Electrochemical Studies of the corrosion inhibition effect of 2-amino-5-ethyl-1,3,4-thiadiazole on low carbon steel in dilute sulphuric acid

[1,2] Roland Tolulope Loto*, [1,2] Cleophas Akintoye Loto and [2]Patricia Abimbola Popoola
[1]*Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria.*
[2]*Department of Chemical, Metallurgical and Materials Engineering,*
Tshwane University of Technology, Pretoria, South Africa.
tolu.loto@gmail.com*

Summary: The electrochemical behaviour of carbon steel in 0.5 M H_2SO_4 was studied in the presence of 2-amino-5-ethyl-1 3 4-thiadiazole (TTD) as inhibitor with the aid of weight loss method, potentiodynamic polarization and open circuit potential measurement technique. The effect of inhibitor concentrations, exposure time, corrosion rate and surface coverage on inhibition efficiency was investigated. Results showed that TTD performed excellently in the acid solution with the inhibition efficiency increasing with increase in inhibitor concentration up to a peak value of 80.67% and 90.5% at maximum concentration from weight loss test and potentiodynamic polarization tests. The compound showed cathodic inhibition tendency in solution with the inhibitor molecules been effectively adsorbed onto the steel surface, stifling the electrochemical reactions responsible for corrosion through the exposure hours. Results from statistical analysis through ANOVA software depicts the overwhelming influence of inhibitor concentration on inhibition efficiency compared to exposure time.

Keywords: Corrosion; Thiadiazole; Sulphuric acid; Inhibition and Steel.

Introduction

The corrosion phenomenon occurs naturally leading to deterioration of metallic alloys and its physical and mechanical properties due to interaction of the alloy with their environment. Corrosion damage cuts across all industries where steel especially carbon steel is applied from pipelines, bridges, petroleum, and chemical processing plants to vehicles, wastewater systems and other marine applications. The economic loss due to corrosion is huge and constitutes a significant proportion of virtually every nation's GDP. Mitigation against corrosion varies widely with numerous methods and corrosion control techniques available however most of them are uneconomical or hazardous to the environment. Corrosion prevention with the use of chemical compounds and derivatives known as inhibitors has been one of the most cost effective and practical techniques for corrosion prevention with a number of researches on them worldwide since addition of inhibitors does not disrupt industrial processes and operations [1-4]. Currently there are efforts to develop environmentally friendly corrosion inhibitors with the use of organic compounds with molecules containing heteroatoms [5-9]. These compounds have been observed to protect steel against corrosion in acidic conditions through adsorption onto the steel surface. This process results in the separation of the steel surface from the acid solutions through physical, physiochemical and or

chemical mechanisms [10]. The strength and duration of protection offered by the organic compounds varies with the types of compound and their molecular structure, configuration and atomic constituents and combination.

Results and discussion

Weight Loss Analysis

Figs (1 and 2) shows the variation of corrosion rate and percentage inhibition efficiency versus exposure time at specific TTD concentrations while Fig. 3 shows the variation of %*IE* with TTD concentration. In H_2SO_4 the steel surface passivates progressively with increase in inhibitor concentration from 0.125% - 0.375% TTD as the cationic molecules of TTD gradually inhibits the corrosive effect of the anionic species (Cl^-/ SO_4^{2-}) by displacing them through competitive adsorption, thereby forming a physiochemical film which strongly adheres to the steel surface. The film is virtually impenetrable and effective till 0.75% TTD. The electrochemical reactions within the test solution modifies in the presence of TTD whereby TTD precipitates adhere to the metal samples through the exposure period. The reactive sites on the specimen surface are totally separated from the corrosive species of the acid chloride solution.

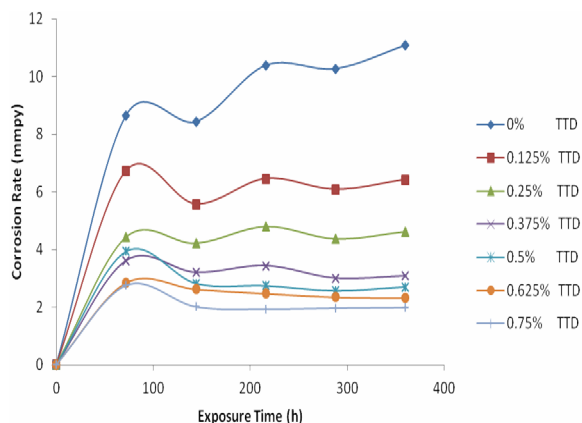*To whom all correspondence should be addressed.

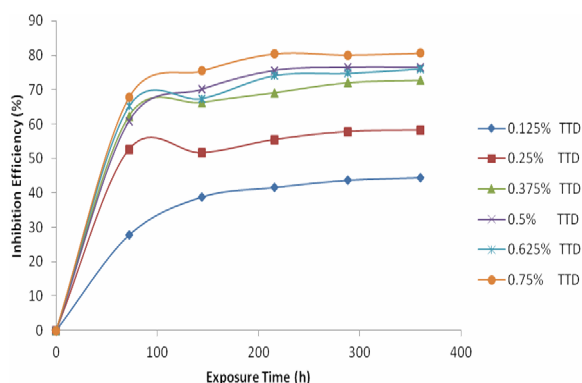Fig. 1:   Effect of percentage concentration of TTD on the corrosion rate of MS in 0.5M H_2SO_4.

Fig. 2:   Plot of inhibition efficiencies of sample (A-G) in 0.5M H_2SO_4 during the exposure period.

Polarization Studies

Fig. 4 shows the potentiodynamic curves of MS in the absence and presence of TTD at specific concentrations in 0.5M H_2SO_4. There is a significant reduction in corrosion rates in the acid solutions despite the differential values in the electrochemical variables. Changes in the anodic and cathodic Tafel constants remained spontaneous due to the influence of TTD on the electrochemical process, thus altering the redox reactions responsible for corrosion. The ability of the inhibitor to strongly adsorb on the steel's surface and effectively minimize corrosion is central to the inhibitive performance of TTD. The inhibitive action is related to the formation of a compact barrier film on the steel electrode surface and is slightly dependent on its concentration in sulphuric acid as observed in Table-1, Fig. 5, due to the instantaneous and effective action of the cationic molecules of the TTD compound.
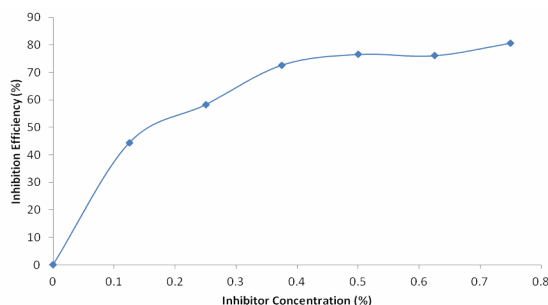

Fig. 3:   Variation of percentage inhibition efficiency of TTD with inhibitor concentration in 0.5M H_2SO_4 solution

TTD showed mixed inhibiting attributes in the acid solutions based on observation of its influence on the Tafel constants of the redox process and the variation of the corrosion potential (E_{cr}) values, but with greater affinity for cathodic inhibition. The values of E_{cr} moved to less noble values at all TTD concentrations. The linear polarization curves in the acid solutions are generally the same indicating similar electrochemical reactions. The maximum displacement of corrosion potential in sulphuric acid solution is 78mV in the cathodic direction thus the inhibitor is conventionally a mixed type inhibitor but cathodic type in action. The mechanism of inhibition results in increase in surface impedance of the cathodic sites [11, 12].
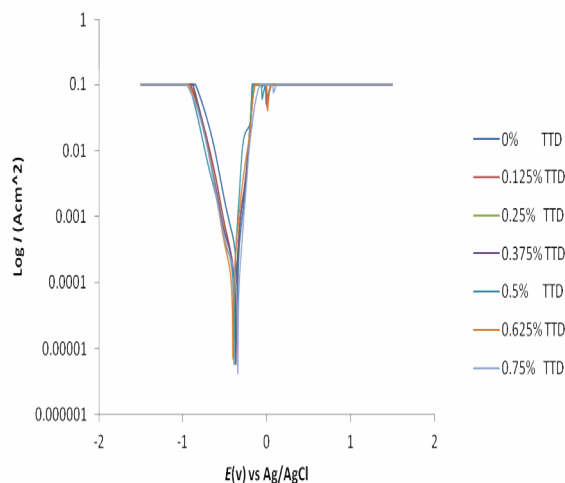

Fig. 4:   Comparison plot of polarization scans for carbon steel in 0.5M H_2SO_4 solution at specific concentrations of TTD (0% -0.75% TTD).

Table-1: Data obtained from polarization resistance measurements for carbon steel in 0.5M H_2SO_4 solution at specific concentrations of TTD.

Sample	Inhibitor Concentration (%)	ba (V/dec)	bc (V/dec)	E_{cr}, Obs (V)	I_{cr} (A/cm²)	i_{cr} (A)	Corrosion rate (mm/yr)	R_p (Ωcm²)	%IE
A	0	0.031	0.052	-0.351	0.000125	0.000207	1.45	40.71	0
B	0.125	0.039	0.026	-0.369	3.95E-05	6.52E-05	0.46	104.03	68.5
C	0.25	0.030	0.067	-0.368	3.11E-05	5.13E-05	0.36	175.62	75.3
D	0.375	0.032	0.028	-0.363	2.17E-05	3.58E-05	0.25	181.36	82.7
E	0.5	0.024	0.035	-0.389	1.92E-05	3.17E-05	0.22	195.27	84.7
F	0.625	0.051	0.017	-0.402	1.43E-05	2.36E-05	0.17	234.89	88.6
G	0.75	0.015	0.027	-0.344	9.39E-06	1.55E-05	0.11	270.49	92.5
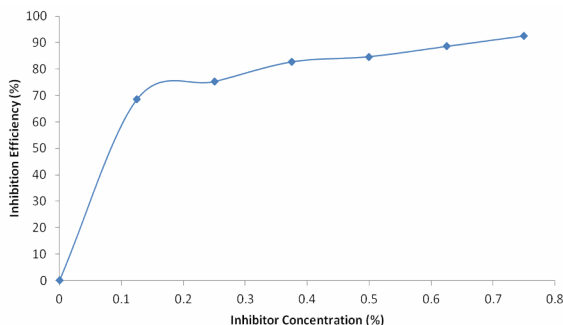
Fig. 5: The relationship between %*IE* and inhibitor concentration for polarization test in 0.5M H_2SO_4 solution/ TTD.

Corrosion inhibition of mild steel in the acid media by TTD as observed from weight loss, open circuit potential measurement potentiodynamic polarization showed that the inhibition efficiency of TTD increased with increase in TTD concentration. Adsorbed TTD molecules on the surface of the steel interfere with cathodic and anodic reaction. Inhibition of the redox reactions depends on the degree of surface coverage of the steel with the adsorbate. Competitive adsorption is assumed to occur on the surface of the steel between the aggressive chloride/sulphate ions and the inhibitor molecule.

Mechanism of Inhibition

It can be assumed that chloride ions are pre-adsorbs on the steel surface and the net positive charge on the surface enhances the specific adsorption of chloride and sulphate ions [13, 14]. The cationic forms of TTD molecules (resulting from protonation in the acid solution) are adsorbed through electrostatic interactions (physical adsorption) between positively charged nitrogen atoms and negatively charged carbon steel surface [15]. The adsorption of the TTD molecules can also occur due to the formation of links between the *d*-orbital of iron atoms, involving the displacement of water molecules from the metal surface, by the electron pairs present on the nitrogen and sulfur atoms and π-orbitals (chemisorption) [15, 16].

TTD being a heterocyclic compound act by adsorption onto the steel surface through the heteroatom and conjugated double bonds within their molecular structures [17]. The presence of heteroatoms (nitrogen and sulfur,) and double bonds in the inhibitor's chemical structure enhance the adsorption process promoting the formation of a chelate on the metal surface, which involves the transfer of electrons from the TTD to metal thereby forming coordinate covalent bond (chemisorption) during the chemical adsorption process [18]. The steel acts as an electrophile, whereas the nucleophile centers of TTD molecule with free electron pairs readily available for sharing results in bond formation and the formation of an impenetrable protective barrier [19]

TTD influenced the kinetics of steel dissolution and its electrochemical behavior. This phenomenon is due to the formation of a thin film of TTD on the metal surface through electrochemical interaction and the adsorption processes as earlier explained. The protective coating separates the steel from the corrosive anions thus preventing Fe atoms from leaving the steel surface to the corrosive solution thereby decreasing the rate of corrosion [20].

Open Circuit Potential Measurement

The effect of TTD compound on the corrosion potential of carbon steel in 0.5M H_2SO_4 as shown in Fig. 6 and Table-2, is highly significant from 0.375% TTD to 0.75% TTD concentration. At these concentrations the potential values is within passivity potentials and the corrosion risk is very low due to the impenetrable film formed on the steel surface physiochemically. Observation of the corrosion potentials through the exposure period from the onset shows the gradual decrease in potential values with time at all concentrations i.e. TTD's influence on the electrochemical process increases progressively and in effect modifies the total redox process to effectively suppress the corrosion reactions.

Table-2: Data obtained from potential measurements for austenitic stainless steel in 0.5M H$_2$SO$_4$ in presence of specific concentrations of the TTD

TTD Concentration	0%	0.125%	0.25%	0.375%	0.5%	0.625%	0.75%
Exposure Time (hrs)							
0	-463	-423	-389	-338	-331	-335	-332
48	-462	-415	-379	-326	-327	-329	-321
96	-455	-409	-372	-319	-324	-323	-315
144	-446	-395	-365	-313	-319	-314	-307
192	-441	-387	-359	-307	312	-309	-298
240	-437	-372	-351	-300	-306	-299	-291
288	-436	-368	-342	-291	-301	-292	-288
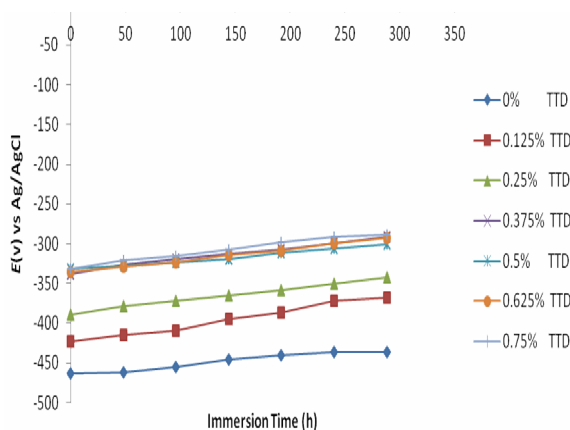
Fig. 6:   Variation of open circuit potential with immersion time for TTD concentrations in 0.5M H$_2$SO$_4$ Adsorption Isotherms and Thermodynamics of the Corrosion Process

The mechanism of corrosion inhibition can be explained on the basis of the adsorption behaviour of the adsorbate on the metal surface. Adsorption isotherms are very important in determining the mechanism of organo - electrochemical reactions. The adsorptive behaviour of the organic compounds is an important part of this study, as it provides important clues to the nature of the metal-inhibitor interaction [21, 22]. Langmuir, Frumkin and Freundlich adsorption isotherms were applied to describe the adsorption mechanism for the inhibiting compounds in acid solutions, as they best fit the experimental results.

The isotherms are of the general form.

$$f(\theta, x)\exp(-2a\theta) = K \qquad (1)$$

where f (θ, x) is the configurational factor which depends upon the physical model and assumption underlying the derivative of the isotherm, θ is the surface coverage, C is the inhibitor concentration, x is the size ration, 'a' is the molecular interaction parameter and K is the equilibrium constant of adsorption process.

The conventional form of the Langmuir isotherm is [23, 24],

$$\left[\frac{\theta}{1-\theta}\right] = K_{ads}C \qquad (2)$$

and rearranging gives

$$K_{ads}C = \left[\frac{\theta}{1 + K_{ads}\,\theta}\right] \qquad (3)$$

where θ is the degree of coverage on the metal surface, C is the inhibitor concentration in the electrolyte, and K_{ads} is the equilibrium constant of the adsorption process.

Langmuir isotherm proposes the following;

I.   The molecular interaction between the adsorbates on the metal surface is fixed.
II.   The Gibbs free energy does not depend on the surface coverage values
III.   There is no effect of lateral interaction among the adsorbates on the value of Gibbs free energy [25].

The plot of C/θ versus AMB concentration (C) (Fig. 7) fitted the Langmuir adsorption isotherm.
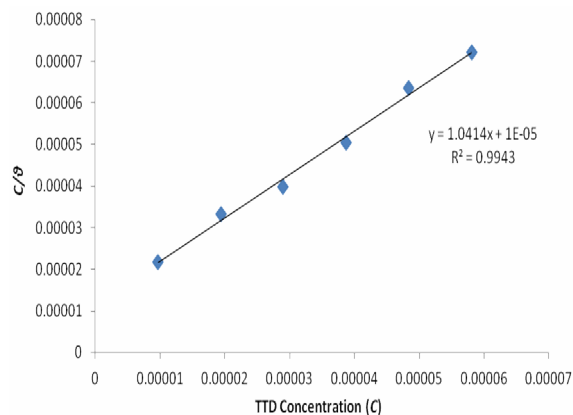
Fig. 7:   Relationship between C/θ and TTD concentration (C) in 0.5 M H$_2$SO$_4$ for MS.

Frumkin isotherm assumes unit coverage at high inhibitor concentrations and that the electrode surface is inhomogeneous i.e. the lateral interaction effect is not negligible. In this way, only the active surface of the electrode, on which adsorption occurs, is taken into account. Frumkin adsorption isotherm can be expressed according to equation 4.

$$\text{Log } C \times \left[\frac{\theta}{1-\theta} \right] = 2.303 \log K + 2\alpha\theta \qquad (4)$$

where K is the adsorption-desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer.

Plots of $\left[\dfrac{\theta}{1-\theta} \right]$ versus inhibitor concentration(C) as presented in Fig. 8 is linear with slight deviation which shows the applicability of Frumkin isotherm. The lateral interaction term (α) calculated from the slope of the Frumkin isotherm (Table-3), shows the intermolecular attraction between the TTD molecules on the surface of MS decreases progressively with increase in TTD concentration; however its overall influence on the inhibition efficiency is negligible.
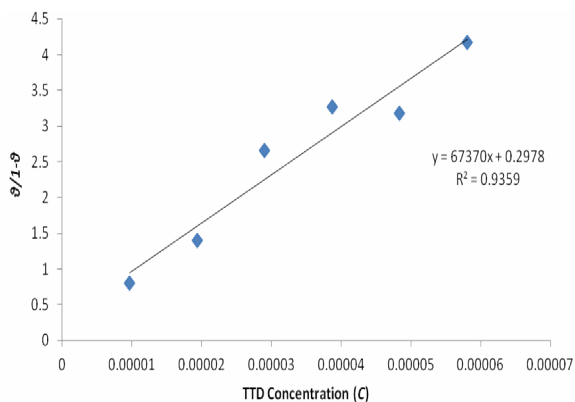

Fig. 8: Relationship between $\theta/1 - \theta$ and TTD concentration (C) in 0.5 M H_2SO_4 for MS.

Table-3: Relationship between lateral interaction parameter and surface coverage (θ) in 3 M H_2SO_4 MS.

Lateral Interaction Parameter (α)	Surface Coverage (θ)
0	0
0.335	0.444
0.255	0.583
0.205	0.727
0.194	0.766
0.196	0.761
0.185	0.807

The plot in Fig. 9 fitted the Freundlich isotherm, according to equation 5, which shows that the relationship between the amount and concentration of TTD molecules absorbed onto the steel varies at different concentrations.

$$\theta = KC^n \qquad (5)$$

$$\log \theta = n\log C + \log K \qquad (6)$$

n is a constant depending on the characteristics of the adsorbed molecule, where $0 < n < 1$, from the plot $n = 0.018$ in H_2SO_4.
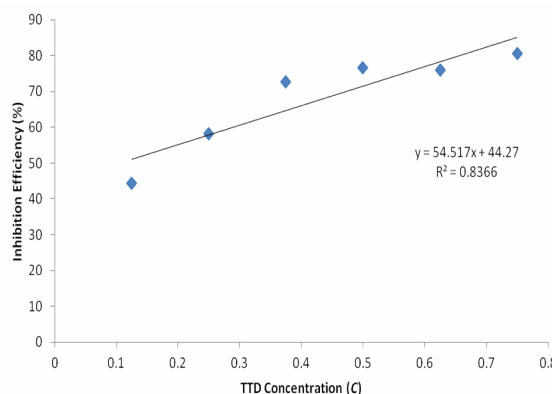

Fig. 9: Relationship between inhibition efficiency and TTD concentrations (C) in 0.5 M H_2SO_4 for MS.

Values of ΔG_{ads} around -20 kJ/mol are consistent with physisorption; those around -40 kJ/mol or higher involve charge sharing to form a coordinate type of bond chemisorption [26]. The value of ΔG_{ads} in H_2SO_4 and HCl for MS under the action of the organic compounds as shown in Table-4 reveals the strong adsorption of TTD molecules onto the steel surface. The negative values of ΔG_{ads} showed that the adsorption of inhibitor molecules on the metal surface is spontaneous. The values of ΔG_{ads} calculated ranged between −38.00 and −40.94 kJ mol^{-1} for TTD (Table-4) in H_2SO_4. The values in H_2SO_4 are consistent with chemical interaction and adsorption onto the MS surface.

The value of ΔG_{ads} obtained shows that the molecules chemisorb on the steel producing a bond resistant to penetration and competitive adsorption from the corrosive species. The intermolecular bonding is sufficiently strong to prevent displacement of adsorbed inhibitor molecules along the surface. The precipitates formed are stable in the acid solution throughout the exposure period.

Table-4: Data obtained for the values of Gibbs free energy, Surface coverage and equilibrium constant of adsorption at varying concentrations of TTD in 0.5 M H_2SO_4 for MS

Samples	Surface Coverage (θ)	Equilibrium Constant of Adsorption (K_{ads})	Free energy of Adsorption (ΔG_{ads}) (kJ/mol)
B	0.444	82589.63	-38.00
C	0.583	72018.72	-37.67
D	0.727	91746.55	-40.94
E	0.766	84482.52	-38.06
F	0.761	65732.3	-37.43
G	0.807	71832.52	-37.66

Table-5: Analysis of variance (ANOVA) for inhibition efficiency of TTD inhibitor in 0.5M H_2SO_4 (at 95% confidence level).

TTD H_2SO_4					Min. MSR at 95% confidence	
Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	Mean Square Ratio	Significance F	F%
Inhibitor concentration	4986.09	5	997.22	98.46	2.71	83.96
Exposure Time	613.22	4	153.30	15.14	2.87	10.46
Residual	202.56	20	10.13			
Total	5801.87	29				

Statistical Analysis

Two-factor single level experimental ANOVA test (F - test) was used to analyse the separate and combined effects of the percentage concentrations of TTD and exposure time on the inhibition efficiency of TTD in the corrosion inhibition of carbon steels in 0.5M H_2SO_4 solutions and to investigate the statistical significance of the effects. The F - test was used to examine the amount of variation within each of the samples relative to the amount of variation between the samples.

The Sum of squares among columns (exposure time) was obtained with the following equations

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \qquad (7)$$

Sum of Squares among rows (inhibitor concentration).

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \qquad (8)$$

Total Sum of Squares

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \qquad (9)$$

The results using the ANOVA test is tabulated in Table-5 as shown below.

The ANOVA results (Table-5, Fig. 10) in the acid solution shows the overwhelming influence of inhibitor concentration on the inhibition efficiency with F - values of 139.41. These are greater than significance factor at $\alpha = 0.05$ (level of significance or probability). The F - values of exposure time in both acids are less significant compared to inhibitor concentration but greater than the significant factor

hence they are statistically relevant with F - values of 15.14. The statistical influence of the inhibitor concentration in H_2SO_4 is 83.96% while the influence of the exposure time is 10.46%. The inhibitor concentration and exposure time are significant model terms influencing inhibition efficiency of TTD on the corrosion of the steel specimen with greater influence from the percentage concentration of TTD.
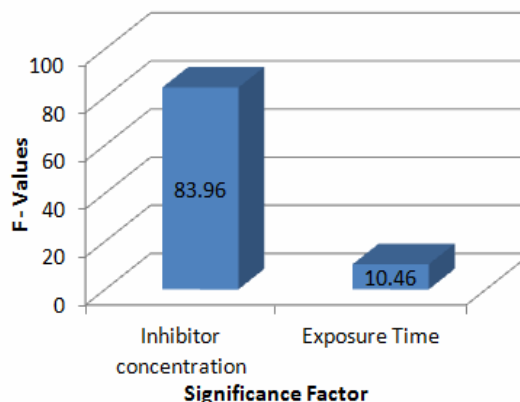

Fig. 10: Influence of inhibitor concentration and exposure time on inhibition efficiency of TTD in 0.5M H_2SO_4.

Experimental

Material

The carbon steel used for this work was obtained in the open market and analyzed at the Applied Microscopy and Triboelectrochemical Research Laboratory, Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, South Africa. The carbon steel has the nominal per cent composition: 0.401 C, 0.169 Si, 0.440 Mn, 0.005 P, 0.012 S, 0.080 Cu, 0.008 Ni, 0.025 Al, and the rest being Fe.

Table-6: Data obtained from weight loss measurements for carbon steel in 0.5M H_2SO_4 at specific concentrations of the TTD at 432 h.

Samples	Corrosion Rate (mm/yr)	Inhibitor Conc. (%)	Inhibition Efficiency (%)	Weight Loss (mg)	Molarity	Surface Coverage (θ)
A	11.08	0	0	2.028	0	0
B	6.43	0.125	44.43	1.127	9.68E-06	0.444
C	4.62	0.25	58.28	0.846	1.94E-05	0.583
D	3.08	0.375	88.66	0.230	0.000029	0.727
E	2.70	0.5	76.58	0.475	3.87E-05	0.766
F	2.32	0.625	76.09	0.485	4.84E-05	0.761
G	1.99	0.75	80.67	0.392	5.81E-05	0.807

Inhibitor

2-amino-5-ethyl-1 3 4-thiadiazole (TTD) a colorless, flake light solid is the inhibitor used. The structural formula of TTD is shown in Fig. 11. The molecular formula is $C_4H_7N_3S$, while the molar mass is 129.18 g mol^{-1}.
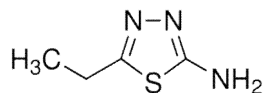
Fig. 11: Chemical structure of 2-amino-5-ethyl-1, 3, 4-thiadiazole (TTD).

TTD was prepared in concentrations of 0.125%, 0.25%, 0.375%, 0.5%, 0.625% and 0.75% respectively.

Test Media

0.5M tetraoxosulphate (VI) acid with 3.5% recrystallised sodium chloride of Analar grade were used as the corrosion test media.

Preparation of Test Specimens

A cylindrical carbon steel rod with a diameter of 14.5 mm was carefully machined and cut into a number of test specimens of average dimensions in length of 6 mm. A 3 mm hole was drilled at the centre for suspension. The steel specimens were then thoroughly rinsed with distilled water and cleansed with acetone for weight loss analysis. The linear polarization technique involved grinding the two surface ends of each specimen with silicon carbide abrasive papers of 80, 120, 220, 800 and 1000 grits before being polished with 6.0 μm to 1.0 μm diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a dessicator before the test.

Weight-loss Experiments

Weighted test species were fully and separately immersed in 200 ml of the test media at specific concentrations of the PPD for 360 h at ambient temperature. Each of the test specimens was taken out every 72 hrs, washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of corrosion rate (mm/y) and percentage inhibition efficiency (%*IE*) (calculated) versus exposure time (h) (Figs. 1 and 2) for the test media and those of inhibition efficiency (%*IE*) (calculated) versus percentage TTD concentration (Fig. 3) were made from Table-6.

The corrosion rate (R) calculation is from this equation 10:

$$R = \left[\frac{87.6W}{DAT}\right] \qquad (10)$$

where W is the weight loss in milligrams, D is the density in g/cm^2, A is the area in cm^2, and T is the time of exposure in hours. The %*IE* was calculated from the relationship in equation 11.

$$\%IE = \left[\frac{W1-W2}{W1}\right] \times 100 \qquad (11)$$

W_1 and W_2 are the corrosion rates in the absence and presence of predetermined concentrations of TTD. The %*IE* was calculated for all the inhibitors every 72 h during the course of the experiment, while the surface coverage is calculated from the relationship:

$$\theta = \left[1 - \frac{W2}{W1}\right] \qquad (12)$$

where θ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent. W_1 and W_2 are the weight loss of carbon steel coupon in free and inhibited acid chloride solutions respectively.

Open Circuit Potential Measurement

A two-electrode electrochemical cell with a silver/silver chloride was used as reference electrode. The measurements of OCP were obtained with Autolab PGSTAT 30 ECO CHIMIE potentiostat. Resin mounted test electrodes/specimens with exposed surface of 165 mm^2 were fully and separately immersed in 200 ml of the test media (acid

chloride) at specific concentrations of TTD for a total of 288 h. The potential of each of the test electrodes was measured every 48 h. Plots of potential (mV) versus immersion time (h) (Fig. 6) for the two test media were made from the tabulated values in Table-3.

Linear Polarization Resistance

Linear polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 165 mm^2. The electrode was polished with different grades of silicon carbide paper, polished to 6.0 μm, rinsed by distilled water and dried with acetone. The studies were performed at ambient temperature with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200 ml of electrolyte, with and without the inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (SCE) was used as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic studies were then made from -1.5V *versus* OCP to +1.5 mV *versus* OCP at a scan rate of 0.00166 V/s and the corrosion currents were registered. The corrosion current density (I_{cr}) and corrosion potential (E_{cr}) were determined from the Tafel plots of potential *versus* log *I*. The corrosion rate (*R*), and the percentage inhibition efficiency (%*IE*) were calculated as follows

$$R = \frac{0.00327 * i_{corr} * eq.wt}{D} \qquad (13)$$

where i_{cr} is the current density in μA/cm^2, *D* is the density in g/cm^3; *eq.wt* is the specimen equivalent weight in grams. The percentage inhibition efficiency (%*IE*) was calculated from corrosion rate values using the equation 14.

$$\%IE = 1 - \left[\frac{R_2}{R_1}\right] \times 100 \qquad (14)$$

R_1 and R_2 are the corrosion rates in absence and presence of TTD respectively.

Statistical Analysis

Two-factor single level statistical analysis using ANOVA test (*F* - test) was performed so as to investigate the significant effect of inhibitor concentration and exposure time on the inhibition efficiency values of the TTD in the acid media.

Conclusion

The performance of TTD on the corrosion inhibition of carbon is slightly dependent on its concentration in sulphuric acid media due to the instantaneous and effective action of the cationic molecules of the TTD compound. TTD showed combined inhibiting attributes in the acid solutions based as a result of its influence on the Tafel constants of the redox process and the variation of the corrosion potential (E_{cr}) values, but with greater affinity for cathodic inhibition. The maximum displacement of corrosion potential in the acid solution is in the cathodic direction thus the inhibitor is theoretically a mixed type inhibitor but cathodic type in action. The inhibition mechanism of TTD on carbon steel was due to adsorption through its functional groups, being absorbed through the pi-electrons of the aromatic rings in its molecular structure, the lone pairs of nitrogen, sulphur and oxygen electrons and as a cationic species. The corrosion potentials throughout the exposure period from the onset shows the gradual decrease in potential values with time at all concentrations i.e. TTD's influence on the electrochemical process increases progressively and in effect modifies the total redox process to effectively suppress the corrosion reactions. ANOVA results in the acid solution shows the overwhelming influence of inhibitor concentration on the inhibition efficiency with a statistical relevance of 83.96%.

Acknowledgement

References

1. G. Q. Liu, Z. Y. Zhu, W. Ke, C. I. Han and C. L. Zeng, *Corrosion Nace*, **57**, 730 (2001).
2. W. D. Collins, R. E. Weyers and I. L. Al-Qadi, *Corrosion Nace*, **49**, 74 (1993).
3. U. J. Ekpe, U. J. Ibok, B. I. Ita, O. E. Offiong and E. E. Ebenso, *Materials Chemistry and Physics*, **40**, 87 (1995).
4. N. O. Eddy, P. A. Ekwumemgbo and P. A. P. Mamza, *Green Chemistry Letters and Reviews*, **2**, 223 (2009).
5. H. Keles, M. Keles, I. Dehri and O. Serindag, *Colloids and Surfaces* A*: Physicochemical and Engineering Aspects*, **320**, 138 (2008).
6. L. Tang, X. Li, L. Li, G. Mu and G. Liu, *Materials Chemistry and Physics*, **97**, 301 (2006).

7. R. Solmaz, G. Kardas, B. Yazıcı and B. Erbil, *Protection of Metals*, **43**, 476 (2007).
8. A. Popova, E. Sokolova, S. Raicheva and M. Christov, *Corrosion Science*, **45**, 33 (2003).
9. G. Kardas and R. Solmaz, *Corrosion Review*, **24**, 151 (2006).
10. A. W. Adamson, *Physical Chemistry of Surfaces*, John Wiley and Sons Inc, (1990).
11. U. M. Eduok, S. A. Umoren and A. P. Udoh, *Arabian Journal of Chemistry*, **5**, 325 (2010).
12. A. J. Trowsdale, B. Noble, S. J. Harris, I. S. R. Gibbins, G. E. Thompson and G. C. Wood, *Corrosion Science*, **38**, 177 (1996).
13. M. Lagrenée, B. Mernari, M. Bouanis, M. Taisnel and F. Bentiss F, *Corrosion Science*, **44**, 573 (2002).
14. F. Bentiss, C. Jama, B. Mernari, H. El Attari, L. El Kadi, M. Lebrini, M. Traisnel and M. Lagrenée, *Corrosion Science*, **51**, 1628 (2009).
15. F. Bentiss, B. Mernari, M. Traisnel, H. Vezin and M. Lagrenée, *Corrosion Science*, **53**, 487 (2011).
16. M. M. El-Naggar, *Corrosion Science*, **49**, 2226 (2007).
17. H. B. Rudresh and S. M. Mayanna, *Surface Technology*, **6**, 139 (1977).
18. M. Ajmal, A. S. Mideen and M. A. Quaraishi, *Corrosion Science*, **36**, 79 (1994)**.**
19. J. Fang and J. Li, **593**, 179 (2002).
20. E. McCafferty, *Corrosion Control by Coating*; Leidheiser, H., Jr., Ed.; Science Press: Princeton, NJ, USA (1979).
21. M. A. Quraishi, F. A. Ansari and D. Jamal, *Indian journal of Chemical Technology*, **11**, 271 (2004).
22. S. T. Hirozawa, *Proc. 8th Eur. Symp. Corros. Inhib*. Ann. University, Ferrara, Italy, **1**, 25 (1995).
23. A. K. Anees, S. Y. Aprael and A. H. K. Abdul, *Journal of the Chilean Chemical Society*, **55**, 150 (2010).
24. M. H. Wahdan, A. A. Hermas, M. S. Morad, Materials Chemistry and Physics, **76**, 111 **(**2002).
25. K. S. Ashish and M. A. Quraishi, *Corrosion Science*, **53**, 1288 (2011).
26. L. M. Vračar and D. M. Dražić, *Corrosion Science*, **44**, 1669 (2002).