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Investigation of Inhibitory Effect of Thiourea on Corrosion of Mild Steel in Dual Purpose Kerosene (DPK) and Premium Motor Spirit (PMS)

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ABSTRACT

The inhibitory effect of thiourea on the corrosion of mild steel in dual purpose kerosene (DPK) and premium motor spirit (PMS) were investigated using gasometric assembly technique. The results revealed that thiourea shows no inhibitory performance in DPK and poor inhibitory effect in PMS. The inhibitory effect of thiourea on mild steel in PMS was found to be consistent with Frumkin adsorption isotherm. The ΔG°_{ads} shows that the adsorption of inhibitor molecules was spontaneous and typical of physical adsorption mechanism. Surface analysis of the mild steel using SEM-EDX confirmed non-inhibitive nature of thiourea in the corrosion of mild steel in DPK and PMS respectively.

KEYWORDS: Mild Steel, gasometric assembly technique, thiourea, corrosion inhibition, petroleum product.

I. INTRODUCTION

Corrosion is the deformation of metals and alloys by the chemical reaction with the environment [1]. Corrosion of metal structures is a major problem that must be regularly addressed in oil industry. Mild steel is the material of choice in oil and gas sector because of its ability to work mechanically and its low cost. [2]. The continual storage and transportation of petroleum product in mild steel materials may lead to corrosion of the metal surface, therefore, an appropriate corrosion inhibitor is urgently needed. The use of corrosion inhibitors of non- toxic type, without heavy metals and inorganic phosphate is of considerable importance [3,4]. The application of inorganic compounds such as chromate and nitrite as corrosion inhibitors is being limited due to its environmental problems [5], therefore an environmentally friendly corrosion inhibitors is urgently needed.

Among available corrosion inhibitors, organic compounds containing a heteroatom, such as nitrogen, oxygen, sulphur and phosphorous or containing double and triple bonds as well as aromatic rings are considered as effective in materials used as anticorrosive inhibitors [2,6]. They have shown great effectiveness in inhibiting corrosion due to film formation on the metal surfaces by adsorption [4,7] and the approach of adsorption depends on the inhibitor's chemical structure and the nature of the solution; acid or base [8]. Thiourea is an organosulphur compound with the formular $SC(NH_2)_2$. The presence of sulphur, Nitrogen and availability of lone pair electrons in thiourea makes it a potential corrosion inhibitor as it facilitate the adsorption of the compound on the metal surface. It has been reported that sulphur containing inhibitors are useful in sulphuric acid solution, while nitrogen containing inhibitors exerts their best efficiencies in hydrochloric acid [4]. Currently, there is limited literature on the corrosion inhibition potential of thiourea of mild steel in petroleum products. In this present work, we investigated the inhibitory effect of thiourea on corrosion of mild steel in dual purpose kerosene (DPK) and premium motor spirit (PMS).

II. EXPERIMENTAL

2.1 Mild Steel Preparation

The mild steel coupon of percentage composition of C(1.64), Mo (0.71), Si (0.39), Al (0.35), Na (0.35), K (0.26), Mg (0.25), O (0.24), S (0.23), P (0.20), Ca (0.20) and remaining as Fe were used for the corrosion studies. The coupons were polished with emery paper and mechanically press cut into 2×2 cm with thickness of $0.041cm^2$ and surface area of $8.0cm^2$. The coupons were degreased in absolute ethanol, dried in acetone and stored in moisture free dessicator before their use. DPK and PMS were collected from NNPC, Owerri, Imo State Mega filling station. The DPK and PMS were employed as the aggressive solution and 200ppm thiourea was used as inhibitor for this study.

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2.2 Gasometric Measurement

The gasometric method described by Okeke *et al* [3] and Uwah *et al* [9] was modified and adopted for the corrosion study. Hydrogen evolutionmeasurements were carried out using gasometric assembly. 200cm3 of the corrodent solution was introduced into the reaction flask connected to the assembly and the initial volume of air in the burette was noted. Then the mild steel coupon was dropped into the corrodent and the reaction flask quickly closed to prevent leakage of hydrogen gas. The change in the volume of hydrogen gas evolved with time was recorded every 1 week by noting the volume change in the level of paraffin oil in the burette for 12 weeks.

The average corrosion rates of the mild steel measured in millimeter per year (MPY), were calculated using method earlier described elsewhere [10-12].

$$\text{Corrosion Rate} = \frac{534H}{\rho AT} \quad (1)$$

Where H is the hydrogen evolution in ml, ρ is the metal density in Mg/M^3, A is the exposed area of the mild steel in M^2, T is the exposure time in hours. The inhibition efficiency (IE) and surface coverage (θ) were calculated using the eqn 2 and 3 respectively.

$$\%IE = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \quad (2)$$

Where CR_{blank} and CR_{inh} are the corrosion rates in the absence and presence of the inhibitor respectively.

$$\theta = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \quad (3)$$

III. Results and Discussion

3.1. Physicochemical Properties of Dual Purpose Kerosene and Premium Motor Spirit

The physicochemical properties of DPK and PMS are presented in Table 1. pH value of DPK and PMS was 7.01 are 5.33 showing the neutrality and acidity of the corrodents. Electrical conductivity indicates the ability of a solution to carry electrical current [10]. The conductivity values of the corrodents were zero showing non ionic conduction and non availability of dissolved salts or ions. The density was 0.7623g/ml and 0.7183/ml for DPK and PMS respectively. The density of the liquids shows floatability of the solvents. Dual purpose kerosene shows high carbon content (81.13ppm) the premium motor spirit (78.83ppm) while PMS shows high sulphur content (231.72ppm) than DPK (224.79ppm). The density content of the samples may be attributed to the carbon contents of the sample.

Table 1: Physicochemical Properties of Dual Purpose Kerosene and Premium Motor Spirit

Parameters	DPK	PMS
pH	7.01	5.33
Conductivity ($\mu S/cm^3$)	0.00	0.00
Carbon content (ppm)	81.13	78.83
Sulphur content (ppm)	224.79	231.72
Density (g/ml)	0.7623	0.7183

3.2. Corrosion Study

The variation of corrosion rate (mmpy), percentage inhibition efficiency and surface coverage evaluated using change in volume of hydrogen gas at 200ppm of thiourea in DPK and PMS for 12 weeks are shown in Table 2 and 3; and Figure 1-3 respectively. The high sulphur content of the corrodents shows that sour corrosion was responsible for the metal dissolution leading to evolution of hydrogen gas [11].

$$H_2S \rightarrow H^+ + HS^-$$
$$HS^- \rightarrow H^+ + HS^{2-}$$
$$2H^+ \text{ Fe} \rightarrow Fe^{2+}_{(s)} + H_{2(g)}$$

Table 2: Corrosion rates and surface coverage for mild steel in DPK in the absence and presence of inhibitor.

Weeks	Corrosion Rate (mmpy)		Surface Coverage
	Blank	inhibitor	
1	0.015	0.258	-16.20
2	0.013	0.228	-16.54
3	0.010	0.194	-18.40
4	0.008	0.187	-22.38
5	0.012	0.190	-14.83
6	0.028	0.180	-5.43
7	0.025	0.155	-5.20
8	0.030	0.145	-3.83
9	0.049	0.152	-2.10
10	0.063	0.142	-1.25
11	0.066	0.134	-1.03
12	0.063	0.124	-0.97

Table 3: Corrosion rates, percentage inhibition efficiency and surface coverage for mild steel in PMS in the absence and presence of inhibitor.

Weeks	Corrosion Rate (mmpy)		%IE	θ
	Blank	inhibitor		
1	0.172	0.046	73.26	0.73
2	0.147	0.030	79.59	0.80
3	0.132	0.052	60.61	0.61
4	0.156	0.110	29.49	0.29

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5	0.160	0.127	20.63	0.21
6	0.153	0.125	18.30	0.18
7	0.166	0.145	12.65	0.13
8	0.178	0.156	12.36	0.12
9	0.188	0.161	14.36	0.14
10	0.189	0.167	11.64	0.12
11	0.178	0.156	12.36	0.12
12	0.183	0.149	18.58	0.19

The corrosion rate of mild steel in DPK in the presence of inhibitor was higher when compared with in the absence of inhibitor. This indicates non inhibitive properties of thiourea in retardation of corrosion rather increases its dissolution in dual purpose kerosene. The surface coverage (θ) recorded in the corrosion study of mild steel in DPK all shows a negative value corresponding to the high rate of metal dissolution in the system. The non inhibitive performance of the inhibitor on mild steel in DPK may be attributed to non adsorption of the inhibitor on the surface of the metal and the neutral nature of the medium as research has shown that sulphur containing inhibitors have good inhibitory effect in acidic medium [4]. The corrosion rate and inhibition efficiency of mild steel in PMS in the presence and absence of inhibitor are presented in Table 3 and Figure 2 – 3.

Inhibition efficiency is the opposite of corrosion rate. The inhibitor applied to prevent corrosion of metals from occurring is considered to be efficient when corrosion rate decreases. The corrosion rate measured in the absence of inhibitor in PMS media shows to be greater than the corrosion rate observed in the presence of inhibitor. The inhibition efficiency of thiourea in inhibiting mild steel in PMS media was observed to decreases with increase in the time of study. The low inhibition efficiency of thiourea obtained in PMS maybe attributed to the acidic nature of the medium because sulphur atom is easily protonated in acid solution [4]. The poor inhibitive property of thiourea observed in this study shows that the organic compound is weakly or not adsorbed onto the metal surface of the metal.

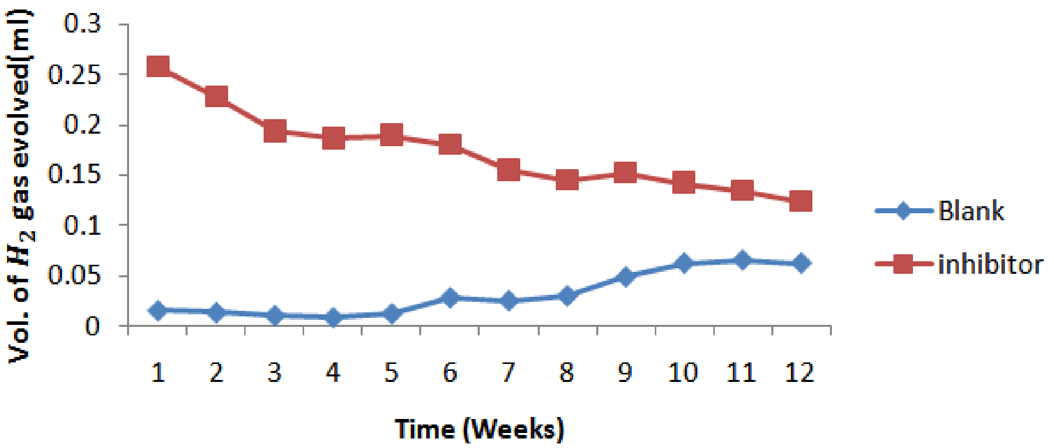

Figure 1: Variation of change in volume of hydrogen gas evolved in DPK with and without thiourea

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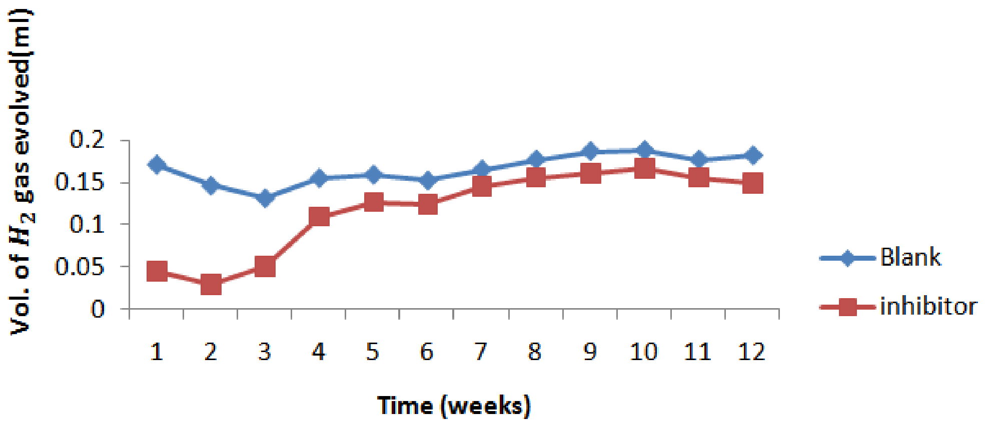

Figure 2: Variation of change in volume of hydrogen gas evolved in PMS with and without thiourea

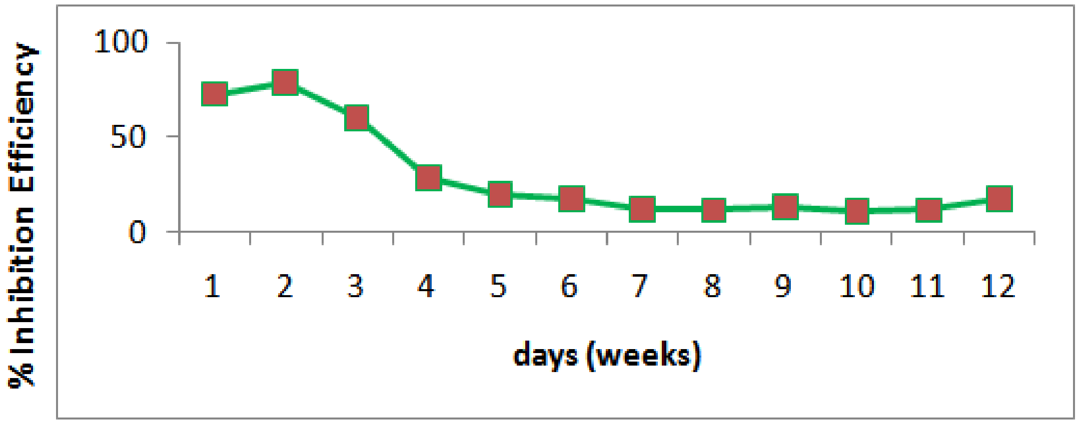

Figure 3: variation of % inhibition efficiency of mild steel in PMS

3.3 Adsorption Isotherm

Adsorption isotherm is used to study the nature and mechanism of interaction of inhibitors to the surface of the metal [6,11]. The degree of surface coverage (θ) of the inhibitor into Frumkin and Flory-Huggins adsorption isotherm were used to study the adsorption characteristics of thiourea. The linear equations of each isotherm were used to find the model of isotherm [12].

Frumkin Isotherm

$$lnC_{inh}\frac{\theta}{1-\theta} = lnK + 2d\theta \quad (4)$$

Flory – Huggins Isotherm

$$log\frac{\theta}{C_{inh}} = logK + xlog(1-\theta) \quad (5)$$

The Frumkin adsorption isotherm assumes that the surface is homogenous or that the lateral interaction effect is not negligible [13]. Flory – Huggins model accounts for surface coverage characteristics of the adsorbed inhibitor. x Indicates the amount of adsorbed water molecules replaced by the inhibitor molecules, d represent the interaction factors among the molecules (repulsion or attraction force) and K is the equilibrium constant in this model obtained from the intercept. x and d are obtained from the slope of the linear graph.

The adsorption equilibrium constants (K) of the inhibitor on the surface of the mild steel in the system is related to the standard Gibb's free energy of adsorption (ΔG°_{ads}) by the following equations [6,7,12].

$$\Delta G^{\circ}_{ads} = -2.303RTlog55.5K_{ads}$$

Where their parameters retains their standard meaning.

Table 4: Adsorption isotherm and standard Gibb's Free energy values for the adsorption of thiourea on mild steel surface in PMS.

Frumkim Isotherm	Values
R^2	0.993
D	482.2
K	8.4×10^{-2}
ΔG°_{ads} (KJ/mol)	-3.88
Flory – Huggins Isotherm	
R^2	0.900
x	-1.31
K	6.28×10^{-4}
ΔG°_{ads} (KJ/mol)	8.46

The parameters of Frumkin, Flory–Huggins adsorption isotherm and standard Gibb's free energy of adsorption are summarised in Table 4. The result revealed that the adsorption process of thiourea follows Frumkin adsorption isotherm because the regression value obtained shows better fit than Flory–Huggins adsorption isotherm. The Frumkin adsorption constants (d) shows that there is interaction among the adsorbed molecules indicating that the interaction among the molecule were not negligible [13]. The result obtained from Frumkin adsorption isotherm shows that the adsorption of the inhibitor on the metal surface was predominately a physisorption process. The standard Gibb's free energy result suggests spontaneous adsorption of inhibitor molecules on the surface of the metal. The low value of ΔG°_{ads} shows that the adsorbed layer of thiourea on the surface of the metal was unstable which resulted to decrease on inhibition efficiency as the time of study increases.

3.4 Surface Analysis

Scanning Electron Microscopy (SEM) micrograph was used to study the surface of mild steel exposed in DPK and PMS in absence and presence of 200ppm thiourea in order to show the nature of molecules adsorbed on the surface of mild steel. SEM micrographs are shown in Figure 4(a-d). The mild steel before immersion was smooth compared to the surface of mild steel immersed in DPK and PMS with or without inhibitor due to dissolution process. SEM-EDX was used to characterise the chemical composition of mild steel used in the study. The percentage weight compositions of the studied mild steel are illustrated in Table 5. From the table, the values of weight percentage composition of iron for mild steel immersed in DPK and PMS without inhibitor was higher when compared with inhibitor. These shows that thiourea did not protect the mild steel against corrosion. The results confirmed the experimental data obtained using gasometric assembly.

Table 5: percentage weight composition of elements obtained from SEM-EDX analysis.

Elements	Pure mild steel	Mild steel in DPK	Mild steel in DPK and inhibitor	Mild steel in PMS	Mild steel in PMS and inhibitor
Fe	95.19	93.55	92.94	90.47	89.23
C	1.64	2.97	2.33	2.93	3.55
Mo	0.71	0.27	0.71	1.94	2.91
Si	0.39	0.65	0.55	0.66	0.67
Al	0.35	0.34	0.40	0.63	0.59
Na	0.35	0.34	0.26	0.14	0.29
K	0.26	0.37	0.21	0.57	0.47
Mg	0.25	0.20	0.15	0.11	0.22
O	0.24	0.59	1.55	0.45	1.51
S	0.23	0.27	0.22	0.00	0.00
P	0.20	0.16	0.29	0.49	0.37
Ca	0.20	0.27	0.07	0.62	0.18
Cr	0.00	0.00	0.16	0.45	0.00
Ti	0.00	0.00	0.16	0.00	0.00

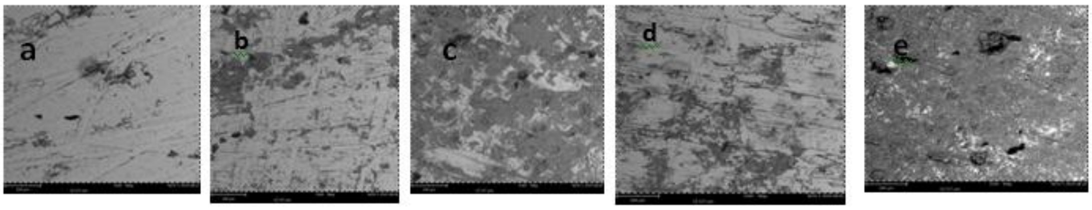

Figure 4: SEM micrograph of (a) mild steel coupon before immersion (b) exposed to DPK in absence of inhibitor (c) expose to DPK in presence of inhibitor (d) exposed to PMS in absence of inhibitor (e) exposed to PMS in presence of inhibitor.

IV. CONCLUSION

The following conclusions were drawn from the results of the experiment.

(i). Thiourea shows poor inhibitive properties on mild steel in premium motor spirit but did not show any inhibition performance in dual purpose kerosene.

(ii).The inhibitive properties of thiourea in PMS was spontaneous and the adsorption characteristics obeys physisorption mechanism which was in conformity with Frumkin adsorption isotherm.

(iii). SEM-EDX analysis confirm that thiourea does not inhibit corrosion of mild steel in DPK and PMS.

Conflict of Interest

The authors have not declared any conflict of interest regarding this work.

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