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Experimental Study of 2-Amino-5-(4-nitrophenyl)-1, 3, 4-Thiadiazole for MS in HCl Solution

Abstract- *The present work aims to study the inhibition performance of new organic inhibitor namely ANTD "2-amino-5-(4-nitrophenyl)-1,3,4-thiadiazole" on corrosion of mild steel (MS) in HCl environment at the concentration of 1.0 M through using weight loss techniques. Weight lost measurements demonstrates the presence of a film on MS surface in existence of organic substance. The inhibition performance of ANTD at various concentrations for mild steel increases with increasing concentration and with an increased in the immersion time and decreased with raising temperatures degrees. The optimal inhibition efficiency of (ANTD), 82%, was achieved for mild steel when immersed with the highest utilized concentration for 6 hrs.*

Keywords- *Mild steel, Corrosion Inhibition, ANTD.*

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1. Introduction

Corrosion of mild steel, may cause constitutional damage and produce variations in physical and/or chemical characteristics of the pipes and other manufacturing equipment. These impacts confirm that corrosion could lead to huge loses if an efficient solution is not figured out. Inhibiting corrosion of MS plays a significant role in many products, chiefly in manufacturing industries that deal with chemicals and utilize of MS. Many of investigations have been done to study efficient ways for inhibitive corrosion. Acids are exceedingly utilized in chemical and petrochemical processes, such as pickling, cleaning, descaling, etc. Inhibitors have the ability to reduce the dissolution rate of mild steel [1–5]. Mild steel is widely employed in industry processes and as a result, it is damaged when exposed to different corrosive processes. The usage of inhibitors is the most workable techniques for protection of mild steel and alloys against corrosion, essentially in corrosive solution [6–8]. The organic molecules, which are employed as inhibitors, can block the metals from oxidation reaction through a certain mechanism [9]. In continuation of previous studies [10–19], herein, we investigate the application of inhibitor (ANTD) (Figure 1) as corrosion inhibition of mild steel coupons in an acidic solution by gravimetric analysis.

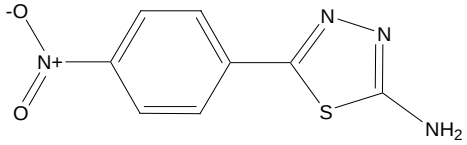

Figure 1: Molecular Structure of 2-amino-5-(4nitrophenyl)-1, 3, 4-thiadiazole

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2. Materials and Methods

I. Synthesis of the inhibitor

Starting materials and usable solvents were bought from Malaysia at Sigma/Aldrich Company. Infrared (FTIR) spectra have been records using FTIR spectrometer instrument 8300/ Shimadzu. CHN "Elemental analysis on carbon, hydrogen and nitrogen" analyses were recorded by CHN elemental analyzer type of 5500 Carlo Erba". The spectra of NMR measured with 300 MHz Ultra Shield utilizing solvent and internal standard "DMSO-d6 and TMS correspondingly". A mixture of 0.01mole 4-nitrobenzoic acid and 0.01mole of the thiosemicarbazide in 16ml of concentrated sulfuric acid have been refluxed for 7h., subsequently, cooled and poured into ice. Filtered and the solid recrystallized from ethanol, yielding, 55%; mp 248-252 oC. FT-IR cm-1; 3400 (NH amine), 1510 and 1340 for the nitro group, 1630 (C=N) and 3150 for C-H aromatic. H- NMR; d: 6.83 ppm (1H, NH2), d: 7.91 ppm (2H, CH, aromatic), d: 8.25 ppm (2H, CH, aromatic). Carbon-NMR in DMSO-d6: 121.6, 127.7, 153.1, 159.0 and 172.6. C-H-N for ANTD; Found (Calculated): C, 43.93% (43.24); H, 3.01% (2.72); N, 24.84% (25.21).

II. Coupons and Environment

MS samples were bought from GamryInc Instruments and applied for the weight loss technique every with an area of 4.5 cm2 with the composition percentages 99.21; 0.21; 0.38; 0.09; 0.05; 0.05 and 0.01 wt % for Fe; C; Si; P; S; Mn and Al, respectively. MS samples have been cleaned according to procedure G1-03- ASTM [20]. The solution of HCl diluted with distilled water has been prepared to utilize of analytical-grade HCl 37% and applied for the experiments. The solution was intended through HCl solution at 1.0 M with various conc. of ANTD: (1-5)x10-1 mM.

III. Gravimetric analysis

Gravimetric analysis has been completed utilizing MS specimens in 1 M HCl in the absence and presence of ANTD. The MS specimens were cleaned and weighted and were immersed for 6 h., at temperatures, "303, 313, 323 and 333" K., in presence and absence of ANTD. Then after MS specimens were removed, cleaned the weighted. The losing in weights was calculated via different in weights of MS specimens that exposure and not exposure. The other characters like CR (corrosion rate), θ (MS surface coverage), and η % (corrosion inhibition efficiency) were estimated according to equations 1-3 [21, 22].

$$C_R = \frac{W}{At} \quad (1)$$

$$\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \quad (2)$$

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \quad (3)$$

Where W=loss in weight (mg), A = (cm2), t = time in h, CR=corrosion rate without ANTD and CR(i) with ANTD.

3. Results and Discussion

I. Gravimetric techniques

Results of gravimetric for specimen of MS in corrosive media at various concentrations of ANTD starting form 0 mM are presented in Figure 2 that represent the impacts of inhibitor concentrations on CR (A) and θ (B) for MS in 1 M HCl. It is an efficient way to optimize the effects of conc. of ANTD on inhibitive performance [23]. The investigation results indicated such increase of ANTD prevent MS from corrosive and the inhibitive performance increases in parallel with increases of concentration of ANTD, as presented in Figure 3. The inhibitor, 2-amino-5-(4-nitrophenyl)-1,3,4-thiadiazole shows inhibition efficiency, (82.0%) at 5x10-1 mM. The excellent corrosion inhibitive performance is imputed to bonding of ANTD molecules with the MS surface, which is confirmed due to heteroatoms "N, O and S" in ANTD molecule and huge molecular structure. In addition, the existence of a benzene group boosts the density of electrons at the efficient center that accelerates the interaction of ANTD with MS [24].

II. Temperature Impacts

Versions of inhibitive effectiveness of (ANTD) on alloy surface in corrosive solution with and without of various ANTD concentrations at temperatures degrees 303K-333K signalize that IE% raise with rising concentration and diminish in parallel with rising temperature degrees (Figure 4). In general, molecules from organic origins have negative absorption and signalize to an exothermic process, so this is why the IE% diminish when the temperature raises.

III. Proposed inhibitive mechanisms

ANTD molecules were adsorbed on alloy and forming a protective layer that bond to the metal

surface. The adsorption mechanisms actions of organic molecules as inhibitors for MS could progress through the following ways.

a. Electrostatically: Ions and metal.

b. Interaction: Unshared electrons of inhibitor molecules with the metal surface.

c. Interaction: Pi-electrons of inhibitor molecules with the metal surface.

ANTD protect the MS surface through the block the catholic reactions and/or anodic reactions and produce in-soluble metal-complex. The IE of ANTD against the corrosion of MS in 1 M corrosive media may be shown according to adsorption site the number, molecular size, charge density, mode of interaction of ANTD with the surface of alloy and capability for forming of metal-complex. Pi-electrons of ANTD and unshared electrons on the hetero atoms (N, O and sulfur) form coordination bonds with MS surface, as shown in Figure 5.

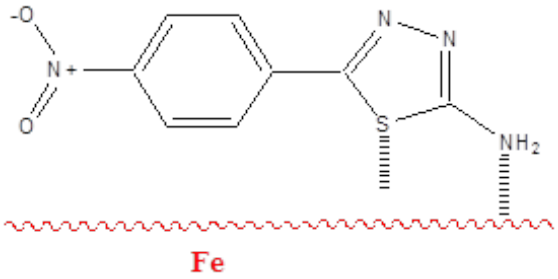

Figure 5: The suggested mechanism of action of the 2-amino-5-(4-nitrophenyl)-1, 3, 4-thiadiazole (ANTD) as a corrosion inhibitor

4. Conclusion

Our work results revealed that ANTD functioned a superior corrosion inhibitor for the surface of mild steel in hydrochloric acid. The superior performance of ANTD at conc. of 5x10-1 mM was 82% but diminished with rising of temp. Degrees that might propose physio-sorption. ANTD is proved as a superior inhibitor with good inhibitive effects due to havening heteroatoms (S, N and O) atoms.

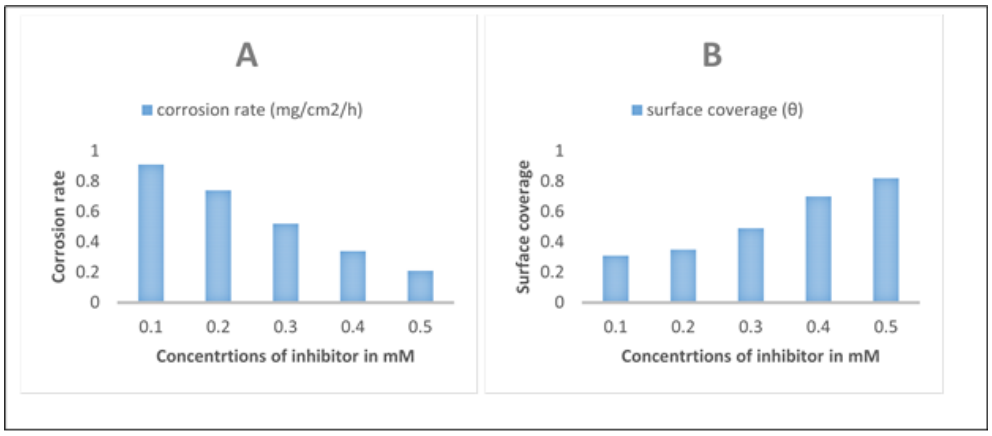

Figure 2: Effect of different concentrations of (ANTD) on corrosion rate and surface coverage (a) and Surface coverage (b) for MS in 1 M HCl.

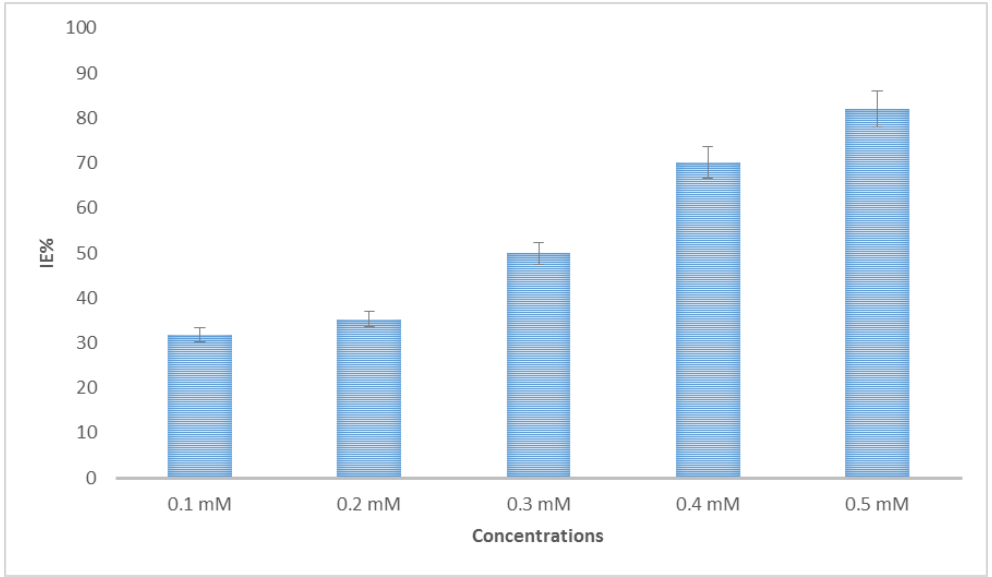

Figure 3: Effect of different concentrations (ANTD) on the inhibition efficiency for MS in 1 M HCl.

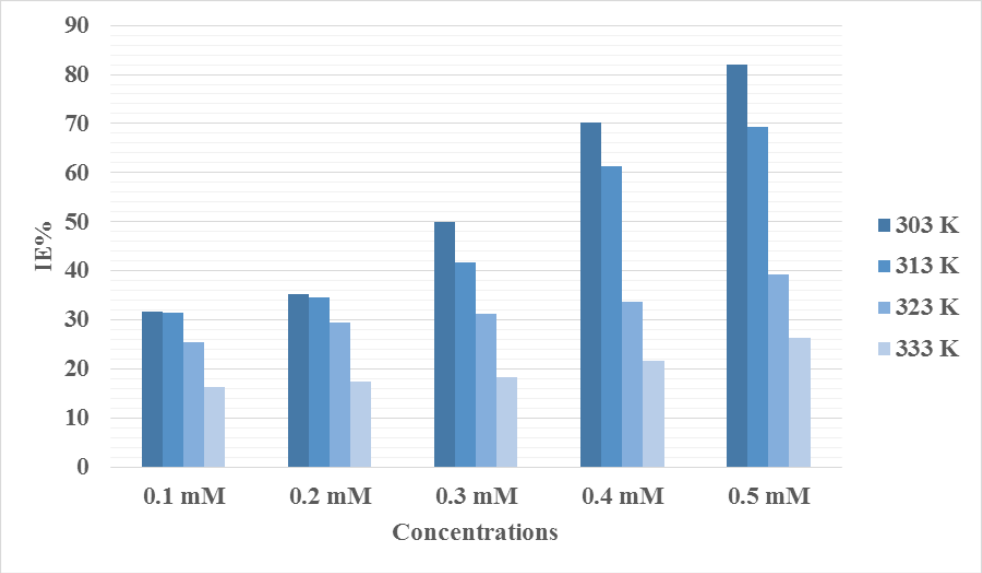

Figure 4: Influences of concentrations vs. temperatures for (ANTD) on corrosion efficiencies.

References

[1] S.K. Shukla, A. Singh and A. Quraishi, "Efficient corrosion inhibitors for mild steel in hydrochloric acid solution," *Int. J. Electrochem*. Sci., Vol. 7, pp. 3371–3389, 2012.

[2] X. Bin, Y. Wenzhong, L. Ying, Y. Xiaoshuang, G. Weinan and C. Yizhong, "Experimental and theoretical evaluation of two pyridinecarboxaldehyde thiosemicarbazone compounds as corrosion inhibitors for mild steel in hydrochloric acid solution," *Corros. Sci*., Vol. 78, pp. 260–268, 2014.

[3] A. Kosari, M.H. Moayed, A. Davoodi, R. Parvizi, M. Momeni, H. Eshghi and H. Moradi, "Electrochemical and quantum chemical assessment of two organic compounds from pyridine derivatives as corrosion inhibitors for mild steel in HCl solution under stagnant condition and hydrodynamic flow," *Corros. Sci*., Vol. 78, pp. 138–150, 2014.

[4] M. Bobina, A. Kellenberger, J. Millet, C. Muntean and N. Vaszilcsin, " Corrosion resistance of carbon steel in weak acid solutions in the presence of L-histidine as a corrosion inhibitor," *Corros. Sci*., Vol. 69, pp. 389–395, 2013.

[5] L. Fragoza-Mar, O. Olivares-Xometl, M. Domínguez-Aguilar, E. Flores, P. Lozada and F. Jiménez-Cruz, "Corrosion inhibitor activity of 1,3-diketone malonates for mild steel in aqueous hydrochloric acid solution", *Corros. Sci*., Vol. 61, pp. 171–184, 2012.

[6] P.S. Desai and S.M. Kapopara, "Inhibiting effect of anisidines on corrosion of aluminum in hydrochloric acid," *Indian Journal of Chemical Technology*, Vol. 16, Part 6, pp. 486–491, 2009.

[7] A.S. Fouda, G.Y. Elewady, and M.N. El-Haddad, "Corrosion inhibition of carbon steel in acidic solution using some azodyes," *Canadian Journal on Scientific and Industrial Research*, Vol. 2, Part 1, pp. 1–18, 2011.

[8] M. Ramananda Singh, K. Bhrara, and G. Singh, "The inhibitory effect of diethanolamine on corrosion of mild steel in 0.5M sulphuric acid medium," *Portugaliae Electrochimica Acta*, Vol. 26, pp. 479–492, 2008.

[9] V.S. Sastri, "Green Corrosion Inhibitors: Theory and Practice," John Wiley & Sons, New York, NY, USA, 2011.

[10] A. A. Al-Amiery, A.Y. Musa, A.H. Kadhum, A.B. Mohamad, "The use of umbelliferone in the synthesis of new heterocyclic compounds," *Molecules*, Vol. 16, pp. 6833–6843, 2011.

[11] A.A.H. Kadhum, A.A. Al-Amiery, A.Y. Musa, A.B. Mohamad, "The Antioxidant Activity of New Coumarin Derivatives," *Int. J. Mol. Sci*., Vol. 12, pp. 5747–5761, 2011.

[12] A.A. Al-Amiery, A.A.H. Kadhum and A.A. Mohamad, "Antifungal Activities of New Coumarins," *Molecules*, Vol. 17, pp. 5713–5723, 2012.

[13] Y.K. Al-Majedy, D.L. Al-Duhaidahawi, K.F. Al-Azawi, A.A. Al-Amiery, A.A.H. Kadhum and A.B. Mohamad, "Coumarins as Potential Antioxidant Agents Complemented with Suggested Mechanisms and Approved by Molecular Modeling Studies," *Molecules* , Vol. 21, pp. 135, 2016.

[14] A.A. Al-Amiery, Y.K. Al-Majedy, A.A.H. Kadhum and A.B. Mohamad, "New Coumarin Derivative as an Eco-Friendly Inhibitor of Corrosion of Mild Steel in Acid Medium," *Molecules*, Vol. 20, pp. 366–383, 2015.

[15] K.F. Al-azawi, "Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solution by an Isatin-aniline Compound," *Molecules*, Vol. 36, Part B, No. 2, 2018.

[16] A.A.H. Kadhum, A. B. Mohamad, L.A. Hammed, A.A. Al-Amiery, N. H. San, A.Y. Musa, " Inhibition of Mild Steel Corrosion in Hydrochloric Acid Solution by New Coumarin," *Materials*, Vol. 7, pp. 4335–4348, 2014.

[17] A.A. Al-Amiery, A.A.H., Kadhum, A. Kadihum, A.B. Mohamad, C.K. How, S. Junaedi, "Inhibition of Mild Steel Corrosion in Sulfuric Acid Solution by New Schiff Base," *Materials*, Vol. 7, pp. 787–804, 2014.

[18] A.A. Al-Amiery, A.A.H. Kadhum, A.H.M. Alobaidy, A.B. Mohamad, P. S. Hoon, "Novel Corrosion Inhibitor for Mild Steel in HCl," *Materials*, Vol. 7, pp. 662–672, 2014.

[19] A.A. Al-Amiery, A.A.H. Kadhum, A.B. Mohamad, S. Junaedi, "Novel Hydrazinecarbothioamide as a Potential Corrosion Inhibitor for Mild Steel in HCl," *Materials*, Vol. 6, pp. 1420–1431, 2013.

[20] A. Standard. G1–03. "Standard Practice for preparing, cleaning, and evaluating corrosion test specimens," *Annual Book ASTM Standards*, Vol. 3, pp. 17–25, 2003.

[21] Q. Deng, H-W. Shi, N-N. Ding, B-Q .Chen, X-P. He, G .Liu, et al. "Novel triazolyl bisamino acid derivatives readily synthesized via click chemistry as potential corrosion inhibitors for mild steel in HCl," *Corros .Sci*. Vol. 57, pp. 220–227, 2012.

[22] Z .Tao, He W, S .Wang, S. Zhang, G. Zhou, "A study of differential polarization curves and thermodynamic properties for mild steel in acidic solution with nitro phenyl triazole derivative," *Corros. Sci*, Vol. 60, pp. 205–213, 2012.

[23] K.F. Al-Azawi, I.M. Mohammed, S. B. Al-Baghdadi, T. A. Salman, H. A. Issa, A.A. Al-Amiery, T.S. Gaaz and A. A. H. Kadhum, "Experimental and quantum chemical simulations on the corrosion inhibition of mild steel by 3-((5-(3,5- dinitrophenyl)-1,3,4-thiadiazol-2-yl) imino)indolin-2-one," *Results Phys*., Vol. 9, pp. 278–283, 2018.

[24] C. Verma, L.O. Olasunkanmia, E.E. Ebensoa, M.A. Quraishi, "Substituents effect on corrosion inhibition performance of organic compounds in aggressive ionic solutions: A review," *J. Mol. Liq.*, Vol. 25, pp. 100–118, 2018.