



Corrosion Inhibition of Carbon Steel X52 by New Schiff Base in HCl Solution

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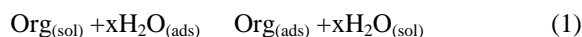
Corrosion
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Adsorption

Abstract

In this study, the inhibition effect of BESB6 Schiff base on carbon steel X52 corrosion in 0.5 M HCl solution was studied. For this aim, electrochemical techniques such as potentiodynamic polarization curves, weight loss (WL) were used. It was shown that, the BESB6 schiff base has remarkable inhibition efficiency on the corrosion of carbon steel in 0.5 M HCl solution. Polarization measurements indicated that, the studied inhibitor acts as mixed type corrosion inhibitor with predominantly control of cathodic reaction. The inhibition efficiency depends on the concentration of inhibitor and reaches 95% at 0.01M BESB6. The remarkable inhibition efficiency of BESB6 was discussed in terms of blocking of electrode surface by adsorption of inhibitor molecules through active centers. The adsorption of BESB6 molecules on the carbon steel surface obeys Langmuir adsorption isotherm.

1. Introduction

The investigation of adsorption of surfactants at solid/liquid interfaces is extremely important in electrochemical studies [1]. Their adsorption on the metal surface can markedly change the corrosion resisting properties of metals [2]. The study of relationship between adsorption and corrosion inhibition is of great importance; since the corrosion inhibition is a surface process and the degree of protection of metal is a function of adsorption [2, 3]. Corrosion in mineral acids represents a terrible waste of both resources and money [4]. Corrosion prevention systems favor the use of environmental chemicals with low or zero environmental impacts. The use of organic molecules as corrosion inhibitor is one of the most practical methods for protecting against the corrosion and it is becoming increasingly popular. The existing data show that organic inhibitors act by the adsorption on the metal surface and protective film formation. The adsorption of organic inhibitors at the metal/solution interface takes place through the replacement of water molecules by organic inhibitor molecules according to following process [5].



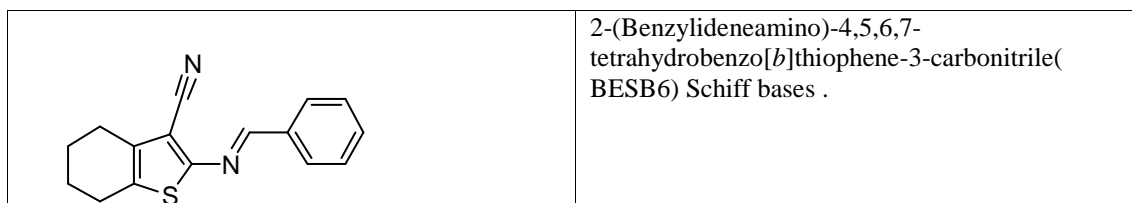
where $\text{Org}_{(\text{sol})}$ and $\text{Org}_{(\text{ads})}$ are organic molecules in the solution and adsorbed on the metal surface, respectively. x is the number of water molecules replaced by the organic molecules. It was shown that organic compounds containing heteroatoms with high electron density such as phosphorus, nitrogen, sulphur, oxygen as well as those containing multiple bonds which are considered as adsorption centers, are effective as corrosion inhibitor [6–9]. It has been also found that the molecules contain both nitrogen and sulphur in their molecular structure have exhibited greater corrosion inhibition efficiency in comparison with those contain only one of these atoms [10–14]. Recently, Schiff base compounds have been of interest in order to obtain efficient corrosion inhibitors since they provide much greater inhibition compared to corresponding amines and aldehydes [15–19]. The presence of $-\text{C}=\text{N}^-$ group in Schiff base molecules enhances their adsorption ability and corrosion inhibition efficiency [20, 21]. We have recently reported BESB6 as corrosion inhibitor for carbon steel [22].

In this study, we have further improved inhibition efficiency of BESB6 by preparing its Schiff base using benzaldehyd. The synthesized Schiff base molecule has additional $\text{C}=\text{N}^-$ bonds as well as a phenyl group which are assumed to be active center of adsorption. Therefore the molecule is expected to show better adsorption ability and corrosion inhibition

efficiency. The aim of this study is to investigate inhibition effect of BESB6 on the carbon steel corrosion in 0.5M HCl solution. For this purpose, potentiodynamic polarization, WL techniques were used.

2. Experimental

2.1. General procedure for the synthesis of 2-(Benzylideneamino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile(BESB6) Schiff bases .



(2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile) (0.89 g, 5 mmol) was dissolved in ethanol and an equimolar amount of the benzaldehyde was added dropwise. The mixture was left to stir at room temperature till the product crashed out from the solvent as precipitated and the reaction mixture was stirred for additional time till the TLC showed complete consumption of the starting materials. The product was filtered off and washed with cold ethanol (2 x 5 mL) and recrystallized from hot ethanol to give the desired product.

2.2. Preparation of electrodes

The working electrode was a cylindrical disc cut from a carbon steel X52 specimen with following chemical composition (wt); C (0.28%), Cr (11%).

The steel disc was mounted in polyester in such a way that only 2.25cm² surface area was in contact with the electrolyte. The carbon steel X 52 specimens was purchased from Mosturod pipe line.co. The surface of working electrode was mechanically abraded using different grades of sand papers, which ended with the 1000 grit, prior to use. The electrode was cleaned by washing with bi distilled water, acetone, bidistilled water, respectively and finally dried with a filter paper. For each test, a freshly abraded electrode was used.

2.3. Test solutions

The test solution was 0.5MHCl solution with and without various concentrations of BESB6 (from 10⁻⁵M to 10⁻³ M). All test solutions were prepared from analytical grade chemical reagents in distilled water. For each experiment, a freshly prepared solution was used. The test solutions were opened to air and the temperature was controlled thermostatically at 300 K.

2.4. Weight loss measurements

Weight loss experiments were carried out using specimens having the dimensions of 4cm. ×5cm×1.2 cm. The specimens were abraded with different grade emery papers, washed with distilled water, degreased with acetone, dried and kept in a desiccator. The specimens were accurately weighted and then immersed in solution containing 0.5MHCl solution with and without various concentrations of Schiff base. After 24 h exposure, the specimens were taken out rinsed thoroughly with distilled water, dried and weighted accurately. The weight loss (WL) in gm⁻² h⁻¹ was calculated using the following equation:

$$WL = \frac{W1 - W2}{St} \quad (2)$$

where W1 and W2 are the average weight of specimens before and after exposure, respectively, S is the total surface area of specimens, t is exposure time.

2.5. Electrochemical measurements

Electrochemical measurements were performed in a double-wall one compartment cell with a three-electrode configuration; a platinum auxiliary electrode, a calomel reference electrode and carbon steel working electrode. The working electrode was immersed in test solution for 15 min. to establish steady state open circuit potential.

3. Results and discussion

3.1. Weight loss measurements

The WL of carbon steel X52 specimens after exposure to 0.5M HCl solution with and without addition of various concentrations of BESB6 was calculated in $\text{gm}^{-2} \text{h}^{-1}$ and the data obtained were given in Table 1. The WL was reduced with increasing Schiff base concentration indicates that the inhibitor molecules act by adsorption on the metal surface.

Table1: Data of carbon steel X52 corrosion in 0.5 M HCl solution devoid of and containing different concentration of BESB6 inhibitor at different exposure times.

Conc., M	1h	24h	48h	72h	96h
1×10^{-5}	60	78	73	69	64.5
5×10^{-5}	66	83	81	75	69
1×10^{-4}	75	92	89	87.5	86
5×10^{-4}	82	92.5	92	91	90
1×10^{-3}	90	95	94	92.5	92.5

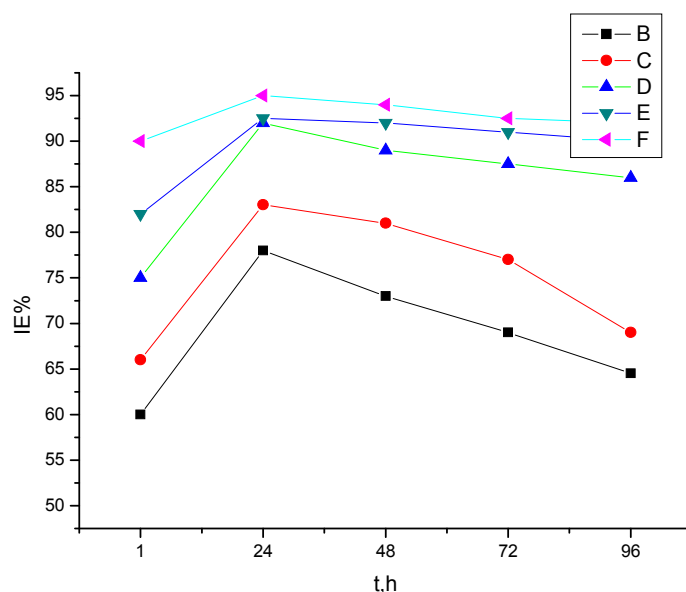


Fig (1): Relation between BESB6 exposure time and inhibition efficiency.

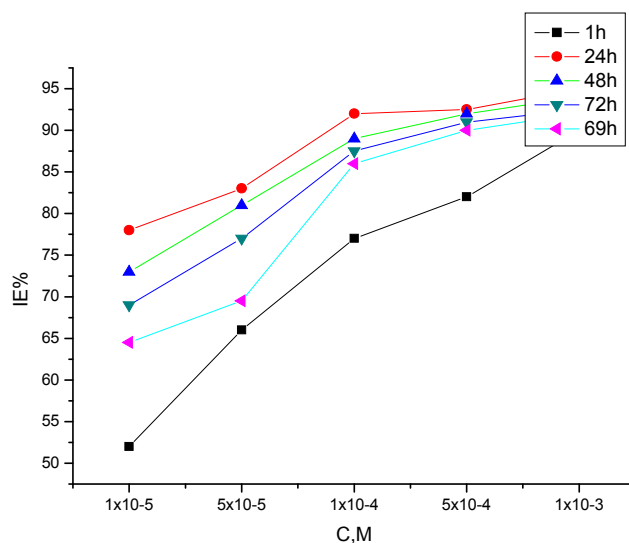


Fig (2): Relation between (BESB6)inhibitor concentrations and inhibition efficiency.

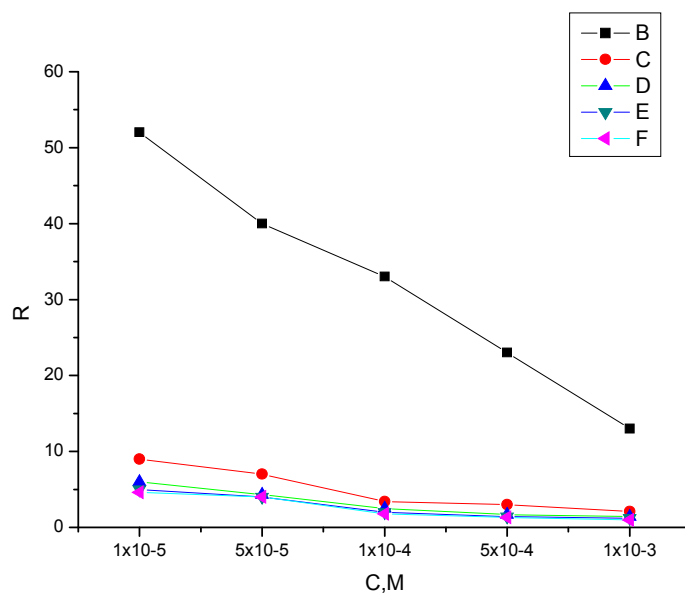


Fig (3): Relation between **BESB6** inhibitor concentrations and corrosion rate.

3.2. Potentiostatic polarization

The potentiodynamic polarization curves of carbon steel X52 in 0.5M HCl solution with various concentrations of BESB6 are shown in Fig. 4. The values of associated electrochemical parameters, i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), and inhibition efficiency (IE%) were calculated from these curves and given in Table 2. The inhibition efficiency IE% was calculated from polarization measurements according to the relation:

$$IE(\%) = \left(\frac{i - i'}{i} \right) \times 100 \quad (3)$$

where i and i' are the uninhibited and the inhibited corrosion current densities, respectively. The values of current densities were obtained by the extrapolation of the current-potential lines to the corresponding corrosion potentials. The weight loss was calculated theoretically with the help of the corrosion current values as can be seen from Table 2.

Table 2: Electrochemical parameters for carbon steel X52 determined from polarization measurements in 0.5M HCl solution without and with various concentrations of BESB6.

Conc. (M)	- E_{corr} (mV)	β_a (mV/Decade)	- β_c (mV/Decade)	I_{corr} (mA)	IE %
Free	493	102	144	0.32	-----
1X10 ⁻⁵	512	95	131	0.2	37.2
5X10 ⁻⁵	506	96	133	0.19	40.5
1X10 ⁻⁴	530	95	111	0.14	56
5X10 ⁻⁴	515	94	110	0.11	65.5
1X10 ⁻³	537	92	125	0.082	74

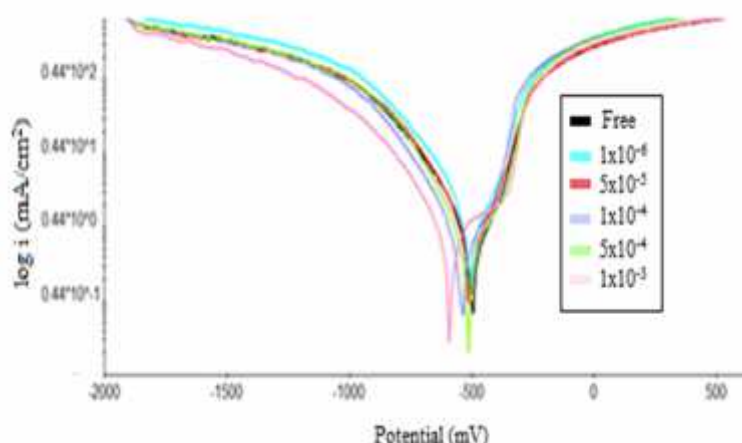
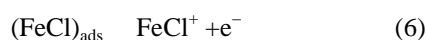
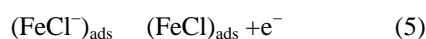
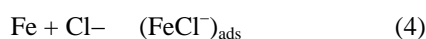


Fig (4): Polarization curves of carbon steel in 0.5M HCl solution without and with the addition of BESB6.

As it can be seen from Fig. 4, the addition of BESB6 to the aggressive solution both reduces anodic metal dissolution and also retards cathodic hydrogen evolution reactions as would be expected. This result is indicative of the adsorption of inhibitor molecules on the active sites of carbon steel. The inhibition is more and more pronounced with the increasing inhibitor concentration. It is also seen clearly from Fig. 4 and Table2 that, the presence of BESB6 in 0.5M HCl solution resulted in shift of corrosion potential towards more negative potentials with respect to that obtained in the absence of inhibitor. These results suggest that the BESB6 can be classified as mixed type corrosion inhibitor with predominantly control of cathodic reaction. The cathodic Tafel slopes decreased in the presence of Schiff base. This result indicates that the addition of BESB6 to the 0.5M HCl solution modifies the mechanism of hydrogen evolution reaction. As it is seen clearly from Fig. 4, the inhibition efficiency of inhibitor is potential dependent on anodic domain. The synthesized Schiff base molecule can acts as corrosion inhibitor on anodic reaction only at low anodic potentials. Between corrosion potential and $-0.350V$, a good inhibition ability was performed suggests formation of a protective layer of adsorbed species at the metal surface [6, 10]. At potentials more positive than $-0.350V$, which is usually defined as the desorption potential [4, 6]; the inhibition efficiency of inhibitor on dissolution reaction reduces. The observed phenomenon may be the result of a significant dissolution of iron, leading to desorption of inhibitor film from the metal surface. In this case, the desorption rate of inhibitor is higher than its adsorption rate [6, 10, 23].

3.3. Inhibition mechanism

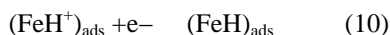
The adsorption of organic molecules on the solid surfaces cannot be considered as purely physical or as purely chemical adsorption phenomenon. The thermodynamic parameters showed that the adsorption BESB6 on the carbon steel surface in 0.5MHCl solution is more chemical adsorption than physical adsorption. Chemical adsorption of BESB6 arises from the donor acceptor interactions between free electron pairs of hetero atoms and π electrons of multiple bonds as well as phenyl group and vacant d orbitals of iron [2, 21, 33]. It has been reported that, the adsorption of heterocyclic compounds occurs with the aromatic rings some times parallel but mostly normal to the metal surface. The orientation of molecules could be dependent on the pH and/or electrode potential. However, more work should be completed to confirm the above arguments [41]. In the case of parallel adsorption of inhibitor molecules, the steric factors also must be taken into consideration. In addition to the chemical adsorption, the inhibitor molecules can also be adsorbed on the steel surface via electrostatic interaction between the charged metal surface and the charged inhibitor molecules if it is possible. The anodic dissolution of iron follows the steps given below [25]:



It is well known that Schiff bases have basic character and expected to be protonated in equilibrium with the corresponding neutral form in strong acid solutions.



It is well known that the chloride ions have a small degree of hydration, and due to specific adsorption, they should be first adsorbed on the positively charged metal surface according to reaction (7). The adsorption of chloride ions creates an excess negative charge towards the solution side of metal and favour more adsorption of cations [46]. Then the inhibitor molecules adsorb through electrostatic interactions between the negatively charged metal surface and positively charged Schiff base molecule (BESB6^+) and form a protective ($\text{FeCl}^- \text{BESB6}^+$)_{ads} layer. In this way, the oxidation reaction of (FeCl^-)_{ads} as shown by reaction steps from (8) to (10) can be prevented [22,40,47]. The cathodic hydrogen evolution reaction may be given as follow:



The protonated Schiff base molecules are also adsorbed at cathodic sites of carbon steel in competition with hydrogen ions that reduce to H₂ gas [22,25,35]. It should also be emphasized that, the large size and high molecular weight of Schiff base molecule can also contribute the greater inhibition efficiency of BESB6 [21].

4. Conclusions

The Schiff base of BESB6 was synthesized and tested as possible corrosion inhibitor for carbon steel x52 in 0.5M HCl solution. According to results obtained, the following points can be emphasized:

- The inhibition efficiency of Schiff base studied depends on its concentration. The excellent inhibition efficiency was attributed to the adsorption of inhibitor molecules and protective film formation on the metal surface.
- The potentiodynamic polarization curves indicated that the BESB6 Schiff base inhibits both anodic metal dissolution and also cathodic hydrogen evolution reactions.

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