



SELF ASSEMBLING MONOLAYERS OF GLYCINE ON CARBON STEEL

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Well-ordered self assembling monolayer's (SAMs) using glycine were formed on the carbon steel surface by immersion method. This leads to ordered, robust monolayers bound to the surface in a bi dentate manner. Monolayer formation takes place when carbon steel is immersed in an aqueous solution containing 60ppm of Cl⁻ and 50 ppm of glycine for 5 minutes, and rinsing the physisorbed molecules in distilled water and heating in a hot air oven. The glycine monolayers on iron oxide steel carbon can withstand rinsing with water, concentrated acid and base exposure. Additionally, these monolayers are stable over the course of one week. The formations of monolayers were confirmed by AFM study and FTIR spectra. The results of this study show that glycine monolayers adsorbed on metal surface can reduce electrochemical activity on the surface, often the first step in corrosion.

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Organic acids such as phosphonic,^{13,14-18} carboxylic,^{19,20-23} hydroxamic,²⁴ and sulfuric¹⁶ acids are capable for forming SAMs by chemisorption on stainless steel,^{25,19,26} aluminium,^{20-22,27} titanium^{13,14,17,18} and copper oxide²⁸ surfaces.

Introduction

Nanometer-sized particles are attracting considerable attention because of their unique properties, including optical, electrical, electrochemical, photo-electrochemical and magnetic properties¹⁻³. Noble metals, such as gold and silver, are hot spots of the research because they can be easily prepared and exist steadily. Moreover, we can manipulate these nano-particles according to our will. Much effort has been done in exploring self-assembled (SA) nanoparticles into ordered structures⁴. Specific structures can provide controlled fabrication of nanometer-sized building blocks with distinctive and useful properties⁵. Polymer-stabilized nanoparticles are usually self-assembled into two-dimensional arrays on the substrate⁶. Yiwei Tan et al.⁷ had reported the self-organization of wire-pattern arrays of Ag nanoparticles. Byeong-Hyeok Sohn⁵ had demonstrated a directed self-assembly of two different kinds of nanoparticles on a block copolymer micellar template. These two particles are gold and iron oxide. The self-assembling process has been investigated to improve corrosion inhibition of metals because self-assembled substances are able to react spontaneously on the metal surface and form compact and stable films^[8]. These films can protect metal from corrosion successfully. Iron is a widely used metal with extensive industrial application and the study of its corrosion inhibition has attracted much attention^{9, 10}.

The first work to use self-assembled films on iron for corrosion protection was self-assembling alkanethiols¹¹. But the application of thiol-compounds is limited due to their toxicity¹². Ilona Felhosi et al.^[12] studied the formation of self-assembled films of alkane monophosphonic acids on iron surface and explained its mechanism of corrosion protection.

In the present work, SAMs of glycine were formed on carbon steel surface by immersion coating (immersing metal surface in an aqueous solution containing 60 ppm of Cl⁻, in the absence and presence of 50 ppm of glycine). The modified samples were characterized by FTIR, and atomic force microscopy (AFM). The formation, uniformity, ordering and bonding of the monolayers accomplished by immersion method have been evaluated.

Experimental Section

Material

Very pure glycine of analytical reagent grade was used in the present study.

Preparation of the substrates

Carbon steel substrates (Composition : wt % : 0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest Fe) of dimensions 1 x 1 x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and stored in oven at 100 °C for 1 h or more.

Formation of monolayers

Immersion deposition monolayers

The cleaned substrates were placed in the oven for 24 h. They were then immersed in an aqueous solution containing 60ppm Cl⁻ in the absence and presence of 50ppm of glycine acid for 5 mts and placed in an oven at 100°C for at least 1 h.

Characterization of the monolayers

FTIR

The substrates were studied using a Perkin Elmer 1600 FTIR spectrophotometer. FTIR spectrophotometer was used to analyze the nature of interaction between the molecules of glycine and the substrate and the alkyl chain ordering the νCH_2 peaks as the reference. The film was removed carefully, mixed with KBr and made into pellets. FTIR spectra were recorded.

Atomic force microscopy

The carbon steel specimen immersed in blank and in the inhibitor solution for a period of 5 mts was removed, rinsed with double distilled water, dried and subjected to the surface examination. Atomic force microscopy (Veeco innova model) was used to observe the samples' surface in tapping mode, using cantilever with linear tips. The scanning area in the images was $5\ \mu\text{m} \times 5\ \mu\text{m}$ and the scan rate was 0.6 HZ / second.

Weight-loss method

Carbon steel specimens in triplicate were immersed in 100 mL aqueous solution containing 60 ppm of Cl^- various concentrations for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution. The inhibition efficiency (IE) was then calculated using the equation:

$$\text{IE} = 100 [1 - (W_2 / W_1)] \%$$

Where W_1 = corrosion rate in the absence of the inhibitor.

W_2 = corrosion rate in the presence of the inhibitor.

Results

Immersion depositon method

FTIR Spectra

A simple procedure of immersing mild steel into an aqueous solution containing 60 ppm of Cl^- and 50 ppm of glycine for 5 minutes led to spontaneous film formation on the carbon steel surface. There is also possibility of formation of iron-glycine film, in the absence of iron oxide, if there is less corrosion or no corrosion of carbon steel. The samples were characterized by FTIR spectra to determine alkyl chain conformation and head group-substrate bonding^{25, 17}. Position of the CH_2 stretching in the infrared spectrum can be used to determine the ordering of the alkyl chain within a film^{22, 29-31}.

For disordered chains, the frequency of the CH_2 stretching is close to that of a liquid alkane (νCH_2 asym $\sim 2924\ \text{cm}^{-1}$) due to the presence of a gauche conformation in the alkyl chains^{30, 32}. For well-ordered alkyl chains the frequency is shifted to lower wave numbers and is close to that of a crystalline alkyl (νCH_2 asym $\sim 2914 - 2918\ \text{cm}^{-1}$) which is considered to have a high degree of order, with all-trans

conformation throughout the alkyl chain. The FTIR spectrum of pure glycine is shown in Fig 1a. The peaks due to νCH_2 sym appear at $2771\ \text{cm}^{-1}$. The FTIR spectrum of iron oxide film formed on metal surface after immersion in 60ppm Cl^- is shown in Fig 1b. The peaks due to iron oxide appear at $\gamma\text{FeOOH} = 1045, 1590\ \text{cm}^{-1}$; $\alpha\text{FeOOH} = 678\ \text{cm}^{-1}$. The peaks due to Fe_3O_4 are absent. The position of the peaks corresponding to νCH_2 asym and νCH_2 sym after immersion in an aqueous solution containing 60ppm of Cl^- and 50 ppm of glycine for 5 minutes and after rinsing in distilled water to remove any physisorbed material or multilayer's, were $2809\ \text{cm}^{-1}$ and $2722\ \text{cm}^{-1}$, respectively (Fig 1c). This indicates that the film is stable, well ordered and strongly bound to the surface.

The IR spectra further indicate that the organic molecules are bound to the surface in a bidentate manner as determined from the shifting of $\nu\text{C}=\text{O}$ and $\nu-\text{OH}$ stretching of the one carboxyl groups of glycine specifically the $\nu\text{C}=\text{O}$ has shifted from 1590 to $1596\ \text{cm}^{-1}$ and νOH has shifted from 3093 to $3416\ \text{cm}^{-1}$. Similar bidentate interaction has been reported for alkyl phosphonic acid on nickel oxide surface³³ and other organic molecules on other oxides^{25, 19, and 17}.

While FTIR spectroscopy can be used to characterize alkyl chain ordering and binding of the molecules to the surface, it cannot determine film thickness and integrity. Therefore, AFM imaging was used to examine the monolayer at nanometer resolution and to verify that the deposition method produces uniform monolayers.

AFM imaging

The comparison of the root mean square (rms) roughness of the unmodified substrate to the modified samples is an indicator of the film uniformity. The rms roughness parameter is a measure of the deviations in the surface from the mean plane within the sampling area³⁴.

Modified surfaces with an rms roughness similar to the control surface are considered to be films of monolayer thickness that follow the contour of the surface, while modified surfaces that have much larger rms roughness than the control are multilayer or non-uniform films^{35, 36}.

The iron oxide control samples had an average rms roughness of 12.06 nm (Fig 2a). The control sample of iron oxide is rough in comparison to model surfaces such as gold and silicon^{37, 38}. Modified samples formed by the immersion method (immersed in 60 ppm of Cl^- and glycine had an rms roughness of 4.3806 nm (Fig 2b). The rms roughness of the substrate did not change very much after the adsorption of glycine molecules suggests uniform deposition of the organic molecules on the surface without aggregate or micelle formation. Therefore it is concluded that within the scope of the analysis, the film formed is a single layer of molecules that follows the contour of the underlying substrate.

The rms roughness values of the films (SAMs) formed on metal surface after immersion in various test solutions are given in Table 1.

The IR spectra of the formed films can be seen on Fig.1.

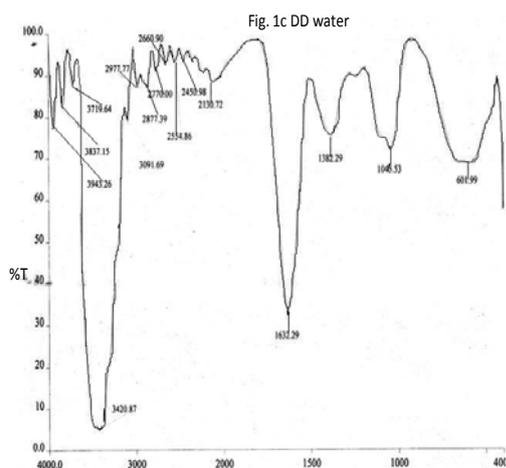
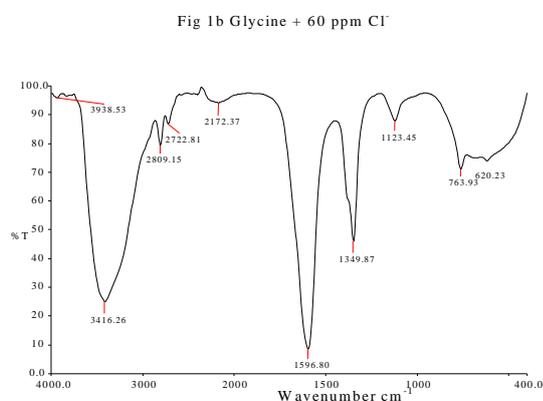
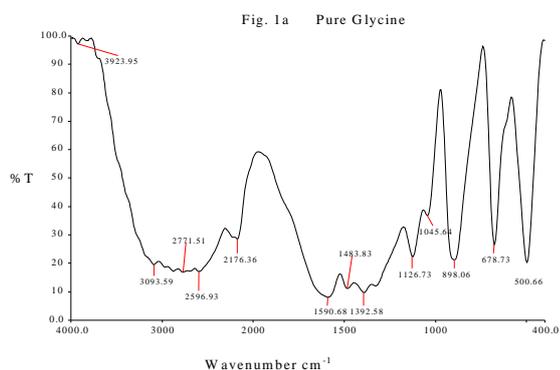


Figure 1. IR spectra of the formed films from

- glycine
- glycine and 60 ppm chloride
- DD water

Table 1. The rms roughness values of the films (SAMs) formed on metal surface immersed in various test solutions.

Test solution	rms roughness of the films (SAMs), nm
Cl ⁻ 60ppm	12.0558
Cl ⁻ 60ppm + Glycine 50ppm	4.38

The rms value of pure glycine molecule is very low (4.38nm) when compared with the rms value of iron oxide formed in the absence of glycine (12.06 nm). This indicates that glycine molecules are adsorbed on the metal surface before the formation of iron oxide on the metal surface. Suppose glycine molecules adsorbed on iron oxide surface then the rms value will be greater than 12.06. But it is not so. Hence it is concluded that glycine is adsorbed on carbon steel surface and not on iron oxide surface.

Stability of monolayer films

The monolayers formed by deposition method were analyzed for stability. After rinsing in water, the samples were left under atmospheric conditions for one day and analyzed. The monolayers remained ordered and bound to the surface as indicated by the lack of change in the FTIR spectra over one day. Stability to acid and base exposure was tested by rinsing modified substrates 1 M HCl or 1 M NaOH. FTIR spectra taken after these treatments remained unchanged.

Film stability and chain ordering can be dependent on alkyl chain length. In general, stability and order increase as the chain length increases^{39, 40-43}. Therefore, a long chain length (> 11 carbons) is commonly used in the formation of SAMs. Substantial disorder is generally found in films formed by short chain molecules, although ordered monolayers of short chain phosphonic acids have been formed on nitinol, titanium and stainless steel oxide^{25, 17, and 44}. In the present study there are only 3 carbons in the chain (H₂N-CH₂-COOH). However, the monolayer is found to be stable. Further research in this line will confirm the proposed concepts.

These conclusions are confirmed by visual observations also. In the blank experiment (60ppm Cl⁻ only) brown film was observed on the metal. In the presence of 50 ppm of glycine brown film was absent and thin interference films (VIBGYOR colour) were noticed.

Analysis of Weight loss Study

The corrosion inhibition efficiencies of glycine in controlling corrosion of carbon steel in aqueous solution containing 60 ppm of Cl⁻ are given in Table 2. It is observed that the inhibition efficiency increases as the concentration of glycine increases upto 100 ppm. However further increases of concentration of glycine leads to a decrease in IE. This is due to the fact that as the concentration of glycine increases, the iron glycine complex formed on the metal surface goes into solution. Hence IE decreases as the concentration of the glycine increases.

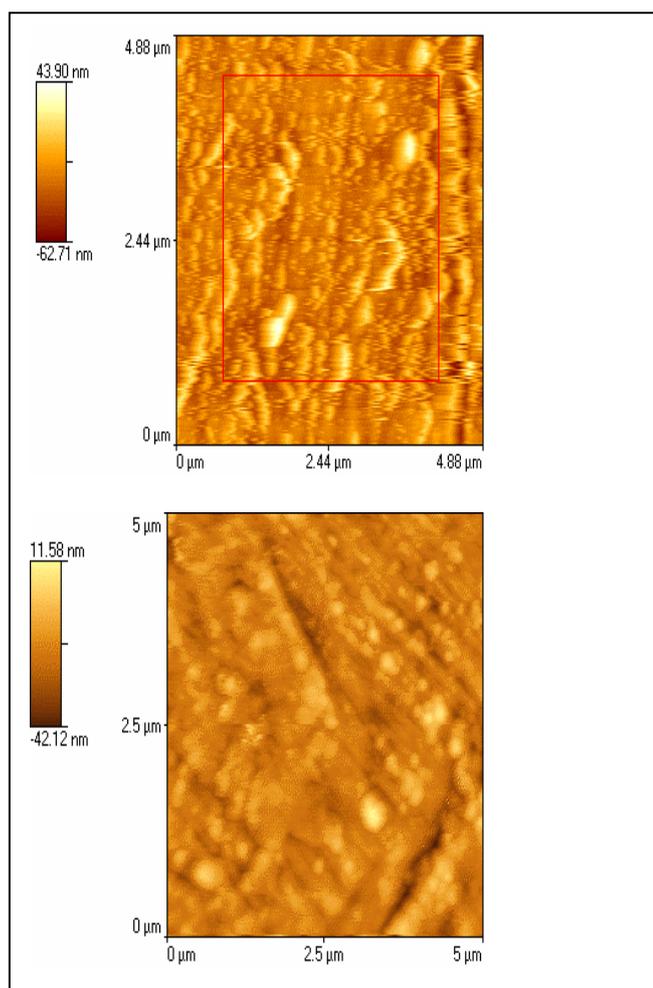


Figure 2. AFM topography images of films formed on carbon steel surface after immerse on in various test solution. Cl⁻ 60ppm; Cl⁻ 60ppm + glycine 50ppm

Discussion

Ordered, complete monolayers of glycine were formed on carbon steel surface. These monolayers were formed using an immersion deposition process. To accomplish monolayer by immersion, a counteraction of 50 ppm of glycine, solution exposure time of 5 minutes and setting temperature of keeping the metal specimens in the oven at 100°C for 1 hr.

Table 2. Inhibition efficiencies of glycine in controlling corrosion of carbon steel in aqueous solution containing 60 ppm of Cl⁻

Glycine (ppm)	Cl ⁻ (60ppm)	
	IE %	CR mmpy
0	-	0.0093
50	70	0.0028
100	75	0.0023
150	65	0.0033
200	60	0.0037

The process of monolayer formation using immersion coating has been described as a sequential process of nucleation, growth and coalescence of densely packed two-dimensional islands, finally covering the entire substrate surface or a large fraction of it^{45, 46-49}.

The average surface coverage for glycine films on iron surface is found to increase monotonically with solution concentration, consistent with a quarter surface density of glycine molecules. It is proposed that the initial islands are nucleated through the adsorption of individual glycine mole from solution^{45, 46, 47}. Therefore a higher concentration of the monomer (100 ppm) in solution leads to more collisions between monomers and subsequent island nucleation becomes more probable leading to a large number of islands on the surface^{46, 50}. For the immersed substrates, increasing the solution concentration leads to the formation of a complete monolayer. When the substrates were heated the bidentate increased, the molecules become thermally mobile and therefore more available for nucleation and / or growth⁵¹.

The molecules in the monolayers formed by immersion method were bound to the carbon steel surface in a bidentate manner. This bonding motif was persistent from deposition through solvent, acid and base rinsing and exposure to atmosphere for one day. A bidentate or monodentate bonding motif is seen between phosphonic acids and various metal oxides such as stainless steel 316L and Zirconium^{25, 17, 44, 52-55}. In the present case, glycine is bonded to carbon steel surface in bidentate manner; since glycine is a monocarboxylic acid and coordination can take place through oxygen atoms of carboxyl groups.

The cause of the differences in bonding motifs has not been determined but may be a function of several factors including oxygen-metal-oxygen distance on the surface, hydroxyl content of the native oxide surface and the coordination sites available on the adsorbate molecules.

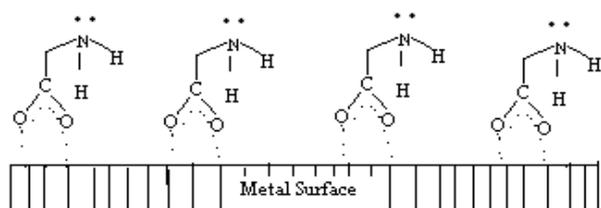
Summary

Well-ordered SAMs using glycine were formed on the oxide of iron carbon steel surface by immersion method. This leads to ordered, robust monolayers bound to the surface in bi dentate manner. Monolayer formation takes place when carbon steel is immersed in an aqueous solution containing 60ppm of Cl⁻ and 50 ppm of glycine for 5 minutes, and rinsing the physisorbed molecules in distilled water and heating in a hot air oven. The glycine monolayers on carbon steel can withstand rinsing with water, concentrated acid and base exposure. Additionally, these monolayers are stable over the course of one week.

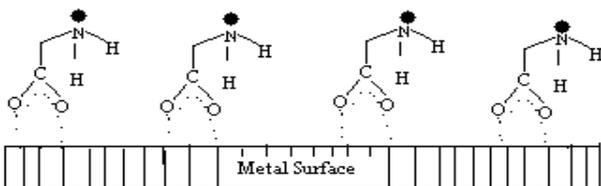
The formations of monolayers were confirmed by AFM study and FTIR spectra. The results of this study show that glycine monolayers adsorbed on metal surface can reduce electrochemical activity on the surface, often the first step in corrosion. Monolayer formation on the carbon steel surface is a significant advance in surface modification of iron oxide and can be used as a building block for future applications in corrosion barriers and electronics.

Scope of the future study

The adsorption of glycine molecule on the carbon steel surface, through the oxygen atoms of the carboxyl group can be represented as follows.



On the nitrogen atom a lone pair of electron is available. On these nitrogen atoms of silver or gold nano particles can be attached if these nanoparticles are generated in *-situ* by suitable methods⁵⁶. Such SAMs containing nano silver or



gold may find applications in biosensors.

● - (Nanometals- Gold or Silver)

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