International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Impact Factor (2012): 3.358

Study the Inhibition Effect of Mequitazine on the Copper Corrosion in Sodium Chloride Solution

Ahmed A. Farag

[1]Additives Laboratory, Petroleum Applications Department, Egyptian Petroleum Research Institute (EPRI)
1 Ahmed El-Zomor St., Nasr City, 11727, Cairo, Egypt

Abstract: ***The corrosion behaviour of copper in aerated 3 wt. % NaCl solution in presence of mequitazine (MQZ), using open circuit potential (OCP), potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) measurements. Polarization measurements indicated that, the studied inhibitor acts as mixed-type inhibitor. The adsorption of MQZ molecules on the copper surface obeys Langmuir adsorption isotherm. The thermodynamic parameters such as the adsorption equilibrium and the free energy of adsorption are calculated and discussed.***

Keywords: Copper, Neutral inhibition, Mequitazine, EIS, Polarization**.**

1. Introduction

Copper is heavily employed in the industry due to its high electrical and thermal conductivities, mechanical workability, and its relatively noble properties. Copper and its alloys have been found in a wide range of applications in many applications such as in electronic industries and communications as a conductor in electrical power lines, in marine industry, such as pipelines for domestic and industrial water utilities including seawater, heat conductors, and heat exchangers, shipbuilding, seawater desalination [1].

However, the high concentration of Cl^- in seawater causes serious corrosion of copper, which has brought enormous economic losses and many potential safety problems to the utilization of marine industry.

Hence, corrosion of copper and its inhibition in a wide variety of media, particularly when they contain chloride ions, have attracted the attention of many investigators [2–7]. Therefore, the investigation of copper corrosion in seawater is an issue of fundamental academic as well as practical significance. Control of copper corrosion can be achieved by many methods, from which the use of corrosion inhibitors is one of the most effective alternatives.

Intense research efforts are being undertaken to find new environmentally friendly compounds as corrosion inhibitors of copper in seawater environment. In general, organic compounds containing polar groups including nitrogen, sulfur and oxygen, and heterocyclic compounds with polar functional groups and conjugated double bonds have been reported to inhibit copper corrosion.

The inhibiting action of these organic compounds is usually attributed to their interactions with the copper surface via their adsorption. Polar functional groups are regarded as the reaction center that stabilizes the adsorption process.

In general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure and the type of the electrolyte solution [8,9]. Many N-heterocyclic compounds have been proved to be effective inhibitors for the corrosion of metals in aqueous media. In the past few years, azoles have been investigated as effective corrosion inhibitors for various environments [10–13]. Azoles are organic compounds containing nitrogen atoms with free electron pairs that are potential sites for bonding with copper and that enable inhibiting action.

The aim of the present is to examine the inhibitory action of Mequitazine (MQZ) (Figure 1) for the corrosion of copper in 3 wt.% NaCl solution. The inhibiting performance of MQZ has been evaluated completely by polarization curves, electrochemical impedance spectroscopy (EIS).

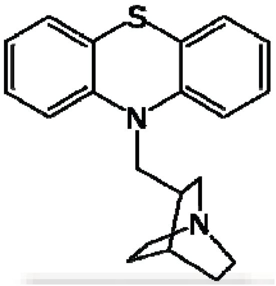

Figure 1: Molecular structures of MQZ

2. Materials and Techniques

Mequitazine (MQZ) and sodium chloride (NaCl) were prepared from Sigma-aldrich Company and used without purification. A standard three-electrode electrochemical cell was used containing platinum wire as the counter electrode, the saturated calomel electrode (SCE) as the reference electrode, and the copper electrode as the working electrode. The working electrodes were prepared from pure copper (99.99 wt.%).

The electrochemical measurements were carried out using Volta lab 40 (Tacussel-Radiometer PGZ301) potentiostate and controlled by Tacussel corrosion analysis software model (Voltamaster 4) at under static condition.

Copper electrode having the area of 1 cm^2 was used as a working electrode. The working electrode was immersed in test solutions for 30 minutes to a establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp}, the electrochemical measurements were performed. The EIS experiments were conducted in the frequency range with high limit of 10^5 Hz and different low limit 10^{-2} Hz at open circuit potential. For potentiodynamic polarization experiments, the potential was scanned from ±250 mV (SCE) around the corrosion potentia at a scan rate of 1 mV s^{-1}, which is acceptable [14, 15].

The impedance data analyses were performed using (Zsimpwin 3.10) software and fitted to its appropriate equivalent circuits. All experiments were performed at 298 K. The experimental results were reproduced and each experiment was carried out three times where a very good agreement was obtained.

3. Results and Discussion

3.1. Open circuit potential behavior

Figure 2 presents the OCP variation of copper as a function of time in aerated 3 wt.% NaCl solutions in the absence and presence of various concentrations of the investigated inhibitor at 303 K.

In NaCl solution, the steady potential was readily attained, corresponding to the free corrosion potential, E_{corr}, of the copper [16]. In inhibited NaCl solution the physical adsorption occurs between the positive charge of protonated inhibitor and negative charge of copper surface.

According to Riggs [17], the classification of a compound as an anodic or cathodic type inhibitor is feasible when the OCP displacement is at least 85 mV in relation to that one measured for the blank solution.

However from Figure 2, the shift in E_{corr} is less than 40 mV in the presence of inhibitors. This shift in E_{corr} is too small for a reasonable classification based on OCP results. Therefore the surfactants can be regarded as mixed-type inhibitors.

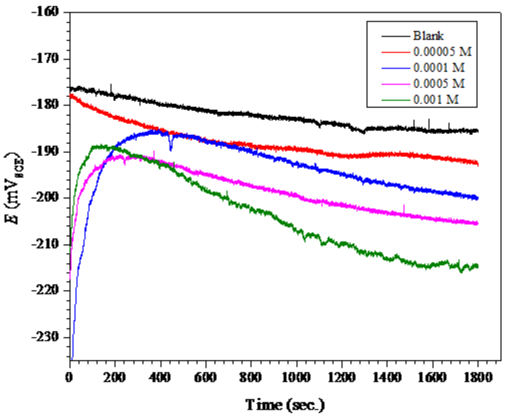

Figure 2: Variation of the OCP of copper vs. time of immersion in 3wt. % NaCl solutions in the absence and presence of various concentrations of MQZ

3.2. Potentiodynamic Curve Measurements

The polarization plots for the copper electrodes with and without MQZ were obtained in 3 wt. % M NaCl solution. Figure 3 shows that the anodic polarization curve for bare copper can be divided into three regions of potential.

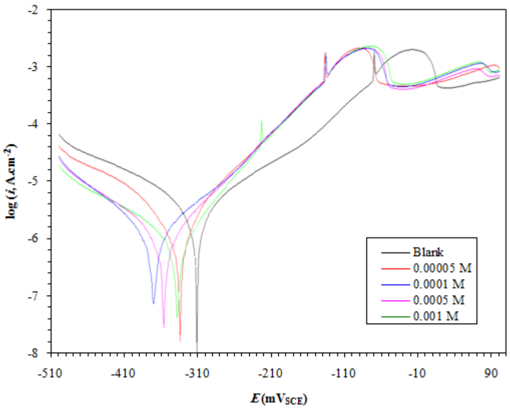

Figure 3: Potentiodynamic polarization curves for the copper electrode in 3wt. % NaCl solutions in the absence and presence of various concentrations of MQZ

The Tafel region indicates the mixed control of the formation of the CuCl film and the diffusion process of the $(CuCl_2)^-$. With the increase of the potential, the formation of the CuCl film starts to be the dominant process, resulting in an active-to-passive transition region, and then the dissolution of the CuCl film or Cu yields the limiting-current region [12,33]. With the increase of the assembly time, the cathodic current density hardly changes while the anodic current density decreases. The inhibition efficiency (η_p) is calculated as the following equation [18,19]:

$$\eta_p = \left(\frac{i_t - i_t^o}{i_t} \right) \times 100 \qquad (1)$$

where i and i^o are uninhibited and inhibited corrosion current densities, respectively. The informative parameters obtained from the polarization curves (Figure 3) are given in Table 1.

Table 1: Polarization parameters for the corrosion of copper in 3 wt. % NaCl in the absence and presence of various concentrations of MQZ at 298 K

MQZ conc. (M)	$-E_{corr}$ (mV$_{SCE}$)	i_{corr} (mA cm^{-2})	β_a (mV dec^{-1})	$-\beta_c$ (mV dec^{-1})	η_p (%)
Blank	-314	9.0	135	158	—
5×10^{-5}	337	3.5	79	129	61.1
1×10^{-4}	342	2.2	71	156	75.5
5×10^{-4}	375	1.4	101	103	85.0
1×10^{-3}	360	1.2	78	104	87.2

MQZ acts as a mixed-type inhibitor. This is seen from the shift to the lower current densities of both anodic and cathodic branches of the potentiodynamic curve compared with the uninhibited solution. The current density decrease is approximately an order of magnitude in the cathodic region more than in the anodic region, together with a shift of E_{corr}

in the cathodic direction. The mixed-type inhibitor character found herein confirms the previous study by El-Sayed et al. [20]. This behavior shows that MQZ is a good inhibition effect for Cu corrosion in 3 wt. % NaCl.

3.3. EIS Measurements

Typical Nyquist impedance plots obtained for the Cu electrode at an open-circuit potential after 30 min immersion under various experimental conditions are shown in Figure 4; symbols represent the measured data and solid lines represent the best fit using the equivalent circuit shown in Figure 5. The parameters obtained by fitting the equivalent circuit and the calculated inhibition efficiency are listed in Table 3. Here, R_s represents the solution resistance, R_{p1} the polarization resistance, Q_1 and Q_2 the constant phase elements (CPEs) and R_{p2} another polarization resistance,. It is seen from Figure 4 and Table 3 that the R_s, R_{p1}, and R_{p2} values recorded for Cu in Cl^- solutions without the inhibitor decrease as the oxygen content increases. This emphasizes the fact that the severity of chloride ions attacks on copper increases as the oxygen content increases. Addition of MQZ to NaCl solution raises the values of R_{p1} and R_{p2}. The constant phase elements (CPEs, Q_1) with their n values near to 1 represent double layer capacitors with some pores; the CPEs decrease upon addition of MQZ and upon increase in its concentration, which are expected to cover the charged surfaces reducing the capacitive effects.

The inhibition efficiency, η_i, of MQZ for the copper electrode can be calculated from the charge transfer resistance as follows [21]:

$$\eta_i = \left(\frac{R_t - R_t^o}{R_t} \right) \times 100 \qquad (2)$$

where R_t and R_t^o are the values of the charge transfer resistance in the presence and absence of MQZ, respectively.

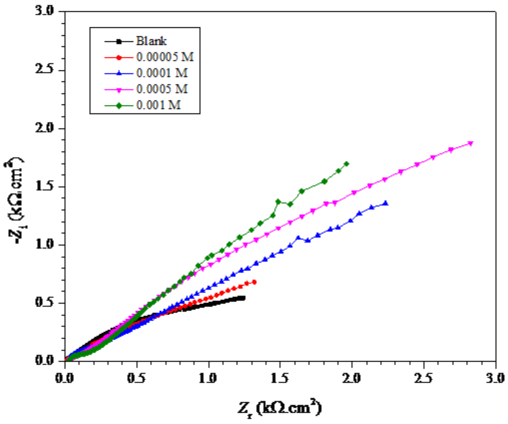

Figure 4: Nyquist plots for the copper electrode in 3wt. % NaCl solutions in the absence and presence of various concentrations of MQZ

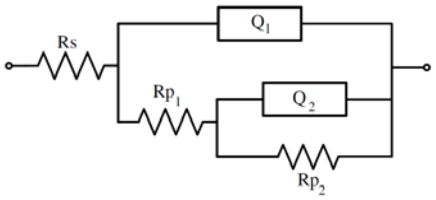

Figure 5: The equivalent circuit used to fit the experimental data presented in Fig. 6. See text for symbols used in the circuit.

Table 3: Parameters obtained by fitting the Nyquist plots shown in Figure 4 with the equivalent circuit shown in Figure 5 for the copper electrode

MQZ conc. (M)	R_s	Q_1	n	R_{p1}	Q_2	n	R_{p2}	η_i
Blank	17.9	4.056E-05	0.75	22.1	0.0003455	0.44	3295	—
5×10^{-5}	17.1	2.515E-05	0.79	50.7	0.0004834	0.41	9261	56.4
1×10^{-4}	15.9	1.238E-05	0.85	97	0.0006829	0.38	44550	77.2
5×10^{-4}	22.7	2.951E-07	0.74	114.8	0.0005062	0.51	11150	80.7
1×10^{-3}	19.3	2.329E-05	0.80	138.7	0.0009445	0.51	44420	84.1

3.4. Adsorption Isotherm

The average values of θ (η/100) obtained from polarization and impedance measurements were tested graphically by fitting different adsorption isotherms, including the Freundlich, Temkin and Langmuir models. The correlation coefficient (R^2) was used to determine the isotherm that best fit the experimental data. A plot of C/θ versus C (Figure 6) gives a straight line with an average correlation coefficient of unity and a slope of nearly unity (1.14) suggests that the adsorption of MQZ molecules obeys Langmuir adsorption isotherm. Langmuir adsorption isotherm expressed by the following equation [22]:

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

where C is MQZ concentration and K_{ads} is the equilibrium constant for the adsorption–desorption process.

The value K_{ads} calculated from the reciprocal of the intercept of isotherm line as 5×10^7 M^{-1}. The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on the copper surface.

The standard free energy of adsorption of the inhibitor (ΔG^{o}_{ads}) on the copper surface can be evaluated with the following equation;

$$\Delta G^{o}_{ads} = -RT\ln(55.5K_{ads}) \qquad (4)$$

According to equation (10) the value of ΔG^{o}_{ads} was calculated as -54.8 kJ mol^{-1}.

The negative value of standard free energy of adsorption indicates spontaneous adsorption of MQZ molecules on the copper surface and also the strong interaction between inhibitor molecules and the metal surface [23].

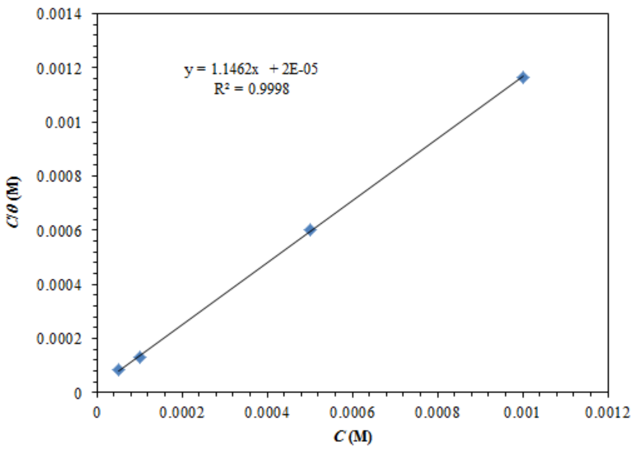

Figure 6: Langmuir adsorption plots of copper in 3 wt. % NaCl solution containing various concentrations of MQZ

Generally, absolute values of ΔG^{o}_{ads} up to 20 kJ mol^{-1} are consistent with physisorption associated with electrostatic adsorption, while those around 40 kJ mol^{-1} or higher are associated with chemisorption as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of metal bonds [24].

Here, the calculated ΔG^{o}_{ads} values are higher than 40 kJ mol^{-1}, indicating that the adsorption mechanism of MQZ on the copper in 3 wt. % NaCl solution is chemical adsorption.

4. Conclusion and Summary

MQZ has been evaluated as a corrosion inhibitor for copper in 3 wt. % NaCl solutions, and the results are summarized as follows:

1. Potentiodynamic polarization measurements indicate that the addition of MQZ decreases the cathodic, corrosion, and anodic currents (mixed-type inhibitor).
2. The adsorption of the MQZ on the copper surface obeys the Langmuir adsorption isotherm.
3. EIS measurements also reveal that the surface and charge transfer resistances increase in the presence of MQZ.

Acknowledgement

The authors are greatly thankful to the Egyptian Petroleum Research Institute (EPRI) fund and support.

References

[1] L. Nu´n´ ez, E. Reguera, F. Corvo, E. Gonzalez, C. Vazquez, Corros.Sci. 47 (2005) 461.
[2] M.M. Antonijevic, S.M. Milic, M.B. Petrovic, Films formed on copper surface in chloride media in the presence of azoles, Corros. Sci. 51 (2009) 1228–1237.
[3] M. Levin, P. Wiklund, C. Leygraf, Bioorganic compounds as copper corrosion inhibitors in hydrocarbon media, Corros. Sci. 58 (2012) 104–114.
[4] F. Altaf, R. Qureshi, S. Ahmed, Surface protection of copper by azoles in borate buffers-voltammetric and impedance analysis, J. Electroanal. Chem. 659 (2011) 134–142.
[5] E.M. Sherif, S. Park, 2-Amino-5-ethyl-1, 3, 4-thiadiazole as a corrosion inhibitor for copper in 3.0% NaCl solutions, Corros. Sci. 48 (2006) 4065–4079.
[6] Z. Khiati, A.A. Othman, M. Sanchez-Moreno, M.-C. Bernard, S. Joiret, E.M.M. Sutter, V. Vivier, Corrosion inhibition of copper in neutral chloride media by a novel derivative of 1,2,4-triazole, Corros. Sci. 53 (2011) 3092–3099.
[7] M. Cubillos, M. Sancy, J. Pavez, E. Vargas, R. Urzua, J. Henriquez-Roman, B. Tribollet, J.H. Zagal, M.A. Paez, Influence of 8-aminoquinoline on the corrosion behavior of copper in 0.1 M NaCl, Electrochim. Acta 55 (2010) 2782–2792.
[8] G. Quartarone, T. Bellomi, A. Zingales, Inhibition of copper corrosion by isatin in aerated 0.5 M H2SO4, Corros. Sci. 45 (2003) 715.
[9] Y.S. Tan, M.P. Srinivasan, S.O. Pehkonen, S.Y.M. Chooi, Effects of ring substituents on the protective properties of self-assembled benzenethiols on copper, Corros. Sci. 48 (2006) 840.
[10] N. Huynh, T. Notoya, S.E. Bottle, D.P. Schweinsberg, Corros. Sci. 42 (2000) 259–274.
[11] A. Popova, M. Christov, S. Raicheva, E. Sokolova, Corros. Sci. 46 (2004) 1333–1350.
[12] A. Dafali, B. Hammouti, R. Mokhlisse, S. Kertit, Corros. Sci. 45 (2003) 1619–1630.
[13] D. Gopi, K.M. Govindaraju, S. Manimozhi, S. Ramesh, S. Rajeswari, J. Appl. Electrochem. 37 (2007) 681–689.
[14] X. Zhou, H.Y. Yang, F.H. Wang, Corros. Sci. 54 (2012) 193–200.
[15] Z. Khiati, A.A. Othman, M. Sanchez-Moreno, M.-C. Bernard, S. Joiret, E.M.M. Sutter, V. Vivier, Corros. Sci. 53 (2011) 3092–3099.
[16] Hui Yu, Kuang-Tsan K. Chiang, Lietai Yang, Threshold chloride level and characteristics of reinforcement corrosion initiation in simulated concrete pore solutions, Constr. Build. Mater. 26 (2012) 723–729.
[17] O.L. Riggs Jr., in: C.C. Nathan (Ed.), Corrosion Inhibitors, second ed., NACE (National Association of Corrosion Engineers), Houston, TX, 1973.
[18] K.F. Khaled, Corrosion control of copper in nitric acid solutions using some amino acids – A combined

experimental and theoretical study, Corros. Sci. 52 (2010) 3225–3234.

[19] W. Chen, S. Hong, H.B. Li, H.Q. Luo, M. Li, N.B. Li, Protection of copper corrosion in 0.5 M NaCl solution by modification of 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium self-assembled monolayer, Corros. Sci. 61 (2012) 53–62.

[20] El-Sayed M. Sherif, A.M. El Shamy, Mostafa M. Ramla, Ahmed O.H. El Nazhawy, 5-(Phenyl)-4H-1,2,4-triazole-3-thiol as a corrosion inhibitor for copper in 3.5% NaCl solutions, Materials Chemistry and Physics 102 (2007) 231–239.

[21] H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, D. Li, J. Appl. Electrochem. 32 (2002) 65.

[22] W.H. Li, Q. He, S.T. Zhang, C.L. Pei, B.R. Hou, J. Appl. Electrochem. 38 (2008) 289–295.

[23] E. Cano, J.L. Polo, A. La Iglesia, J.M. Bastidas, Adsorption 10 (2004) 219–225.

[24] G. Quartarone, L. Ronchin, A. Vavasori, C. Tortato, L. Bonaldo, Corros. Sci. 64 (2012) 82–89.

Author Profile

Ahmed A. Farag received the B.Sc., Master and Ph.D. degrees in Chemistry from Science Faculty, Al-Azhar University/ Egypt in 2002, 2007 and 2011, respectively. I worked in National Research Center (NRC), Polymers and Pigments Department/Egypt until 2007. Now I am working in Egyptian Petroleum Research Institute (EPRI), Petroleum Applications Department/Egypt from 2007 until now.