CYCLIC VOLTAMMETRIC AND AFM STUDY OF CORROSION INHIBITION AND ADSORPTION BEHAVIOR OF SODIUM DODECYL SULPHATE-ZN²⁺ ON CARBON STEEL IN AQUEOUS MEDIUM

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ABSTRACT

The inhibition of corrosion of Sodium Dodecyl Sulphate and the synergistic effect with Zn²⁺ taking place on the surface of carbon steel in well water medium were studied using mass reduction technique, cyclic voltammetry (CV), Atomic Force Microscopy (AFM), FTIR and Contact Angle measurement. The effects showed that there is a protective layer formed on the surface of carbon steel and also that the protective layer is stable even in presence of 3.5% sodium chloride solution. This confirms that there was a formation of self-assembled monolayer on the surface of the carbon steel and there was a synergistic effect occurs among Zn²⁺ and Sodium Dodecyl Sulphate.

Keywords: SDS, Corrosion Inhibition, Synergistic Effect, Carbon Steel.

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INTRODUCTION

Corrosion is known as the destruction of resources caused by the contact of the metal surfaces by the corrosive environment. The destruction attributed to metal decay has become a major difficulty in the worldwide financial system. Metal deterioration remains an electrochemical process that is taking place between a metal and its environment including both oxidation and reduction reactions.¹ Oxidation occurs at anode and reduction occurs at cathode of the surface of the metal.

A lot of machinery components in petroleum production industry like drilling gears, production vessels and downhole tubular are fabricated from carbon steel.² Corrosion can destruct the materials which are used to make automobiles, pipelines, systems, bridges and buildings, petroleum refineries³. Hence it is important to protect metals from destruction.

Corrosion inhibitors have been used to reduce metal corrosion in various industries and also there are many scientific pieces of evidence for the inhibitors which decrease corrosion on metals.^{4,5,6,7,8}

Among organic, inorganic, mixed and surfactant inhibitors, an essential corrosion-resistant device is surfactant. Surfactant molecules will form micelles and the hydrophobic effect enhances adsorption of the functional groups present in the surfactant molecule onto the metal surface and forming a protective layer even at low surfactant concentrations.⁹ This layer reduces corrosion of the metal. Benefits of surfactants are great inhibition effect, lesser price, eco-friendly and easy making and so on.¹⁰

For the present work Sodium Dodecyl Sulphate which is an anionic surfactant has been selected for reducing corrosion effect taking Zn²⁺ by means of the co-inhibitor.

The following work will explain:

- The efficiency of corrosion inhibition of SDS in reducing the destruction of carbon steel in the presence and absence of Zn²⁺

- ii. The formation of the protective film on carbon steel by atomic force microscopy (AFM) and FT-IR spectroscopy
- iii. The systematic characteristics through cyclic voltammetry study
- iv. An appropriate mechanism meant for inhibition of corrosion.

EXPERIMENTAL

Materials and Solutions

The rectangular samples (1 X 4 X 0.2cm) of carbon steel were used for weight loss measurements. For cyclic voltammetry measurements, cylindrical carbon steel electrodes were routinely polished with emery paper, rinsed using double distilled water, degreased using trichloroethylene and dehydrated at room temperature.

AnalaR sample of Sodium Dodecyl Sulphate, analytical reagents $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and sodium chloride were used for the experimental investigations.

Electrochemical Measurements

Components of three-electrode cell assembly for this work are a working electrode (Carbon steel), a counter electrode (Platinum wire) and a reference electrode (Saturated calomel) were used for recording cyclic voltammogram.

Surface Analysis by FT-IR Spectroscopy

Perkin-Elmer 1600 FT-IR spectrometer was used to record the spectrum of the powder (KBR pellet).

Contact Angle Measurements

To fit the proper water drop shape and also to analyze the contact angle between the water droplet and surface of the carbon steel an instrument with VCA Optima XC software was used.

Atomic Force Microscopy Characterization (AFM)

To find out the surface morphology of the metal Veeco Innova model was used. Scanning has been done in the tapping mode, $50\mu\text{m} \times 50\mu\text{m}$ was the scan area in the image and 0.6 Hz S^{-1} was fixed as the scan rate.

Mass Loss Technique

Traditional mass loss tests were carried out in a well water medium using rectangular carbon steel at room temperature for 24 hours.

RESULTS AND DISCUSSION

Electrochemical Techniques

Cyclic Voltammetric Technique

Cyclic voltammetry is an important electrochemical technique which is adopted for analyzing the electrochemical characteristics of an analyte solution.¹¹

The Cyclic Voltammogram of Polished Carbon Steel Immersed in 3.5% NaCl Solution

The cyclic voltammogram recorded for the number of one cycle for the polished carbon steel dipped in 3.5% sodium chloride is given in Fig.- 1(a). On observing a peak during anodic sweep at -425 mV which is called a metal dissolution peak. Once the polarisation at anodic side of metal reaches a definite critical potential, a peak appeared at -100mV is corresponding to the pitting potential (E_{pit}), that is the pitting potential for polished carbon steel surface is appeared at more negative side due to corrosion. Because it does not have any protective coating of film on the surface of the metal.

Whereas there are two peaks appeared on cathodic sweep, one peak appeared on -420mV indicating the reduction of corrosion product and another peak appeared at -1.10V which is known as reduction of iron oxide product and the reduced corrosion current density occurs at $-1.0 \times 10^{-3}\text{A}$. When the metal dissolves, there is a formation of $\text{Fe}(\text{OH})_2$ and/or FeO film on the surface of the metal. As a result of high polarizability of the Chloride ions, the Cl^- ions are adsorbed on the surface of the metal than that of OH^-

ions. The adsorbed Cl^- ions enter the FeO film on the imperfections in the FeO film. When Cl^- ions approach the surface of the metal that will stimulate the local corrosion.

Cyclic Voltammogram for Polished Carbon Steel Surface Immersed in Well Water for One Day

The Cyclic Voltammogram recorded for the number of one cycle for the polished metal dipped for one day in a well water medium. A protective film has been found on the surface of the metal. The metal with this protective film was immersed in 3.5% sodium chloride solution is given in Fig.- 1(b). It is detected that on anodic sweep, the metal dissolution peak does not appear. Absence of electrons on the metal surface indicating the reasonable stability of the protective film formed on the metal surface.

When the anodic polarisation of carbon steel reaches a certain critical potential, A peak appeared at 150mV when the anodic polarisation approaches critical potential which is corresponding to the pitting potential. This shows that in a well water medium, there is a formation of protective film on the surface of the metal as a result of the existence of many anions and cations in well water. When this electrode containing this protective film is dipped in 3.5% sodium chloride and on recording cyclic voltammogram is observed that the protective film is not broken; it seems to be stable hence, the potential is moved towards the anodic part (+150mV). This shows that there should be a stable iron, iron oxide protective film and other iron compounds on the surface of the metal.

During the cathodic sweep reduction of pitting corrosion, the product peak is moved to -500mV shows the possibility of pitting corrosion. The iron oxide reduction peak is moved from -1.10V to -1.30 V; that is towards more negative side and its current density is $-1.30 \times 10^{-3} \text{A}$ indicating that the film is unstable that is unreactive.

Cyclic Voltammogram for Polished Carbon Steel Surface Containing 50 ppm of Zn^{2+} and 200 ppm of SDS in Well Water for One Day

The Cyclic Voltammogram recorded for the number of one cycle of polished metal, dipped in well water containing 50 ppm of Zn^{2+} and 200 ppm of SDS for one day. A protective film was found on the surface of Carbon steel. The carbon steel surface having this protective film was dipped in 3.5% sodium chloride solution is given in Fig.- 1(c). It is detected that for the period of anodic sweep, metal dissolution was not observed but a passive region is noticed without the transfer of an electron from the surface of the carbon steel. In the passive region the corrosion resistance increases due to the formation of thin surface film. The passive film becomes stable and corrosion rate falls to very low value and hence protects the metal against further oxidation. Pitting potential (E_{pit}) peak appears at 1.5V that is shifted to more positive side because of the presence of Fe^{2+} -inhibitor stable complex on the carbon steel surface.

During the cathodic sweep, absence of pitting corrosion product peak reveals the absence of pitting corrosion under the experimental conditions. The peak due to the reduction of FeO peak to iron is moved from -1.10V to -1.72V that is more negative side and its current density is shifted from $-1.0 \times 10^{-3} \text{A}$ to $-5.2 \times 10^{-3} \text{A}$. This confirms the development of compact and stable Fe^{2+} -inhibitor complex and there is also a possibility of deposition of Zn^{2+} -inhibitor complex on the metal surface and hence it can tolerate the attack of Cl^- ions present in 3.5% sodium chloride.

FT-IR Spectra

FT-IR spectroscopy is a powerful tool used to analyze the formation of the protective film on the carbon steel surface.¹² The FT-IR spectrum (KBr pellets) for pure SDS and the FTIR spectrum (KBr pellets) for the protective film formed on the metal surface that is dipped in SDS and Zn^{2+} solution are represented in Fig.-s 2 (a,b). The FT-IR spectrum (KBr pellets) for the protective film that is formed on the metal surface after dipping in 50 ppm of Zn^{2+} and 200 ppm of SDS solution is represented in Fig.- 2(b). It is observed that there is a decrease in $\text{S}=\text{O}$ stretching frequency from 1291.8 to 1239.0cm^{-1} and decrease in $\text{S}-\text{O}$ stretching frequency from 446.3cm^{-1} to 429.14cm^{-1} . There is a decrease in $\text{S}-\text{O}-\text{C}$ bands from 908.2cm^{-1} to 850.5cm^{-1} respectively. These decrease in frequencies representing that the electron clouds of $\text{S}=\text{O}$ and $\text{S}-\text{O}$ are moved to Fe^{2+} bring about the development of $\text{SDS}-\text{Fe}^{2+}$ complex on the surface of the carbon steel. The band at 531.6cm^{-1} is indicating $\text{Fe}-\text{O}$ stretching vibration. The bands at 894.81cm^{-1} and 758.2cm^{-1} are caused by $\text{Zn}-\text{O}$ stretching and bending vibrations respectively.

Fig.-1: Cyclic Voltammogram of (a.) Polished Metal Dipped in 3.5% Sodium Chloride Solution, (b.) Metal Dipped in Well Water for One Day, (c.) Metal in Well Water with 50 ppm of Zn^{2+} and 200 ppm of SDS for One Day

Fig.-2: FT-IR Spectra for (a) Sodium Dodecyl Sulphate (Pure Form), (b) Carbon steel dipped in Zn^{2+} and Sodium Dodecyl Sulphate Solution.

Table-1: Contact Angle Values for Carbon Steel (Polished) and Carbon Steel Dipped in Zn^{2+} (50 ppm) and Sodium Dodecyl Sulphate (200ppm) in Well Water Medium.

S. No.	Carbon Steel (polished)	Carbon Steel Dipped in Zn^{2+} (50 ppm) and Sodium Dodecyl Sulphate (200ppm) in Well Water Medium
1	66°	85.4°

Contact Angle Measurements

Table-1 representing the contact angle values between water droplets and the carbon steel surface with and without protective film while dipping the metal in a well water medium.¹³ The contact angle values are given as 66°, 85.4° for polished carbon steel and the carbon steel dipped in well water medium respectively. This increase in contact angle value (19.4°) in presence of Sodium Dodecyl Sulphate explaining the development of self-assembling monolayer on the surface of the metal by chemical deposition method. This can be confirmed by the aliphatic -CH stretching frequencies slightly moved from 2851cm^{-1} to 2880cm^{-1} and from 2980cm^{-1} to 2919.4cm^{-1} . This kind of lower shifts representing the free -CH groups and are confirming the development of monolayer on the surface of the carbon steel. Fig.-3(a,b) indicating that there is a reasonable increase in hydrophobicity and the rate of corrosion inhibition.

Fig.-3: Contact Angle Value for (a) Carbon Steel (Polished), (b) Carbon Steel Dipped in Zn^{2+} (50 ppm) and Sodium Dodecyl Sulphate (200ppm) in Well Water Medium

Atomic Force Microscopy

Atomic Force Microscopy (AFM) has been used to find out the surface morphology of various metal surfaces.¹⁴ From Table- 2 the R_a , R_q and (P-V) values that are average roughness, root-mean-square roughness and the maximum peak-to-valley (P-V) height values for carbon steel in various environments have been obtained. 16.49 nm, 20.75 nm and 107.26 nm are the R_a , R_q and (P-V) values for the polished carbon steel respectively. From Fig.-4 (a,b, c) and 5 (a, b, c) it is observed that there is a roughness on the surface of the polished carbon steel because of atmospheric corrosion. 85.37 nm, 118.65 nm and 118.65 nm are the R_a , R_q and (P-V) values for the carbon steel dipped in well water medium respectively. Fig.-4(b) and 5(b) shows few pits on the carbon steel surface when dipped in well water without the inhibitor. 24.28 nm, 31.85 nm and 253.91 nm are the R_a , R_q and (P-V) values for the carbon steel dipped in Zn^{2+} (50 ppm) and Sodium Dodecyl Sulphate (200 ppm) in well water medium respectively. Fig.-4(c) and 5(c) shows the smoother carbon steel surface because of the formation of Fe^{2+} -SDS complex and $\text{Zn}(\text{OH})_2$ on the surface of the carbon steel and hence increases the corrosion inhibition efficiency.

Table-2: Atomic Force Microscopic Values

Sample	Average Roughness (R_a) (nm)	RMS Roughness (R_q) (nm)	Maximum Peak-to-valley height (P-V) (nm)
Carbon steel (Polished)	16.49	20.75	107.26
Carbon steel dipped in well water medium	85.37	118.65	631.13

Carbon steel dipped in Zn^{2+} (50 ppm) and Sodium Dodecyl Sulphate (200 ppm) in well water medium	24.28	31.85	253.91
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Fig.- 4: Two Dimensional Atomic Force Microscopic Images for (a) Carbon Steel (Polished), (b) Carbon Steel Dipped in Well Water Medium, (c) Carbon Steel Dipped in Zn^{2+} (50 ppm) and Sodium Dodecyl Sulphate (200 ppm) in Well Water Medium

Synergistic Effect of Zn^{2+} and Sodium Dodecyl Sulphate

Mass Loss Method

Table- 3 representing the corrosion rate and corrosion inhibition efficiency values for carbon steel dipped in various inhibitor environments and it is observed from this Table- that there is a synergistic effect occurs among Zn^{2+} and Sodium Dodecyl Sulphate. The combination of 50 ppm of Zn^{2+} and 200 ppm of Sodium Dodecyl Sulphate shows 92% Corrosion inhibition efficiency. When the carbon steel dipped in Zn^{2+} and Sodium Dodecyl Sulphate separately there is a considerable decrease in corrosion inhibition efficiency that is 16% and 40% respectively.

The increase in corrosion inhibition efficiency is due to the formation of Fe^{2+} -SDS complex on the anodic part of the surface of the carbon steel and preferably controlling anodic reaction. Formation of $\text{Zn}(\text{OH})_2$ on the cathodic part of the surface of the carbon steel and preferably controlling cathodic reaction hence confirming the synergistic effect among Zn^{2+} and Sodium Dodecyl Sulphate.

Fig.-5: Three Dimensional Atomic Force Microscopic Images for (a) Carbon Steel (Polished), (b) Carbon Steel Dipped in Well Water Medium, (c) Carbon Steel Dipped in Zn^{2+} (50 ppm) and Sodium Dodecyl Sulphate (200 ppm) in Well Water Medium

Table-3: Corrosion Rates (CR) and the Inhibition Efficiencies (IE) gained from the Mass Loss Method for Zn^{2+} and Sodium Dodecyl Sulphate System Dipped in Well Water Medium for One Day

SDS (ppm)	Zn^{2+} (0 ppm)		Zn^{2+} (25 ppm)		Zn^{2+} (50 ppm)	
	CR (mdd)	IE%	CR (mdd)	IE%	CR (mdd)	IE%
0	18.18	-	18.18	-	18.18	-
50	13.82	24	15.99	12	14.27	16
100	13.09	28	5.82	68	4.36	76
150	12.36	32	5.09	72	3.64	80
200	10.91	40	3.99	78	2.91	84
250	13.09	28	3.27	82	1.45	92

Outline of Corrosion Inhibition Mechanism is Given Below

- Carbon steel is dipped in a well water medium containing 50 ppm Zn^{2+} and 200 ppm Sodium Dodecyl Sulphate inhibitor system.
- There is a formation of Zn^{2+} and Sodium Dodecyl Sulphate complex in the solution and then this complex is spread to the carbon steel surface.
- On the carbon steel surface, Zn^{2+} and Sodium Dodecyl Sulphate complex are converted into Iron and Sodium Dodecyl Sulphate complex that is more stable in nature.
- Fe^{2+} -Sodium Dodecyl Sulphate complex is formed on the anodic part and $\text{Zn}(\text{OH})_2$ is formed on the cathodic part of the carbon steel surface.

- This confirms that the protective film is having Fe^{2+} -Sodium Dodecyl Sulphate and $\text{Zn}(\text{OH})_2$.

CONCLUSION

From the above data, the observations are given below,

- FT-IR spectral data confirm the development of protective film on the surface of the carbon steel.
- Contact angle values explain the hydrophobicity of the surfactant
- AFM images show the surface morphology of carbon steel.

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