Synergistic Effect of Iodide Ion and 1-(2H)-Phthalazinone on Galvanic Corrosion of Aluminum and Mild Steel in 1.0 M HCl

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Received: 20 July 2011 / Accepted: 2 October 2011 / Published: 1 November 2011

The corrosion inhibitive effects of 1-(2H)-phthalazinone (PTO) on the coupled metals of aluminium and mild steel in 1.0 M HCl solution and the synergistic influence of potassium iodide (KI) on the inhibition efficiency were assessed. The galvanic potential and galvanic current were measured in blank solution, presence of 1 mM of PTO, presence of 0.1% KI and combination of PTO and KI. Result showed that the presence of PTO has significantly reduced galvanic current from 1160 μ A cm⁻² to 69.9 μ A cm⁻². In addition, the presence of both PTO and KI in solution decreased the galvanic current to value even further to 0.75 μ A cm⁻² while the galvanic current increased to -2000 μ A cm⁻² in presence of KI alone in the solution,.

Keywords:

1. INTRODUCTION

Corrosion of aluminum and its alloys have been a subject of numerous studies due to their high technological value and wide range of industrial applications especially in aerospace and house-hold industries. Aluminum and its alloys are reactive materials and are prone to corrosion. Aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their advantages [1]. Mild steel is a well-known material. It is used widely in industries for various applications. However, in industries, mild steel will undergo corrosion. Thus, there is a shortcoming of mild steel [2].

In the equipment that transmits oilfield production liquids; there is direct contact between different metals. Besides that, copper alloys, carbon steels, aluminium alloy, low-alloy steels and

stainless steels are normally combine for downhole and surface pump assemblies. These galvanic couples may bring to the corrosion problems. Hydrochloric acid is one of the most commonly used acids in today's industrialized world. Its applications include chemical cleaning and processing, acid treatment of oil wells and other applications. The wide use of this acid has led to the concentration of this study on the corrosive effects of this acid on carbon steel, which is a versatile component in many industrial structures [3].

Organic compounds have become accepted as effective inhibitors of metal corrosion in various media. Compounds containing nitrogen, oxygen, sulfur, or phosphorous have particularly been reported as efficient corrosion inhibitors. The protective efficiency is based on adsorption ability of their molecules, where the resulting adsorption film acts as a barrier separating the metal from the corroding medium.

The inhibitors act at the interphase created by corrosion product between the metal and aqueous corroding solution. Thus the nature of inhibitor interaction and efficiency may be dependent on the chemical, mechanical and structural characteristics of this layer [2].

Synergism has become one of the most important effects in inhibition processes and serves as the basis for all modern corrosion inhibitor formulations.

Synergistic effect is the upgrading of inhibition efficiency of organic compounds in the presence of some anions, particularly halide ions [4]. It is thought that the anions are able to improve adsorption of the organic cations in solution by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism thus results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions [4].

In this research, the galvanic potential, E_g and the galvanic current, I_g of the couples Al2024 and mild steel were recorded using zero resistance ammeter (ZRA) measurements over a two hours period in blank, 1mM PTO, KI alone, and combination of 1mM PTO and 0.1% KI in 1.0 M HCl.

2. EXPERIMENTAL

Al2024 and mild steel were used as the working electrodes. Both of the working electrodes were cylinder shape with exposure surface area of 3cm². The composition of aluminium alloy Al2024 was 3.8 wt. % Cu, 0.1 wt. % Cr, 0.5 wt. % Fe, 1.2 wt. % Mg, 0.3 wt. % Mn, 0.5 wt. % Si, 0.15 wt. % Ti, 0.25 wt. % Zn, Mn balanced with Al. The composition of mild steel was Fe, 99.21; C, 0.21; Si, 0.38; P, 0.09; S, 0.05; Mn, 0.05; Al, 0.01. The ASTM Standard procedure, G1-03 was followed to clean the specimens. The measurements were carried out in 1.0 M hydrochloric acid at 30°C in absence and presence of 1mM of PTO as corrosion inhibitor. The test was repeated using KI alone and the combination of 1mM of PTO and 0.1% of KI. The molecular structure of PTO is shown in Fig. 1 as below:



Figure 1. The molecular structure of phthalazinone (PTO)

The Gamry Instrument Potentiostat/Galvanostat/ZRA model of 600 was used by applying zero potential between the dissimilar metals. This allows the E_g and I_g to be recorded simultaneously versus time. The coupling of Al2024 and mild steel was installed in bi-metallic shaft from pine instrument, USA and immersed in 1.0 M HCl solution for about two hours. The ions concentrations of Al³⁺ and Fe²⁺ after 120 minutes of ZRA test were determined using atomic adsorption spectroscopy (AAS). The Atomic Adsorption Spectrometer used was Analyst 800 from Perkin Elmer Instruments.

3. RESULTS AND DISCUSSION

3.1. Zero Resistance Ammeter Measurements

The galvanic E_g and I_g of mild steel and Al2024 were recorded 120 minutes in blank and presence of 1 mM PTO, only 0.1% KI and the combination of 1mM PTO and 0.1% KI in 1.0 M HCl solution at 30°C as shown in Fig. 2, 3, 4 and 5, respectively.



Figure 2. Change in galvanic current and galvanic potential of mild steel and Al2024 coupling in 1.0 M HCl solution at 30°C



Figure 3. Change in galvanic current and galvanic potential of mild steel and Al2024 coupling in 1.0 M HCl solution at 30°C with 0.1% KI



Figure 4. Change in galvanic current and galvanic potential of mild steel and Al2024 coupling in 1.0 M HCl solution at 30°C with 1 mM phthalazone

For blank solution, the initial galvanic current was 1150 μ A cm⁻² and galvanic potential was -597 mV. A stable galvanic current about 1550 μ A cm⁻² and galvanic potential about -630 mV (SCE) was establish at 40 to 60 minutes. After that, the galvanic current was decrease to 1160 μ A cm⁻² and -595 mV. The stable galvanic current and potential from 40 to 60 minutes indicate that the stabilization of oxide layer of the metals. The abrupt drop in potential is use to the partial passive film damage [5]. Negative current refers to electron flow from aluminum to mild steel [6]. The current passes from mild steel to aluminum because the electrode potential of mild steel is higher than aluminum before coupling [7].



Figure 5. Change in galvanic current and galvanic potential of mild steel and Al2024 coupling in 1.0 M HCl solution at 30°C with both 0.1% KI and 1 mM phthalazone

In presence of 1mM PTO, stable galvanic potential reach -643 mV after 20 minutes and galvanic current at about 69.9 μ A cm⁻². This result shows that presence of PTO has significantly decreased both the galvanic current and the galvanic potential. Decrease of the galvanic current reflects that the corrosion of both metals were inhibited. Musa et al. [6] and Whitten et al. [8] have reported that the galvanic current, Ig and galvanic potential, Eg decreased with addition of inhibitor. In case of KI alone, the galvanic current was increased to -2000 μ A cm⁻² after 90 minutes. The galvanic potential in this case was shift to -650 mV and reach steady state after 7 minutes. It can be seen that the galvanic potential is around -643 to -650 mV with presence of 1 mM PTO, 0.1% KI and both. This indicated that presence of PTO and KI has makes the passive film more stable if compare to blank HCl solution.

The presence of both 1 mM PTO and 0.1% KI in solution decreases the galvanic current even further to -0.75 μ A cm⁻² and shift the galvanic potential to lower direction, -650 mV after 30 minutes. This result reveals that KI shows synergistic effect on galvanic corrosion of mild steel and Al2024. The strong chemisorptions of iodide ions on the metal surface facilitate the adsorption of the protonated inhibitor molecule. Stabilization of adsorbed iodide ions with PTO lead to greater inhibition of galvanic corrosion [9].

From potentiodynamic measurements of single electrode corrosion, PTO was found as a mixed-type inhibitor [10, 11] which can inhibit the cathodic process of mild steel and anodic process of Al2024 in 1.0 M HCl solution. When the galvanic coupled electrode was immersed in HCl solution, cathodic area of mild steel will carries more negative excess charge and anodic area of Al2024 will carries positive excess charge. As a result, the protonated inhibitor molecules will tend to adsorbed on

the mild steel surface than Al2024 surface. The inhibition effect on the cathodic process of mild steel electrode is enhanced whereas the inhibition effect on the anodic process of Al2024 is weakened. The results show that in presence of PTO or both PTO and KI, the galvanic current and galvanic potential were decreased.

3.2. Atomic Adsorption Spectroscopy

The ions concentrations of Al^{3+} and Fe^{2+} after 120 minutes of ZRA test were determined using atomic adsorption spectroscopy (AAS) and listed in Table 1.

	Al^{3+} (mg/L)	Fe^{2+} (mg/L)
Blank	321.40	3.66
0.1% KI	144.30	5.76
1 mM Phthalazone	47.33	2.93
1 mM Phthalazone + 0.1% KI	32.29	1.03

Table 1. Result of atomic adsorption spectroscopy

Results show that the aluminum ions, AI^{3+} shown higher concentration than mild steel ions, Fe^{2+} in all studied solutions. This can be explained by the transfer of electron from aluminum to mild steel and aluminum became sacrificial anode to protect mild steel. In presence of KI, the AI^{3+} was decreased almost to half while Fe^{2+} increased to double, this was due to presence of KI has stabilized the passive film of aluminum whereas it does not have any effect on mild steel surface. In addition of PTO, both AI^{3+} and Fe^{2+} were decreased to 47.33 and 2.93 mg/L, respectively. This indicates that PTO was inhibited the both metal from corrosion. The lowest values of AI^{3+} and Fe^{2+} ions concentration were found in presence of both PTO and KI solution. The synergistic effect of KI with PTO has the greatest effect to inhibit the galvanic corrosion of mild steel and Al2024. These results were in line with trend from those obtained from ZRA tests.

4. CONCLUSION

The results show that in presence of PTO or both PTO and KI, the galvanic current and galvanic potential were decreased. It was found that in presence of PTO or both PTO and KI, the galvanic current shifts to more positive direction and galvanic potential shifts to more negative direction. Atomic adsorption spectroscopy (AAS) results revealed that the aluminum ions, AI^{3+} concentration are higher than mild steel ions, Fe^{2+} in all studied solutions. The lowest values of AI^{3+} and Fe^{2+} ions concentrations were found in presence of both PTO and KI in 1 M HCl solution.

ACKNOWLEDGEMENTS

We gratefully acknowledge National University of Malaysia (No. UKM-GGM-NBT-037-2011) for support of this work

References

- 1. A.A. El Maghraby, The Open Corrosion Journal 2(2009) 189
- 2. A.Y. Musa, A. A. .B. Rahoma, A. Amir H. Kadhum, A. B. Mohamad, H. Mesmari, *J. Mol. Struc.* 969 (2010) 233
- 3. A.Y. Musa, A. A. H. kadhum, M. S. Takriff, A. B. Mohamad, Int. J. Surf. Sci. Eng. 5 (2011) 226
- 4. E.E, Ebenso, H. Alemu, S. A. Umoren, I. B. Obot, Int. J. Electrochem. Sci. 3(2008) 1325
- 5. M.G. Pujar, N. Parvathavarthini, R. K. Dayal, H. S. Khatak. Int. J. Electrochem. Sci. 3(2008) 44
- 6. A.Y. Musa, A. B. Mohamad, A. A. H. Kadhum, Y. B. A. Tabal, *J. Mater. Eng. and Perform.* 20(2011)394
- 7. M. Hara, Y. Shinata, S. Hashimoto, Corr. Sci. 39(1996) 627
- 8. L. Whitten, J. Boivin. Electrochemical Testing of Corrosion Inhibition for Galvanically Coupled Alloys. Northern Area Western Conference. (2006) Alberta, Canada
- 9. M. Bouklah, B. Hammouti, A. Aouniti, M. Benkaddour, A. Bouyanzer, *App. Surf. Sci.* 252(2005) 6236
- 10. A.Y. Musa, A. A. H. Kadhum, A. B. Mohamad, M. S. Takriff, E. P. Chee, *Current Applied Physics*, 2011, doi:10.1016/j.cap.2011.07.001
- 11. A.Y. Musa, A. B. Mohamad, A. A. H. Kadhum, M. S. Takriff, L. T. Tien, Corr. Sci., 2011,
- 12. doi:10.1016/j.corsci.2011.07.010

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