

Corrosion Inhibition Studies Of *Ficus Abutilifolia* On N-80 Oil Well Tubular Steel In 15% Hydrochloric Acid Solution

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ABSTRACT

The corrosion inhibition of oil well tubular steel (N-80 steel) in well acidizing solution (15% Hydrochloric acid) by extract of *Ficus Abutilifolia* (FA) was studied using weight loss technique. Maximum inhibition efficiency (and surface coverage) was obtained at an optimum concentration. However, increase in temperature decreased the inhibition efficiency at the temperature range studied. The inhibition efficiencies were compared to a standard oil well acidization corrosion inhibitor, Propargyl Alcohol. Optimum inhibition efficiency for the tubular steel in the presence of *Ficus Abutilifolia* were 57.40% at 60°C and 52.57% at 90°C while those for Propargyl Alcohol were 90.97% at 60°C and 67.50% at 90°C. The phenomenon of physical adsorption has been proposed from the heat of adsorption values of all inhibitors studied (-9.35686 to -2.65846 kJ/mol). Activation energy values indicates a surface reaction.

Keywords: Corrosion inhibition, oil well steel, *Ficus Abutilifolia*, hydrochloric acid, Activation energy

1. INTRODUCTION

In industries such as pulp and paper industry, power generation, underground structures, chemical and oil industries, metals are used in over 90% of construction process (Osarolube et al., 2004). Iron and steel are the most commonly used materials in the fabrication and manufacturing of oil field operating platforms because of their availability, low cost, ease of fabrication, and high strength (Umezurike, 1998; Nwoko and Umoru, 1998).

Corrosion of metals generally occurs in the presence of oxygen and moisture and involves two electrochemical reactions (oxidation and reduction). Oxidation occurs at anodic site and reduction occurs at cathodic site. In acidic medium hydrogen evolution reaction predominates (Atul, 2007).

Hydrochloric acid is used during oil well acidization to increase the productivity of crude petroleum oil and gas wells.

In view of the fact that the acidizing acid (HCl) Corrodes the tubular steel, steps must be taken so as to ensure that acid attack on the metal is as minimal as possible.

The effective way of protecting the oil well tubular material is by using organic corrosion inhibitors (Jayaperumal et al, 2000).

A variety of organic compounds are effective corrosion inhibitors under acid conditions including acetylenic alcohols, aromatic unsaturated aldehydes, -alkenyl phenones, nitrogen- and sulfur-containing heterocyclic compounds, quaternary ammonium salts, and condensation products of carbonyls and amines (Schmitt, 1984; Cizek, 1994; Brindsi et al, 1981; Raman and Labine, 1996).

Among these compounds, acetylenic alcohols are widely used as acid inhibitors in industry because of their commercial viability and effectiveness. However, these inhibitors produce

toxic vapors under acidic conditions. Because of this, a need exists for development of new acidizing inhibitors. Plant extracts of *Ficus Abutilifolia* have been studied with a view to evaluate their corrosion inhibition properties on N-80 steel in 15% hydrochloric acid (HCl). This plant extract was chosen because they are more environmentally benign and less toxic than the conventional propargyl alcohol used for oil well acidization.

Therefore the objectives of this research work are as follows:

- I. To study the corrosion rate of N-80 stainless steel in 15% Hydrochloric Acid solution.
- II. To study the effectiveness of *Ficus Abutilifolia* as an inhibitor in 15% Hydrochloric Acid.
- III. To ascertain the correlations between varying corrosion parameters and corrosion rate of N-80 stainless steel in 15% HCl with and without extracts of ficus *Abutilifolia* using corrosion kinetic and thermodynamic models.
- IV. To compare the inhibition efficiency of *Ficus Abutilifolia* with that of a standard oil well corrosion inhibitor, propargyl alcohol.

2.0. EXPERIMENTAL METHODS

2.1. Materials

The steel sample used for this research work, as – received was obtained from S,C,C Nigeria Ltd Abuja, Nigeria. The alloy composition of the steel is given in Table 1

TABLE 1: the high strength low alloy steel is a commercial micro-alloyed steel (in hot-rolled condition) with the following percentage alloy:

TABLE 1: PERCENTAGE ALLOY COMPOSITION OF HIGH STRENGTH LOW ALLOY STEEL(IN HOT-ROLLED CONDITION)

Element	C	Mn	Si	P	S	Mo	V	Ti	Al	Fe
% composition	0.220	1.200	0.250	0.025	0.025	0.001	0.004	0.002	0.051	BAL

2.2 Inhibitors

Two inhibitors were used for this research work. These includes the standard inhibitor for acidization, Propargyl Alcohol and extract of *Ficus Abutilifolia*.

The Propargyl alcohol was obtained from chemical store while the plant extract (*Ficus Abutilifolia*) were obtained from the forest in Zaria. The extract of *Ficus Abutilifolia* were obtained using a soxhlet according to the conventional methods. The phytochemical analysis is given in table 2.

Table 2 Phytochemical analysis of *Ficus Abutilifolia* (FA)

CHEMICAL CONSTITUENT	FA
ALKALOIDS	–
ANTHRAQUINONE	+
SAPONINS	–
TANNINS	+
STEROIDS AND TERPENOIDS	+
NITROGEN	+
SULPHUR	+

3.0 PROCEDURE

Prior to the experiment, the as – received steel (60mmx50mmx15mm) bars were sectioned into coupon of sizes 20mm x 10mm x 3.5 mm and polished with emery papers(220-800 grades).The specimens were the washed with distilled water followed by degreasing in absolute ethanol, dried in acetone, weighed and stored in a moisture free desiccators prior to use (NACE, 1984).

The experimental set up consists of a reaction vessel (250 ml three – necked round bottom flask with a condenser inserted into it) containing the HCl corrodent and inhibitor in which the sample, tied with thread, is /are suspended and then immersed in the corrodent.

The set up is placed in thermostated water bath/heating mantle at 45°C, 60°C, 75°C, 90°C. The corroded coupons were then retrieved from the set up at 0.5 hour interval for 2.5 hours. Each set of coupons was dipped into saturated

ammonium acetate solution at room temperature, to terminate the corrosion reaction. They were washed by scrubbing with a light brush and dried in acetone and finally in an oven maintained at 80 °C. The weight loss of the coupons was evaluated in grams as the difference in the weight of the coupons before and after the test.

The loss of weight of coupons is evaluated in grams as the difference in weight of the coupons before and after the test (Orubite et al, 2004)

$$W = (W_i - W_f)g \quad (1)$$

Where W = weight loss of coupon.

W_i = initial weight of coupon

W_f = final weight of coupon,

Each reading is report as an average of three (3) experimental reading.

The corrosion rate of coupons in different corrosion medium is calculated from weight loss using the formula (NACE, 1984)

$$\text{Corrosion Rate (mpy)} = 534W/DAT \quad (2)$$

Where W= weight loss (mg)

D = Density of specimen (g/cm³)

A = Area of specimen (in²)

T = Exposure time (Hrs)

4.0. RESULTS AND DISCUSSION

4.1 Weight loss Studies

Table shows the values weight loss(in grams), corrosion rate (in mpy), inhibition efficiency (IE%), surface coverage (θ) and obtained at different concentration of the inhibitors in 15% Hydrochloric acid solution for an immersion period of 2.5 hours. The corrosion inhibition efficiency (IE) of the inhibitors is calculated using the formula (Ekpe et al, 1994).

$$E\% = [1 - W_1 / W_2] \times 100\% \quad (3)$$

$$\theta = [1 - W_1 / W_2] \quad (4)$$

Where W_1 = weight loss in the presence of inhibitors

W_2 = weight loss in the absence of inhibitor at the same temperature.

= surface coverage

TABLE 3 Values of weight loss,corrosion rate,inhibition efficiency at various temperatures for propargyl alcohol (PA) and extract of *Ficus Abutilifolia* (FA).

Temp (°C)	Conc (ppm)	FA				PA			
		Wt Loss (g)	Corr.Rate (mpy)	Inh.Eff (%)	Surface Coverage (θ)	Wt Loss (g)	Corr.Rate (mpy)	Inh.Eff (%)	Surface Coverage (θ)
45	0	0.100807	1062.510	-	-	0.100807	1062.510	-	-
	1000	0.071422	752.7917	29.14976	0.291498	0.021206	223.509	86.75036	78.96376
	3000	0.057645	607.5759	42.81647	0.428165	0.0168	177.0698	89.50328	83.33449
	5000	0.051895	546.9778	48.52044	0.485204	0.01392	146.722	91.3023	86.19144
	7000	0.051505	542.8648	48.90732	0.489073	0.01072	112.9886	93.30202	89.36582
	9000	0.072205		761.042	28.37303	0.28373	0.009699	102.2307	93.93975
60	0	0.231287	2435.457	-	-	0.231287	2435.457	-	-
	1000	0.137703	1450.016	40.46215	0.404622	0.0302	317.6929	83.98606	0.839861
	3000	0.111693	1176.123	51.70825	0.517082	0.0249	262.4337	86.77151	0.867715
	5000	0.099736	1050.215	56.87803	0.56878	0.0245	258.1466	86.98761	0.869876
	7000	0.09906	1043.1	57.17019	0.571702	0.0182	191.3845	90.35289	0.903529
	9000	0.098517	1037.389	57.40467	0.574047	0.0170	179.031	90.97559	0.909756
75	0	0.293615	3091.771	-	-	0.293615	3091.771	-	-
	1000	0.185906	1957.59	36.68375	0.366838	0.0510	536.68	81.3718	0.813718
	3000	0.149542	1574.676	49.06871	0.490687	0.0433	456.2922	84.16206	0.841621
	5000	0.133887	1409.83	54.40048	0.544005	0.0429	452.0967	84.30769	0.843077
	7000	0.130913	1378.518	55.41324	0.554132	0.0349	367.542	87.24259	0.872426
	9000	0.13044	1373.538	55.57431	0.555743	0.0338	355.6627	87.65492	0.876549
90	0	0.189169	1993.840	-	-	0.189169	1993.840	-	-

	1000	0.170459	1796.633	9.890627	0.098906	0.0846	890.4508	55.27808	0.552781
	3000	0.164467	1731.84	13.05816	0.130582	0.0725	763.2212	61.67448	0.616745
	5000	0.148218	1560.735	21.64784	0.216478	0.0730	768.934	61.41017	0.614102
	7000	0.143021	1506.014	24.39512	0.243951	0.0625	658.4303	66.96076	0.669608
	9000	0.130724	1377.83	30.89565	0.308957	0.0614	646.7177	67.54225	0.675423

It could be seen from table 3 that the addition of inhibitor to the acid had reduced the corrosion rate. The inhibition efficiency increased with increase in concentration of inhibitors and decreased with increase in temperature.

We can observe from Table 3 that, as the reaction temperature is increased from 45°C to 90°C, the inhibition efficiency decreases. Inhibition efficiencies decreases from 57.4% at 60°C to 30.9% at 90°C for FA while efficiency decreases from 93.9% at 45°C to 67.5% at 90°C for PA.

This decrease in inhibition efficiency with increase in temperature can be attributed to the decrease in the protective nature of the inhibitive film formed on the metal surface (or desorption of the inhibitor molecules from the metal surface) at higher temperatures. This suggests physical adsorption mechanism. Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between the two processes at a particular temperature. With increase of temperature, the equilibrium between adsorption and desorption processes is shifted to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperature (Jamal and Anwar 2010).

Physical (electrostatic) adsorption takes place when when inhibition efficiency decreases with rise in temperature while chemisorptions takes place when inhibition efficiency increases with increase in temperature (Umoren et al, 2007). Thus, it is appropriate to say that decreasing temperature favours the inhibition efficiency of FA and PA on steel in hydrochloric acid.

4.2 Kinetic Considerations

The corrosion reaction is a heterogeneous one, composed of anodic and cathodic reactions with the same or different rate (James and Akaranta, 2009). It is on this basis that kinetic analysis of the data is considered necessary. In this present study, the initial weight of steel

coupon at time, t is designated W_i , the weight loss is ΔW and the weight change at time t , $(W_i - \Delta W)$ or W_f .

When $\log W_f$ was plotted against time (in days), a linear variation was observed, which confirms a first-order reaction kinetics with respect to tubular steel in HCl solutions, formulated (Peter et al, 2010) as :

$$\text{Log } W_f = \text{log} W_i - kt \quad (5)$$

where W_i is the initial weight before immersion, k is the rate constant and t is time.

From the rate constant values, the half-life values, $t_{1/2}$, of the metal in the test solutions were calculated using the equation:

$$t_{1/2} = 0.693/k \quad (6)$$

Another important kinetic parameter, apparent activation energy, E_a , was calculated from the Arrhenius equation (Abiola and Oforka, 2002, Ebenso et al, 2002, Orubite et al, 2004)

$$\log(r_2/r_1) = E_a/2.303[1/T_1 - 1/T_2] \quad (7)$$

Where r_1 and r_2 are the corrosion rates at temperatures T_1 and T_2 .

The values of the rate constants, k (obtained from the slopes of the plots in Fig. 1), half-life values, $t_{1/2}$, and activation energy are presented in Table 4 and 5.

Table 4. Values of rate constant, half life and activation energy for FA at various concentrations

Temp Conc(ppm)	RATE CONSTANT, $k(\text{DAY}^{-1}) \times 10^{-3}$				Half-life, $t_{1/2}$ (DAYS) $\times 10^2$				ACTIVATION ENERGY, kJmol^{-1}		
	45°C	60°C	75°C	90°C	45°C	60°C	75°C	90°C	45°C- 60°C	60°C- 75°C	75°C- 90°C

Blank	26.73	31.07	45.21	68.09	0.26	0.22	0.15	0.10	9.53	24.00	27.95
1000	16.68	20.31	30.61	47.60	0.42	0.34	0.23	0.15	13.01	25.91	29.98
3000	14.25	16.99	24.98	38.36	0.49	0.41	0.28	0.18	11.77	25.51	29.67
5000	12.70	15.52	22.53	34.59	0.55	0.45	0.31	0.20	12.63	25.38	29.73
7000	12.97	15.50	22.53	34.48	0.53	0.45	0.31	0.20	10.90	25.95	29.54
9000	12.94	15.47	22.31	34.40	0.54	0.45	0.31	0.20	11.01	25.40	30.20
									11.48	25.36	29.51

Table 5. Values of rate constant, half life and activation energy for PA at various concentrations

Temp Conc(ppm)	RATE CONSTANT, k (DAY^{-1}) $\times 10^{-3}$				Half-life, $t_{1/2}$ (DAYS) $\times 10^2$				ACTIVATION ENERGY, kJmol^{-1}		
	45°C	60°C	75°C	90°C	45°C	60°C	75°C	90°C	45°C- 60°C	60°C- 75°C	75°C- 90°C
Blank	26.73	31.07	45.21	68.09	0.26	0.22	0.15	0.10	9.53	24.00	27.95
1000	3.89	5.89	8.68	14.81	1.78	1.18	0.80	0.47	20.67	33.72	35.50
3000	3.08	4.43	7.82	12.38	2.25	1.57	0.89	0.56	23.12	35.57	36.06
5000	2.62	4.76	7.52	12.64	2.64	1.46	0.92	0.55	33.21	36.04	37.23
7000	2.12	3.34	6.09	11.06	3.27	2.07	1.14	0.63	30.97	41.97	40.87
9000	1.86	3.01	5.83	11.02	3.72	2.30	1.19	0.63	32.93	44.15	41.92
									25.07	35.91	36.59

From Tables 4 and 5, there is a general decrease in the rate constants from 45°C – 90°C with increasing concentrations of FA and PA (Tables 4 and 5). The increase in half-life ($t_{1/2}$) with increase in concentration shown when FA and PA are present further supports the inhibition of the steel in 15% HCl by the additives. The increase in half life indicates more protection of the metals by the FA and PA (James and Akaranta, 2009). On the basis of the experimentally determined activation energy value (11.5 kJ/mol at 45°C – 60°C, 29.5 kJ/mol at 75°C-90°C for FA and 25 kJ/mol at 45°C – 60°C, 36.6 kJ/mol at 75°C-90°C for PA), the additive is physically adsorbed on the coupons. These values are higher than the value of 9.5 kJ/mol obtained for the blanks indicating that the corrosion reaction of steel is retarded by FA and PA (Ebenso, 2003). These values are also lower than the threshold value (80kJ/mol) required for chemical adsorption indicating that FA and PA inhibit the tubular steel corrosion via physical adsorption mechanism (Ekop and Eddy, 2008).

Therefore, it is probable that a multilayer protective coverage on the entire tubular steel surface was obtained.

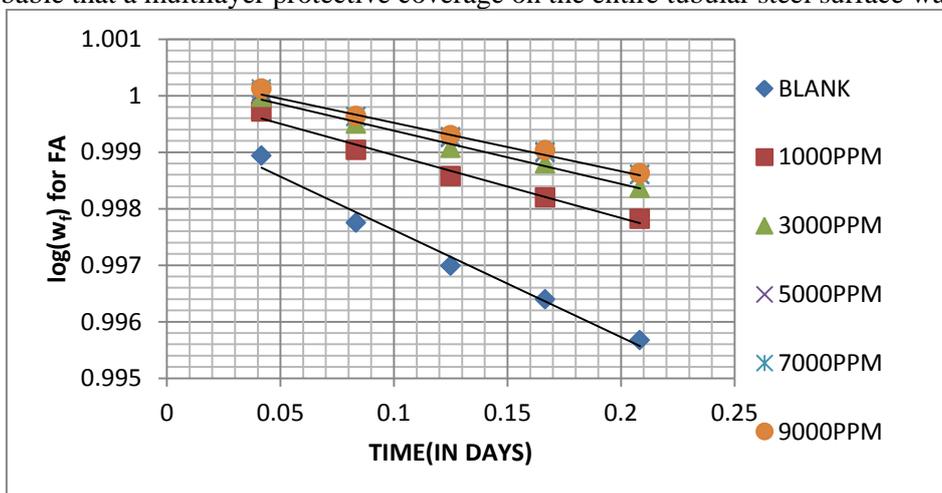


FIG 1 VARIATION OF LOG W_f WITH TIME (DAYS) FOR TUBULAR STEEL COUPONS IN 15% HCl SOLUTION CONTAINING FA AT 30°C

4.3 Thermodynamic Considerations

One of the thermodynamic tools used in the determination of inhibition mechanism is the standard heat of adsorption, Q_{ads} .

Q_{ads} could be calculated using the following equation (Orubite et al, 2004).

$$Q_{ad} = 2.303R \text{Log} \left[\frac{\theta_2}{1 - \theta_2} \right] - \log \left[\frac{\theta_1}{1 - \theta_1} \right] \frac{T_1 T_2}{T_2 - T_1} \text{ KJ mol}^{-1} \quad (8)$$

Where θ_1 and θ_2 are degrees of surface coverage at temperature T_1 and T_2 by different inhibitor. Values of Q calculated from Equation 8 are recorded in Table 6. The values ranged from -9.36 to -2.66KJ/mol for FA and -35.55 to -21.09 KJ/mol for PA indicating that the adsorption of the inhibitors on the surface of the steel is exothermic.

Table 6 values of heats of adsorption at various concentrations and temperatures for FA and PA

CONC(PPM)	HEATS OF ADSORPTION(kJ/mol) of FA			CONC(PPM)	HEATS OF ADSORPTION(kJ/mol) of PA		
	318K-333K	333K-348K	348K-363K		318K-333K	333K-348K	348K-363K
BLANK	-	-	-	BLANK	-	-	-
1000	-9.43	-5.62	-6.35	1000	-13.03	-11.75	-9.39
3000	-4.56	-3.18	-3.72	3000	-15.41	-13.53	-9.75
5000	-5.69	-2.62	-3.44	5000	-26.50	-14.05	-11.15
7000	-2.47	-3.60	-3.01	7000	-23.32	-20.21	-15.03
9000	-2.66	-2.57	-4.22	9000	-25.27	-22.53	-16.17

4.4 Adsorption Behaviour

The observed inhibition of the corrosion of tubular steel in the HCl solutions with increase in the inhibitor concentration can be explained by the adsorption of the components of the inhibitor on the metal surface. From a theoretical standpoint, the inhibition action of organic molecules has been regarded as a simple substitution process, in which an inhibitor molecule (I) in the aqueous phase substitutes and x is number of water molecules adsorbed on the surface (Atkins and De Paula,2002 and El-Awady et al,1992).



The inhibitor molecules may then combine with Fe^{2+} ions on the metal surface, forming metal-inhibitor complex. The resulting complex, depending on its relative solubility could either inhibit or catalyse further metal dissolution. Plant extracts are viewed as an incredible rich source of naturally synthesized chemical compounds. These large numbers of different chemical compounds may form adsorbed intermediates (organo-metallic complexes) such as Fe-I (Gunasekaran and Chauhan,2004 and El-Etre et al, 2005) which may either inhibit or catalyse further metal dissolution.

CONCLUSIONS

The results presented in this paper show that extracts from the leaves of *Ficus Abutilifolia*(FA) and propargyl alcohol(PA) inhibit the corrosion of N-80 steel in HCl solutions to a reasonable extent.

The inhibition efficiencies of the inhibitors(FA and PA) increased with increase in concentration and decreased with increase in temperature and followed the trend: PA>FA. From the trend in inhibition efficiencies, inhibitors, present at highest concentration in the corrodent, is assumed to contribute significantly to the adsorbed organic compounds responsible for the inhibitive effects of the inhibitors. The adsorbed species formed insoluble [Fe-I] complex due to their interactions with the dissolved iron ions. The methanolic extract can be considered as a source of relatively cheap, ecofriendly and effective acid corrosion inhibitor. Based on the trend of inhibition efficiency with temperature and from the obtained values of activation energy and heat of adsorption,the corrosion inhibition is attributed to chemical adsorption of the phytochemical components of the plant on the surface of the tubular steel.

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