Direct RESEARCH JOURNALS

Direct Research Journal of Chemistry and Material Science
Vol.7 (1), pp. 1-6, March 2020
ISSN 2354-4163
DOI: https://doi.org/ 10.26765/DRJCMS623398016
Article Number: DRJCMS623398016

https://directresearchpublisher.org/drjcm/

*Full Length Research Paper*

# Synthesis and corrosion inhibition study of mild steel in 0.5 M hydrochloric acid by 1-((2-arbamoylguanidino) (furan-2-ylmethyl) urea

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Received 3 March 2020; Accepted 20 March, 2020

The corrosion inhibition of mild steel in, 0.5M HCl solution by 1-((2-arbamoylguanidino) (furan-2-ylmethyl) urea (CFU) was investigated using weight loss experiment at different temperature (30°C, 40°C, 50°C). The CFU was synthesized and characterized using FTIR and $^1$HNMR. The finding indicates that CFU acts as an effective corrosion inhibitor for mild steel in hydrochloric acid solution. The inhibition efficiency and surface coverage of mild steel increased with increasing concentration of CFU, but reduced as temperature increases. Langmuir adsorption isotherm and freundlick adsorption isotherm were used to deduce that the adsorption mechanism was physical adsorption. The estimation of the adsorption also determined the free Gift's energy at the range of -12KJmol$^{-1}$ to -14KJmol$^{-1}$, which implies that the reaction was spontaneous. The inhibitive ability of CFU was attributed to the presence of oxygen, nitrogen and aromatic furan in its structure.

**Keywords:** Inhibition, efficiency, 1-((2-Carbamoylguanidino) (furan-2-ylmethyl) urea, adsorption

## INTRODUCTION

Corrosion of metals is a natural phenomenon which proceeds until inhibited. Since metals are used in different technological structures and in various environments, protection of metallic structures is pertinent (Orie *et al*, 2015; Okorosaye – Orubite and Ngobiri, 2017). The use of mild steel as construction material in industrial sectors has become a great challenge for corrosion engineers or scientists nowadays. In practice, most of the acidic industrial applications such as refining crude oil, acid pickling, industrial cleaning, acid descaling, oil–well acid in oil recovery and petrochemical processes use mild steel as their material. Hydrochloric acid is one of the most widely used agents in the industrial sector (Hussin *et al*., 2016). Due to the aggressiveness of acid solution to mild steel, the use of inhibitor to prevent the metal dissolution process will be inevitable (Ostovari et al., 2009). Recent researches on corrosion inhibition had centred on natural inhibitors which are non toxic, eco friendly and readily available obtained from plants. Some of the evidences where bio-renewable green chemical were used for corrosion inhibitors are Carica papaya (Okoafor and Ebenso, 2010) water hyacinth (Oloruntoba et al., 2012), bread food peel (Orie and Christian, 2015), Tinosporacrispa (Hussin *et al*., 2016) Citrus aurantium leaves (Hassan *et al.,* 2016), Folic Acid (Orie et al., 2015), extract of red onion skin (James and Akarenta, 2002), Karanj (Pongama pinnate ) seed, (Singh *et al.,* 2011). 1-((2-Carbamoylguanidino) (furan-2-ylmethyl) urea is a heterocyclic organic compound containing furan ring, methine, amine, Carbamoyl group and imine group. It has a molecular mass of 240.10, the melting range of 108-110°C and is

perfectly soluble DMSO (Orie *et al*., 2018). 1-((2-Carbamoylguanidino) (furan-2-ylmethyl) urea is obtained from furfural. Furfural is a heteroaromatic aldehyde (furan-2-carbaldehyde) produced from a variety of agricultural by-products (Ngochindo, 1995) and is obtained by hydrolysis and dehydration of pentose carbohydrates contained in lignocelluloses (Machado *et al.,* 2016). Furfural is an indispensable chemical that is potentially relevant to the economy of a developing country on the platform that it is a bio-renewable chemical, readily available, cheap, and that could also be seen as a possible feedstock for most consumers in developing countries (Yen *et al*, 2014). Recently, furfural has gained attention as a potential chemical for organic synthesis and its derivatives have vast applications both in chemical and pharmaceutical industries (Yen *et al*., 2014; Orie *et al*., 2018). The structure of CFU is shown blow (Figure 1): 1-((2-Carbamoylguanidino)(furan-2-ylmethyl) urea have conjugated aromatic furan structure, N and O heteroatom with free electron pairs that are available to bond with metal surface. The use of CFU as corrosion inhibitor has not been reported. The aim of this work is to investigate the effectiveness of CFU as corrosion inhibitor for mild steel in 0.5M HCl medium at 303K, 313K, and 323K.

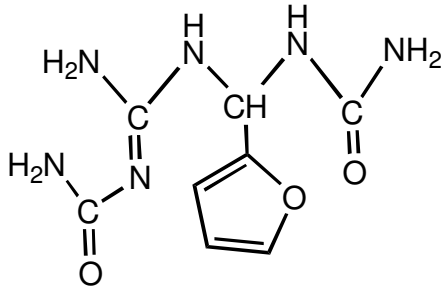


**Figure 1**. The structure of 1-((2-Carbamoylguanidino) (furan-2-ylmethyl) urea.

## MATERIAL AND METHODS

### Synthesis of 1-((2-Carbamoylguanidino) (furan-2-ylmethyl)) urea

The furfural used in this study was bought from chemical store. The deteriorated furfural was purified by vacuum distillation at the temperature of 65°C to 80°C. The procedure adopted in the synthesis of 1-((2-Carbamoylguanidino) (furan-2- ylmethyl) urea was earlier reported by Orie *et al.* (2018). The purified furfural (40 mL, 0.48 mol), urea (40 g, 0.63 mol) and distilled water (9 mL) were placed in a flat-bottomed flask (250 mL) and the mixture heated in a water bath at a temperature of 60°C for 1 h, 40 min with vigorous stirring. Thereafter, NaOH (2 mL of 20% of solution) was added and the heating continued for 20 min. The mixture was cooled in an ice bath and the resulting brown precipitate filtered, washed with n-hexane, recrystallized from methanol and the crystal dried in an oven at 50°C (Figure 2).

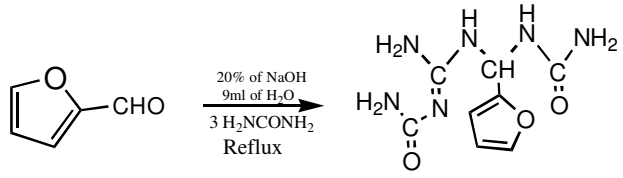



**Figure 2**. Equation 1. Synthesis of 1-((2-Carbamoylguanidino) (furan-2-ylmethyl)) urea.

### Preparation of mild steel coupon

The corrosive environment, 0.5M HCl prepared according to known standards. Mild steel sheets with composition, (C, 0.16-18%, Mn 0.7-0.9%, P 0.0 4%, Si 0.40% and S, 0.04%) were obtained from the Engineering workshop of the university of Port Harcourt Choba Rivers State Nigeria. They were cut into 4cm/3cm sizes of 1.0mm thickness. The coupons were perforated at the top centre with holes of diameter 2.0mm to allow passage of thread. They were mechanically cleaned and scrubbed with sandpaper to expose shining surfaces, degreased in absolute ethanol and dipped in acetone and finally dried in an oven at 40°C. Dried coupons were stored in desiccators before use. The initial weight of the coupons was taken, using an analytical weighing balance. Each weight was an average of three replicate measurements.

### Solutions preparation

About 0.5 M HCl solutions were prepared by the dilution of 37% HCl using distilled water. The concentration range of CFU employed was varied from $1.07x10^{-5}$M to $2.5 x10^{-5}$M. This concentration range was chosen upon the maximum solubility of CFU. The powder, CFU was first dissolved in DMSO before it was diluted to standard solution.

### Weight loss measurement

The rectangular mild steel specimens of dimension 4 cm/ 3 cm sizes of 1.0 mm thickness were immersed (complete immersion) in 100 mL of deaerated electrolyte in the absence and presence of different concentrations of CFU at different temperature of 303 K, 303K and 323K. The weight loss of mild steel specimens was determined after 24 hours of immersion for the duration of 7 days. The following formulas were used to calculate some essential parameters to aid decision on the level of inhibitions.

$$\text{Inhibition Efficiency (IE\%)} = \frac{W_B - W_i \quad X100}{W_B 1} \quad (1)$$

$$\text{Surface coverage } (\theta) = \frac{W_I}{W_B} \quad (2)$$

$$\text{Longmuir adsorption isotherm, } \frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

$$\text{Freundlich adsorption isotherm, } \theta = K_{ads.} C^{-n} \quad (4)$$

$$\text{Gibbs free energy, } K_{ads} = 1/55.5e^{(-dG/RT)} \quad (5)$$

Where $\theta$ is the surface coverage, IE is the inhibitor efficiency, C is the inhibitor concentration, $W_i$ and $W_b$, weight of coupon in presence and absence of inhibitors, $K_{ads}$ equilibrium adsorption constant, and n is constant. Equations 1, 2, 4 and 5 can be drawn as shown in (Figure 3, 4, 5 and 6). The Gibbs standard free energy of adsorption of the organic inhibitor can be estimated by means of Eq. (5).

As shown in (Table 2), the higher correlation coefficients ($R^2$) were obtained via using Langmuir adsorption isotherm. Generally, a higher value of $K_{ads}$ accompanying with higher trend to adsorb on mild steel surface, on the other hand, equilibrium constant of adsorption ($K_{ads}$) was noticed to decrease with increase in temperature, similar results was reported in the literature (Umoren et al., 2011). The values of free energy of adsorption, $dG_{ads}$, are negative which exposes the spontaneity of adsorption process and the stability of the adsorbed film on the metal surface. The obtained values of the adsorption free energy are around -20 kJ/mol, which is an indication of physical adsorption.

## RESULTS AND DISCUSSION

### FTIR Spectrum For (1-((2-Carbamoylguanidino) (furan-2-ylmethyl)) urea

The IR data analysis of the product identified the presence of imine group (1532.87cm$^{-1}$), a carbamoyl group (1666.55 cm$^{-1}$) and methine (2885.23 cm$^{-1}$) (Figure 3). This IR data analysis is in line with Orie *et al* (2018). The $^1$H-NMR analysis of the product in DMSO showed multiplet peaks in the range (δ) 6.54-7.53 ppm which corresponds to the furan ring. The peak at 6.23 ppm is due to the proton around the methine group while the peak in the 5.6 ppm is assigned to proton around carbamoyl group. 13C-NMR data analysis indicates the presence of carbon from furan (106.12-154.75 ppm), imine (158.52 ppm), carbamoyl group (160.15ppm) and methane (50.6 ppm). The proton NMR data analysis showed in Emmanuel *et al. (2013)* and with Orie *et al.* (2018).

### Inhibition efficiency and concentration

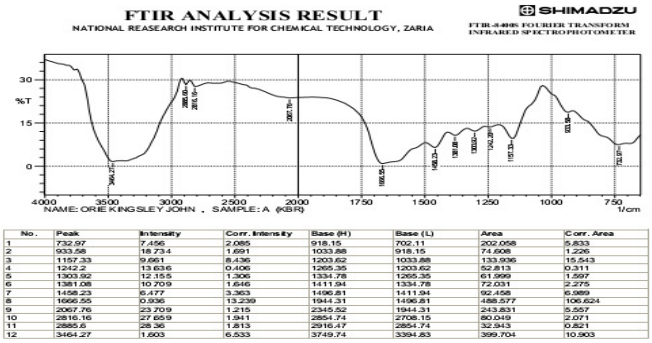
The data shown in (Table 1), explains the relationship of inhibition efficiency, concentration and temperature. The solution with the concentration, 2.5x10$^{-5}$M of the inhibitor has the highest inhibition efficiency of 70% at 30$^o$C temperature. There was decrease in inhibition efficiency, as the temperature of the system increased from 30$^o$C to 50$^o$C. This detail is shown in (Table 1 and Figure 4) and the observation is in line with Ostovari et al., 2009; Hussin *et al*., 2016 and Orubite andNgobiri, (2017).

### Longmuir Adsorption Isotherm of CFU

Elucidation of adsorption mechanism from the experimental data requires estimation of the adsorption modes of the inhibiting species (whether molecular or ionic). The predominant adsorption mode will be dependent on factors such as the inhibitors composition, chemical changes and the nature of the surface charge on metal (Umoren et al., 2011). The linear graph between C/Θ versus C in (Figure 5) shows that CFU obeys the Langmuir isotherm at the concentration and temperature of the metal. It supports the assertion that the mechanism of corrosion inhibition is due to the formation and maintenance of a protective film on the metal surface and the additive covers both the anode and cathode sites through uniform adsorption following Langmuir isotherm. The inhibitory action of CFU should be attributed to the adsorption of its component on the mild steel surface. The presence of N, O, C = O, N-H, C-O, and N-hetero cyclic ring in CFU are responsible for the inhibitive effect of CFU. The linear plot with high correlation coefficient (0.967) and slope of about unity (0.966) clearly reveals that the surface adsorption process of CFU on the mild steel surface obey the Langmuir adsorption isotherm and adsorption is temperature dependant, this estimation is in line with Ostovari *et al.*(2009).

### Freundlich Isotherm

Freundlich adsorption isotherm is commonly used to describe the adsorption characteristic for the heterogeneous surface (Ituen *et al.,* 2017). Figure 6 reveals Freundlich adsorption isotherm of CFU on the surface of the mild steel and is given by equation 5. The straight line graph produced by ploting lnΦ against




| No. | Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|---|---|---|---|---|---|---|---|
| 1 | 732.97 | 7.456 | 2.085 | 918.15 | 702.11 | 202.058 | 5.833 |
| 2 | 933.58 | 18.734 | 1.691 | 1033.88 | 918.15 | 74.608 | 1.226 |
| 3 | 1157.33 | 9.661 | 8.436 | 1203.62 | 1033.88 | 133.936 | 15.543 |
| 4 | 1242.2 | 13.636 | 0.406 | 1265.35 | 1203.62 | 52.813 | 0.311 |
| 5 | 1303.92 | 12.155 | 1.306 | 1334.78 | 1265.35 | 61.999 | 1.597 |
| 6 | 1381.08 | 10.709 | 1.646 | 1411.94 | 1334.78 | 72.031 | 2.275 |
| 7 | 1458.23 | 6.477 | 3.363 | 1496.81 | 1411.94 | 92.458 | 6.989 |
| 8 | 1666.55 | 0.936 | 13.239 | 1944.31 | 1496.81 | 488.577 | 106.624 |
| 9 | 2067.76 | 23.709 | 1.215 | 2345.52 | 1944.31 | 243.831 | 5.557 |
| 10 | 2816.16 | 27.659 | 1.941 | 2854.74 | 2708.15 | 80.049 | 2.071 |
| 11 | 2885.6 | 28.36 | 1.813 | 2916.47 | 2854.74 | 32.943 | 0.821 |
| 12 | 3464.27 | 1.603 | 6.533 | 3749.74 | 3394.83 | 399.704 | 10.903 |

**Figure 3**. The spectra of 1-((2-Carbamoylguanidino) (furan-2-ylmethyl)) urea.

**Table 1.** Inhibition efficiency and concentration.

| Inhibitors concentrations | Average percentage inhibition | | |
|---|---|---|---|
| **Moldm$^{-3}$** | **30°C** | **40°C** | **50°C** |
| 1.07 x $10^{-5}$ | 40.4 | 36.0 | 34.0 |
| 1.43 x $10^{-5}$ | 48.0 | 42.0 | 34.1 |
| 1.79 x $10^{-5}$ | 56.8 | 44.1 | 43.3 |
| 2.14 x $10^{-5}$ | 63.9 | 53.9 | 51.0 |
| 2.50 x $10^{-5}$ | 70.0 | 66.0 | 60.4 |


**Figure 4**. Surface coverage and concentration of inhibitor.

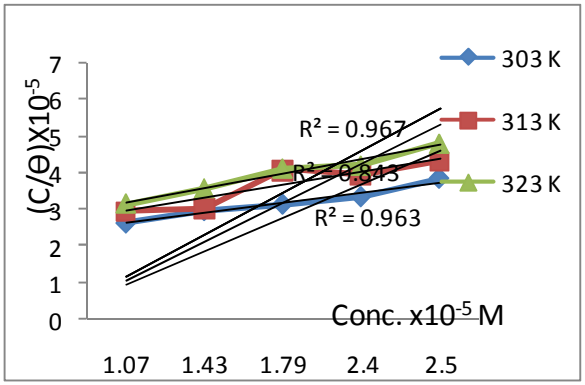



**Figure 5**. Longmuir adsorption isotherm of CFU on mild steel in 2M HCl at different temperature.

concentration of inhibitor and the slop of 1/n obeyed Freundlich adsorption isotherm, and is in line with Okoafor and Ebenso, (2010). The data in (Table 2) show the correlation coefficient of the Langmuir adsorption

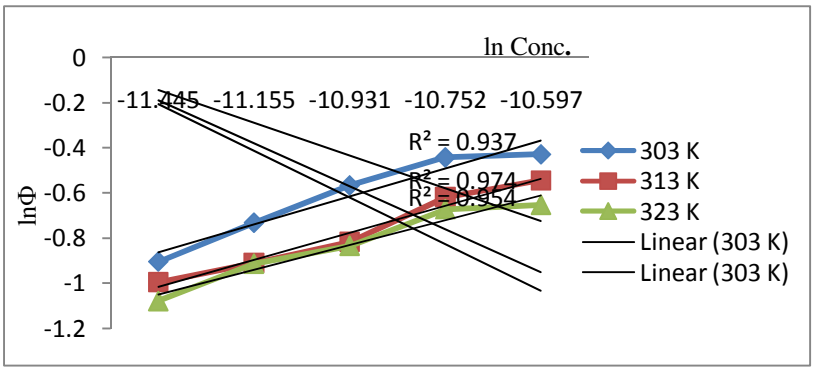



**Figure 6**. Freundlich adsorption isotherm of CFU on mild steel in 2M HCl at different temperature.

**Table 2.** Effect of temperature and thermodynamic parameters.

| **Langmuir** | Adsorpsion | Isotherm | Freundlich | Adsorpsion | Isotherm | |
|---|---|---|---|---|---|---|
| **T K** | $K_{ads}$l/ml | dG/ KJmol. | $R^2$ | $K_{ads}$l/ml | N | $R^2$ |
| 303 | 3.636 | -13.369 | 0.967 | 1.159 | 8.065 | 0.939 |
| 313 | 2.532 | -12.869 | 0.963 | 1.135 | 8.403 | 0.974 |
| 323 | 3.635 | -14.252 | 0.843 | 0.988 | 9.174 | 0.954 |

isotherm and freundlich adsorption isotherm, and they indicate that an increase in temperature leads to a increase in an equilibrium constant of adsorption.

## Effect of temperature and thermodynamic parameters

The values of free energy of adsorption, $dG_{ads}$, shown in (Table 2) are negative which expose the spontaneity of adsorption process and the stability of the adsorbed film on the metal surface. The obtained values of the adsorption free energy are around -20 kJ/mol indicates physical adsorption (Hussin and Kassim, 2011; Aljourani *et al*., 2009). Generally, the values of $dG_{ads}$ around -20 kJ $mol^{-1}$ or less and negative are known to be associated with physical adsorption (electrostatic interactions between the inhibitor and charged surface) while those around -40 kJ $mol^{-1}$ or more negative is are known to be associated with chemisorption (charge sharing or transferring from organic molecules to the metal surface and form a coordinate type of metal bond) (Benali *et al*., 2007). From this estimation, it can be concluded that CFU is physically adsorbed on the charged mid steel surface thus creating an electrostatic interaction.

## Conclusion

1-((2-Carbamoylguanidino) (furan-2-ylmethyl) urea which was synthesized and characterized using FTIR and $^1$HNMR ,has been found to be an effective inhibitor for mild steel in 0.5M HCl. This research exploited the weight loss method and the maximum inhibition efficiency was 70% at 303K. The efficiency of inhibition decreased with an increase in temperature. Langmuir adsorption isotherm and Freundlick adsorption isotherm were used to study the adsorption mechanism to be physical adsorption. The estimation of the adsorption determined the free Gift's energy at the range of -12 $KJmol^{-1}$ to -14 $KJmol^{-1}$. The inhibitive ability of CFU was attributed to the presence of oxygen, nitrogen and aromatic furan in its structure.

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