

Full Paper

Corrosion Inhibition and Adsorption Behavior of 1-(1-Naphthalenylmethyl)quinolinium Chloride on Mild Steel in Hydrochloric Acid Medium

Ali Reza Rezaierod*, Ali Reza Rahimi and Mosayeb Chaghazardi

Electrochemistry and Inhibitors Group, Environmental Protection Department, Research Institute of Petroleum Industry (RIPI), Azadi sport complex Blvd., Tehran, Iran

* Corresponding Author, Tel.:00982148255228; Fax: 00982148255231

E-Mail: rezaierodar@ripi.ir (A. Rezaierod)

Received: 13 June 2014 / Received in Revised form: 15 November 2014 /

Accepted: 21 November 2014 / Published online: 31 December 2014

Abstract- The inhibition behavior of 1-(1-Naphthalenylmethyl) quinolinium chloride (NMQ) on the corrosion of mild steel in 1.00 M hydrochloric acid has been investigated. Weight loss measurements, potentiodynamic polarization and electrochemical impedance (EIS) techniques were used to study the corrosion inhibition process. The results revealed that maximum corrosion protection was 99% at 50 ppm of NMQ. Polarization measurements indicate that inhibitor has mainly cathodic inhibition effects and therefore control of hydrogen evolution is done. From EIS measurements it is found that charge transfer resistance values increased and double layer capacitance values decreased by increasing the inhibitor concentration. The adsorption of NMQ on the mild steel follows the Langmuir isotherm model, calculated value of adsorption free energy was (-43.6) kJ mol⁻¹ and adsorption constant was 10^{7.5}.

Keywords- 1-(1-Naphthalenylmethyl) quinolinium, Corrosion Inhibitor, Adsorption isotherm

1. INTRODUCTION

Acidic solutions are used for different purposes in several industrial processes such as acid pickling and oil well acidizing [1]. Acid inhibitors used in these processes for corrosion

protection and thereby increase the operation life of materials. Most of acid inhibitors are aliphatic or aromatic compounds with nitrogen, sulfur or oxygen atoms in their functional groups [2-5]. M.A. Quraishi and coworkers have been reported Inhibition of steel corrosion by some triazole derivatives in HCl [6]. These inhibitors protect steel more than 200 ppm concentration. N-heterocyclic amines have been used as corrosion inhibitor for iron protection in perchloric acid [7]. *T*-Cinnamaldehyde has been used for the corrosion inhibition of steel in acidic media [8]. Quinolines and their derivatives have been applied as corrosion inhibitors for acidic media, Moreover quinaldine and quinaldic acid have been used for corrosion protection of mild steel in 0.5 M HCl [9]. Prabhu and his co workers investigated the corrosion inhibition of Quinol-2-thione compounds for mild steel in hydrochloric acid [10]. F.Zucc and coworkers have reported corrosion inhibition of 1-(1-Benzenemethyl) quinolinium chloride for nickel in HClO₄ Solution using the electrochemical quartz crystal microbalance [11]. The aim of the present work is to study the inhibition effect of 1-(1-Naphthalenylmethyl) quinolinium chloride on the corrosion of mild steel in 1.00 M hydrochloric acid. The synthesized compound has 4 aromatic rings and is an ammonium salt (type 4), these characteristics cause different behavior in adsorption and corrosion protection of this inhibitor (In comparison to other quinoline compounds). Electrochemical behavior and adsorption of this inhibitor in acidic media is not investigated before, and this study revealed that this compound shows a good corrosion inhibition (%90) in low concentration (30 ppm).

2. EXPERIMENTAL WORK

2.1. Materials

Fig. 1 shows the molecular structure of 1-(1-Naphthalenylmethyl) quinolinium chloride [C₂₀H₁₆N.Cl]. For synthesis of NMQ, 50 g of Quinoline (Aldrich, 98%, Germany) and 68 grams of 1-Chloromethyl-Naphthalen (Aldrich, 98%) were mixed in 50ml of propan-2-ol (Merck, Germany, 99%) and refluxed for 6 hours at 95 °C (m.p. 120 °C) [12,13].

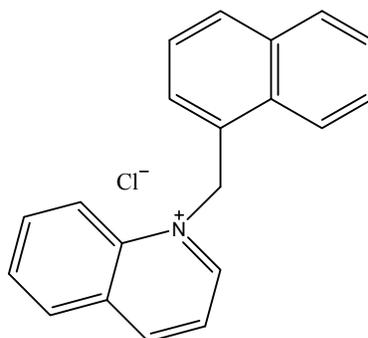


Fig.1. The chemical structure of 1-(1-Naphthalenylmethyl) Quinolinium Chloride (NMQ)

The 1.00 M hydrochloric acid was prepared by dilution of analytical grade 37% HCl (Merck, Germany) with double-distilled water. Mild steel samples (C1010 from Esfahan steel company, IRAN) have the chemical composition (wt%) as follows: C, 0.18, Si, 0.28, Mn, 0.29, P, 0.4, S, 0.05 and remain Fe.

2.2. Corrosion measurements

Electrochemical experiments were carried out using IM6 (Zahner Elektrik company, Germany) P/G stat instrument under continuously stirring conditions. A graphite rod and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The cylindrical shape working electrode with exposed area of 1.6 cm² was dipped in 1.00 M hydrochloric acid solution. Before each experiment, the working electrode was abraded with wet SiC paper (grades 320-800), polished with emery paper to mirror surface, degreased with acetone and finally immersed in the corrosive media. In impedance measurements, the applied frequency ranged from 100 kHz to 10 mHz and impedance data were obtained at the open circuit corrosion potential of the working electrode. The electrode potential was allowed to stabilize for 60 minutes before starting the experiments. In the potentiodynamic polarization measurements the potential scan rate was 0.5 mV s⁻¹, and before recording the polarization curves, the open-circuit potential was allowed to be stabilized. The potential scanned primarily in the cathodic direction from the corrosion potential and subsequently in the anodic direction.

Weight loss measurements were carried out using mild steel plates with 0.3×10×70 mm dimensions dipped in 500 ml of test solution (containing different concentrations of NMQ) for 10 hr. Before each experiment, coupons were abraded with wet SiC paper (grades 320-800), polished with emery paper, then washed with double distilled water, degreased with acetone, dried and finally immersed in test solution.

3. RESULTS AND DISCUSSIONS

3.1. Potentiodynamic Polarization measurement

The anodic and cathodic polarization behavior of mild steel in the presence and absence of NMQ in 1.00 M HCl is shown in Fig. 2 and the values of corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic slopes (b_a and b_c) and inhibition efficiency ($IE\%$) are given in Table 1. $IE\%$ is calculated using the following equation:

$$IE\% = \frac{I_{corr} - I_{inh}}{I_{corr}} \times 100 \quad (1)$$

In which I_{corr} and I_{inh} are the corrosion current values without and with inhibitor respectively. The results showed that I_{corr} values decreased with increase in the concentrations of NMQ and lowest I_{corr} was obtained at 50 ppm of the corrosion inhibitor.

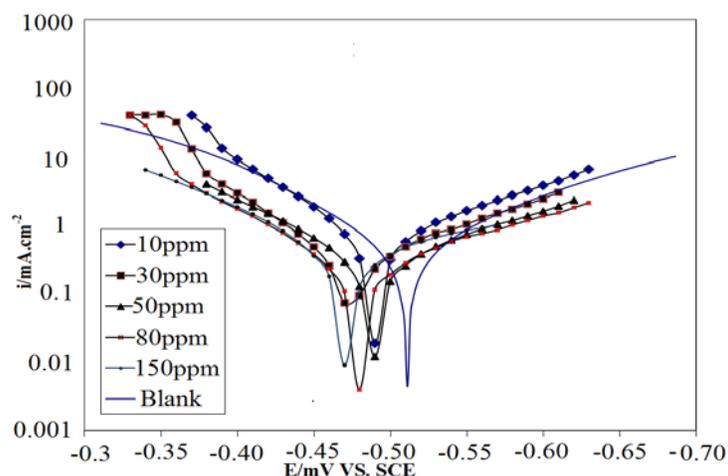


Fig. 2. Polarization curves for different concentrations of inhibitor at room temperature

The values of Tafel slopes show that the corrosion inhibition may be due to the control of hydrogen evolution reaction. The values of $IE\%$ increase with addition of inhibitor concentration. The anodic Tafel slope and E_{corr} are almost constant when the inhibitor is added, showing that the inhibitor's presence modifies the mechanism of the hydrogen reduction and it also suggests that NMQ is a cathodic type corrosion inhibitor.

Table 1. The values of corrosion current density (I_{corr}), corrosion Potential (E_{corr}), Tafel slopes (b_a and b_c) and inhibition efficiency (IE)

Parameter	Blank	30 ppm	40 ppm	50 ppm	80 ppm	150 ppm
E_{corr}/V	-0.508	-0.489	-0.487	-0.472	-0.488	-0.467
$I_{corr}/A\ cm^{-2}$	4.83E-03	29E-05	10E-05	4.78E-05	4.91E-05	9E-05
$b_a/V\ dec^{-1}$	0.090	0.080	0.088	0.086	0.0103	0.098
$b_c/V\ dec^{-1}$	0.122	0.133	0.138	0.157	0.167	0.170
$IE/\%$	-	94	98	99	99	98

3.2. Electrochemical Impedance spectroscopy

The Nyquist plots obtained from electrochemical impedance measurements of mild steel in 1.00 M HCl containing different concentrations of NMQ are presented in Fig. 3 and charge-transfer resistance (R_p) and capacitance (C_{dl}) are shown in Table 2. It is apparent from these plots that impedance response of 1.00 M HCl has obviously altered after addition of inhibitor.

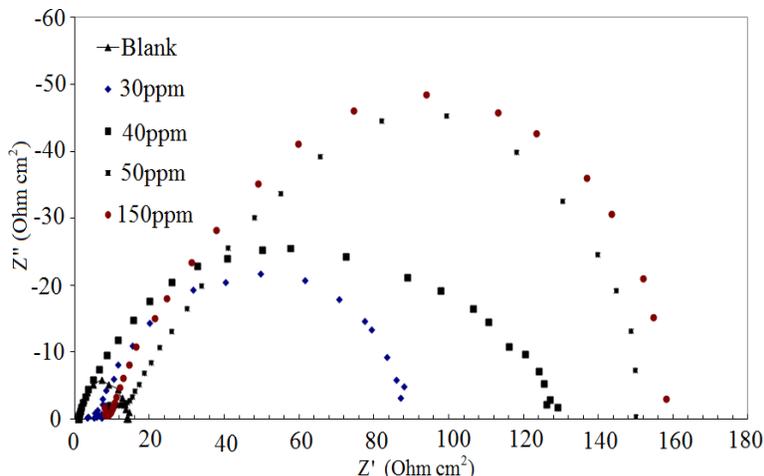


Fig. 3. Nyquist plots for various concentrations of inhibitor at room temperature

From Table 2 data it is concluded that charge-transfer resistance values increase and capacitance values decrease with increasing the inhibitor concentration. Decrease in the C_{dl} Values may be due to decrease in local dielectric constant because of replacement of water molecules at the metal surface by molecules of NMQ molecules. It has been reported that the adsorption of corrosion inhibitor molecules on the metal surface is characterized by lower capacitance [14-15].

Table 2. Electrochemical impedance parameters for mild steel in 1.00 M HCl with various content of NMQ

NMQ (ppm)	$R_p(\Omega.cm^2)$	$C_{dl} (\mu F.cm^{-2})$
Blank	8	650
30	90	160
40	130	37
50	150	41
150	155	40

3.3. Weight loss measurements

Weight loss measurements were carried out by immersion of test coupons in 500 ml acidic solution. The percentage of inhibition efficiency ($IE\%$) was calculated using the following equation [4]:

$$IE\% = \frac{W_o - W_i}{W_o} \times 100 \tag{2}$$

Where w_o and w_i are the weight losses in the absence and presence of inhibitors in corrosive

solution. Table 3 gives the corrosion rate and inhibition efficiency for various concentration of inhibitor in corrosive solution obtained from weight loss experiments at 30 °C after 6 h of immersion. Results shown in the Table 1 revealed that IE% increased with increase in the concentration of inhibitor, but at a concentration of 50 ppm is reached maximum protection (97%).

Table 3. Corrosion rate and inhibition efficiency for various concentrations of inhibitor at 30 °C after 6 h

C / ppm	Corrosion Rate / mpy	IE %
Blank	430±6	-
10	220±2	49
30	52±1	87
40	29±1	93
50	13±1	97
80	14±1	94
150	14±1	94

Further increase in inhibitor concentration provided no more protection. The reason for increase in IE% with time and concentration may be because of the adsorption of NMQ molecules on the surface of mild steel and regularly covering of all sites of the steel surface and forming a uniform molecular layer (or layers) on the surface [16].

Table 4. Weight loss measurement results for Blank and for 50 ppm inhibitor containing solution at different temperatures

T / °C	CR(mpy)/ Blank	CR(mpy)/ 50ppm NMQ	IE %
30	430	13	97
40	750	52	93
50	1570	140	91
60	2510	295	88

3.4. Effect of temperature

Weight loss measurements for 50 ppm of inhibitor at 30, 40, 50 and 60 °C were shown in Table 4. As shown, inhibition efficiency decreases with increasing temperature because the temperature can modify the electrostatic interaction between inhibitor molecules and iron

surface and decrease adsorption of inhibitor. Increase in the corrosion rate at high temperatures may be related to increase in the solubility of the protective layer of inhibitor which covers the surface of metal.

3.5. Adsorption isotherm

Adsorption of organic molecules on the metal surface depends mainly on the electronic characteristics, charge and nature of the metal surface, adsorption of solvent and other ionic species, temperature and on the electrochemical potential at solution-interface and the chemical structure of organic molecules [17]. The corrosion inhibitor adsorption isotherms that used in research articles include Langmuir, Flory-Huggins, Temkin, Toth, Frumkin, Parsons, Hill de Boer, Dhar-Flory-Huggins and Bockris-Swinkels [18]. The values of the surface coverage corresponding to different concentrations of NMQ were used to find the best adsorption isotherm and the best was obtained with Langmuir adsorption isotherm which is expressed by equation (3):

$$\log \frac{\theta}{1-\theta} = \log C + \log K \quad (3)$$

Fig. 4 shows the adsorption isotherm plot of NMQ on the surface of mild steel in 1.00 M HCl. The linear relationship of $\log \theta/(1-\theta)$ versus $\log C$ showed that inhibitor obeyed Langmuir adsorption isotherm.

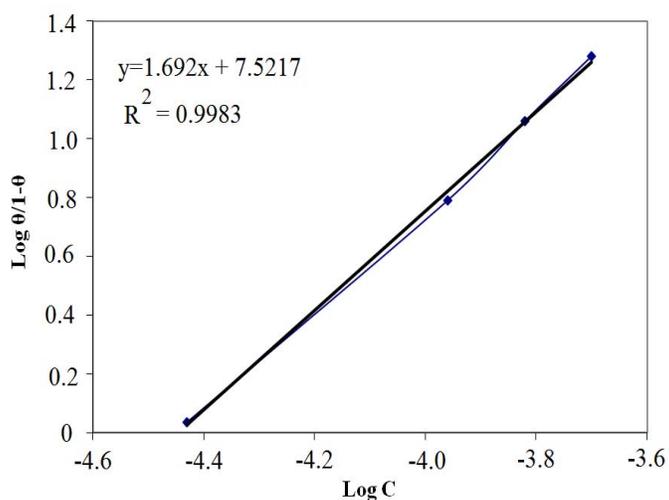


Fig. 4. Langmuir plot for NMQ adsorption on the surface of mild steel in 1.00 M HCl at 303 K

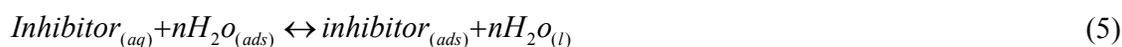
Calculated value of "K" (equilibrium Constant) for the adsorption reaction was $10^{7.5}$.

Adsorption free energy (ΔG°_{ads}) was calculated by using the following equation:

$$\Delta G^{\circ}_{ads} = -RT \cdot \ln K_{ads} \quad (4)$$

$$\Delta G^{\circ}_{ads} = -8.32 \times 303 \ln 10^{7.5} \quad \text{then:} \quad \Delta G^{\circ} = -43.6 \text{ kJ mol}^{-1}$$

Negative value of ΔG°_{ads} indicates spontaneous adsorption of NMQ on the metal surface, and values of the adsorption free energy less than (-40) kJ mol⁻¹ have typically been correlated with the electrostatic interactions between inhibitor molecules and charged metal surface (physisorption) [19]. This behavior can be explained as a result of the displacement process of water molecules during adsorption of inhibitor on mild steel surface according Eq. (5) [20-21].



Where "n" is the size ratio of inhibitor molecule to water molecule, and it represents the number of water molecules replaced by one molecule of inhibitor.

Inhibitors containing electronegative atoms such as nitrogen in NMQ and aromatic double bonds act through a process of surface adsorption, because of electrostatic interaction between ion pairs electrons of inhibitor and Fe atoms of metal. Electron transfer can occur between nitrogen ion pairs and vacant orbitals of iron atoms. It is usually accepted that corrosion inhibition of organic inhibitors is result of formation of adsorption layer as a film barrier, thus isolating the metal from the corrosive media [22]. The possible reaction centers for adsorption of inhibitor on Fe-hydrochloric acid interface are unshared electron pair on nitrogen and π electrons on aromatic rings. Strong adsorption of chloride present in the solution on the metal surface brings about a negative charge favoring the adsorption of cationic inhibitors thus the protonated inhibitor molecules may be adsorbed on the metal surface through electrostatic mechanism between the positively charged nitrogen atom and the negatively charged metal surface [23]. The number of heteroatom and aromatic rings in the molecule, their charge density, and molecular size and conformation of inhibitor can affect adsorption process [24-26].

4. CONCLUSION

Corrosion inhibition behavior of NMQ has been investigated by different techniques in this paper. Polarization and electrochemical impedance measurements showed high values of polarization resistance and low corrosion current density values for 50 ppm concentration of inhibitor in 1.00 M HCl. It indicates strong protection of mild steel by 50 ppm of inhibitor in 1.00 M HCl Acid. The adsorption of inhibitor on mild steel surface was consistent with Langmuir isotherm. The value of heat of adsorption ΔG_{ads} was negative, which indicate the spontaneous adsorption of NMQ on the metal surface.

REFERENCES

- [1] B. Mernari, H. Elattari, and M. Traisnel, *Corros. Sci.* 40 (1998) 391.
- [2] S. P. Fakrudeen, H. C. Ananda Murthy, and V. B. Raju, *J. Chil. Chem. Soc.* 57 (2012) 1364.
- [3] T. Sethi, A. Chaturvedi, R. K. Upadhyay, and S. P. Mathur, *J. Chil. Chem. Soc.* 52 (2007) 1206.
- [4] U. Achuthakini, P. Shetty, S. D. Shetty, A. Isloor, and R. Herle, *J. Chil. Chem. Soc.* 55 (2010) 56.
- [5] I. B. Obot, N. O. Obi-Egbedi, and N. W. Odozi, *Corros. Sci.* 52 (2010) 923.
- [6] M. A. Quraishi, and S. Ahmad, *British Corros. J.* 32 (1997) 297.
- [7] K. B. Samardzija, and K. F. Khaled, *Anti-corros. Meth. Mater.* 52 (2005) 11.
- [8] F. B. Growcock, *Corrosion* 45 (1989) 1003.
- [9] E. E. Ebenso, I. B. Obot, and L. C. Murulana, *Int. J. Electrochem. Sci.* 5 (2010) 1574.
- [10] R. A. Prabhu, and T. V. Venkatesha, *Mater. Chem. Phys.* 108 (2008) 283.
- [11] F. Zucc, M. Fonsati, and G. TrabANELLI, *J. App. Electrochem.* 28 (1998) 441.
- [12] W. W. Frenier, and D. G. Hill, *Corrosion. NACE International Paper No. 04407* (2004).
- [13] W. W. Frenier, *Us Patent 5096618* (1992).
- [14] M. Benabdellah, R. Touzani, and A. Aouniti, *Mater. Chem. Phys.* 105 (2007) 373.
- [15] K. A. Ramaki, and M. Hagiwara, *Corros. Sci.* 5 (1987) 87.
- [16] C. M. A. Brett, *Corros. Sci.* 33 (1992) 203.
- [17] I. B. Obot, N. O. Obi-Egbedi, and S. A. Umoren, *Int. J. Electrochem. Sci.* 4 (2009) 863.
- [18] M. Guzman, R. Lara, and L. Vera, *J. Chil. Chem. Soc.* 54 (2009) 123.
- [19] S. Martinez, and I. Stern, *Appl. Surf. Sci.* 199 (2002) 83.
- [20] M. A. Quraishi, and S. K. Shukla, *Mater. Chem. Phys.* 113 (2009) 685.
- [21] S. Zhang, Z. Tao, S. Liao, and F. Wu, *Corros. Sci.* 52 (2010) 3126.
- [22] E. E. Ebenso, *Bull Electrochem.* 19 (2003) 209.
- [23] Y. I. Kuznetsov, *Organic Inhibitors of Corrosion of Metals.* Plenum Pub., NW (1981).
- [24] N. Soltani, M. Behpour, and S. M. Ghoreishi, *Corros. Sci.* 52 (2010) 1351.
- [25] I. B. Obot, and N. O. Obi-Egbedi, *Corros. Sci.* 52 (2010) 198.
- [26] I. B. Obot, and N. O. Obi-Egbedi, *Corros. Sci.* 52 (2010) 657.