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Hydrophobicity and Corrosion Inhibition by Self Assembling Nano Films on metal surface – An Over View

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" Hydrophobicity and Corrosion Inhibition by Self assembling nano films on metal surface "

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Abstract

Self assembling nano films of surfactants on mild steel surface has been assembled by immersion method. These films have been analysed by AFM study. Contact angle measurement reveals the hydrophobic nature of the protective film. This film offers better corrosion inhibition efficiency as revealed by weight loss method

Keywords:

Self assembling nano films , surfactant films on mild steel surface, AFM , Contact angle , corrosion inhibition , hydrophobicity.

Introduction

Self-assembly is a process in which a disordered system of pre-existing components forms an organized structure or pattern as a consequence of specific, local interactions among the components themselves, without external direction. When the constitutive components are molecules, the process is termed molecular self-assembly.

Self assembling nanofilms have many potential applications in many areas such as non-wetting surface, corrosion inhibition, lubrication, monolayer lithography, biocompatible surfaces, etc. Self assembling nano layers are found to be hydrophobic and hence prevent water molecules reaching the metal surface. Hence corrosion of metals is prevented by self assembled nano films formed on metal surface. The water repelling nature of nano layers can be compared with "Lotus Effect", wherein water droplets roll down the lotus leaves whereby self cleaning effect also takes place. Self assembling molecules have been used to control corrosion of metals [1-11].

Behpour and Mohammadi have investigated the inhibition properties of aromatic thiol selfassembled monolayer for corrosion protection[4]. Formation of inositol hexaphosphate monolayers at the copper surface from a Na-salt of phytic acid solution has been reported by Yang et al [8]. Self-assembling adhesion promoters for corrosion resistant metal polymer interfaces have been devised by Maege et al. [11].

Self assembled mono layers are found to hydrophobic in nature. This is confirmed by measuring the contact angle of the metal surface. As the contact angle increases, hydrophobicity increases, wettability decreases, and corrosion resistance of the surface increases[12- 15]. When the contact is greater than 80°, the surface is considered as hydrophobic. The surface becomes super hydrophobic, when the contact is greater than 140°. It is observed that when surfactants are used as inhibitors, self assembling takes place and the surface becomes hydrophobic and corrosion resistant [12, 13, 15]. Benzotriazole also creates hydrophobic surface [14].

In the present work self assembling of some surfactants on mild steel surface has been investigated.

Experimental

High purity chemicals were used in the present study. Nano films were formed on the metal surface such as mild steel by the simple immersion method for a period of one day in an aqueous medium containing suitable concentration of the inhibitors.

Weight loss method

Mild steel specimens of the dimension $1 \times 4 \times 0.2$ cm were used in the present study. The composition of the carbon steel is: specimens Composition (wt %): 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron.

The metal specimens in triplicate were immersed in a suitable medium for one day. Weight of the metal specimens was measured before and after immersion. Corrosion rates and the inhibition efficiency (IE) were calculated using the formula:

IE= 100[$(w_1 - w_2)/w_1$] % ,where, w_1 = corrosion rate in the absence of inhibitors; w_2 = corrosion rate in the presence of inhibitors.

Contact Angle

The contact angle measurements on the 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 5 mL 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, the average values with standard deviations ±2 are reported.

Atomic Force Microscopy

All atomic force microscopy images were obtained in a VECCO lab incorporation AFM instrument in contact mode in air. The scan size of all the AFM images are 50 μ m × 50 μ m areas at a rate of 6.68 μ m/second.

Root-mean-square roughness, average roughness, and peak-to-valley value were calculated.

AFM image analysis was performed to obtain the average roughness, R_a (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, R_q (the average of the calculated height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to- valley height in five adjoining sampling heights).

Results and Discussion

Inhibition of corrosion of mild steel in well water by self assembling nano films of surfactants

Inhibition efficiencies (IE %) of various surfactant systems like CTAB-Zn²⁺, SDS-Zn²⁺, Tween20-Zn²⁺, Tween80-Zn²⁺, TritonX100-Zn²⁺ in controlling corrosion of carbon steel immersed in well water in the presence and absence of inhibitor system for one day have been evaluated. Inhibition efficiency has been evaluated by weight loss method.

Analysis of results of weight loss method

Inhibition efficiencies (IE %) of various systems like CTAB-Zn²⁺, SDS-Zn²⁺, Tween20-Zn²⁺, Tween60-Zn²⁺, Tween80-Zn²⁺, TritonX100-Zn²⁺ in controlling corrosion of carbon steel immersed in well water in the presence and absence of inhibitor system for one day are comparatively given in Table 1.

Table 1: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system and the inhibition efficiencies (IE %) obtained by weight loss method.

System	CR, mdd	IE %
Blank	18.18	-
CTAB (200 ppm) + Zn ²⁺ (50	0.73	96
ppm)		
SDS (200 ppm) + Zn ²⁺ (50	1.45	92
ppm)		
Tween 80 (200 ppm) + Zn ²⁺	1.82	90
(50 ppm)		
Tween 60 (200 ppm) + Zn ²⁺	2.18	88
(50 ppm)		
Tween 20 (200 ppm) + Zn ²⁺	2.73	85
(50 ppm)		
Triton X 100 (200 ppm) +	2.91	84
Zn²+ (50 ppm)		

From the above table 1, it is observed that CTAB (200 ppm) + Zn^{2+} (50 ppm) has good inhibition efficiency. The inhibition efficiency of various surfactants are in the following order:

CTAB (200 ppm) + Zn^{2+} (50 ppm) > SDS (200 ppm) + Zn^{2+} (50 ppm) > Tween 80 (200 ppm) + Zn^{2+} (50 ppm) > Tween 60 (200 ppm) + Zn^{2+} (50 ppm) > Tween 20 (200 ppm) + Zn^{2+} (50 ppm) > Triton X 100 (200 ppm) + Zn^{2+} (50 ppm)

Atomic Force Microscopy

Atomic force microscopy is a powerful technique for gathering roughness statistics from a variety of surfaces. AFM is becoming an accepted method of roughness investigation[16,17].

The AFM images of the surface of polished metal, polished metal immersed in well water and in various inhibitor environments were recorded. The AFM parameters derived from these images are summarized in Table2.

Table 2: AFM data for carbon steel surface immersed in inhibited and uninhibited environments.

Samples	Roughness, nm		Maximum peak to valley height, nm
	RMS (R _q)	Average (R _a)	_
Polished	20.75	16.49	107.26
Well water	118.65	85.37	631.13
СТАВ	75.30	55.31	526.23
SDS	31.85	24.28	253.91
Tween 80	29.22	17.36	271.68
Tween 60	46.56	39.07	219.01
Tween 20	79.19	63.08	348.96
Triton X 100	81.47	62.07	490.05

It is observed that for polished metal, the AFM parameters namely R_q , R_a and P-V are low. For corrosive medium surface, these parameters are verified. For various inhibitor systems, these parameters are in between the extreme cases. The smoothness of surface is correlated to effective corrosion inhibition efficiency.



The self assembling model of CTAB is shown in Fig.1 as an example.

Fig.1. Self assembling model of CTAB

The rolling down of the water drops on the hydrophobic surface is shown in Fig.2.





2.11 Contact Angle measurements

When self-assembling monolayers are formed on metal surface, the surface becomes hydrophobic. Hence it becomes water repellent. Water molecules cannot 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.

It is observed that for water droplet on polished carbon steel surface the contact angle is 66° . In the case of metal surface immersed in the corrosion medium (well water) containing 200 ppm of CTAB and 50 ppm of Zn²⁺, 200 ppm of SDS and 50 ppm of Zn²⁺, 200 ppm of Tween 80 and 50 ppm of Zn²⁺, 200 ppm of Tween 60 and 50 ppm of Zn²⁺, 200 ppm of Tween 20 and 50 ppm of Zn²⁺, 200 ppm of Triton X 100 and 50 ppm of Zn²⁺ the increase in contact angle are given as

follows 91.1°, 85.4°, 84.5°, 84°, 81.7°, 81.1° respectively. Thus, it is evident that in presence of corrosion inhibitor (CTAB), because of formation of self-assembling monolayers, contact angle increases; hydrophobicity increases and hence corrosion inhibition increases shown in Figure 3 (a-g).







Figure 3: Contact angle measurement for carbon steel syrface immersed in

Well water (blank)

- (a) Well water containing 200 ppm of CTAB and 50 ppm of Zn²⁺
- (b) Well water containing 200 ppm of SDS and 50 ppm of Zn²⁺
- (c) Well water containing 200 ppm of Tween 80 and 50 ppm of Zn^{2+}
- (d) Well water containing 200 ppm of Tween 60 and 50 ppm of Zn²⁺
- (e) Well water containing 200 ppm of Tween 20 and 50 ppm of Zn²⁺
- (f) Well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

Conclusion

Weight loss method reveals that the greater inhibition efficiency of CTAB than the other surfactants comparatively.

Contact angle measurement explains the hydrophobic nature of surfactant FILM.

AFM images show the surface morphology of metal FILM.

Summary

Self assembling nano films of surfactant films on mild steel surface have been formed by immersion method. These films have been analysed by AFM study. Contact angle measurement reveals the hydrophobic nature of the protective film. This film offers better corrosion inhibition efficiency.

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