

Corrosion Behavior of Mild Steel in Hydrochloric Acid Solutions

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The corrosion behaviour and mechanism for mild steel in hydrochloric acid solutions was studied by chemical (hydrogen evolution, HE & mass loss, ML) and electrochemical (electrochemical impedance spectroscopy & potentiodynamic polarization) methods at 25° C. The chemical results revealed that mild steel corrodes in HCl solutions with a reaction constant of 0.56 and the corrosion rate increases with the increase in acid concentration. Microstructural studies for mild steel after immersion in HCl solutions of different concentrations showed general and pitting corrosion and the latter becomes more pronounced at higher level of HCl concentration. Accordingly, it was found that R_{ct} value decreases while both C_{dl} and i_{corr} values increase with increasing HCl concentration. PDP results revealed that the steel dissolution is anodically controlled. Estimation of the ratio Z/v_s from PDP data indicated that mild steel dissolution occurs via multistep mechanism. This mechanism involves two steps each of them is characterized by one electron release and one of them is the rate determining step. The rate determining step may involve adsorbed $[FeOH]_{ads}$ and/or $[FeClOH]_{ads}^-$ groups.

Keywords: Mild steel; Corrosion; Hydrochloric acid; Impedance; Polarization

1. INTRODUCTION

Mild steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions [1]. Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of hydrochloric acid. This acid is very corrosive to most of the common metals and alloys [2].

The aim of this work is to investigate the corrosion behaviour and mechanism for mild steel in solutions of HCl (0.25-2.5 mol dm⁻³) at 25 °C by using chemical (hydrogen evolution, HE and Mass

loss, ML) and electrochemical (electrochemical impedance spectroscopy, EIS and potentiodynamic polarization, PDP) methods. The morphology of mild steel surface before and after immersion in HCl solutions was examined at different concentrations of the acid.

2. EXPERIMENTAL PART

2.1. Materials

Corrosion tests by chemical and electrochemical measurements were performed using rods prepared from mild steel having the composition: 0.02% (P), 0.37% (Mn), 0.03% (S), 0.01% (Mo), 0.039% (Ni), 0.21% (C) and the remainder is Fe. The electrode preparation and pretreatment for chemical and electrochemical measurements were described in previous work [3].

2.2. Solutions

The solutions of HCl in the concentration range from 0.25 to 2.50 mol dm⁻³ were prepared from analytical grade concentrated HCl (BDH company) using bidistilled water.

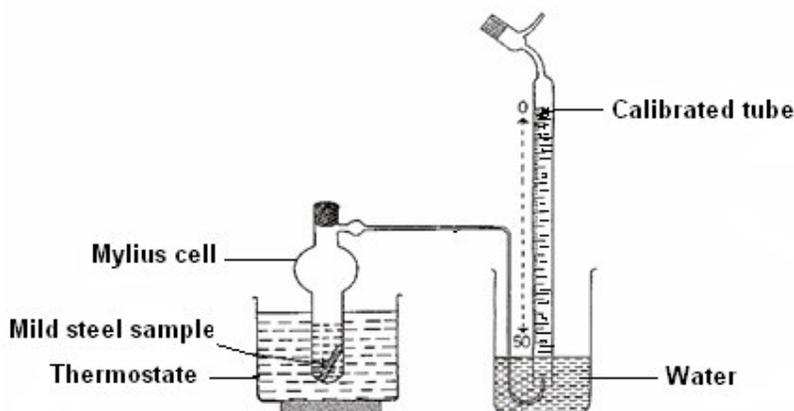


Figure 1. Schematic diagram of the system used in chemical measurements

2.2. Procedures

2.2.1. Chemical measurements

The apparatus and procedures for HE and ML determination of corrosion rates can be described as below:

50 ml of tested solution were placed in a cell of Mylius type (Fig. 1) and a degreased, weighed mild steel specimen was introduced into the solution. The time was recorded and H₂ evolved was collected in a calibrated tube by downward displacement of water over time interval of 90 min. A plot

of H_2 evolved per unit area ($ml\ cm^{-2}$) against time (min.) in the presence of different concentrations of the studied inhibitors produced a straight lines with slope represents the rate of H_2 evolved (ρ_{HE} , $ml\ cm^{-2}\ min^{-1}$). At the end of each experiment of HE, the mild steel specimen was withdrawn from the tested solution, washed thoroughly with bidistilled water followed by acetone and dried with air, then weighed again. The rate of mass loss (ρ_{ML} , $g\ cm^{-2}\ min^{-1}$) was calculated as follows:

$$\rho_{ML} = \frac{m_b - m_a}{S \cdot t_{\infty}} \quad (1)$$

Where m_b and m_a are the mass of mild steel specimen before and after immersion in the tested solution, respectively, S is the surface area of the specimen and t_{∞} is the end time of each experiment.

2.2.2. Electrochemical measurements

EIS and PDP measurements were run on ACM Gill AC instrument connected to Samsung computer (Bridge DVD ASUS 8X max.) by using a conventional electrochemical cell of three electrodes are mild steel as working electrode, $Ag/AgCl_{(s)}/KCl_{saturated\ (aq)}$ as reference electrode and platinum wire as auxiliary electrode, Figure 2. The EIS measurements were performed at open circuit potential after 15 min. of immersion in the tested solution with amplitude of 10 mV. The covered frequency range was 30 KHz to 0.5 Hz. The charge transfer resistance (R_{ct}) values have been calculated from the difference in the impedance at low and high frequencies.

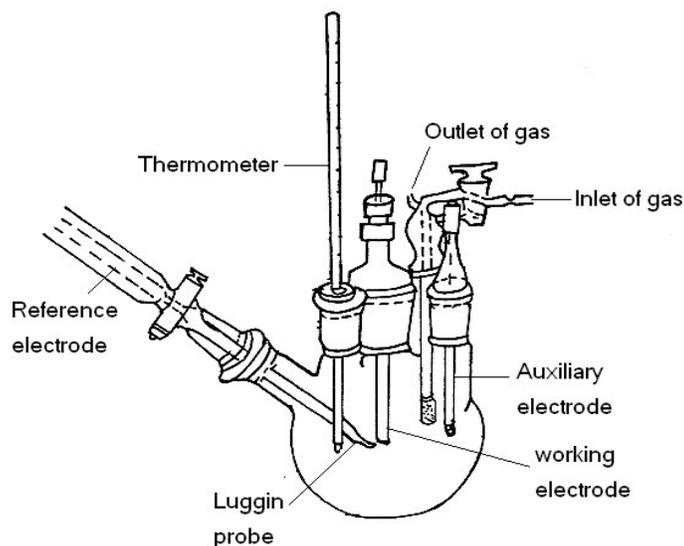


Figure 2. Schematic diagram for the electrochemical cell

The capacitance of the double layer (C_{dl}) values are estimated from the frequency (f) at which the imaginary component of the impedance ($-Z''$) is maximum and obtained from the equation:

$$f(-Z''_{\max.}) = \frac{1}{2\pi \cdot C_{dl} R_{ct}} \quad (2)$$

The PDP measurements were carried out after the impedance test, at sweep rate of 60 mV min^{-1} and within the potential range from -700 to -300 mV . Tafel lines extrapolation method was used for detecting $i_{corr.}$ and $E_{corr.}$ values for the studied systems. Because of the presence of a degree of non-linearity in the part of the obtained polarization curves, the corresponding anodic and cathodic Tafel slopes (β_a and β_c) were calculated as a slope of the points after corrosion potential (E_{corr}) by $\pm 50 \text{ mV}$ using a computer least square analysis.

2.2.3. Morphological study

The morphological of mild steel surface was studied by making photomicrograph of the surface before and after immersion in HCl solutions of different concentrations. The specimens were examined using an optical microscope (Leitz METALLUX3, WETZLAR, Germany).

It must be noted that all measurements were conducted in aerated, stagnant solutions at $25 \text{ }^\circ\text{C}$.

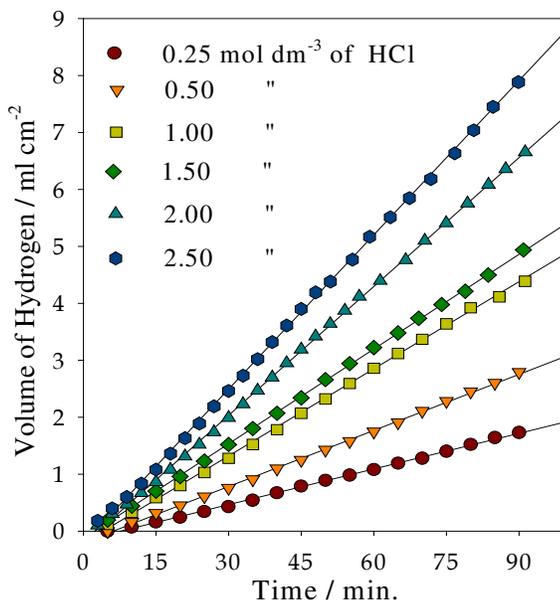


Figure 3. Volume of hydrogen evolved versus time for mild steel corrosion in HCl solutions of different concentrations at $25 \text{ }^\circ\text{C}$.

3. RESULTS AND DISCUSSION

3.1. Hydrogen Evolution and Mass loss Measurements

Data are plotted for volume of H_2 gas evolved against time in minutes for 0.25 to 2.50 mol dm^{-3} of HCl concentrations and presented in Fig. 3. Slopes of such lines are estimated and taken as the rates

of corrosion reaction as mentioned before. The good linearity in the relations indicates the absence of insoluble film on the metal surface during corrosion.

Table 1. Corrosion rates for mild steel sample at different concentrations of HCl solutions at 25 °C.

c_{HCl} (mol dm ⁻³)	0.25	0.5	1.0	1.5	2.0	2.5
$\rho_{\text{HE}} \times 10^2$ ml cm ⁻² min ⁻¹	2.083	3.308	5.157	5.658	7.645	9.106
$\rho_{\text{ML}} \times 10^5$ g cm ⁻² min ⁻¹	5.841	8.143	12.214	13.060	17.756	20.986

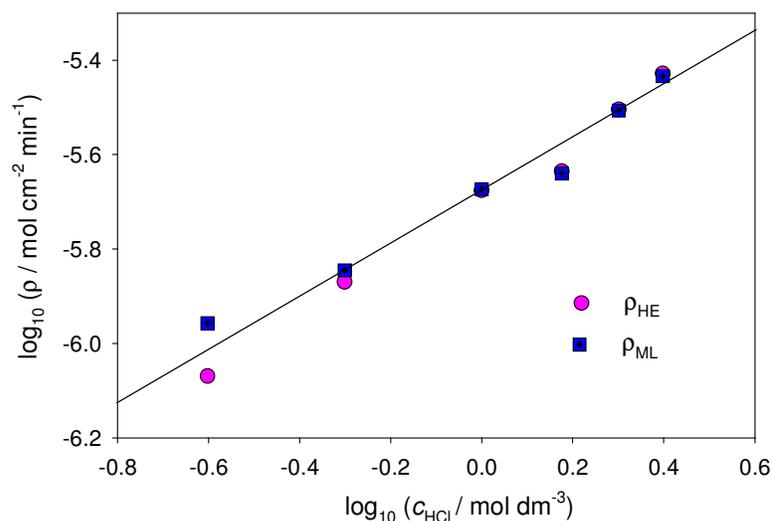


Figure 4. Plot of $\log_{10}(\rho / \text{mol cm}^{-2} \text{min}^{-1})$ vs $\log_{10}(c_{\text{HCl}} / \text{mol dm}^{-3})$

The calculated corrosion rates (ρ_{HE} and ρ_{ML}) obtained from HE and ML measurement, respectively, against concentrations are tabulated in Table 1. As observed, both ρ_{HE} and ρ_{ML} increase with increasing of acid concentration, indicating acceleration behaviour for the metal dissolution. This result is expected because with increasing acid concentration, both acidity and Cl⁻ ion concentration are increased too. According to Oakes and West [4], iron dissolution in HCl solutions depends principally upon the chloride ion activity over the pH range 0.0 to -0.6. While at more negative pH values and at high chloride ion activity, the corrosion rate is more dependent upon pH. On the other hand, Gad Allah et al.[5] pointed out that iron dissolution in HCl solutions depends on H⁺ ion more than the Cl⁻ ion.

It was known that corrosion rates (ρ_{HE} and ρ_{ML}) can be correlated with the acid concentration by the following equation [6]:

$$\log_{10} \rho = \log k + B \log_{10} c_{\text{HCl}} \quad (3)$$

where k is the specific reaction rate constant, B is the reaction constant and c_{HCl} is the amount concentration of HCl solution. k value represents the corrosion rate when the concentration of acid is equal to unity. The hydrogen evolution and mass loss is produced by the same reaction:

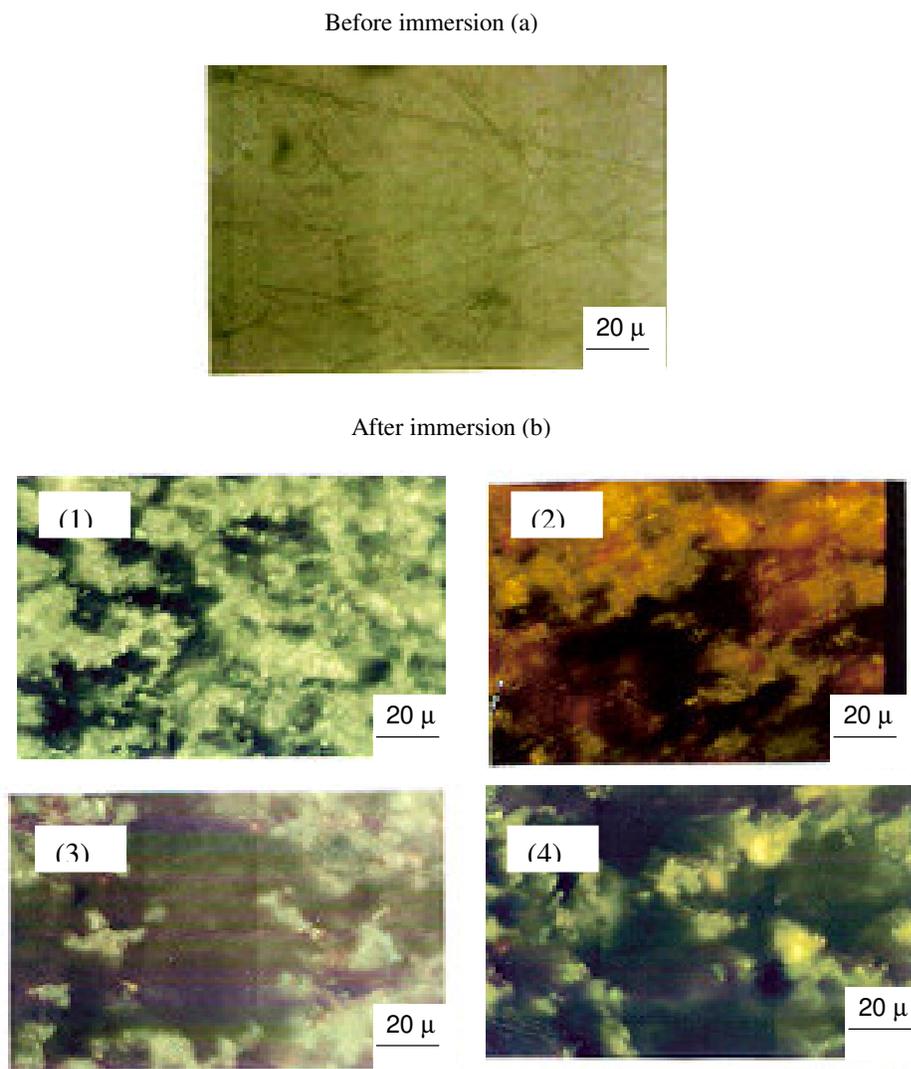
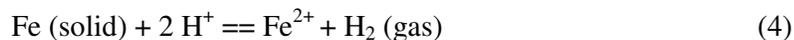


Figure 5. Micrographs for mild steel surface in (a) before and (b) after immersion for 90 min at 25 °C in HCl solutions: (1) 0.25; (2) 1.00; (3) 1.50 and (4) 2.50 mol dm⁻³.

So to estimate the reaction constant, the corrosion rates obtained from HE and ML methods must be converted to the same unit (mol cm⁻² min⁻¹) by assuming that the HE reaction occurred at 1.01325×10⁵ Pa. Figure 4 gives the relation log₁₀ρ (ρ, mol cm⁻² min⁻¹) versus log₁₀ c_{HCl} for the studied sample. Figure 4 shows that there is discrepancy between ρ_{HE} and ρ_{ML} only at the lowest HCl concentrations. The straight line in this figure correlates all points (even that showed discrepancy

between ρ_{HE} and ρ_{ML}) with good correlation coefficient of 0.969. The estimated B and k values are 0.56 and $2.07 \times 10^{-6} \text{ mol cm}^{-2} \text{ min}^{-1}$, respectively. Mathur and Vasudevan [6] reported that iron corrodes in HCl solution by a reaction constant of 0.56 indicating good consistency with that obtained in the present work.

Microstructural studies for mild steel surface were performed before and after immersing the studied specimen in the tested solution for 90 min. at 25°C and illustrated in Figure 3. Before exposure to the corrosive solution, parallel features on the clean polished steel surface which are associated with polishing scratches were observed, Figure 5(a). Examination of Figures 5(b) revealed that the corrosion attack (general and pitting corrosion) becomes more pronounced as HCl concentration increases. At acid concentrations $\leq 1.00 \text{ M}$, Figures 5(1b and 2b), the pits were partly closed, deep and did not contain visible deposit, while at acid concentrations $> 1.00 \text{ M}$, Figures 5(2b-4b), the pits were open and their diameter was very large. These pits were full of black corrosion products. These observations can be explained on the basis of Cl^- ion activity and the extent of its contribution in acceleration metal dissolution [7].

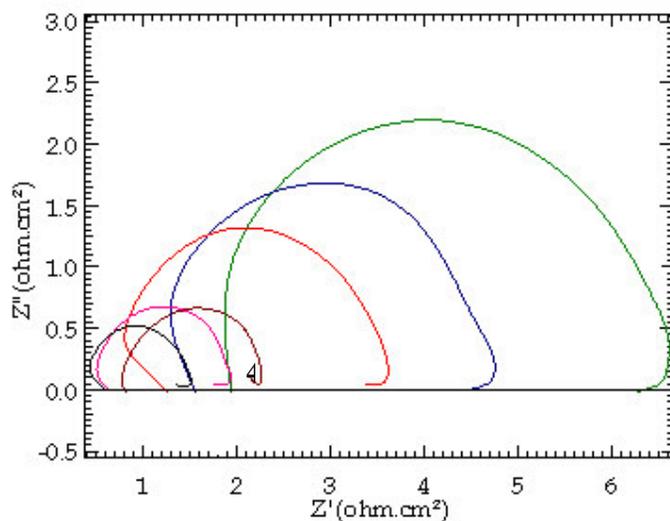


Figure 6. Nyquist plots for mild steel in HCl solutions of (1) 0.25, (2) 0.50, (3) 1.00, (4) 1.5, (5) 2.00 and (6) 2.50 mol dm^{-3} at 25 °C

2.2. Electrochemical impedance spectroscopy measurements

The corrosion of mild steel specimen in aerated HCl solutions of different concentrations, was investigated by EIS at the open circuit potential at 25° C. Figure 6 shows clearly that Nyquist plots for mild steel in the tested acid solutions are characterized by depressed semicircles at high to medium frequencies and small inductive loops at low frequencies. The previous electrochemical systems can be represented by the simplified Randle equivalent circuit, Fig. 7, which shows parallel combination of a charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}), both in series with solution resistance (R_s). According to the electrochemical theory, R_{ct} is inversely proportional to the corrosion

current density (i.e. corrosion rate), so it is analogous to the use of polarization resistance in the Stern-Geary equation [8]:

$$i_{\text{corr.}} = \frac{\beta'}{R_{\text{ct}}} \quad (4a)$$

$$i_{\text{corr.}} \cdot R_{\text{ct}} = \beta' \quad (4b)$$

$$\text{where } \beta' = \frac{\beta_a \cdot \beta_c}{2.303(\beta_a + \beta_c)}$$

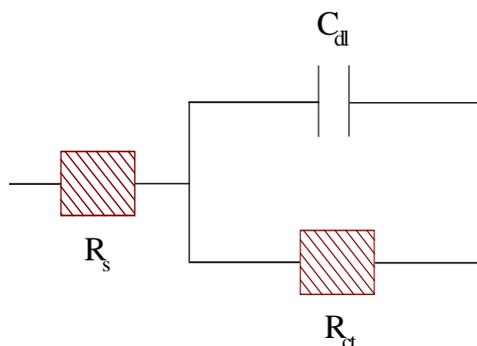


Figure 7. Schematic diagram for the simplified Randle equivalent circuit.

All values of R_{ct} , C_{dl} , $i_{\text{corr.}}$ and β' have been estimated. Figure 8 represents the variation of R_{ct} , C_{dl} , $i_{\text{corr.}}$ and β' as a function of HCl concentration. All experimental results obtained from EIS measurements may be interpreted as follows:

- 1) The depression in the semicircles is a characteristic behavior for solid electrodes and often referred to a frequency dispersion have been attributed to roughness and inhomogeneities of solid surfaces [9].
- 2) The well defined capacitive loop suggests that the corrosion process occurs under charge transfer control (activation control) [10, 11], and as the HCl concentration increases, the diameter of the capacitive loop (i.e. R_{ct}) decreases, Figure 8(a). While C_{dl} and $i_{\text{corr.}}$ values tend to increase, Figure 8(b & c), respectively.
- 3) The inductive loop may indicate the occurrence of localized attack (pitting corrosion by Cl^- ions) [12].
- 4) $i_{\text{corr.}}$ is strictly inversely proportional to R_{ct} as indicated from the constant value of β' at all studied concentrations of HCl, Figure 8(d). The average value of the proportionality constant β' is about 0.0261 V which is within the range of β' (0.010-0.030 V) that recorded for steel in acid media [13].

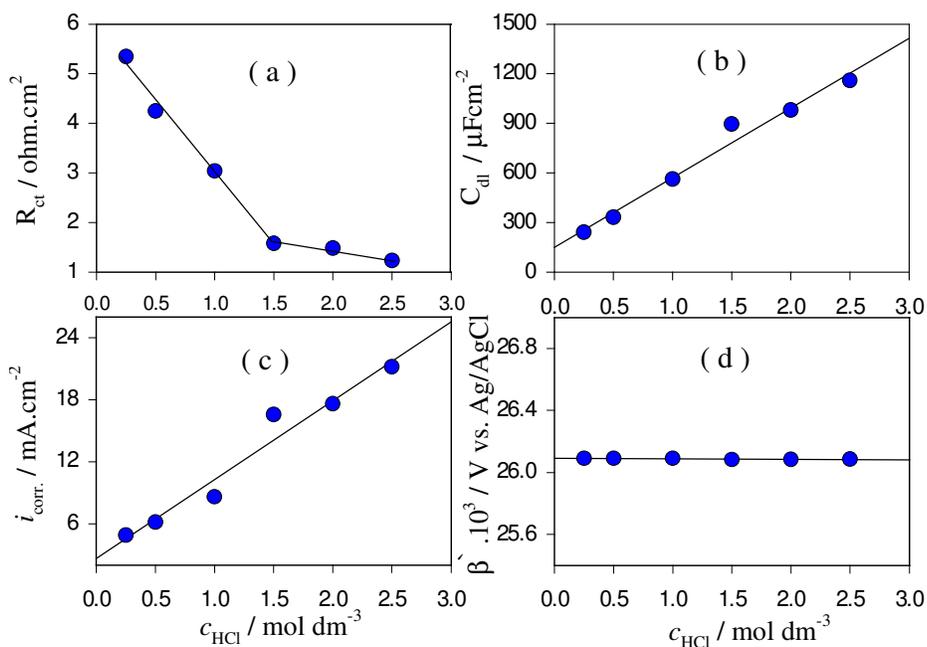


Figure 8. Variation of R_{ct} , C_{dl} , i_{corr} and β' with c_{HCl} at 25 °C.

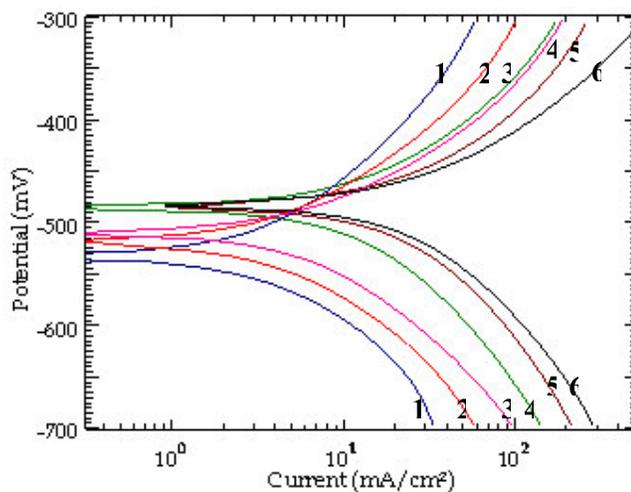


Figure 9. PDP curves for mild steel in HCl solutions of (1) 0.25, (2) 0.50, (3) 1.00, (4) 1.5, (5) 2.00 and (6) 2.50 mol dm⁻³ at 25 °C.

3.3. Potentiodynamic polarization measurements

The effect of aerated HCl solutions of different concentrations on the anodic and cathodic polarization behavior of mild steel electrode have been investigated at 25°C, Figure 9. The polarization

curves show that both the anodic and cathodic polarization curves were shifted to higher current densities and the corrosion potential ($E_{\text{corr.}}$) of the working electrode is shifted into the noble (positive) direction with increasing acid concentration.

Table 2. Potentiodynamic polarization parameters for mild steel corrosion in HCl solutions of different concentrations at 25 °C.

c_{HCl} (mol dm^{-3})	$-E_{\text{corr.}}$ (V)	$i_{\text{corr.}}$ (mA.cm^{-2})	β_a (V.dec^{-1})	$-\beta_c$ (V.dec^{-1})
0.25	0.534	3.913	0.075	0.087
0.5	0.519	6.896	0.075	0.087
1.0	0.508	10.205	0.075	0.087
1.5	0.484	13.836	0.075	0.087
2.0	0.480	17.497	0.075	0.087
2.5	0.477	20.230	0.075	0.087

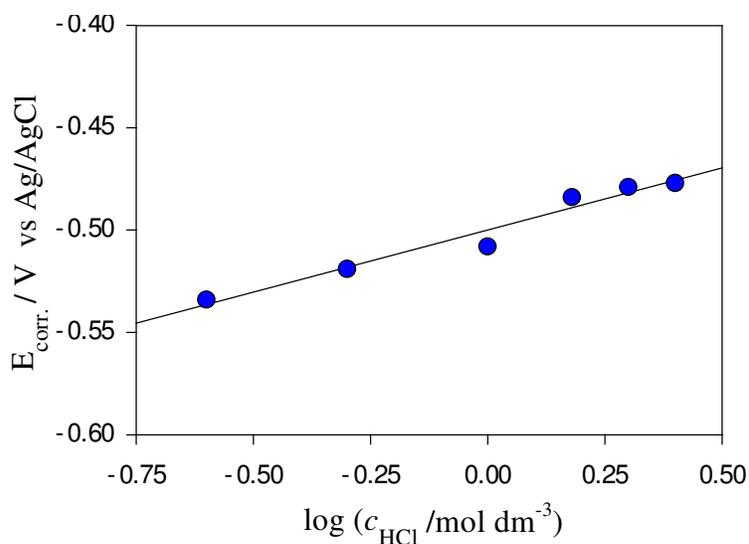


Figure 10. The relation between $E_{\text{corr.}}$ for mild steel and $\log c_{\text{HCl}}$ at 25 °C.

Values of corrosion potential ($E_{\text{corr.}}$), corrosion current density ($i_{\text{corr.}}$) and both anodic and cathodic Tafel slopes (β_a and β_c , respectively) were estimated and listed in Table (2) and the obtained results are interpreted as follows :

1. Tafel slopes (β_a and β_c): As shown, both anodic and cathodic Tafel slopes are not changed by increasing HCl concentration, which indicates that the mechanism of metal dissolution does not change with increasing acid concentration. However the PDP results are in agreement to the work of

Chin and Nobe [7] show that the polarization curves have two quite distinct Tafel slopes and at low polarization potentials, the rate of iron dissolution is accelerated by chloride ions with anodic Tafel slope of 0.075 V/dec^{-1} .

2. Corrosion current density (i_{corr}): It was observed, that i_{corr} value increases with increasing HCl concentration, indicating that the corrosion rate is increased with acid concentration.

3. Corrosion potential (E_{corr}): E_{corr} Value is shifted to more positive potentials with increasing HCl concentration, indicating that the polarization occurs mostly at the anode, hence the corrosion rate is said to be anodically controlled [14]. The estimated average value of E_{corr} (-0.484 V) is in good agreement with that recorded by Ashassi and Seifzadeh [11] for steel corrosion in 1.0 M HCl at 25°C . However, the linear relation between E_{corr} and $\log c_{\text{HCl}}$ is illustrated in Figure 10 and can be given by the following equation [12]:

$$E_{\text{corr}} = E_{\text{corr}}^{\circ} + \frac{\ln 10 RT}{ZF} \log_{10} c_{\text{HCl}} \quad (5)$$

where E_{corr}° is the corrosion potential when the acid concentration equal to unity, R is the universal gas constant, T is the absolute temperature, Z is the number of electrons involved in the corrosion reaction, F is the Faraday constant and c_{HCl} is the amount concentration of HCl. The estimated value of E_{corr}° is about -0.500 V which is similar to that recorded in Table 2 for mild steel sample in 1.0 M HCl . At 25°C and for Z equal to unity the theoretical slope of equation (5) equals $\frac{\ln(10) RT}{ZF} = 0.05916 \text{ V}$ which is in good consistency with the slope obtained from regression analysis of E_{corr} vs. $\log c_{\text{HCl}}$ (0.061 V). However, the deviation of Z from the expected value ($Z=2$ electrons) may be related to multistep process for electron release during the metal dissolution. So, a stoichiometric number (ν_s) must be involved in the previous relation as follows:

$$E_{\text{corr}} = E_{\text{corr}}^{\circ} + \frac{\ln 10 RT \nu_s}{ZF} \log_{10} c_{\text{HCl}} \quad (6)$$

ν_s indicates how many times the elementary act, which determines the rate of the overall electrode reaction, must occur for the end product to be formed. If we considered that the net charge transferred during the electrode reaction is equal to Z and small deviation from equilibrium is occurred, a charge equal to Z/ν_s will be transferred in a once occurring rate determining step (**r.d.s.**) [15]. By taking into account the slope of the relation in Figure 6 which is in accordance of Equation 6, one can calculate the net charge transferred in the rate determining step and it was found equal to one electron ($Z/\nu_s \approx 1$ electron). Moreover the ratio Z/ν_s is also calculated from the following equation [15]:

$$Z/v_s = \beta^{\circ} \left(\frac{1}{\beta_a} - \frac{1}{\beta_c} \right) \quad (7)$$

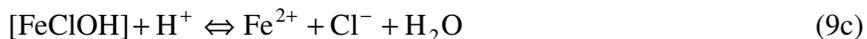
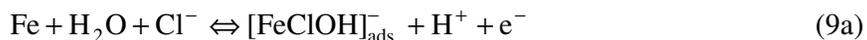
where $\beta^{\circ} = 2.303 \frac{RT}{F}$. By introducing the value of both β_a and β_c , Table 2, in Equation (7), the resultant value of the ratio (Z/v_s) is approximately of unity which is in good agreement with the result obtained from the slope of the relation in Equation (6).

If we assume that the electrochemical reaction of iron corrosion involves transfer of two electrons, then there are two steps ($v_s = 2$) each one represents transfer of one electron and one of them may be considered the rate determining step. This result is in good agreement with the mechanisms that are suggested for iron dissolution [7, 16] in:

(i) aqueous solutions:



(ii) aqueous solutions containing Cl^- ions:



Where $[\text{FeOH}]_{\text{ads.}}$ and $[\text{FeClOH}]_{\text{ads.}}^-$ are the adsorbed intermediates which each of them is involved in the rate determining step (Equations 8b and 9b, respectively) of mild steel dissolution according to mechanism (i) and (ii), respectively. It must be pointed out that the presence of Cl^- ions does not exclude dissolution through the $[\text{FeOH}]_{\text{ads.}}$ intermediate in chloride free acid media, as the two mechanisms can proceed simultaneously [17].

4. CONCLUSIONS

- The studied mild steel corrodes in HCl solutions with a first order reaction and the corrosion rate increases with the increase in acid concentration.
- Microstructural studies for mild steel after immersion in HCl solutions of different concentrations showed general and pitting corrosion and the latter becomes more pronounced at higher level of HCl concentration.
- It was found that R_{ct} value decreases while both C_{dl} and i_{corr} values increase with increasing HCl concentration.
- PDP results revealed that the steel dissolution is anodically controlled.

- Calculations for the ratio Z/v_s from PDP data indicated that mild steel dissolution occurs via multistep mechanism. In this mechanism electron release occurs in two steps each of them involves one electron and one of them is the rate determining step. The rate determining step may involve adsorbed $[\text{FeOH}]_{\text{ads}}$ and/or $[\text{FeClOH}]_{\text{ads}}^-$ groups.

References

1. S. D. Shetty, P. Shetty and H. V. S. Nayak, *J. Serb. Chem. Soc.* 71 (10) (2006) 1073
2. M. G. Fontana. Corrosion Engineering. 3rd Ed., McGraw-Hill Book Company, New York, (1987) 346.
3. E. A. Noor, *Corros. Sci.* 47 (2005) 33
4. G. Oakes and J. M. West, *Br. Corros. J.* 4 (1969) 66
5. A. G. Gad Allah, N. Nassif and T. Mikhail, *Annali di Chimica* 82 (1992) 49
6. P. B. Mathur and T. Vasudevan, *Corrosion (NACE)* 38(3) (1982) 171
7. R. J. Chin and K. Nobe, *J. Electrochem. Soc.* 119 (11) (1972) 1457
8. M. Stern and A. L. Geary, *J. Electrochem. Soc.* 104 (1957) 56
9. M. Metikos-Hukovic, R. Babic, Z. Grubac and S. Brinic, *J. Appl. Electrochem.* 24 (1994) 772
10. S. Muralidharan, M. A. Quraishi and S. V. Iyer, *Portug. Electrochim. Acta* 11(1993) 255
11. H. Ashassi-Sorkhabi and D. Seifzadeh, *Int. J. Electrochem. Sci.* 1(2006) 92
12. A. A. Mazhar, S. T. Arab and E. A. Noor, *J. Appl. Electrochem.* 31(2001) 1131
13. V. I. Sorokin, *Zashita Metallov* 5 (1993) 712
14. H. H. Uhlig, Corrosion and Corrosion Control. 2nd Ed., John Wiley & sons Inc. (1971).
15. L. I. Antropove, Theoretical Electrochemistry. English translation, Mir Publishers: Moscow, (1977) 401.
16. D. R. Macfarlane and S. I. Smedley, *J. Electrochem. Soc.* 133 (11) (1986) 2240
17. L. Meszaros, B. Lengyel, T. Garai and G. Trabanelli, *Acta Chim. Hung.* 127 (1) (1990) 113