Available online at www.worldnewsnaturalsciences.com

World News of Natural Sciences

WNOFNS 10 (2017) 26-38 EISSN 2543-5426

Kinetics and Thermodynamic Studies of Corrosion Inhibition of Mild Steel Using Methanolic Extract of *Erigeron floribundus* (Kunth) in 2 M HCl Solution

F. E. Abeng[1, 2,*], V. D. Idim[1,2], P. J. Nna[1,3]

[1]Department of Pure and Applied Chemistry, University of Calabar, P.M.B. 1115, Calabar, Nigeria

[2]Department of Chemical Sciences, Cross River University of Technology, P.M.B. 1123, Calabar, Nigeria

[3]Department of Chemistry, Ignatius Ajuru University of Education, P.M.B. 5047, Port Harcourt, Nigeria

*E-mail address: fidelisabeng@yahoo.com

*Tel: +2348035664813

ABSTRACT

The investigation of kinetics and thermodynamics of the corrosion of a mild steel in a 2 M HCl solution using methanolic extract of *Erigeron floribundus* was carried out by means of gravimetric techniques. The results obtained indicate that the extract retarded corrosion. The inhibition efficiency was seen to increase with increase in concentration of the inhibitor, as well as with increase in temperature. The values of activation energy (E_a) obtained indicate a chemisorption mechanism, whereas the value of Gibbs free energy (ΔG^o_{ads}) indicates a spontaneous adsorption of the extract components on the metal surface. Kinetic modelling of the experimental data obeys first order reaction. The adsorption of methanolic extract of *Erigeron floribundus* onto the mild steel surface followed the Langmuir adsorption isotherm model. Therefore, the extract functions as a good corrosion inhibitor for mild steel in hydrochloric acid.

Keywords**:** *Erigeron floribundus*, corrosion inhibition, kinetics, Adsorption mechanism

1. INTRODUCTION

Figure 1. *Erigeron floribundus* (Kunth)
https://inpn.mnhn.fr/espece/cd_nom/611690

Organic compounds containing polar functional groups such as nitrogen, sulfur and oxygen in conjugated system have been reported to be effective corrosion inhibitors for steel [1]. Some plants extracts contain a mixture of polar functional group and thus possess multiple active centers. The study of corrosion inhibition of plants' extracts has been on the increase in recent times. Generally the inhibitive effect of plants extract is attributed to the adsorption of organic substances on the metal surface by blocking active sites or forming a protective barrier on steel surfaces [2, 3].

The effectiveness of inhibition by the adsorbed inhibitor system will be determined by the energy released on forming the metal-inhibitor bond compared to the corresponding changes when the pure acid reacts with the metal [1, 4]. In recent years, natural compounds, such as herbal plants are employed as corrosion inhibitor, in order to develop new cleaning chemicals for green environment, *Erigeron floribundus* is well known and reputed medicinal plant traditionally used for the treatment of skin disorders by the rural population as well as those from the urban area. This species is widespread in Nigeria [5, 6]. The main purpose of this study is to investigate the inhibitive potential of methanolic extract of *Erigeron floribundus* as an eco-friendly corrosion inhibitor on a mild steel in 2 M HCl solution using gravimetric technique. The summary of plants extracts used as corrosion inhibitors have recently been given in [1-5] and [7-16] (**Figure 1**).

2. EXPERIMENTAL METHODS

2. 1. Preparation of specimen

Mild steel specimens, had a composition of 0.6% Mn; 0.36% P; 0.15% C; 0.07% S, and 98.79% Fe, and the specimens used in this work were obtained from Physics Department, University of Calabar - Nigeria. The mild steel was mechanically pressed and cut to coupons of dimension 40.0 × 12.0 × 0.8 mm, with the surface area of 10.10 cm^2.

2. 2. Preparation of the plant extract

The fresh parts of *Erigeron floribundus* were obtained within the premises of Faculty of Agriculture Cross River University of Technology, Calabar. The fresh plant was washed with water, air dried, powdered and extracted with methanol for 24 hours. The methanol solution was filtered and refluxed further to obtain a concentrated solution. The clear dark brown methanol concentrated solution was dried under vacuum to get a semi-solid liquid [14]. 8 g of semi-solid liquid, that is methanol extract, was dissolved in 2 M HCl solution and kept for 24 hours. The resultant solution was filtered and stored. From the stock solution (8 g /L), inhibitor test solutions of concentrations: 0.1, 0.5, 1.0, 2.0, and 4.0 g /L were prepared using serial dilution method. These solutions were then used for the corrosion test [15].

2. 3. Gravimetric measurement

Weighed test specimens were fully immersed separately for 5 hours in each of the beakers containing the extract for the five sets, the same process as above was done for the beaker containing only 2 M HCl solution. Each of the test specimens was taken out every one hour, washed with distilled water, raised with ethanol, dried in acetone, and re-weighed [7]. From the weight loss data, the corrosion rates (*CR*) were calculated from eq. 1:

$$CR = \frac{WL}{A \cdot t} \times 1000 \ (\mathrm{mg \cdot cm^{-2} \cdot h^{-1}}) \qquad 1$$

where *WL* is the weight loss data, *A* the specimen surface area, and *t* the immersion period.

Thus from corrosion rate, the inhibition efficiency *IE*% was evaluated using eq. 2.

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

where *IE*% is the inhibition efficiency, CR_{blank} is the corrosion rate for the blank, while CR_{inh} is the corrosion rate for inhibited solution [8].

3. RESULTS AND DISCUSSION

3. 1. Effect of temperature on corrosion inhibition of mild steel in 2 M HCl solution

The variation of weight loss *WL*, corrosion rate *CR* and inhibition efficiency *IE*% obtained from experimental measurements of mild steel after immersion in 2 M HCl solution at the temperature of 303 K, 313 K, 323 K, and 333 K, as a function of concentration in the presence of methanol extract of *Erigeron floribundus*, is shown in **Figs**. **1**, **2**, and **3**.

The results show that weight loss and corrosion rate values decrease from uninhibited to inhibited solution at each temperature. The decrease is payable to the inhibitive effect of the plant extract and these effects increased with an increase in concentration of the plant extract. Inspection of Fig. 3 reveals that the inhibition efficiency increases with increase in the concentration of the methanol extract, and increases with increase in temperature.

This could be attributed to the phytochemical components present in the plant extract, which were adsorbed in the mild steel-solution interface [6]. Inhibition efficiency and corrosion rate of the mild steel in various concentrations of methanol extract with temperature are summarized in **Table 1**.

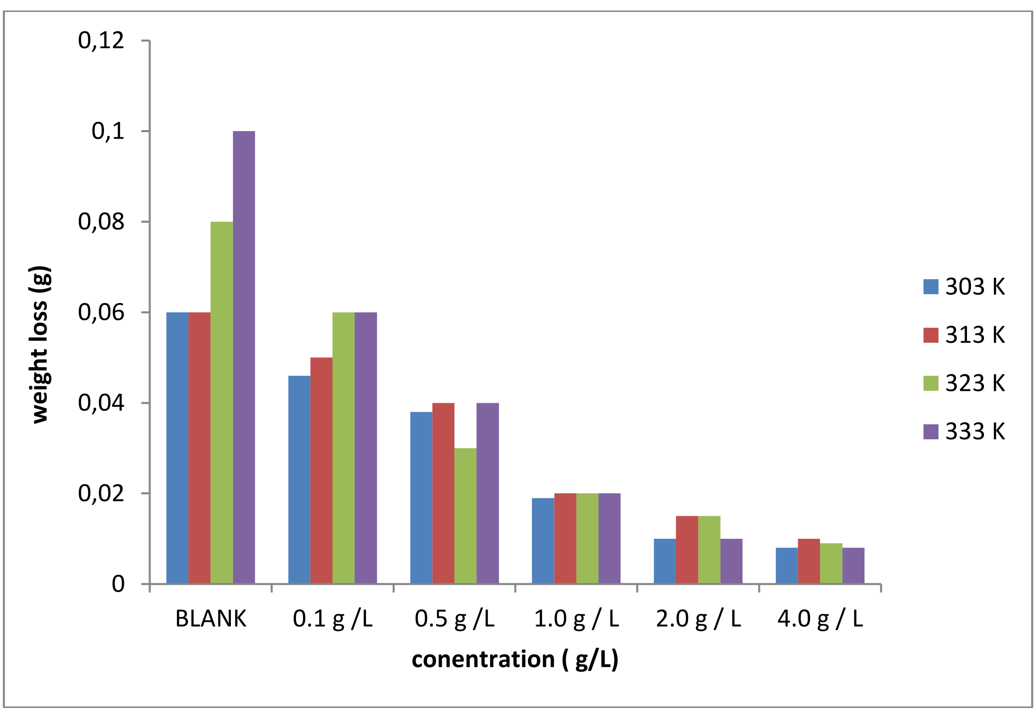

Fig. 1. Variation of weight loss of Mild steel in 2 M HCl solution as a function of concentration in the presence of methanol of *Erigeron floribundus* extract

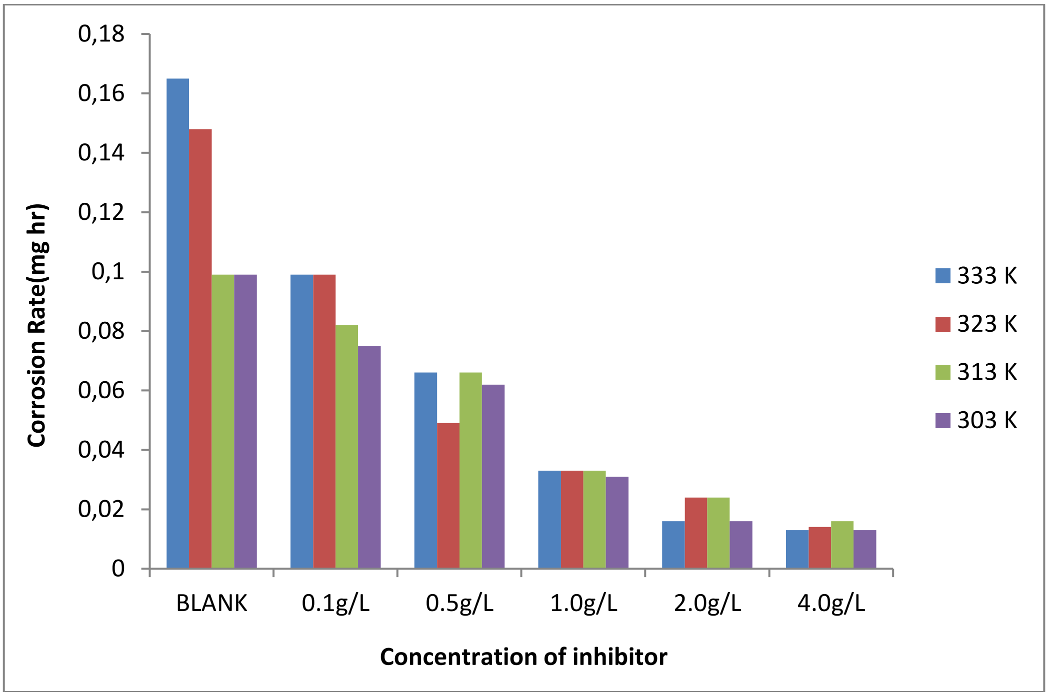

Fig. 2. Variation of corrosion rate of Mild steel in 2 M HCl solution as a function concentration in the presence of methanol of *Erigeron floribundus* extract

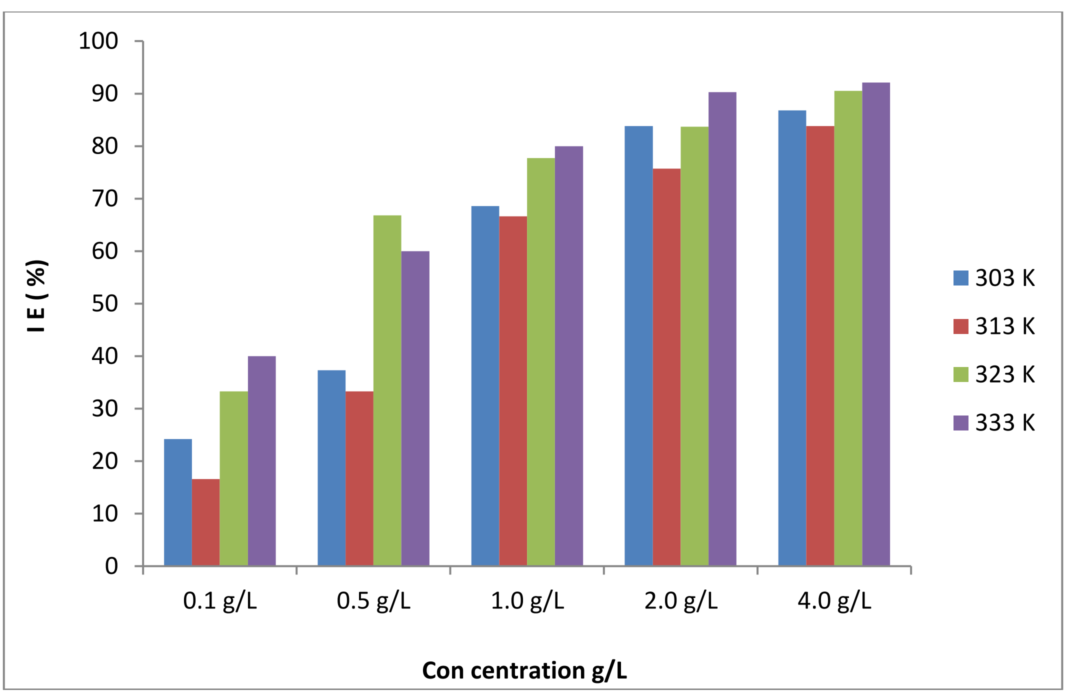

Fig. 3. Variation of inhibition efficiency of Mild steel in 2 M HCl solution as a function of concentration in the presence of methanol of *Erigeron floribundus* extract

Table 1. Effect of various temperatures on a mild steel corrosion in 2 M HCl solution containing various concentrations of methanol extract of *Erigeron floribundus.*

	303 k		313 K		323 K		333 K	
Con (g/L)	*IE*%	*CR*(mg/h)	*IE*%	CR(mg/h)	*IE*%	*CR*(mg/h)	*IE*%	*CR*(mg/h)
BLANK		0.099		0.099		0.148		0.165
0.1	24.2	0.075	16.6	0.082	33.3	0.099	40.0	0.099
0.5	37.3	0.062	33.3	0.066	66.8	0.049	60.0	0.066
1.0	68.6	0.031	66.6	0.033	77.7	0.033	80.0	0.033
2.0	83.8	0.016	75.7	0.024	83.7	0.024	90.3	0.016
4.0	86.8	0.013	83.8	0.016	90.5	0.014	92.1	0.013

3. 2. Kinetics and thermodynamics of the corrosion inhibition of mild steel in 2 M HCl solution

The corrosion rate of most reactions increases as temperature is increased, like the corrosion rate displayed in Table 1. It has been found experimentally that a plot of ln *k* against 1/*T* gives a straight line. This behaviour is normally expressed mathematically by introducing two parameters, one representing the intercept and the other the slope of the straight line, and writing the expression as eq. 3

$$\ln k = \ln A - \frac{Ea}{RT} \qquad 3$$

where *A* is the pre-exponential factor, *E*a is the activation energy, collectively this two quantities are called Arrhenius parameters, while *R* is gas constant, *T* is absolute temperature, *k* represents the rate constant or corrosion rate [17].

The Arrhenius plot obtained from eq.3 gave a straight line graph, as shown in **Fig. 4**, with the slope of $-Ea / 2.303\ R$. Analysis of temperature dependence of inhibition efficiency, as well as comparison of the corrosion activation energies in the absence and presence of inhibitor gives insight into the possible mechanism of inhibitor adsorption. An increase in inhibition efficiency with a rise in temperature, with analogous decrease in corrosion activation energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of formation of chemically adsorption film, whereas a decrease in inhibition efficiency with rise in temperature, with corresponding increase in corrosion activation energy in the presence of inhibitor compared to its absence, is recognized as a physical adsorption mechanism [6,11]. The inhibition efficiency with temperature, obtained in Table 1 and Fig. 3, suggests chemisorption of the phytochemical constituents of the plant extract on the surface of the metal. In order to confirm this, corrosion activation energies, E_a for the mild steel dissolution in 2 M HCl solution, in the absence and presence of the methanol extract, were obtained from the plot of ln *CR* versus 1/*T* and are listed in **Table 2**. In the corrosion of mild steel in 2 M HCl solution weight at time after post treatment of coupons is chosen as w_f , when ln w_f / w_o was plotted against time, in hours, a linear variation was observed, which confirms the first order reaction kinetics with respect to the mild steel in 2 M HCl solution, formulated as

$$\ln \frac{wf}{wo} = -k \cdot t \qquad 4$$

where w_o is the initial weight before immersion, *k* is the rate constant, and *t* is time. The values of the rate constants, obtained from the slopes of the plot in **Fig. 5**, are obtainable in Table 2.

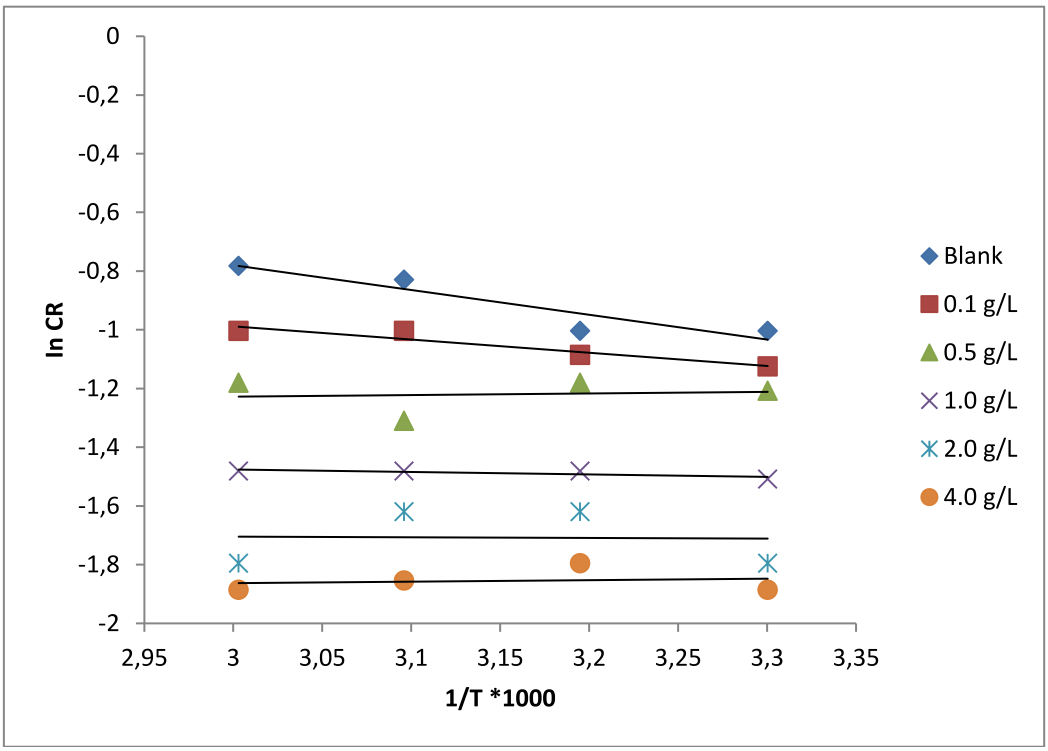

Fig. 4. Arrhenius plot for the mild steel in 2 M HCl solution in different concentrations of methanol extract of *Erigeron floribundus.*

Table 2. Calculated values of activation energy, enthalpy, entropy, rate constant, and half life for mild steel coupon in 2 M HCl solution containing methanol extract of *Erigeron floribundus.*

Conc. (g/L)	*Ea* kJ/mol	Δ*H* kJ/mol	Δ*S* kJ/mol	Rate Con.	Half Life	R^2
BLANK	16.16	13.51	–22.67	4.12	0.422	0.999
0.1	8.59	59.54	–49.3	3.04	0.495	0.999
0.5	10.33	–36.76	–82.84	2.20	0.552	0.998

1.0	15.89	−10.33	−79.65	1.58	0.625	0.999
2.0	4.21	−22.01	−87.55	1.32	0.681	0.999
4.0	9.57	−16.84	−94.79	0.57	2.722	1.000

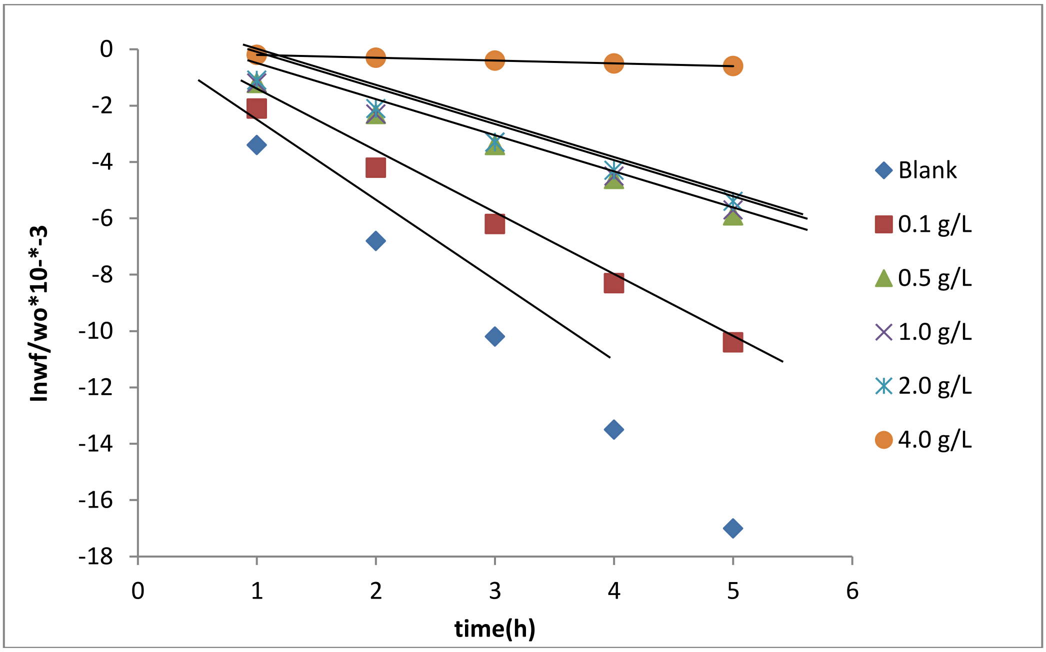

Fig. 5. Plot of ln $\frac{wf}{wo}$ against time for mild steel coupons in 2 M HCl solution containing the methanol extract of *Erigeron floribundus* at various concentrations.

The results obtained reveal that the rate constant decreases with the increase in concentaration of methanol extract of *Erigeron floribundus*. From the rate constant values, the half life values, $t_{1/2}$ of the metal in the test solutions were calculated from the equation 5:

$$t_{1/2} = \frac{0.693}{k} \qquad 5$$

and the deduced data are also listed in Table 2. The half life values were observed to increase with the increase in concentration of the methanol extract of *Erigeron floribundus,* indicating decrease in the dissolution rate of the metal in the solution with the increase in concentration of the inhibitor.

The transition state equation was used to calculate some thermodynamic parameters (ΔH_{ads} and ΔS_{ads}) for the adsorption of methanol extract of *Erigeron floribundus* on the mild steel surface.

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \qquad 6$$

where *CR* is the corrosion rate for mild steel in 2 M HCl solution, *R* is gas constant, *T* is the temperature, *N* is the Avogadro's number, *h* is the Planck constant., ΔS_{ads} is the entropy of the adsorption and ΔH_{ads} is the enthalpy of adsorption of the inhibitor on the mild steel surface. From the logarithm of both sides of eq. 6, eq. 7 was obtained,

$$\log (CR/T) = \log R/N\cdot h + \Delta S_{ads}/ 2.303R - \Delta H_{ads}/2.303\, R\cdot T \qquad 7$$

The plots of log (*CR*/*T*) against 1/*T* for methanol extract of *Erigeron floribundus* were linear, the slopes and intercept of the transition state plot (**Fig. 6**) are equal to $-\Delta H_{ads}$ / 2.303*R* and (log $R/N\cdot h + \Delta S_{ads}/ 2.303R$), respectively. The values of ΔH_{ads}, calculated from the slope of the plot were positive in blank and 0.1 g /L, and negative in 0.5, 1.0, 2.0 g/L, and 4.0 g/L, ΔH_{ads} values of adsorption of methanol extract of *Erigeron floribundus* on mild steel surface exhibited both, endothermic and exothermic reactions, respectively. On the other hand, the values of ΔS_{ads}, calculated from the intercept of the transition state plot, are negative. This shows that there is an increase in the degree of disorderliness, indicating that there is a bigger association of the inhibitor's molecules rather than dissociation [2, 3].

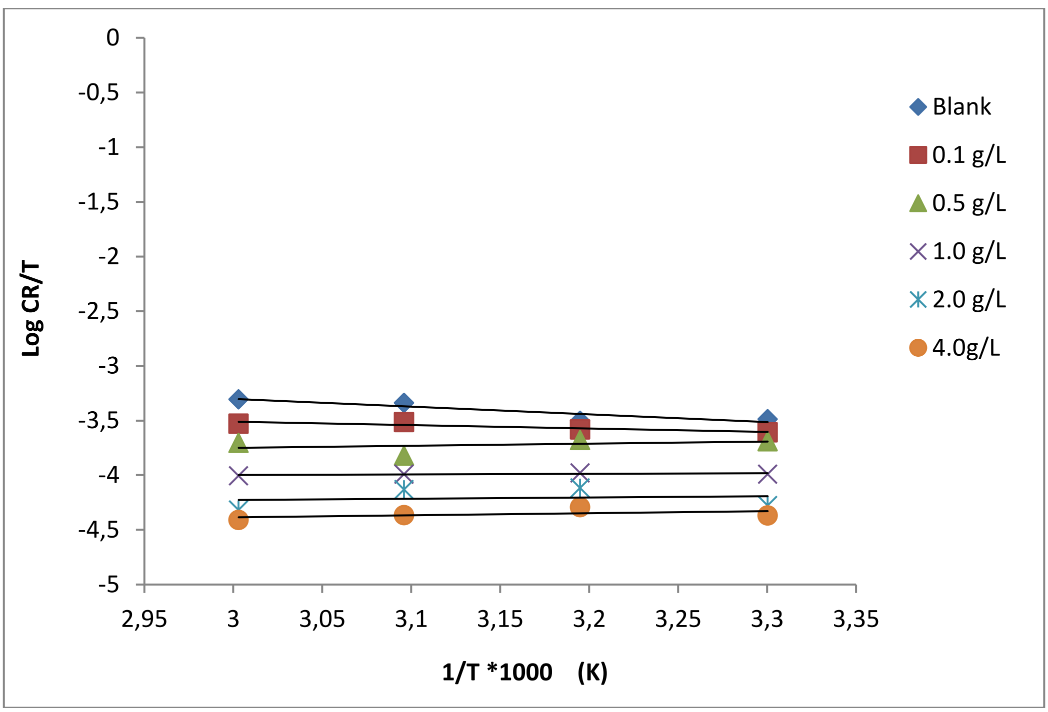

Fig. 6. Variation of log (*CR*/*T*) with 1/*T* for the inhibition of mild steel corrosion in 2 M HCl solution by methanol extract of *Erigeron floribundus*

We observed a progressive raise in the thermodynamic parameters (ΔH_{ads} and ΔS_{ads}), presented in Table 2, with increasing in the concentration of methanol extract of *Erigeron floribundus* which confirms that methanol extract of *Erigeron floribundus* is the adsorption inhibitor for the corrosion of mild steel in 2 M HCl solution.

3. 3. Adsorption behaviour

The experimental inhibition of the corrosion of mild steel in 2 M HCl solution increases with increase in the concentration of the extract, and this can be explained by the adsorption of the constituent of the extract on the metal surface. From a hypothetical point of view, the inhibition action of the organic molecules has been regarded as a simple substitution process, in which an inhibitor molecule in aqueous phase substitution with any number of water molecules is adsorbed on the metal surface [7]

$$\ln h + yH_2O \leftrightarrow \ln h_{(ads)} + yH_2O_{(aq)} \qquad 8$$

The inhibitor molecules may then mingle with Fe^{2+} ions on the metal surface, forming metal-inhibitor complex. The resulting complex, depending on the relative solubility, could either inhibit or catalyse further metal dissolution. Methanol extract of the plant is viewed as an incredible rich source of naturally synthesized chemical compounds.

These large numbers of different chemical components may form adsorbed intermediates (organic-metallic complexes) [7]. Most researchers claim that particular compound in a plant extract is solely responsible for the inhibition ability. In a real sense it is not true, since most plant extracts are composed of numerous organic compounds capable of either inhibiting or accelerating the corrosion processes. The net antagonistic and synergistic action of the phytochemical components of the plant is what is actually recorded as the inhibition efficiency of the methanol extract of the plant [4, 7].

Like most medicinal plants, *Erigeron floribundus* is composed of numerous naturally occurring compounds, with some of these compounds being isolated and characterized from the plant. These include: alkaloid, phenol, triterpenes, sterol, flavonoids, cardiac glycosides, and tannins [5, 6].

Most of these compounds have complex molecular structures, large molecular weight and significant number of oxygen, sulfur, and nitrogen atoms integrated in the structure. These compounds can adsorb on the metal surface through the lone pairs of the electrons present on their oxygen, sulfur, and nitrogen atoms. The adsorption of such compounds on the metal surface creates a barrier for charge and mass transfer, leading to a decrease in the interaction between the metal and the corrosive atmosphere. As a result, the corrosion rate of the metal decreases [12, 13].

The experimental data were applied to different adsorption isotherm models. It was found that the experimental data fitted the Langmuir adsorption isotherm (**Fig. 7**) which may be formulated as [9, 10]:

$$\frac{Cinh}{\theta} = \frac{1}{bads} + C_{inh} \qquad 9$$

where θ is the surface coverage, C_{inh} is the concentration of the inhibitor and b_{ads} is the adsorption-desorption equilibrium constant. The adsorption-desorption equilibrium constant, obtained from the intercept of the Langmuir adsorption isotherm plots and linear regression coefficient were used to determine the best fit. The results obtained for ΔG_{ads} and b_{ads} are shown in **Table 3**.

Table 3. Calculated values of equilibrium constant and free energy of the adsorption at different temperatures.

Temp., K	b_{ads}	ΔG_{ads} kJ/mol	R^2
313	0.038	–39.72	0.998
333	0.036	–40.03	0.999

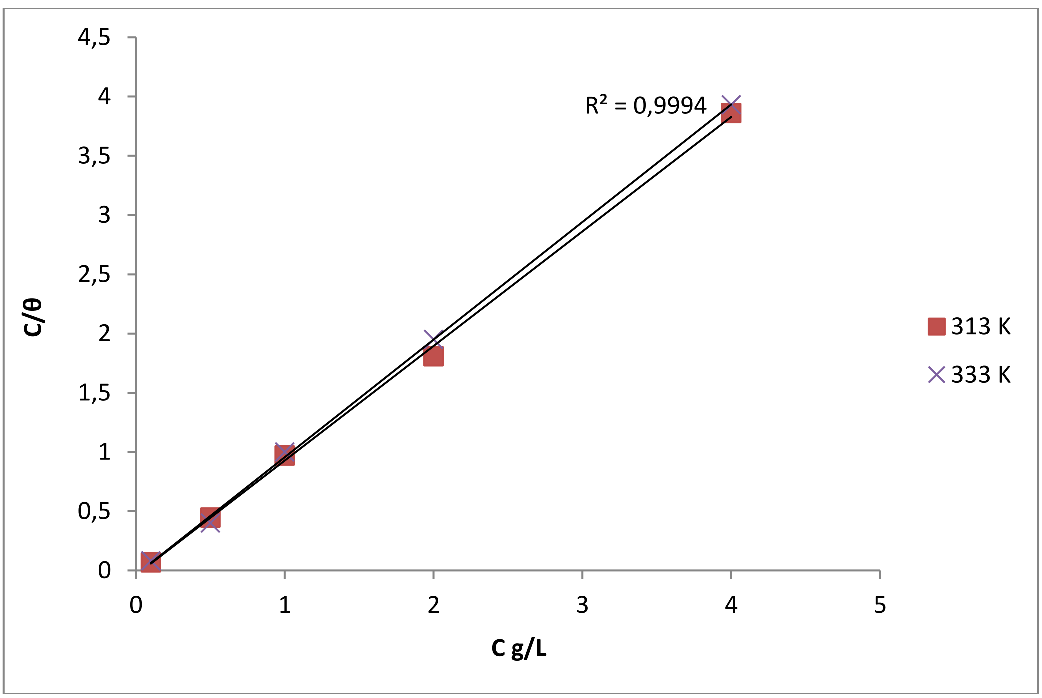

Fig. 7. Langmuir adsorption isotherm of methanol extract of *Erigeron floribundus.*

The values obtained for ΔG^{o}_{ads} were negative indicating that the adsorption process is spontaneous. Generally, the values of ΔG^{o}_{ads} less than –20 kJ·mol^{-1} signify physic-sorption and values more negative than –40 kJ·mol^{-1} signifying chemisorptions [7, 9, 10]. The results listed in Table 3 show that ΔG^{o}_{ads} values are more negative than –20 kJ·mol^{-1}. This reveals that the adsorption of the inhibitor on the metal surface is spontaneous and confirms chemisorption's mechanism.

4. CONCLUSIONS

The results presented in this paper show that the methanol extract from *Erigeron floribundus* inhibits the corrosion of mild steel in 2 M HCl solution to a reasonable extent. The inhibition efficiency of the methanol extract increased with increasing concentration of the inhibitor with temperature. The inhibition process followed the first order reaction kinetics. It has been observed that the positive and negative values obtained for the enthalpy show a mixed reaction process such as endothermic and exothermic reactions. Also the value of entropy is negative, indicating association mechanism, and negative value of the free energy reveals that the reaction process is spontaneous. Adsorption isotherm mechanism followed the Langmuir adsorption.

Acknowledgement

The authors thank the management of corrosion and electrochemistry research laboratory, Department of Pure and Applied Chemistry, University of Calabar, Calabar, Nigeria.

References

[1] N.O. Eddy, S.A. Odoemelam, I N. Ama, Ethanol extract of ocimum gratissimum as a green corrosion inhabitor for the corrosion of mild steel in H_2SO_4. *Green Chem. Lett. Rev.* 3 (2010) 165-172.

[2] N.O. Eddy, P.A. Mamza, Inhibitive and adsorption properties of ethanol extract of seeds and leaves of Azadirachta indica on the corrosion of mild steel in H_2SO_4. *Electrochem. Acta* 27 (2009) 443-456.

[3] N.O. Eddy, E.E. Ebenso, Corrosion inhibition and adsorption properties of ethanol extract of *Gongronema latifolium*on mild steel in H_2SO_4. *Pigm. Resin. Tech.* 39 (2010) 77-83.

[4] A.W. Elyn-Amira, A.A. Rahim, H. Osman, K. Awang, P.B. Raja, Corrosion inhibition of mild steel in I M HCl solution by *Xylopia ferruginea* leave from different extract and partition. *Int. J. Electrochem. Sci*. 6 (2011) 2998-3016.

[5] Y.J.H. Galani, J. Nguefack, D.C. Dakole, D. Patchayo, F.R. Fouelefack, P.H. Amvan Zello, Antifungal potential and phytochemical analysis of extracts from seven Cameroonian plants against late blight pathogens phytophthora infestans. *Int. J. Curr. Micr. and App. Sci.* 2 (2013) 140-154.

[6] F.H. Trabi, M.W. Kone, N.F. Kuoame, Antifungi activity of Erigeron floribundus from Cote d lvoire West Africa. *Tropical J. Pharm. Res.* 7 (2008) 975-979.

[7] P.C. Okafor, E.E. Ebenso, U.J. Ekpe, *Azadirachta indica* extracts as corrosion inhibitor for mild steel in acid medium. *Int. J. Electrochem. Sci.* 5 (2010) 978-993.

[8] B. U. Ugi, F. E. Abeng, Corrosion inhibition effects and Adsorption characteristics of ethanol extract of king Bitter root (Andrographis paniculata on mild steel in 1.0 M HCl and H_2SO_4 acid media. *Fountain J. Nat. Appl. Sci.* 2 (2013) 10-21.

[9] F.E. Abeng, P.J. Nna, U J. Ekpe, Corrosion inhibitive properties and adsorption of ethanol extract of *Phyllanthus amarus* on mild steel in HCl. *Reiko Int. J. Sci. Tech. Res.* 5 (2014) 33-42.

[10] P.S. Desai, S.M. Kapopara, Inhibitory Action of Xylenol Orange on Aluminium in HCl solution. *Indian J. Chem. Tech.* 21 (2014) 139-145.

[11] S.F. Desouza, S.R. Goncalves, A. spinelli, Assessment of caffeine Adsorption onto mild steel surface as an Eco-friendly corrosion inhabitor. *J. Brazil Chem. Soci.* 25 (2014) 81-90.

[12] O.O. Fadare, A E. Okoronkwo, E.F. Olasehinde, Assessment of anticorrosion potential of extract ficus aspertoliamiq (moraceae) on mild steel in acidic medium, *Afr. J. Pure Appl. Chem.* 10 (2016) 8-22.

[13] K.C. Ferreira, F.B. Cordeiro, J.C. Nuries, H. Orofino, M. Magalhaes, A.G. Torres, E.D. Elia, Corrosion inhibition of carbon steel in HCl solution by Aqueous Brown onion peel extract. *Int. J. Electrochem. Sci.* 11 (2016) 406-418.

[14] G.A. Ijuo, H.F. Chanhul, I.S. Energy, Kinetic and Thermodynamic studies of corrosion inhibition of mild steel using Bridelia ferruginea extract in acidic environment. *J. Adv. Electrochem*. 2 (2016) 107-112.

[15] P. Arockiasamy, X. Queen Rosart Sheela, G. Thenmozhi, M. Franco, W. J. Sahayaraj, R. Jaya Santhi, Evaluation of corrosion inhibition of mild steel in 1 M HCl solution by Molligo cerviana. *Int. J Corros*. 5 (2014) 6791-6798.

[16] F.E. Abeng, U.J. Ekpe, A.I. Ikeuba, B.U. Ugi, P.J. Nna, Inhibitive action of alkaloids and non alkaloid fraction of ethanolic extracts of *Phyllanthus amarus* on the corrosion of mild steel in HCl solution. *Global J. Pure Appl. Sci.* 19 (2013) 107-117.

[17] P. Atkins, J. Depaula, Physical Chemistry. Eight Ed., Oxfort Press, Oxfort, 2010.

(Received 27 March 2017; accepted 14 April 2017)