Research Article

Corrosion inhibition of carbon steel by tween 20 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.

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INTRODUCTION

Corrosion is a natural process, which converts refined metal to their more stable oxide. It is the gradual destruction of materials (usually metals) by chemical reaction with their environment. In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal, and results in a distinctive orange colouration. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term degradation is more common. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases. A corrosion inhibitor is a chemical compound that, when added to a liquid or gas, decreases the corrosion rate of a material, typically a metal or an alloy. The effectiveness of a corrosion inhibitor depends on fluid composition, quantity of water, and flow regime. Nowadays, surfactants are widely used and find a very large number of applications in the petroleum industry. Surfactant inhibitors have many advantages, for example, high inhibition efficiency, low price, low toxicity, and easy production [1-4]. Moreover, the investigation of surfactants adsorbed on metal surfaces is extremely important in electrochemical studies such as corrosion inhibition, adhesion, lubrication, and detergency [4].

Several surfactants have been used as substitutes for mercury. The surfactants inhibit zinc corrosion by their adsorption on zinc [5-7]. The polar groups of surfactants are adsorbed on while the non-polar groups escape from the surface of zinc to form a protective layer that inhibits the corrosion of zinc. It has been found that the surfactants containing polyoxyethylene group are more effective than other surfactants as zinc corrosion inhibitors [8-11].

EXPERIMENTAL SECTION

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 well water containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} 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(w2/w1)] %

Where,

w_1= corrosion rate in absence of inhibitor
w_2= 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.

Potentiodynamic polarization study

This study was carried out using EG & G electrochemical impedance analyzer model 6310. A three-electrode cell assembly was used. Carbon steel was used as working electrode, platinum was used as counter electrode and saturated calomel electrode(SCE) was used as reference electrode. Corrosion potential, corrosion current and Tafel slopes were calculated.

Contact Angle Measurement

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 Tween 20 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 (Tween 20) are given in Tables 1 to 3. The inhibition efficiencies (IE) are also given in these Tables. The inhibition efficiencies of the Tween 20-Zn2+ systems as a function of concentrations of Tween 20 are shown in Fig. 1.

It is observed from Table 1 that Tween 20 shows some inhibition efficiencies. 200 ppm of Tween 20 has 32% inhibition efficiency, as the concentration of Tween 20 increases, the inhibition efficiency increases. This is due to the fact that as the concentration of Tween 20 increases, the protective film (probably iron Tween 20 complex) formed on the metal surface. At concentrations ≥ 250 ppm of Tween 20, 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: Tween 20-Zn^{2+} (0 ppm)
Immersion period: One day

Tween 20 (ppm)	Zn2+ (ppm)	CR (mdd)	IE%
0	0	18.18	-
50	0	14.91	18
100	0	14.18	22
150	0	13.45	26
200	0	12.36	32
250	0	13.09	28

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Influence of Zn²⁺ on the inhibition efficiencies of Tween 20

The influence of Zn²⁺ on the inhibition efficiency of Tween 20 is given in Table 2. It is observed that as the concentration of Tween 20 increases the IE increases. Similarly for a given concentration of Tween 20 IE increases as the concentration of Zn²⁺ increases. At concentrations ≥ 250 ppm of Tween 20, 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 Tween 20 and Zn²⁺. For example, 0 ppm of Zn²⁺ has 18 percent IE; 0 ppm of Tween 20 has 14 percent IE. Interestingly their combination has a high IE, namely 88 percent.

In the presence of Zn²⁺ more amount of Tween 20 is transported towards the metal surface. On the metal surface Fe²⁺- Tween 20 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 Tween 20.

$Fe \rightarrow Fe^{2+} + 2e^-$ (Anodic reaction)
$Fe^{2+} + Zn^{2+}$- Tween 20 complex $\rightarrow Fe^{2+}$- Tween 80 complex $+Zn^{2+}$
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (Cathodic reaction)
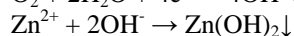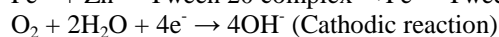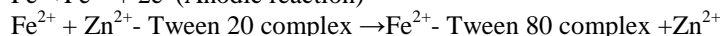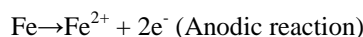$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$

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: Tween 20-Zn²⁺ (50 ppm)
Immersion period: One day

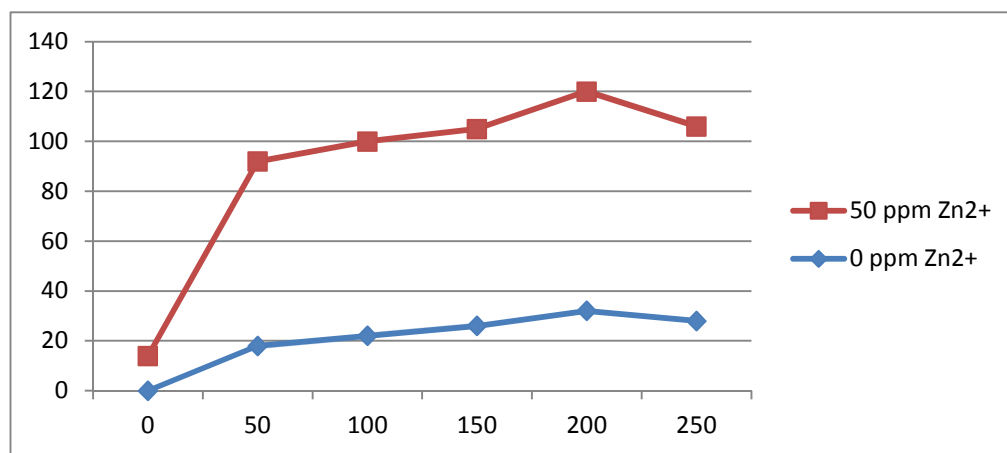| Tween 20 (ppm)	Zn²⁺ (ppm)	CR (mdd)	IE%
0	0	18.18	-
0	50	-	14
50	50	4.73	74
100	50	3.99	78
150	50	3.82	79
200	50	2.18	88
250	50	3.99	78

Fig.1: Corrosion rates (CR) of carbon steel immersed in various test solutions

Analysis of potentiodynamic polarization study

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process. If a protective film is formed on the metal surface, the linear polarization resistance value (LPR) increases and the corrosion current value (ICorr) decreases.

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Figure 2, the corrosion parameters are given in Table 4. When carbon steel was immersed in well water the corrosion potential was -828mV Vs SCE. When Tween 20 (200 ppm) and Zn²⁺ (50 ppm) were added to the above system the corrosion potential shifted to the noble side -810mV Vs SCE. This shows that the corrosion potential difference is very small therefore behaving like mixed type inhibitor which controls both anodic and cathodic reaction to an equal extent. This suggests 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 potentiodynamic polarization study

System	ECorr mV Vs SCE	bc mV Vs decade	ba mV Vs decade	ICorr A/cm^2	LPR ohmcm^2
Well water	-828	6.052	6.091	8.915x10-7	35319.7
Well water + Tween 20 (200 ppm)+Zn^{2+} (50ppm)	-810	6.302	6.309	6.368 x10-7	47656.7
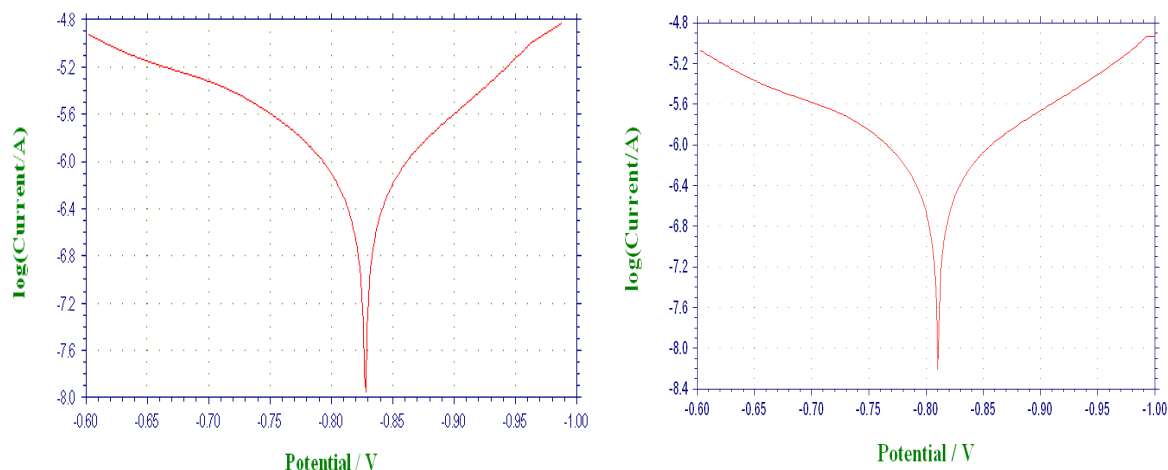
Figure 2: Polarization curves of mild steel immersed in various test solutions
Well water (blank) (b) Well water + Tween 20 (200 ppm)+Zn^{2+} (50ppm)

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 Tween 20 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 Tween 20 and 50 ppm Zn2+ is shown in Figure 6b. The peak at 3450 cm^{-1} is due to OH- stretching. The C=O stretching frequency has Shifted from1641.19 cm^{-1} to 1645.1 cm-1.This observation suggest that Tween 20 has coordinated with Fe2+ on metal surface through oxygen atom of resulting in the formation of Fe^{2+}- Tween 20 complex on the anodic sites of the metal surface. The peak at 674 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 1112.11 cm^{-1} is shifted to 1250 cm^{-1}. The CH$_2$ band is shifted from 1352.9 cm^{-1} to 1420 cm^{-1}. The band at 1458.84 corresponding to benzene ring is shifted to 1506.1 cm^{-1}. The C-H band at 851.69 cm^{-1} suggests disubstituted benzene is shifted to890 cm^{-1}. Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe^{2+}- Tween 20 and Zn(OH)$_2$.
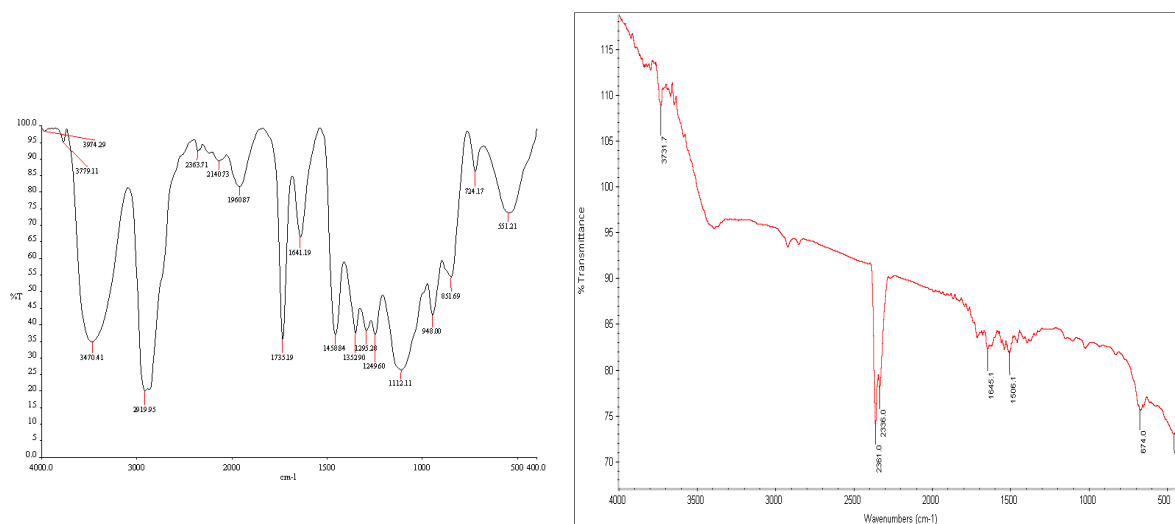
Figure 3: FTIR Spectrum of (a) Pure Tween 20 (b) Well water + Tween 20 (200ppm) + Zn^{2+}(50ppm)

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

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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 80.35◦. It is interest in note that in the presence of inhibitor, the contact angle increases to 14.35◦.

Table 4 Contact angle measurement for polished metal and metal surface after immersion in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn2+

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 Zn2+
1.	66◦	80.35◦

Thus, it is evident that in presence of corrosion inhibitor (Triton X 100) , because of formation of self assembling monolayers contact angle increases ; hydrophobocity increases and hence corrosion inhibition increases figure 4a and 4b.
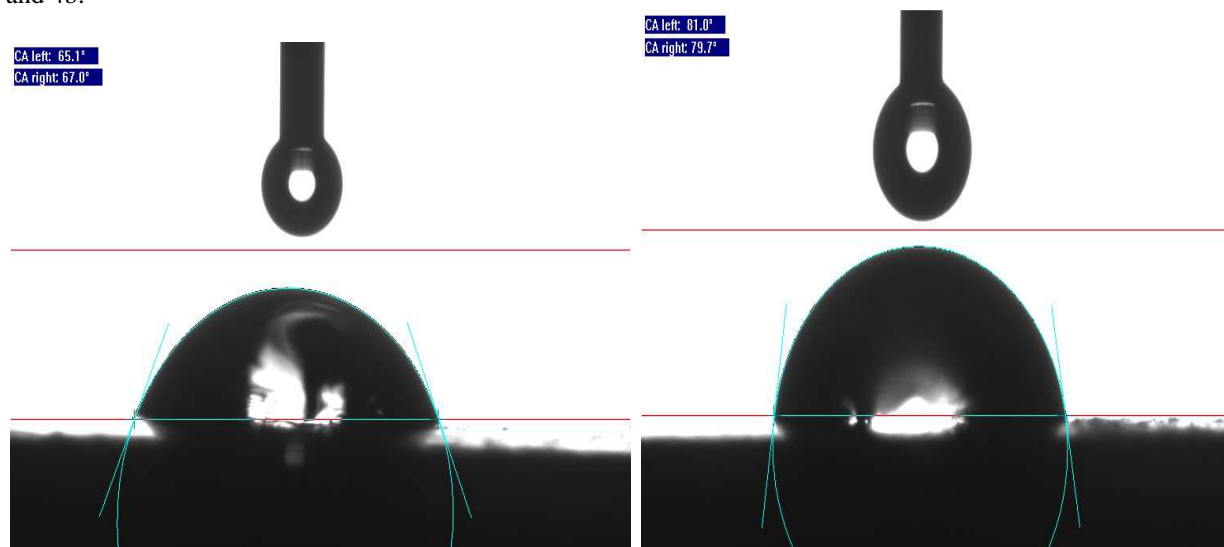

Figure 4: Contact angle measurement for (a) polished metal (b) Contact angle measurement for metal surface after immersion in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

**Mechanism of Corrosion inhibition**

The results of the weight-loss study show that the formulation consisting of 200 ppm Tween 20 and 5 ppm of Zn^{2+} has 88 % IE in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn^{2+} and Tween 20. 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+}-Tween 20 complex and Zn(OH)$_2$. In order to explain these facts the following mechanism of corrosion inhibition is proposed.

When the solution containing well water, 5 ppm Zn^{2+} and 200 ppm of Tween 20 is prepared, there is formulation of Zn^{2+}-Tween 20 complex in solution.

When carbon steel is immersed in this solution, the Zn^{2+}-Tween 20 complex diffuses from the bulk of the solution towards metal surface.

Zn^{2+}-Tween 20 complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe^{2+}-TWEEN 20 complex, which is more stable than Zn^{2+}-Tween 20.

On the metal surface Zn^{2+}-TWEEN 20 complex is converted into Fe^{2+}-Tween 20 on the anodic sites, Zn^{2+} is released.

Zn^{2+}-Tween 20 + Fe^{2+} →Fe^{2+}-Tween 20 + Zn^{2+}
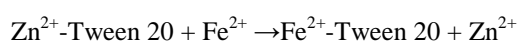
The released Zn^{2+} combines with OH- to form Zn(OH)2 on the cathodic sites.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$$
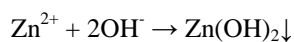
Thus the protective film consists of Fe^{2+}-TWEEN 20 complex and $Zn(OH)_2\downarrow$

In presence of inhibitor system self-assembling monolayers of TWEEN 20 are formed on the metal surface. So, hydrophobicity and hence corrosion inhibition increases. This is supported by FTIR spectra and contact angle measurement.

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