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Outstanding inhibitive effect of colchicine on aluminium alloy 6061 corrosion

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Abstract

The corrosion protection ability of colchicine (CC) on Aluminium alloy 6061 (AA6061) in 3.5% NaCl medium was examined by potentiodynamic polarization, electrochemical impedance, and chronoamperometric techniques. About 99 % of protection efficiency was achieved by 2 mM concentration of CC in 3.5% NaCl solution. The adsorption of CC on AA6061 surface obeys Langmuir isotherm by following both physisorption and chemisorption mechanism. Variation in the surface morphology of inhibited and uninhibited metal samples was examined by scanning electron microscopy.

Keywords

Corrosion inhibitor; Aluminium alloy; Potentiodynamic polarization; Electrochemical impedance spectroscopy, Adsorption isotherm

Introduction

Aluminium alloy 6061 (AA6061) has a remarkable technological importance and extensive applications in industries and machineries due to low cost, light weight, high thermal and good corrosion resistance properties [1]. The corrosion resistance behaviour develops from the ability of metal to form a natural oxide film on its surface [2,3]. However, the localized corrosion takes place in an aggressive chloride medium and it leads to the breakdown of passive layer and resulted in pit formation [4,5]. Thus, chemical inhibitors are widely employed to minimize the corrosion of AA6061 in chloride media. Numerous organic compounds having N, S, and O atoms along with π

electrons have been studied as proficient corrosion inhibitors for aluminium and its alloys in 3.5 % NaCl solution [6-10]. But, now a day, the drug molecules find much attention in the field of corrosion inhibition. This is due to the strong chemical activity, low toxicity and negligible negative impact of drug molecules on the environment [11- 13].

The drug molecules inhibits metallic corrosion by the process of adsorption and the magnitude of adsorption depends on nature of the metal, mode of adsorption, chemical structure of the inhibitor, and type of corrosion media [14]. As a result colchicine (CC) drug molecule which is an oral anti-inflammatory agent used for the treatment of gout, familial Mediterranean fever and pericarditis [15,16] has been chosen based on its structural considerations. CC contains one nitrogen and six oxygen atoms along with large number of π -electrons in the six and seven membered ring system which may induce the adsorption behaviour of molecule on the metal surface. Meanwhile, according to literature study, there is no report found on the corrosion inhibition studies of CC in 3.5 % NaCl medium. Hence in the present investigation, the anticorrosive ability of CC on AA6061 in 3.5 % NaCl solution has been explored by electrochemical techniques and surface analysis.

Experimental

Preparation of Metal Samples.

The surface of AA6061 (Bhandari Metal House, K.R. Market, Bangalore, India) having composition 0.25 % Cu, 1.0 % Mg, 0.60 % Si, 0.20 % Cr and remainder being Al was polished with different grades of emery papers (grade No. 400, 600, 800, 1000, and 1200). Afterwards, the polished specimen was immersed in 10 % NaOH solution for 30 sec, degreased with acetone and rinsed by millipore water, dried and stored in desiccator. The AA6061 specimens of 1 cm² area (exposed) with a 5 cm long stem isolated with araldite resin were used for electrochemical measurements.

Preparation of solutions

Corrosive medium was prepared from AR grade NaCl by using millipore water. The millipore water was obtained from Elix 3 Milli-pore system (Resistivity greater than 18 M Ω cm at 25 °C). CC was obtained from Ramdev Chemicals India Pvt. Ltd., Mumbai and its structure is given in Figure 1. The different concentrations (1.0, 1.5, 2.0 mM) of inhibitor solutions were prepared by dissolving specified amount of CC in 3.5 % NaCl solution. All the experiments were carried out in static condition and 3.5 % NaCl solution exhibit pH 6 and the same pH has been maintained for each concentration of inhibitor solutions. Each experiment was carried out in triplicate, and the average values are reported.

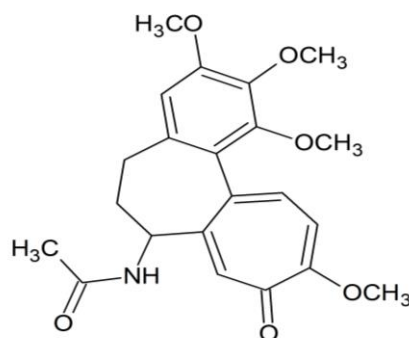


Figure 1. The structure of CC [16]

Electrochemical measurements

The electrochemical measurements were conducted in a three electrode conventional glass cell using CHI 660C electrochemical analyzer (CH instruments, Austin, USA). An AA6061 specimen (of 1 cm² area), a platinum wire, and a Ag/AgCl electrode were used as working, auxiliary, and reference electrodes for all the experiments. Prior to each potentiodynamic polarization and electrochemical impedance spectroscopic measurements (EIS), a stabilization period of 30 min was allowed to establish a steady state open circuit potential (OCP).

Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were carried out over a potential range of -200 mV to +200 mV at OCP with a scan rate of 0.5 mV s⁻¹. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic (β_a), and cathodic (β_c) Tafel slopes were generated from the software installed in the instrument. The inhibition efficiency $\eta_T / \%$ was evaluated from i_{corr} values using the following expression:

$$\eta_T / \% = \frac{i_{\text{corr}}^{\circ} - i_{\text{corr}}}{i_{\text{corr}}^{\circ}} \times 100 \quad (1)$$

where i_{corr}° and i_{corr} are the corrosion current densities without and with CC, respectively.

Electrochemical impedance measurements

The impedance measurements were carried at OCP in the frequency range 1 mHz to 100 kHz with 5 mV sine wave as the excitation signal. Impedance data were analyzed using ZSimp-Win 3.21 software. The percentage efficiency $\eta_Z / \%$ was evaluated from total resistance (R_t) values using the following equation

$$\eta_Z / \% = \frac{R_t - R_t^{\circ}}{R_t} \times 100 \quad (2)$$

Where R_t° and R_t are the total resistance (where R_t is the sum of R_1 and R_2) in the absence and presence of CC, respectively.

Chronoamperometric measurements

The chronoamperometric experiments were carried out by polarizing the working electrode anodically at -0.68 V (Ag/AgCl) for 600 s in 3.5 % NaCl solution.

Surface morphological studies

The surface morphology of AA6061 samples after immersion in corrosive medium in the absence and presence of inhibitor was analyzed using scanning electron microscope (JEOL, JSM 6400, JEOL Datum Shanghai Co. Ltd., Shanghai, PRC).

Results and discussion

Potentiodynamic polarization (PDP) measurements

The potentiodynamic polarization curves obtained for AA6061 in 3.5 % NaCl solution with or without CC are presented in Figure 2. It is evident from the figure that, both the cathodic and anodic curves are shifted towards lower current density in inhibited solution compared to NaCl

solution. As a result it can be considered that both oxygen reduction and Al dissolution process are limited by CC and thus it acts as a mixed type inhibitor.

The corrosion kinetic data obtained from potentiodynamic polarization curves for AA6061 in 3.5 % NaCl having different concentrations of CC are tabulated in Table 1. It can be visualized from the table that by increasing the concentration of CC there exist a slight variation in both β_a and β_c values and E_{corr} values shifted towards more positive direction. This infers the formation of strongly adsorbed CC film on AA6061 surface.

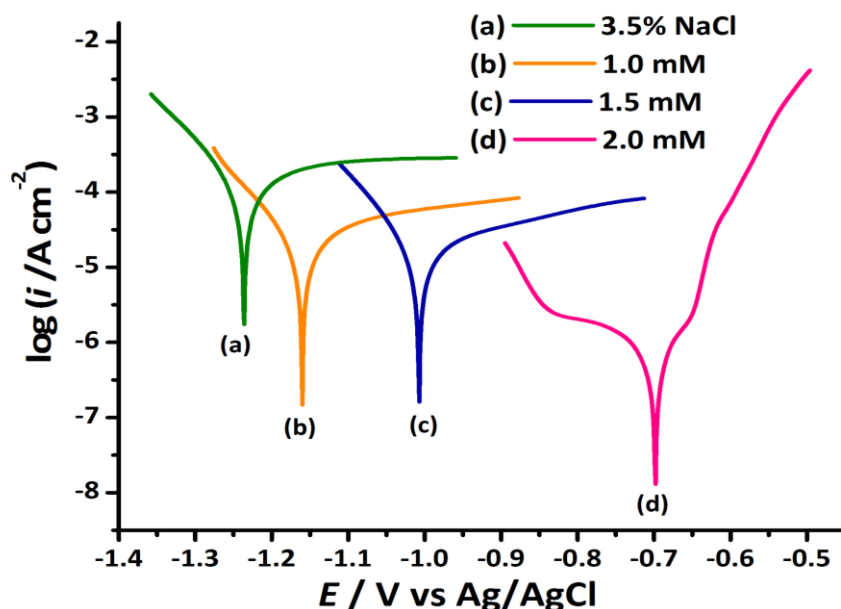


Figure 2. Potentiodynamic polarization curves obtained for AA6061 in 3.5 % NaCl in the absence and presence of CC.

Usually, in 3.5 % NaCl media, aluminium experience pitting corrosion because of the presence of destructive chloride ions. Hence, AA6061 dipped in 3.5% NaCl shows high i_{corr} value. But the i_{corr} values get reduced in presence of CC. This specifies that in inhibited solution the CC molecules adsorb on the Al surface and decreases the aggressiveness of Cl^- ions as well as protect the surface from being pitted. This suggests that CC inhibits the corrosion of AA6061 in 3.5 % NaCl solution and its efficiency increases with the increase of its content in the solution.

Table 1. Potentiodynamic polarization parameters obtained for AA6061 in 3.5 % NaCl in the absence and presence of CC

C / mM	$-E_{corr} / V$	$-\beta_c / mV \text{ dec}^{-1}$	$\beta_a / mV \text{ dec}^{-1}$	$i_{corr} / \mu A \text{ cm}^{-2}$	$\eta_T / \%$
Blank	1.236	10.063	2.308	162.5	
1.0	1.160	11.516	2.876	25.08	85
1.5	1.007	11.367	2.805	20.17	88
2.0	0.698	21.923	2.417	0.6728	99

On the other hand, it is apparent from the Figure 2 that a wide passive region can be witnessed in the anodic curve obtained for 2 mM CC. This may be attributed to the formation of stable inhibitor film on the oxide layer which results in 99 % protection efficiency. By reviewing these results, it can be concluded that CC behaves as a potential corrosion inhibitor for AA6061 by inhibiting the corrosion of aluminium by blocking the active sites of the metal surface.

Electrochemical impedance spectroscopy (EIS)

EIS analysis was carried out to get information on the corrosion and inhibition mechanism of AA6061. The electrochemical impedance diagrams in the form of Nyquist and Bode plots obtained for AA6061 in 3.5 % NaCl in the absence and presence of CC are given in Figures 3 and 4, respectively. The EIS results were simulated by an electrical equivalent circuit shown in the inset of Figure 3. In this circuit, R_s represents the solution resistance, R_1 is the charge transfer resistance corresponding to the corrosion reaction at the Al/solution interface, R_2 represents the polarization resistance, which reflects the protective property of the film, CPE_1 and CPE_2 represents the constant phase elements (CPE) as a substitute for the double-layer capacitance (C_{dl}). The impedance of CPE is defined as

$$Z_{CPE} = Q^{-1} (j\omega)^{-n} \quad (3)$$

where Q is the CPE constant, ω is the angular frequency, $j^2 = -1$ is the imaginary number and n is the CPE exponent which gives details about the degree of surface inhomogeneity resulting from surface roughness, inhibitor adsorption, porous layer formation etc.

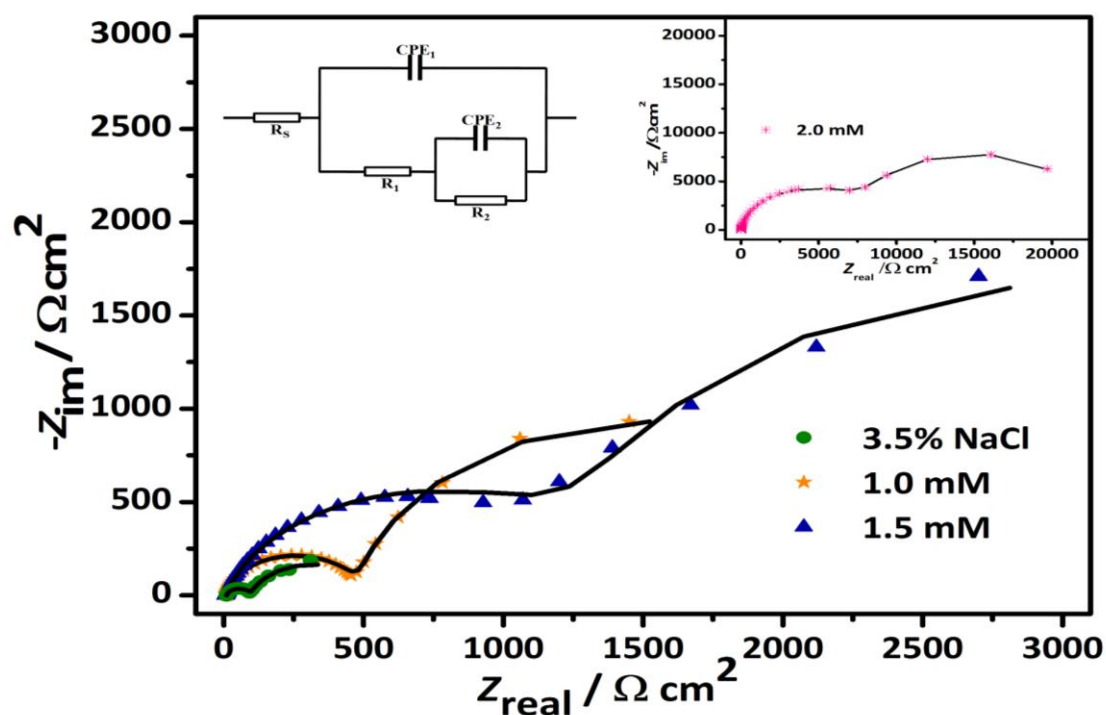


Figure 3. Nyquist plots for AA6061 in 3.5 % NaCl in the absence and presence of different concentrations of CC.

Two capacitive loops were observed in Nyquist plots. The first capacitive loop at higher frequencies is related to the sum of charge transfer resistance and accumulation resistance (some free molecules or ions or corrosion products), while the second capacitive loop at lower frequencies corresponds to the film resistance. The diameter of these capacitive loops gets increased with increasing CC concentration and signifies the adsorption of inhibitor molecules on the metal surface. The adsorption of inhibitor molecules at the AA6061/NaCl solution interface results in an increase of polarization resistance and reduces the corrosion rate of AA6061 [17].

Table 2. Electrochemical impedance parameters obtained for AA6061 in 3.5 % NaCl in the absence and presence of different concentrations of CC

C / mM	$R_s / \Omega \text{ cm}^2$	$Q_1 / \mu\Omega^{-1} \text{ S}^n \text{ cm}^{-2}$	n_1	$R_1 / \Omega \text{ cm}^2$	$Q_2 / \mu\Omega^{-1} \text{ S}^n \text{ cm}^{-2}$	n_2	$R_2 / \Omega \text{ cm}^2$	$\eta_z / \%$
Blank	10.12	171.8	0.865	87.12	12060	0.811	442.5	
1.0	10.68	71.05	0.913	483.6	3562	0.912	2116	80
1.5	6.934	155.2	0.827	1427	2322	0.920	3597	89
2.0	6.891	24.47	0.936	9259	309.4	1.000	13620	98

Data from Table 2 reveal that increasing the concentration of CC in chloride media leads to an increase in resistance value and decrease in CPE values. The decrease in Q_1 and Q_2 values may be due to the decrease in local dielectric constant and/or an increase in the electrical double layer thickness [18]. This infers CC acts via adsorption at the AA6061/NaCl solution interface. Meanwhile the increase in R_1 and R_2 values point out that the amount of CC molecules adsorbed on the metal surface increases and the adsorbed inhibitor molecules forms a protective film on the electrode surface and consequently become a barrier to hinder the mass and charge transfer, resulting in an increase in the protection efficiency.

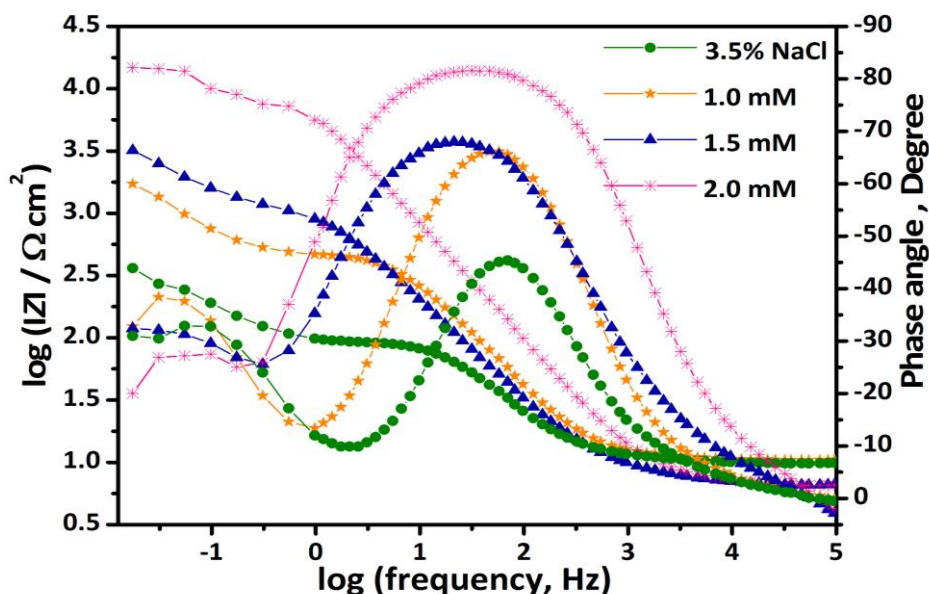


Figure 4. Bode plots for AA6061 in 3.5 % NaCl in the absence and presence of different concentrations of CC.

The Bode diagrams (Figure 4) that was plotted using the same experimental data in the Nyquist format. In the lower frequency range, impedance modulus (Z_{mod}) gives information regarding the corrosion resistance behavior of metal samples. In Figure 4, Z_{mod} values increases with increasing CC concentration compared to uninhibited solution and it reveals the better corrosion inhibition performance of CC in NaCl medium. Compared to uninhibited solution, the new phase shift is observed in the inhibited solutions. This means that the formation of inhibitor film changes the electrode interfacial structure and results in an extra time constant [19]. Hence two time constants can be evidenced in Figure 4 and this indicate that there are two major electrochemical kinetic processes on the electrode surface: the high frequency part is due to the adsorption of the CC molecule and the formation of the inhibitor film; the second time constant at medium frequency is due to the electrochemical corrosion process. Moreover, the inhibition effect is more remarkable

and the middle frequency phase becomes loftier and wider at higher concentration [19] of CC (2 mM). These suggest the formation of compact, stable protective film of CC on AA6061 surface in 3.5 % NaCl solution.

Chronoamperometric (CA) measurements

The chronoamperometric experiments were performed so as to get information on the corrosion behaviour of AA6061 in 3.5 % NaCl solution in the absence and presence of CC at less negative potentials. The experiments were carried out by polarizing the working electrode anodically at -680 mV (vs. Ag/AgCl) for 600 s [20]. The current density values were obtained during the electrooxidation of AA6061 in 3.5 % NaCl solution in the absence and presence of different concentrations of CC and the chronoamperometric curves are illustrated in Figure 5.

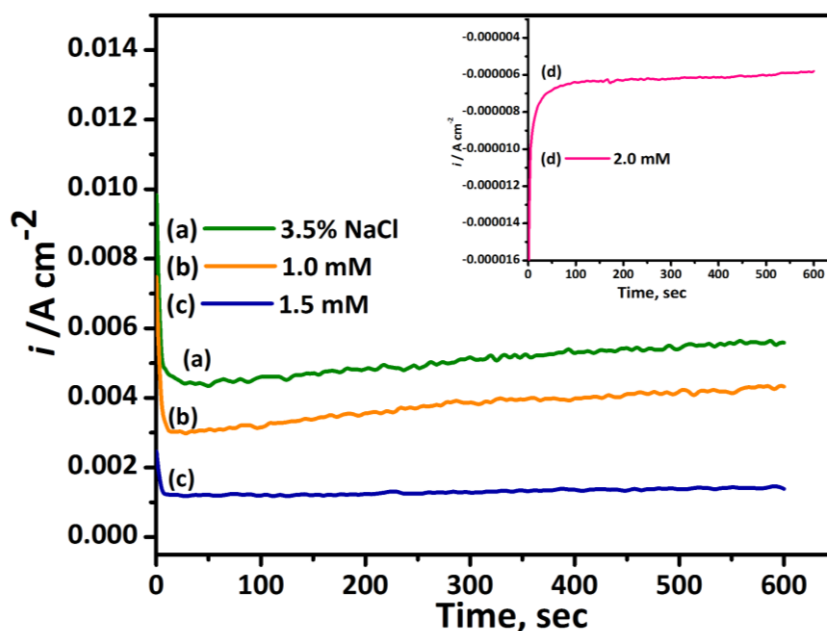


Figure 5. Chronoamperometric curves obtained for AA6061 in 3.5 % NaCl in the absence and presence of different concentrations of CC.

The absolute current of AA6061 in uninhibited solution is comparatively higher than inhibited solution. The addition of CC in to NaCl solution results in a reduction in the absolute current of AA6061 from the first moment till the end of the measurement. Besides, a significant decrease in the current was observed by increasing the concentration of CC. This supposes that CC improves the anticorrosive nature of AA6061 in 3.5 % NaCl solution and hence it can be considered as a potential corrosion inhibitor.

Adsorption isotherm

The anticorrosive ability of metals can be improved by the adsorption of organic molecules and ions at the metallic surface. The molecular structure, electronic properties and distribution of charge in inhibitor molecules, the nature and surface charge of the metal, and the type of corrosive medium [21] have great influence on the process of adsorption of inhibitors on metal surface. In order to gain information on the adsorption behaviour of CC on AA6061 surface, the data obtained from the PDP and EIS techniques were tested with several adsorption isotherms. Many attempts were made to fit experimental data with adsorption isotherms like Langmuir, Flory-Huggins, Temkin, and Freundlich isotherms [22-24] (Equations 4-7).

Langmuir adsorption isotherm:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C, \tag{4}$$

Flory – Huggins adsorption isotherm:

$$\log\left(\frac{\theta}{C}\right) = \log K_{ads} + a \log(1 - \theta), \tag{5}$$

Temkin adsorption isotherm:

$$\theta = \frac{1}{f} \ln K_{ads} C, \tag{6}$$

Freundlich adsorption isotherm:

$$\log \theta = \log K_{ads} + n \log C, \tag{7}$$

where C is the inhibitor concentration, θ is the degree of surface coverage defined as $\eta/100$ and K_{ads} is the adsorptive equilibrium constant, f is the factor of energetic inhomogeneity, and the parameter a is the number of water molecules replaced by inhibitor molecules on the metal surface.

The experimental data were fitted to Langmuir, Flory–Huggins, Temkin, and Freundlich isotherms and the corresponding curves are illustrated in Figure 6. In the present investigation, the best fit was obtained with Langmuir adsorption isotherm and the plot of C/θ against C clearly indicates that the linear regression coefficient (R^2) and the slope values are very close to 1. This reveals that the adsorption of CC on AA6061 obeys the Langmuir adsorption isotherm.

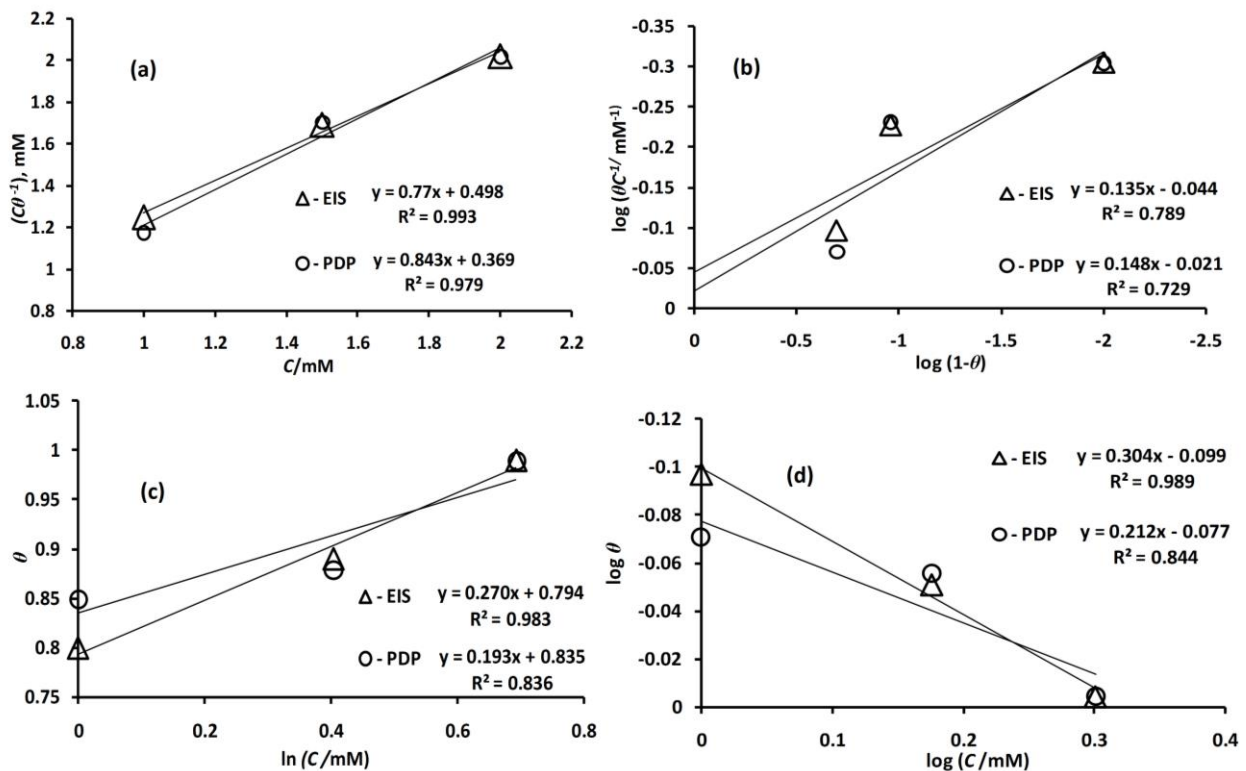


Figure 6. Adsorption isotherm plots obtained for the CC on the surface of AA6061 in 3.5 % NaCl (a) Langmuir, (b) Flory-Huggins, (c) Temkin and (d) Freundlich isotherms

The equilibrium constant, K_{ads} is related to the standard Gibbs free energy of adsorption $\Delta G^{\circ}_{\text{ads}}$ by the relation:

$$K_{\text{ads}} = \frac{1}{55.5} \exp\left(\frac{\Delta G^{\circ}_{\text{ads}}}{RT}\right) \quad (8)$$

where R is the universal gas constant, T is the thermodynamic temperature and 55.5 is the molar concentration of water in the solution.

Generally, the values of $\Delta G^{\circ}_{\text{ads}}$ around -20 kJ mol^{-1} or lower are consistent with physisorption and those around -40 kJ mol^{-1} or higher involves chemisorption [25]. In the present work, the values of $\Delta G^{\circ}_{\text{ads}}$ obtained for the adsorption of CC from PDP and EIS analysis are -29.93 and $-29.18 \text{ kJ mol}^{-1}$, respectively. This ensures that the adsorption of CC on AA6061 involves both physisorption and chemisorptions. Meanwhile, the negative value of $\Delta G^{\circ}_{\text{ads}}$ suggests the spontaneity of the adsorption of the CC molecules and the stability of the adsorbed layer on AA6061 surface.

Surface morphological studies

Figure 7 shows the surface morphology of AA6061 samples after immersion in 3.5 % NaCl in the absence and presence of 2 mM CC. It can be clearly seen from the Figure 7a that AA6061 surface is strongly damaged with numerous pits in the absence of CC due to dissolution of metal in NaCl medium. But a smoother surface free from pits can be observed in the Figure 7b due to the presence of CC which results in the formation of protective layer on AA6061. This signifies that CC hinders the dissolution of Al and thereby it reduces the pitting corrosion of AA6061 in 3.5 % NaCl.

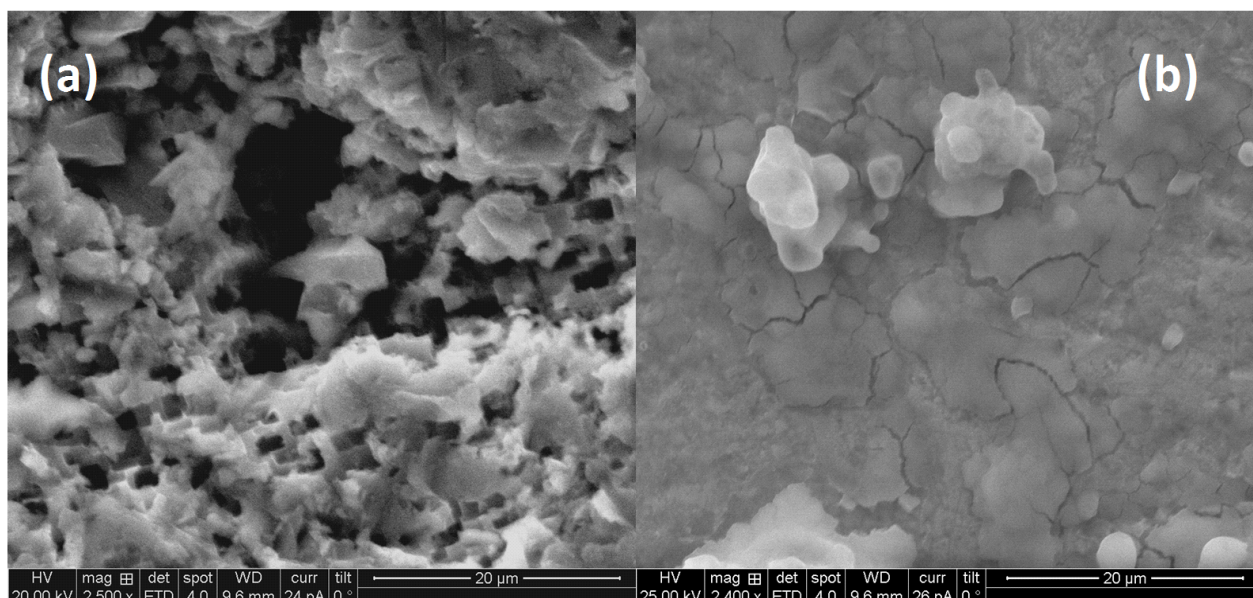


Figure 7. SEM micrographs of AA6061 immersed in (a) 3.5 % NaCl and b) 3.5 % NaCl + 2.0 mM CC

Mechanism of corrosion inhibition

Aluminium has more electronegative potential value and hence, it undergoes oxidation very easily in an oxidizing media. This phenomenon leads to the formation of oxide layer (Al_2O_3) on its surface by both cathodic and anodic reactions [26]. The mechanism of formation of oxide film on AA6061 surface is shown in Figure 8a.

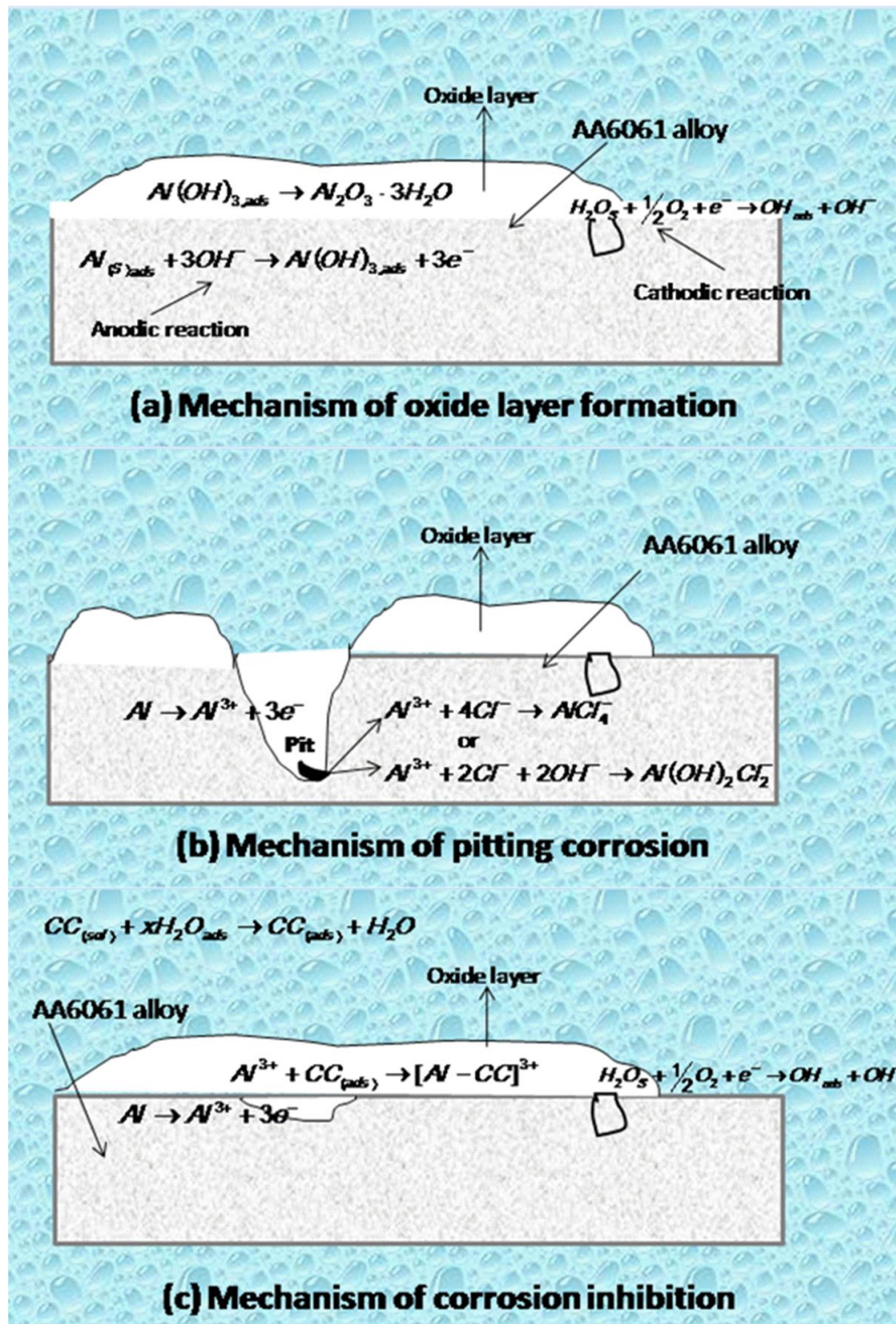


Figure 8. Mechanism of AA6061 corrosion and its inhibition by CC in 3.5 % NaCl.

The presence of oxide layer on metal surface induces corrosion resistance property. However, in 3.5 % NaCl medium, aluminium undergoes pitting corrosion which results in the depletion of oxide layer. The mechanism of pitting corrosion is depicted in Figure 8b. In the presence of 3.5 % NaCl media, the stability of the oxide layer decreases due to the presence of aggressive chloride ions [7]. The aggressive chloride ions penetrates through the oxide film and breakdown the aluminium oxide formed on the metal surface [27]. Then the adsorbed chloride ions reacts with Al^{3+} in the oxide lattice and results in the formation of oxychloride complexes, $Al(OH)_2Cl_2^-$ [28-31]. The oxychloride complex reduces the stability of oxide film and intensifies the dissolution rate of aluminium [20].

On the other hand, all the experimental results reveal that the corrosion of AA6061 can be minimized in presence of CC. The electrochemical studies disclose that the inhibition performance of CC occurs through the process of electrostatic interaction. The mechanism of corrosion inhibition is given in Figure 8c. The inhibitor CC get adsorbed on metal surface by donor acceptor interactions between free electron pairs of four oxygen atoms present in the methoxy group and π electrons of the phenyl ring and the vacant orbital of aluminium atom. According to the quantum chemical studies carried out by our research group, nitrogen and oxygen atoms, and π - electrons in the phenyl ring and cycloheptatrienone ring, are the main active sites of adsorption of CC on metal surface [32]. As a result, CC gets adsorbed on AA6061 surface through these active sites and it prevents the formation of oxychloride complexes and inhibits metal dissolution reaction.

Conclusions

The pitting corrosion of AA6061 can be minimized in the presence of CC in 3.5 % NaCl solution. CC acts as a proficient corrosion inhibitor through the process of adsorption. The PDP, EIS and CA studies disclose that CC forms a protective film on metal surface which results in an improvement in anticorrosive nature of AA6061 in NaCl medium. The adsorption of CC on AA6061 surface follows Langmuir adsorption isotherm via comprehensive adsorption mechanism. Variation in the surface morphology of metal samples also reveals the corrosion protection ability of CC.

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