

# Inhibition of corrosion by poly(*N*-hexadecylaniline)/docosanol mixed Langmuir–Blodgett films on copper in sea water

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## Abstract

Electrochemical and weight loss techniques have been used for investigation of inhibition of corrosion on copper metal by Langmuir–Blodgett (LB) films of poly(*N*-hexadecylaniline)/docosanol in sea water. LB films of poly(*N*-hexadecylaniline)/docosanol were deposited onto the copper specimens. The open-circuit potential and potentiodynamic polarization curves were observed to shift in noble direction, which indicated that these LB films could inhibit the corrosion of copper metal in sea water.

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## 1. Introduction

Inhibition is a preventive measure against corrosive attack on metallic materials. It consists of the use of compounds which, when added in small concentrations to an aggressive environment, are able to decrease corrosion of the exposed metal. The compounds most often used as corrosion inhibitors are nitrogen, sulfur and oxygen containing compounds [1–5]. These compounds get adsorbed onto the surface of metal from the bulk of environment forming a film at the metal surface. Benzotriazole and its derivatives have been used as corrosion inhibitors for copper in different environments [6–8]. A number of conducting polymers such as polyaniline, polypyrrole, poly(*o*-toluidine) and poly(*o*-anisidine) have also been used as corrosion inhibitors for copper [9–12]. If these inhibitors are pre-adsorbed onto the metal surface in the form of well-organized molecular layer of controllable thickness, then one can expect better prevention of corrosion [13]. The Langmuir–Blodgett (LB) technique is one of the best techniques to produce very thin films of ordered structures with controllable thickness at molecular level [14].

The fabrication of LB films of inhibitors was achieved by amphiphilization of inhibitors [15,16]. 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 metal surface can be performed. In this communication, we present the corrosion inhibition of copper by LB films of poly(*N*-hexadecylaniline)/docosanol in sea water. The pure poly(*N*-hexadecylaniline) monolayer was not stable on air/water interface due to lack of amphiphatic balance. However, the addition of docosanol leads to stable film. The LB films of the mixture of both compounds in 1:1 ratio have been fabricated onto well-polished copper specimens for present study. A set of 2, 6 and 10 monolayer LB films deposited on copper surface have been prepared to study the effect of number of LB films on inhibition of corrosion of copper in sea water.

## 2. Experimental

Poly(*N*-hexadecylaniline) has been prepared and characterized by the method described in our previous paper [17]. For weight loss and electrochemical experiments 1 cm<sup>2</sup> copper (HCL 99.9% purity) specimens were polished succes-

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sively with 1/0 to 1/4 grade emery papers and washed with benzene followed by a hot analytical grade soap solution, and finally with triple distilled water. After polishing and washing they were degreased by ultrasonating in acetone for few minutes, dried and stored in a vacuum desiccators.

Formation and deposition of the LB films on copper substrate have been done using NIMA trough (Model-2000, NIMA Technology, England). Triple distilled water was used as subphase and chloroform (HPLC grade) was used as the spreading solvent. All the experiments were performed at room temperature ( $25 \pm 2^\circ\text{C}$ ). Monolayers of poly(*N*-hexadecylaniline) mixed with docosanol in 1:1 ratio were produced by dissolving them in chloroform and spreading on water subphase. After waiting about 15 min to allow the solvent to evaporate, the compression was slowly begun at a continuous speed of  $5\text{ cm}^{-2}\text{ min}^{-1}$  and a surface pressure ( $\pi$ ) versus area (*A*) isotherm was recorded. Deposition of LB films have been done by dipping the copper substrate into the water subphase having monolayer of poly(*N*-hexadecylaniline)/docosanol at air/water interface.

Weight loss experiments were carried out in 500 ml conical flask containing 250 ml of synthetic sea water (3.4% NaCl). The inhibition efficiency (IE) of LB films was calculated after 2–9 weeks using 2, 6 and 10 monolayers of LB films deposited on copper metal. After the experiments, specimens were removed from the sea water and washed thoroughly with triple distilled water, dried and weighted.

LB films coated copper specimens were used for electrochemical studied in three-electrode cell containing 250 ml sea water at room temperature ( $25 \pm 2^\circ\text{C}$ ). The exposed area of the working electrode was  $1\text{ cm}^2$ . Anodic and cathodic polarization curves were obtained potentiodynamically after 48 h of film fabrication, with a sweep rate of  $5\text{ mV s}^{-1}$  by a corrosion measurement system (EG & G PAR 273A). The scanning electron micrographs (SEM) of the specimens were taken by a scanning electron microscope (JSM-840).

### 3. Results and discussion

#### 3.1. Fabrication of Langmuir–Blodgett films

Surface pressure ( $\pi$ ) versus area (*A*) isotherms of poly(*N*-hexadecylaniline) and mixed poly(*N*-hexadecylaniline)/docosanol have been shown in Fig. 1. The pure poly(*N*-hexadecylaniline) monolayer was found to be unstable at air/water interface. But a stable monolayer could be fabricated by adding docosanol. The  $\pi$ –*A* isotherm of mixed film is steeper and contains less “liquid condensed phase” as compared to that of pure poly(*N*-hexadecylaniline), indicating the formation of better monolayer. The collapse pressure of these monolayer was  $\sim 55\text{ mN m}^{-1}$ .

The stability of the films has been studied by measuring the change in molecular area as a function of time at a constant surface pressure. It has been observed that the area of the mixed films did not change appreciably as a function of time.

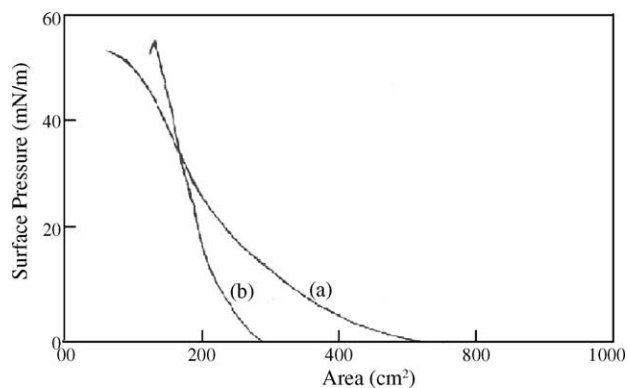


Fig. 1. Surface pressure ( $\pi$ ) vs. area (*A*) isotherms of: (a) poly(*N*-hexadecylaniline), (b) 1:1 poly(*N*-hexadecylaniline)/docosanol.

This result indicates that the monolayer of the mixed poly(*N*-hexadecylaniline) with docosanol was quite stable under the studied condition. The mixed monolayer has been further studied to see the hysteresis by repeatedly compressing and expanding. It has been observed that there was no hysteresis, indicating that the systems are capable of forming stable monolayer.

Deposition of poly(*N*-hexadecylaniline)/docosanol has been done by dipping the copper substrate into the water subphase having monolayer of mixed poly(*N*-hexadecylaniline)/docosanol at air/water interface with a target pressure of  $15\text{ mN m}^{-1}$ . Dipping speed was  $10\text{ mm min}^{-1}$  for the downward and upward. Between subsequent dips, the samples were allowed to dry in the air for 10 min, to avoid re-transferring of the last deposited monolayer on the water surface. The transfer ratio for the upward and downward dip was comparable to each other indicating Y-type deposition of the LB films [18]. Transfer ratios were between 0.8 and 1.0 during the Y-type deposition of multilayers.

#### 3.2. Weight loss studies

The fabricated LB films on copper substrate were used for weight loss experiments. The results of weight loss experiments have been given in Table 1. It is clear from the weight loss data that there is increase in inhibition efficiency (IE) with the increase in number of monolayers of poly(*N*-hexadecylaniline)/docosanol. Maximum inhibition is

Table 1  
Percentage inhibition efficiency (measured in weight loss in mg) of corrosion of copper in the presence of LB films in sea water (3.4% NaCl) at  $25 \pm 2^\circ\text{C}$

Time (days)	Control	Number of monolayers		
		2	6	10
20	2.21	0.53 (75.9)	0.23 (89.6)	0.13 (94.2)
30	3.64	0.83 (77.2)	0.32 (91.1)	0.20 (94.6)
40	4.12	0.91 (77.9)	0.34 (91.7)	0.24 (94.3)
50	4.99	1.12 (77.6)	0.40 (91.9)	0.23 (95.4)
60	5.81	1.32 (77.3)	0.57 (90.2)	0.27 (95.3)

Data in parentheses are inhibition efficiency in percentage (%).

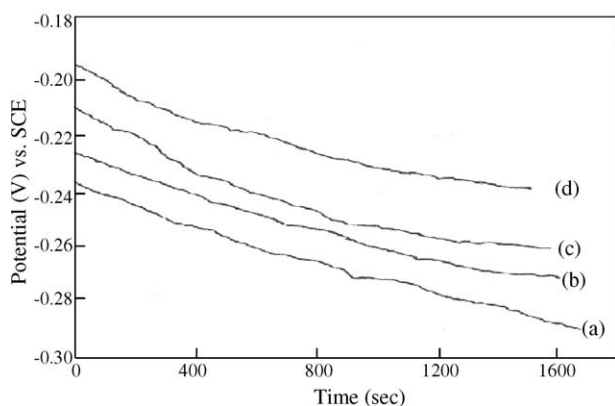


Fig. 2. Variation of corrosion potential of copper exposed to sea water (3.4% NaCl) with different monolayers of 1:1 poly(*N*-hexadecylaniline)/docosanol: (a) control, (b) two monolayers, (c) six monolayers, (d) 10 monolayers.

obtained in the presence of 10 monolayers of LB films on copper surface.

The inhibition efficiency have been calculated by the following equation:

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

where  $a$  is the average weight loss of the copper specimens without LB films and  $b$  is the average weight loss of copper specimens coated with LB films.

The effect of contact time of the copper specimens with sea water has been also studied. It has been observed that the LB films of poly(*N*-hexadecylaniline)/docosanol inhibit the corrosion of copper effectively even after 8 weeks with very high inhibition efficiency  $\sim 95\%$ , indicating that these films are very stable on the copper surface for a long period.

### 3.3. Corrosion potential

The variation of open-circuit potential with time of copper specimens with and without LB films, exposed to synthetic sea water, have been shown in Fig. 2. It has been found that the open-circuit potential shifts towards the positive direction in the presence of LB films of poly(*N*-hexadecylaniline)/docosanol on the copper surface from the bare metal. The shift of corrosion potential towards noble direction in the presence of LB films suggests the protective action of poly(*N*-hexadecylaniline)/docosanol for corrosion in sea water.

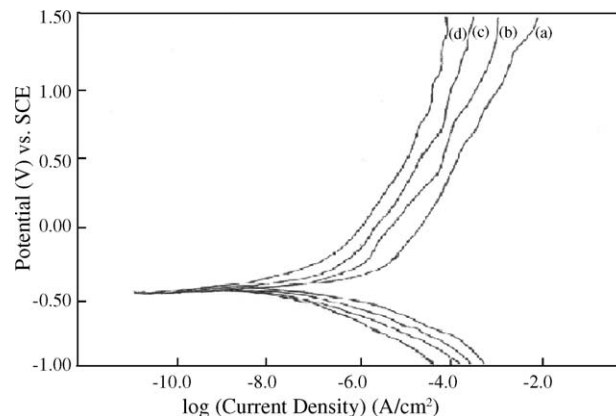


Fig. 3. Potentiodynamic polarization curves of copper exposed to sea water (3.4% NaCl) with different monolayers of 1:1 poly(*N*-hexadecylaniline)/docosanol: (a) control, (b) two monolayers, (c) six monolayers, (d) 10 monolayers.

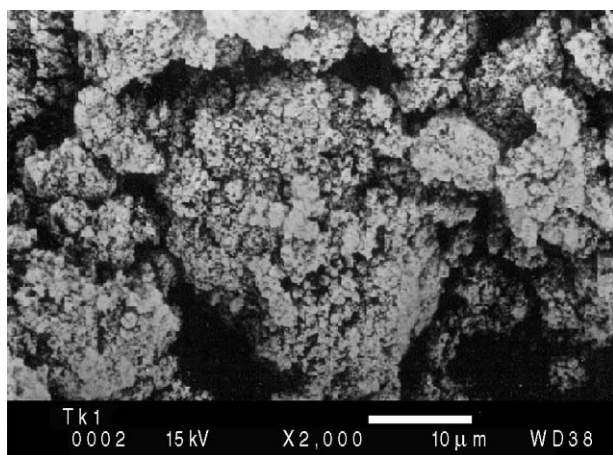
### 3.4. Potentiodynamic polarization studies

The electrochemical experiments were carried out on the specimens of copper coated with LB films of poly(*N*-hexadecylaniline)/docosanol in the synthetic sea water. The corrosion behaviour and corrosion rate were calculated and results are given in Table 2. It has been observed that these films inhibit the corrosion of copper metal. It has been observed that the LB films of 10 monolayers was most effective in protection of corrosion. Potentiodynamic polarization curves of copper in the control (uncoated) and in the presence of different monolayers of poly(*N*-hexadecylaniline)/docosanol have been shown in Fig. 3. It is clear from these curves that LB films reduced the corrosion rate by affecting both cathodic and anodic reactions or redox reaction occurring at solution/metal interface. The passivation of the copper specimens increased with increasing the number of monolayer of poly(*N*-hexadecylaniline)/docosanol. The shift in corrosion potential of copper with modification by poly(*N*-hexadecylaniline)/docosanol multilayer was not significant. This indicates that the poly(*N*-hexadecylaniline)/docosanol monolayers inhibit the corrosion possibly by blocking effect as proposed by Guo et al. [16]. These films act as a barrier at solution/metal interface and thus prevent the corrosion of copper in marine environment. 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 [19]. The

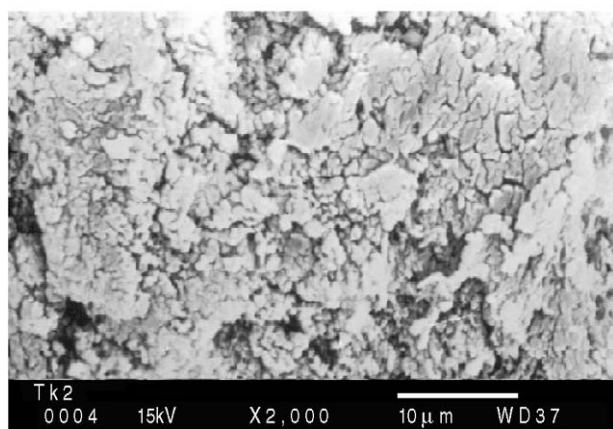
Table 2

Electrochemical parameters for the corrosion of copper in the presence of LB films in sea water (3.4% NaCl) at  $25 \pm 2^\circ\text{C}$

No. of monolayers	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\text{A cm}^{-2}$ )	Corrosion rate ( $\text{milli-inch year}^{-1}$ )
Control	-446.3	$3.24 \times 10^{-6}$	2.99
2	-430.2	$4.13 \times 10^{-7}$	0.381
6	-378.6	$2.98 \times 10^{-7}$	0.275
10	-377.2	$1.10 \times 10^{-7}$	0.102



(a)



(b)

Fig. 4. SEM photographs of copper specimen exposed in 3.4% NaCl solution: (a) copper, (b) copper coated with 10 monolayers of mixed LB film of poly(*N*-hexadecylaniline)/docosanol.

surface of the copper specimen becomes almost completely blocked in the presence of 10 monolayers, thus showing very high inhibition efficiency (95.3%). Scanning electron micrographs (SEM) of copper specimen exposed in solution of 3.4% NaCl shows localized attack (Fig. 4a), whereas the SEM of copper coated with 10 layers of mixed LB film of poly(*N*-hexadecylaniline)/docosanol shows less localized attack (Fig. 4b).

#### 4. Conclusion

LB films of mixed poly(*N*-hexadecylaniline)/docosanol was found to be more stable than the pure poly(*N*-hexadecylaniline). Mixed LB films were successfully deposited on the copper specimen. Mixed LB films were found to be very effective in inhibiting the corrosion of copper in sea water. The inhibition efficiencies increased with increasing the number of monolayers of poly(*N*-hexadecylaniline)/docosanol.

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