

ADSORPTION CHARACTERISTICS AND CORROSION INHIBITION OF ZINC IN ACID SOLUTION BY DIMETHYLGLYOXIME

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Abstract

Corrosion inhibition of Zinc in H₂SO₄ solution by DMG at 308 and 318K was studied using the weight loss technique. The weight loss data were used for further calculations of some corrosion parameters. The percent inhibition efficiency (%I_E) increased with concentration of DMG. Temperature increased the corrosion rate but decreased the inhibition efficiency between 308 and 318K in the absence and presence of the inhibitor respectively. Physical adsorption is proposed from Ea values obtained. The increase in the percent inhibition efficiency as well as the surface coverage (θ) indicated that the adsorption of DMG on the reaction sites of H₂SO₄ plays an important role in the adsorption process. The presence of -C=O and -N=N-, etc groups in DMG was found to have contributed greatly to the inhibition process by interacting with zinc surface.

Keywords: zinc metal, dimethylglyoxime, weight loss, corrosion inhibition, physisorption

Introduction

Corrosion may be considered as the partial transformation of a metal or an alloy to a combined state when there is an interaction with the environment (Ladd, 1998). It is a costly business and the protection of materials such as zinc from corrosion is necessary.

Zinc has widely been used commercially as roofing sheets in housing industry due to its high quality and long lasting appearance, zinc is used as a protective coating for steel (Uppal and Bhatia, 2002). It is also used for galvanizing iron, in order to protect it from corrosion and in making alloys like brass.

Corrosion of metals/alloys such as zinc, aluminium, magnesium, mild steel, stainless steel etc causes tremendous harm to many nations economy. Corrosion inhibition of metals such as zinc and mild steel has therefore received considerable attention over the years due to the role of zinc in most industries (Ita and Offiong, 1997; Abdel-Gaber, 2008; Orubite-Okorosaye and Oforka, 2007 and Onen, 2009). Corrosion inhibition of zinc is therefore of great academic and industrial concern.

Organic compounds containing nitrogen, sulphur, and oxygen atoms usually act as good corrosion inhibitors. Thus, in N – tetracycline compounds, adsorption take place through nitrogen heteroatom, conjugated double bonds or aromatic rings in their structures (Abdel et al, 2010). It has been established that the use of chemical inhibitors of zinc corrosion remains the most practical and most effective means of preventing corrosion (Okafor et al, 2008).

It is generally assumed that corrosion inhibition is performed by adsorption of the additives to the metal interface. It is known that the potential difference between the inhibitor and the metal surface is due to a non – uniform distribution of electric charges at the interface (Abdel et al, 2010, Abiola and James, 2010).

Dimethylglyoxime was chosen because it is less expensive and easy to handle as a corrosion inhibitor. This study is limited to the use of zinc and Dimethylglyoxime, DMG, as inhibitor. Furthermore, the investigation makes use of weight-loss technique at 308K and 318K.

Although the study was limited to the use of zinc metal and DMG, as the inhibitor, it is expected that the chosen inhibitor can be

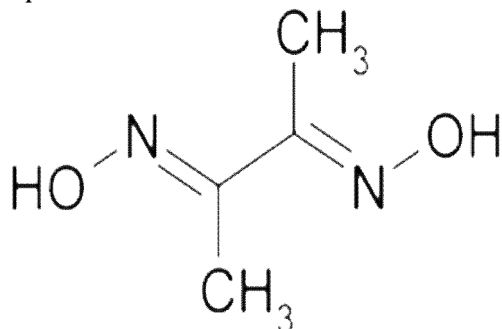


Figure 1: Molecular Structure of Dimethylglyoxime.

METHODOLOGY

Materials Preparation

The zinc sheets for this investigation were obtained from Mubi Market, Adamawa State. The zinc sheets were mechanically press cut into 5.0 x 4.0 cm and thickness of 6.0×10^{-3} cm. The sheets were used without further polishing. They were however, degreased in absolute ethanol, dried in propanone and stored in moisture free desiccators before corrosion studies commenced. The average mass of the coupons was 7.98 – 8.02 g and total surface area of the coupons exposed was 18.4 cm^2 (Onen, 2006).

Weight loss Measurements

Five 250 mL, beakers containing separately 0.10M, 0.20M, 0.30M, 0.40M and 0.50M H_2SO_4 solution were placed in thermostated water baths at 308K and 318K. Previously weighed zinc coupons were immersed in each of the beakers. They were retrieved at 24 hourly intervals progressively for 168 hours (7days). The coupons were washed several times in distilled water, cleaned and dried in propanone and reweighed. The difference in mass (mg) of the coupons was recorded as the weight loss of zinc in each case. Each of the reported readings was an average of two experimental readings was recorded to the nearest 0.001g

used on other metals such as Al, Mg and alloys etc.

on a digital electronic balance (Adventurer) (Ebenso et al, 2004).

The second part of the study involved measurement of weight loss after introduction of the inhibitor (DMG) in five sets of 250 mL beakers maintained at 308K and 318K. The previously weighed zinc coupons were introduced into all the beakers containing different concentrations of DMG. Each coupon was retrieved from the inhibitors solutions at 24 hourly intervals for a period of 168 hours. The zinc coupons were washed, dried and reweighed. The difference in mass recorded for a period of 168 hours (7 days) was recorded as the weight loss in (mg).

Corrosion rates for zinc in 0.50M MH_2SO_4 and different concentrations of DMG were determined for 168 hours immersion period from weight loss using the formula

$$\text{Corros rate} = \frac{\Delta W}{DAT} \quad (1)$$

where ΔW is weight loss(g), D is the density of the metal, A is the area of zinc coupons and T is the time of exposure (hours) (Onen, 2004).

The percent inhibition efficiency ($\%I_E$) was calculated using the expression

$$\%I_E = \frac{R_o - R_1}{R_o} \times 100 \quad (2)$$

where R_o and R_1 are the corrosion rates in uninhibited and inhibited in H_2SO_4 solutions respectively (Onen, 2004).

The surface coverage (θ) at each concentration of the inhibitor was determined using the relation

$$\theta = 1 - \frac{R_1}{R_o} \quad (3)$$

where R_o and R_1 are corrosion, rates, the absence and presence respectively of inhibitor in H_2SO_4 solutions at the same temperature (Onen, 2004).

Results and Discussion

Effect of H_2SO_4 Concentration and Temperature on the Corrosion Process

Figure 2 and Table 1 show the variation of weight loss and corrosion rate with time, t (days) for zinc in H_2SO_4 at 308K and 318K. It was observed that weight loss/corrosion rate (mdd) of zinc increased with increasing concentration of H_2SO_4 and temperature. Similar observation has been made by several workers on corrosion of metals in H_2SO_4 solution (Onen, 2006, Ibok et al, 1995). This could be attributed to an increase in the rate of diffusion of active species in the corrosion process. More so, rate of chemical reactions generally increase with increase in concentration and temperature.

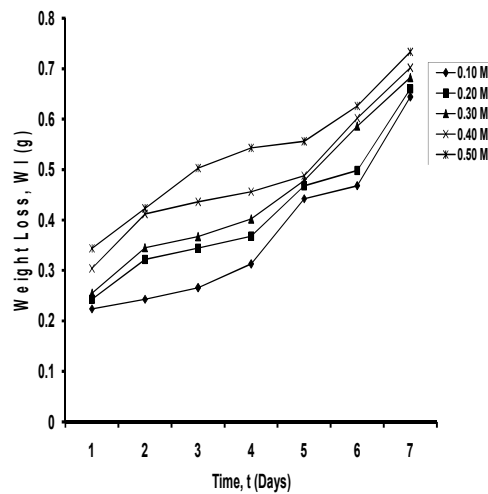
Effect of (DMG) Concentration on Zinc Corrosion

Variation of weight loss with time, t (days) for zinc corrosion in 0.50M H_2SO_4 with various concentrations of DMG at 308K is shown on Figure 3. Similar plots were obtained at 318K. The graphs reveal that weight loss was lowest at 0.0010M of DMG (highest concentrations of inhibitors studied).

This indicates that DMG inhibits the corrosion of zinc to an appreciable level, with inhibitor concentration and at a low temperature. With the addition of the inhibitor (DMG) the inhibition efficiency ($\%I_E$) and the surface coverage were found to increase while corrosion rates decrease with increasing concentration in order, 0.0010M DMG efficiency (67.97%) and (2.20×10^{-5} mdd) corrosion rate but inhibition efficiency decreases with increasing temperature (308K-318K). This shows that the inhibitor function effectively at lower temperatures which suggest physisorption. This agrees with earlier reports by Onen (2004) and Ebenso et al (2004).

Table 1: Corrosion Parameters of Zinc Corrosion in 0.50M H₂SO₄ containing DMG from Weight loss measurements

Inhibitor Conc. (M)	Weight loss (g)		Corrosion Rate (mdd) x10 ⁻⁵		Inhibition Efficiency(%I _F)		Surface Coverage (θ)	
	308K	318K	308K	318K	308K	318K	308K	318K
Blank	0.459	0.579	5.13	6.47	-	-	-	-
DMG	0.258	0.35	2.88	3.9	55.43	38.7	0.55	0.3
0.0001		5		7		2		9
0.0003	0.241	0.33	2.69	3.7	58.48	42.5	0.59	0.4
0.0005		4		2		0		3
0.0007	0.212	0.31	2.37	3.4	63.38	46.1	0.63	0.4
0.001		3		9		0		6
	0.200	0.29	2.23	3.3	65.55	48.3	0.66	0.4
		9		4		4		8
	0.191	0.282	2.20	3.15	67.97	51.31	0.68	0.51

Figure 2: Plot of Weight loss, W_t, with time, t (days) for Zinc corrosion in different concentrations of H₂SO₄ at 308K

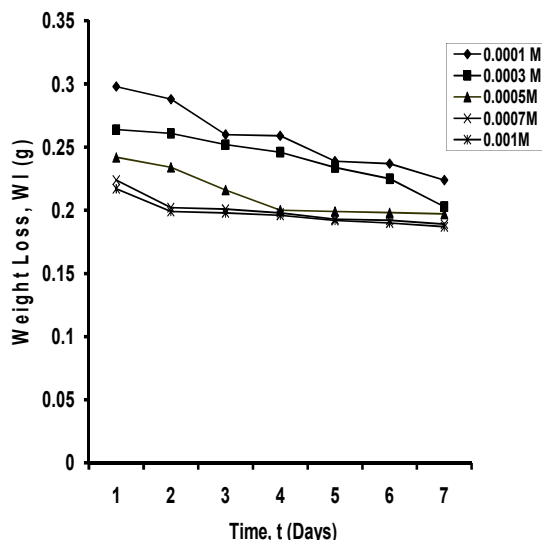


Figure 3: Weight loss, W_t , versus time, t (days) for Zinc corrosion in $0.50M H_2SO_4$ with various concentrations of DMG at 308K

Kinetic and Thermodynamic Consideration of the Results

The activation energy values presented in Table 2 were computed from the modified equation.

$$E_a = 2.303R \frac{T_1 T_2}{T_2 - T_1} \log \frac{\rho_2}{\rho_1} \quad (4)$$

where ρ_1 and ρ_2 are corrosion rate at 308K and 318K respectively (Akhmetov et al,1989).

The values of rate constant, k recorded in Table 2 were obtained from plots of $\log A_d$ versus time (days) as shown in Figures 4 and 5.

The half life, $t_{1/2}$ values presented in Table 2 were calculated using the equation (5).

$$t_{1/2} = \frac{0.693}{k} \quad (5)$$

The values of heat of adsorption, Q_{ads} (in Table 2) were computed from the relation:

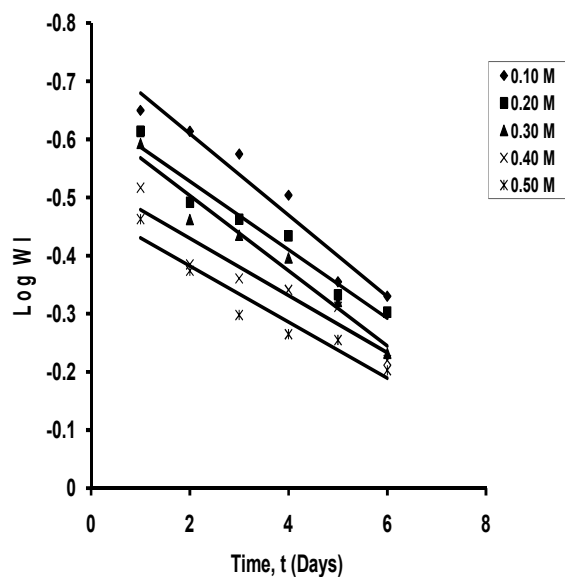
$$Q_{ads} = 19.147 \left(\log \frac{\theta_2}{1 - \theta_2} - \log \frac{\theta_1}{1 - \theta_1} \right) \left(\frac{T_1 T_2}{T_2 - T_1} \right) \quad (6)$$

where θ_1 and θ_2 are degree of surface coverage at 308K and 318K respectively (Yadav,1999).

All the values of Q_{ads} are negative for zinc corrosion (Table 2). This is an indication that adsorption and inhibition efficiency decrease with increase in temperature. The negative values of Q_{ads} imply also that the adsorption process is spontaneous which agrees with earlier findings by other authors (Onen, 2006; Ebenso et al, 1999)

Table 2: Kinetic and Thermodynamic data for Zinc Corrosion in 0.50M H₂SO₄ containing DMG from Weight loss measurements

Inhibitor Conc. [M]	Rate constant, k (sec ⁻¹) x 10 ⁻²		Half life, t _{1/2} (sec) x 10 ¹		Activation energy, E _a (kJmol ⁻¹)		Heat of adsorption, Q _{ads} (kJmol ⁻¹)	
	308K	318K	308K	318K	308K	318K	308K	318K
Blank	2.14	1.98	3.22	3.50	18.90			
DMG	3.34	3.12	2.07	2.22	26.14	-26.80		
0.0001	3.82	3.55	1.81	1.95	26.40	-24.93		
0.0003	4.36	3.98	1.58	1.74	31.52	-26.50		
0.0005	4.79	4.27	1.45	1.63	32.90	-24.82		
0.0007	4.98	4.52	1.35	1.53	29.32	-24.13		
0.001					29.26	-25.44		
Average								

Figure 4: Plot of log W₁ versus time, t (days) for Zinc corrosion in different concentrations of H₂SO₄ at 308K

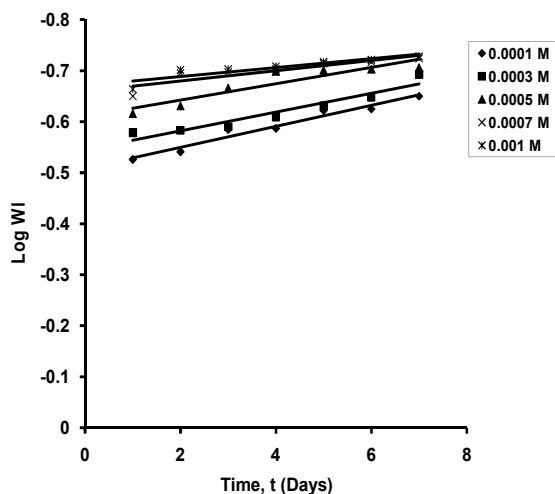


Figure 5: Plot of $\log W_1$ versus time, t (days) for Zinc corrosion in different concentrations of inhibitor (DMG) at 308K

Adsorption Consideration of the Results

An inspection of Table 1 and Figure 6, show that the inhibition efficiency ($\%I_E$) and surface coverage (θ) increase with inhibitor concentration and decrease with increasing temperature. This further attests to physical adsorption (physisorption) mechanism at high concentrations. Lower surface coverages are observed because very little interactions between the adsorbed species took place. The surface coverage data implies that the adsorption of the inhibitor (DMG) on the zinc interface may be due to electrostatic force between the adsorbates and the atoms on the metal surface. This assertion confirms the observations earlier published (Onen, 2004, Ekpe et al, 1995).

To establish the extent of adsorption of inhibitor molecules on the zinc surface, inhibition efficiency ($\%I_E$) was plotted against inhibitor concentration for zinc corrosion by DMG at 308K and 318K as shown in Figure 6. The extent of adsorption of inhibitor molecules on the zinc surface was further established by plotting C/θ against C at 308K and 318K as shown in Figure 7. The data obtained, for the inhibitor studied between 308K and 318K were found to fit Langmuir adsorption isotherm. This is an indication that corrosion inhibition of zinc is due to the formation and maintenance of a protective coating on the metal surface (Ebenso et al, 2004).

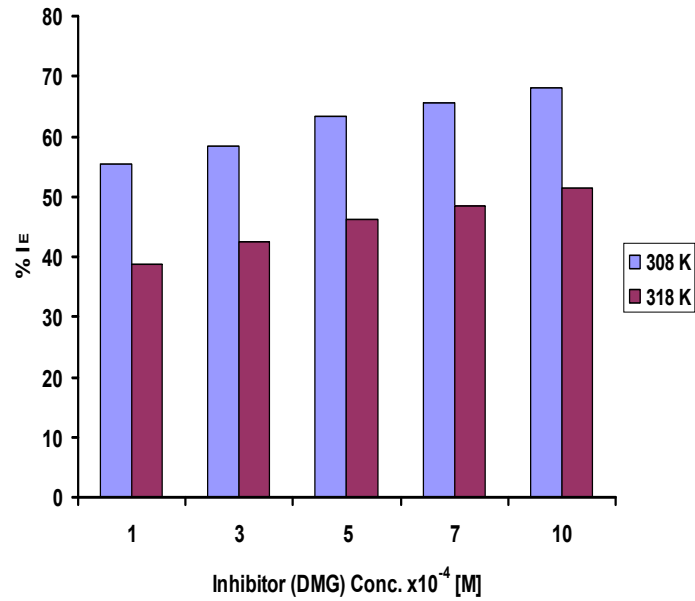


Figure 6: Plot of % I_E versus inhibitor (DMG) concentration [M] for Zinc corrosion at 308K and 318K

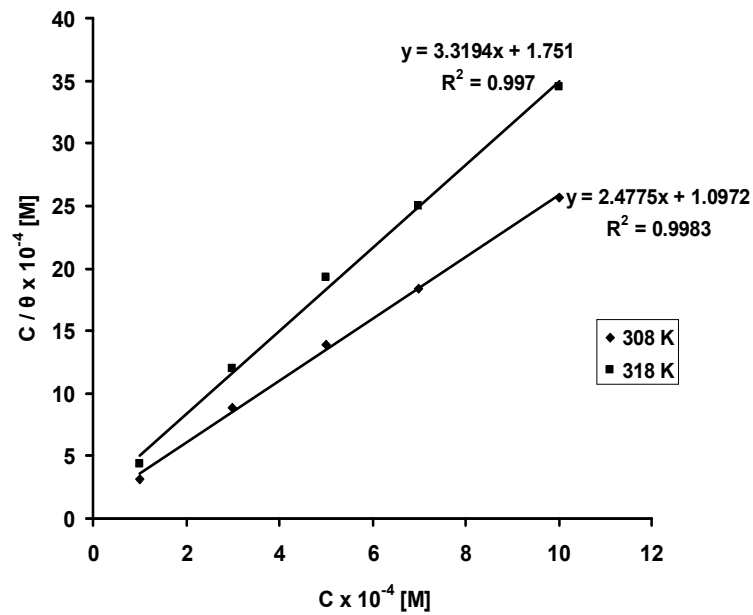


Figure 7: Langmuir adsorption isotherm plotted as C / θ versus C for Zinc corrosion containing DMG at 308K and 318 K

Inhibition Mechanism

Table 2 shows calculated values of rate constant (k), half life $t_{1/2}$, and activation energy E_a . The average value of the activation energy E_a , (29.26 kJmol^{-1}) for the compound studied is less than 40 kJmol^{-1} , indicating that the compound was physically adsorbed on the zinc surface. Physical adsorption requires that the average E_a be less than or equal to 40 kJmol^{-1} and the percent inhibition efficiency should be increased at lower temperatures. This agrees with earlier report by Onen (2006).

Influence of Molecular Structure of Inhibitor on Corrosion Inhibition of Zinc

The results obtained from this study (Table 1) show the molecular structure of the inhibitor (DMG) (shown in Figure 1), must have contributed greatly to the its inhibition effectiveness. The overall structure is stabilized by hydrogen bonds. More so, DMG have carbon and nitrogen atoms as its substituents. The C and N-atoms are known to be centres of adsorption onto the metal (Ebenso et al, 1999). Electron densities on C and N-atom are made available to the electron accepting methyl group which stabilizes the compound at the reaction site.

The compound studied, inhibited the acid corrosion of zinc. The assertion that inhibition increased with high molecular masses

according to which, the number of substituents on the functional groups of the inhibitor increases made by (Ebenso et al, 1999) and Ita and Offiong, 1997) was not applicable in this case since the molar mass of DMG is just 92.0 mol^{-1} .

As the substituent groups increase on adsorption sites, interaction between the atoms reduces thus exposing more adsorption sites to favour attractions between the inhibitor molecules and zinc surface. This in turn increases inhibition efficiency. It suffices it to mention that inhibition efficiency may decrease or increase with the number of substituents on the functional groups of the inhibitor depending on whether the substituents are electron-withdrawing or electron donating.

Conclusion

DMG shows good performance as corrosion inhibitor in $0.5 \text{MH}_2\text{SO}_4$. The DMG inhibits the corrosion by getting adsorbed on the metal surface following Langmuir adsorption isotherm. The values of Q_{ads} at 308K and 318K are all negative implying that the inhibitor is strongly adsorbed on zinc surface and that the adsorption is spontaneous. The weight loss (g) decreases with increase in inhibitor concentration while the inhibition efficiency ($\%I_E$) increased with increase in inhibitor concentration and decrease with increase in temperature.

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