Inhibition of Copper Corrosion in Aqueous Sodium Chloride Solution by N-Octadecylbenzidine/ 1-Docosanol Mixed Langmuir-Blodgett Films

A. Jaiswal, R.A. Singh, and R.S. Dubey***

ABSTRACT

Mixed Langmuir-Blodgett (LB) films of N-octadecylbenzidine (NODB)/l-docosanol were deposited onto a copper surface to investigate the inhibition of corrosion of copper in 3.4% sodium chloride (NaCl) solution by weight loss, corrosion potential, and potentiodynamic polarization measurements. The surface of the copper specimen before and after corrosion was also examined by scanning electron microscopy (SEM). The mixed monolayers of NODB/1-docosanol inhibited the corrosion of copper efficiently. The inhibition efficiency increased with the number of monolayers, and the maximum inhibition of about 94% was obtained by 10 monolayers of NODB/1-docosonal. The inhibition has been explained on the basis of "blocking action" of LB films of NODB/1-docosonal on the copper surface.

KEY WORDS: copper, electrochemical testing, Langmuir-Blodgett film, N-octadecylbenzidine, sodium chloride

INTRODUCTION

Corrosion inhibitors are used to protect metal surfaces in aggressive environments. The compounds most often used as corrosion inhibitors are nitrogen-containing organic compounds (aliphatic and aromatic amines),[1-3] oxygen, and sulfur-containing compounds.[4-5] Several of these compounds have been studied as corrosion inhibitors for copper and its alloys in different environments.[6] Examples include heterocyclic compounds, such as benzotriazole and its derivatives,[7-9] 2-mercaptobenzotrizole,[4-5] and 2-mercaptobenzimidazoles,[10-11] that have been used to inhibit corrosion in neutral aqueous solutions, seawater, and, in some cases, solutions contaminated with sulfide ions. Other examples include thiourea and potassium ethyl xanthate used in 0.1 M sodium chloride (NaCl) and 1 M sodium perchlorate ($NaClO_4$) media,[8] a polymer of a 3-amino 1,2,4-triazole unit used in a 3% NaCl medium,[12] and benzohydroxamic acid used in chloride solutions to inhibit copper corrosion.[13]

A possible way to inhibit corrosion may be through the chemical modification of the metal surface by adsorbing molecules of inhibitors in well-organized homogeneous monolayers or multilayers.[14-15] The Langmuir-Blodgett (LB) film technique[16-17] and the self-assembly technique[18-19] produce well-organized thin films on the metal surface and could be used as powerful tools for this purpose.

Particularly, the LB film technique enables the fabrication of organized thin films of controllable thickness at the molecular level.[16] Corrosion inhibition by LB films is likely to require fewer inhibitors, and the study of the extent of corrosion inhibition as a function of the exact amount of inhibitor and exact inhibitor film thickness adsorbed onto the metal surface can be performed.

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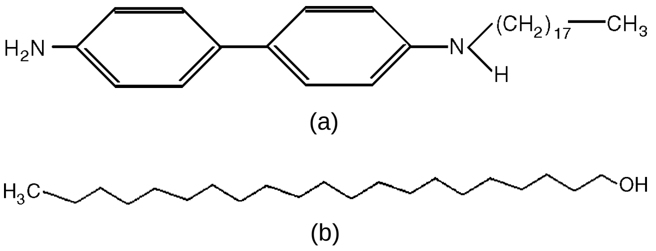


FIGURE 1. *Molecular structures of: (a) NODB and (b) 1-docosanol.*

A few attempts have already been made in this direction in recent years.[20-23] The self-assembled monolayers (SAM) derived from the adsorption of n-alkanethiolates onto a freshly evaporated copper surface were found to protect metal from oxidation.[20] The SAM were assumed to be providing a barrier to the transport of oxygen to the copper surface. Angstrom level changes in the thickness of the SAM (e.g. ~ 6 Å), resulted in a decrease in the rate of oxidation by 60%. Similarly, the SAM of n-alkanthiols was found to protect gold from corrosion in aqueous bromine solution.[21]

Recently, studies have been conducted on LB film-modified metal surfaces in order to evaluate the corrosion inhibition effect of these films.[22-23] Wolpers, et al., have produced monomolecular LB films of n-octadecyltrichlorosilane (n-OTS) and chlorodimethyloctadecylsilane (CODS) on iron and nickel metal substrates in order to protect the reactive metal surface against corrosive species like H_2O, O_2, and sulfur dioxide (SO_2).[22] The corrosion protection properties of the LB films were analyzed with the scanning Kelvin microprobe (SKM) and results showed that a reasonable corrosion protection could be obtained by organic LB films if the organic monolayers were compact and bound to the metal surface by strong chemical bonds. Guo, et al., deposited LB film monolayers of hexadecyltrimethylammoniumbromide (HTAB) onto a carbon steel surface to investigate the inhibition of corrosion by these films.[23] The LB monolayers of HTAB deposited on carbon steel were found to have excellent stability in both neutral and acidic aqueous solutions, and it was observed that these films efficiently inhibited the corrosion of steel in both media. In neutral media, inhibition was explained on the basis of the simple blocking effect, whereas, in the acidic environment, one more phenomena played an important role. The positively charged HTAB monolayers did not allow the free transport of H^+ ions of acidic media through and thus helped prevent corrosion. This phenomenon is termed "charge effect."

Organic amines have been known as efficient inhibitors of metallic corrosion in various environments for many years.[1-2] The monolayer behavior of several amines with long chains at the air/water interface and the transfer properties of the monolayers to the solid substrates have been investigated by several workers.[24-26] In the present work, LB films of 1:1 M N-octadecylbenzidine (NODB)/1-docosanol were fabricated onto a well-polished copper specimen. The pure NODB was not able to form a stable monolayer at the air/water interface, and the addition of 1-docosanol with NODB led to a stable LB film. The corrosion behavior of copper surfaces modified with NODB/1-docosanol mixed LB films were studied in a 3.4% NaCl solution. The electrochemical measurements were carried out to monitor corrosion behavior. The corrosion inhibition effect of LB films on copper was also studied by the weight loss measurements and by scanning electron microscopy (SEM).

EXPERIMENTAL PROCEDURES

NODB has been synthesized and characterized by techniques reported elsewhere.[27] 1-docosanol was obtained from Fluka[†] and used without further purification, and chloroform (high-performance liquid chromatographic [HPLC] grade) was used as the spreading solvent. The structures of NODB and 1-docosanol are shown in Figures 1(a) and 1(b), respectively. Commercial grade copper (99.9% purity) obtained from Hindustan Copper, Ltd. (Rajsthan, India) has been used to prepare the test specimens. Analytical grade NaCl was purchased from Sigma and used without further purification. Triple-distilled water was used for making all electrolytic solutions.

Sample Preparation

Copper Specimen — Rectangular coupons (1 cm by 2 cm) were sheared from the sheets of copper (1-mm thick). The surface of the copper was polished sequentially with 1/0 to 4/0 grade emery paper and washed with benzene (C_6H_6) followed by a hot analytical grade soap solution and, finally, triple-distilled water. After washing, the samples were degreased with 99% ethanol for 30 min. All copper specimens thus prepared were dried and stored over silica gel in a vacuum desiccator.

Deposition of LB Film — Formation of Langmuir films and deposition of LB films have been studied on a commercial LB set-up (Model 2000[†], NIMA Technology, England). Triple-distilled water was used as a subphase. All the experiments were performed at room temperature (25 ± 2°C). Mixed monolayers were produced by blending both components (NODB and 1-docosanol) in equimolar ratio in solution. The mixture was spread on the clean water surface of the trough. After allowing ~ 15 min for the solvent to evaporate, the compression was slowly begun at a continuous speed of 5 cm^2/min and the surface pressure-molecular area (π-A isotherm) was recorded.

[†] Trade name.

The mixed monolayers were transferred onto the well-polished copper surface by the vertical dipping method. For deposition, compression was performed in a step-by-step manner to reach the target pressure. After each increase of the surface pressure, a waiting time of ~ 10 min allowed the system to reach equilibrium. Steps of 2 mN/m were usually chosen. The dipping was performed at the surface pressure of 30 mN/m and a dipping speed of 5 mm/min. Test specimens with 2, 4, 6, 10, 14, and 20 monolayer LB films deposited on the copper surface were prepared to study the effect of the number of monolayers of LB films on inhibition of copper corrosion.

Weight Loss and Electrochemical Experiments

For the weight loss experiments, a portion of the copper specimen covered by the LB films was cut carefully and immersed in 250 mL of 3.4% NaCl solution kept in an Erlenmeyer flask. The flasks containing test specimens were kept in an electrochemically regulated thermostat maintained at 30°C.

The specimens were weighed on an electronic balance within an accuracy of ± 0.001 mg before and after immersion testing. After the experiments, the specimens were removed from the corrosive media, washed thoroughly with triple-distilled water, dried, and weighed. Triplicate experiments were performed in each case, and mean values of the weight losses were recorded. The inhibition efficiency (IE) of LB films was calculated from the weight loss after 3 to 4 weeks.

The electrochemical investigations were carried out in a three-electrode cell containing 500 mL of 3.4% NaCl solution. The three ports provided on the cell permitted the use of a three-electrode system: a Luggin capillary containing a saturated calomel electrode (SCE) as the reference electrode inserted into its wide opening at the upper end of the capillary, a very high density spectroscopic grade graphite rod as the counter electrode, and the copper specimen (1 cm by 1 cm) modified with LB films on both the sides as the working electrode. The edges of the copper specimen (1-mm thick) were coated with lacquer before exposure to the corrosive environment. The specimens, with an area of 2 cm^2, were connected to the working electrode with a screw. Electrochemical measurements were performed using a microprocessor-based corrosion measurement system (CMS-1000†, Gamry Instruments, Inc., U.S.).

SEM

Copper specimens exposed to the 3.4% NaCl solution were removed and dried by washing successfully with increasing (50, 75, and 100%) concentrations of acetone (CH_3COCH_3). The SEM photographs of bare and LB film-modified copper specimens were taken with the help of a JEOL ISM 840† scanning electron microscope, before and after corrosion experiments, to compare the surface morphology in both the cases.

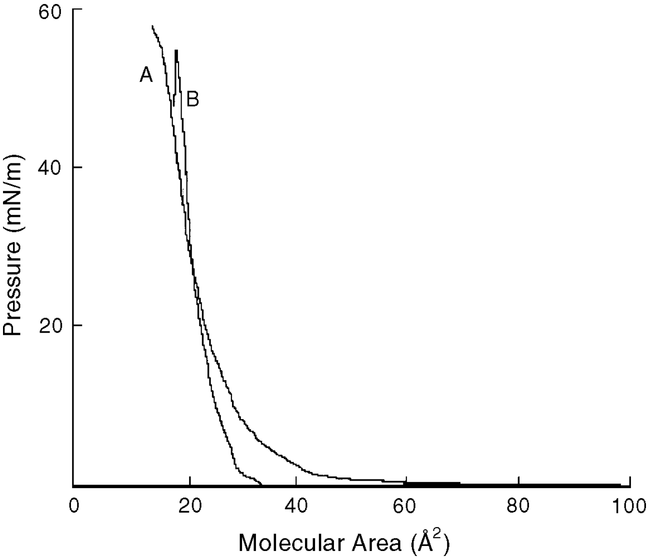


FIGURE 2. *Surface pressure (π)-molecular area (A) isotherms of: (A) NODB and (B) 1:1 NODB/1-docosanol.*

RESULTS AND DISCUSSION

Fabrication of LB films on Copper Substrates

The pure NODB monolayer was found to be unstable at the air/water interface, but stable monolayers could be formed by adding 1-docosanol. The π-A isotherms for monolayers of pure NODB and the NODB/1-docosanol mixture (1:1 M ratio) are shown in Figure 2. The isotherm of the mixed film was steeper and contained less "condensed liquid phase" than pure NODB, indicating the formation of a better monolayer in the former case. Also, the mixed films were found to be more stable than pure NODB films at different surface pressures (viz., 30, 35, and 40 mN/m). The collapse pressure of these monolayers was ~ 55 mN/m, and the area per molecule of NODB calculated from the π-A isotherms was ~ 27 Å^2.

Mixed LB films of the above materials were fabricated successfully. Figure 3 shows the bar chart of the transfer of 10 mixed monolayers from the air/water interface to the copper surface. Y-type depositions, with 79 ± 2% transfer during down stroke and 97 ± 2% transfer during up stroke, were obtained.

Weight Loss Studies

The results of weight loss experiments in 3.4% NaCl solution are shown in Figure 4 as a plot of IE vs numbers of monolayers. The IE was calculated by the following equation:

$$\mathrm{IE} = \frac{a - b}{a} \times 100$$

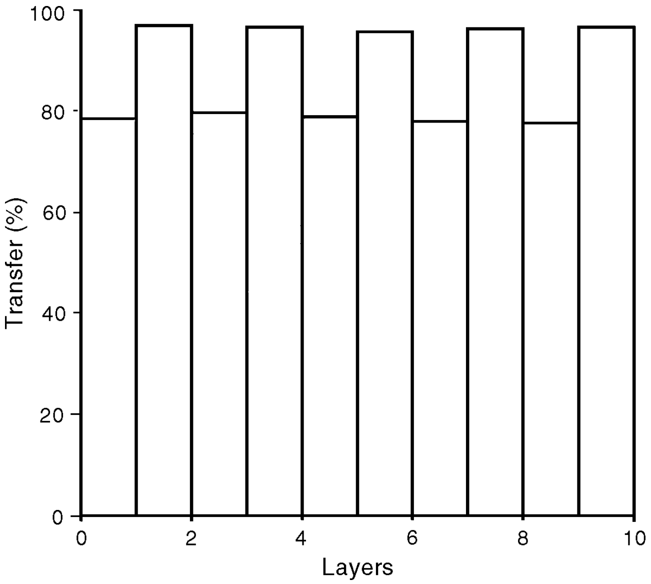


FIGURE 3. *Bar chart showing percentage transfer of mixed monolayer of 1:1 NODB/1-docosanol from the water surface to the copper substrate vs the number of monolayers.*

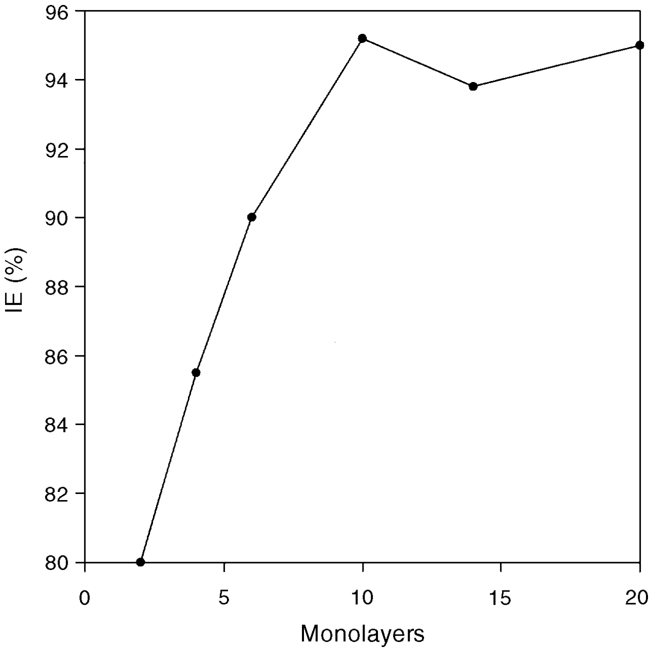


FIGURE 4. *Corrosion IE of mixed monolayers of 1:1 NODB/1-docosanol on copper as a function of number of monolayers.*

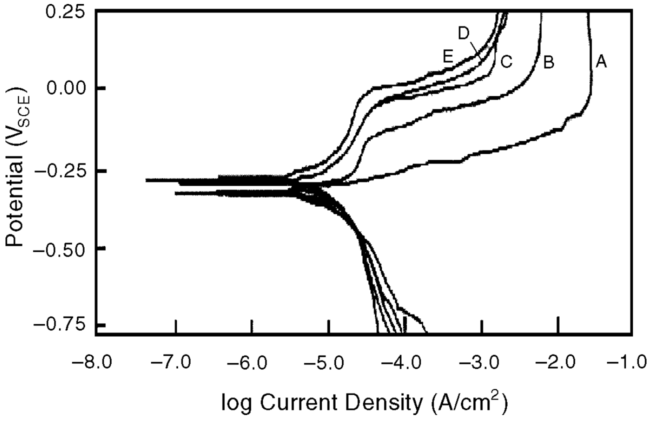


FIGURE 5. *Potentiodynamic polarization curves of copper exposed to 3.4% NaCl solution: (A) control, (B) in presence of 5 ppm benzidine in 3.4% NaCl solution, (C) 2 monolayers, (D) 6 monolayers, and (E) 10 monolayers of NODB/1-docosanol LB films on copper.*

where a is the average weight loss of the copper specimens without LB films and b is that for specimens coated with NODB/1-docosanol LB films, in a corrosive environment.

It is clearly observable that the IE increased with the increase in the number of monolayers of NODB/1-docosanol LB films up to 10 monolayers and then became almost constant on further increase in the number of monolayers from 14 to 20.

Another important observation that can be made from these data is that the LB films of NODB/1-docosanol inhibited the corrosion of copper effectively even after eight weeks with a very high IE (~ 92%), indicating that these LB films are very stable and exist on the copper surface for a fairly long period.

Electrochemical Studies

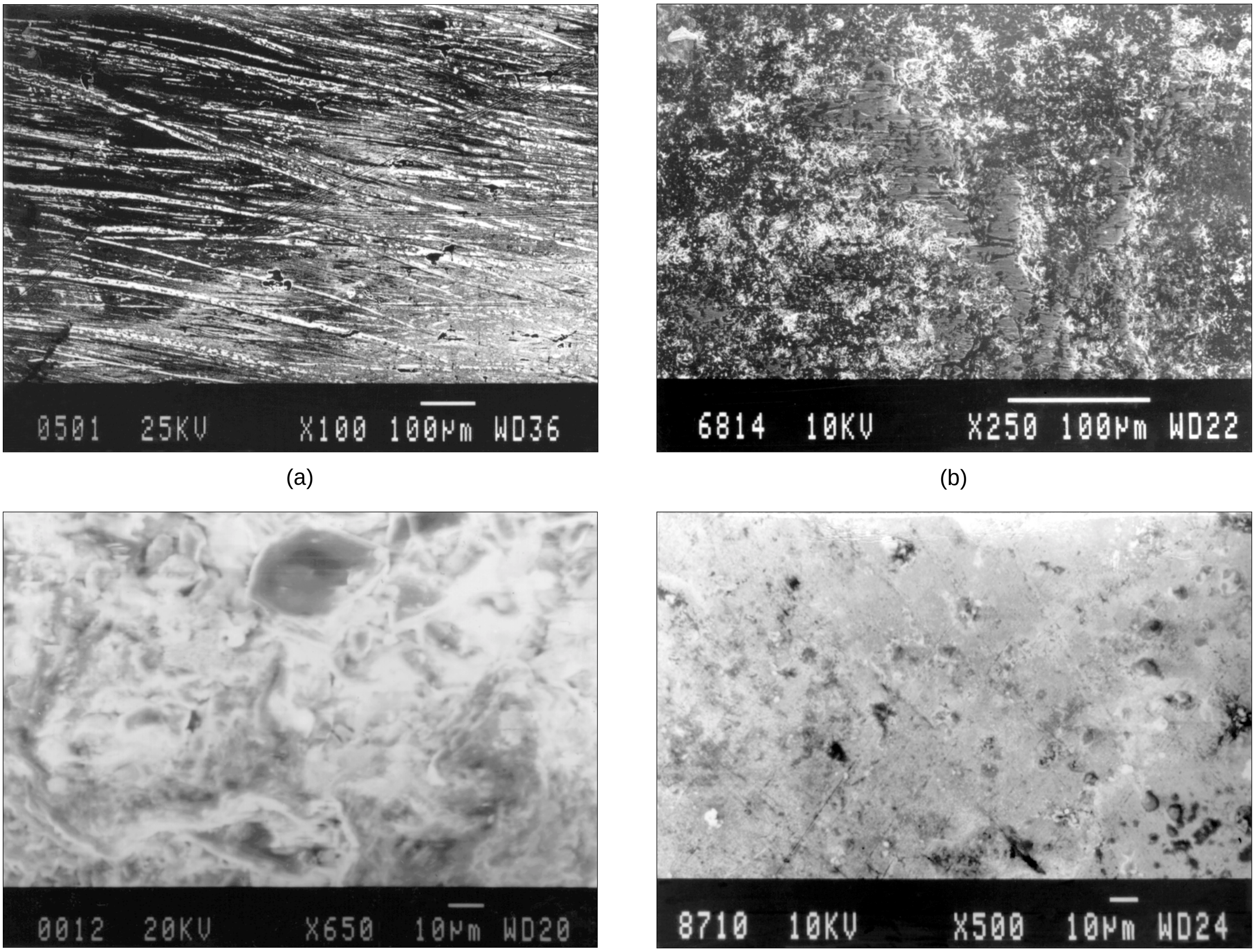
The potentiodynamic polarization curves of copper specimens with and without LB films of NODB/1-docosanol exposed to 3.4% NaCl solution are shown in Figure 5. Measurements of corrosion IE by electrochemical and weight loss methods were also made on adding benzidine to the bulk electrolyte. The results obtained from these studies were then compared with those obtained for experiments conducted with LB films (Figure 5 [B]). It is noticeable from the figure that although the anodic polarization curves shifted towards the lower current density region in both the above cases, it was more pronounced in the presence of LB films. Maximum shifting was observed in the presence of 10 monolayer LB films. The nature of the cathodic polarization curves remained almost the same in both the presence and absence of LB films. The corrosion potential showed only an insignificant shift towards the positive direction in the case of LB films modified copper surface. Various electrochemical parameters obtained from the polarization curves such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel constant (β_a), cathodic Tafel constant (β_c), polarization resistance R_p, corrosion rate expressed in mm/y, and IE are summarized in Table 1. Several observations could be made from these data:

— LB films of NODB/1-docosanol inhibit the corrosion of copper in 3.4% NaCl solution more effectively than benzidine.

TABLE 1

The Electrochemical Parameters Showing the Inhibition Effect of Mixed LB Films of Different 1:1 NODB/1-Docosanol Monolayers on Corrosion of Copper in 3.4% NaCl at 25 ± 2°C

Parameters	E_{Corr} (mV)	I_{Corr} (A/cm²)	β_C (mV/decade)	β_A (mV/decade)	R_P (Ω-cm²)	Corrosion Rate (mm/y)	IE (%)
Control	–294.1	6.41×10^{-5}	5.16×10^{4}	387.7	3.25×10^{3}	2.550	—
5 ppm benzidine	–301.8	1.08×10^{-5}	936.4	285.3	5.26×10^{3}	0.635	72
2 monolayers	–301.7	8.78×10^{-6}	434.1	278.8	8.40×10^{3}	0.308	86
6 monolayers	–284.6	6.44×10^{-6}	424.8	284.1	1.15×10^{4}	0.226	90
10 monolayers	–284.4	3.94×10^{-6}	360.5	228.0	1.54×10^{4}	0.139	94



(a) (b)

(c) (d)

FIGURE 6. *SEM photographs of copper: (a) polished, (b) exposed in 3.4% NaCl solution showing localized attack, (c) coated with mixed LB film of NODB/1-docosanol, and (d) showing less localized attack in the presence of LB films.*

— IE increases with the number of monolayers.

— I_{corr} decreases with the increasing number of monolayers.

— A film containing 10 or more monolayers of NODB/1-docosanol is most effective.

— The shift in corrosion potential of copper modified by NODB/1-docosanol multilayers is not very significant, indicating that the NODB/1-docosanol monolayers inhibit the corrosion possibly through the blocking effect, as proposed by Guo, et al.[23]

The surface of the copper specimen became almost completely blocked in the presence of 10 monolayers of NODB/1-docosanol. The high stability of these films on the copper surface was possibly attributable to their strong adsorption onto the metal surface, which is very important for excellent corrosion inhibition. The possible explanation for such adsorption could be given on the basis of ion-dipole interaction. The negative end dipoles forming LB films strongly bond to the positively charged copper surface.

SEM

SEM photographs of bare and LB film-modified copper specimens were taken before and after the exposure of these specimens to the corrosive environments. Figures 6(a) through 6(d) show the SEM photographs of the freshly polished copper surface, the copper surface modified with 10 monolayers of NODB/1-docosanol, and the surface after exposure to 3.4% NaCl solution for 30 days. The corrosion inhibition effect of LB films on the copper surface can be clearly seen from these photographs. The copper specimen modified with NODB/1-docosanol LB films shows less localized attack in 3.4% NaCl solution (Figure 6[d]) as compared to the bare metal, where the localized attack (i.e. pitting) can be significantly distinguished (Figure 6[b]).

CONCLUSIONS

❖ Mixed LB films of NODB/1-docosanol have been deposited onto a copper surface with excellent stability in 3.4% NaCl solution. These LB films have been found to be very effective in inhibiting copper corrosion. The IE increases with increasing number of monolayers, and maximum efficiency has been observed in the presence of 10 monolayers of NODB/1-docosanol. The simple blocking of the metal surface caused by these monolayers has been proposed to account for the inhibition of corrosion.

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