



Corrosion inhibition of carbon steel by triton X 100 self-assembling monolayers

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ABSTRACT

Well-ordered self-assembled mono layers using Triton X 100 were formed on the carbon steel surface by immersion method. This leads to ordered, strong mono layers bound to the surface. Monolayer formation takes place when carbon steel is immersed in well water in presence of 200 ppm of Triton X 100 and 50 ppm of Zn²⁺ for one day and rinsing the adsorbed molecules in distilled water and heating in a hot air oven. The formulations of mono layers were confirmed by FTIR spectra. The self-assembled mono layers were tested by polarization and SEM analysis. The nano film is found to be hydrophobic in nature. This is confirmed by measurement of contact angles.

Key words: Self-assembled mono layers, carbon steel, Triton X 100, hydrophobicity, Polarisation, SEM, contact angle.

INTRODUCTION

Self-assembled monolayers (SAMs) are well ordered molecular assemblies, formed suddenly by chemisorptions through the molecule head group. Once adsorbed to the surface, these molecules arrange themselves through Van der Waals interaction among long aliphatic chains [1–3]. SAMs have paying attention widespread and seize vast promise for application in numerous areas e.g. corrosion resistance, biosensors and microelectronics. The adsorption and corrosion inhibition behavior of 1-tetradecylphosphonic acid selfassembled monolayers on the differently structured surfaces of 2024 and 1 060 aluminum alloys have been investigated [4]. Self assembled monolayers (SAMs) of hydroxamic acids on the carbon steel surface have been investigated [5]. The self assembling behavior and inhibition effect of dodecane thiol self-assembled monolayers (SAMs) on copper surface were investigated [6]. Self-assembly systems for example alkanethiol on gold have been intensively investigated [7-11]. In recent times, attention was focused on other organic molecules and active metal substrates, such as iron, aluminium, zinc [12-14]. In this work, we have evaluated the corrosion inhibition properties of Cetyl-Trimethyl-Ammonium Bromide (TRITON X 100) SAMs on carbon steel. The present work is undertaken (i) to evaluate the inhibition efficiency of Cetyl-Trimethyl-Ammonium Bromide (TRITON X 100) SAMs for the corrosion of carbon steel (ii) to analyze the protective film SAMs on carbon steel by FTIR spectra (iii) to understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization studies (iv) to study the hydrophobization of the Cetyl-Trimethyl-Ammonium Bromide (TRITON X 100) monolayers by contact angle measurements. (v) to propose a suitable mechanism for corrosion inhibition.

EXPERIMENTAL SECTION

2.1 Preparation of the specimens

Carbon steel specimens (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest Iron) of the dimensions 1.0x4.0x0.2cm were polished to a mirror finish and degreased with trichloroethylene, and used for the weight-loss method and

surface examination studies.

Weight-loss method

Carbon steel specimens in triplicate, were immersed in 100ml of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn²⁺ for one day. The weight of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. The corrosion products were cleansed with Clarke's solution. The corrosion inhibition efficiency(IE) was then calculated using the equation

$$IE=100[1-(w_2/w_1)] \%$$

Where,

w₁= corrosion rate in absence of inhibitor

w₂= corrosion rate in presence of inhibitor

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by various surface analysis techniques.

FTIR spectra

These spectra were recorded in a Perkin-Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr and made into pellets, and the FTIR spectra were recorded.

AC impedance spectra

The instrument and cell set up used for polarization study was used to record AC impedance spectra also. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

$$R_t = (R_s + R_t) - R_s$$

Where R_s = solution resistance

$$C_{dl} = 1/2\pi R_t f_{max} \quad (4)$$

Where f_{max} = frequency at maximum imaginary impedance.

AC impedance spectra were recorded with initial E(v) = 0, high frequency (Hz) = 1x10⁵, low frequency (Hz) = 1, amplitude (V) = 0.005 and quiet time (s) = 2.

Contact angle measurements

The contact angle measurements on surfaces were performed on a VCA Optima instrument equipped with a CCD camera for imaging. The deionized water under static conditions with a drop volume of 5mL was employed to determine the contact angle. VCA Optima XC software provided with instruments was used for fitting the drop shapes to find the contact angle of water on the surface. This measurement was repeated three times for each sample, and the average values with standard deviations ±2 degree are reported.

RESULTS AND DISCUSSION

Synergistic effect of TritonX 100 and Zn²⁺ system

Analysis of weight loss method

Corrosion rates (CR) of carbon steel immersed in well water in the absence and presence of inhibitor (TritonX 100) are given in Tables 1 and 3. The inhibition efficiencies (IE) are also given in these Tables. The inhibition efficiencies of the TritonX 100 -Zn²⁺ systems as a function of concentrations of TritonX 100 are shown in Fig. 1.

It is observed from Table 1 that TritonX 100 shows some inhibition efficiencies. 200 ppm of TritonX 100 has 32% inhibition efficiency, as the concentration of TritonX 100 increases, the inhibition efficiency increases. This is due to the fact that as the concentration of TritonX 100 increases, the protective film (probably iron TritonX 100 complex) formed on the metal surface. At concentrations ≥ 250 ppm of TritonX 100, the protection efficiency decreases. It may be due to the fact that these molecules aggregate together to form micelles. They are not uniformly absorbed on the metal surface. Hence corrosion inhibition efficiently decreases.

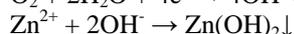
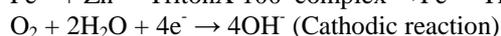
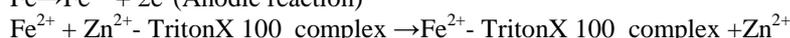
Table 1: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method*Inhibitor system: TritonX 100-Zn²⁺ (0 ppm)**Immersion period: One day*

TritonX 100 (ppm)	Zn ²⁺ (ppm)	CR (mdd)	IE%
0	0	18.18	-
50	0	15.99	12
100	0	14.72	19
150	0	14.36	21
200	0	12.36	32
250	0	13.27	27

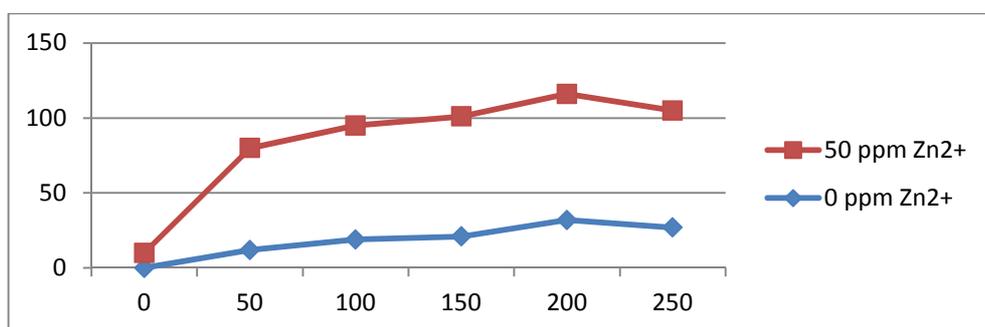
Influence of Zn²⁺ on the inhibition efficiencies of TritonX 100

The influence of Zn²⁺ on the inhibition efficiencies of TritonX 100 is given in Table 2. It is observed that as the concentration of TritonX 100 increases the IE increases. Similarly for a given concentration of TritonX 100 IE increases as the concentration of Zn²⁺ increases. At concentrations ≥ 250 ppm of TritonX 100, the protection efficiency decreases. It may be due to the fact that these molecules aggregate together to form micelles. They are not uniformly absorbed on the metal surface. Hence corrosion inhibition efficiently decreases. It is also observed that a synergistic effect exists between TritonX 100 and Zn²⁺. For example, 0 ppm of Zn²⁺ has 12 percent IE; 0 ppm of TritonX 100 has 10 percent IE. Interestingly their combination has a high IE, namely 84 percent.

In the presence of Zn²⁺ more amount of TritonX 100 is transported towards the metal surface. On the metal surface Fe²⁺- TritonX 100 complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is controlled. The cathodic reaction is the generation of OH⁻, which is controlled by the formation of Zn(OH)₂ on the cathodic sites of the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Zn²⁺ and TritonX 100.

**Table 2: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method***Inhibitor system: TritonX 100 -Zn²⁺ (50 ppm)**Immersion period: One day*

TritonX 100 (ppm)	Zn ²⁺ (ppm)	CR (mdd)	IE%
0	0	18.18	-
0	50	16.36	10
50	50	5.82	68
100	50	4.36	76
150	50	3.64	80
200	50	2.91	84
250	50	3.99	78

**Figure 1: Corrosion rates (CR) of carbon steel immersed in various test solutions***Analysis of AC impedance spectra*

AC impedance spectra (electrochemical impedance spectra) have been used to confirm the formation of protective on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl}) decreases and the impedance log (Z/ohm) value increases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (TritonX 100 -Zn²⁺) are

shown in Figures 3 (a,b) (Nyquist plots) and Figures 4 (a,b) and Figures 5 (a,b) (Bode plots). The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Bode plots are also given in Table 3.

It is observed that when the inhibitors TritonX 100 (200 ppm) + Zn^{2+} (50 ppm) are added, the charge transfer resistance (R_t) increases from $1011.4 \Omega cm^2$ to $1127.0 \Omega cm^2$. The C_{dl} values decreases from $4.9823 \times 10^{-5} F/cm^2$ to $4.4154 \times 10^{-5} F/cm^2$. The impedance value [$\log(Z/\Omega cm)$] increases from 3.16 to 3.20. These results lead to the conclusion that a protective film is formed on the metal surface.

Table 3: Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from AC impedance spectra

System	Nyquist plot		Bode plot Impedance value $\log(Z/\Omega cm)$
	$R_t \Omega cm^2$	$C_{dl} F/cm^2$	
Well water	1011.4	4.9823×10^{-5}	3.16
Well water + TritonX 100 (200ppm) + Zn^{2+} (50ppm)	1127.0	4.4154×10^{-5}	3.19

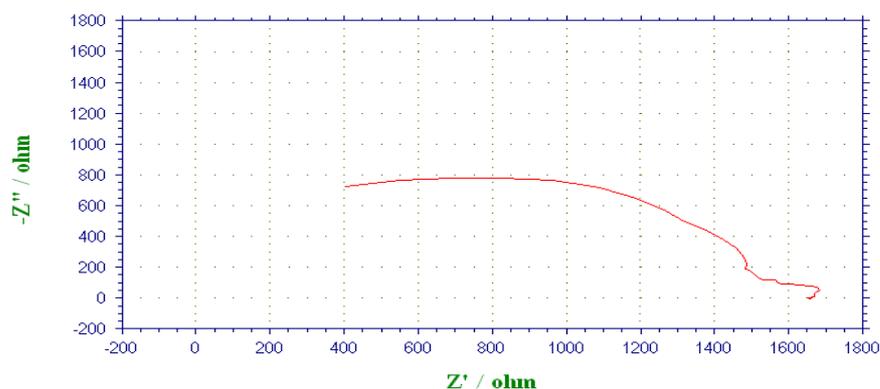


Figure 3: AC impedance spectra of carbon steel immersed in various test solution (Nyquist plot) (a) Well water (blank)

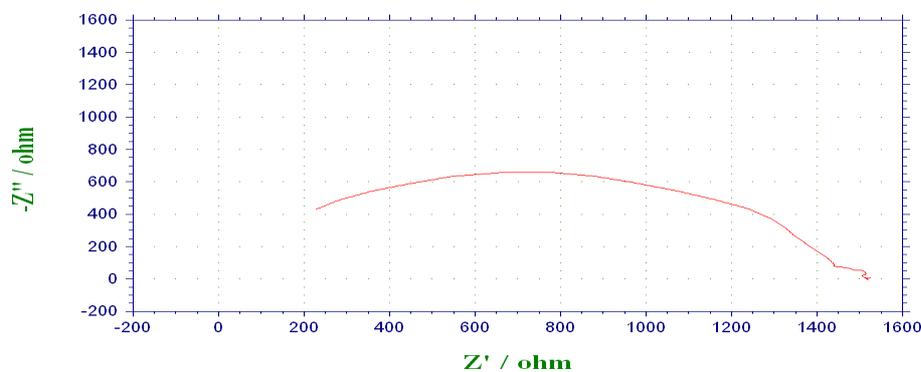


Figure 3: AC impedance spectra of carbon steel immersed in various test solution (Nyquist plot) (b) Well water + TritonX 100 (200ppm) + Zn^{2+} (50ppm)

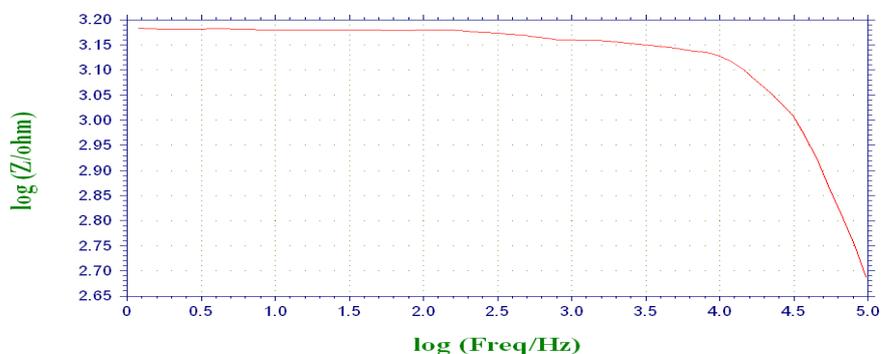


Figure 4: AC impedance spectra of carbon steel immersed in various test solution (Impedance Bode plot) (a) Well water (blank)

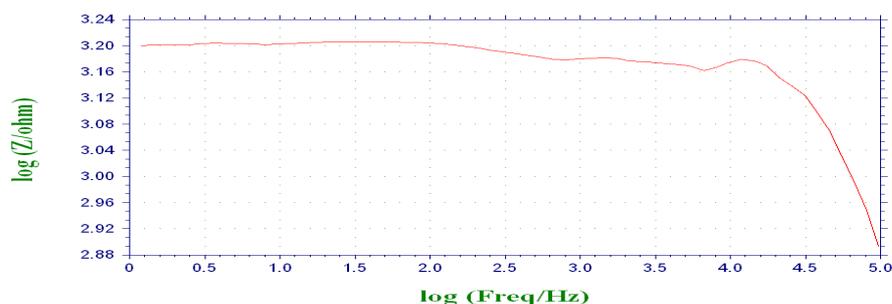


Figure 4: AC impedance spectra of carbon steel immersed in various test solution (Impedance Bode plot) (b) Well water + TritonX 100 (200ppm) + Zn^{2+} (50 ppm)

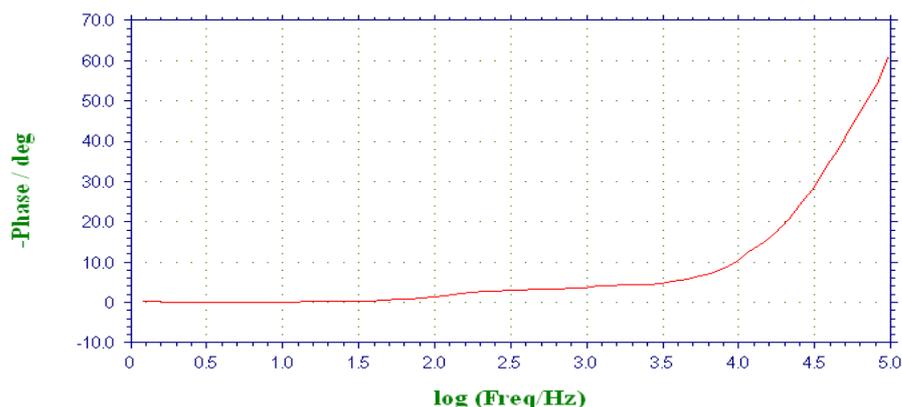


Figure 5: AC impedance spectra of carbon steel immersed in various test solution (Phase Bode plot) (a) Well water (blank)

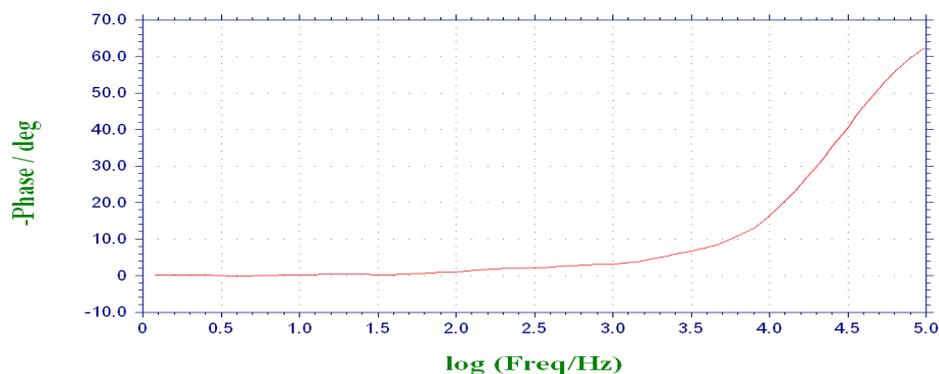


Figure 5: AC impedance spectra of carbon steel immersed in various test solution (Phase Bode plot) (b) Well water + TritonX 100 (200ppm) + Zn^{2+} (50ppm)

Analysis of FTIR spectra

FTIR spectra have been used to analysis the protective film formed on the metal surface. The FTIR spectrum (KBr) of pure TritonX 100 is shown in Figure 6a. The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 200 ppm of TritonX 100 and 50 ppm Zn^{2+} is shown in Figure 6b. The peak at 3410.2 cm^{-1} is due to OH- stretching. The C=O stretching frequency has Shifted from 1609.17 to 1627.4 cm^{-1} . This observation suggest that TritonX 100 has coordinated with Fe^{2+} on metal surface through oxygen atom of resulting in the formation of Fe^{2+} - TritonX 100 complex on the anodic sites of the metal surface. The peak at 687 cm^{-1} corresponds to Zn-O stretching. This confirms that $Zn(OH)_2$ is formed on the cathodic sites of the metal surface. The spectrum exhibits a strong C-O-C band at 1113.5 cm^{-1} is shifted to 1300 cm^{-1} . The CH₂ band is shifted from 1354.55 cm^{-1} to 1450 cm^{-1} . The C-C band is shifted from 1609.17 cm^{-1} to 1630 cm^{-1} . The band at 1458.6 corresponding to benzene ring is shifted to 1460 cm^{-1} . The C-H band at 837.63 cm^{-1} suggests disubstituted benzene is shifted to 800 cm^{-1} . Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe^{2+} -TritonX 100 and $Zn(OH)_2$.

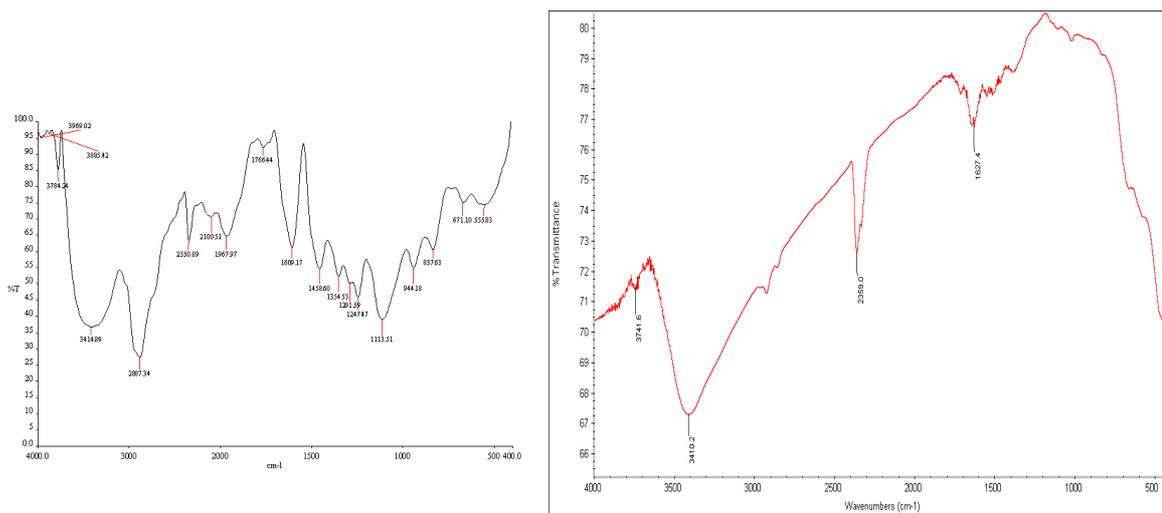


Figure 6. FTIR Spectrum of (a) Pure TritonX 100 (b) Well water + TritonX 100 (200ppm) + Zn^{2+} (50ppm)

Contact Angle measurements

When self Assembling monolayers are formed on metal surface, the surface becomes hydrophobic hence it becomes water repellent. Water molecules can not sit on the metal surface this is very similar to lotus effect (water droplets rolling on lotus leaves) so corrosion is prevented. As the hydrophobicity increases corrosion inhibition nature also increases.

Contact angles of water droplets formed on various metal surfaces are given in the following table 4. It is observed that for water droplet on polished mild steel surface the contact angle is 66° . In the case of metal surface immersed in the corrosion medium (well water) the contact angle increases 81.7° . It is interest in note that in the presence of inhibitor, the contact angle increases to 15.7° .

Table 4 Contact angle measurement for polished metal and metal surface after immersion in well water containing 200 ppm of Triton X 100 and 5 ppm of Zn^{2+}

S.No	Contact angle value for polished metal	Contact angle value for metal surface after immersion in well water containing 200 ppm of Triton X 100 and 5 ppm of Zn^{2+}
1.	66°	81.7°

Thus, it is evident that in presence of corrosion inhibitor (Triton X 100) , because of formation of self assembling monolayers contact angle increases ; hydrophobicity increases and hence corrosion inhibition increases figure 7a and 7b.

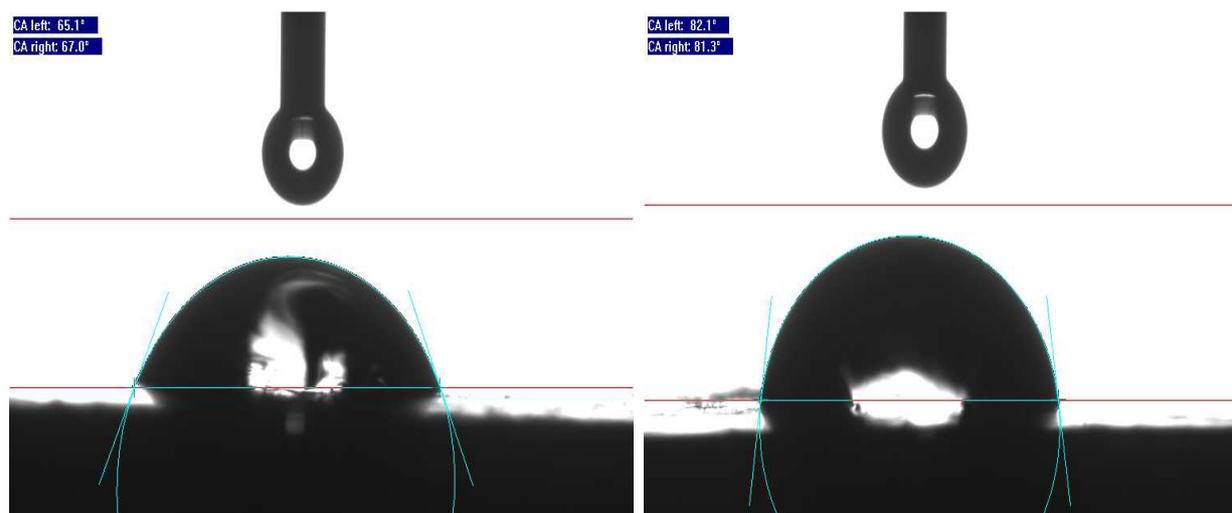


Figure 7(a) Contact angle measurement for polished metal (b) Contact angle measurement for metal surface after immersion in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

Formation of monolayers can be confirmed by analysis of the position of aliphatic –CH stretching frequency appear at 1354.55 cm^{-1} in figure 6a. In the presence of inhibitor Triton X 100 monolayers are formed on the metal surface by chemical deposition method. In this case the aliphatic –CH stretching frequency appear at 1450 cm^{-1} . There is the shift is not very much hence it is concluded that the aliphatic –CH groups are free. This confirming the formation of monolayers on the metal surface.

Mechanism of Corrosion inhibition

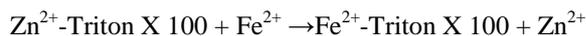
The results of the weight-loss study show that the formulation consisting of 200 ppm Triton X 100 and 50 ppm of Zn^{2+} has 84 % IE in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn^{2+} and Triton X 100. Polarization study reveals that this formulation functions as mixed type inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+} -Triton X 100 complex and $\text{Zn}(\text{OH})_2$. In order to explain these facts the following mechanism of corrosion inhibition is proposed.

When the solution containing well water, 50 ppm Zn^{2+} and 200 ppm of Triton X 100 is prepared, there is formulation of Zn^{2+} -Triton X 100 complex in solution.

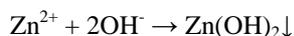
When carbon steel is immersed in this solution, the Zn^{2+} -Triton X 100 complex diffuses from the bulk of the solution towards metal surface.

Zn^{2+} -Triton X 100 complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe^{2+} -Triton X 100 complex, which is more stable than Zn^{2+} -Triton X 100.

On the metal surface Zn^{2+} -Triton X 100 complex is converted into Fe^{2+} -Triton X 100 on the anodic sites, Zn^{2+} is released.



The released Zn^{2+} combines with OH^- to form $\text{Zn}(\text{OH})_2$ on the cathodic sites.



Thus the protective film consists of Fe^{2+} -Triton X 100 complex and $\text{Zn}(\text{OH})_2 \downarrow$

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