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Kinetics of the Corrosion of Mild Steel in Petroleum-Water Mixture Using Ethyl Ester of Lard as Inhibitor

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Abstract

Ethyl Esters of Lard (EEL) has been investigated as a mild steel corrosion inhibitor in petroleum-water mixture by weight-loss tests at different concentrations (0.1g/l, 0.2g/l, 0.3g/l, 0.4g/l and 0.5g/l) of inhibitor, and at temperatures of 303 K, 313 K, 323 K and 333 K. Results show that inhibition efficiency increases as the inhibitor concentration increases, decreases with temperature, and follows the Langmuir adsorption isotherm. It was found that the adsorption of the ethyl ester of Lard on mild steel is by physical adsorption. For the trans-esterification process, the optimal parameters needed for the optimal yield of the ester were: reaction time of 120 minutes, temperature of $75^{o}C$*, content of catalyst of 1% and alcoholic content of 72* cm^3*.*

Keywords: *Corrosion inhibitor, ethyl ester, Lard, mild steel, petroleum-water mixture.*

Introduction

Mild steel is one of the most preferred materials for industry due to its easy availability and excellent physical properties (Sinnott and Towler 2009). However, its use is restricted in certain media like acidic environments and other corrosive mediums because of the susceptibility towards corrosion. It is cheaper than wrought iron and stronger and more workable than cast iron. Corrosive environments have received a considerable amount of attention because of their attack on materials (Khadom, *et al*. 2009). Mild steel has practical importance, for example in the acid pickling of iron and steel, chemical cleaning of the scale in metallurgy, oil recovery and petrochemical industry and other electrochemical systems. During chemical processes, metals suffer from corrosion in acid solutions at elevated temperatures.

Generally, increased corrosion-resistance can only be obtained at increased cost. However, the actual material-related costs incurred in a project will depend on the corrosivity of the environment and other factors (Ebenso and Obot 2010). Due to the wide applications, studies on the corrosion of metals in organic medium have attracted considerable interest in recent years (Ashassi-Sorkhabi and Seifzadeh 2008). One way of protecting mild steel from corrosion is to use corrosion inhibitors. It has been found earlier that the corrosion caused by the aqueous organic solvents can be effectively controlled by the use of corrosion inhibitors. Use of suitable inhibitors for a system can not only extend the life of the materials in use but could also enable the use of a less expensive inhibitor (Khadom, *et al*. 2009). Most corrosion inhibitors protect the corrosion of metals when they are adsorbed on the surface of the metal (Ashassi-Sorkhabi and Seifzadeh 2008; Eddy and Odoemelam 2008). The adsorption and inhibitive properties of some corrosion inhibitors containing hetero-atoms in their long carbon chain/aromatic structure have also been

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studied (Eddy, *et al*. 2008). Studies have also been conducted on the adsorptive and inhibitive properties of some natural products (Ashassi-Sorkhabi and Nabavi-Amri 2000). In most of these studies, these properties are found to be strongly influenced by the chemical structure of the compound, the corrosive medium, temperature, concentration of the inhibitor, period of contact, etc. Adsorption characteristics of an inhibitor can be studied by the use of adsorption isotherms and the application of the theory of thermodynamics (Ashassi-Sorkhabi and Seifzadeh 2008).There are reports that vegetable oils and their derivatives are potentially important substitutes or extenders for conventional corrosion inhibitors as they are renewable alternative resources (Yordanov and Petkov 2008). Esters of non-edible oils (castor seed oil and rubber seed oil) have also been reportedly used to inhibit mild steel corrosion in HCl and petroleum-water mixtures (Undiandeye *et al*. 2011). Experiment has revealed that the presence of water in petroleum enhances the corrosion rate of mild steel. The higher the percentage of water, the higher the corrosion enhancement (John, *et al*. 2004). In petroleum industries, metal surfaces come in contact with emulsions of oil in water or water in oil. During refining processes, crude oil is usually pumped through pipelines to tank batteries which separate the oil from gas and water (Khadom, *et al*. 2009). In this investigation, the authors have chosen carbon steel to study corrosion inhibition, in petroleum having acetic acid and NaCl. The inhibitor chosen is the Ethyl Ester of Lard (EEL). Many restaurants in the western nations have eliminated the use of lard (pig fat) in their kitchens because of the religious and health-related dietary restrictions of many of their customers. The great amounts of waste animal fat, produced at several slaughter houses and other meat processing units, might be an attractive and cheap raw material for use as corrosion inhibitor. The use of waste lard as raw materials for corrosion inhibition has three major advantages: i) it does not compete with the food market; ii) recycles waste; and iii) reduces production costs (Eddy and Odoemelam 2008). Other waste materials that can be used for corrosion inhibition are the waste frying oils (Eddy and Odoemelam 2008; Eddy, *et al*. 2008; Ashassi-Sorkhabi and Nabavi-Amri 2000; Yordanov and Petkov 2008). Due to the scarce availability of these low cost materials, their use at an industrial scale is limited; however, lard might be an attractive alternative. The information about corrosion rate and kinetic parameters may be helpful in the corrosion control. Equations like the transition state theory (Eq. (1)) and the Arrhenius equation (Eq. (2)) can be used to estimate activation parameters for some systems (Khadom, *et al*. 2009):

$$r = (RT/Nh)\exp(-\Delta H/RT)\exp(\Delta S/R), \quad (1)$$

$$r = A\exp[-E/(RT)]. \quad (2)$$

Chemical kinetics is the study of rates of chemical processes. It includes investigations of how different experimental conditions can influence the rate of a chemical reaction and yields information about the reaction mechanism, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. Like in many chemical reactions, corrosion rate increases with an increase in concentration of the corrosive medium. Corrosion rate data as a function of concentration of corrosive medium can be used to show the rate dependence of petroleum-water mixture concentration. Mathur and Vasudevan (1982) proposed a model given as:

$$r = k\exp(BC), \quad (3)$$

where C is the acid concentration and B is the constant for the reaction studies.

This can be compared with the well-known equation for chemical reaction studies:

$$r = k\,c^n. \quad (4)$$

The purpose of this research is to study the effect of temperature and concentration on mild steel corrosion in petroleum-water mixture. This will be done using the Arrhenius equation, transition state equation, and reaction rate kinetic equation. The parameters contained in Eqs. (1)-(4) are defined in Table 1.

Experimental Set Up

The specimens were mechanically polished with silicon carbide abrasive paper, degreased with acetone, washed in double distilled water and finally dried. Each metal coupon was of the size 5.0×2.0×0.3 cm. Before polishing, a hole of about 0.1 cm in diameter was drilled on each coupon. The average weight of the mild steel was 10 g. The composition of the mild steel, as analyzed with the ARL 3460 Metal Analyzer, Optical Emission Spectrometer at the Aluminum Smelting Company of Nigeria, ALSCON, Ikot-Abasi, Akwa-Ibom State, Nigeria, was: C-0.14, Si-0.03, Mn-0.32, S-0.05, P-0.2, Ni-0.01, Cu-0.01, Cr-0.01 and Fe-Balance (wt%). Weighed samples were immersed in 200 ml of petroleum-water mixture with and without different concentrations of the inhibitor for various intervals of time. They were then taken out and immersed in saturated sodium carbonate solution to remove residual solutions and then washed thoroughly with washing liquor, rinsed with distilled water, dried and reweighed. The parameters used for the study are:

- Time: 24 h, 48 h, 72 h, 96 h, 120 h, 144 h.
- Concentration of the inhibitors: 0.1 g/l, 0.2 g/l , 0.3 g/l, 0.4 g/l, 0.5 g/l.
- Temperatures: 303 K, 313 K, 323 K, 333 K.

The corroding petroleum-water mixture was prepared by adding a mixture of brine and ethanoic acid to the petroleum. This is according to the method described by Ashassi-Sorkhabi and Seifzadeh (2008). Briefly, each litre of petroleum-water mixture contains 20% NaCl and 8% ethanoic acid. The brine was prepared by dissolving 117 g of NaCl in 1 litre of water. The lard was first heated at 100°C to eliminate residual water and then cooled to near the reaction temperature (60°C). The ester was produced according to the method given by Yordanov and Petkov (2008).

Table 1. Parameters used in Eqs. (1)-(4).

Parameter	Definition
r	Corrosion rate
A	Pre-exponential factor
E	Activation energy(J/mol)
R	Gas constant (8.314 J/mol K)
T	Absolute temperature (K)
H	Enthalpy of activation
S	Entropy of activation
N	Avogadro's Number (6.022×10^{23})
h	Plank's constant (6.626×10^{-34})
C	Inhibitor Concentration
B	Constant for reaction studies
K	Reaction rate constant
N	Order of reaction

Care was taken to ensure accurate measurement of component materials. The process uses 100% excess ethanol (99% purity) to speed the reaction. An error in ethanol measurement will affect reaction speed, ester purity and cost. An excess ratio of KOH to lard will result in production of an unusable soap, while a deficit ratio of KOH to lard will result in an ester of reduced purity (Undiandeye *et al.* 2011).

Results and Discussion

Using Design-Expert® Version 8 software (Stat-Ease, Inc. 2010) for Design of Experiments (DOE), the conversion of the esters was optimized and the optimal parameters for highest conversion were: reaction time of 120 minutes, temperature of 75°C, content of catalyst of 1% and alcoholic content of 72 cm^3. Table 2 shows the corrosion rate of mild steel in petroleum-water mixture in the presence of different concentrations of the inhibitor at different temperatures.

Table 2. Effect of temperature and inhibitor concentration on the corrosion rate of mild steel.

		303 K		313 K		323 K		333 K	
S/N	Conc. (g/l)	CR (g/cm^{2}hr) $\times10^{-5}$	IE%	CR (g/cm^{2}hr) $\times10^{-5}$	IE%	CR (g/cm^{2}hr) $\times10^{-5}$	IE%	CR (g/cm^{2}hr) $\times10^{-5}$	IE%
1	Blank	15.19	-	28.21	-	33.42	-	36.89	-
2	0.1	0.825	94.50	1.645	94.12	2.395	92.84	13.68	62.92
3	0.2	0.608	95.89	1.302	95.44	2.322	93.05	13.58	63.19
4	0.3	0.434	97.01	0.955	96.55	2.261	93.23	13.06	63.53
5	0.4	0.284	98.05	0.651	97.70	2.101	93.72	12.35	66.53
6	0.5	0.255	98.32	0.556	98.03	1.971	94.10	12.12	67.15

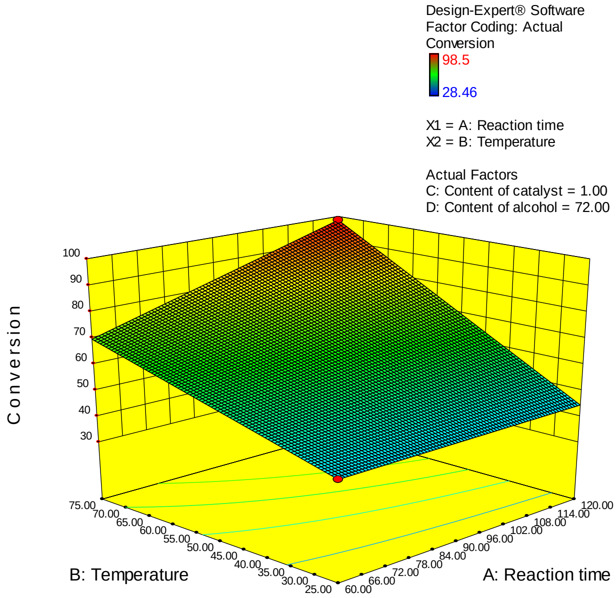

Fig. 1. Influence of temperature and reaction time on conversion.

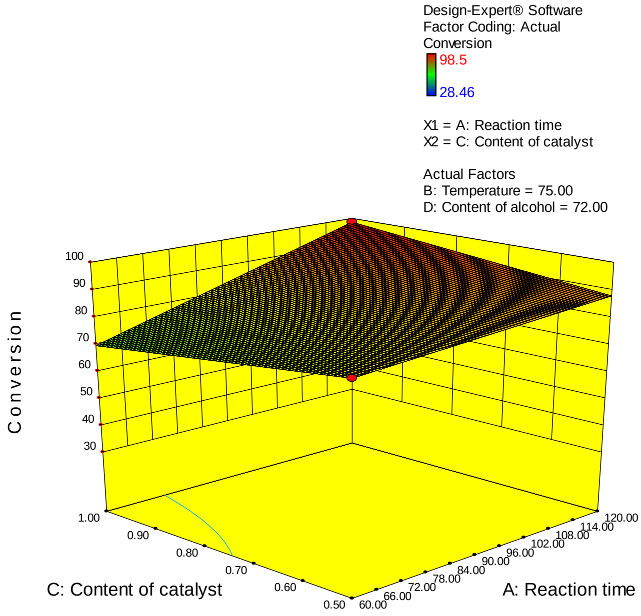

Fig. 2. Influence of content of catalyst and reaction time on conversion.

As shown in Table 2, the corrosion rate of mild steel increases with an increase in temperature but reduces with increase in inhibitor concentration. Figures 1 and 2 show the influence of these optimal parameters on conversion.

Activation Energy and Frequency Factor: The average values of activation energies and frequency factors are evaluated using Eq. (2) by plotting ln(r) against 1/T as shown in Fig. 3. These values are shown in Table 3.

Table 3. Values of A and E using Eq. (2).

Concentration	Values of A (/day) E13	Values of E (kJ/ mol)	Regression values (R)
0.0	7.3	13.50	0.945
0.1	25.43	67.43	0.932
0.2	38.56	75.10	0.965
0.3	59.33	83.70	0.976
0.4	76.35	94.32	0.987
0.5	89.78	97.85	0.939

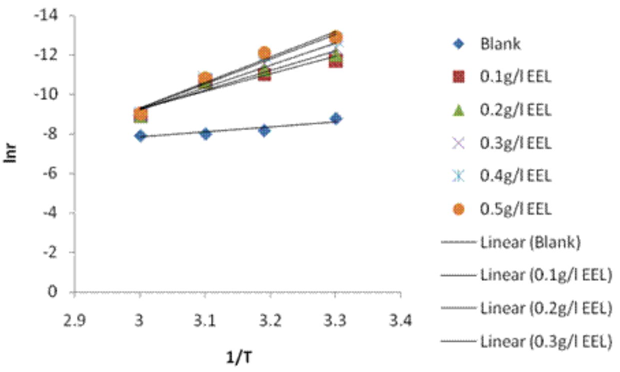

Fig. 3. Arrhenius plot for mild steel corrosion in petroleum-water mixture in the absence and presence of different concentrations of Ethyl Ester of Lard, EEL.

As can be seen from Table 3, the activation energy increased with inhibitor concentration. This shows that a decrease in corrosion rate occurs as more inhibitor is added to the mixture. It is evident from the table that E (activation energy) values in the presence of the inhibitors are higher than that in the absence of inhibitor. The higher activation energies imply a slow reaction and that the reaction is very sensitive to temperature. Thus, increase in activation energies in the presence of EEL inhibitors signifies physical adsorption (Undiandeye *et al*. 2011). This is also true of the pre-exponential factor. This increase in E and A, due to increase in inhibitor concentration, were also reported by Eddy and Odoemelam (2008), Eddy *et al*. (2008), Ashassi-Sorkhabi and Nabavi-Amri (2000), Yordanov and Petkov (2008), and Undiandeye *et al*. (2011). To find the values of H and S, Eq. (1) was rearranged to give a straight line equation. The rearranged equation is:

$$\ln(r/T) = \ln[R/(Nh)]+\Delta S/R-\Delta H/(RT). \quad (5)$$

Graphs of ln(*r*/*T*) against 1/*T* are plotted as shown in Fig. 4 and used to evaluate the values of *H* and *S*. These are shown in Table 4 for all concentrations.

Table 4. Values of *H* and *S* from Eq. (5).

Concentration (g/l)	H (kJ/mol)	S (kJ/mol K)	R
0.0	37.87	-231.87	0.932
0.1	57.87	-167.21	0.913
0.2	68.95	-157.43	0.974
0.3	73.76	-132.11	0.986
0.4	86.11	-120.99	0.954
0.5	94.47	-105.84	0.968

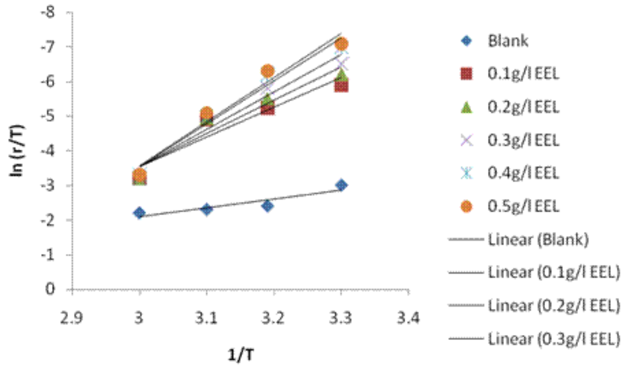

Fig. 4. Transition state plot for mild steel corrosion in petroleum-water mixture in the absence and presence of different concentrations of Ethyl Ester of Lard, EEL.

As seen from Table 4, the values of *H* increased with increasing concentration of inhibitor. This indicates that at lower concentration of inhibitor, the corrosion needs low energy to occur. This means that the energy barrier of corrosion reaction increase as the concentration of inhibitor increase and activated complex or transition state complex can be formed faster in the blank solution. In addition, the positive values of *H* both in the absence and presence of EEL reflect the endothermic nature of the steel dissolution process. The values of *S* are shown to be highest in the solution containing 0.5 g/l of inhibitor. The negative values of entropy of activation both in the absence and presence of inhibitor imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. This implies that there is more disorderliness in the blank solution. This disorderliness reduces with an increase in inhibitor concentration. Umoren *et al*. (2008), Kinani and Chtaini (2007), and Chauhan and Gupta (2009) also reported this trend. In both Tables 3 and 4, the linear regression coefficients are very close to unity. This indicates a strong dependence of ln(*r*) from 1/*T* (Ebenso and Obot 2010).

Rate Constant and Reaction Constants

To obtain the kinetic constants, Eqs. (3) and (4) are rearranged to obtain linear correlations:

$$\ln(r) = \ln(k) + BC; \qquad (6)$$

$$\ln(r) = \ln(k) + n\ln(C). \qquad (7)$$

By plotting ln(*r*) versus *C* (Fig. 5) and ln(*r*) versus ln(*C*) (Fig. 6), respectively, values of *B*, *k* and *n* are obtained and tabulated in Table 5.

The value of *k* denotes the ability of corrosion for mild steel. Table 5 clearly shows that *k* decreases after addition of EEL to the petroleum-water mixture solution, which indicates that the corrosion of mild steel is drastically inhibited by the EEL inhibitor.

Table 5. Kinetic parameter values.

Concentration (g/l)	*B* (g/cm^{2}day)	*K* (g/cm^{2}day)	*n*
Blank	0.145	0.253	1.54
0.1	0.457	0.167	1.34
0.2	0.576	0.148	1.23
0.3	0.621	0.146	1.31
0.4	0.698	0.121	1.22
0.5	0.856	0.109	1.35

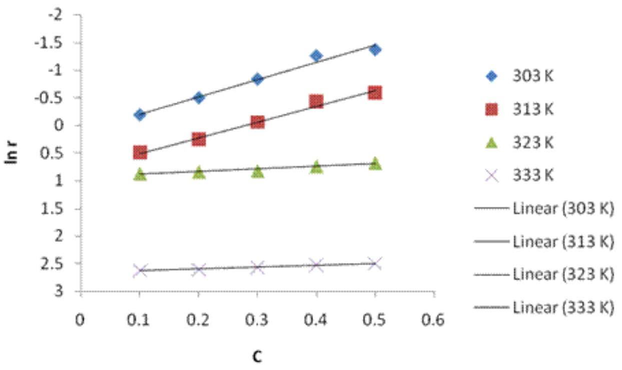

Fig. 5. Relationship between ln(*r*) and *C*.

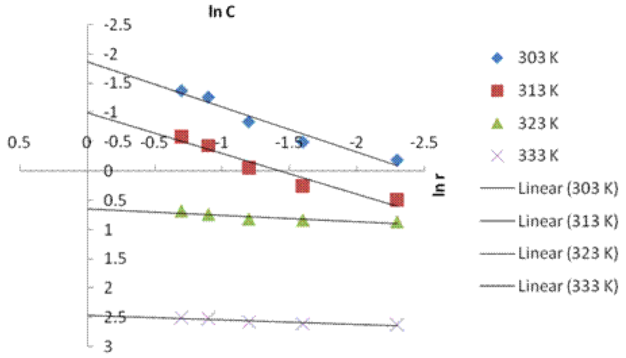

Fig. 6. Graph of ln(*r*) versus ln(*C*).

The values of *B* obtained in inhibited solution is higher than in uninhibited solution, which indicates that the extent of change of *r* with *C* in inhibited petroleum-water mixture is higher than in uninhibited solution (Ebenso and Obot 2010). The values of *n* are all close to unity implying that the reaction approximates first order. The kinetics of the corrosion of mild steel in petroleum-water mixture containing various concentrations of EEL, was also studied by plotting values of -log(weight loss) versus time (*t*) for various combinations of inhibitor-petroleum-water solutions as shown in Fig. 7 . The plots are linear, with R^2 values very close to unity. Therefore, the kinetics of the corrosion of mild steel in petroleum-water mixture can be represented according to the following equation:

$$-\log(W) = k_1 t/2.303, \qquad (8)$$

where *W* is the weight loss, k_1 is the first order reaction rate constant and *t* is the time in days. Values of k_1 obtained from the slopes of the plots (at various concentrations of the inhibitor) are presented in Table 6. Also, for a first order reaction, the relationship between the rate constant and half-life can be written as follows (Umoren *et al*. 2008):

$$t_{1/2} = 0.693/k_1. \qquad (9)$$

Calculated values of $t_{1/2}$ are also presented in Table 6. From the results obtained, it is significant to note that the half-life increases with increasing concentration of EEL which suggests that the half- life of mild steel in petroleum-water mixture increases with increasing concentration of the inhibitor.

A look at Table 6 reveals that the values of *k* relate closely with the values presented in Table 5. This confirms that the corrosion of mild steel in the mixture follows first order.

Table 6. Half-life of mild steel in petroleum-water mixture.

	Parameters		
Conc. (g/l)	k_1 (day^{-1})	$t_{1/2}$ (days)	R^2
Blank	0.22	3.15	0.9203
0.1	0.16	4.33	0.9818
0.2	0.14	4.95	0.9920
0.3	0.14	4.95	0.9837
0.4	0.12	5.76	0.9022
0.5	0.11	6.30	0.9598

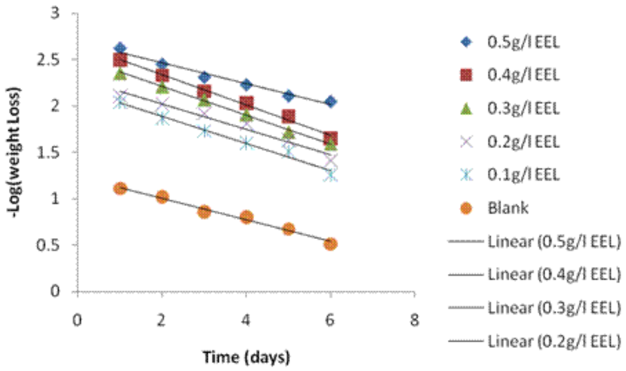

Fig. 7. Relationship between -log(*W*) and time.

As shown in Table 6, the half-life of mild steel increases steadily with an increase in the concentration of the inhibitor.

Adsorption Isotherms

Adsorption isotherms are very important in understanding the mechanism of inhibition of corrosion reaction of mild steel. The most frequently used adsorption isotherms is the Langmuir isotherms. Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and the adsorbent (Eddy *et al*. 2008). Assumptions of Langmuir relate the concentration of the adsorbate in the bulk of the electrolyte (*C*) to the degree of surface coverage (*θ*) according to the equation (Eddy and Odoemelam 2008):

$$C/\theta = 1/K + C, \qquad (10)$$

where *k* is the equilibrium constant of adsorption. Taking logarithm of both sides of the equation gives;

$$\log(C/\theta) = \log(C) - \log(K). \qquad (11)$$

By plotting values of log(*C*/*θ*) versus values of log(*C*), straight line graphs were obtained as shown in Fig. 8.

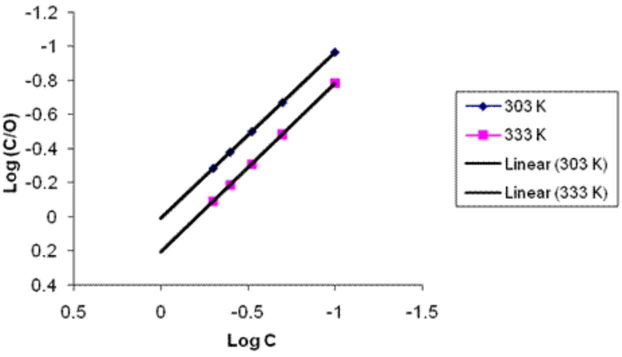

Fig. 8. Langmuir curve fitting for adsorption of EEL on mild steel electrode in petroleum water mixture.

The applicability of Langmuir adsorption isotherm to the adsorption of EEL on mild steel confirms the formation of multimolecular layer of adsorption where there is no interaction between the adsorbate and the adsorbent (Eddy *et al*. 2009).

In order to investigate the retention of the protection offered by the EEL, the mild steel samples taken out of the solutions containing 0.5 g/l of the inhibitor after mass loss measurements were dried in a desiccator for various times, then transferred into fresh petroleum-water mixture without inhibitor for 2 hours of immersion time. Figure 9 shows the variation of protection efficiency with the drying time.

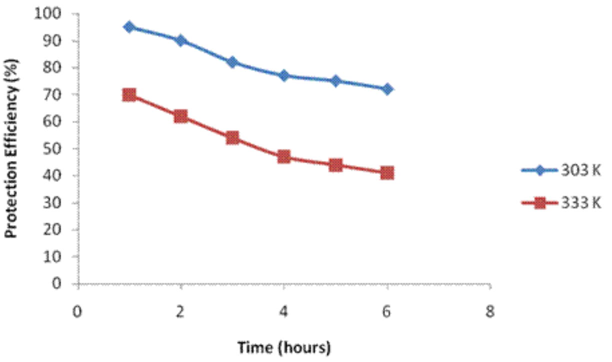

Fig. 9. Variation of protection efficiency against drying time for mild steel samples at 303 K.

It can be seen that the protection provided by the esters was retained and that the degree of retention decreased with increasing drying time.

Conclusion

From the results obtained, the following conclusions can be drawn:

- The EEL is a good corrosion inhibitor of mild steel in petroleum-water mixture.
- The inhibition of mild steel by EEL approximates a first order reaction.
- Inhibition efficiency increased with increase in concentration of the EEL.
- Activation energies were higher in the presence of EEL than in the blank environment.
- The adsorption of both the EEL on mild steel fits into the Lagmuir model.
- An increase in the concentration of EEL brings about an increase in the half-life of mild steel in the petroleum-water mixture.

References

Ashassi-Sorkhabi, H.; and Nabavi-Amri, S.A. 2000. Corrosion inhibition of carbon steel in petroleum/water mixtures by *N*-containing compounds. Acta Chimica Slovenica 47: 507-18.

Ashassi-Sorkhabi, H.; and Seifzadeh, D. 2008. Analysis of raw and trend removed EN data in time domain to evaluate corrosion inhibition effects of New Fuchsin dye on steel corrosion and comparison of results with EIS. J. Appl.Electrochem.38: 1,545-52.

Chauhan, J.S.; and Gupta, D.K. 2009. Corrosion inhibition of titanium in acidic media containing fluoride with bixin. E-J. Chem. 6: 975-8.

Ebenso, E.E.; and Obot, I.B. 2010. Inhibitive properties, thermodynamic characterization and quantum chemical studies of secnidazole on mild steel corrosion in acidic medium. Int. J. Electrochem. Sci. 5: 2,012-35.

Eddy, N.O.; and Odoemelam, S.A. 2008. Inhibition of the corrosion of mild steel in acidic medium by penicillin V potassium. Adv. Natur. Appl. Sci. 2: 225-32.

Eddy, N.O.; Odoemelam, S.A.; and Odiongenyi, A.O. 2008. Ethanol extract of Musa acuminate peel as an eco-friendly inhibitor for the corrosion of mild steel in H_2SO_4. Adv. Natur. Appl. Sci. 2: 35-42.

Eddy, N.O.; Odoemelam, S.A.; and Odiongenyi, A.O. 2009. Inhibitive, adsorption and synegistic studies on ethanol extract of *Gnetum aricana* as green corrosion inhibitor for mild steel in H_2SO_4. Green Chemistry Lett. Rev. 2: 111-9.

John, R.C.; Pelton, A.D.; Young, A.L.; Thompson, W.T.; Wright, I.G.; and Besmann, T.M. 2004. Assessing corrosion in oil refining and petrochemical processing. Mater. Res. 7: 163-73.

Khadom, A.A.; Yaro, A.S.; Kadum, A.A.H.; AlTaie, A.S.; and Musa, A.Y. 2009. The effect of temperature and acid concentration on corrosion of low carbon steel in hydrochloric acid media. Amer. J. Appl. Sci. 6: 1,403-9.

Kinani, L.; and Chtaini, A. 2007. Corrosion inhibition of titanium in artificial saliva containing fluoride. Leonardo J. Sci. 6: 33-40.

Mathur, P.B.; and Vasudevan, T. 1982. Reaction rate studies for the corrosion of metals in acids - I, Iron in mineral acids. Corrosion 38: 171-8.

Sinnott, R.K.; and Towler, G. . Chemical Engineering Design. 5th ed. Elsevier Science & Technology, Butterworth-Heinemann Ltd., Oxford, England, UK.

Stat-Ease, Inc. 2010. Design-Expert® Version 8. Stat-Ease, Inc., Minneapolis, MN, USA.

Umoren, S.A.; Obot, I.B.; and Ebenso, E.E. 2008. Corrosion inhibition of aluminium using exudate gum from *Pachylobus edulis* in the presence of halide ions in HCl. E-J. Chem. 5: 355-64.

Undiandeye, J.A.; Okewale, A.O.; Etuk, B.R.; and Igbokwe, P.K. 2011. Investigation of the use of ethyl esters of castor seed oil and rubber seed oil as corrosion inhibitors. Int. J. Basic Appl. Sci. 11: 48-54.

Yordanov, D.; and Petkov, P. 2008. Investigation of ethyl esters of fatty acids as corrosion inhibitors. J. Univ. Chem. Technol. Metall. 43: 405-8.