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Stability of Layer Forming for Corrosion Inhibitor on Mild Steel Surface under Hydrodynamic Conditions

Ahmed Y. Musa[1,*], *Abdul Amir H. Kadhum*[1], *Abu Bakar Mohamad*[1], *Abdul Razak Daud*[2], *Mohd Sobri Takriff*[1], *Siti Kartom Kamarudin*[1], *Norhamidi Muhamad*[3]

[1] Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, Bangi, 43600, Selangor, Malaysia
[2] School of Applied Physics, Universiti Kebangsaan Malaysia, Bangi, 43600, Selangor, Malaysia
[3] Department of Mechanical and Material Engineering, Universiti Kebangsaan Malaysia, Bangi, 43600, Selangor, Malaysia
[*]E-mail: ahmed.musa@ymail.com

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Change of open circuit potential (OCP) with immersion time, Tafel polarization, and electrochemical impedance spectroscopy (EIS) were performed to investigate the corrosion inhibitor layer forming on mild steel surface. 4-Amino-5-phenyl-4H-1, 2, 4-trizole-3-thiol (APTT) was used through out the experiments as the corrosion inhibitor in this study. The investigation was conducted under hydrodynamic conditions with different pickling solutions of 0.5M HCl and 2.5M H_2SO_4 at 30 °C. The hydrodynamic conditions experiments were simulated using the rotating cylinder electrode (RCE). In both solutions, the values of OCP were shifted to more positive direction, the corrosion current densities were decreased, and charge transfer resistances were increased with flow velocity, respectively. The fitted data recoded from EIS were in line with those of polarization measurements. Experimental results obtained from change of OCP with immersion time, Tafel polarization, and EIS measurements showed indicated that the formation and the development of the inhibitor layer in both pickling solutions were flow velocity dependence.

Keywords: Mild steel, Corrosion inhibitor layer, hydrodynamic conditions

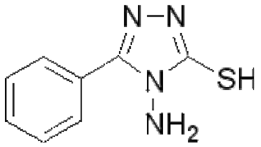
1. INTRODUCTION

Mild steel is still the material most commonly used for pipes in the industry. Both scale and corrosion products have negative effects on the pipe performance of the equipment, which requires periodic de-scaling and cleaning in acid pickling solutions. Therefore, corrosion of mild steel and its inhibition in acid solutions have attracted attention from numerous previous of investigators [1-11].

Corrosion inhibitors were reported to exhibits an effective way of metal lost by minimize the percentage metal loss during pickling process, due to eliminates some of the undesirable reaction connected with destructive effects of acid pickling solutions on mild steel surface and prevents its dissolution. Compounds containing nitrogen, sulphur and oxygen have been reported as inhibitors [12–16].

Most of the investigations on organic inhibitors have been investigated under static conditions. There are few studies in the literatures on the effect of hydrodynamic conditions on performance of inhibitors under laminar or turbulent flow. Some authors have investigated the effect of flow on corrosion of metals and alloys such as nickel–aluminium–bronze (NAB) [17, 18], stainless steel [19, 20], Cu–Ni alloys [21–25] and carbon steel [26] in different corrosive solutions. Fluid velocity is one of the most important parameters to be considered during corrosion and corrosion inhibition of metals, due to the flow affects both in the anodic and cathodic reactions, and in the inhibitor mass transport

In the investigation described working, a rotating-cylinder electrode was used to simulate the effect of hydrodynamic conditions on the corrosion inhibitor layer formed on mild steel surface in different acid pickling solutions. The acid pickling solutions used were 2.5M H_2SO_4 and 0.5M HCl. Change of open circuit potential with immersion time, Tafel polarization, and electrochemical impedance spectroscopy were used to investigate the effect of hydrodynamic conditions on the corrosion inhibitor layers. The compound of 4-Amino-5-phenyl-4H-1, 2, 4-trizole-3-thiol (APTT) was used as corrosion inhibitor through out the investigation, in which the inhibition performance has been confirmed by earlier investigation [12]. The molecular structure of APTT is shown as follows:



2. EXPERIMENTAL PART

The working electrode employed in this work is made from mild steel, with the chemical compositions to be as follows: 0.08 wt.% C, 0.25 wt.% Si, 0.45 wt.% Mn, 0.03 wt.% P, 0.03 wt.% S, and the balanced with Fe. The rotating cylinder electrode was designed for application with a Gamry Instrument Potentiostat/Galvanostat/ ZRA, model AFMSRCEP rotator. The dimensions of the RCE were 1.2 cm in diameter and 0.78 cm in length. The RCE effective area is 2.94 cm^2. The experiments were performed at flow velocities of U_1=25, U_2=50 and U_3=100 cm s^{-1} at 30°C in aerated 2.5M H_2SO_4 and 0.5M HCl solutions. The Reynolds number for a rotating cylinder electrode with outer diameter, *d* (cm) was calculated according to the relation [27]:

$$\mathrm{Re} = \frac{Ud\rho}{\mu}$$

where ρ, μ, and U are the solution density , absolute viscosity of the solution, and linear velocity (cm s^{-1}). In general, for a rotating cylinder, when the Reynolds number is greater than 200, the flow may be considered as turbulent [28]. The calculated Reynolds number values as presented on Table 1 confirmed that the experiments were performed under turbulent flow conditions in both acid pickling solutions.

The working electrode was first mechanically polished using SiC paper in successive grades from 200 to 1500, washed with deionized water thoroughly and degreased with absolute ethanol and dried at room temperature.

Table 1. Variation in Reynolds number for various flow velocities in 2.5M H_2SO_4 and 0.5M HCl at 30°C.

Solution	μ (g cm^{-1} s^{-1})	ρ (g cm^{-3})	U (cms^{-1})		
			25	50	100
				Re	
2.5M H_2SO_4	0.0175	1.1718	2008	4017	8035
0.5M HCl	0.0083	1.012	3658	7316	14631

A glass water jacket cell with 175 ml capacity made of Gamry consist of three electrodes namely for working, graphite bar counter and reference electrodes was used. The reference electrode was a saturated calomel electrode (SCE).

The measurements were carried out in both aerated 2.5M H_2SO_4 and 0.5M HCl. 4-amino-5-phenyl-4H-1, 2, 4-trizole-3-thiol (APTT) inhibitor was used throughout the experiments. It was reported that a 4×10^{-4} M of inhibitor would be sufficient to obtain a good protective efficiency in acidic solution [12]. The solution was freshly prepared from analytical grade chemical reagents using distilled water. For each run, a freshly prepared solution as well as a cleaned set of electrodes was used.

Electrochemical measurements were performed using Gamry Instrument Potentiostat/Galvanostat/ ZRA, these include Gamry framework system based on the Ref 600, Gamry applications that include OCP, potentiodynamic scan and EIS are DC105 and EIS300 software. The potentiodynamic current-potential curves were swept from -0.2 to 0.2 V_{SCE} at a scan rate of 0.166 mV s^{-1}. Impedance measurements were carried out using AC signals of amplitude 10 mV peak to peak at OCP in the frequency range 100 KHz to 1Hz. The OCP of the working electrode was measured as a function of immersion d of 60 min

3. RESULTS AND DISCUSSION

3.1. OCP with immersion time measurements

The OCPs of mild steel were monitored over 60 min. from the moment of immersion in the respective solutions at 30 °C. Fig. 1 A, B represent the effects of absence and presence of APTT inhibitor along with different flow velocities by the varying the OCP of mild steel with time in both the acid pickling solutions. The mixed nature of the inhibitor [12] induces a continuous shift in OCP (i.e E_{corr}) towards nobler potentials, indicating the spontaneous adsorption of inhibitor on metallic surface.

Corrosion potential stabilization occurs after almost 10 min. of immersion time in 0.5M HCl and 2.5M H_2SO_4 solutions, respectively. In both plateaus, potential values rise up in stagnant inhibitive solution which is due to the inhibition effect exhibited by APTT [12]. For flow velocities of U = 50, and 100 cm s^{-1}, the OCP becomes more positive compared to stagnant conditions, it means that the surface becomes nobler with increased flow velocity which can probably due to more oxides formation on metal surface in high flow velocity. In addition at higher flow velocities, the presence of dissolved oxygen and H^+ ions on metal surface are increased and could lead to formation of more oxides and more positive values of OCP [29].

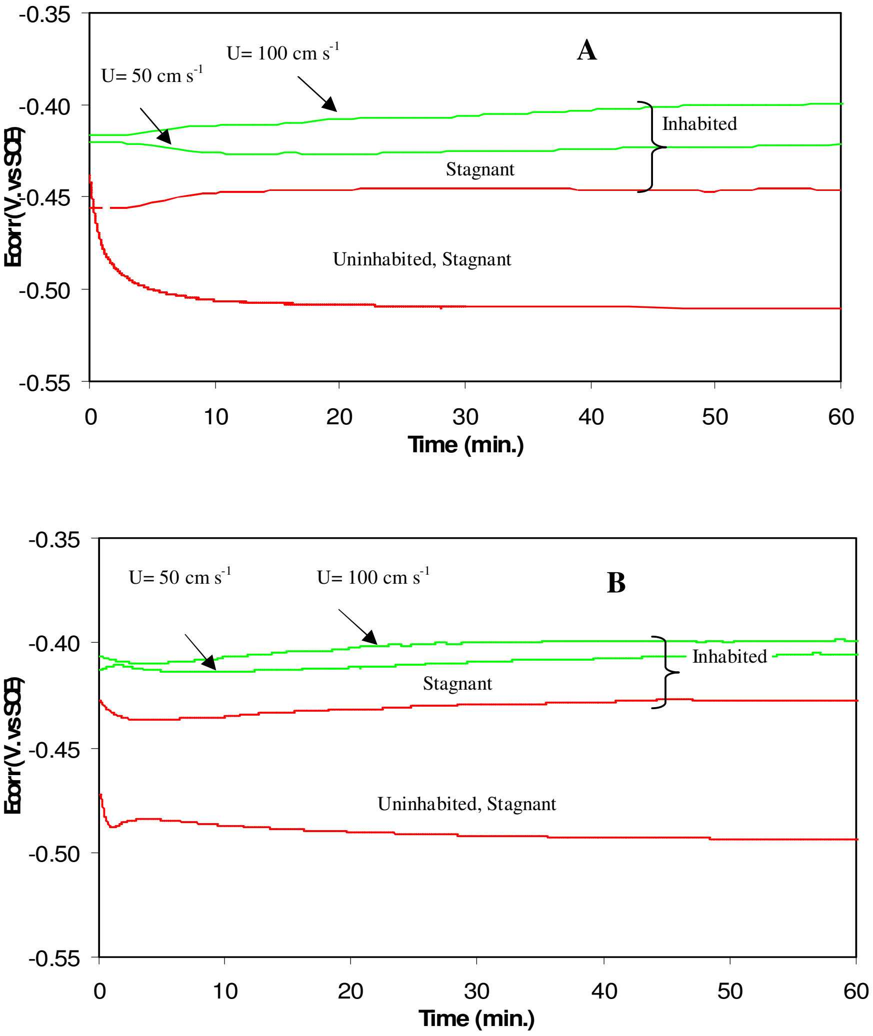


Figure 1. OCP vs. time during 60 min. for mild steel in both (A) 0.5M HCl and (B) 2.5M H_2SO_4 solutions with 4× 10^{-4} M of APTT at different flow velocities.

3.2. Polarization curves

The current - potential curves obtained for three flow velocities of 25, 50 and 100 cm s^{-1} in both solutions of 0.5M HCl and 2.5M H_2SO_4 with 4 $\times 10^{-4}$M of APTT are as shown in Fig 2 and Fig.3 respectively. The numerical values of the variation of corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (β_a), and cathodic Tafel slope (β_c) with flow velocity at 30 °C for both solutions are depicted in Table 2. In Fig. 2 and Fig.3, the cathodic current densities increased with flow velocity, which may be explained by an increase in the oxygen supply to the metal surface while the anodic current densities were decreased along with flow velocity, which mean that the anodic dissolution of metal reduced with flow velocity. The flow velocity caused a shift in corrosion potential toward the positive values, thus the cathodic current densities increased and the anodic current densities decreased [30].

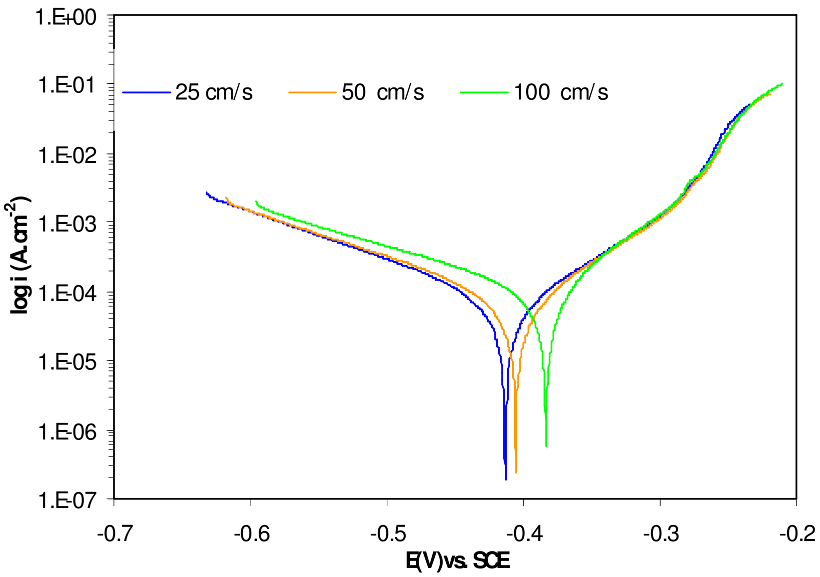


Figure 2. Polarization curves for mild steel in 0.5M HCl solution with 4× 10^{-4} M of APTT at different flow velocities.

Table 2. Electrochemical parameters for mild steel in the presence of 4×10^{-4} M APTT in 0.5M HCl and 2.5M H_2SO_4 at different flow velocities

Solution	*U* (cms^{-1})	i_{corr}($\mu A.cm^{-2}$)	E_{corr}(mV)	β_c(V/dec)	β_a(V/dec)
HCl	25	46.7	413	126	77.4
	50	51.5	404	104	57.6
	100	23.5	383	129	53.2
H_2SO_4	25	43.3	391	106	54.3
	50	38.8	388	103	49
	100	26.6	389	102	51

It's obvious from Table 2 in both solutions, the E_{corr} shifted to more positive direction while the i_{corr} reduced with flow velocity, respectively.This trend confirms results obtained from OCP measurements. As mentioned in Section 3.1, this behavior for inhibited solutions shows that the mild steel surface has become nobler in high flow rates, probably due to more oxide formation on surface. The reduction of i_{corr} with flow velocity confirms these results.

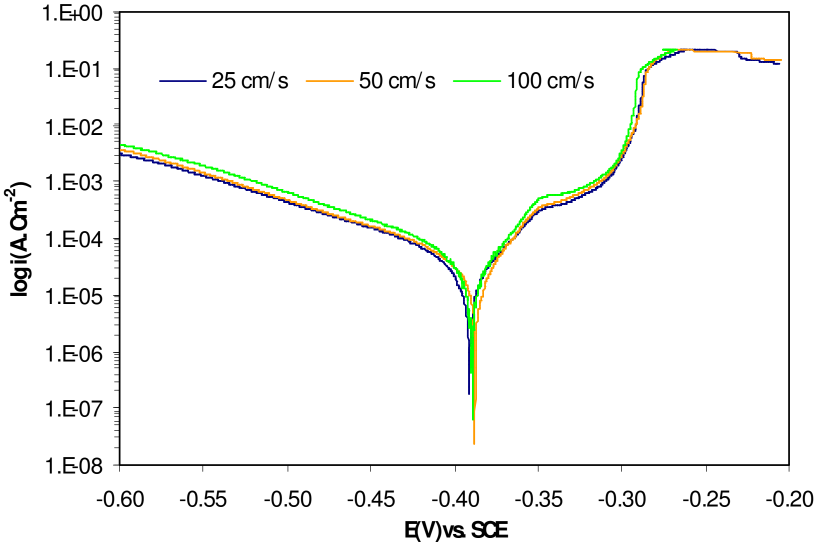


Figure 3. Polarization curves for mild steel in 2.5M H_2SO_4 solution with 4× 10^{-4} M of APTT at different flow velocities.

It is generally accepted that the first step in the adsorption of an organic inhibitor on a metal surface usually involves replacement of one or more water molecules adsorbed at the metal surface [31]:

$$Inh_{(sol)} + xH2O_{(ads)} \rightarrow Inh_{(ads)} + xH2O_{(sol)} \qquad (1)$$

The inhibitor may then combine with freshly generated Fe^{2+} ions on steel surface, forming metal inhibitor complexes [32]:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (2a)$$

$$Fe^{2+} + Inh_{(ads)} \rightarrow [Fe\text{-}Inh]_{(ads)}{}^{2+} \qquad (2b)$$

The resulting complex, depending on its relative solubility, can either inhibit or catalyze further metal dissolution. It is insufficient to form a compact complex with the metal ions at low concentrations of APTT in the solution, so that the resulting adsorbed intermediate will be readily soluble in the acidic environment. But at relatively higher concentrations more APTT molecules become available for complex formation, which subsequently diminishes the solubility of the surface layer, leading to improved inhibiting effect [32].However, hydrodynamic conditions can also affect the inhibition of metal corrosion, flow can increase mass transport of inhibitor molecules that causes more inhibitor presence at metal surface. This effect can improve the inhibition performance[33].Nevertheless hydrodynamic conditions can increase mass transport of metal ions (Fe^{2+}), produced during metal dissolution, from electrode surface to the bulk of solution and hence lead to less $[Fe\text{-}Inh]^{2+}$ complex presence on electrode; this is a harmful effect for inhibition performance. In addition the high shear stress resulted from high flow velocity can also separate inhibitor layer or adsorbed $[Fe\text{-}Inh]^{2+}$ complex and cause more desorption from metal surface which acts as a negative factor on inhibition efficiency [33].

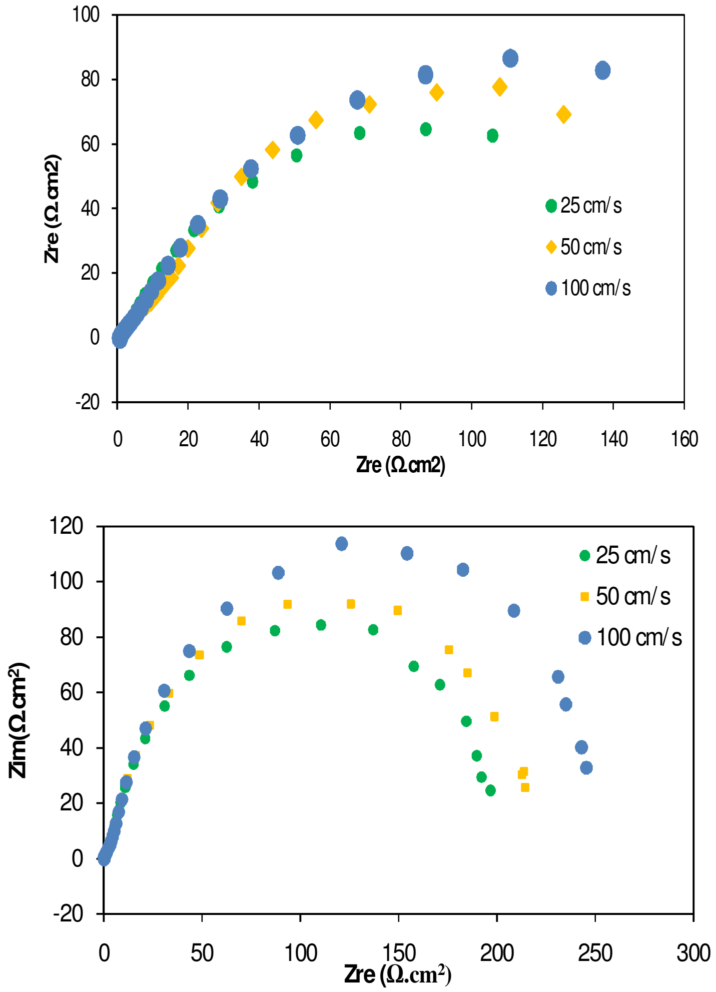


Figure 4. Nyquist plots for mild steel after 60min of immersion in (A) 0.5M HCl and (B) 2.5M H_2SO_4 solution with 4× 10^{-4} M of APTT at different flow velocities.

3.3. EIS measurements

To quantify turbulent flow influence on film formation and stability, EIS spectra were recorded on the working electrode for three flow velocities by Nyquist format in both acid pickling solutions with 4×10^{-4} M of APTT, Fig 4 A, B. The impedance spectra for both acid pickling solutions shows that the Nyquist plot has tow loops: one loop of which is much smaller than the other one in high frequency range, and one loop in low frequency range with capacitive behaviour. The loop at lower frequency is due to the corrosion electrochemical process [34, 35].

The loop at high frequency range would be due to the inhibitor film [34,35]because a surface dielectric layer normally has a small time constant and so has a phase angle shift in the high frequency range [35]. The magnitude of the impedance increases from the beginning and up to the end of the experiments as shown in Nyquist plots, Fig.4 A, B; this suggests that the flow velocity greatly but gradually changed the corrosion kinetics on the electrode surface.

The equivalent circuit models used to fit the experimental; results are previously reported [34]. The values of the parameters, obtained from the fit, are reported in Table 3. It can be seen that R_{ct} increased with flow velocity in both solutions. These results are in line with those obtained from polarization measurements.

Table 3. EIS fitted data for mild steel in 0.5M HCl and 2.5M H_2SO_4 solution with 4×10^{-4} M of APTT at different flow velocities.

Solution	*U* (cms^{-1})	R_{ct} *(ohm.cm²)*	C_{dl} $(\mu F.cm^{-2})$
HCl	25	175.3	724.2
	50	223	582.5
	100	236	437.6
H_2SO_4	25	157.4	413.8
	50	217.7	332.9
	100	258.7	258.7

As described in Section 3.2, fluid flow has several effects on the behaviour of inhibitor. On one hand, it can improve the performance of inhibitor through increase of inhibitor mass transport toward metal surface; on the other hand, less $[Fe\text{-}Inh]^{2+}$ complex may be formed on electrode because of increased mass transport of Fe^{2+} ions from metal surface toward bulk of solution, the adsorbed inhibitor layers and $[Fe\text{-}Inh]^{2+}$ complex may also be desorbed from surface more quickly under hydrodynamic conditions. The balance of these opposite effects determines the overall changes of corrosion inhibition process with flow velocity.

4. CONCLUSIONS

The influence of hydrodynamic conditions on the formation and stability of corrosion inhibitor layer formed on mild steel surface during pickling process was investigated. The investigation involved change of OCP with immersion time, Tafel polarization, and EIS. The fitted data recoded from EIS were in line with those of polarization measurements. The investigation showed that in both solutions, the corrosion current density decreased and charge transfer resistances were decreased with the flow velocity, while, E_{corr} shifted toward more positive values as the flow velocity increased. The results also revealed that the formation and the development of the inhibitor layer in both pickling solutions were dependent on the respective flow velocities.

It was found that the flow has several different effects on inhibition performance. On one hand it can increase the inhibitor mass transport from bulk to electrode surface and on the other hand it leads to more desorption of adsorbed inhibitor molecules; high flow velocity can also lead the Fe^{2+} ions, formed during metal dissolution, move away from metal surface and causes to less $[Fe\text{-}Inh]^{2+}$ complex presence on electrode surface which can have a negative effect on surface protection. The balance of these different phenomena will determines the overall corrosion inhibition process with flow.

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