Mathematical Modeling of Corrosion Inhibition Behavior of Low Carbon Steel in HCl Acid

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Abstract: In this study, the nonlinear region of polarization curve near the corrosion potential can be discussed depending on data of over potential as a function of current densities. These data can be analyzed by suggestion a mathematical model take into account the effect of mass transfer on activation process. This model was used to evaluate the values of polarization resistance $R_p$ in presence and absence of phenylthiourea (PTU) as a corrosion inhibitor of low carbon steel in hydrochloric acid. The values of polarization resistance obtained by mathematical model compared with these obtained by Tafel parameters. The suggested $\beta$-model was very useful in evaluating the values of $R_p$. The maximum value of polarization resistance was 775.5 m$\Omega$ cm$^2$ at 30°C and 1M HCl in presence of 1 g L$^{-1}$ PTU, while the minimum value was 3.1 m$\Omega$ cm$^2$ at 60°C and 5 M HCl in absence of PTU. These results indicate that the polarization resistance values increased with increase in PTU concentration and decreases with increase in both temperature and acid concentration.

Key words: Current density, Stern and Geary equation, polarization resistance, phenylthiourea, over potential

INTRODUCTION

Many researches and literature concentrated on corrosion inhibition, but few of them deal with the effect of inhibitor concentration on polarization resistance. The polarization resistance is a measure of a metal to undergo corrosion in a certain environment, it is a slope of the potential-current (E-i) curve at the corrosion potential, i.e.,

$$R_p = \frac{\partial E}{\partial i_{corr}}$$

The shape of this curve around the corrosion potential and hence $R_p$, is determined by the sum of the partial E-i curve both anodic and cathodic half reaction (Bardal, 2004) The shape of both curves, in turn, depends on the respective kinetic parameters of their reaction. The current-potential curve of corroding metal is rather complex non-linear equation; hence a general analytical solution for $R_p$ is equally complex. Under some conditions, the E-i relation reduces to a simple form and hence a simple analytical solution for $R_p$ can be obtained. The Stern and Geary equation (Bardal, 2004) which can be written in equation as:

$$R_p = \frac{b_n b}{2.3RT} \frac{n}{\eta}$$

where, $\eta$ is over potential (i.e., $E-E_{corr}$), $i_{corr}$ is corrosion current density (A cm$^{-2}$), $b_n$ and $b$ are anodic and cathodic Tafel slopes (mV). Equation 1 assumed that the applied current is a linear function of electrode potential (about 10 mV around corrosion potential) and slope of this linear relationship is $R_p$. Equation 1 will have high percent of error because of the non-linearity of ($\eta$-i) relationship near the corrosion potential. According to Stern, the quotient ($\partial i/\partial E$) or ($\Delta E/\Delta i_{corr}$) is called the polarization resistance by analogy to resistance = (V/I) from conventional electricity. Other has suggested that the inverse of ($\Delta E/\Delta i_{corr}$) is called the conductance by obvious analogy to the inverse of electrical resistance, which is called the conductance (Allen and Faulkner, 2001).

Recently, Mansfield (2005) stated that, as new experimental technique mature and are more commonly used, various misconception and misnomers are sometimes perpetuated, which, when used often enough, are considered to be truth. Some of these myths, misconception and misnomers are the linear polarization

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technique. There exists the polarization resistance (P₀) technique and linear polarization technique, but there is no Linear Polarization Resistance (LPR) technique (Mansfield, 2005). As pointed out many years ago by El-Feky and Walter, 2000) polarization curves recorded in the vicinity of the corrosion potential (E_cor) are linear only in the exceptional case that the anodic (b⁺) and cathodic (b⁻) Tafel slopes are equal, i.e., b⁺ = b⁻. In the general case there can be appreciable curvature at E_cor. It is surprising that the little use is made of experimental data recorded for determining P₀ values to calculate Tafel slopes and i_cor values from data in pre-Tafel region (Sastri et al., 2007).

The term polarization resistance (P₀) must not be confused with resistance polarization (R). P₀ is polarization resistance at electrode/solution interface, knowing P₀ one can calculate electrochemical reactions rates (Sastri, 2001). P₀ represents the charge transfer resistance resulting from the separation of charges across the solid interface to the outside edge of the double layer. While R represents the resistance through the bulk solution (R_b) and the resistance of any films present on the working electrode surface (R_w) (i.e., R = R_b + R_w) (Trethewey and Chamberlain, 1996). The goal of this research is to study the effect of temperature, acid concentration and inhibitor concentration on polarization resistance. Two models suggested to evaluate the values of P₀, one of them take into account the effect of mass transfer on the activation control corrosion reaction and the deviation of P₀ from linearity. While, the other model is Stern and Geary equation which neglect the effect of mass transfer and assuming that the corrosion reaction is completely activation control.

**MATERIALS AND METHODS**

Specimens of cylindrical shape with outside diameter of 1.96 cm and a length of 0.5 cm, of low carbon steel were used. The specimens were first decreased with anular benzene and acetone and then annealed in a vacuum at 600°C for 1 h and cooled to room temperature. Samples were abraded in sequence under running tap water using emery paper of grade number 220, 320, 400 and 600 then washed with running tap water followed by distilled water, dried with clean tissue, immersed in acetone and benzene, kept in desiccators over silica gel bed until use. Corrosion cell has four necks, one was fitted with working electrode, one for immersing a thermometer in order to observe the test temperature and the other one had a spherical joint for manipulating the lugging capillary probe. The probe was adjusted to be in a distance not more than 2 mm from the working electrode. The fourth necks input graphite electrode. All potential values were measured in reference to Saturated Calomel Electrode (SCE). DC power supply which is equipped with current and voltage limiters offers better stability and control, its type is 6236B, triple output supply Hewlet Packard, USA. In present study, the corrosion reaction of low carbon steel in 1, 3 and 5 M HCl, at 30, 40, 50 and 60°C, in presence of 0.1, 0.75 and 1 g L⁻¹ phenylthiourea (PTU) as a corrosion inhibitor were studied. The low carbon steel working electrode specimens have the following chemical composition C 0.041 wt.%, Mn 0.311%, P 0.05%, S 0.007% and the remainder is iron.

**Mathematical model derivation:** The generalized equation for the polarization curve for metal corroding is given in Eq. 2 (Bockris et al., 1993):

\[
i = i_{corr} \exp \left( \frac{2.303F}{b_+} \lambda \exp \left( \frac{-2.303F}{b_-} \right) \right)
\]

where, \(\lambda\) is mass-transport correction factor,

\[
\lambda = \frac{1}{1 + \frac{i_{corr}}{i_{corr0}}} \exp \left( \frac{-2.303F}{b_-} \right)
\]

and the dimensionless factor \(i_{corr}/i_{corr0}\) can be substituted by \(\beta\). The cathodic part of the equation is mathematically equivalent to those of Albayra et al. (1973) and Flitt and Schweinsberg (2005), but it is expressed in a more general and easily applicable form. Massiani et al. (1984) use a correction factor of \((1-i\beta)\) in place of \(\lambda\). The expression of Britz and Hougaard (1983) can be shown to be an approximation of Eq. 2 when \(i_{corr}/i_{corr0} \ll 1\).

If the exponential terms of Eq. 2 are expanding in series, we come to the equation of polarization curve by the way of degree polynomial:

\[
i(\eta) = C_0 + C_1 \eta + C_2 \eta^2 + C_3 \eta^3 + \ldots + C_n \eta^n
\]

where, \(C_0, C_1, C_2, \ldots, C_n\) are constants. Equation 3 is a non-linear equation of \((\eta-i)\) relationship. The coefficient of \(\eta\) in Eq. 3 can be obtained by a non-linear estimation method using a statistical computer program from the set of experimental points of current densities vs. over potentials for the corrosion of low carbon steel in 1, 3 and 5 M HCl acid in absence and presence of 0.75 and 1 g L⁻¹ phenylthiourea (PTU) as a corrosion inhibitor, at different temperatures of 30, 40, 50 and 60°C. Equation 3 can be written in the form of the Macalaurin formula as (Andrei and Alexander, 2007):

\[
i(\eta) = \left( \frac{2}{b_+} \right) \eta + \frac{1}{2!} \left( \frac{2}{b_+} \right)^2 \eta^2 + \ldots + \frac{1}{n!} \left( \frac{2}{b_+} \right)^n \eta^n
\]
By comparison of Eq. 3 with Eq. 4, the polynomial coefficient can be written as:

$$C_1 = 2.303 \ln \left( \frac{1}{b_p} + \frac{1}{b_n} (1-\beta) \right).$$ (5)

The dimensionless factor \(i_{corr}/i_0\) or \(\beta\) can be used to determine the corrosion mechanism. The values of \(\beta\) have two limiting cases; \(\beta \to 0\) the corrosion kinetic is subjected by slow charge transportation; at \(\beta = 1\) the limiting stage of total process is the depolarizer transport to electrode surface. It was suggested that in the range of \(\beta < 0.05\) and \(\beta > 0.95\), it is possible to use the simplified form of Eq. 2 and 5, (for activation and diffusion mechanism) with out precision of calculations evaluation. The approach that suggested here was to use the values of the second coefficient of \(\beta\)-model to evaluate the value of \(P_x\), i.e., by using Eq. 5. It is clear that when \(\beta = 0\), \(C_1 = (1/P_x)\). This analysis may take into account the nonlinearity of polarization curve near the corrosion potential.

**RESULTS AND DISCUSSIONS**

Polarization experiments were carried out in acid solutions at different inhibitor concentration for each temperature and acid molarities as shown in Table 1 which shows the values of \(P_x\) at different conditions. Table 1 shows 48 experimental tests.

The effect of inhibitor concentration on values of \(P_x\) was calculated as mentioned previously from the values of \(C_1\) obtained from \(\beta\)-model. These values compared with the values obtained using Tafel extrapolation method depending on the values of \(b_p\) and \(b_n\) (i.e., \(P_x = b_p/(2.303 i_{corr}(b_p+b_n))\)). As shown in Fig. 1-6, the values of \(P_x\) in presence of inhibitor were higher than the values in absence of inhibitor. The values of polarization resistance decrease with both acid concentration and temperature increasing.

Figure 1 and 2 shows the effect of inhibitor concentration on polarization resistance. The values of \(P_x\) in presence of inhibitor were higher than the values in absence of inhibitor, which indicates that the resistance to the corrosion was increased. The values of polarization resistance \(P_x\) represent the charge resistance resulting from the separation of the charges across the solid interface to the outside edge of the double layer, these values were increased by increasing of inhibitor's

![Fig. 1: Variation of polarization resistance with inhibition concentration at 30°C at different acid concentration](image)

**Table 1: Polarization resistance of steel in HCl at different inhibitor concentration, temperature and acid concentration**

<table>
<thead>
<tr>
<th>Inhibitor concentration (g L⁻¹)</th>
<th>Temperature (°C)</th>
<th>HCl (M)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tr>
<td>0</td>
<td>30</td>
<td></td>
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<td>175.95</td>
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</table>
Fig. 2: Variation of polarization resistance with inhibition concentration at 40°C at different acid concentration.

Fig. 3: Variation of polarization resistance with acid concentration at different PUT concentration at 50°C.

Fig. 4: Variation of polarization resistance with acid concentration at different PUT concentration at 40°C.

Fig. 5: Variation of polarization resistance with temperature at different PUT concentration at 5 M HCl.

concentration. This suggests that as inhibitor concentration increase the fraction of surface of metal which covered by inhibitor will increase and this may prevent or reduce the charge transfer from the metal to the solution and hence, increase the value of \( P_b \). Mahmoud (2005) studied the inhibition effect of Pyrazol on the corrosion of metal in 1 M hydrochloric acid. The values of \( P_b \) are deduced for the working electrode from the slopes of the straight lines obtained from potential-current plots (\( \Delta E/\Delta I \)), he found that the values of \( P_b \) for the working electrode increase by increasing the concentration of inhibitors, which is the same as in present study.

Figure 3 and 4 show the selective effect of acid molarities on polarization resistance. In absence of inhibitor the values of \( P_b \) reduced as acid concentration increased. Normally, as the concentration of corrosive acid media is increased, the corrosion rate is likewise increased. This is primarily due to the fact that the amounts of hydrogen ions, which are active species, are increased. It is known that corrosion process consists of two or more partial reactions. For the corrosion of steel in acids, on of the reactions being the anodic reaction consists of an oxidation of the metal so that it changes from metallic state to an ionic state, \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2e \), while, the cathodic reaction occurs at different site from the anodic one, as follows \( 2\text{H}^+ + 2e \rightarrow \text{H}_2 \). Both cathodic and anodic reactions proceed at the same rate during electrochemical corrosion. Therefore, increasing in hydrogen ions concentration will encourage the hydrogen evolution or cathodic reaction and at the same time, this will leads to increase in anodic reaction, i.e., increasing in separation of metallic ions. This behavior will reduce the resistance of metal to the corrosion as acid concentration increased. The same behavior observed in presence of inhibitor, the values of \( P_b \) also reduced as acid concentration increased. The values of \( P_b \) were higher in
Fig. 6: Variation of polarization resistance with temperature at different PUT concentration at 1 M HCl

presence of inhibitor due to the formation of protective layer which reduces the corrosion process.

Temperature increases the rate of almost all chemical reaction (Shreir et al., 2000). Like most chemical reactions, the rates of corrosion of metal in aqueous acid solutions increase with temperature increasing and this leads to reduction in metal resistance. Therefore, as shown in Fig. 5 and 6, the polarization resistances decrease by increasing in temperature at any acid concentration. In presence of inhibitor, the effect of increasing in temperature on inhibited acid-metal reaction can be highly complex. The rate of the uninhibited, acid-metal, heterogeneous reaction increased and the fraction of the metal surface covered by adsorbed inhibitor changes, usually decrease (Philippe, 2002). These two reasons increase the corrosion rates and decrease the resistance of metal. Therefore, the same behavior of \( P_e \) observed in the presence of different concentration of PUT at different acid concentration. Generally, the values of \( P_e \) obtained by \( \beta \)-model were lower than that obtained using Tafel parameters. This \( \beta \)-model behavior explain the mixed influence of mass transfer and activation effect on corrosion process which leads to decrease the metal resistance, while the second model neglecting the mixed effect and hence a higher values of polarization resistance were obtained.

**CONCLUSION**

The values of \( P_e \) were obtained from the set of data of over potential as a function of current densities. The values of \( P_e \) increased by increasing in inhibitor concentration and this may be, due to the formation of protective film which increases the resistance of metal to corrosion. The values of \( P_e \) decreased with both temperature and acid concentration increase. This attributed to the increasing in corrosion rates with hydrogen ion concentration and with temperature increase, which lead to reduction in metal resistance. The highest value of polarization resistance was 775.5 \( \Omega \) cm\(^2\) at 30\(^\circ\)C and 1 M HCl in presence of 1 g L\(^{-1}\)PUT, while the lower value was 3.1 \( \Omega \) cm\(^2\) at 60\(^\circ\)C and 5 M HCl in absence of PTU. These results indicating the improvement of polarization resistance by increasing inhibitor’s concentration and decreasing of temperature.

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