**EXPERIMENTAL STUDY FOR THE INFLUENCE OF POSITION OF ACETYL SUBSTITUENT ON QUINOLINE FOR INHIBITION OF ALUMINIUM CORROSION IN HYDROCHLORIC ACID SOLUTION**

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**Abstracts**

Some selected acetylquinolines performance on inhibition of aluminium corrosion and effect of acetyl substituent at 5, 6 and 8 on quinoline  in hydrochloric acid was investigated experimentally through weight loss, EIS and PDP. For  weight loss, Five acetylquinolines (5-ACQ), six acetylquinolines (6-ACQ), and eight acetylquinolines (8-ACQ)  were used in varying mass and temperature  in different  concentration of HCl. The adsorption characteristics of these inhibitors were found to be consistent with longmuir isotherm, both physical and chemical mechanisms all played a significant role. Comparatively, the corrosion rate, mass loss, inhibition efficiency and the degree of surface coverage obtained from the weight loss indicated the superiority of six acetylquinoline 6-ACQ) performance followed by Five acetylquinolines (5-ACQ) and eight acetylquinoline (8-ACQ) has the least corrosion inhibition performance under the same conditions. The speed of the inhibition process proceeded via first order kinetics for all the systems. SEM and FTIR were used to characterised the surface morphology and the functional group before and after corrosion study. The Nyquist plot from impedance data and the parameters also indicated same behaviour  as the weight loss. The Tafel plot polarization data and the parameters shows the same trends. The results of the EIS and PDP are found to be relatively consistent with that of  weight loss. All the molecules showed very good corrosion inhibition efficiency, 6-ACQ molecule  gives better aluminium corrosion inhibitor than other two molecules.

**Keywords:** *Acetylquinoline, aluminium, corrosion, substituent, position, inhibition, performance*

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**INTRODUCTION**

Literature has already established that; the study of corrosion inhibition activity by some organic molecules and their derivatives on metals has been the subjects of investigations in the quest to design a befitting inhibitor on the basis of properties and environment of the metal in question[1]. However, a wide range of organic inhibitors offers desirable attributes such as non-toxicity, a variety of choices and readily availability[2]. However, they cannot universally protect all metals in the same aggressive media, thus prompting the search for efficient metal or medium-specific inhibitors. Consequently, organic inhibitors of various classes have been the subject of intensive research interest as potential materials for the surface protection of ferrous and non-ferrous metals and their alloys against aggressive environments [3],[4]. The extent of adsorption of inhibitors on the metal surface depends on many factors: (i) the nature of the metal, (ii) the mode of adsorption of the inhibitor and (iii) the surface condition [5]. The adsorption theory of corrosion inhibition of metal postulating that the adsorption of an inhibitor is generally over the entire metal surface, as was first proposed by Hackerman [5]. Just like iron, aluminium is globally widespread in application, and as one of the less noble non-ferrous metal it has a strong tendency to undergo all forms of corrosion in different environments. The extraction of aluminium from its ore (bauxite) is virtually energy extensive and economically expensive necessitating the needs for protection against severe corrosion problems. Nowadays, the use of acidic media in pickling, facility cleaning and descaling is indispensable in so many industries [6]. Hydrochloric acid is a common acidic medium for these purposes because it is more economical, efficient and less troublesome compared to other mineral acids. Even though aluminium is effectively passive in neutral aqueous environment, it is strongly predisposed to corrosion in acidic media even as dilutes as acid rain water.In the actual facts, Cl- from various sources including neutral salts, has the ability to cause pitting corrosion at vulnerable spots of passive film-protected non-ferrous metal[6].The protection of aluminium and its oxides against the corrosive action of chloride ions in aqueous medium has been extensively investigated. A great number of inhibitors has been studied, and several number of their actions with regard to corrosion inhibition of aluminium has been reported in the literature[7]. Organic corrosion inhibitors are preferred due to their environmental friendly and effectiveness at wide range of temperatures. The efficiency of organic inhibitor depends on the size of the organic molecule, aromaticity, type and number of bonding atoms or groups in the molecule (π and σ bonds), nature and surface charge, the distribution of charge in the molecule and the type of aggressive media[8]. The presence of polar functional groups with S, O or N atoms in the molecule, heterocyclic compounds and pi electrons present in the molecule also increases the efficiency of these organic corrosion inhibitors[8]. The use of computational chemistry such as density functional theory (DFT), molecular dynamic simulation (MD), Monte carlo (MC) simulation and quantitative structure-activity relationship (QSAR) modelling has been applied for study of corrosion inhibition properties of organic molecules. Aromatic rings has mostly been regarded as the zones through which certain inhibitors can protect etching of metals[9]. Functional group attached to aromatic ring also has great role in corrosion inhibition of metals generally.

Acetylquinolines are nitrogenous bicyclic heterocyclic compounds with molecular formula of C11H9NO, as such it is expected to show a reasonable good effectiveness against metallic corrosion because of its association with high electron density (10-π and 2-nonbonding electrons). Quinoline derivatives containing polar substituent such as acetyl group can effectively adsorb and form highly stable chelating complexes with surface metallic atoms through coordination bonding. The available studies for corrosion inhibition of quinoline molecules focuses on the nature and type of functional groups ( being substituted or non-substituted) attached to the molecule in use[10]. To our knowledge, this is the first investigation for the effect of position of substituent groups in corrosion inhibition for aluminium in acidic environment. However, aside from aromaticity, functional group and the type of substituent, corrosion inhibition efficiency of heterocyclic compound can also be influence by the nature and position of substituent attached to the molecule[11]. This study is aimed at justifying the claim, being very scanty or non from the literature.

**2.0 Materials And Methods**

**2.1 Materials**

The inhibitors which are the quinoline derrivatives (5, 6, and 8-acetylquinolines) three in number, were obtained from the Aldrich Chemical Co. Ltd, (Gillingham Dorset - England), all with 99% purity. The inhibitors were used without further purification. Other materials are the distilled water, ethanol; with 96%, purity,hydrochloric acid; with 37% purity and specific gravity of 1.175-1.185 g/20oC and diethyl ether; with 99.5% purity and specific gravity of 0.713-0.714. The aluminium plate used in this study composed of 98.9% Al , 0.5% Fe and 0.48% Si with traces of other elements which includes: Ti, V, Mn, Ni Cu, Ga etc in negligible amount, falling within the class of wrought aluminium. The metal coupons used in this experiment were mechanically cuts and optimized (5.0cm × 3.0cm × 0.11cm) degreased in ethanol, rinsed in acetone, air dried and preserved in moisture free desiccators prior to corrosion study. Doubly distilled water was used to prepare test solution of the corrodent by diluting 37% HCl from Sigma-Aldrich[12].

**2.2 Mass Loss Measurement**

The Metals coupons (5.0 cm × 3.0 cm × 0.11 cm) obtained was firstly weighed, suspended with the aid of Pyrex glass hooks tightened on a rod horizontally placed end to end held by retort stands such that 4.0cm × 3.0cm of the test metal is immersed each in 80ml of 0.2M, 0.4M and 0.6M HCl solution containing different concentrations of inhibitor (0.0, 0.2, 0.4, and 0.6 g/L) . Contact was allowed for 5 h at 303, 313 and 323K. The coupons were then withdrawn at predetermined intervals of time, washed, rinsed in diethyl ether, dried and reweighed. The mass losses was recorded. The above procedure was tested for all the three acetylquinolines. Each experiment was carried out three times [13].The mass measurements was performed on Mettler FA2004 electronic balance. From the mass loss data, corrosion rate (CR, in gh–1cm–2), the degree of surface coverage (θ) and Inhibition efficiency I (%) were computed using Equations [14]:

Weight Loss = W1 - W2  3.1

*θ =* 1 - 3.2

% *IE*= × 100 3.3

*CR* (*gh*-1*cm*-2) = 3.4

Where W1 is the initial masses (g) of Al and W2 is the final mass after time t, θ is the degree of surface coverage of the inhibitor, A is the area of the Al coupon (cm2), t is the immersion time (h).

**2.3 Electrochemical Measurements**

**2.3.1 Impedance Measurement**

Electrochemical Impedance tests was carried out after OCP at 303 ± 1K, 0.4MHCl without and with 0.2g/L inhibitor for each system in a three electrode cell using a Gamry interface 5000E potentiostat (Louis Drive Warminster, PA 18974, USA) equipped with complete Gamry frameworkversion 7.9.0 and Gamry Ecchm Analyst version7.9.0 , with V3 Studio software over a frequency range of 100 kHz - 10 mHz, with a signal amplitude of 5mV. A graphite rod was used as counter electrode and Ag/AgCl electrode was used as the reference electrode. The latter was connected via a Luggin’s capillary. Measurements was performed in aerated and unstirred solutions after 30 minutes immersion in the test solutions. The working electrodes was prepared from square sheets of aluminium with 1cm2 of the area exposed to the test solution [15]. Origin lab software was used for the data handling which gives the Nyquest plot of each system. The charge transfer resistance values were obtained from the diameter of the semi circles of the Nyquist plots. The inhibition efficiencies of the inhibitors was also calculated from the charge transfer resistance values [16].

**2.3.2 Potentiodynamic Polarization**

Potentiodynamic polarization studies was performed after OCP in 0.4 M HCl at 303 K using a Gamry interface 5000E potentiostat (Louis Drive Warminster, PA 18974, USA) equipped with complete Gamry frameworkversion 7.9.0, having an acquisition system installed with NOVA software package version 1.8 and a three-electrode electrochemical cell: the metal coupons of surface area 1 cm2 as working electrode, an Ag/AgCl reference electrode and a graphite counter electrode. Aluminium samples for electrochemical experiments were of dimension 1.0 cm × 1.0 cm ×0.11 cm. These were subsequently sealed with epoxy resin in such a way that only one square surface of area 1.0 cm2 was left uncovered. The exposed surface was degreased in acetone, rinsed with distilled water, and air dried. The aluminium metal was polarized between –1,000 and 2,000 mV at a certain scan rate of 0.333 mV s-1 and 303K. From the polarization test data for inhibited aluminium in acid medium,the electrochemical parameters such as Tafel slopes, corrosion potential, corrosion current and corrosion rate were calculated. The linear region of anodic and cathodic curves was extrapolated with 0.0016V/sec scan rate. From the Tafel analysis; corrosion current density, corrosion rate, linear polarization resistance and corrosion potential were obtained in a static solution [16]. The inhibition efficiency IE (%) was also computed. Each test was runs in triplicate. Measurements was performed in 0.4 M acid solutions containing 0.2g/L mass of the test inhibitors. The inhibition efficiency (%IE) was deduced from the linear polarization resistance (LPR) and potentiodynamic polarization-corrosion rate (PP-CR) which was used as criteria for assessment of corrosion resistance of aluminium in corrosive environments using the following equations:

*%IE*  =× 100 3.5

Where *CRo*and *CR* are corrosion rates of the materials in the presence and absence of inhibitors respectivel[17].

**2.4 Surface characterization**

To understand the type and nature of corrosion on the aluminium, the resulting surfaces before and after corrosion, were examined on Phenom ProX model (Netherlands) scanning electron microscope at accelerating voltages of 5.00kV. Infrared spectra of the adsorbed inhibitors were recorded using SHIMADZU FTIR-8400S Fourier Transform Infrared Spectrometer (FTIR) over a frequency range of 400-4000cm-1. Elemental analysis of aluminium test plates was performed on Mini pal 4 PW 4030 energy dispersive X-ray fluorescence spectrometer (EDXRF) installed with Mini Pal analytical software. The specimens were stimulated by a potential of 30 kV and a current of 1 mA for 10 min.

**3.0 Results and Discussion**

**3.1 Weight Loss Analysis**

The corrosion inhibition performance profile of 5-ACQ, 6-ACQ and 8-ACQ systems for the anti-corrosion effect on aluminium via weight loss experiment is shown in the figures 3.1 to 3.5 below. Starting with figure 3.1, the profile indicates a progressive decrease in weight loss with increase in the inhibitors masses (g/L) at 303K for all the three system (5-ACQ/0.2MHCl on Al, 6-ACQ/0.2MHCl on Al and 8-ACQ/0.2MHCl on Al) concurrently under the same condition. The vertical height of the bars in figure 3.1 to 3.3 is a function of the amount of weight lost by the aluminium in test for the blank and the inhibited case for all the systems. This is in agreement with the fact that the presence of inhibitor molecule prevent the corrodent molecules (acid) from having full contact with the metal surface such that a barrier has been created in between which could be physically or chemically depending on the adsorption characteristics [18]. Here we can think of it this way : without the inhibitor, the metal surface is like a smooth, flat surface. When the corrodent molecules collide with the metal surface, they have to overcome a lot of resistance to get past the surface and start the corrosion reaction. However, when an inhibitor is introduced, it behave like a small bumps on the surface of the metal. The corrodent molecules can now get a better grip on the metal surface because of the inhibitor molecules. In this situation, the corrodent molecules don't have to overcome as much resistance to start the corrosion reaction. So the presence of the inhibitor molecules effectively reduces the activation energy required for the reaction to occur.

The variation of the inhibitors mass from 0.0, through 0.2, 0.4 to 0.6g/L shown in figures 3.1 to 3.3 profile, leads to decrease in mass loss of the aluminium at all temperatures and all corrodent concentration. This is because the increase in the inhibitor mass leads to an increase in the number of inhibitor molecules available to interact with the corrodent molecules and reduce the activation energy. It's just like putting more bumpers on the metal surface to make it easier for the corrodent molecules to attach.

**Figure 3.1:** Weight loss of aluminium in 0.2M HCl at 303k using inhibitors 5-ACQ, 6-ACQ and 8-ACQ with varying mass of inhibitor for each system.

**Figure 3.2:** Weight loss of aluminium in 0.2M HCl at 313k using inhibitors 5-ACQ, 6-ACQ and 8-ACQ with varying mass of inhibitor for each system.

**Figure 3.3:** Weight loss of aluminium in 0.2M HCl at 323k using inhibitors 5-ACQ, 6-ACQ and 8-ACQ with varying mass of inhibitor for each system.

Also figures 3.1, 3.2 and 3.3 gave a clear situation for the effect of varying temperature from 303K, 313K and to 323K. There's increase in weight loss of the metal as the temperature increases. This has been reported by many scholars [16]. It's because at elevated temperature the inhibitor molecules becomes segregated and more porous on the metal surface. This allows some contacts between the metal and the corrodent molecules hence more mass loss than the room temperature[16].

Another observable effect from all figures 3.1, 3.2 and 3.3 is that 6-ACQ has the lowest weight loss ( shortest bar ) for all the inhibitor mass at all temperature. This is a clear indication that 6-ACQ is more adsorbed on the metal surface than the remaining inhibitors, and so regardless of the inhibitor dose applied, 6-ACQ exhibits relatively lower mass loss compared to 5-ACQ and 8-ACQ, indicating clearly its superior anti-corrosion efficiency.

**Figure 3.4:** Weight loss of aluminium in 0.4M HCl at 303k using inhibitors 5-ACQ, 6-ACQ and 8-ACQ with varying mass for each system.

**Figure 3.5:** Weight loss of aluminium in 0.6M HCl at 303k using inhibitors 6-ACQ, 5-ACQ and 8-ACQ with varying mass for each system.

Figures 3.4 and 3.5 shows an increase in corrodent concentration with increase in mass loss of the metal serially irrespective of temperature and inhibitor mass. Corrosion was more rapid in 0.6M, followed by 0.4M and 0.2M has the lower corrosion of metal both in the absence and in the presence of inhibitor at all temperature . This may be attributed to the breakdown of the air-formed passive film and the initiation of pitting, which is traditionally followed by steady state corrosion conditions, due to cathodic reaction [17]. In most cases, the reason for varying the concentration of the corrodent in corrosion inhibition study is to allow study of how the adsorption behaviour changes with corrosiveness of the environment. it will also help to determine the optimal concentration of inhibitor for a given level of corrosion. As the concentration of the corrodent increases, the activation energy for the reaction decrease. This is because there are more corrodent molecules available to react, so they can provide more energy to overcome the energy barrier and start the reaction[17].

**Figure 3.6:** Corrosion Rate of aluminium in 0.2M HCl at 303k with varying inhibitor mass for each system.

**3.2 Corrosion rate analysis**

Corrosion rate is a measure of how quickly a material corrodes or goes into solution[18]. It can be expressed in terms of the amount of material lost over time, such as milligrams per square meter per day. Corrosion rate is an important factor to consider when studying corrosion inhibition, as the goal generally is to reduce the rate of corrosion[18]. The figure 3.6 is the profile of the corrosion rate in 0.2MHCl at 303K with varying inhibitor mass for each system. It can be observed from the above figure that the rate of attack slows down in the presence of inhibitors. As the concentration of the corrosion inhibitor increases, the corrosion rate tends to decrease[18]. This is because the inhibitor molecules adsorbed onto the metal surface forms a protective layer that prevents the metal from coming in contact with the corrosive environment [19]. The more the number of inhibitor molecules present,, the thicker the protective layer and the slower the corrosion rate. The figure 3.6 indicates that the corrosion rate is slower with 6-ACQ as inhibitor being the inhibitor with shorter bar. 6-ACQ has been observed to be more attracted on the metal surface than other inhibitors used here. In this study, the corrosion rate is in the order 8-ACQ > 5-ACQ > 6-ACQ. The molecules have the same molecular mass and equal number of atoms, but there's noticeable difference in terms of performance in reduction of corrosion rate among them.

**Figure 3.7**: %IE for corrosion of aluminium in 0.2M HCl at 303k with varying inhibitor mass for each system.

**Figure 3.8**: %IE for corrosion of aluminium in 0.2M HCl at 313k with varying inhibitor mass for each system.

**Figure 3.9**: %IE for corrosion of aluminium in 0.2M HCl at 323k with varying inhibitor mass for each system.

The profiles shown in figures 3.7, 3.8 and 3.9 are the percentage inhibition efficiency (%IE) in 0.2M HCl at 303K, 313K and 323K respectively with varying inhibitor mass for each system. Inhibition efficiency of a given molecule is the percentage reduction in corrosion rate when a corrosion inhibitor is added [19]. The above figures shows an increase in the vertical height of the bar with increase in the inhibitor mass for each of the inhibitor, which is the direct increase in the percentage inhibition efficiency as the mass of the inhibitor is increased at all temperatures. Also here unlike the weight loss and the corrosion rate, the percentage inhibition efficiency increased with increase in the inhibitor mass and decreased with elevation of temperature[20]. Also here, despite the fact that the three molecules used here (5-ACQ, 6-ACQ and 8-ACQ) are comparably of the same molecular mass and number of atoms, but observably the molecule 6-ACQ has the higghest percentage inhibition efficiency followed by 5-ACQ with 8-ACQ having the least. This can also be observed from table 3.1 which indicates the variation of inhibitor mass and temperature in 0.2M HCl. Both the values of the mass loss and the percentage inhibition efficiency are in consistent with the figures above. There are possible reasons for the difference in the corrosion rate and the percentage inhibition efficiencies among the three molecules which will be discuss after consideration of other experimental results (PDP and EIS).

Table 3.1 : Mass loss of the aluminium and the inhibition efficiency of each inhibitor using masses of 0.2g, 0.4g and 0.6g in 0.2M Hydrochloric Acid (Corrodent) at 303k, 313k and 323k

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| S/N | Inhibitor | Conc.g/L | Average mass loss (g) at 303k | %IE | Average mass loss (g) at 313k | %IE | Average mass loss (g) at 323k | %IE |
|  | Blank | 0 | 0.2110 | 0 | 0.2810 | 0 | 0.3061 | 0 |
| 1 | 5-ACQ | 0.2 | 0.1206 | 47 | 0.15 | 33 | 0.1602 | 31 |
| 0.4 | 0.0615 | 61 | 0.1102 | 46 | 0.1312 | 46 |
| 0.6 | 0.0201 | 85 | 0.0701 | 56 | 0.1102 | 54 |
| 2 | 6-ACQ | 0.2 | 0.1101 | 50 | 0.1351 | 44 | 0.1401 | 38 |
| 0.4 | 0.0513 | 76 | 0.1004 | 59 | 0.1211 | 55 |
| 0.6 | 0.0113 | 98 | 0.0502 | 70 | 0.0931 | 67 |
| 3 | 8-ACQ | 0.2 | 0.127 | 32 | 0.1768 | 30 | 0.1854 | 28 |
| 0.4 | 0.0751 | 53 | 0.1188 | 43 | 0.1635 | 37 |
| 0.6 | 0.0427 | 62 | 0.0784 | 53 | 0.1124 | 49 |

The table 3.1 clearly shown the increase in mass loss with temperature increase, decrease in mass loss and increase in percentage inhibition efficiency with increase in inhibitor concentration which has also been reported by many authors [20]. From the observation of the parameters in the table, 6-ACQ has the better inhibitive performance follwed by 5-ACQ and 8-ACQ has the lower performance under the same conditions. But generally all the molecules performances in terms of corrosion inhibition for aluminium in HCl environment are very good. The ultimate goal of using corrosion inhibitor is to prevent or minimized severe chemical attack on the metal surface to reasonable percentage which leads to economic and social consequences [20].

**3.2 kinetic study**

**Table 3.2** : Kinetics for Corrosion of aluminium using 0.4g s of each inhibitor in 0.4M Hydrochloric Acid (Corrodent) at varying temperature.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Inhibitor** |  | | **5-ACQ** | |  | |
| **Temp.** | 303K | | 313K | | 323K | |
| **1st order**  **2nd order** | k1 | R2 | k1 | R2 | k1 | R2 |
| 0.019 | 0.999 | 0.022 | 0.998 | 0.025 | 0.997 |
| 0.006 | 0.542 | 0.014 | 0.S | 0.015 | 0.498 |

**Inhibitor** **6-ACQ**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Temp.** | 303K | | 313K | | 323K | |
| **1st order**  **2nd order** | k1 | R2 | k1 | R2 | k1 | R2 |
| 0.016 | 0.999 | 0.020 | 0.999 | 0.024 | 0.999 |
| 0.005 | 0.952 | 0.003 | 0.697 | 0.015 | 0.396 |

**Inhibitor 8-ACQ**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Temp.** | 303K | | 313K | | 323K | |
| **1st order**  **2nd order** | k1 | R2 | k1 | R2 | k1 | R2 |
| 0.016 | 0.999 | 0.021 | 0.998 | 0.022 | 0.999 |
| 0.010 | 0.842 | 0.011 | 0.568 | 0.008 | 0.699 |

Tables 3.2 presented details of the kinetic parameters obtained from weight loss experiments for aluminium corrosion in HCl solutions using acetylquinolines at different temperatures. The value of the rate constant and the R-square value are the parameters for establishing the kinetics of chemical reaction at varying temperature [20]. In almost all systems, the R-square values are more close to unity for the first order results than that of the second order, and with higher values of the rate constant. This confirmed the fact that the corrosion inhibition of alumunium with acetylquinolines followed the first order kinetic. The first and the second order kinetic rate constant was obtained using equations 3.6 and 3.7 below:

In = *k*1(s-1) or In = *k*1 3.6

= k2t + 3.7

Where [Ao] is the initial mass of the metal, [A] is the mass corresponding to time t, *k*1 and k2 are the first and second order rate constant respectively [21].

**3.3 Activation parameters**

In order to calculate the values of activation energies and heat of adsorption, study of the effect of temperature on the corrosion of aluminium in varying HCl concentrations containing various masses of inhibitors is of paramount important and the following Arrhenius Equations werer used:

*CR* = *Aexp* [22]. 3.8

Taking logarithm of both sides at a particular temperature gives Equation 3.9, while at two different temperatures gives Equation 3.10 as follows:

log(*CR*) = log*A* - [22]. 3.9

log = [22]. 3.10

3.11

Where *θ1* and *θ2* are the degrees of surface coverage at the temperatures T1 and T2 respectively [23]. At constant pressure, the value of *Qads* approximate enthalpy of adsorption (Δ*Hads*).

The free energy change of adsorption, ΔGoads, is calculated using Equation 3.12 [23]:

ΔG0ads = - RT ln (55.5 x Kads) 3.12

Where 55.5 is the molar concentration of water in solution, *R* and *T* remain the same as described above and Kads was obtained from the intercept of a plot of *θ* against log*C*. For adsorption to take place, ΔGads must be negative. Now, ΔSads is always negative, because the adsorbed atoms or molecules lose degrees of freedom in the process. As a result, ΔHads also supposed to be negative showing that most of the adsorption processes are exothermic. Generally, the values of ΔG0ads around -20 kJmol-1 correspond to physisorption while those above -40 kJmol-1 correspond to chemisorption [24]. The heat of adsorption *Qads*, which can also be defined by equation 3.10 depends on the energies of the bonds formed between the adsorbed atoms and the metal surface[24].

The activation energy is the minimum energy required for the corrosion reaction to occur, while the heat of adsorption is the energy released when the inhibitor molecules are adsorbed on to the metal surface. The activation energy is related to the overall corrosion reaction, while the heat of adsorption is specific to the interaction between the inhibitor molecules and the metal surface[25].

**Table 3.3**: Activation Energy, Ea (kJ/mol) and Qads (kJ/mol) of Different Inhibitor Systems of 0.2, 0.4 and 0.6g/L on Aluminium at 313K and 323K Obtained through Weight Loss Method.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  | 5-ACQ(g/L) | |  |  |  |
|  |  | 0.00 |  | 0.2 |  | 0.4 |  | 0.6 |
| Corrodent concentration | Ea | Qads | Ea | Qads | Ea | Qads | Ea | Qads |
| 0.2M | 33.05 | 0.00 | 19.66 | -34.76 | 14.14 | -43.21 | 11.12 | -87.21 |
| 0.4M | 28.18 | 0.00 | 20.54 | -28.91 | 15.08 | -33.75 | 14.32 | -70.22 |
| 0.6M | 23.25 | 0.00 | 22.66 | -25.24 | 19.41 | -27.81 | 18.46 | -67.70 |
|  |  |  |  | 6-ACQ(g/L)  0.2 | |  |  |  |
|  |  | 0.00 |  | 0.4 |  | 0.6 |
| Corrodent concentration | Ea | Qads | Ea | Qads | Ea | Qads | Ea | Qads |
| 0.2M | 33.05 | 0.00 | 11.29 | -84.03 | 5.54 | -93.76 | 4.17 | -107.61 |
| 0.4M | 28.18 | 0.00 | 15.25 | -66.73 | 7.82 | -78.33 | 5.31 | -90.23 |
| 0.6M | 23.25 | 0.00 | 18.92 | -54.89 | 10.83 | -63.63 | 7.78 | -83.25 |
|  |  |  |  | 8-ACQ(g/L)  0.2 | |  |  |  |
|  |  | 0.00 |  | 0.4 |  | 0.6 |
| Corrodent concentration | Ea | Qads | Ea | Qads | Ea | Qads | Ea | Qads |
| 0.2M | 33.05 | 0.00 | 18.44 | -27.91 | 16.35 | -33.95 | 14.98 | -65.52 |
| 0.4M | 28.18 | 0.00 | 20.21 | -23.64 | 17.81 | -27.88 | 16.08 | -57.21 |
| 0.6M | 23.25 | 0.00 | 23.12 | -19.53 | 21.16 | -23.32 | 19.64 | -33.59 |

The table 3.3 show a decrease in activation energy with increase in corrodent concentration without inhibitor. This is in consistent with the theory of chemical reaction, since collision of molecules that leads to chemical reaction. the gravity of this collision depends on the distance between the molecules [26]. When the concentration of the corrodent is increased, more molecules are introduce into the system and the distance between them is shortened hence less energy is required for activation of the reaction. So the higher the concentration of the corrodent, the lower will be the activation energy for the corrosion reaction[26].

The difference in activation energy and heat of adsorption with and without inhibitor suggest that the presence of the inhibitor is changing the mechanism of the corrosion [27]. Without inhibitor, the rate of corrosion is directly proportional to the concentration of the corrodent, and there is no heat of adsorption because the corrodent is not forming a bond with the metal surface. As shown in the table 3.3 with inhibitor, activation energy decreases as inhibitor mass increases, indicating that the inhibitor is lowering the barrier to the reaction and increasing the rate of corrosion. This could be due to the formation of a new bond between the inhibitor and the metal surface, which has a lower activation energy. The increase in activation energy with increasing corrodent concentration when inhibitor is present suggest that the inhibitor is creating a barrier that make it harder for the corrodent to react with the metal surface. This could be due to formation of the layer of inhibitor molecules on the metal surface that blocks the corrodent from reaching the surface[27].

The increase in the heat of adsorption also suggests that a bond is being formed between the inhibitor and the metal surface[28]. Table 3.3 indicated that 6-ACQ has lower activation energy and higher heat of adsorption compared to the other molecules, followed by 5-ACQ and 8-OHQ has highest activation energy. This could be due to the unique structure of 6-ACQ which allows it to interact with the metal surface in a way that lowers the energy barrier for the reaction.

**Table 3.4:** Enthalpy, ΔHads (kJ/mol) and Entropy, ΔSads (kJ/mol/K) Values Obtained with and without Different Inhibitors Systems of 0.2, 0.4 and 0.6g/L on Aluminium through Weight Loss Method.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  | 5-ACQ(g/L) |  |  |  |  |
| Corrodent concentration | 0.00  ΔHads | ΔSads | 0.20  ΔHads | ΔSads | 0.40  ΔHads | ΔSads | 0.60  ΔHads | ΔSads |
| 0.2M | 32.92 | 0.197 | 26.04 | 0.217 | 22.47 | 0.229 | 17.47 | 0.239 |
| 0.4M | 42.28 | 0.182 | 31.31 | 0.201 | 26.37 | 0.214 | 22.84 | 0.228 |
| 0.6M | 51.77 | 0.167 | 40.17 | 0.194 | 37.32 | 0.199 | 29.87 | 0.204 |
|  |  |  |  | 6-ACQ(g/L) |  |  |  |  |
| Corrodent concentration | 0.00  ΔHads | ΔSads | 0.20  ΔHads | ΔSads | 0.40  ΔHads | ΔSads | 0.60  ΔHads | ΔSads |
| 0.2M | 32.92 | 0.197 | 20.25 | 0.211 | 17.91 | 0.234 | 15.38 | 0.249 |
| 0.4M | 42.28 | 0.182 | 26.13 | 0.202 | 21.45 | 0.201 | 18.32 | 0.223 |
| 0.6M | 51.77 | 0.167 | 31.31 | 0.189 | 27.79 | 0.196 | 21.93 | 0.214 |
|  |  |  |  | 8-ACQ(g/L) |  |  |  |  |
| Corrodent concentration | 0.00  ΔHads | ΔSads | 0.20  ΔHads | ΔSads | 0.40  ΔHads | ΔSads | 0.60  ΔHads | ΔSads |
| 0.2M | 32.92 | 0.197 | 26.23 | 0.210 | 23.55 | 0.228 | 19.89 | 0.236 |
| 0.4M | 42.28 | 0.182 | 32.54 | 0.202 | 28.87 | 0.213 | 23.28 | 0.223 |
| 0.6M | 51.77 | 0.167 | 43.52 | 0.179 | 36.65 | 0.198 | 30.87 | 0.204 |

From the table 3.4, the corrodent concentration increases, the enthalpy of the system increases which means that the system is becoming more energetically more favourable for the corrosion reaction to take place. This is because of the fact that the corrodent is the reactant in the corrosion reaction[29]. T he decrease in *ΔSad* with increasing corrodent concentration also is an interesting issue, since the system is becoming more ordered as the corrodent molecules are added. However, the opposite trends are observed for the system with inhibitor mass. This suggest that the inhibitor is disturbing the corrosion reaction and making the system less energitic[30]. The ΔHads and *ΔSad* values have opposite trends as the corrodent concentration increases. This is likely due to the fact that the inhibitor is having two different effects on the system[30]. On the one hand it is blocking the corrosion reaction, which decreases the system's enthalpy. On the other hand it is increasing the disorder of the system, which increases the system's entropy. The net effect of these two opposing effects is obseved in table 3.4 . This is a fascinating example of how two opposing forces can have a complex interaction to determine the overall properties of the system. The ΔHads and *ΔSad* values for 6-ACQ has better precision than other two inhibitors. This is justifying the superiority of the 6-ACQ in terms of corrosion inhibition performance on the aluminium surface in hydrochloric acid environment.

Generally, the inhibitors effects on the corrosion reaction can be summerized in two main points. First the inhibitor is blocking the reaction and preventing the loss of metal from the surface. Second, the inhibitor is increasing the disorder of the system, which may be helping to prevent the formation of corrosion products[31]. The overall effect of inhibitor is to reduce the rate of corrosion reaction and to prevent the damage caused by corrosion. This is very useful in practical applications where corrosion prevention is important[31].

The observations from table 3.4 reveal that the difference seen in the inhibition efficiencies in the table 3.1 does not emerged from the size of the substituent, but comes probably from the substituent position. In other word, the size of a substituent attached to quinoline has no significant effect on the corrosion inhibition of aluminium in HCl solution. This reflects the characteristics of liquid or solid reactions likely to be aluminium dissolution due to ineffective inhibition [32].

**Table 3.5:** Langmuir Adsorption Isotherm Parameters Obtained from the Adsorption of the Inhibitors on Aluminium Surfaces at Different Temperatures.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | 303K | | | 313K | | | 323K | | |
| Inhibitor | Corr.Conc. | R2 | Slope | Kads | R2 | Slope | Kads | R2 | Slope | Kads |
| 5-ACQ | 0.2MHCl | 0.999 | 0.305 | 1.341 | 0.977 | 0.571 | 0.825 | 0.958 | 0.628 | 0.688 |
| 0.4MHCl | 0.998 | 0.413 | 0.830 | 0.997 | 0.512 | 0.777 | 0.964 | 0.459 | 0.587 |
| 0.6MHCl | 0.995 | 0.475 | 0.721 | 0.894 | 0.479 | 0.697 | 0.974 | 0.498 | 0.550 |

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | 303K | | | 313K | | | 323K | | |
| Inhibitor | Corr.Conc. | R2 | Slope | Kads | R2 | Slope | Kads | R2 | Slope | Kads |
| 6-ACQ | 0.2M HCl | 0.998 | 0.329 | 0.941 | 0.999 | 0.655 | 0.644 | 0.992 | 0.681 | 0.625 |
| 0.4M HCl | 0.999 | 0.490 | 0.892 | 0.999 | 0.529 | 0.546 | 0.983 | 0.563 | 0.539 |
| 0.6M HCl | 0.989 | 0.315 | 0.733 | 0.998 | 0.410 | 0.501 | 0.997 | 0.436 | 0.428 |

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | 303K | | | 313K | | | 323K | | |
| Inhibitor | Corr.Conc. | R2 | Slope | Kads | R2 | Slope | Kads | R2 | Slope | Kads |
| 8-ACQ | 0.2MHCl | 0.999 | 0.414 | 0.869 | 0.999 | 0.592 | 0.620 | 0.997 | 0.669 | 0.517 |
| 0.4MHCl | 0.999 | 0.561 | 0.784 | 0.998 | 0.626 | 0.576 | 0.998 | 0.671 | 0.459 |
| 0.6MHCl | 0.999 | 0.313 | 0.691 | 0.989 | 0.427 | 0.505 | 1.000 | 0.517 | 0.435 |

**3.4 Adsorption Study**

The adsorption isotherms provide valuable information on the nature of interaction between the inhibitor molecules and the metal surface. The surface coverage (θ) of the adsorbed molecules can be determined by dividing the inhibition efficiency values of the weight loss runs with 100 [33]. The results obtained for θ were analyzed using Langmuir, Temkin, Flory Huggins and El-Awardy adsorption isotherm equations as given by equations 3.13, 3.14, 3.15 and 3.16 respectively.

C = 1 + C 3.13

θ K

θ = -lnlogKads - lnC

2α 2α 3.14

log(θ) = logK + xlog (1- θ) 3.15

C

log θ = logK + ylog C 3.16

(1- C)

where *C* is the concentration of the inhibitor in g/L and Kads is the equilibrium constant of the adsorption process. The Langmuir adsorption isotherm parameters are shown in Table 3.5 The linear regression coefficient is close to unity for almost all the inhibitors. The degrees of surface coverage, θ, at various concentrations of the selected quinolines at 303 and 323 K were the data used for plotting the isotherms. The data were tested with the different adsorption isotherm equations viz Langmuir, Temkin, Flory-Huggins and El-Awady show the parameters of linearisation of each adsorption model[34].

The surface coverage obtained from IE% values fitted all the adsorption models since the values of the regression coefficient, R2 , were mostly greater close to unity in Langmuir for all the three systems [35]. But the Langmuir adsorption isotherm fited the best with almost all the systems have R2 values close to unity. Sometimes, it may be sufficient to confirm inhibitor adsorption from data which fit the isotherms. Often times, it is also desirable to extend the scope to include deduction of thermodynamic parameters associated with the adsorption process using the relationship between the adsorption equilibrium constant (kads) and the standard free energy of adsorption, ∆Gads[36].



Figure 3.10: Impedence responses at the metal/acid interface for the corrosion of aluminium in the absence and in the presence of 0.4g/L 5-ACQ, 6-ACQ and 8-ACQ inhibitors in 0.4M HCl at 303k**.**

The figures 3.10 depict the characteristics impedance responses at the metal/acid interface for the corrosion of aluminium in the absence and in the presence of 0.4g/L each inhibitor in 0.4M HCl. The impedance spectra for the Nyquist plots of aluminium in the acid solutions in the absence and presence of the hydroxyquinolines were appropriately analyzed by fitting to the equivalent circuit model Rs (Cdl  Rct), which has been previously used to model the metal/acid interface[37], [38].

**Table 3.6 :** Impedance data for the corrosion of aluminium in 0.4 M HCl in the absence and presence of 0.4g/L Inhibitor for each system at 303 K.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| System Rct (Ω cm2 ) Cdl (μΩ-1Sncm-2) N IE% | | | | |
| HCl (Blank) 134.5 3.56 0.86 0.00 | | | | |
| 5-ACQ | 689.8 | 1.39 | 0.82 | 66.45 |
| 6-ACQ | 1185.5 | 0.62 | 0.97 | 92.21 |
| 8-ACQ | 115.4 | 2.71 | 0.84 | 45.79 |

The corresponding impedance parameters are presented on Table 3.6. The increase in Rct values in inhibited systems which signifies an increase in the diameters of the Nyquist semicircles with a corresponding decrease in the double layer capacitance (Cdl), confirms the corrosion inhibiting properties of the quinolines . The observed decrease in Cdl values, which normally corresponds to alteration of the double layer thickness can be attributed to the adsorption of the quinolines (with lower dielectric constant compared to the displaced adsorbed water molecules) on the metal/acid interface, thereby protecting the metal from the corrosive effect of the aggressive acids[38]. However, 6-ACQ has largest amplitude among the three acetylquinolines tested as observed from figure 3.10 and highest percentage inhibition efficiency as shown on table 3.6 which further justified its corrosion inhibition superiority compared to 5-ACQ and 8-ACQ. The amplitude of the Nyqquist plots, the magnitude and trend of the obtained inhibition efficiencies %IE presented are in agreement with those determined from weight loss measurements.

****Figure 3.11: Polarization at the metal/acid interface for the corrosion of aluminium in the absence and in the presence of 0.4g/L 5-ACQ, 6-ACQ and 8-ACQ inhibitors in 0.4M HCl at 303k**.**

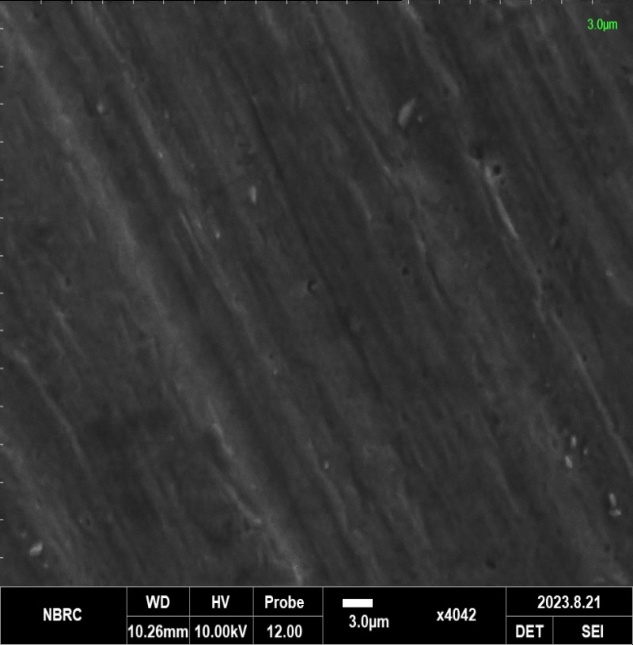
From Table 3.7, it can be clearly seen that, the insertion of aluminium in the corrodent (HCl) of 0.4M concentration without inhibitor gives higher value of both the icorr and the corrosion rate at room temperature, but they tend to decrease as the inhibitors are introduce in the corrosive solution, which in turn leads to some degrees if inhibition. For the first system with 5-ACQ (5-Acetylquinoline) of 0.4g/L, lower the icorr value of 17.20µA to 600.00 µA was obtained, while the corrosion rate and inhibition efficiency achieved were 385mpy and 42.16% respectively.

The potentiodynamic polarization plots in figure 3.11 above show that the inhibitor affects both the anodic metal dissolution and cathodic hydrogen evolution reactions . In some of the inhibitors used, the cathodic Tafel lines are parallel for all the inhibitors, which indicates that the inhibitor molecules just slightly change the cathodic hydrogen evolution reaction[39].

**Table 3.7** : Potentiodynamic polarization data for the corrosion of aluminium in 0.4 M HCl in the absence and presence of 0.4g/L Inhibitor for each system at 303 K.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| System | BetaA(V/d) | BetaC(V/d) | icorr(µA) | Ecorr(mV) | CR (mpy) | %IE |
| Blank | 188.2e-3 | 414.2e-3 | 617.20 | -998.0 | 11.02e3 | 0.00 |
| 5-ACQ | 128.9e-3 | 150.9e-3 | 477.00 | -861.00 | 306.50 | 68.32 |
| 6-ACQ | 130.0e-3 | 246.4e-3 | 2.340 | -797.0 | 1.500e3 | 95.60 |
| 8-ACQ | 121.6e-3 | 170.8e-3 | 600.0 | -898.0 | 385.40 | 65.53 |

The corrosion potential (*E*corr) values from Table 3.7 show that the addition of inhibitor shifts the corrosion potential to positive side. When the corrosion potential changes noticeably with the introduction of an inhibitor, the inhibitor is claimed to work by blocking the active sites [40]. On the other hand, a negligible change in *E*corr upon the addition of an inhibitor indicates that the inhibitor works by geometric blocking effect [40], [41]. Hence, in these systems, the inhibitors are believed to work by blocking the active sites. Also from Table 3.7, it is observed that the *I*corr value decreases with inhibitor addition, whereas the *E*corr increases. Such a trend of increase in *E*corr accompanied with a drop in *I*corr is suggestive of corrosion inhibition and increased surface hydrophobicity, which could be attributed to the inhibitor molecules adsorbed on aluminium surface [41]. In the present study, the largest shift caused in the *E*corr upon inhibitors addition are mostly 45 mV and less, and both cathodic and anodic processes are affected, indicating that the inhibitors surely works as mixed type [42].

 Figure 3.12: Micrograph of the Raw Aluminium image prior to corrosion study.

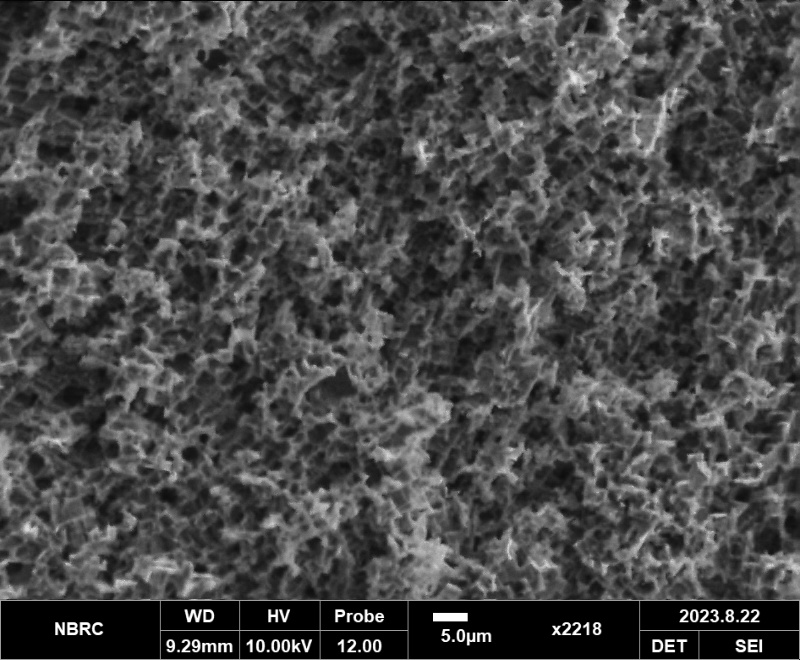


Figure 3.13Micrographs of Aluminium after dipping in 0.4M HCl for 5 hour without inhibitor.

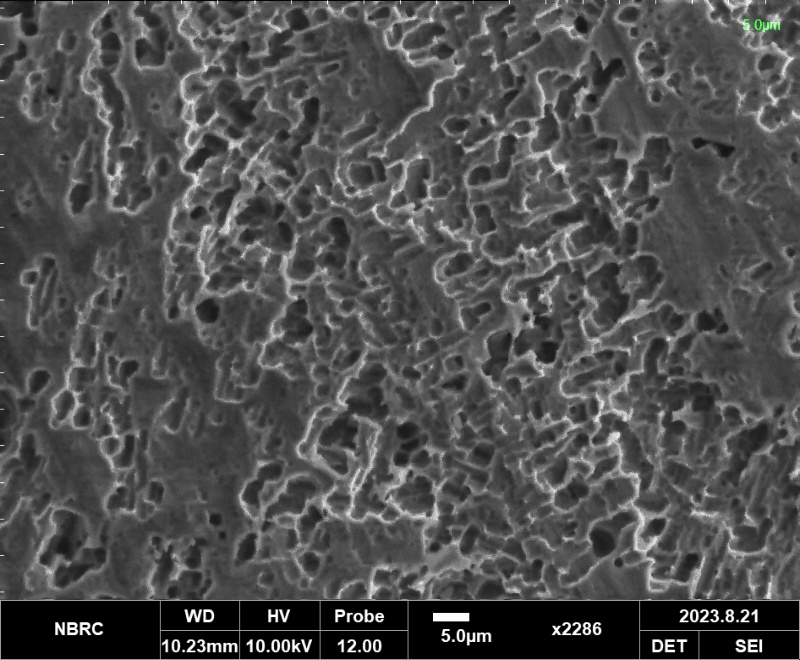


Figure 3. 14 : Micrographs of Aluminium after dipping in 0.4M HCl for 5 hour with 0.4g/L 5-ACQ inhibitor.

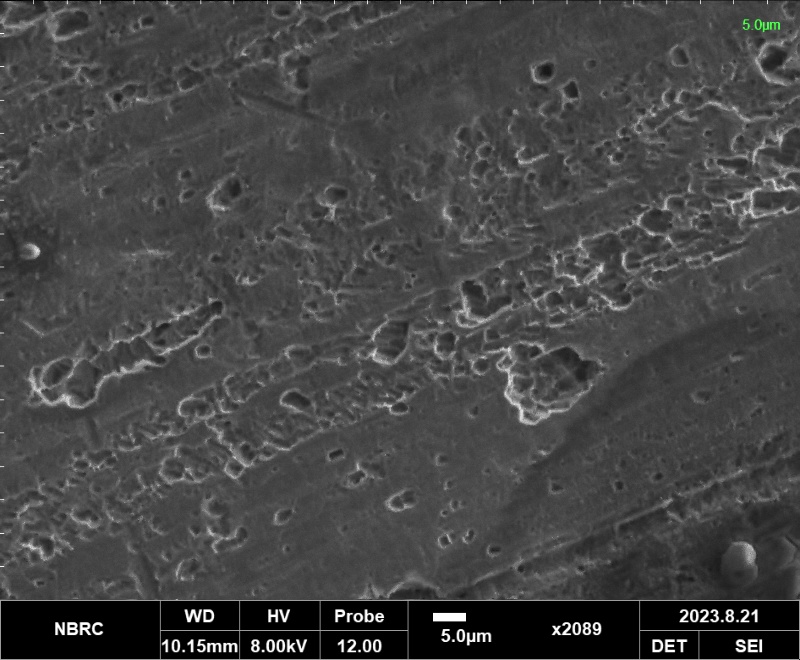


Figure 3. 15 : Micrographs of Aluminium after dipping in 0.4M HCl for 5 hour with 0.4g/L 6-ACQ inhibitor.

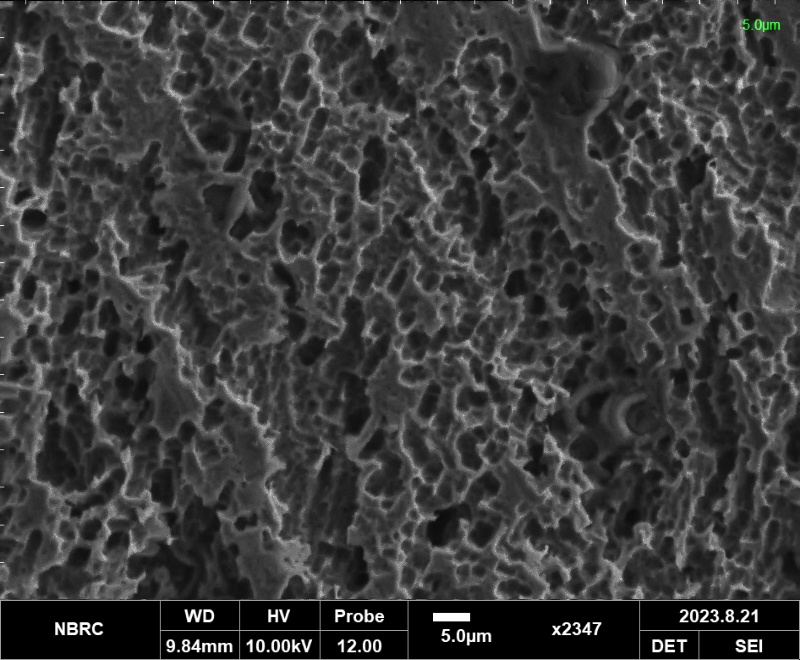
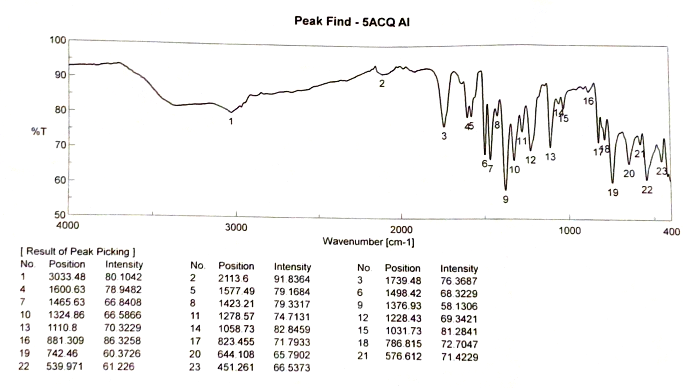
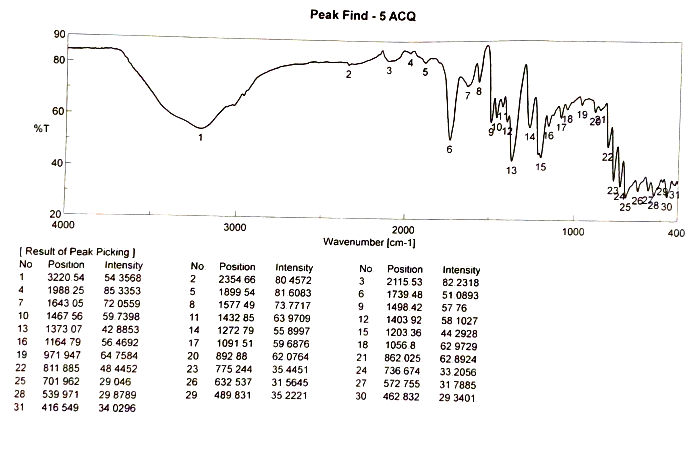


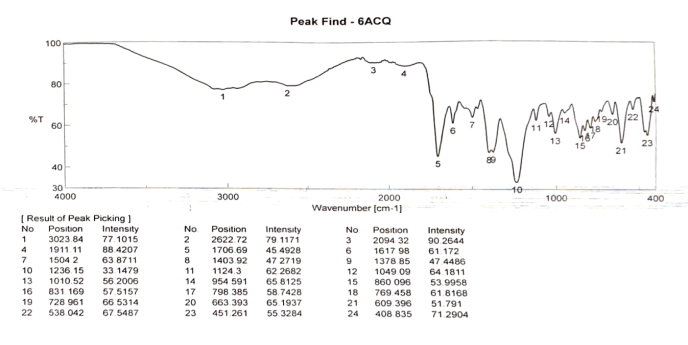
Figure 3. 16 : Micrographs of Aluminium after dipping in 0.4M HCl for 5 hour with 0.4g/L 8-ACQ inhibitor.

Figure 3.12 shows the morphology of the aluminium surface prior to corrosion study, which indicates a smooth and clear surface. Figure 3.13 is the micrograph of the same surface after been immersed in 0.4M HCl solution without the inhibitor. Corrosion pits are clearly observed on the surface after 5 hours of immersion, which indicates the effects of the aggressive environment.

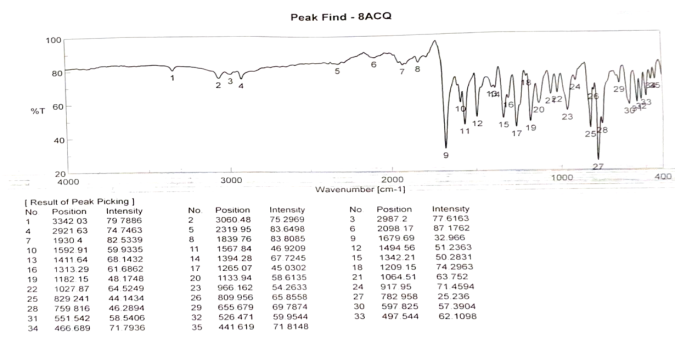
Figures 3.14,3.15 and 3.16 shows the micrographs of each of the samples immersed in 0.4M with 0.2g/L 5-ACQ, 6-ACQ and 8-ACQ inhibitors respectively. It is clearly seen that the samples immersed in medium with inhibitors each shows a thick layer, which would have been formed from deposition of corrosion products and inhibitor molecules. The unprotected sample shows formation of more pits. The surface becomes hydrophobic with the addition of an inhibitor, which also confirms adsorption of the quinoline derrivatives molecules on the surface of the aluminium and formation of film to protect the surface, which is typical for mixed inhibitors [43]. However, figure 3.15 which is the surface using 6-ACQ inhibitor, shows more uniform layer on the aluminium protected surface which means more corrosion protection than 5-ACQ and 8-ACQ inhibitors. This is in consistent with the weight loss and the electrochemical experiments.



**Figure 3.17 :** FTIR spectra of Aluminium corrosion products after immersion in 0.4MHCl with and without 0.4g/L 5-ACQ at 303K

C:\Users\DELL\Desktop\PIC\6ACQ.TIF 

**Figure 3.18 :** FTIR spectra of Aluminium corrosion products after immersion in 0.4MHCl with and without 0.4g/L 6-ACQ at 303K

C:\Users\DELL\Desktop\PIC\8-ACQ.TIF 

**Figure 3.19 :** FTIR spectra of Aluminium corrosion products after immersion in 0.4MHCl with and without 0.4g/L 8-ACQ at 303K

**3.5 Fourier Transform IR Analysis**

The FTIR spectra of the acetylquinolines derivatives on the surface of aluminium is shown in figure 3.17, 3.18 and 3.19 for 5-ACQ, 6-ACQ and 8-ACQ respectively. The appearance of a strong peaks around 1703cm-1, 1715cm-1and 16875cm-1 are due to the C**=**O bond in 6-ACQ, 5-ACQ and 8-ACQ respectively, the peak around 1610cm-1 corresponds to the aromatic ring, the nitrogen atom in the molecule have a peak around 1410cm-1 and the peak around 1605cm-1 stands for the carbon-carbon double bond generally for all the acetylquinoline molecules. The o.4g/L of the acetylquinolines in 0.4MHCl without insertion of the aluminium coupon shows clear the presence of acetyl-carbon bond, aromatic ring, nitrogen and carbon-carbon double bond. However, upon insertion of the aluminium in the solution, the spectra shows some new peaks 575cm-1, 455cm-1 and 357cm-1. These peaks are due to the metal-oxygen bond (M-O), metal-ligand bond and metal-nitrogen bond respectively. The peaks corresponding to C**=**O stretching at 1715cm-1 shifted to 1735cm-1 for 6-ACQ, 1703cm-1 shifted to 1720cm-1 for 5-ACQ, and 1687cm-1 shifted to 1705cm-1 for 8-ACQ, the aromatic ring at 1610cm-1 changes to 1515cm-1, peak of nitrogen which appears around 1410cm-1 shifted to 1420cm-1 in 6-ClQ and 8-ClQ, but has disappeared in 6-ClQ molecule. From the FTIR, Such a shift is attributed to the interaction of the acetylquinoline molecules with the metal surface [43]. A major interesting thing to consider is the effect of the substituent position on the FTIR spectrum. The positions 5,6 and 8 are all orthor positions relative to the nitrogen atom, so they are close to the region of high electron density around the nitrogen. These means that the substituents at these positions can experience some electronic effects known as mesomeric effect which stabilize the electron density of the aromatic ring, and affect their FTIR spectra and hence significant difference in percentage corrosion inhibition among the molecules. The high stretching value of the C**=**O peak and the nitrogen and disappearance of the peak of N which is seen with 6-ACQ, is an evidence of bonding of aluminium surface with the chloroquinoline molecules. This reaffirmed the fact that the mechanism proceeded via both physical and chemical adsorption[43].

**3.6 Mechanism of Inhibition**

Naturally, the test aluminium plate before corrosion study have air passive film of aluminium oxides on their surface due to oxidation as shown in equation (3.17) [43].

4Al + nH2O + 3O2 → 2Al2O3(H2O)n 3.17

However, the dissolution of the aluminium in the aggressive medium (acid solution) can be represented in equation (3.18) [43]

Al → Al3+ + 3e- 3.18

The quinoline derivatives used here are the 5-ACQ, 6-ACQ and 8-ACQ are of the same molecular mass and similar structure. The interaction of aluminium with these molecules generally involves formation of complex between the aluminium ion and the oxygen and nitrogen atoms of the acetylquinoline molecule. The complex is hydrophobic and act as corrosion inhibitor by blocking the active sites on the aluminium surface, thus preventing the reaction between the aluminium and the corrosive medium[44]. The most likely chemical equation for this interaction is presented in the equation (3.19)

Al3+ + C9H7OCH3N + 6H2O →[Al(C9H7OCH3N)3 (H2O)3] 3.19

Here the aluminium ion (Al3+) is complexed with three molecules of the acetylquinoline and three molecules of water forming a product that is hydrophobic. The interaction involves the formation of a coordinate covalent bond between the aluminium ion and the oxygen atom of the acetylquinoline molecule. Furthermore, the FTIR peaks, the difference in the inhibition efficiency shown by the molecules despite having the same mass and structure is believed to come from orientation of the substituent (acetyl group) position on the parent quinoline molecule. At position 6, acetyl group is more available to participate in the interaction with the aluminium via oxygen than other positions 5 and 8. This gives the superior performance to 6-ACQ.

**3.7 Conclusion**

The effects of acetyl substituent position on quinoline used as corrosion inhibitor for aluminium in hydrochloric acid was successfully investigated experimentally. Out of the three acetylquinolines ( 5-acetylquinoline, 6-acetylquinoline and 8-acetylquinoline), 6-acetylquinoline (6-ACQ) showed highest corrosion inhibition efficiency under all conditions. The results obtained from mass loss, potentiodynamic polarisation and impedance measurement support these observations. The position of the acetyl substituent on the quinoline molecule showed some influence in the corrosion inhibition performance for aluminium in acidic environment. Scanning electron micrographs confirmed that 6-ACQ has more uniform blockage of the etching sites on the acid-stricken aluminium slabs. Based on this, we can say that 6-ACQ is an effective corrosion inhibitor for aluminium in acid medium because it forms a stronger bond with the metal surface and lowers the activation energy for the corrosion reaction. This suggest that 6-ACQ is a promising candidate for use in industrial applications where corrosion prevention is necessary. From the FTIR, the significant shift in wave-number is attributed to the interaction of the acetylquinoline molecules with the metal surface. The high stretching value of the acetyl peak and the nitrogen and even disappearance of the peak of N which is seen with 6-ACQ, is an evidence of bonding of aluminium surface with the acetylquinoline molecules. This reaffirmed that the mechanism is a mixed adsorption.

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