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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 P_R 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 β -model was very useful in evaluating the values of P_R . The maximum value of polarization resistance was $775.5 \text{ m}\Omega \text{ cm}^2$ at 30°C and 1M HCl in presence of 1 g L^{-1} PTU, while the minimum value was $3.1 \text{ m}\Omega \text{ cm}^2$ 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 decreased 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.,

$$P_R = \left(\frac{\partial E}{\partial i} \right)_{E = E_{\text{corr}}}$$

The shape of this curve around the corrosion potential and hence P_R , 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 P_R is equally complex. Under some conditions, the E-i relation reduces to a simple form and hence a simple analytical solution for P_R can be obtained. The Stern and Geary equation (Bardal, 2004) which can be written in equation as:

$$P_R = \left(\frac{\partial \eta}{\partial i} \right)_{\eta=0} = \frac{b_a b_c}{(2.303 i_{\text{corr}} (b_a + b_c))} \quad (1)$$

where, η is over potential (i.e., $E - E_{\text{corr}}$), i_{corr} is corrosion current density (A cm^{-2}), b_a and b_c 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 P_R . Equation 1 will have high percent of error because of the non-linearity of (η -i) relationship near the corrosion potential. According to Stern, the quotient ($\partial \eta / \partial i$) or ($\Delta E / \Delta i_{\text{app}}$) is called the polarization resistance by analogy to resistance = (E/I) from conventional electricity. Other has suggested that the inverse of ($\Delta i_{\text{app}} / \Delta E$), is called the corrodance 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

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

The term polarization resistance (P_R) must be not confused with resistance polarization (R). P_R is polarization resistance at electrode/solution interface, knowing P_R one can calculate electrochemical reactions rates (Sastri, 2001). P_R 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_s) and the resistance of any films present on the working electrode surface (R_f) (i.e., $R = R_s + R_f$) (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 P_R , one of them take into account the effect of mass transfer on the activation control corrosion reaction and the deviation of P_R 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 analar 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):

$$i = i_{corr} \left(\exp\left(\frac{2.3\Delta E}{b_c}\right) - \lambda \exp\left(-\frac{2.3\Delta E}{b_c}\right) \right) \tag{2}$$

where, λ is mass-transport correction factor,

$$\lambda = \frac{1}{1 - \frac{i_{corr}}{i} + \frac{i_{corr}}{i} \exp\left(-\frac{2.3\Delta E}{b_c}\right)}$$

and the dimensionless factor (i_{corr}/i) can be substituted by β . The cathodic part of the equation is mathematically equivalent to those of Albaya *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/i) in place of λ . The expression of Britz and Hougaard (1983) can be shown to be an approximation of Eq. 2 when (i_{corr}/i) <<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:

$$i(\eta) = C_0 + C_1\eta + C_2\eta^2 + C_3\eta^3 + \dots + C_n\eta^n \tag{3}$$

where, $C_0, C_1, C_2, \dots, C_n$ are constants. Equation 3 is a non-linear equation of (η - i) relationship. The coefficient of η 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 Maclaurin formula as (Andrei and Alexander, 2007):

$$i(\partial_i) = \left(\frac{\partial i}{\partial \eta}\right)_{\eta=0} \eta + \frac{1}{2!} \left(\frac{\partial^2 i}{\partial \eta^2}\right)_{\eta=0} \eta^2 + \dots + \frac{1}{n!} \left(\frac{\partial^n i}{\partial \eta^n}\right)_{\eta=0} \eta^n \tag{4}$$

By comparison of Eq. 3 with Eq. 4, the polynomial coefficient can be written as:

$$C_1 = 2.303i_{corr} \left\{ \left(\frac{1}{b_a} \right) + \left(\frac{1}{b_c} \right) (1-\beta) \right\} \quad (5)$$

The dimensionless factor (i_{corr}/i_0) or (β) can be used to determine the corrosion mechanism. The values of β have two limiting cases; $\beta \rightarrow 0$ 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 β -model to evaluate the value of P_R , i.e., by using Eq. 5. It is clear that when $\beta = 0$, $C_1 = (1/P_R)$. This analysis may take into account the nonlinearly 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_R at different conditions. Table 1 shows 48 experimental tests.

The effect of inhibitor concentration on values of P_R was calculated as mentioned previously from the values of C_1 obtained from β -model. These values compared with the values obtained using Tafel

extrapolation method depending on the values of b_a , b_c and i_{corr} (i.e., $P_R = b_a b_c / (2.303 i_{corr} (b_a + b_c))$). As shown in Fig. 1-6, the values of P_R 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_R 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_R 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

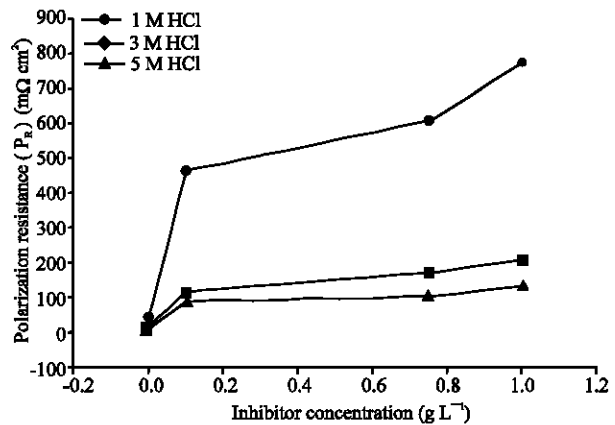


Fig. 1: Variation of polarization resistance with inhibition concentration at 30°C at different acid concentration

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

Inhibitor concentration (g L ⁻¹)	Temperature (°C)	P _R (mΩ cm ²)					
		HCl (M)					
		1		3		5	
		β-model	Tafel	β-model	Tafel	β-model	Tafel
0	30	40.11	40.94	17.15	22.45	11.31	13.850
0.1		463.30	494.05	115.60	117.12	88.76	110.280
0.75		607.20	614.76	170.10	175.95	101.00	141.670
1.0		775.50	795.46	206.00	208.50	133.30	145.150
0	40	14.30	21.23	12.80	19.81	4.50	9.880
0.1		171.10	185.93	83.20	100.75	58.00	89.180
0.75		220.70	243.16	140.10	132.10	170.88	90.191
1.0		258.90	337.90	173.00	190.68	118.00	104.570
0	50	12.10	19.55	7.50	10.55	5.10	9.470
0.1		122.20	130.55	21.40	30.45	11.10	17.550
0.75		170.30	199.22	32.30	55.55	13.30	18.910
1.0		196.60	230.41	45.40	60.11	17.70	25.130
0	60	10.90	14.39	5.40	6.46	3.10	5.200
0.1		101.30	110.25	15.30	14.98	10.70	22.610
0.75		120.10	130.71	22.22	33.13	11.12	12.890
1		150.50	170.31	43.11	50.10	15.33	20.310

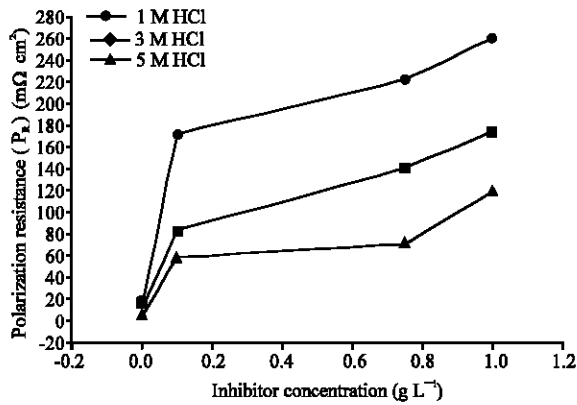


Fig. 2: Variation of polarization resistance with inhibition concentration at 40°C at different acid concentration

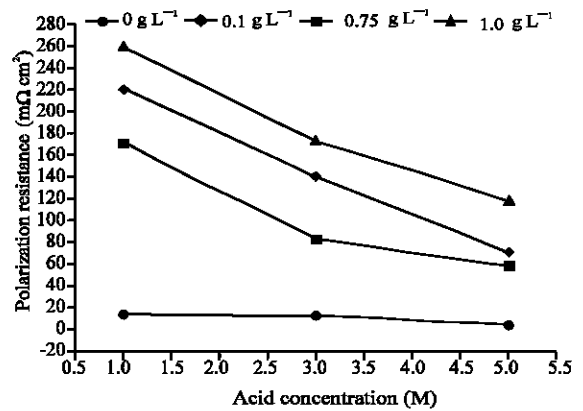


Fig. 4: Variation of polarization resistance with acid concentration at different PUT concentration at 40°C

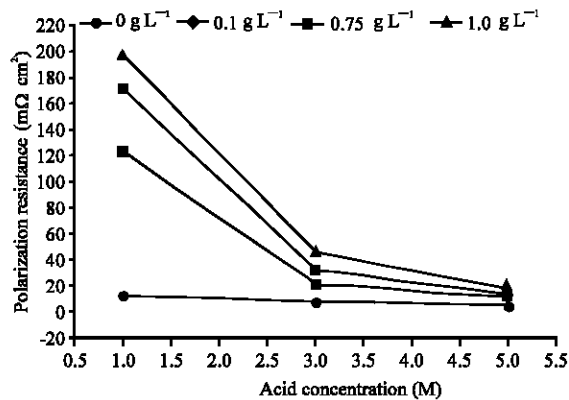


Fig. 3: Variation of polarization resistance with acid concentration at different PUT concentration at 50°C

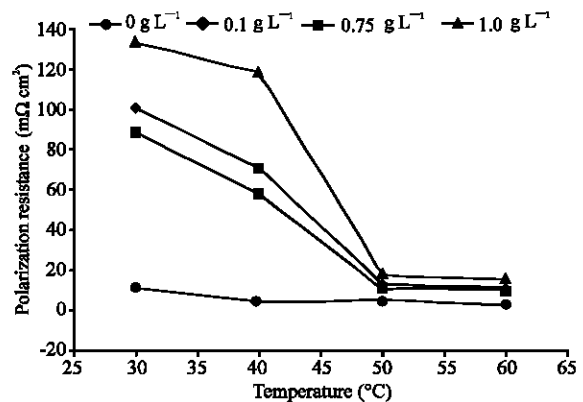


Fig. 5: Variation of polarization resistance with temperature at different PUT concentration at 5 M HCl

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_R . Mahmoud (2005) studied the inhibition effect of Pyrazol on the corrosion of metal in 1 M hydrochloric acid. The values of P_R 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_R 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_R 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, one 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, $Fe \rightarrow Fe^{++} + 2e$, while, the cathodic reaction occurs at different site from the anodic one, as follows $2H^+ + 2e \rightarrow H_2$. 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 lead 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_R also reduced as acid concentration increased. The values of P_R were higher in

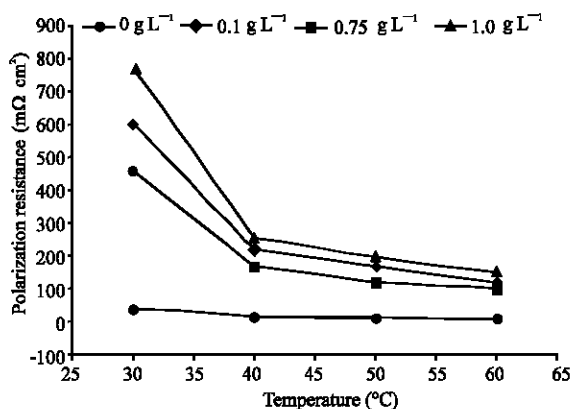


Fig. 6: Variation of polarization resistance with temperature at different PUT concentration at 1 M HCl

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_R observed in the presence of different concentration of PTU at different acid concentration. Generally, the values of P_R obtained by β -model were lower than that obtained using Tafel parameters. This β -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_R were obtained from the set of data of over potential as a function of current densities. The values of P_R 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_R 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 mΩ cm² at 30°C and 1 M HCl in presence of 1 g L⁻¹ PTU, while the lower value was 3.1 mΩ cm² at 60°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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REFERENCES

- Albaya, H.C., O.A. Cobo and J.B. Bessone, 1973. Some consideration in determining corrosion rates from linear polarization measurements. *Corrosion Sci.*, 13: 287-287.
- Allen, J.B. and L.R. Faulkner, 2001. *Electrochemical Methods Fundamentals and Applications*. 2nd Edn., John Wiley and Sons, Inc., London.
- Andrei, D. and V.P. Alexander Manzhurov, 2007. *Handbook of Mathematics for Engineers and Scientists*. Taylor and Francis Group, LLC., ISBN: 1584885025.
- Bardal, E., 2004. *Corrosion and Protection*. Springer-Verlag Ltd., London.
- Bockris, J., N.G. Smart and M. Gamboa-Aldeco, 1993. Corrosion mechanisms of iron in concentrated acidic zinc chloride media. *Corrosion Sci.*, 34: 759-777.
- Britz, D. and G. Hougaard, 1983. Effects of mixed activation and transport control of the cathodic process on corrosion current measurements. *Corrosion Sci.*, 23: 987-987.
- El-Feki, A.A. and G.W. Walter, 2000. Corrosion rate measurements under conditions of mixed charge transfer plus diffusion control including the cathodic metal ion deposition partial reaction. *Corrosion Sci.*, 42: 1055-1070.
- Flitt, H.J. and D.P. Schweinsberg, 2005. Evaluation of corrosion rate from polarization curves not exhibiting a Tafel region. *Corrosion Sci.*, 47: 3034-3052.
- Mahmoud, S.S., 2005. Corrosion behavior and its inhibition of a copper-iron alloy in hydrochloric acid solution. *Corrosion*, 12: 1127-1135.
- Mansfield, F., 2005. Editorial: Misconceptions and misnomers. *Corrosion*, 61: 1019-1019.

- Massiani, Y., J.P. Crousier, J. Galea and R. Romanetti, 1984. Determination des parametres des courbes de polarisation a l'aide d'un programme de calcul par regression non lineaire. Application a la corrosion d'un metal en milieu acide en presence d'oxygene dissous. *Electrochim Acta*, 29: 1679-1679.
- Philippe, M., 2002. *Corrosion Mechanisms in Theory and Practice*. 2nd Edn., Marcel Dekker, Inc., USA., ISBN: 0 8247 0666-8.
- Sastri, V.S., 2001. *Corrosion Inhibitors Principles and Applications*. Johan Wiley and Sons Publisher, New York, ISBN: 0-471-97608-3.
- Sastri, V.S., E. Ghali and M. Elboudjaini, 2007. *Corrosion Prevention and Protection*. Johan Wiley and Sons Publisher, USA.
- Shreir, L.L., R.A. Jarman and G.T. Burstein, 2000. *Corrosion, Metal/Environment Reactions*. 3rd Edn., Butterworth-Heinemann, Britain.
- Trethewey, K.R. and J. Chamberlain, 1996. *Corrosion for Science and Engineering*. 2nd Edn., Longman, USA., ISBN: 0582238692.