

Research Article

Corrosion Inhibition of Aluminium in HCl by Amine Modified Epoxy Resin

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N-Butyl amine has been grafted unto Dow epoxy resin. The product was evaluated as an acid inhibitor by gravimetric techniques. The reduction in corrosion of aluminium in 1 M HCl solution was 92% at 30°C and 83% at 60°C with an inhibitor concentration of 100 ppm. The corrosion rate at this concentration was 3.0×10^{-2} and 1.5×10^{-1} mm/yr at 30° and 60°C. For the specimens in HCl without inhibitor at 10-hour immersion period, the corrosion rate was 3.8×10^{-1} and 8.6×10^{-1} mm/yr, respectively, at 30° and 60°C. Data obtained correlate with Langmuir isotherm.

1. Introduction

Aluminium and its alloys find extensive application in the construction of heat exchangers, radiators, and related components in water cooling/treatment facilities. It is often observed that such facilities may suffer corrosion damage from ingress of chlorides and other extraneous anions as a result of inadequate provision for corrosion mitigation such as faulty design features and nonintroduction of suitable corrosion inhibitors into the system. Pitting corrosion at crevices and under sediments is often encountered in such industrial situations.

The use of organic inhibitors is the most economical and practical method of protecting metals against aqueous corrosion [1–3]. These inhibitors contain heteroatoms such as Sulphur, Oxygen, and Nitrogen in their structures in addition to multiple bonds and may contain cyclic hydrocarbons as well [3–6]. The mechanism of inhibition of these organic compounds is thought to be by adsorption which may depend on the number of heteroatoms and the surface area of the corroding metal/alloy [7, 8].

Various investigators [8–13] have researched on polymers as corrosion inhibitors because of their large surface areas,

cost effectiveness, and inherent stability. These polymers have been reported to be very efficient at low concentrations in very aggressive media although efficiencies vary widely as a result of differences in composition. Chemically modified polyurethane [14] gave about 95% inhibition efficiency for mild steel corroding in acidic medium. On the other hand, polyacrylamide [15] achieved an efficiency of about 63% for aluminium corroding freely in 0.5 M HCl solution.

In order to contribute towards the search for suitable corrosion inhibitors of polymeric origin, in the present investigation, a Dow epoxy resin was chemically modified with n-butyl amine at suitable temperatures and examined as corrosion inhibitor for aluminium in 1 M HCl solution.

2. Experimental

2.1. Materials. 99.99% aluminium with nominal impurities of 0.004 wt% Fe, 0.002 wt% Cu, and 0.003 wt% Si was made into electrodes measuring 10 mm × 10 mm × 1 mm. The epoxy resin, Resin 828, is a product of Dow Chemicals, USA, while all other chemicals employed in this investigation are laboratory grade reagents from BDH Chemicals, UK.

2.2. Methods

2.2.1. Inhibitor Formulation. The inhibitor employed in this investigation was synthesised by mixing in a 500 mL beaker, equal moles of epoxy resin which had amber colouration, and n-butyl amine in a water bath, set at a controlled temperature of 100°C. A consistent brown coloured product, Amine Modified Epoxy Resin (AMER), was obtained after 30 mins of constant stirring.

The various concentrations of inhibitor were obtained by serially diluting 1 g/litre solution of the inhibitor with the corrodents of interest, 1 M HCl solution.

2.2.2. Corrosion Measurements. The aluminium electrodes were etched in 10% NaOH solution for 3 mins, rinsed in running doubly distilled water and thereafter desmuted in 50% HNO₃ for 2 mins, rinsed in doubly distilled water and in acetone, dried in air for 10 minutes prior to being stored in desiccators. Triplicate experiments, at 30°C and 60°C were performed by separately immersing 10 preweighed electrodes, with exposed area of 2.3 cm², in 200 mL of 1 M HCl contained in 250 mL beakers for times ranging from 1 hr to 10 hrs. After each period of immersion, the electrodes were washed in running distilled water for 3 mins while scrubbing the surfaces with a soft brush and later in acetone for 30 sec. After drying in a stream of cool air, the electrodes were reweighed. The mean of the weight changes were taken as the weight change for each period of immersion. Similar procedure was performed in 1 M HCl with different concentrations of AMER as inhibitor of interest.

3. Results and Discussions

3.1. Corrosion Rates. For the calculation of corrosion rates, the relationship in (1) as described by Jones [1] and other authors [15–17] was employed

$$CR = \frac{87.6\Delta wt}{\rho_A t}, \quad (1)$$

where CR is the corrosion rate in mm/yr, Δwt is the weight loss, ρ_A is the density of Aluminium in g/cm³, and t is the time of exposure.

The efficiency of the inhibitor, %Inh., was obtained from the following equation

$$\%Inh. = \left[\frac{CR_O - CR_1}{CR_O} \right] \times \frac{100}{1}, \quad (2)$$

where CR_O and CR_1 are Corrosion rates without and in the presence of inhibitor, respectively.

θ , the surface coverage, is given by the relationship, $\theta = [(CR_O - CR_1)/CR_O]$, where all the symbols have their usual meanings.

The weight loss and corrosion rates of aluminium specimens in hydrochloric acid at both 30°C and 60°C are displayed in Figures 1 and 2, respectively. The rate of change in weight at 30°C increased rapidly between 1 and 2 hours with a rate that decreased with time between 2 and 10

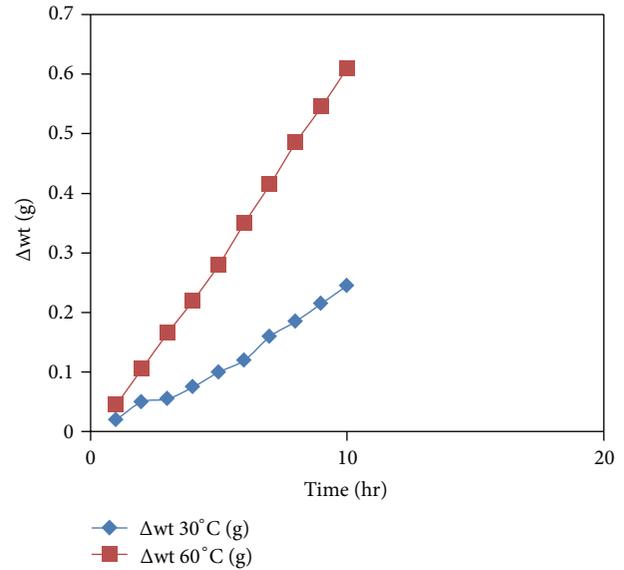


FIGURE 1: Weight loss of aluminium with time of immersion in 1 M HCl at 30°C and 60°C.

hours of immersion in HCl. The initial rapid increase in weight loss is consistent with the rapid dissolution of the amphoteric air formed oxide skin on aluminium in acidic media which exposes freshly prepared aluminium surface to rapid dissolution of the substrate metal.

However, the decrease in rate of dissolution may be attributed to the formation of corrosion products at cathodic sites on the aluminium electrode. Such corrosion products will retard the corrosion process for a while before they are subsequently dissolved by the acidic medium to reveal further areas of the specimen and corrosion processes will proceed.

At 60°C, the weight loss is linear with time of immersion in HCl solution as all corrosion products formed are dissolved rapidly in the warm corrodent.

The gravimetric method for corrosion studies is a time tested and reliable technique. Several authors have reported good correlation between this technique and gasometric, impedance, and polarisation techniques [16–20]. The corrosion rate of aluminium in HCl at 60°C (Figure 2) increased at a rate which decreased with exposure time and was maximum at 8.6×10^{-2} mm/yr at 10 hours. On the other hand, the corrosion rate at 30°C was at its peak, 3.5×10^{-2} mm/yr, after 2 hours of exposure in the corrodent which corroborates the weight loss measurement described earlier. Thereafter, the corrosion rate decreased to about 2.2×10^{-2} mm/year at 3 hours of exposure, beyond which steady increase in corrosion rate was observed and was about 3.5×10^{-2} mm/yr at 10 hours in HCl solution.

From Figure 3, the corrosion rates decreased exponentially as the concentration of the inhibitor was increased. Thus, it can be safely inferred that the inhibitor reduced the corrosion rates of aluminium at both 30°C and 60°C.

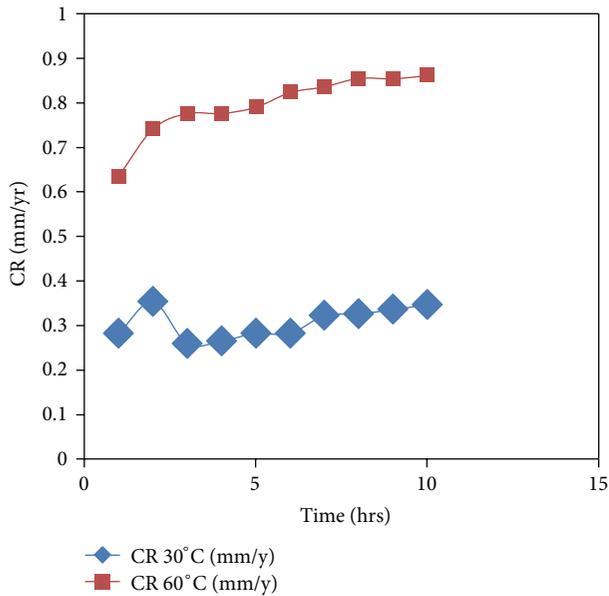


FIGURE 2: Corrosion rates of aluminium in 1M HCl at 30°C and 60°C.

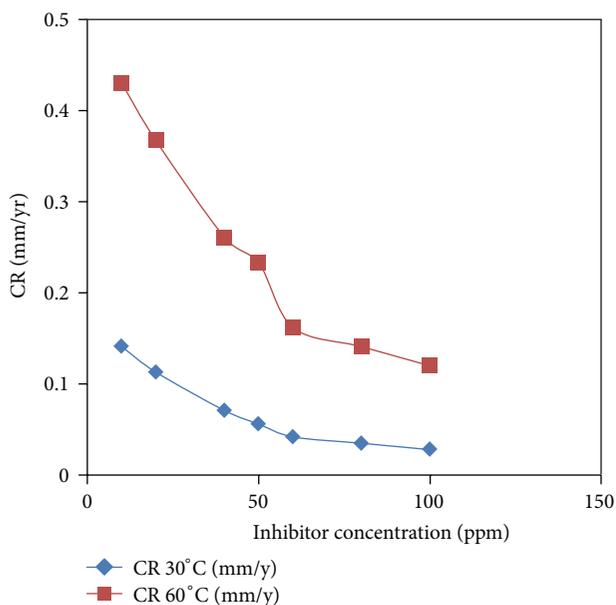


FIGURE 3: Corrosion rates of aluminium in 1M HCl solution in the presence of various concentrations of inhibitor (AMER).

Displayed in Figure 4 is the percent inhibition which increases with increase in the concentration of the inhibitor. Inhibitors of organic origin inhibit corrosion by adsorbing on metals in corroding systems. The increase in % inhibitor efficiency was more pronounced at concentration levels between 40 and 60 ppm probably as the surface of the corroding aluminium specimens became saturated with adsorbed inhibitor species. The efficiency of the inhibitor

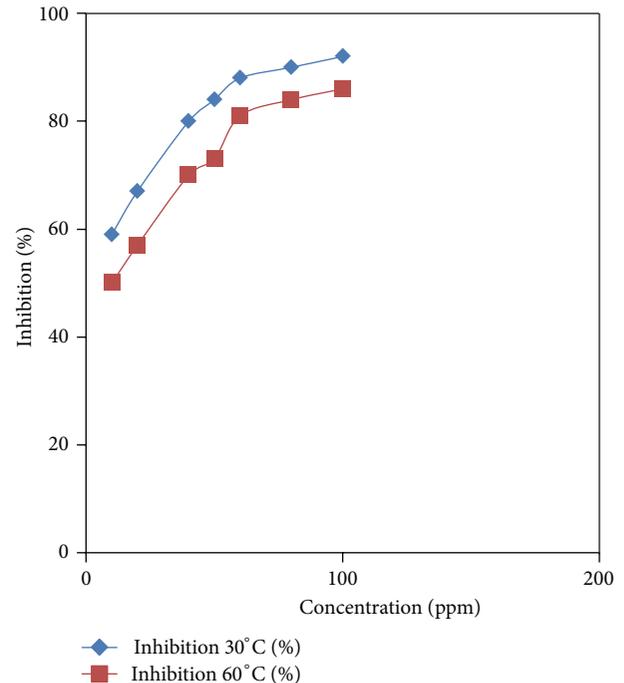


FIGURE 4: Variation of % inhibition with concentration of inhibitor (AMER) at 30°C and 60°C.

was better at lower temperatures and this may be attributed to desorption of inhibitor molecules from the corroding surface at high temperatures as described by El-Etre [18] and Abdallah [19]. However, AMER was more effective at 30°C with an efficiency of about 92% as against 86% at 60°C, with an inhibitor concentration of 100 ppm.

Furthermore, the energy of activation, E_a , for the corrosion reactions in the presence and absence of corrosion inhibitor obtained from the condensed Arrhenius equation (3) is 40.11 kJ/mol and 28.54 kJ/mol, respectively. The increase in E_a in the presence of inhibitor further demonstrates that there was a hindrance placed on the electrochemical reaction path on the substrate by some adsorbed inhibitor species. With a positive E_a value, the mechanism of inhibition is likely to be by physical adsorption [21–23] of the inhibitor species

$$\log \left[\frac{CR_{60}}{CR_{30}} \right] = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]. \quad (3)$$

The interpretation of adsorption isotherms has been employed by several authors [24–27] to describe the mode(s) of interaction of inhibitor molecules with corroding surfaces in various media in which, the values for surface coverage of inhibitors, θ , were plotted against concentration to fit Frumkin [28] or, C versus θ/C to establish a Langmuir [29] type of adsorption isotherm. Displayed in Figure 5 are curves for Langmuir adsorption.

Displayed in Figure 5 are curves of Langmuir adsorption for AMER at both 60° and 30°C where it can be observed that the inhibitor obeys this adsorption isotherm. From observed data, it is obvious that the adsorption isotherm curves are

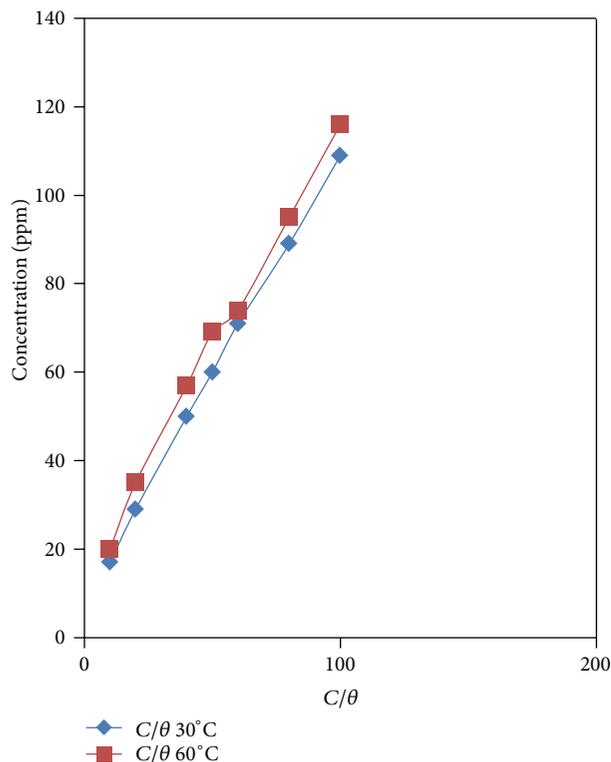


FIGURE 5: Test of variables to fit Langmuir adsorption isotherm.

neither in agreement with Temkin nor Frumkin adsorption isotherms, respectively. Thus there are no interactions among the adsorbed inhibitor molecules on the corroding surfaces [28].

The heat of adsorption, Q_{ads} , can be obtained from the relationship

$$Q_{ads} = 2.303R \left[\log \frac{\theta_2}{1-\theta_2} - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right] \left[\frac{T_1 T_2}{T_2} - T_1 \right], \quad (4)$$

where T_1 is the temperature of the corroding system at 30°C and T_2 the corresponding temperature at 60°C. θ_1 is the surface coverage of the inhibitor at 30°C while θ_2 is the surface coverage at 60°C.

The calculated approximate value of Q_{ads} is -17.52 kJ/mol. The negative value of Q_{ads} is consistent and agrees with the findings of other researchers [20, 21] that for physisorption, the heat of adsorption is generally negative and positive values indicate mechanism by chemisorption [20].

4. Conclusions

Amine modified epoxy resin (AMER) effectively reduced the corrosion rate of aluminium in hydrochloric acid by physically adhering to the corroding metallic surface.

The data obtained from the gravimetric studies correlate with the Langmuir adsorption isotherm which indicate that

there are no interactions among the adsorbed inhibitor species. However, the reactions at the electrolyte/aluminium interface was sufficiently interrupted by the inhibitor species to lower the corrosion rates by 92% and 86% at 30° and 60°C, respectively.

The corrosion rates of aluminium in 1 M hydrochloric acid in the presence of 100 ppm of AMER at 10 hours of exposure are 3.0×10^{-2} and 1.5×10^{-1} mm/yr, respectively at 60° and 30°C. On the other hand, for specimens exposed in hydrochloric acid without AMER for the same period, the corrosion rates are 3.8×10^{-1} and 8.6×10^{-1} mm/yr at 30° and 60°C.

The mechanism of inhibition is proposed by physical adsorption of the inhibitor species on the corroding aluminium surface.

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