Corrosion Inhibition Properties of Dioctyl Phthalate on Mild Steel in 0.5 M Sulphuric Acid Medium

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Abstract

The corrosion inhibition properties of dioctyl phthalate on mild steel in 0.5 M H_2SO_4 medium was carried out using the weight loss method at temperature range of 303 K to 313 K for three hours. The concentration of the inhibitor was set at a range of 0.01 M to 0.07 M and a maximum reaction time of three (3) hours. The adsorption of the inhibitor on the surface of the mild steel was studied using Langmuir, Freundlich and the newly proposed Adejoh – Ekwenchi Isotherm. The maximum inhibition efficiency obtained for the corrosion of mild steel in H_2SO_4 was 85.11% at a temperature of 303 K. All values of ΔH_{ads} were found to be positive indicating the endothermic nature of the dissolution of the mild steel. The values of entropy of adsorption ΔS_{ads} was found to increase with increase in concentration of the inhibitor indicating that the rate determining combination step is a more orderly arrangement relative to the initial state. The values of E_{ads} and those of ΔH_{ads} varied in a similar manner, and the average values of $E_{ads} - \Delta H_{ads}$ equals 2.41 kJmol^{-1}, which is very close to the value of RT (2.51 kJmol^{-1}) indicating that the adsorption process is unimolecular in nature. The values of ΔG_{ads} and K_{ads} for the corrosion inhibition studies of mild steel in 0.5 M H_2SO_4 and dioctyl phthalate as the inhibitor were found to be suggestive of a physisorption mechanism. The adsorption values were in agreement with the three isotherms employed, with Freundlich isotherm as best fit for the modelling of the adsorption of dioctyl phthalate on mild steel in acid medium.

Keyword: Mild steel, Dioctyl Phthalate, Weight loss, Corrosion inhibition.

Introduction

Corrosion is a major industrial problem all over the world and a nightmare to most manufacturing and construction companies. According to the American Galvanizers Association, steel corrosion is an expensive problem costing about $2.2 trillion annually [1]. Although corrosion could be said to be nature's method of recycling, or of returning of a metal to its lowest energy form, it is an insidious enemy that destroys our cars, plumbing systems, buildings, bridges, engines, factories etc [2]. In Nigeria, especially in the oil producing states where there is a large amount of emitted acid gases, zinc roofs and metallic parts have been corroded and appear as a brownish colour on the surfaces. These tends to be washed down by rain leading to a considerable reduction in metal thickness and loss of strength, which may as a result leads to perforation of roofs and leaking [3].

Corrosion inhibitors are classified into inorganic and organic corrosion inhibitors, the mechanism of corrosion can be described as; chemical adsorption or chemisorption of the inhibiting material to the surface of the steel or by combination between inhibitor ions and metallic surface [4, 5].

Phthalates are esters of 1,2-benzenedicarboxylic acid. The most widely used phthalates are the dibutyl phthalates and the dioctyl phthalate [6]. Dioctyl phthalate (DOP) with IUPAC nomenclature dioctyl benzene-1,2-dicarboxylate, is a clear, colourless, and viscous liquid with a slight, characteristic odor, soluble in ethanol, ether, mineral oil, and the majority of organic solvents, immiscible with water, resistant to hydrolysis and air oxygen activity. Its high plasticizing efficiency, fusion rate, viscosity, low volatility, UV-resisting property, water-extracting proof, cold-resisting property, and also good softness, found a lot of applications in many offshoots of the industry [7].

Many researchers reported that the inhibition effect mainly depends on some physico-chemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and so on [8,9]. Most of the research conducted on corrosion inhibition are through the use of plant extracts; from the juice of grapes [10], *Zenthoxylum alatum* plant extract [11], extract of *Ricinus communis* var minor [12], *Newbouldia leavis* leaf extract [13], leaf extract of *Euphorbia hirta* [14], e.t.c. Most of these extracts studied do not give a clear view of the compound in the extract responsible for the inhibition process, and as such makes the application ambiguous. This particular study is centred on one compound – dioctyl phthalate, and described it corrosion inhibition properties, hence its mechanism of adsorption on the surface of the mild steel.

Materials and Method

All the materials used for this research are of analytical grade. The method used for the study of the corrosion inhibition properties of Dioctyl phthalate on mild steel is the weight loss method [15], with coupons of size 5 cm by 4 cm, and thickness of 0.5 mm obtained from the mechanical workshop of the University of Jos, Nigeria.

Determinations

The evaluation of the inhibition efficiency (%I) was determined from the weight loss measurement at temperatures ranging from 303K to 318K [16]. The kinetic and thermodynamic parameters were determined as described below. The adsorption parameters and surface coverage were also determined as outlined below.

Determination of Parameters

The data obtained from the experiment above was used to determine the following parameters;

Inhibition Efficiency (%IE) and Surface Coverage (θ)

The inhibition efficiency (%IE) and the surface coverage (θ) were determined from the following equations

$$\%I = [1 - (\frac{W0 - Wt}{W})] \, X \, 100$$

$$\theta = 1 - (\frac{W0 - Wt}{W}) \hspace{4cm} 1$$

Where W_0 = initial weight of the mild steel before suspending in the solutions,

   W= weight of the mild steel without the inhibitor, that is, weight in blank solution, and;

   Wt = weight of the mild steel with the inhibitor

The inhibitor efficiency gives important information about the performance of the inhibitor in various medium [17]

Corrosion Rate

This is a method of monitoring corrosion. The rate of corrosion C_r, is the weight loss per unit area per unit time of a metallic material [17]. This is given by the equation

$$C_r \, (mg \; cm^{-2} \; hr^{-1}) = \frac{W0 - Wt}{A\,T} \qquad\qquad 2$$

Where A = surface area of the coupon (cm^2)

T = time of exposure in hrs

W_0 – Wt = weight loss

Thermodynamic Parameters

These parameters tell more of the adsorption properties of the inhibitor. This includes the Activation energy of adsorption E_{ads}, the heat of adsorption Q_{ads}, enthalpy of activation $\triangle H_{ads,}$ entropy $\triangle S_{ads}$ and free energy change $\triangle G_{ads}$.

1. **Activation Energy E_{ads}:** this is the energy that adsorbing species must acquire in order to be adsorbed on the surface of the mild steel to form a protective monolayer. This is obtained from a modified form of the Arrhenius equation [18];

$$C_r = A \, e^{-Eads/RT}$$

This equation can be linearized to give

$$\ln C_r = \ln A - (E_{ads}/RT) \qquad\qquad 3$$

Where C_r = rate of corrosion
A = a frequency factor
R = Gas constant (Atm. L. mol^{-1} K^{-1})
T = temperature (K)

A graphical plot of $\ln C_r$ against $1/T$, gives a straight line graph with slope equals to E_{ads}/R and an intercept of $\ln A$ [18]. The values of E_a greater than 20kJ indicate that the adsorption process is controlled by the surface reactions. [19]

Heat of Adsorption Q_{ads}

This parameter is used to tell whether an adsorption process is endothermic or exothermic. A positive value of Q_{ads} indicates an endothermic process while a negative value indicates exothermic process of adsorption. This can be evaluated from equation 3.4 reported by [20]

$$Q_{ads} = 2.303R \left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right) \right] \times \left(\frac{T_1 \times T_2}{T_2 - T_1}\right)$$

Where θ_1 = is the initial surface coverage at temperature T_1

θ_2 = is the final surface coverage at temperature T_2

R = the gas constant

Equation 3.4 can be written as;

$$\frac{Q_{ads}}{RT} = \ln\left(\frac{\theta}{1-\theta}\right) \qquad 4$$

A graphical plot of $\ln\left(\frac{\theta}{1-\theta}\right)$ against 1/T gives the value of the Q_{ads} obtained from the slope of the graph which is Q_{ads}/R. Negative Q_{ads} values indicate an exothermic adsorption process. This exothermic reaction can either be physisorption or chemisorption. This can be distinguished by considering the values of the heat of adsorption. Value of energy less than 40kJ is indicative of physical adsorption, otherwise, chemical adsorption. [20]

Enthalpy of Adsorption ΔH_{ads} and Entropy of Adsorption ΔS_{ads}

The enthalpy of adsorption and the entropy of adsorption (H_{ads} and S_{ads}) can be determined from the Eyring transition state equation;

$$C_r = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{ads}}{R}\right) \exp\left(-\frac{\Delta H_{ads}}{RT}\right)$$

Rearranging the equation gives;

$$\ln\frac{C_r}{T} = \ln\frac{R}{Nh} + \left(\frac{\Delta S_{ads}}{R}\right) - \left(\frac{\Delta H_{ads}}{RT}\right) \qquad 5$$
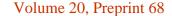
A plot of $\ln C_r/T$ against 1/T is a straight line with a slope equal to $\frac{\Delta H_{ads}}{R}$ and the intercept of the graph is equal to $\ln\frac{R}{Nh} + \left(\frac{\Delta S_{ads}}{R}\right)$. Where C_r is the corrosion rate, T is the temperature in Kelvin, N is the Avogadro's number 6.03×10^{23} mol^{-1}, h is the Planck's constant 6.62×10^{-34} Js, and R is the gas constant. The values of ΔH_{ads} indicates whether the adsorption is endothermic ($+\Delta H$) and exothermic ($-\Delta H$). [21]

Free Energy of Adsorption (ΔG^o_{ads})

This value also indicates the type of adsorption mechanism, whether by physical or chemical adsorption mechanism. Values of ΔG^o_{ads} from −20kJ or more indicates physical adsorption mechanism, while values of −40kJ or less is an indicative of chemical adsorption.

This value was calculated from the equation below;

$$K_{ads} = \left(\frac{1}{55.5}\right)\exp\left(-\frac{\Delta G_{ads}}{RT}\right)$$
$$\ln K_{ads} = \ln\left(\frac{1}{55.5}\right) - \left(\frac{\Delta G_{ads}}{RT}\right)$$

$$\triangle G_{ads} = - RT(\ln 55.5K_{ads}) \qquad\qquad 6$$

Where K_{ads} is the equilibrium constant for the adsorption of the inhibitor on mild steel surface, which is obtained from the adsorption isotherm given by equation 3.9 – 3.11, T is the Absolute temperature of the system, R is the gas constant, and C is the concentration of the inhibitor. [22]

Kinetic Parameters

Corrosion reactions are usually first order and are expected to obey the equation of a first order reaction as given below

$$\ln w_f = \ln w_i - kt \qquad\qquad 7$$

$$\ln w_f/w_i = -kt$$

$$\ln w_i/w_f = kt$$

Where w_i and w_f are respectively the weights of the mild steel in blank acid solution and after immersion in the inhibitor solution. This value tells how fast the adsorption process is taking place. A plot of $\ln(w_i/w_f)$ against t, gives a straight line with a slope which is equal to k [12].

Also the half life of this process was determined from the value of the rate constant that was obtained from above using

$$t_{1/2} = \frac{\ln 2}{k} \qquad\qquad 8$$

Adsorption Studies

The variation at constant temperature of the surface coverage of adsorbing species with the concentration or pressure of the adsorbing solutes is known as the adsorption isotherm. Adsorption parameters obtained from adsorption studies give important information that will help in understanding the type of adsorption taking place during the inhibition. Adsorption isotherms are important in the optimization of the adsorption mechanism and aiding the understanding of the surface properties of the inhibitor. [23].

Most frequently used adsorption isotherms are Langmuir, Freundlich, Frumkin, Temkin, Forry – Huggins, BET, e.t.c. The newly proposed Adejo – Ekwenchi isotherm was also used to confirm the claims about its effectiveness in deciphering the mechanism of adsorption.

The isotherms used to test the linearity of the adsorption results are;

Langmuir $\qquad \left(\dfrac{C}{\theta}\right) = \dfrac{1}{k} + C \qquad$ 9

Freundlich $\qquad \log \theta = \log k + n\log C \qquad$ 10

Adejoh – Ekwenchi $\qquad \log\left(\dfrac{1}{1-\theta}\right) = \log K_{AE} + b\log C \qquad$ 11

k is the equilibrium constant for adsorption in all the equations. The values of k, gives information about how favourable the inhibition process is, and higher values of k indicates favourable adsorption process. C is the concentration of the solution of the inhibitor. [24, 25]

Results and Discussion

The corrosion inhibition properties of Dioctyl phthalate was determined at temperature ranges of 303 – 313 K, in 0.5 M H_2SO_4 solution. The average initial weight of the mild steel coupon before immersion into the inhibitor solution is 2.512 g. Table 1 represents the weight loss of mild steel at different concentration of the inhibitor in 0.5 M H_2SO_4 solution as the inhibitor.

Table 1: weight loss of mild steel in inhibitor and 0.5 M H_2SO_4 solution at different temperatures

Conc. of inhibitor (M) in 0.5M H_2SO_4	Weight Loss (g) (303 K) $(w_0 - w_t)$			Weight Loss (g) (308 K) $(w_0 - w_t)$			Weight Loss (g) (313 K) $(w_0 - w_t)$		
	1 hr	2hr	3hr	1 hr	2hr	3hr	1 hr	2hr	3hr
Blank	0.0362	0.0424	0.0512	0.0471	0.0537	0.0611	0.0563	0.0623	0.0713
0.01	0.0257	0.0365	0.0401	0.0366	0.0426	0.0523	0.0459	0.0549	0.0645
0.03	0.0128	0.0212	0.0386	0.0261	0.0317	0.0478	0.0351	0.0442	0.0522
0.05	0.0023	0.0083	0.0158	0.0155	0.0216	0.0321	0.0248	0.0324	0.0411
0.07	0.0011	0.0026	0.0071	0.0103	0.0149	0.0218	0.0137	0.0209	0.0340

The percentage inhibition efficiency (%IE) was calculated according to equation (1a) and the values obtained at different concentration of the inhibitor and different temperatures in 0.5 M H_2SO_4 solution are recorded in Table 2.

Table 2: Percentage Inhibition Efficiency (%IE) of the inhibitor on mild steel in 0.5M H_2SO_4

Conc. Of inhibitor in 0.5M H_2SO_4	% IE at 303K			% IE at 308K			% IE at 313K		
	1 Hr	2Hrs	3Hrs	1 Hr	2Hrs	3Hrs	1 Hr	2Hrs	3Hrs
Blank	0	0	0	0	0	0	0	0	0
0.01	29.0055	13.9151	21.6797	22.2930	20.6704	14.4026	18.4725	11.8780	9.53717
0.03	64.6409	50.0000	24.6094	44.5860	40.9683	21.7676	37.6554	29.0530	26.7882
0.05	93.6464	80.4245	69.1406	67.0913	59.7765	47.4632	55.9503	47.9936	42.3562
0.07	96.9613	93.8679	86.1328	78.1316	72.2533	64.3208	75.6661	66.4526	52.3142

Also, the surface coverage of the inhibitor solution on mild steel was calculated according to equation (1b). Table 3, represents the surface coverage (θ) of the inhibitor on mild steel in 0.5 M H_2SO_4 solution

Table 3: Surface coverage (θ) of the inhibitor on mild steel in 0.5M H$_2$SO$_4$

Conc. Of inhibitor in 0.5M H$_2$SO$_4$	θ at 303K			θ at 308K			θ at 313K		
	1 Hr	2 Hrs	3 Hrs	1 Hr	2 Hrs	3 Hrs	1 Hr	2 Hrs	3 Hrs
Blank	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.01	0.2901	0.1392	0.2168	0.2229	0.2067	0.1440	0.1847	0.1188	0.0954
0.03	0.6464	0.5000	0.2461	0.4459	0.4097	0.2177	0.3766	0.2905	0.2679
0.05	0.9365	0.8043	0.6914	0.6709	0.5978	0.4746	0.5595	0.4799	0.4236
0.07	0.9696	0.9387	0.8613	0.7813	0.7225	0.6432	0.7567	0.6645	0.5231

The rate of corrosion of mild steel in solution of the inhibitor was also calculated according to equation 2. These values are represented in Table 4 for the inhibitor in 0.5 M H$_2$SO$_4$.

Corrosion rate (Cr) increases with increasing temperature from 303 K to 313 K in H$_2$SO$_4$ medium, and the corrosion rate decreases with increase in the concentration of the inhibitor. This is because as the concentration of the inhibitor increases, more molecules of the inhibitor become available to cover the surface of the mild steel, preventing it from the grip of the corrodant.

Table 4: Corrosion rate (Cr) of the mild steel in inhibitor/0.5M H$_2$SO$_4$

Conc. Of inhibitor in 0.5M H$_2$SO$_4$	Cr at 303K			Cr at 308K			Cr at 313K		
	1 Hr	2 Hrs	3 Hrs	1 Hr	2 Hrs	3 Hrs	1 Hr	2 Hrs	3 Hrs
Blank	0.0018	0.0011	0.0009	0.0024	0.0013	0.0010	0.0028	0.0016	0.0012
0.01	0.0013	0.0009	0.0007	0.0018	0.0011	0.0009	0.0023	0.0014	0.0011
0.03	0.0006	0.0005	0.0006	0.0013	0.0008	0.0008	0.0018	0.0011	0.0009
0.05	0.0001	0.0002	0.0003	0.0008	0.0005	0.0005	0.0012	0.0008	0.0007
0.07	0.0001	0.0001	0.0001	0.0005	0.0004	0.0004	0.0007	0.0005	0.0006

As presented in table 2, there is a significant increase in inhibition efficiency as the concentration of the inhibitor increases and it could be observed that the efficiency decreases with increase in temperature. This is suggestive of a physisorption mechanism of adsorption of the inhibitor onto the surface of the metal [16].

Thermodynamic Considerations/parameters

Activation energy of adsorption E_{ads}, the quantity of energy Q_{ads} involved in the adsorption process, the enthalpy of adsorption ΔH_{ads}, and the entropy of the system ΔS_{ads}, where determined according to equations, 3b, 4b and 5b respectively. The results obtained for these parameters are shown in Table 5.

Table 5: Thermodynamic parameters of the dioctyl phthalate inhibitor in 0.5 M H_2SO_4 solution at different concentrations of the inhibitor

Concentration of inhibtor (moldm^{-3}) in 0.5M H_2SO_4	Activation energy of Adsorption		Heat of Adsorption		Enthalpy of adsorption and Entropy of Adsorption			Free Energy of Adsorption	
	E_{ads} (kJ)	R^2	Q_{ads} (kJ)	R^2	ΔH_{ads} (kJ)	ΔS_{ads} (JK^{-1})	R^2	ΔG_{ads} (kJ)	R^2
Blank	38.67	0.998			32.29	-2.76	0.988		
0.01	50.84	0.997	-46.53	0.989	43.23	-2.28	0.984	-46.5	0.989
0.03	89.15	0.974	-87.55	0.932	77.1	-0.74	0.947	-87.55	0.932
0.05	211.81	0.932	-193.92	0.894	185.54	4.25	0.894	-194	0.894
0.07	226.20	0.883	-184.45	0.802	197.12	4.72	0.837	-184.5	0.802

A change in the value of E_{ads} in the presence of the inhibitor may be due to the modification of the mechanism of the corrosion process in presence of adsorbed inhibitor molecules. Bouyanzer et'al in Ejikeme et'al [26] indicated that generally, higher values of E_{ads} in presence of additives support physical adsorption mechanism whereas an unchanged or lower value of E_{ads} for inhibited systems compared to the blank is indicative of chemisorption mechanism. From table 5, it can be seen that the values of the activation energies for the inhibited systems are higher than that of the uninhibited or blank system. This is an indication of a physisorption mechanism of adsorption.

The values of Enthalpy of adsorption and Entropy of Adsorption; ΔH_{ads} and ΔS_{ads} were obtained from the graphical plot of the Eyring transition state equation (equation 6). The values of ΔH_{ads} and E_{ads} are nearly the same in 0.5 M H_2SO_4, and are higher in the presence of the inhibitor. This indicates that the energy barrier of the corrosion reaction increased in the presence of the inhibitor without changing the mechanism of dissolution [27]. The positive values of ΔH_{ads} for both corrosion processes with and without the inhibitor reveal the endothermic nature of the mild steel dissolution process and indicate that the dissolution of steel is difficult [27]. The values of entropy of adsorption ΔS_{ads} listed in Table 5 for 0.5M H_2SO_4, clearly showed that entropy of activation increases in the presence of the

studied inhibitor compared to free acid solution. The negative Q_{ads} values indicate that adsorption and inhibition efficiency (Table 2) decreases with rise in temperature which is in line with the findings of Onen *et al*, [15] and indicates that the adsorption of the inhibitor to the surface of the mild steel is spontaneous, and also, this is indicative of a strong interaction between the inhibitor and the mild steel [15].

Adsorption Studies

Three isotherms were selected for the adsorption study; these are Langmuir, the Freundlich and the newly proposed Adejoh – Ekwenchi isotherms.

Table 6: Values for adsorption studies of the inhibitor on mild steel in 0.5 M H_2SO_4 solutions at different temperatures.

Temperature (K)	Langmuir Isotherm		Freundlich Isotherm			Adejoh–Ekwenchi Isotherm		
	K_L	R^2	K_F	n_F	R^2	K_{AE}	B	R^2
303	37	0.965	5.25	0.732	0.782	41.4	0.814	0.705
308	25	0.961	4.47	0.772	0.907	6.97	0.413	0.765
313	18.5	0.857	5.86	0.889	0.996	4.56	0.317	0.934

"b" (from the Adejoh – Ekwenchi Isotherm) is a parameter called "variation factor" and it relates the surface coverage by the adsorbate to the change of adsorbate bulk concentration. A decrease in the value of b with rise in temperature is an indication of physical adsorption mechanism, while increase or fairly constant in its value with rise in temperature shows the mechanism of adsorption to be chemical adsorption [24]. K_{AE} is the isotherm adsorption equilibrium constant known as Adejo–Ekwenchi constant. Just like any isotherm it is a temperature dependent parameter, which gives the adsorption strength. High value of it is indicative of favourable adsorption process. It can be seen that K_{AE}, followed the required trend similar to those of Langmuir and Freundlich, indicating a favourable adsorption process. It can also be seen that the values of "b" decreases with increase in temperature. This supports the claims by Adejoh et' al, [24] that the mechanism for this type of trend is physisorption. This is in line with all the experimental data analysed previously in this research.

The positive adsorption equilibrium constant K_F (Freundlich Isotherm) values are indication of favourable adsorption. The parameter n_F in the Freundlich isotherm relates to intensity of adsorption and it varies with heterogeneity of the material [28], and the value is always positive, but not an integer, with typical value is 0.6 [29]. The average value of n_F is 0.798 for

the inhibitor in 0.5 M H_2SO_4 indicating that this adsorption process can reasonably be modelled by Freundlich isotherm and is heterogeneous [16]. The adsorption equilibrium constant K_{ads} (for all the Isotherms tested) decreases with increase in experimental temperature in the corrosion media, indicating that the interactions between the adsorbed molecules and the metal surface are weakened and consequently, the adsorbed molecules could become easily removable. Such data explains the decrease in the inhibition efficiency with increasing temperature [30].

Free Energy of Adsorption ΔG^o_{ads}

The standard free energy of adsorption, ΔG°_{ads}, which can characterize the interaction of adsorbed molecules and metal surface, was calculated using Equation 10. The values of K_{ads} were determined from the different isotherm plots, and are represented in table 7 for 0.5 M H_2SO_4 solution. The negative values of ΔG°_{ads} ensure the spontaneity of adsorption process and stability of the adsorbed layer on the metal surface. Generally, the values of ΔG°_{ads} below 40kJ/mol are consistent with physisorption, while those above 40 kJ/mol, involve chemisorption [31]. From table 7 below, the values of the standard free energy of adsorption are negative. This indicates that the adsorption process is spontaneous. The values also, were found to be below 40 kJ/mol; which concur with the aforementioned physisorption mechanism for the adsorption process in 0.5 M H_2SO_4 solution.

Table 7: values for the standard free energy of adsorption ΔG^o_{ads} of the solution of the inhibitor in 0.5 M H_2SO_4 at different temperatures

Isotherm	Temperature (K)	K_{ads}	R^2	ΔG^o_{ads} (kJ/mol)
Langmuir	303	37	0.965	−19.21
	308	25	0.961	−18.53
	313	18.5	0.857	−18.04
Freundlich	303	5.25	0.782	−14.30
	308	4.47	0.907	−14.12
	313	5.86	0.996	−15.05
Adejoh – Ekwenchi	303	41.4	0.705	−19.50
	308	6.97	0.765	−15.26
	313	4.56	0.934	−14.40

Kinetic Parameters

The corrosion of mild steel follows a first order rate law with respect to the concentration of the inhibitor [32]. A decrease in the rate constant k, with increase in temperature indicates that the rate of the mild steel corrosion is greatly reduced in the presence of the inhibitor (dioctyl phthalate) in H_2SO_4 Solution. The half – life presented in table 8, indicates that the life span of the mild steel is increased as the temperature increased[32].

Table 8: rate constant k, and half – life $t_{1/2}$ of mild steel in the inhibitor/0.5 M H_2SO_4 solution at different temperatures

Temperature (K)	Rate Constant k (hr⁻¹)		
	k (hr⁻¹)	R²	$t_{1/2}$ (hr)
303	0.79	0.943	0.877
308	0.233	0.993	2.975
313	0.134	0.982	5.173

Summary

Dioctyl phthalate can be said to be a good corrosion inhibitor, and gave a maximum percentage inhibition efficiency of 85.11% at a concentration of 0.07 M of the inhibitor in 0.5 M H_2SO_4 solution at a temperature of 303 K.

The Freundlich adsorption isotherm was found to be the best fit for the adsorption studies of the corrosion inhibition of dioctyl phthalate in H_2SO_4 medium with an average R^2 value of 0.9. It was also discovered that the Adejoh – Ekwenchi Isotherm can be used to model adsorption process for corrosion inhibition studies.

All values of $\triangle H_{ads}$ were found to be positive indicating an endothermic nature of the dissolution of the mild steel. The values of entropy of adsorption $\triangle S_{ads}$ was found to increase with increase in concentration of the inhibitor indicating that the rate determining combination step is a more orderly arrangement relative to the initial state.

It was also discovered that the values of E_{ads} increases with increase in the concentration of the inhibitor. The values of E_{ads} and those of $\triangle H_{ads}$ varies in a similar manner, and the average values of $E_{ads} - \triangle H_{ads}$ equal to 2.41 kJmol⁻¹, which is very close to the value of RT (2.51 kJmol⁻¹) indicating that the adsorption process is unimolecular in nature[16].

All values of Q_{ads} were found to be negative, indicating that the process of adsorption of the inhibitor on mild steel is exothermic and spontaneous. It also indicates strong interaction between the inhibitor and the mild steel surface.

The corrosion kinetics showed an adherence to first order kinetics and the half- life values showed that the presence of the inhibitor extends the lifespan of the mild steel.

The values of $\triangle G_{ads}$ and K_{ads} for the corrosion inhibition studies of mild steel in 0.5 M H_2SO_4 and dioctyl phthalate as the inhibitor were found to be suggestive of a physisorption mechanism.

Conclusion

The corrosion inhibition properties of dioctyl phthalate were determined in 0.5 M H_2SO_4 solution and at a temperature range of 303 to 313 K using the weight loss method. The results obtained, showed that dioctyl phthalate is a good corrosion inhibitor of mild steel. This efficiency was found to decrease with increasing temperature and increases with increase in the concentration of the inhibitor. The most suitable isotherm to be used for modelling the corrosion inhibition studies of the dioctyl phthalate is the Freundlich adsorption isotherm. The values obtained for the newly proposed Adejoh – Ekwenchi isotherm agrees with the predictions of Adejoh and Ekwenchi, such that their isotherm can also be used in modelling adsorption processes. Physisorption mechanism was proposed for the adsorption of dioctyl phthalate in 0.5 M H_2SO_4 and 1.0 M HCl solution on mild steel.

Acknowledgement

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