Self-assembling nano films on metal surface as corrosion inhibitors

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Abstract

Self-assembling molecules form protective layers on metal surfaces Self assembled nanofilms of adipic acid, N-cetyl-N,N, N-trimethyl ammonium bromide, Tween- 60, Sodium dodecyl sulphate and an aqueous extract of banana peel have been formed on the surface of carbon steel by the immersion method. The formation of the nanofilms has been confirmed by Fourier Transform Infrared spectral study and Atomic Force Microscopy Study. The corrosion inhibitive nature of the protective film has been estimated by the classical weight loss method and electrochemical study such as polarization study. The hydrophobic nature of the protective film has been investigated by measurement of contact angles of the protective films. The hydrophobic surfaces may find application in various exciting fields such as corrosion protection, raincoats, water proof surfaces and biomaterials. Copyright © 2017 VBRI Press.

Keywords: Self assembling nanofilm, corrosion inhibition, hydrophobic surfaces, AFM, FTIR, contact angle measurement, hydrophobicity.

Introduction

Corrosion can be considered as a natural process. This spontaneous process is thermodynamically favorable. The rate of corrosion can be controlled by many methods. Use of corrosion inhibitors is one such method. These inhibitors may be classified as anodic type, cathodic type or mixed type. This classification depends on whether they control anodic reaction or cathodic reaction or both type of reactions, predominantly. A good inhibitor is expected to be water soluble and hydrophobic (to displace water from metal surface). The corrosion inhibitors should have a good delivery mechanism also.

Nanotechnology is one of the hottest fields, which draws attention from all over the world and has the potential to outdate most of the technology existing today. Nanomaterials are very important because they have very special properties which may lead to new and exciting application including corrosion control [**1**]. Nanoparticles-based corrosion inhibitors offer better corrosion protection efficiency than the ordinary ones, because as the size of the particle decreases the surface area for a given mass and hence the number of active centers increases. Finally, this leads to efficient chemisorptions/physisorption of nanosized inhibitors on corroding metal surfaces. So, enhanced corrosion inhibition efficiency can be realized where nanoparticles/nano films are used as corrosion inhibitors.

Self-assembling nanofilms can be formed on the metal surface or metal oxide surface by various techniques which include simple immersion method in a suitable solvent containing the molecules to be assembled on the metal surface. Molecules can be assembled on nickel [**2- 9**], which is a key component in the electronic industry and an important alloying constituent in many biometrials. Self-assembling nanofilm can be formed on copper surface [**10-14**] and carbon steel surfaces [**15,16**].

Self-assembling nanofilms have many potential applications in many areas such as non-wetting surface, corrosion inhibition, lubrication, monolayer lithography, biocompatible surfaces,etc [**17-19**]. 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 rolled down the lotus leaves whereby self-cleaning effect also takes place.

Self-assembling monolayer of n-alkanoic acids **[20-21**] and alkyl phosphonic acids [**19-22**] have been investigated. In the present work the corrosion inhibitive efficiencies of self-assembled nano films of glycine, adipic acid, N-cetyl-N,N,N-trimethyl ammonium bromide, Tween 60, Sodium dodecyl sulphate and an aqueous extract of banana peel have been evaluated. Because of the deposition of hydrophobic films on the surface of the metal the corrosion inhibition efficiency will increase.

Experimental

All the chemicals used in the present study are very pure chemicals. Nano films were formed on the surface of the metal such as carbon steel by the simple immersion technique for a duration of one day in an aqueous medium which contains suitable concentration of the inhibitors.

Weight loss method

Carbon steel specimens of the dimension 4 x 1 x 0.2 cm were used in the present work. 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 carbon steel samples in triplicate were dipped in a suitable medium for a period of one day. Weight of the metal specimens was measured before and after immersion. Corrosion rates and the inhibition efficiency (IE) were determined using the formula:

IE= 100[(r1- r2)/r1] % ,where, r1 = corrosion rate in the absence of inhibitors; r2 = corrosion rate in the presence of inhibitors.

FTIR

A Perkin-Elmer -1600 spectrometer was used to record FTIR spectra. KBr pellet method was used. The protective film was removed and made into KBr pellet to record the spectrum. The resolving power was 4 cm-1.

Contact angle

A VCA Optima instrument, provided with a CCD camera was used to measure the contact angle of the protective film formed on the metal surface. A drop volume of 5 mL was used to determine the contact angle. The experiment was repeated thrice.

Polarization studies

A CHI – Electrochemical workstation with impedance, Model 660A was used to record Polarization curves using a three-electrode cell assembly (Block diagram 1). A saturated calomel electrode (SCE) was used reference electrode Platinum was used as the counter electrode. Mild steel was employed as working electrode. Corrosion parameters were calculated.

AC impedance spectra

The instrument used for polarization study was used for AC impedance study also. The spectra were recorded in the same three electrode cell assembly. AC impedance parameters such as the charge transfer resistance (Rt) and the double layer capacitance (Cdl) were determined.

Results and discussion

Self assembled nanofilm of adipic acid (AA) and corrosion inhibition

Adipic acid has the ability to control the corrosion of carbon steel in chloride medium (60 ppm of Cl^-). This has been evaluated by classical weight loss method. The formulation consisting of 50 ppm of AA prevents the corrosion of carbon steel by 86%. AA molecules form self-assembling monolayers of nanofilm on carbon steel. When water molecules sit on this surface, they will be simply rolled down, because the nanofilms function as asperities, just like in lotus effect. These asperities function as water repellent surface. Hence, water molecules hesitate to reach the metal surfaces and thus corrosion resistance increases. In presence of self assembled nanofilm, contact angle increases, wetability decreases and hydrophobicity increases and hence corrosion resistance increases. The stability of protective film was evaluated by immersing the metal surface in 1N H_2SO_4 and also in 1N NaOH Solution. The analysis of FTIR spectra of these films after immersion in either acid or base revealed that the protective film is stable. There was no substantial change in FTIR spectra of these surface films.

FTIR spectra

Presence of two peaks (2811 and 2726 cm-^{1}) in the region of 2700 to 3000 cm-^{1}, corresponding to γ-CH_2 symmetry and γ-CH_2 unsymmetry indicated that the self assembled film formed on the surface the metal is stable. **Fig. 1(a)** represents the FTIR spectrum (KBr) of adipic acid . When mild steel is immersed in 60 ppm of Cl^- and adipic acid a protective film is formed on the surface of the metal. This is represented in **Fig. 1(b)**. The shifting of carbonyl stretching frequency and OH stretching frequency confirmed the formation of Fe^{2+-}Adipic acid complex on the surface of the metal.

AFM studies

The AFM images of various surface are shown in **Fig. 3**. The roughness values of the nanofilm formed on metal surface in the absence and presence of adipic acid are given in **Table 1**.

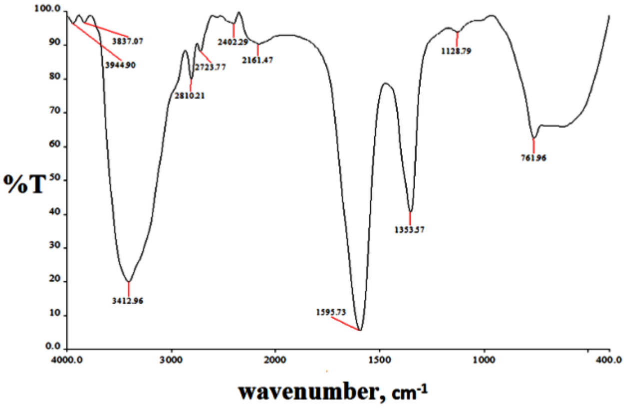

Fig.1: FTIR spectrum of pure Adipic acid (AA).

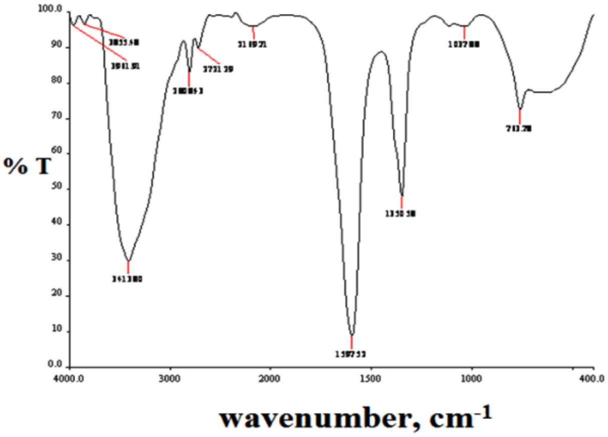

Fig.2. FTIR spectrum of film (Adipic acid + Cl^- 60 ppm).

Table. 1. Roughness values of the self-assembled nanofilms produced on surface of metal immersed in various media.

Test Solution	Roughness of the films, (RMS), nm
Cl^- 60 ppm	12.0558
Cl^- 60 ppm + AA 50 ppm	11.5167

It is observed that in the presence of Adipic acid, the film is of 11.8833nm thick; which is lower than that of iron oxide formed on the surface of metal, in the presence of chloride ions (and in the absence of adipic acid). This indicated that the protective nanofilm is anchored on the metal surface, even before the process of corrosion started. Had the film formed on iron oxide, the thickness of the film would have been greater than 12.0558 nm. But it is not so. Hence, it is inferred that the nanofilm is produced on the surface of the metal even before the process of the corrosion started because of the presence of AA nanofilm, chloride ion is not able to reach the metal surface. Hence corrosion rate decreases and corrosion inhibition increases **[23]**.

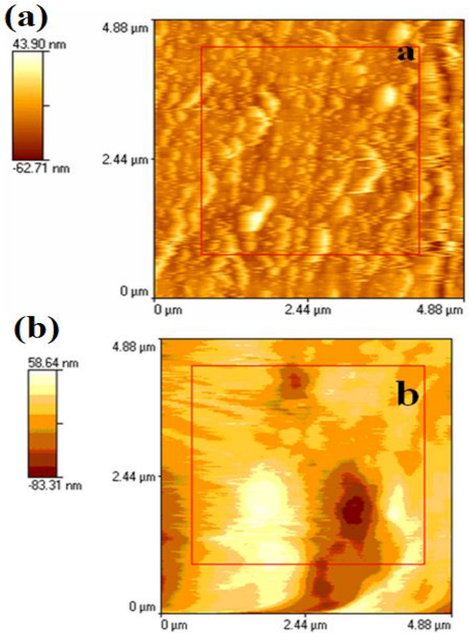

Fig. 3. (a). Cl^- ppm (b) Cl^- 60ppm + Adipic acid 50 ppm.

Electrochemical studies

The protective film formed on the surface of the metal can be proved by polarization study and AC impedance spectra [**24-30**]. Upon formation of a protective film on the surface of the metal, linear polarisation resistance (LPR) value increases and corrosion current value decreases. Further, charge transfer resistance value increases and double layer capacitance value decreases. The impedance value increases. Based on the these concepts, it is inferred from **Table 2** and **Fig. 4** that, adipic acid after the formation of self-assembled nanofilms on the metal surface, the corrosion resistance of carbon steel in chloride medium increases, when adipic acid is added.

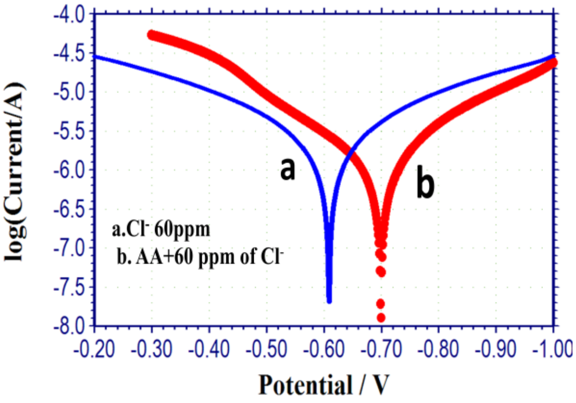

Fig. 4. Polarization curves. (a) carbon steel immersed in aqueous solution containing 60 ppm of Cl^- (b) AA+60 ppm of Cl^- .

Table 2. Corrosion parameters of carbon steel immersed in solution having 60 ppm of Cl^- and inhibitor.

AA ppm	E_{corr} mVvs SCE	b_c mV/decade	b_a mV/decade	LPR Ohm cm^2	I_{corr} A/cm^2
0	-608	183	189	23319.1	$1.735x10^{-6}$
50	-715	166	157	26664.4	$1.315x10^{-6}$

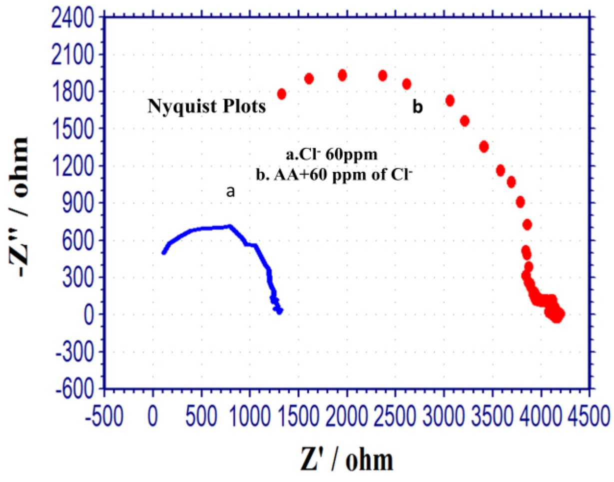

Fig. 5. AC Impedance spectra (Nyquist Plots). (a) Carbon steel in solution containing 60 ppm of Cl^- (b) solution having 60 ppm of Cl^- + 50 ppm of adipic acid.

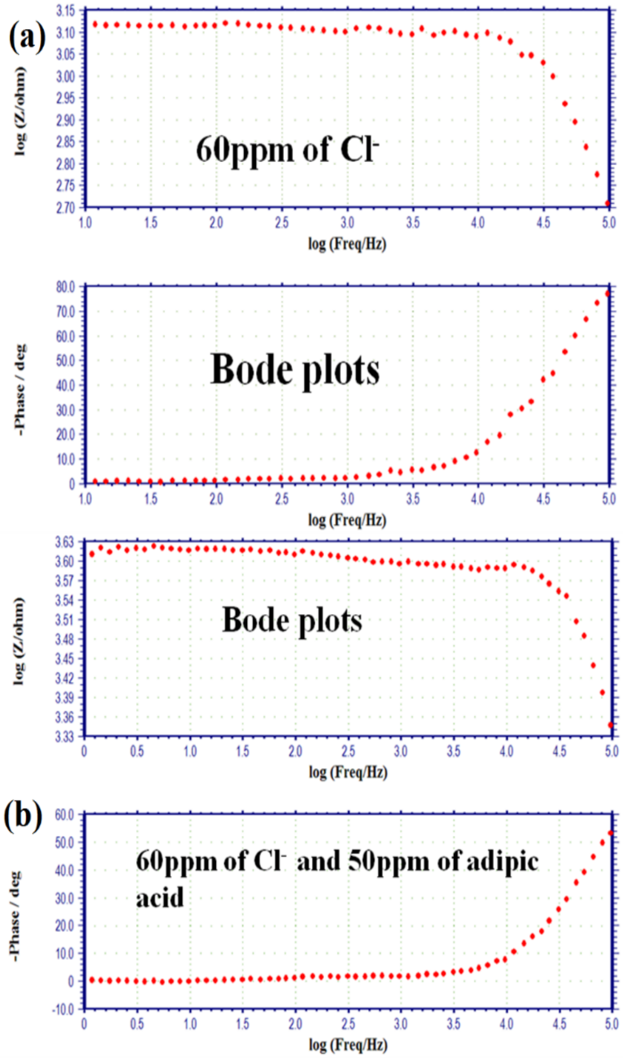

Fig. 6. AC Impedance spectra (Bode plots). (a) Carbon steel immersed in solution containing 60 ppm of Cl^-. (b) Carbon steel immersed in solution containing 60 ppm of Cl^- and 50 ppm of adipic acid.

Self-assembled nanofilm of CTAB *and corrosion inhibition*

The corrosion inhibitive effect of N-cetyl-N, N, N-trimethyl ammonium bromide (CTAB) nanofilm has been investigated by weight loss method. CTAB has the ability to control corrosion of carbon steel in well water. The formulation consisting of 50 ppm of Zn^{2+} and 200 ppm of CTAB offers 96% of corrosion inhibition efficiency.

Analysis of AFM spectra

Fig. 7, Table. 4, confirmed the formation of self assembled CTAB nanofilms on the surface of the metal. When mild steel is placed in well water having CTAB (200 ppm) and Zn^{2+} (50 ppm), the RMS (Rq) roughness is 75.30 nm. The film is in the nano meter level. The thickness of the film is found to be higher than that of the polished metal; but it is thinner than that of the film that is formed on the surface of metal after immersion in the corrosive medium.

Similar observations have been made in the case of maximum peak to valley height and average roughness and. All these lead to the conclusion that a nano film is produced on the surface of the metal, which enhances the corrosion inhibition offered by the nano film.

The presence of protective film of CTAB **Fig. 8(a)** on the surface of metal is further proved by FTIR spectral analysis **Fig. 8(b).** The C-N stretching frequency has shifted from1136 to 1024 cm^{-1}. This confirms that CTAB is coordinated with Fe^{2+}, through N-atom.

Contact angle measurement study reveals that in presence of CTAB, the contact angle of bare polished metal increases from 60 to 84.5^o **[Fig. 9(a) (b), Table. 5]**.

Thus, in presence of nanofilm of self-assemble CTAB, the contact angle increases; hydrophobicity increases, wettability decreases and corrosion resistance increases. The formation of protective film is further supported by polarization study [**Fig. 10**, **Table. 6**].

In presence of CTAB, there is increase in linear polarization resistance value and decrease in corrosion current value. These observations indicate that a protective film is present on the metal surface. This prevents the corrosion of the metal.

Self-assembled nanofilm of Tween-60 system and corrosion inhibition

The nano film of Tween- 60 **(**schematic diagram 2), has corrosion inhibitive nature. It controls the corrosion of carbon steel in well water for one day. Weight loss method reveals that the system consisting of 200 ppm of Tween-60 and 50 ppm of Zn^{2+} offers 88% of corrosion inhibition efficiency.

The polarization study **[Table 7 & Fig. 11]** proves the formation of protective layer on the metal surface in presence of Tween-60. This is revealed by the fact that, in presence of Tween-60, there is an increase in linear polarization value and decrease in corrosion current value.

Formation of protective layer, on the metal surface is further confirmed by FTIR spectra. Shift in stretching frequencies of various functional groups, namely, carbonyl oxygen, alcoholic oxygen and –C-O-C- oxygen are noticed.

Contact angle measurements **[Fig 13 (a)-(b)**, **Table 8]**, suggest that when Tween-60 is used as inhibitor, the contact angle increases from 66^0 to 84.0^0. Hence hydrophobicity increases and corrosion resistance increases.

It is observed from AFM investigation that **[Fig. 14, Table 9]**, nanofilm is produced on the surface of the metal. A nanofilm, of 46.56 nm thickness is formed on the metal surface, in the presence of inhibitor. It is noted that this thickness is higher than that of control, but lower than that of blank. In the presence of the inhibitor, the maximum peak-to-valley height decreases when compared with the blank value (that is in the absence of Tween-60 inhibitor).

Self-assembled nanofilm of sodium dodecyl sulphate (SDS) and corrosion inhibition

Nanofilm of SDS (Schematic Diagram 3) has been used to control corrosion of carbon steel in well water. Weight loss method reveals that the formulation consisting of 200 ppm of SDS and 50 ppm of Zn^{2+} offers 92% of inhibition efficiency.

The formation of protective film on the metal surface **[Fig. 15, Table 10]** has been asserted by using polarization study. It is observed that there is increase in the linear polarization resistance value and decrease in corrosion current value in presence of inhibitor system.

The formation of protective film on the surface of the metal has been proved by FTIR spectra. The S=O stretching frequency deceases from 1219.8 cm^{-1} to 1239.0 cm^{-1}. This confirmed the formation of Fe^{2+} -SDS complex on the surface of the metal.

Contact angle measurement study reveals that the contact angle increases from 66° to 85.4° **Fig. 17**. **(A)(B), Table. 11**. This suggests that in presence of SDS nanofilm, the wettability decreases; hydrophobicity increases and inhibition efficiency increases.

Analysis of AFM spectra **Fig18, Table12** reveals that the thickness of the nanofilm is 31.85 nm. In presence of this nanofilm the maximum peak to valley height.

Corrosion inhibition by self-assembling nanofilm formed on metal surface by an aqueous extract of banana peels

An aqueous extract of banana peels forms nanofilm on carbon steel surface immersed in seawater. Weight loss method reveals that the formulation which consists of 4ml of the extract Zn^{2+} offers 98% of inhibition efficiency. This is due to the formation of nanofilm of the active principle of banana peel. **[Fig 19. Schematic Diagram 4].**

The formation of a protective film on the metal surface has been confirmed by polarization study **[Table 13, Fig. 20].** It is observed that there is increase in LPR value and decrease in corrosion current value.

The FTIR spectra confirmed the formation of protective film on the metal surface. Shifts in the stretching frequencies of the corresponding polar groups have been observed.

The AFM image [**Fig. 22, Table 14**], also confirms the formation of nanofilm of 8.45 nm thickness on the metal surface. The peak to valley of protective film also decreases from 89.10 nm to 38.63 nm in presence of inhibitor system.

Conclusion

- Corrosion inhibition by nanomaterials is a new field which has attracted many researchers [**31**].
- In the present study, the corrosion inhibition offered by the nanofilms has been confirmed by the classical weight loss method and polarisation study.
- The hydrophobicity of protective films is confirmed by contact angle measurement.
- These hydrophobic surfaces may find applications in preparing raincoats, water proof caps, shoes, glass windows of cars and biocompatible surfaces.

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Author's contributions

Conceived the plan: SR, RJR, SSP; Performed the expeirments: SR, RJR; Data analysis: SR, RJR, SSP ; Wrote the paper: SR, RJR, SSP . Authors have no competing financial interests.

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