The corrosion inhibition of mild steel by 2-ethyl-3-methylquinazolin-4(3H)-ones in sulphuric acid medium

RINKI GOEL* and WEQAR A. SIDDIQI

1Department of Applied Science & Humanities, Faculty of Engineering and Technology, Jamia Millia Islamia, New Delhi - 110 025 (India).

(Received: August 08, 2009; Accepted: October 15, 2009)

ABSTRACT

The inhibition of the corrosion of mild steel in 0.5 M H₂SO₄ by 2-ethyl-3-methylquinazolin-4(3H)-ones inhibitor (EMQ) has been investigated at various concentrations of the inhibitor as well as at different temperature using Weight loss and Electrochemical measurement techniques. The effect of the temperature on the corrosion behaviour with addition of different concentrations of EMQ compound was studied in the temperature range of 298K - 318K. Polarization curve reveals that EMQ compound is temperature independent but inhibition efficiency increases with increase in inhibitor concentration. Changes occurred in impedance parameters (Change transfer resistance, Rt and Double-layer capacitance, Cdl) were indicative of adsorption of EMQ on the metal surface leading to the formation of a protective film. Adsorption of EMQ on the mild steel surface is found to obey the Langmuir adsorption isotherm. The mild steel samples were also analyzed by Scanning Electron Microscopy (SEM). The protection efficiency increases with increasing inhibitor concentration in the range of 10-7 to 10-3 M but slightly decreases with increase in temperature.

Key words: Mild Steel, Corrosion inhibitors, Acid medium, Electrochemical Impedance Spectroscopy.

INTRODUCTION

Inhibitors are widely used for protection of materials from corrosion in acid environments. Usually, inhibitors protect the metal by adsorbing onto the surface and retard metal corrosion in aggressive media, so selecting the appropriate inhibitor for metal is very important.

Some studies¹-³ have shown that the inhibition of the corrosion process is mainly decided by the formation of an inhibitor and a vacant d orbital of a metal. So, most of the excellent inhibitors are organic compounds containing nitrogen⁴,¹², sulphur⁵, ⁷, ¹¹ oxygen⁶,⁸-¹⁰ and Schiff base¹³. An interesting phenomenon is that Schiff bases systematically display considerably stronger corrosion inhibition efficiencies than the corresponding amines¹⁴,¹⁵. The explanation lies in the presence of unoccupied-orbitals in the schiff base molecule, which enables electron back donation from the transition metal d-orbitals and stabilise the existing metal inhibitor bond. An important feature regarding practical applicability is that many Schiff bases can conveniently be synthesised from relatively cheap starting material.

The aim of this work is to study the inhibition efficiency and the effect of temperature on the inhibition action of 3-ethyl-2-methylquinazoline-4(3H)-ones (EMQ) on the corrosion of mild steel in 0.5 M H₂SO₄ media using Weight loss, Galvanodynamic polarization and Electrochemical impedance spectroscopy.

EXPERIMENTAL

Inhibitor

3-ethyl-2-methylquinazoline-4(3H)-ones was studied for corrosion inhibition action on steel. The compound 3-ethyl-2-methylquinazoline (EMQ) was synthesized by following the procedure given elsewhere (16) and recrystallised compound was taken. Fig. 1 gives the chemical structures of the compound.
Specimens
Mild steel specimens, having composition (% by mass) of C (0.017%), Si (0.017%), Mn (0.85%), P (0.0047%) and Fe (Bal), of the size of 1 cm³ were used for the Gravimetric measurements. The working electrodes with an exposed area of 0.5 cm² in the Electrochemical measurement were covered with epoxy araldite, polished with emery paper (100, 360, 600, 800, 1000 grit) rinsed with double distilled water, degreased in acetone and dried for use later. AR grade chemicals were used for the preparation of solutions.

Corrosive Medium
The aggressive solutions used were made of AR grade H₂SO₄ and appropriate concentrations of acid were prepared using bidistilled water. The concentration range of EMQ employed was 10⁻⁷ to 10⁻³ in the presence and absence of 0.5 M sulphuric acid.

Gravimetric Measurements
The weight loss of the rectangular steel specimens in 0.5 M H₂SO₄ with and without the addition of different concentrations of EMQ compound was determined after a 6h period of immersion, at a temperature of 298K, 308K and 318K in air atmosphere without bubbling. The inhibition efficiency (%) of the inhibitor is calculated using Equation 1:

\[ \% IE = \frac{W_0 - W}{W_0} \times 100 \]  

Where, \(W_0\) and \(W\) are weight losses without and with inhibitor.

The corrosion rate (17) of mild steel is calculated using Equation 2:

\[ \mu = \frac{3.45 \times 10^5 W}{ADT} \]  

Where, \(W\) = weight loss (g), \(D\) = Density of mild steel specimen (g cm⁻³), \(A\) = Area of the coupon (cm²), \(T\) = exposure time (h).

Electrochemical Measurements
Electrochemical experiments are performed in a conventional three electrode glass cell assembly with a mild steel rod as the working electrode (We), platinum foil as the auxiliary electrode (Ce) and saturated calomel as a reference electrode. The electrolytic solution was an acidic solution maintained at 298K in air atmosphere without bubbling.

Polarization Measurement
The anodic and cathodic polarization measurements are done under Galvanostatic condition. The potentials were scanned primarily in the cathodic direction from corrosion potential and then subsequently in the anodic direction. The electrode was held in the test solution for few seconds, prior to measurements, to ensure reliable corrosion potential. The percentage inhibition efficiency (%) is calculated using Equation 3:

\[ \% IE = \frac{I_{corr}^o - I_{corr}}{I_{corr}^o} \times 100 \]  

Where, \(I_{corr}^o\) and \(I_{corr}\) are the corrosion current densities in the absence and presence of inhibitor.

Electrochemical Impedance Spectroscopy (EIS)
Impedance spectroscopy measurements are carried out in the frequency ranging from 42 Hz to 5 MHz using LCR HI-Tester (H10K1 3532-50). Various impedance parameters like Polarization resistance (Rp) and Double layer capacitance (Cdl) are determined and Nyquist plots of mild steel in uninhibited and inhibited acid solutions, containing different concentration of EMQ compound were obtained.
SEM and FTIR studies

The surface morphology of the steel samples was investigated after anodic polarization using SEM technique (JSM 840 Jeol). FT-IR spectra (in KBr pellets) were recorded on a Nicolet Protege 460 Spectrophotometer.

RESULTS AND DISCUSSION

Weight Loss Measurements

The values of percentage inhibition efficiency (%IE) and corrosion rate (µcorr) obtained from Weight loss method, at various concentrations of inhibitor and different temperatures, are summarized in Table 1. It has been found that the EMQ compound inhibits the corrosion of mild steel in 0.5 M H₂SO₄ solution at all concentrations used in this study i.e. 10⁻⁷ to 10⁻³ M.

It has also been observed that the inhibition efficiency of the compound increases with the increase in concentration as shown in Fig. 2. It can be seen from Fig. 3 that inhibition efficiency decreases with an increase in temperature from 298K to 318K.

Polarization Measurement

Anodic and Cathodic polarization were studied with different concentration of EMQ inhibitor in 0.5M H₂SO₄ solution. The effect of different inhibitor concentration on the corrosion kinetic parameters such as anodic and cathodic tafel slopes (a, c), Ecorr, Icorr, surface coverage (θ) and inhibition efficiency obtained using polarization measurement technique at 298K are summarized in Table 2 and plotted in Figure 4. An inspection of these results reveals the following:

- Increase of both anodic and cathodic tafel slopes indicates a mixed anodic and cathodic effect on the corrosion mechanism (18) i.e. mixed inhibitor.
- Corrosion current is increasing with increasing temperature. The inhibition efficiency decreases with decrease in the concentration of the additive. The adsorption takes place though the lone pair of electrons of hetero atom (N & O) which helps in very uniform coverage of metal surface.
- The adsorption at higher concentration during ion pair mechanism is very effective resulting in strong inhibition action. The extent of blockage of active sites is reduced with the decrease in concentration and with temperature, the gap between adsorption and desorption becomes shorter leading to higher extent of corrosion. There is an irregular trend in the change of cathodic and anodic tafel slope values proving that inhibition is not exclusively taking place adsorption alone but is also due to the mixed effect of blocking sites as well as by the formation of (M-OH-In) ads or (M-In-OH) ads or (M-In) ads onto the metal surface.

It is interesting to note that the values of IE given by polarization are higher than those obtained by weight loss measurements. These results may be due to the fact that the electrochemical measurements were carried out on freshly prepared solutions. The inhibitor has produced a noticeable decrease in the corrosion current density at all the concentrations and temperatures. This decrease in the corrosion rate could be due to the pair adsorption between protonated molecule and the metal surface and d – p interaction between lone pair of electrons of nitrogen and oxygen atom, electrons of the aromatic ring and vacant dorbital of metal atom. Both physical and chemisorption could affect this barrier.

Electrochemical Impedance Spectroscopy (EIS)

The corrosion behavior was studied for different concentrations of inhibitor at room temperature. Rp values were calculated from the difference in impedance at lower and higher frequencies (19) and Cdl values were obtained using the Equation 4 by determining the frequency at which the imaginary component of the impedance was the maximum. The deduced EIS parameters are collected in Table 3.

\[
C_{dl} = \frac{1}{2\pi f \left(\frac{-Z'_{max}}{Z''_{max}}\right) R_p} \quad ...(4)
\]

A typical set of Nyquist plots (Fig. 5) shows that impedance spectra were similar to a single circle but not a perfect loop (20). The inhibition efficiency increased markedly with increase in inhibitor
Table 1: Corrosion parameters obtained from Weight loss measurements for various concentrations of inhibitor at different temperatures in 0.5 M H₂SO₄

| Temp. (K) | Concentration (M) | Weight Loss (G) | μcorr (cm h⁻¹) | IE (%) |
|-----------|-------------------|-----------------|----------------|--------|
| Blank     | 10⁻⁷ M            | 0.0786          | 2.22           | 77.0   |
| 298       | 10⁻⁵ M            | 0.0145          | 0.4096         | 81.55  |
|           | 10⁻³ M            | 0.007           | 0.197          | 90.09  |
| Blank     | 10⁻⁷ M            | 0.158           | 4.46           | -      |
| 308       | 10⁻⁵ M            | 0.0475          | 1.34           | 69.9   |
|           | 10⁻³ M            | 0.0289          | 0.816          | 81.7   |
| Blank     | 10⁻⁷ M            | 0.5487          | 15.5           | -      |
| 318       | 10⁻⁵ M            | 0.1997          | 5.64           | 63.6   |
|           | 10⁻³ M            | 0.1183          | 3.3            | 78.4   |

Table 2: Corrosion parameters obtained from Polarization measurements for various inhibitor concentrations at different temperatures in 0.5 M H₂SO₄

| Temp. (K) | Conc. (M) | E_corr (mV) | Log I_corr (µA Cm⁻²) | θ | βₐ (mV/dec) | βₐ (mV/dec) | IE (%) |
|-----------|-----------|-------------|----------------------|---|--------------|--------------|--------|
| Blank     | 525       | 3.59        | -                    | - | 114.285      | 109.5        | -      |
| 298       | 10⁻⁷ M    | 525         | 2.9                  | 0.763 | 55.4         | 96.7         | 77.0   |
|           | 10⁻⁵ M    | 500         | 2.8                  | 0.853 | 52.7         | 77.2         | 82.2   |
|           | 10⁻³ M    | 479         | 2.4                  | 0.922 | 50.0         | 106.4        | 91.9   |
| Blank     | 518       | 3.66        | -                    | - | 50           | 81.67        | -      |
| 308       | 10⁻⁷ M    | 520         | 3.18                 | 0.5322 | 25.3         | 53.4         | 62.9   |
|           | 10⁻⁵ M    | 494         | 3.1                  | 0.824 | 25.4         | 69.5         | 69.5   |
|           | 10⁻³ M    | 520         | 2.9                  | 0.895 | 55.6         | 100          | 81.6   |
| Blank     | 520       | 3.8         | -                    | - | 80.76        | 69.964       | -      |
| 318       | 10⁻⁷ M    | 525         | 3.4                  | 0.369 | 53.7         | 97.6         | 62.2   |
|           | 10⁻⁵ M    | 511         | 3.3                  | 0.808 | 64.2         | 86.1         | 64.4   |
|           | 10⁻³ M    | 517         | 3.1                  | 0.864 | 47.6         | 76.2         | 78.4   |

Table 3: Impedance parameters obtained using Electrochemical Impedance method in 0.5 M H₂SO₄ at 298K

| Concentration (M) | Rp (cm²) | Capacitance, Cdl (µF cm⁻²) | IE (%) |
|-------------------|----------|----------------------------|--------|
| 0.5 M H₂SO₄       | 53       | 600                        | -      |
| 10⁻⁷ M            | 172      | 339                        | 77.1   |
| 10⁻⁵ M            | 352      | 165.5                      | 82.0   |
| 10⁻³ M            | 607      | 96.5                       | 92.1   |
concentration. The Cdl (Cdl = \( \gamma /d \)) values tend to decrease which was resulted due to the displacement of the H\(_2\)O molecules by the inhibitor molecules at the interface of the electrical double layer, which suggested that the two inhibitor molecules function by adsorption at the metal solution interface (21), and the charge transfer between the solution and metal surface had been inhibited sharply. Increase in \( R_p \) indicates that the corrosion resistance from the adsorption film formed by the inhibitor on the metal surface has increased, resulting in decrease of the corrosion rate. It can be seen that at the minimum concentration, inhibition efficiency of EMQ increased rapidly, which may have resulted from the contact adsorption film. From the values of \( R_p \) and Cdl, it can be deduced that EMQ showed good inhibition effect with increase in the working concentration.

**Thermodynamic Parameters**

In order to understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbate on the steel surface must be known. The degree of surface coverage (\( \theta /1-\theta \)) for different concentrations of inhibitor has been evaluated from polarization measurements. The data were tested graphically by fitting to various isotherms. A straight line was obtained on plotting Log (\( /1-\)) against Log C shown in Fig. 6, suggesting that the adsorption of the compound on mild steel surface follows Langmuir adsorption isotherm model\(^2\).  

**Adsorption isotherm**

The inhibition efficiency of EMQ compound is determined by their adsorbility on the surface of the corroding metal. The values of degree of surface coverage (q) of mild steel by adsorption of different concentration of EMQ compound, calculated using Equation 5, have been inserted into Table 2. The degree of coverage \( \theta \) was found to increase with increase in the concentration of additive and decreases with the increase in the temperature where mono layer adsorption occur on the steel surface, the Langmuir adsorption isotherm (22) may be expressed by equation 5:

\[
\frac{\theta}{1-\theta} = AC \exp \left( -\frac{\Delta H}{RT} \right) \quad \text{(5)}
\]
Where T is temperature, A is independent constant, C is inhibitor concentration, R is gas constant, H is heat of adsorption and \( \theta \) is surface coverage by the inhibitor molecule.

Equation (5) can be converted to logarithmic scale as given below:

\[
\log \frac{\theta}{1 - \theta} = \log A + \log C - \frac{\Delta H_{ads}}{2.303RT} \quad (6)
\]

Fig. 7 shows the Plot of log \((1/\theta)\) versus \((1/T)\) at different additive concentrations. The slope of the linear parts of curves is equal to \(-H/2.303R\). The average heat of adsorption, \(H_{ads}\) were calculated at different concentrations of inhibitor using Equation 6 and are summarized in Table 4. The negative values of \(H_{ads}\) reflect the exothermic behavior of EMQ compound on the metal surface.

| Concentration (M) | \(E_a\) (kJ mol\(^{-1}\)) | \(-\Delta H\) (kJ mol\(^{-1}\)) |
|-------------------|-----------------|-----------------|
| 0.5M H\(_2\)SO\(_4\) | 3.70            | -               |
| 10\(^{-5}\)       | 6.10            | 9.12            |
| 10\(^{-3}\)       | 8.22            | 8.29            |
| 10\(^{-2}\)       | 9.13            | 9.16            |

Table 4: Thermodynamic parameters at various inhibitor concentrations in 0.5M H\(_2\)SO\(_4\)
The activation energy of the corrosion process is calculated using the Equation 7:

\[ K = A \exp \left( -\frac{E_a}{RT} \right) \]  

...(7)

Where, \( E_a \) is the activation energy, \( A \) is the frequency factor, \( T \) is the absolute temperature, \( R \) is the gas constant and \( K \) is the rate of metal dissolution reaction and is directly related to corrosion current density \( I_{corr} \) (14). The values of \( E_a \) can be calculated from the slopes of straight line obtained from Fig. 8. The values of \( E_a \) obtained at different concentration of compound are summarized in table 4, agrees with the order of inhibition efficiency. The activation energy is higher in the presence of additives than in its absence. During the corrosion reaction mechanism, the charge transfer is blocked with adsorption of EMQ molecules to the metal surface, causing the increase in the activation energy (23, 24). The higher values of \( E_a \) are good evidence for the chemisorptions mechanism of EMQ compound on the steel surface.

**Morphological investigation**

Microstructural studies of mild steel in 0.5 M H2SO4 in absence and presence of a certain concentration of compound at 298K were performed. It is clear that the corrosion attack was more pronounced in the absence and presence of low inhibitor concentration (10-7M) of the studied inhibitor at 298K temperature (Fig. 9a, 9b), while the film formed on the metal surface becomes more protective with increase of inhibitor concentration (10-3 M) at 298K (Fig. 9c). This is attributed to the involvement of compound in the interaction with the active sites of metal surface, resulted in enhanced surface coverage of the metal so that there is a contact between metal and the aggressive medium.

**IR Studies**

The compound formed on the corroded steel specimens after polarization were scrapped, collected and subjected to FT-IR spectral studies. The involvement of NH group, C=C and C=O in interaction reaction with metal surface atom could be proved by the respective IR spectra. The shift in the adsorption peaks from NH (3422-3400), C=O...
(1717-1700), C=C (751-719) further the intensity of the peaks stretching frequency is decreased which implies that the shift peaks in this compound is coordinated to Fe+2 resulting in the formation of a Fe+2 inhibitor complex on the metal surface.

CONCLUSION

The inhibition efficiency of designed molecules increases by increasing the inhibitor concentration, but it decreases with increase in testing temperature. The order of inhibition efficiency was correlated with the modification of the molecular structure of inhibitor, while the decrease in inhibitor efficiency with temperature was ascribed to the thermodynamic parameters due changes in the nature of molecular interactions.

The galvanostatic polarization curve indicates that EMQ compound inhibits both anodic metal dissolution and cathodic hydrogen evolution reaction. This is mixed type inhibitor.

AC impedance plots of mild steel show that polarization resistance increases with increase in inhibitor concentration.

The adsorption of EMQ molecules on the metal surface from 0.5 M H2SO4 solution obeys Langmuir adsorption isotherm. The negative sign of the Hads indicates that the adsorption process is spontaneous and exothermic.

The increase in activation energy after the addition of EMQ compound to the 0.5 M H2SO4 solution indicates that the adsorption is more physical than the chemical.

The analysis of the SEM images suggests that the corrosion of the mild steel is mainly through pitting and the addition of inhibitor to the aggressive solution results into the formation of the protective film on mild steel surface.

ACKNOWLEDGEMENTS

The authors are thankful to the Prof. Alimuddin and Mr. Khalid Mujasam Batoo, Department of Applied Physics, A.M.U. Aligarh, India for providing necessary laboratory facilities to perform impedance measurements.

REFERENCES

1. Khamis E, Corrosion 46: 476 (1990).
2. Schweinsberg D, George G and Nanayakkara A, Corros Sci. 28: 33 (1988).
3. Tang L B, Mu G N and Lu G H, Corros Sci 45: 2251 (2003).
4. Bentiss F, Traisnel M and Lagrenee M, Corros Sci 42: 127 (2000).
5. Abd-El-Nabey B A, Khamis E, Ramadan M, Sh and El-Gindy A, Corrosion 52: 671 (1996).
6. Queraishi M A and Jamal D, Corrosion 56: 983 (2000).
7. Arab S T and Noor E A, Corrosion 44: 122 (1993).
8. Lagrenee M, Mernari B, Chabi N, Traisnel M, Vezin H, and Bentiss F Corros Sci 43: 951 (2001).
9. Abid E L, Ibrahim M A M and Khalid K F, Mater Chem Phys 70: 268 (2001).
10. Martinez S and Stern I, Appl. Surf Sci 199: 83 (2002).
11. Ebenso E E, Mater Chem Phys 79: 58 (2003).
12. Damborenea J De, Bastidas J M and Vazquez A J, Electrochim Acta 42: 455 (1997).
13. Nosseini M, Mertens S F L, Ghorbani M and Arshadi M R, Mater Chem Phys 70: 800 (2003).
14. Desai M N, Desai M B, Shah C B and Desai S M, Corros Sci 26: 827 (1986).
15. Shokry H, Yusa M, Sekine I, Issa R M, El-Baradic H Y and Gomma G K, Corros Sci 40: 2173 (1998).
16. Mishra P, Gupta P N and Shady A K, J Ind Chem Soc 68: 618 (1991).
17. Olivares O, Likhanova N V, Gomez B, Navarrete J, Serrano M E, Arce F and Hallen J M, Appl Surf Sci 252: 2894 (2006).
18. Abdallah M, Corros Sci 44: 717 (2002).
19. Bentiss F, Lagrene M, Traisnel M and Hornez C, Corros Sci 41: 789 (1999).
20. Mansfeld F, Kending M W and Tsai S, Corrosion 37: 301 (1981).
21. Mccafferty E and Hackerman N, J Electro Chem Soc 119: 146 (1972).
22. Saliyan V R and Adhikari AV, Corros Sci 50: 51 (2008).
23. Osman M M, El-Ghazaway R A and Sabagh M A, Mater Chem Phys 80: 55 (2003).
24. Amer M A, Khamis E and Alsenani G, J Applied Electro Chem 32: 149 (2002).