



Corrosion Mitigation of Aluminium in 3.65% NaCl Medium Using Hexamine

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Abstract

This study reports the performance of Hexamine as a useful corrosion inhibitor on Aluminium alloy in 3.65% NaCl at ambient temperature and a constant pH of 7. The corrosion-protective ability of Hexamine was investigated utilizing potentiodynamic polarization procedures, computational studies and mass loss estimates. The result from the research unveils that Hexamine hinders the corrosion of Aluminium alloy in sodium chloride solution. The inhibition effect was due to the blockage of the active site of the metal surface by the adsorbed molecule of Hexamine thereby forming a thin layer which minimizes the intrusion of chloride ion into the mobile sites of Aluminium alloy, leading to the reduction of corrosion current density. The deteriorations in mass by the inhibited Aluminium alloy were discovered to decrease as the mass of mass concentration of Hexamine increases. The outcome of the experiment indicated that Hexamine offered inhibition performance of 47.1%, which may likely increase as mass concentration increases. Polarization curve confirmed that Hexamine in 3.65% NaCl at ambient temperature behaved as a mixed-type inhibitor, reducing the corrosion rate and increasing the polarization potential. Adsorption of Hexamine molecules on the Aluminium alloy was attested to follow Langmuir adsorption isotherm with correlation regression coefficient (R^2) value of 0.8408. The Morphology study via SEM micrograph affirms the adsorption of Hexamine molecules on the surface of the Aluminium alloy.

Keywords Hexamine · Aluminium · Inhibition · Langmuir and corrosion

1 Introduction

The mechanism of corrosion investigations of aluminium and its alloy are still of essential interest because of their technological value and technical applicability, particularly in the machine, aerodynamics, household devices, packages and a photoelectric material [1]. Aluminium alloys are also predominantly used in marine applications where lighter weight materials and good mechanical properties are required [2].

Marine corrosion occurs with components of machinery and piping that are used in seawater or saline water. Exposure of parts can be constant or occasional. Vessels or ships, pipelines, maritime structures, are common cases of systems that encounter marine corrosion [3]. Degradation of aluminium and aluminium alloys has continued as discussion of several researchers due to their significance in contemporary development and vast industrial applications [4, 5]. Comparatively, aluminium and its alloy display better resistance to corrosion than iron and mild steel on exposure to a caustic environment, which was credited to a thin oxide layer that builds on them [6, 7]. Nevertheless, copious subjects linked to the corrosion of Aluminium and its alloy in a saline environment unveil that they are predisposed to damages by corrosion on exposure to chloride atom [8–13]. Consequently, adequate corrosion assuring means should be employed. Example of these practical measures is the application of inhibitors. A number of investigations have been conducted to present inhibitors suitable for diverse destructive media [14–17], however, some of the tested inhibitors have been found to have an awkward impact on the climate [18]. Thus, it is necessary to examine the makeup of an

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inhibitor before using. It is worthy of note that, a huge measure of chemical inhibitors have been discovered to exhibit strong inhibitive action amidst moderate toxicity, however, the bulk of them are high-priced compared to natural or organic corrosion inhibitors.

Organic inhibitors like Hexamine have grown in relevance in recent years because of their environmentally friendly nature. Hexamine as an antibiotic finds various engineering applications [19]. Metal corrosion defence by the inhibitive organic compounds is a function of their ability to adsorb on the base metal surface creating barrier layers against corrosive species in the media [20]. Organic inhibitors protective strength in corrosion reduction is a function of numerous determinants such as the quality of the metal surface, the nature of eroding media and the chemical composition of the inhibitor [21, 22]. Those determinants make it imperative for prudent selection of inhibitors for metals. Corrosion inhibition by Hexamine had been widely used. The study of corrosion inhibitory performance of Hexamine on cast iron pipes in aqueous salt solution of 2% NaCl revealed that Hexamine minimized the pipes corrosion, offering maximum corrosion efficiency of 52.9% after 288 h of exposure [23]. Mild steel embedded in concrete with 0.5% of Hexamine after 180 days of exposure was discovered to have been inhibited by 43.52% [24]. The choice of Hexamine is as a result of its inhibitory action which could be linked with various factors such as the structure of its molecules, adsorption ability, distribution and synergy of molecules on the metallic surface [4, 25]. This study examines the inhibitive capacity of Hexamine on the corrosion of Aluminium alloy in seawater 3.65% NaCl solution. The performance of Hexamine on the inhibition of Aluminium alloy was examined applying potentiodynamic polarization methods, mass loss techniques, computational comparisons and SEM micrographs.

2 Experimental Procedures

2.1 Sample Preparation

The Aluminium alloy coupons utilized for these studies are of the dimension of (20×20×2) mm. The synthetic composition in (wt %) is given in Table 1. These coupons were later cleaned with sandpapers of varying degrees and washed with distilled water. All specimens' mass was registered and specified accordingly. 3.65% NaCl solution was prepared using doubled distilled water which served as the corrosive medium. The mass of the Hexamine whose molecular composition is shown in Fig. 1 was varied in 3.65% NaCl simulated solution

for each potentiodynamic polarization analysis conducted. 200 ml of solution was prepared for all the corrosion and mass loss measurement.

2.2 Potentiodynamic Polarization Experiment

Autolab PGSTAT 101 Metrohm potentiostat including NOVA software of version 2.1.2 was employed for this electrochemical experiment. The Aluminium alloy coupon was fused to cable and installed on a resin. Aluminium alloy served as the practical electrode. A graphite rod was adopted as the counter electrode and silver chloride electrode (SCE) serves as the reference electrode. Potentiodynamic polarization curves were acquired from the potential of -2.0 V to -0.5 V vs. open circuit potential at a sweep rate (scan rate) of 0.005 m/s.

The practical electrode (Aluminium alloy) was dipped into the electrolyte (3.65% NaCl solution) for 10 min to accomplish the steady-state potential. The same technique was carried out with four different Aluminium alloy specimens altering the concentration of Hexamine in four different 200 ml of 3.65% NaCl solution and the outcomes were recorded. To ensure reproducibility each experiment was carried out four times. The polarization potential (E_{corr}), and current density (j_{corr}) data were estimated from the Tafel plots. The surface coverage (θ) and the percentage inhibition efficiency (% IE) were computed from Eqs. 1 and 2 [27–30].

$$\theta = 1 - \frac{j_{\text{corr}}}{j_{\text{corr}}^0} \quad (1)$$

$$\text{IE}\% = 1 - \frac{j_{\text{corr}}}{j_{\text{corr}}^0} \times 100 \quad (2)$$

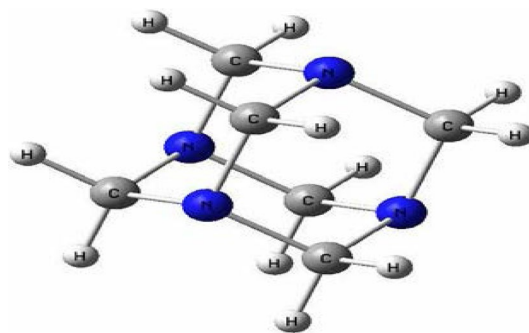


Fig. 1 Molecular structure of Hexamine [26]

Table 1 Composition of Aluminium alloy (% w)

Element	S	F	Cu	Mn	Mg	Cr	Ti	Ca	Zr	V	Al
% w	0.157	0.282	0.0025	0.024	0.51	0.023	0.006	0.0011	0.002	0.0035	Bal

Table 2 Polarization data for Hexamine inhibited and uninhibited Aluminium alloy

Samples	E_{corr} (V)	j_{corr} ($\mu\text{A}/\text{cm}^2$)	Cr (mm/year)	Pr (Ω)	IE (%)
Control	-1.3082	0.497	0.58634	238.54	0
Al-0.3HX	-1.3239	0.412	0.48564	336.41	17.1
Al-0.6HX	-1.252	0.371	0.41216	402.49	25.4
Al-0.9HX	-1.2458	0.329	0.38131	468.36	34.0
Al-1.2HX	-1.3075	0.263	0.24926	594.96	47.1

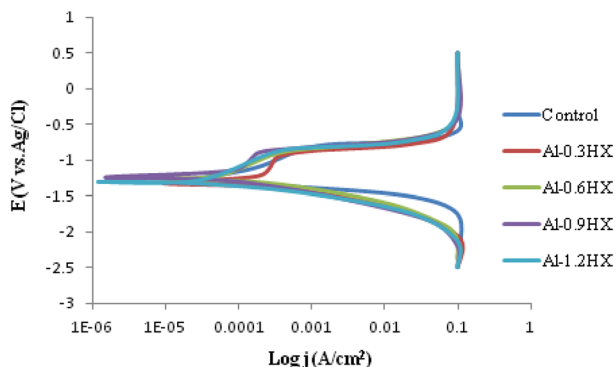


Fig. 2 Potentiodynamic polarization curves for Hexamine inhibited and uninhibited Aluminium alloy

j_{corr} , inhibited corrosion current densities. j_{corr}^0 , uninhibited corrosion current density.

3 Results and Discussion

3.1 Potentiodynamic Polarization Measurement

Potentiodynamic polarization data of uninhibited and inhibited Aluminium alloy in 3.65% NaCl are shown in Table 2. Their equivalent polarization curves are presented in Fig. 2, implying that polarization had occurred. This was affirmed by the presence of both cathodic and anodic branch [31, 32]. Tafel extrapolation of the current–potential lines was used to obtain j_{corr} ; the corrosion current densities and the corresponding values of corrosion potentials (E_{corr}) as presented in Table 2. The values of corrosion rate (Cr) and polarization potential (Pr) were likewise generated from the Tafel curve. Notably, the presence of Hexamine produced a reduction in corrosion rate by pushing the anodic and cathodic polarization curves in the region of the lower values of current densities. The reduction in current density could be attributed to the blockage of active sites of the Aluminium alloy [32]. However, there was a slight disparity in E_{corr} values on altering the mass concentration of Hexamine as observed in Fig. 2, confirming that Hexamine is a mixed-type inhibitor in 3.65% NaCl at room temperature [29, 33, 34].

3.2 Open Circuit Potential (OCP) Measurement

The OCP is the potential in a working electrode relative to the electrode in reference while there is no current or potential existing in the cell. The change in the open circuit potential results in polarization. This is due to the flowing current across the electrode/electrolyte interface [35]. Figure 3 presents the open circuit potential (OCP) versus time curves for Aluminium alloy in 3.65% NaCl. Meticulous analysis of the OCP vs. time curves shows that Hexamine moves the steady-state potential toward a more negative

Fig. 3 Evolution of open circuit potential (OCP) vs. exposure time for inhibited and uninhibited Aluminium alloy in 3.65% NaCl solution

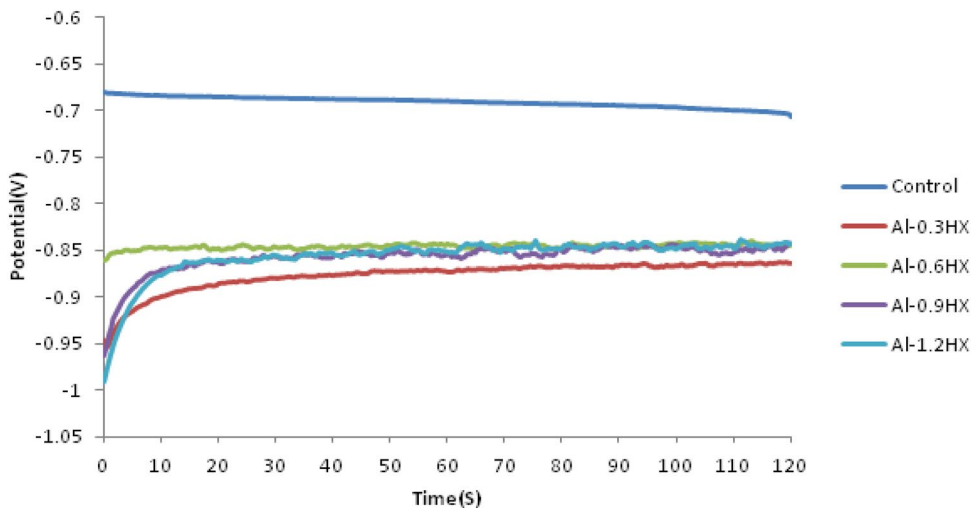
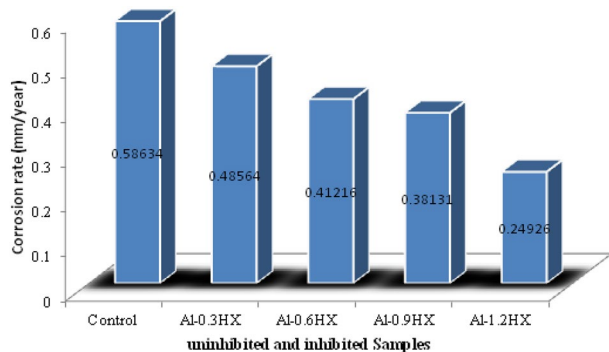


Table 3 Mass loss, surface coverage and C/θ

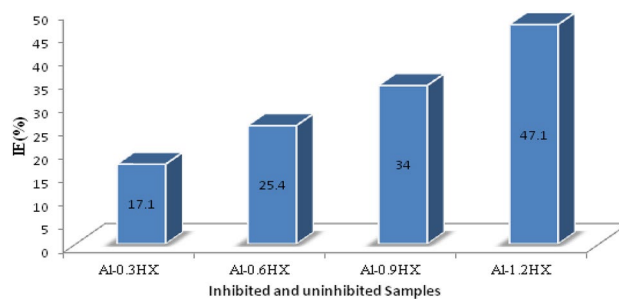
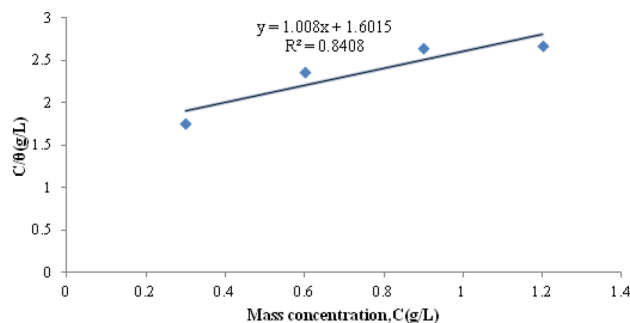
Samples after immersion	Mass concentration of Hexamine, C (g/l)	Mass loss (mg)	Surface coverage (θ)	C/θ
Control	0	14.68	0	0
Al ₁	0.3	12.16	0.171	1.754
Al ₂	0.6	10.89	0.254	2.362
Al ₃	0.9	8.27	0.340	2.647
Al ₄	1.2	7.34	0.471	2.667

**Fig. 4** Representation of rate with respect to the inhibited and uninhibited Aluminium alloy

path. The contradictory shift of the curves with respect to the uninhibited Aluminium alloy intimates that the cathodic reaction was predominant. More so, there are striking variations in the characteristics of the curved compared to the uninhibited sample. The OCP values for the inhibited samples were between -0.99V and -0.86V within the first 5 s. This later moved to less negative values between 0.89 and -0.85 . The OCP vs. time curve for the samples were close to straight line indicating the achievement of steady-state potential [36, 37].

3.3 Mass Loss Measurement and Corrosion Rate

Measurement of mass loss after the electrochemical test was carried out using the OHAUS pioneer TMPA1214 model are presented in Table 3. Mass loss effects show that introduction of Hexamine into the 3.65% NaCl medium minimizes corrosion. The mass loss of Aluminium alloy diminishes slightly as the mass concentration of Hexamine increases. This behaviour is an indication that the mass loss rate had been altered. Figure 4 reveals the effect of Hexamine on the corrosion rate of Aluminium alloy. In accordance with the work of author ref [38], the rate of corrosion reduced as the concentration of Hexamine increases. As presented in Fig. 4 the corrosion rate of the uninhibited Aluminium alloy has the highest corrosion rate.

**Fig. 5** Variation of inhibition efficiency as the mass concentration of Hexamine increases**Fig. 6** Langmuir adsorption isotherm for Hexamine inhibited samples

3.4 Mechanism of Inhibition Efficiency and Adsorption Study

The values of corrosion current (j_{corr}) in Table 2 were found to reduce with a rise in the concentration of Hexamine, symbolizing the adsorption of Hexamine on the exterior of Aluminium alloy [39]. The adsorption minimizes the effect of the Chloride ion. This is the reason for the increase in corrosion inhibition efficiency of Hexamine as the mass concentration increases. As shown in Fig. 5 the maximum inhibition efficiency was 47.1% for the 1.2 g/l inhibited sample.

An adsorption mechanism necessitated the calculation of C/θ and C for the potentiodynamic polarization system using Langmuir adsorption isotherm and a linear correlation [40–42]. Equation 3 shows the Langmuir isothermal adsorption act. This provides an extensive understanding of metal inhibitor synergy and the metallic-complex actions in the coverage region. The Langmuir isothermal plot in Fig. 6 on the surface characteristics presents a linear correlation with the increase in the concentration of the inhibitor revealing the continuous adsorption of the inhibitor on the surface of Aluminium alloy. The value of R^2 for Langmuir adsorption isothermal was 0.8408. This R^2 value is a similar range as those of ref [42, 43]. This revealed that the

corrosion protection of Aluminium alloy by Hexamine had been accomplished because R^2 is close to unity.

The Langmuir adsorption isothermal law,

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (3)$$

C , concentration of the corrosion inhibitor; θ , degree of surface coverage; k adsorption equilibrium constant.

3.5 SEM Micrograph Studies

The SEM micrographs of the Hexamine inhibited samples after the corrosion experiment are shown in Fig. 7a–d. The micrographs show the surface topography and morphological deterioration of the Hexamine inhibited samples as a result of the chemical reaction of the corrosive ion in the chloride medium. Flakes indicating corrosion products such as oxides and hydroxide of Aluminium can be observed [44]. Notably, the flakes on the surface of Fig. 7d were found to be less. The reduction in flake could be as a result of the increase in the mass concentration of Hexamine. Comparatively, minimal breakdown of passive film was noticed with Fig. 7d; however, the thin layer covering formed by Hexamine molecules gives protection against corrosion in all the

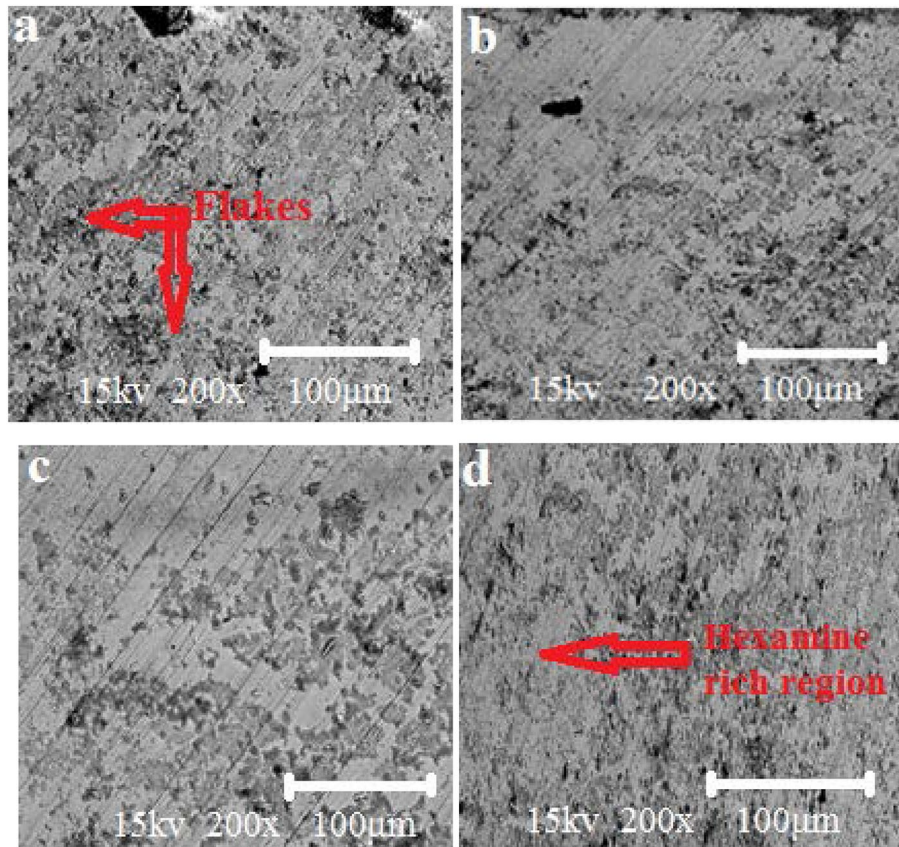
cases. The combined effort of the heteroatom of Hexamine enables its adsorption on the interface of aluminium via physical and chemical reaction mechanism [45].

The inhibitory action of Hexamine could also be traceable to the availability of four amine groups with lone pair, donor nitrogen atoms in the molecule of Hexamine which adsorb on the surface of Aluminium alloy to resist its corrosion. More so, the presence of methylene group closer to the lone pair donor atom improves the electron density of Nitrogen atom and via inductive effect, strengthens Hexamine [46].

4 Conclusions

- The corrosion studies of Aluminium alloy were carried out at ambient temperature using 3.65% NaCl and the result shows that Hexamine enhanced the corrosion resistance of the alloy in saline environment. The inhibitory efficiency increases with increase in mass concentration of Hexamine.
- The adsorption of Hexamine molecule on the Aluminium alloy surface follows Langmuir adsorption isotherm. The correlation regression coefficient of $R^2 = 0.8408$ was obtained in 3.65% NaCl solution. The value of R^2 is close

Fig. 7 SEM Micrograph of **a** Al-0.3HX sample, **b** Al-0.6HX sample, **c** Al-0.9HX sample and **d** Al-1.2HX sample



to unity which shows that the inhibitor was effectively adsorbed.

- The potentiodynamic polarization investigations show that Hexamine acted as a mixed-type inhibitor. This was confirmed by the Tafel curves.
- The morphology study shows the formation of thin film on the surface of Aluminium alloy immersed in 3.65% NaCl in the presence of Hexamine. The adsorption of Hexamine molecules was confirmed by the SEM micrographs

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