# The Effect of Triethylene Tetramine on the Corrosion Behavior of Carbon Steel in H<sub>2</sub>S-HCl-H<sub>2</sub>O system at 90 °C

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The inhibitive effect of triethylene tetramine (TETA) as a neutralizer for the carbon steel in  $H_2S$ -HCl- $H_2O$  system at 90 °C was investigated by weight loss method, electrochemical impedance spectroscopy (EIS), potantiodynamic polarization techniques and scanning electron microscopy (SEM). The results showed that the addition of TETA to  $H_2S$ -HCl- $H_2O$  system inhibited the anodic reaction and reduced the corrosion rate of carbon steel due to adsorption of TETA molecules on the metal surface. The maximum inhibition efficiency of TETA was adjusting pH value to 6.05 with 10.1 mmol/L TETA additions in  $H_2S$ -HCl- $H_2O$  system.

Keywords: A. Steel; A. Acid solutions; B. EIS; B. SEM; C. Acid inhibition.

## **1. INTRODUCTION**

Corrosion has always been an inevitable part of petroleum refining operations. Corrosion process of carbon steel in acid environment, representative of atmospheric distillation plants, is a very important scientific and technological topic in the petroleum industry [1-3]. Corrosion of the steel in petroleum oils is almost always the result of associated sulfur compounds, naphthenic acid, carbon dioxide gas or salts in the oils [4]. After desalting process, salts and sulphide compounds dissolved in crude oil can provoke the formation of a corrosion aqueous solution whose chemical composition involves the presence of both hydrochloric acid (HCl) and hydrogen sulfide (H<sub>2</sub>S) [2, 3].

Because it is inexpensive and readily available carbon steel is probably used for a dominant material for the components in refinery plants [5]. Unfortunately, the corrosion aqueous solution

containing both HCl and  $H_2S$  is very aggressive causing varied damages on carbon steel during plant operation in primary distillation plants. Corrosion processes of carbon steel can be severe if the chloride content is high in a primary distillation plant. Therefore, ammonia, corrosion inhibitors or neutralizers are widely used to prevent or minimized metal dissolution in acid solution [6]. It is noteworthy that control of a constant pH with ammonia is difficult, but neutralizing amines buffer the aqueous solution so that pH control is easier over a wide range of amine concentrations [5]. Amines are well known inhibitors for acid solution and are known to exert the high degree of protection for ferrous materials [7]. Several previous works have been performed related to the inhibition properties of amines on the corrosion of iron and steel in acid solutions [1, 6, 8-10]. In these literatures, there are studies of the inhibitive effect of cyclic and aliphatic primary amines [1, 8, 9], secondary amines [6] and tertiary amines [10] on the corrosion phenomena. However, chemical compositions of these solutions are different to those found in real-life operation of the primary distillation plants and few researches on the corrosion inhibitive effect of tetramines have been carried out at the temperature of the condensation system in primary distillation plants, which usually is greater than 70 °C.

Recently, the influences of  $H_2S$  and HCl concentration on the corrosion behavior of carbon steel at 90 °C have been respectively investigated in literatures [11, 12]. The results have shown that both  $H_2S$  and HCl exhibited acceleration to the cathodic hydrogen evolution but had not influence on the anodic iron dissolution [11, 12]. In the solution with high acidity, some inhibitors maybe not have the best affection. Therefore, triethylene tetramine (TETA) as a typical neutralizing compound is chosen to decrease pH value of the acid solution of the condensation system of primary distillation plants in Lanzhou Petrochemic Company (LPC), China National Petroleum Corporation (CNPC). In the present work, the effect of triethylene tetramine (TETA) on carbon steel corrosion process in acid solution has been investigated using weight loss method, electrochemical measurements and scanning electron microscopy (SEM) at 90 °C.

#### **2. EXPERIMENT**

Experiments were conducted at atmospheric pressure in a glass cell as described previously [11, 12]. A typical three-electrode cell was used with a saturated calomel electrode (SCE) (GD-II, BRICEM, China) as the reference electrode, a large piece of platinum foil with a surface area of over  $4.0 \text{ cm}^2$  as the counter electrode, and a SAE-1020 carbon steel specimen as the working electrode. The temperature of electrolyte solutions was controlled with a bath at  $90 \pm 1$  °C. Residual H<sub>2</sub>S was absorbed by gas absorbent.

The specimens employed for the present study were SAE-1020 carbon steel, whose main compositions were 0.20 wt.% C, 0.32 wt.% Si, 0.56 wt.% Mn, 0.033 wt.% P, 0.032 wt.% S and Fe as the balance.

Square specimens of the carbon steel ( $10.0 \text{ mm} \times 10.0 \text{ mm} \times 2.5 \text{mm}$ ), which exposed a  $1.0 \text{ cm}^2$  surface to the electrolyte, were machined from the steel sheet and embedded in epoxy resin mold. Prior to each experiment, the electrode surface was sand blasted to 1000 grade, degreased with acetone, cleansed with distilled water and dried in a compressed hot air flow.

The concentrated solutions whose concentration was 0.25 mol/L Na<sub>2</sub>SO<sub>4</sub>, 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> and 0.5 mol/L Na<sub>2</sub>S were prepared with analytical grade chemicals and distilled water, respectively. 0.25 mol/L Na<sub>2</sub>SO<sub>4</sub> was used as the based solution. The acidic solution (5.9 mol/L H<sub>2</sub>S + 0.03 mol/L HCl) was prepared from the concentrated Na<sub>2</sub>S solution and the concentrated H<sub>2</sub>SO<sub>4</sub> solution and the analytical regent grade HCl as described previously [11]. The concentration of H<sub>2</sub>S in the test solution was referred to concentration of the solution of the condensation system of primary distillation plants of LPC. So the acidic solution in the present work was 0.25 mol/L Na<sub>2</sub>SO<sub>4</sub> with 5.9 mol/L H<sub>2</sub>S and 0.03 mol/L HCl, whose pH value was 2.75. The precise concentration of H<sub>2</sub>S was determined by the iodometric titration method with triplicate to make sure the results reproducible and reliable and pH value of the test solution was measured using a pH meter (PHSJ-4A, SPSIC, China).

To study the effect of a neutralizing compound on the carbon steel corrosion process, TETA was employed as a major composition of the neutralizer commonly used in LPC to adjust pH of the acid solution of the condensation system of primary distillation plants. TETA is the commercial name of N,N'-bis(2-aminoethyl)-1,2- ethylenediamine. The chemical structure of TETA was shown in Fig. 1.



Figure 1. Structure of triethylenetetramine (TETA) molecule.

TETA was added into the acidic solution (pH = 2.75) with different content to obtain different pH value solution. The solutions used in the test were listed in Table 1.

Table 1. Concentration of TETA in the solution of carbon steel.

| Acidic Solution  | TETA Concentration<br>/ mmol/L | pН   | T / °C |
|--|--------------------------------|------|--------|
| 0.25 mol/L Na <sub>2</sub> SO <sub>4</sub> + 5.9 mol/L | 0                              | 2.75 | 90     |
| $H_2S+0.03 \text{ mol/L HCl}$                          | 4.5                            | 4.11 | _      |
|  | 7.7                            | 5.28 |        |
|  | 10.1                           | 6.05 |        |
|  | 15.1                           | 6.46 |        |
|  | 19.4                           | 7.13 |        |
|  | 24.5                           | 8.09 | —      |

TETA concentration was 4.5 mmol/L while pH value of solution was 4.11, 7.7 mmol/L to pH 5.28, 10.1 mmol/L to pH 6.05, and 24.5 mmol/L to pH 8.29, respectively.

Specimens were cut into 10.0 mm ×10.0 mm ×2.5 mm specimens for immersion tests and three specimens used for each series were measured for good reproducibility. Weight loss experiments were done according to the method described previously [11, 12]. The inhibition efficiency ( $\eta_{WL}$ ) and corrosion rates ( $\nu$ ) (g m<sup>-2</sup> h<sup>-1</sup>) were determined by using the following equations:

$$\eta_{\rm WL} \% = \frac{w_0 - w_i}{w_0} \times 100 \tag{1}$$

$$v = \frac{W_0 - W_1}{A \times t} \tag{2}$$

where,  $w_0$  is weight loss in absence of inhibitor,  $w_i$  is weight loss in presence of inhibitor;  $W_0$  (g) and  $W_1$  (g) are the original weight and final weight of specimens, respectively; A (m<sup>2</sup>) is the exposed surface area of specimens, and t (h) represents the immersion time.

Potentiodynamic polarization curves measurements were performed at a potential scan rate of 0.333 mV s<sup>-1</sup>. The potential range was from -0.30 V to 0.30 V vs. open circuit potential (OCP). All potentials reported in this paper were measured with respect to the SCE. The inhibition efficiency ( $\eta_P$ ) was determined by using the equations (3) [13, 14]:

$$\eta_{\rm P}\% = \frac{i_{\rm corr} - i_{\rm corr}}{i_{\rm corr}} \times 100 \tag{3}$$

where  $i_{corr}$  and  $i_{corr}$  are the corrosion current density in the absence and in the presence of TETA, respectively.

Excited by a sinusoidal perturbation signal of 5 mV amplitude, EIS measurements were carried out at OCP over the frequency from 100 kHz to 10 mHz. The data were acquired in four cycles at each frequency, for providing good precision at all frequencies. The experimental data were analyzed using the commercial software ZsimpWin<sup>®</sup>. The inhibition efficiency,  $\eta_{CT}$ , is calculated by the charge transfer resistance that is obtained from Nyquist plots, according to the following equation [7, 14]:

$$\eta_{\rm CT} \% = \frac{R_{\rm ct} - R_{\rm ct}}{R_{\rm ct}} \times 100$$
(4)

where  $R_{ct}$  and  $R'_{ct}$  are the charge transfer resistance values in the absence and presence of TETA, respectively.

For better reproducibility, all above electrochemical measurements were repeated more than three times and were carried out using IVIUMSTAT ELECTROCHEMICAL INTERFACE (IVIUM TECHNOLOGIES, Netherlands) controlled by PC.

The corrosion morphology of carbon steel was characterized by SEM (Cambridge S240). The energy used for analysis was 20 kV. To observe the corrosion morphology under the corrosion products, the corrosion products were removed using the chemical products-cleanup method (ISO 8407:1991) [15].

#### **3. RESULTS AND DISCUSSION**

3.1. Weight loss measurements



**Figure 2.** Variations of the corrosion rates(v) and inhibition efficiencies( $\eta$ ) as a function of pH value in the sour solutions without or with TETA at 90 °C.

Fig. 2 showed the variations of the inhibition efficiencies and corrosion rates obtained from weight loss measurements in absence and presence of different concentrations of TETA in the acidic solution with 5.9 mol/L H<sub>2</sub>S and 0.03 mol/L HCl (pH = 2.75) after 1 h immersion at 90 °C. It had been found that the corrosion rate was 9.11 g m<sup>-2</sup> h<sup>-1</sup> in the acidic solution (pH = 2.75), while it was 2.91, 0.76, 0.68, 2.07, 3.12 and 5.79 g m<sup>-2</sup> h<sup>-1</sup> for pH value was 4.11, 5.28, 6.05, 6.46, 7.13 and 8.09 with added different concentrations of TETA in the acidic solution, respectively. TETA inhibited the corrosion of carbon steel and the inhibition efficiency ( $\eta_{WL}$ ) of TETA increased with pH value up to a maximum (92.6 %) at a pH of 6.05 while the concentration of TETA was 10.1 mmol/L and then it decreased. The inhibition efficiency ( $\eta_{WL}$ ) of TETA were 0%, 68.1%, 91.6%, 92.6%, 77.3%, 65.8%, 36.5% for pH value being 2.75, 4.11, 5.28, 6.05, 6.46, 7.13 and 8.09, respectively. These results indicated that the addition of TETA decreased the metal dissolution rate and showed maximum inhibition efficiency at pH 6.05 while the concentration of TETA was 10.1 mmol/L.

#### 3.2. Potentiodynamic polarization measurements



**Figure 3.** Potentiodynamic polarization curves of carbon steel in 5.9 mol/L H<sub>2</sub>S and 0.03 mol/L HCl solutions containing different concentrations of TETA at 90 °C.

Fig. 3 showed a set of polarization curves for the carbon steel in aerated acidic solutions without and with addition of TETA at 90 °C. In each case, the polarization measurement was performed after the corrosion potential reached an approximately stable value to ensure the reaction system was in the steady state. It could be seen that anodic reactions of the carbon steel corrosion were inhibited with the addition of TETA in the acidic solution.

**Table 2.** Corrosion parameters obtained from potentiodynamic polarization curves and inhibition efficiencies for carbon steel in 5.9 mol/L H<sub>2</sub>S and 0.03 mol/L HCl solution in the absence and presence of TETA at 90 °C.

| 0 2.75 -0.64 0.07 0.37 451.0 —       | TETA<br>Concentration /<br>mmol/L | рН   | $E_{ m corr}$ / ${ m V}_{ m SCE}$ | $b_{\rm a}$ / V dec <sup>-1</sup> | $b_{\rm c}$ / V dec <sup>-1</sup> | $i_{\rm corr}$ / $\mu { m A~cm}^{-2}$ | $\eta_{ m P}$ % |
|--------------------------------------|-----------------------------------|------|-----------------------------------|-----------------------------------|-----------------------------------|---------------------------------------|-----------------|
|                                      | 0                                 | 2.75 | -0.64                             | 0.07                              | 0.37                              | 451.0                                 | —               |
| 4.5 4.11 -0.60 0.06 0.22 120.6 73.3  | 4.5                               | 4.11 | -0.60                             | 0.06                              | 0.22                              | 120.6                                 | 73.3            |
| 7.7 5.28 -0.59 0.13 0.14 50.8 88.7   | 7.7                               | 5.28 | -0.59                             | 0.13                              | 0.14                              | 50.8                                  | 88.7            |
| 10.1 6.05 -0.57 0.13 0.15 38.2 91.5  | 10.1                              | 6.05 | -0.57                             | 0.13                              | 0.15                              | 38.2                                  | 91.5            |
| 15.1 6.46 -0.58 0.14 0.19 47.2 89.5  | 15.1                              | 6.46 | -0.58                             | 0.14                              | 0.19                              | 47.2                                  | 89.5            |
| 19.47.13-0.520.100.2678.982.5        | 19.4                              | 7.13 | -0.52                             | 0.10                              | 0.26                              | 78.9                                  | 82.5            |
| 24.5 8.09 -0.50 0.11 0.60 248.0 45.0 | 24.5                              | 8.09 | -0.50                             | 0.11                              | 0.60                              | 248.0                                 | 45.0            |

Values of associated electrochemical parameters such as corrosion potential ( $E_{corr}$ ), cathodic and anodic Tafel slopes ( $b_c$  and  $b_a$ ), corrosion current density ( $i_{corr}$ ) obtained by extrapolation of the Tafel lines and the inhibition efficiency ( $\eta_P$ ) of TETA in each case were listed in Table 2.

As it could be seen from these polarization results (Table 2), the  $i_{corr}$  values decreased with increasing pH value of the solutions, reaching a minimum when pH was 6.05 (TETA concentration was 10.1 mmol/L), and then started to increase. The addition of TETA led to a change of anodic and cathodic Tafel slopes besides decreasing both currents, which indicated that TETA inhibited the anodic reaction greater extents than the cathodic one and reduced metal dissolution. Furthermore, the inhibition efficiency ( $\eta_P$ ) increased with pH in the solutions up to a maximum (91.5 %) as pH was about 6.05 (TETA concentration was 10.1 mmol/L), and then it decreased.

By comparing polarization curves in the absence and presence of TETA (Table 2), it was observed that the addition of TETA shifted the corrosion potential in the positive direction, depending on pH of the solutions adjusted with TETA. The value of the corrosion potential is influenced by two competitive reactions of cathodic process and anodic process [16, 17]. From Fig. 3, TETA inhibited the anodic reaction to greater extents than the cathodic one. As a result, the corrosion potential of the carbon steel displayed the characteristic of positive shift with the addition of TETA.

#### 3.3. Electrochemical impedance spectroscopy (EIS)



**Figure 4.** Typical Nyquist diagrams of carbon steel in aerated acidic solutions in the absence and presence of different concentrations of TETA at 90 °C.

Fig. 4 displayed the impedance spectra obtained for the carbon steel in the solutions mentioned in Table 1. It could be observed that the shape and size of these impedance spectra strongly depended

on pH value of the solutions. As can be found in Fig.4, the impedance diagrams measured in the acidic solutions without addition of TETA (pH = 2.75) displayed two well-separated capacitive loops. However, with the addition of TETA the impedance diagrams displayed one loop. From analysis with Bode plot, we considered that there are still two time constants in the impedance diagrams of the solution with adding TETA. Deviation from perfect circular shape refereed to the frequency dispersion of interfacial impedance which arises due to the roughness and other inhomogeneities of the surface [7, 18-20]. It was also observed from Fig.4 that the capacitive loop increased in size with the increase of addition of TETA. All impedance plots could be analyzed by the equivalent circuit [11, 12, 21, 22] in Fig. 5. The circuit employed allowed the identification of both solution resistance ( $R_s$ ) and charge transfer resistance ( $R_{ct}$ ). Values of the elements corresponding to adsorptive characteristics of the system (the adsorptive capacitance, CPE<sub>a</sub>, and the adsorptive resistance,  $R_a$ , of corrosion products) were also obtained. In order to give more accurate fit results, the constant phase elements (CPE) were substituted for capacitors.

**Table 3.** Fitting results of EIS data for carbon steel in 5.9 mol/L H<sub>2</sub>S and 0.03 mol/L HCl solution in the absence and presence of TETA at 90 °C.

| TETA<br>Concentration<br>(mmol/L) | рН   | $R_{\rm s}$<br>( $\Omega$ cm <sup>2</sup> ) | CPE <sub>dl</sub><br>Y <sub>0</sub> ×10 <sup>-3</sup><br>( $\Omega^{-1}$ cm <sup>-2</sup> s <sup>n</sup> ) | $n_1$ | $R_{\rm ct}$<br>( $\Omega$ cm <sup>2</sup> ) | CPEa<br>$Y_0$<br>$(\Omega^{-1} \operatorname{cm}^{-2} \operatorname{s}^n)$ | <i>n</i> <sub>2</sub> | $R_{\rm a}$<br>( $\Omega$ cm <sup>2</sup> ) | $\eta_{ m Rct}$ % |
|-----------------------------------|------|---|--|-------|--|--|-----------------------|---|-------------------|
| 0                                 | 2.75 | 6.24  | 2.65   | 0.78  | 21.23  | 0.31   | 0.86                  | 15.10                                       |                   |
| 4.5                               | 4.11 | 5.75  | 8.68   | 0.87  | 102.10                                       | 0.054  | 0.97                  | 33.43                                       | 79.21             |
| 7.7                               | 5.28 | 5.79  | 5.92   | 0.83  | 127.60                                       | 0.019  | 0.93                  | 71.18                                       | 83.36             |
| 10.1                              | 6.05 | 4.88  | 4.48   | 0.81  | 201.40                                       | 0.024  | 0.92                  | 199.50                                      | 89.46             |
| 15.1                              | 6.46 | 4.94  | 5.27   | 0.86  | 135.50                                       | 0.022  | 0.95                  | 89.79                                       | 84.33             |
| 19.4                              | 7.13 | 6.17  | 4.39   | 0.88  | 59.87  | 0.025  | 0.87                  | 25.20                                       | 64.40             |
| 24.5                              | 8.09 | 4.70  | 11.95  | 0.62  | 36.49  | 0.011  | 0.69                  | 18.17                                       | 41.82             |



**Figure 5.** Equivalent circuit used to simulate the EIS diagrams obtained from carbon steel in aerated sour solutions without or with TETA at 90 °C.

Table 3 showed representative parameter values of the fitting results to EIS data obtained for carbon steel using the equivalent circuit of Fig. 5. From Table 3,  $R_{ct}$  increased from the value of 21.23  $\Omega$  cm<sup>2</sup> for the acid solution (pH 2.75) to 201.40  $\Omega$  cm<sup>2</sup> in the solution containing TETA 10.1 mmol/L at pH 6.05, and then decreased remarkably with increasing of pH value from 6.05 to 8.09. However, all the results of  $R_{ct}$  obtained in the solutions with TETA were higher than that obtained in the absence of TETA, which implied that TETA had an inhibition effect on the corrosion process of carbon steel in the solution at 90 °C.

## 3.4. Analysis of corrosion morphology





**Figure 6.** SEM micrographs of surface morphology of carbon steel in 5.9 mol/L H<sub>2</sub>S and 0.03 mol/L HCl solutions without and with TETA (a) without TETA; (b) without TETA and with the corrosion product removed; (c) 4.5 mmol/L; (d) 4.5 mmol/L and with the corrosion product removed; (g) 10.1 mmol/L; (f) 10.1 mmol/L and with the corrosion product removed; (g) 19.4 mmol/L; (h) 19.4 mmol/L and with the corrosion product removed; (i) 24.5 mmol/L; (j) 24.5 mmol/L and with the corrosion product removed.

The morphologies of carbon steel surface after 1 h immersion in the absence and presence of TETA solutions at 90 °C were shown in Fig. 6. The typical cotton-like corrosion products formed on the surface of carbon steel in the absence of TETA solution, pH 2.75, could be observed. With the addition of TETA, it is clearly showed that a mass of corrosion products formed on carbon steel surface could also be observed. However, the compactness of corrosion products film strongly depended on the addition of TETA in the solutions. When carbon steel immersed in the solution added with 10.1 mmol/L TETA, the corrosion products were very compact (Fig. 6c). With the increase of addition of TETA, the corrosion products were broken down (Fig. 6e) or became loose (Fig. 6g), leading to the decrease of protective performance of the corrosion products film.

After removing the corrosion products on the carbon steel surface, the morphologies of carbon steel surface displayed different characteristics in the acidic solutions without and with TETA. Some of granulated compounds absorbed on the carbon steel surface could be observed in the presence of

TETA, which could be produced by the interaction between the adsorption of TETA molecule and the corrosion products formed in sour environment [1, 7] (Fig. 6d, f, h). Meanwhile, the amount of granulated compounds seemed to decrease with increasing of addition of TETA from 10.1 mmol/L to 24.5 mmol/L. Additionally, it could be found that areas of localized corrosion spots appeared with crater-like shapes on the carbon steel surface in the solutions at 19.4 mmol/L TETA (Fig. 6f) and 24.5 mmol/L TETA (Fig. 6h), which could be associated with the decrease of the inhibition efficiency of TETA when addition of TETA increased to 19.4 mmol/l, and up to 24.5 mmol/L.

#### 3.5. Mechanism of inhibition

Amines may be adsorbed on the metal surface in the form of neutral molecules, involving the displacement of water molecules from the metal surface [23-25]. For getting adsorbed on the steel surface from the solutions, each amine molecule displaces 'n' molecules of water. Therefore, thermodynamics of the exchange of adsorbate between the bulk solution and the interface depends on the relative size of the adsorbate [7]. Such competitive adsorption process of amine molecule from solution is similar to a quasi-chemical substitution process and can be described by the following formula [7, 26]:

$$\operatorname{Amines}_{(s)} + n\operatorname{H}_2\operatorname{O}_{\operatorname{ads}} \to \operatorname{amines}_{\operatorname{ads}} + n\operatorname{H}_2\operatorname{O}_{(S)}$$
(5)

The thermodynamics of this reaction depends on the number of water molecules 'n', which replaced by the amine.

It is noteworthy that amines may also adsorb through electrostatic interactions between the positive charged nitrogen atom and the negative charged metal surface [27]. Strong adsorption of amine molecules is not always a direct combination of the molecule with the steel surface. It is believed that the adsorption of the amine can be influenced by anions in acidic solutions [28, 29]. In acidic solution, chloride ions may be first adsorbed at the steel/solution interface at the corrosion potential through electrostatic attraction force. Additionally, the HS<sup>-</sup> anions can absorb on the carbon steel, acting as bridges facilitating the adsorption of inhibitor [30]. Being specifically adsorbed, these anions create an excess negative charge towards the solution and favour more adsorption of the cations [31, 32]. Therefore, the ammonium cations are able to electrostatically adsorb on the carbon steel surface covered with primarily adsorbed Cl<sup>-</sup> or HS<sup>-</sup> ions in the acidic solution.

The obtained results of the series of experiments showed that, the addition of the under testing neutralizing compound decreased the corrosion process of carbon steel in the given aqueous media, which meant that TETA had ability to form a protective film on the metal surface [7]. However, this ability of protective film strongly depended on the pH value of the solution. The inhibitive efficiency of TETA increased with the increase of pH value, reaching a maximum at pH 6.05 (TETA concentration was 10.1 mmol/L), and then started to decrease. As pH value increased with increasing concentration of TETA, more molecules would be adsorbed on the steel surface due to the electrostatic attraction or van der Waals forces between the amine molecules and steel. As a result, more water

molecules at the corroding interface were replaced. Meanwhile, the corrosion products film formed on the carbon steel surface and became compact (Fig. 6c), leading to the inhibitive efficiency of TETA increasing. However, as soon as all the active sites became saturated with the amine, the development of the inhibitor layer was gradually slowed down. Furthermore, high level concentration of amine inhibitor leaded instability of the corrosion products film resulting in electrochemical activation between corrosion agents of the acidic solution and the steel surface [33]; as a consequence the film easily broken or became loose (Fig. 6 e and g); it exposed fresh steel surface areas to the highly corrosive environment, leading to a localization corrosion attack (Fig. 6 f and h). Therefore, the inhibition efficiency decreased after the pH value increasing up to 6.05.

The corrosion data by polarization curves (Fig. 3) in presence of amine suggested that inhibition of dissolution of carbon steel occurred, through the adsorption of amine at the local anodic as well as cathodic sites, especially at the anodic sites. The effect of TETA on the anodic partial reaction is mainly attributed to the chemisorptions of the amine on the carbon steel surface through coordination bond formation between the steel and the electron pair on the nitrogen atom [7]. The lone pair electrons of the nitrogen atom in the amine could form co-ordination bond with the iron by sharing the electrons with the unfilled levels. Therefore, each molecule of TETA could form bond with two iron atoms and effectively covers the carbon steel surface (Fig. 7).



Figure 7. Illustration of adsorption of TETA at steel surface [7]

As a result, the anodic process of carbon steel was obviously restrained in the presence of TETA. On the other hand, the cathodic reaction of carbon steel in the acidic solutions displayed the hydrogen evolution reaction. Presence of TETA did not much effect the shape of the curves but shifted the corrosion current towards a lower value. According to Sanyal et al. [34], amine molecules may form 'onium ion' and get adsorbed on the cathodic regions of the metal surface due to electrostatic attraction in acid solutions. The onium ion may obstruct the passage of ions to the cathodic surface.

## 4. CONCLUSION

1. The addition of TETA to  $H_2S$ -HCl- $H_2O$  system at 90 °C reduced the corrosion rate of carbon steel due to adsorption of TETA molecules on the metal surface.

3. Potentiodynamic polarization indicated that TETA inhibited the anodic reaction greater extents than the cathodic one and reduced metal dissolution.

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