1: Potentiodynamic curves of mild steel in (a) 1 M HCl, (b) 1 M HCl + 2.0 mM of K1, (c) 1 M HCl + 2.0 mM of K2 and (d) 1 M HCl + 2.0 mM of K3 at different temperatures.

In Figure 2, it demonstrates the Arrhenius plot of mild steel in 1 M HCl as previously discussed in the absence and with addition of 2.0 mM Schiff base inhibitors. The graph of log i_{corr} vs. 1/T in this figure presents linear line having slope of ($-E_a$/R). The calculated E_a presented as in Table 3 demonstrate the values of E_a for K2 is lower compared to the 1 M HCl while for K1 and K3 are higher than the blank solution. The inhibition efficiencies correlate to the activation energies for organic inhibitors are classified into three categories which also related to the temperature effects [10]:

1. Inhibitors in whose presence the inhibition efficiency increases with temperature increased while the value of E_a for the corrosion process is lower than that obtained in the uninhibited solution.
2. Inhibitors whose inhibition efficiency does not change with temperature variation. The apparent activation energy does not change with the presence and absence inhibitors.
3. Inhibitors in whose presence the inhibition efficiency decreases with temperature increased while the value of E_a for the corrosion process is higher than that obtained in the uninhibited solution.

The increase of inhibition properties along with the increase in temperature indicates chemisorption type of adsorption [11] while the decrease in inhibition efficiencies suggests the physical adsorption on the surface of metal [12]. Generally, presence of π electron in the benzene ring and C=N bond in the studied planar Schiff base structure facilitates the adsorption interaction of organic inhibitor as electron donator to the metal surface since iron acts as electron acceptor in the chemisorption bond [13]. Thus, it can be recommended that K2 ligand form strong chemisorptive bond even at 55°C hence provide better protection on mild steel surface compared to the other studied Schiff base ligands since K2 have –Cl substitution at the para-position in phenyl ring and the –Cl assist N in formation of this type of bond to the iron surface [14]. The adsorption mechanism for inhibitors depends on the functional group available in that structure molecule, because certain groups adsorbed at different degree [15].

Table 3. Thermodynamic parameters for adsorption of studied inhibitors on the mild steel surface in 1 M HCl

Inhibitor	**E_a (kJ/mol)**
1 M HCl	26.31
K1	59.11
K2	25.82
K3	51.07

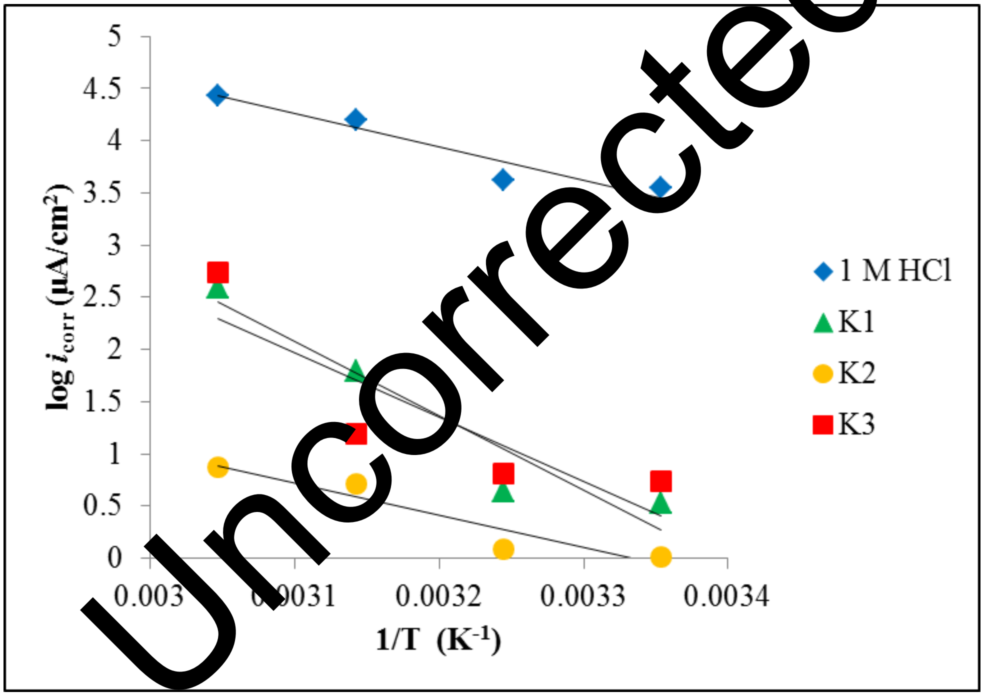


Figure 2: Arrhenius plot obtained from mild steel current density in 1 M HCl

The K1 and K3 organic inhibitors having E_a higher than that found in 1 M HCl suggesting the type of adsorption formed between inhibitor and iron predominantly is physisorption. In an acidic solution, some Schiff bases are protonated and exist in cationic form along with the molecular Schiff base in the solution. The already adsorbed chloride ions from the electrolyte at the iron surface causes the cationic form of the inhibitors of K1 and K3 adsorbed via electrostatic interaction. Generally, methoxy (-OCH_3) substituent as in K3 is known to have high inhibition efficiency since it is an electron donating group due to the lone pair of oxygen atom increases the electron density of aromatic ring thus π electrons readily adsorbed to the surface of metal [16,17]. However, the adverse effect from this group it is bulkier compared to K1 and causes steric hindrance thus easily desorp from the iron surface at highest investigated temperature [18]. This leads to the increase of corrosion of iron due to the attack of aggressive solution to the exposed sites on its surface.

Conclusion

Studied Schiff base inhibitors are effective corrosion inhibitors for mild steel in the test solution in the presence of optimum concentration of inhibitors compared to the blank solution of 1 M HCl even at elevated temperature. The inhibiting properties of K2 is due to chemisorption of the Schiff base molecule on the iron surface while K1 and K3 physical adsorption is affected by surface charge interaction between adsorbed chloride and the protonated form of inhibitors. The adsorption of these Schiff bases on the iron surfaces contribute to the high inhibition efficiencies of studied inhibitors in 1 M HCl. From the temperature effect, the activation energy parameter is calculated.

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