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Adsorption kinetics of 2-chloroacétophénone and 4-bromoacétophénone thiosemicarbazone on Oueme Valley clays (R. Benin)

Tadjou DO REGO¹,², Serge Fredys Rodrigue O. SENOU¹,³, Fidèl DIMON³, Salome KPOVIESSI², Alban HOUNGBEME¹, Coffi AZANDEGBE ENI³, Georges C. ACCROMBESSI², Jacques POUPAERT⁴ and Fernand A. GBAGUIDI¹,²*

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2-chloroacetophenone-thiosemicarbazone and 4-bromoacetophenone-thiosemicarbazone are compounds endowed with numerous pharmacological properties. In order to produce therapeutic agents using clay as excipient, this paper deals with the absorption kinetics of a clay originating from Oueme valley in Benin. A prospection in this area gave rise to the collection of 4 samples classified according to their color (yellow, white, black, and red). Toxicity studies performed on larvae gave no evidence of toxicity. These clays are highly hydrophilic and can accept a high load of organic material. The white clay, which is the least acidic, shows the best adsorption capacity. Additional experiments were carried out with this clay in ethanol. Best adsorption was obtained after 2 h. Adsorption isotherms indicate low affinity between the clay and the thiosemicarbazones and can be modelized using Langmuir and Freundlich’s models.

Key words: Clay, thiosemicarbazones, kinetic, absorption, larval toxicity, desorption.

INTRODUCTION

2-chloroacetophenone thiosemicarbazone and 4-bromoacetophenone thiosemicarbazone are interesting pharmacomolecules whose usefulness has been proved in microbiology (Fatondji 2011). On the other hand, clay is a
natural material with various therapeutic applications (antibacterial, antiseptic).
In Benin, this natural resource still awaiting exploitation is available in the Oueme valley and is scarcely used by local population to cure ulcers, muscular lesions, and persistent diarrhea. In order to incorporate these thiosemicarbazones into clays as excipients to improve their therapeutic efficacy, the clay must be endowed with good capacities of sorption and desorption of these organic compounds. The aim of this paper is to follow up the evolution of the clay adsorption of 2-chloroacetophenone thiosemicarbazone (2-CAT) and 4-bromoacetophenone thiosemicarbazone (4-BAT) in ethanol.

EXPERIMENTAL

Materials
Young shrimp larvae (Artemia salina) were used as biological material. 2-chloroacetophenone-thiosemicarbazone (2-CAT) and 4-bromoacetophenone-thiosemicarbazone (4-BAT) used as adsorbates were previously synthesized, purified and characterized in the Laboratory of Organic Chemistry and Physical Synthesis (LACOPS / UAC). Their physicochemical characteristics are summarized in Table 1.

White, yellow, black and red consumables clay, were taken from the Oueme valley, in the township Dangbo and Aguegue (southern of Benin). A portion of each sample was dried in an oven at 105 ± 2°C, powdered, sieved to 180 μm and stored for the sorption study. The second parts were kept in plastic boxes at room temperature for toxicity studies, because freezing may reduce their sensitivity (Caquet., 2011).

Characterization of clays
Water and organic material content, acid-base nature, specific surface area and cation exchange capacity of each sample of clays were determined.

Water content
Water content was determined by Audigié et al. (1978) method.

Organic material content
Clay's organic material content is measured according to NF EN 12879 norm.

<table>
<thead>
<tr>
<th>Adsorbats</th>
<th>2-CAT</th>
<th>4-BAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₆H₅ClN₃S</td>
<td>C₆H₅BrN₃S</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>227.72</td>
<td>272.16</td>
</tr>
<tr>
<td>Melting point</td>
<td>157-158</td>
<td>198-199</td>
</tr>
<tr>
<td>Front report</td>
<td>0.88</td>
<td>0.80</td>
</tr>
</tbody>
</table>

pH measurements
The pH was measured following the method proposed by Aïssata (2009).

Cation-exchange capacity (C.E.C.)
Cation-exchange capacity (CEC) is the maximum quantity of total cations, of any class, that a soil is capable of holding, at a given pH value, available for exchange with the soil solution. It is expressed as milliequivalent of hydrogen per 100 g of dry soil (mₑq/100 g).

Specific surface
The specific area in m²/g is assessed by methylene blue colorimetry according to Hicham El (2006).

Cytotoxicity test on shrimp larvae
The test is performed against Artemia salina Leach by the method of Michael et al. (1956) resumed by Vanhaecke et al. (1981) and Sleet and Brendel (1983) and proposed in the literature as a simple bio-assay method for assessment of preliminary toxicity of natural active products (Solis et al., 2001). The eggs of A. salina were incubated in sea water until hatching of young larvae (48 h). Then, series of solutions of each tested clay sample at varying and progressive concentrations were prepared. A defined number of larvae, (sixteen) were introduced into each solution. All solutions and control solution containing no active substance were left under stirring for 24 h. Counting under a microscope the number of dead larvae in each solution was used to evaluate the toxicity of the solution. In the case where there was death in the control medium, the data was corrected by Abbott's formula:

% death = [(test - control) / control] × 100 (Abbott, 1925).

Data (dose-response) are transformed by logarithm and the LC₅₀ were determined by linear regression (Hafner et al., 1977). Tests were carried out in triplicate.

Adsorption kinetics of 2-CAT and 4-BAT in ethanol

Sorption technique
The initial concentrations of thiosemicarbazone were: 0.0625, 0.125, 0.25 and 0.5 mg/ml. 0.02 g of clay (< 180 μm) is mixed with 2 ml of an ethanolic solution of thiosemicarbazone. The suspensions are stirred for 10 h at room temperature. The supernatant is assayed by high performance thin layer chromatography (HPTLC) after centrifugation to determine the
Table 2. Physicochemical characteristics of consumables clays.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Yellow clay</th>
<th>Black clay</th>
<th>Red clay</th>
<th>White clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (%)</td>
<td>36.70</td>
<td>54.73</td>
<td>33.38</td>
<td>59.95</td>
</tr>
<tr>
<td>M.O. (%)</td>
<td>14.34</td>
<td>23.84</td>
<td>18.12</td>
<td>13.76</td>
</tr>
<tr>
<td>C.E.C (mₑq/100 g)</td>
<td>23.79</td>
<td>20.13</td>
<td>22.21</td>
<td>16.01</td>
</tr>
<tr>
<td>S.S. (m²/g)</td>
<td>3.32</td>
<td>2.29</td>
<td>2.46</td>
<td>4.82</td>
</tr>
<tr>
<td>pH medium KCl</td>
<td>3.54±0.01</td>
<td>3.29±0.01</td>
<td>4.18±0.03</td>
<td>5.02±0.03</td>
</tr>
<tr>
<td>pH medium H₂O</td>
<td>4.65±0.00</td>
<td>4.17±0.01</td>
<td>5.12±0.01</td>
<td>6.04±0.02</td>
</tr>
</tbody>
</table>

Figure 1. Dose-response curves illustrating the sensitivity of shrimp larvae to clay species.

Analyses of the thiosemicarbazones

Thiosemicarbazones are analyzed by CCMHP densitometer (Camag TLC Scanner III) at 300 nm. A mother solution (1 mg·mL⁻¹) is prepared in ethanol and further diluted to get concentrations of 0.0625, 0.125, 0.25 and 0.5 mg/ml used for standardization. HPTLC plates (Silica gel 60 F254S Merck®) are developed using a toluene: acetonitrile mixture (6 : 7, v/v).

RESULTS AND DISCUSSION

Physicochemical parameters of the clays

As can be seen in Table 2, the studied clays are rather hydrophilic with a content of water ranging between 33.38 and 59.95%. The white (59.95%) and black clays (54.73%) are notably more hydrophilic than the red (33.38%) and yellow clays (36.70). Clay's CEC values are found in the range 16.01 and 23.79 mₑq / 100 g. These figures are satisfactory since Morel (1996) found for kaolinite values between 5 and 15 mₑq / 100 g, for illite and chlorite values between 10 and 40 mₑq / 100 g. These clays exhibit a weak adsorption capacity in accordance with their low specific area (2.29 – 4.82 m²·g⁻¹). The white clay exhibits the highest specific surface. Clay's pH figures are all below 7, attesting to their acidic character. Yellow, red and black clays are found clearly more acidic (3.5 ≤ pH ≤ 5), than the white one (6.04).

Larval toxicity

The shrimp larvae are sensitive to clays. We noticed a gradual increase in the number of dead larvae gradually as the extract concentration increased (Figure 1). The LC50 (Table 3) compared to the values of table drawn by...
Table 3. LC50 value of the various supplies clays.

<table>
<thead>
<tr>
<th>CL50 value (mg/mL)</th>
<th>Yellow clay</th>
<th>Black clay</th>
<th>Red clay</th>
<th>White clay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.17</td>
<td>0.10</td>
<td>0.17</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Table 4. Correspondence between LC50 and toxicity.

<table>
<thead>
<tr>
<th>CL50</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL50 &gt; 100 μg/mL ou 0.1 mg/mL</td>
<td>-</td>
</tr>
<tr>
<td>100 μg/mL &gt; CL50 ≥ 50 ou 0.05 mg/mL</td>
<td>++</td>
</tr>
<tr>
<td>50 μg/mL &gt; CL50 ≥ 10 g/mL ou 0.01 mg/mL</td>
<td>++</td>
</tr>
<tr>
<td>CL50 &lt; 10 μg/mL</td>
<td>+++</td>
</tr>
</tbody>
</table>

- No toxic, + Low toxicity, ++ : Moderate toxicity, +++ : High toxicity.

Table 5. Isotherm parameters studied 2-CAT and 4-BAT for white clay.

<table>
<thead>
<tr>
<th>Models</th>
<th>Settings</th>
<th>qm</th>
<th>b</th>
<th>RL</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>2-CAT</td>
<td>-1.35.10⁻⁵</td>
<td>-17.386</td>
<td>0.999 – 0.996</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>4-BAT</td>
<td>-2.03.10⁻⁵</td>
<td>-3.640</td>
<td>0.556 – 0.843</td>
<td>0.97</td>
</tr>
<tr>
<td>Freundlich</td>
<td>2-CAT</td>
<td>1/n</td>
<td>4.20</td>
<td>kᵢ = 4.426</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>4-BAT</td>
<td>1/n</td>
<td>1.86</td>
<td>kᵢ = 5.14.10²</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Figure 2. Kinetics test of adsorption 4-BAT on the white clay in ethanol medium.

Mireille (1995) sparkling (Table 4) shows that these clays are not toxic. Thus, consumables clays of the valley can be used without toxicological risk. In view of these results of LC50 figures (Table 5) compared with those established by Mireille (1995) demonstrate the lack of toxicity of these clays.

Adsorption kinetics of 2-CAT and 4-BAT in ethanol

According to Figures 2 and 3, adsorption kinetics of 2-CAT and 4-BAT on white clay shows that there is no apparent equilibration time for adsorption of thiosemicarbazones by this clay and that adsorption is
Figure 3. Kinetics test of adsorption 2-CAT on the white clay in ethanol medium.

Figure 4. Adsorption isotherms of 4-BAT on white clay in ethanol medium at 25 ± 2°C.

reversible. After a fast initial phase, adsorption is maximal after 2 h. Desorption follows the same kinetic behaviour and reaches a plateau after 2 h. Thiosemicarbazone's adsorption is considerably influenced by its initial concentration in ethanol. Maximal sorption goes up to 63% for 4-BAT and 89% for 2-CAT after 2 h equilibration.

Sorption isotherm of 2-CAT and 4-BAT

A sorption isotherm (also adsorption isotherm) describes the equilibrium of the sorption of a material at a surface (more general at a surface boundary) at constant temperature. It represents the amount of material bound at the surface (called the sorbate) as a function of the material present in the solution. In this study, sorption isotherms were determined at room temperature after 2 h equilibration and were found of the concave S-shape type, suggesting a low affinity of the white clay (Figures 4 and 5 and Table 5) for thiosemicarbazone derivatives according to Giles et al. (1974). Modeling of these isotherms give intensity parameters which fit with those computed following to the models of Langmuir and Freundlich ($R^2 > 0.8$).

Conclusion

Selected clays originating from Oueme valley of Benin are not toxic. They are highly hydrophilic, rich in organic materials and are of acidic nature. They exhibit low specific area and CEC comparative analysis of their characteristics shows that the white clay, less acidic and hydrophilic shows the best adsorption capacity. Adsorption isotherms suggest a low affinity between the white clays and thiosemicarbazones and can be
rationalized following the models of Freundlich and Langmuir. Adsorption kinetics demonstrates that adsorption is reversible and optimal after 2 h.

Conflict of Interest

The author(s) have not declared any conflict of interests.

REFERENCES

A kinetic study was carried out using spectrophotometric approach on the oxidation of nine differently substituted 2-aryl-trans-decahydroquinolin-4-ones by Cetyltrimethylammonium dichromate (CTADC) as oxidant at 30°C and in aqueous acetic acid (50%) containing catalytic amount of sulphuric acid (6N). The reactions were studied at 350 nm. The reaction was found to follow second order kinetics. The substitution of methyl group at position three of the decahydroquinoline ring and the presence of electron releasing groups in the aryl group increased the rate of oxidation of the substrates. The change in the rate of oxidation with temperature and solvent composition was also studied. The products formed during the oxidation were also confirmed by using high-performance liquid chromatography (HPLC) and spectral analysis.

Key words: 2-aryl-trans-decahydroquinolin-4-ones, kinetics, oxidation, Cetyltrimethylammonium dichromate (CTADC).

INTRODUCTION

The kinetic studies on the oxidation of different aliphatic (Singh et al., 1982; Mahadevappa and Swamy 1988; Singh et al., 1978a; Chiba et al., 1995), alicyclic (Mushran et al., 1976; singh et al., 1978b; Karnojitzky 1981), aromatic (Ogata and Sawaki 1972; Manivannan and Maruthamuthu 1986; Khandual et al., 1973; Annapoorna et al., 1998; Devries et al., 1995) ketones and a series of 2,6-diaryl-4-piperidones (Kumabe et al., 2001; Selvaraj et al., 1979) have been studied extensively by various workers and suitable mechanisms have been proposed. Recently the kinetics of oxidation of present ketones were reported in aqueous acetic acid using thallium(III), cerium(IV) and lead(IV) (Satyanarayana et al., 2010, 2013a, b) as oxidizing agents. In the present study CTADC was selected as oxidizing agent, as it is found to be selective, mild phase transferring and chemoselective oxidant (Patel and Mishra, 2007a, 2004b; Sahu et al., 2005; Patel and Mishra, 2006c, d). It was found to
oxidize aromatic amines and thiols to the corresponding coupled dehydrogenated products (Patel and Mishra, 2004b), aldoximes to the nitriles (Sahu et al., 2005), cholesterol to 7-dehydrocholesterol (Patel and Mishra, 2006c), arylthiourea to corresponding urea (Sahoo et al., 2010), alcohols to ketones (Vimala et al., 2009), oxidation of diols (Patel et al., 2008f) selectively. However, the study of the kinetics of oxidation of 2-aryl-trans-decahydroquinolin-4-ones with CTADC was not reported so far. The present investigation was taken up with a view to identify whether the complex reagent CTADC useful for oxidation of the said ketones and also to identify the possible products during oxidation process. Hence, it is considered to investigate the kinetics of oxidation of 2-aryl-trans-decahydroquinolin-4-ones and also to study the effect of substituent(s) in aryl group and in the heterocyclic ring. This prompted the authors to carry out the investigation on a total nine compounds (1-9) (Figure 1).

**EXPERIMENTAL**

**Reagents and apparatus**

**Preparation of ketones**

The ketones were prepared by the method developed by Balliah and Natarajan (1981), and purified by recrystallization from suitable solvents to constant melting points. All the samples were dried in vacuum before use. Cetyltrimethylammonium dichromate (CTADC) was prepared by the known method (Patel et al., 2005) and its purity was checked by estimating Cr(VI) iodometrically (Vogel, 1961).

**Acetic acid**

Acetic acid glacial (Excelar), supplied by ‘Qualigens Fine Chemicals’, was refluxed with chromium trioxide for 6 h and fractionally distilled. The fraction boiling at 390-391K was collected and was used.

**Other reagents**

Cetyltrimethylammonium bromides, Potassium dichromate, Potassium iodide, Sulphuric acid used were all A.R grade. Doubly distilled water was used for all purposes.

**Instrument**

The instrument used was analytical technologies UV/visible spectrophotometer of Model Spectro2080.

**Kinetic procedure**

The oxidation kinetics of 2-aryl-trans-decahydroquinolin-4-ones by CTADC in the presence of aqueous acetic acid using a UV-Vis spectrophotometric method and all the kinetic measurements were carried out at 350 nm (Figure 2). The measurements were performed in 50:50(v/v) acetic acid: water containing 6N H₂SO₄ at 30°C. The temperature was controlled by using thermostat of accuracy ±0.1°C. The required amount of CTADC solution was prepared by dissolving the necessary amount of CTADC in the solvent medium. The solutions of the substrates (ketones) were
prepared by dissolving the appropriate quantity of the compounds in the same solvent, so that the concentration of the ketones was maintained always higher than the concentration of CTADC. The reaction was initiated by mixing CTADC to ketones and the progress of the reaction was followed spectrophotometrically by monitoring the decrease in absorbance at 350 nm. The second order conditions were followed for determining the rates of the reactions.

**Product analysis**

A mixture of ketone and CTADC was allowed to react in aqueous acetic acid (50%, v/v) in presence of sulphuric acid (6.0 N). The concentration of CTADC was maintained slightly excess than the concentration of ketone. The resulting mixture was kept aside at 30°C temperature for 2 to 3 days. The mixture turned reddish green, indicating the formation of reduced Cr (III). After that the reaction mixture was neutralized with saturated solution of sodium carbonate, extracted with ether and the combined ether extract separated and the crude product was obtained after distillation of the ether layer.

**Stoichiometry**

The stoichiometry of the reaction was determined by allowing a known excess of the oxidant CTADC to react with the substrate in solvent medium at 30°C and the un-reacted CTADC was estimated. The stoichiometry was found to be in the mole ratio of 1:1 for oxidant to substrate.

\[ R_2C=O + \text{CTADC} \rightarrow \text{Product} + \text{Cr(III)} \]

**Calculation of the rate constants**

The rate constants were calculated using the second order rate equation:

\[ k_2 = \frac{2.303}{t \ (a-b)} \log \frac{b(a-x)}{a(b-x)} \]

Where, \( a \), Initial concentration of substrate in moles/lit; \( b \), Initial concentration of CTADC in moles/lit.

**RESULTS AND DISCUSSION**

A kinetic study was made on the oxidation of 2-aryl-trans-decahydroquinolin-4-ones (1 to 9) by using CTADC as oxidizing agent in aqueous acetic acid (50%) medium. The reaction was found to follow over all second order kinetics. The rate constants obtained for the selected substrates were given in Table 1.

An examination of the rate constants for the oxidation of 2-aryl-trans-decahydroquinolin-4-ones 1 to 3 (where there is no methyl group at 3\textsuperscript{rd} position) and those of corresponding 3-Methyl-2-aryl-trans-decahydroquinolin-4-ones 5, 6 and 7 (where there is methyl group at 3\textsuperscript{rd} position) revealed that the latter series of compounds 5, 6, and 7 were oxidized at a faster rate than former series of compounds 1 to 3. This observation is as expected as the electron-releasing inductive effect of methyl group in heterocyclic ring enhances the rate of oxidation of these series of compounds. However, the observation made in the present investigation was found to be contrary to the observations made by us in earlier studies for same compounds with metal ions Ti(III), Pb(IV) and Ce(IV) (Satyanarayana et al., 2010, 2013a, 2013b). The results of the study were given in Table 2.

The introduction of electron releasing and electron withdrawing substituent’s on the phenyl group at ortho- and para- positions had provided useful information to know the structure-activity relationship of these compounds. Substitution at ortho and para positions of aryl ring is expected to produce negligible effect on the rate of oxidation, because aryl ring is far away from the reaction centre. But the substituents at ortho and para positions played a vital role on rate of oxidation. This may be mainly due to the polar effect exerted by the substituents. The electron releasing groups increased the rate of oxidation. For example for compounds 1 to 3, the rate of oxidation

<table>
<thead>
<tr>
<th>S/No.</th>
<th>Compound</th>
<th>( k_2 \times 10^2 \text{ Mole}^{-1} \text{ Sec}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-ph-4-one</td>
<td>07.53 + 0.12</td>
</tr>
<tr>
<td>2</td>
<td>2-(p-tolyl)-4-one</td>
<td>10.48 + 0.15</td>
</tr>
<tr>
<td>3</td>
<td>2-(p-OMe)-4-one</td>
<td>14.12 + 0.11</td>
</tr>
<tr>
<td>4</td>
<td>2-o-Cl-Ph-4-one</td>
<td>20.81 + 0.25</td>
</tr>
<tr>
<td>5</td>
<td>3-Me-2-ph-4-one</td>
<td>29.08 + 0.32</td>
</tr>
<tr>
<td>6</td>
<td>3-Me-2-(p-tolyl)-4-one</td>
<td>39.23 + 0.20</td>
</tr>
<tr>
<td>7</td>
<td>3-Me-2-(p-OMe)-4-one</td>
<td>16.27 + 0.02</td>
</tr>
<tr>
<td>8</td>
<td>3-Me-2-(p-Cl)-4-one</td>
<td>20.03 + 0.06</td>
</tr>
<tr>
<td>9</td>
<td>1,3-di-Me-2-ph-4-one</td>
<td>22.31 + 0.21</td>
</tr>
</tbody>
</table>

Temp = 30°C, H\(^+\) = 6.0 N, Solvent = 50% AcOH.

x. Amount of CTADC reacted in time t (seconds); t. Reaction time in seconds.
was found to be increased with increase in electron releasing nature of the substituent at $p$-position of phenyl ring. But, the trend was not followed for compound 7 that is, for $p$-methoxy substituted compounds in case of 3-methyl substituted compounds 5 to 7. This may be because highly bulky methoxy substituent on phenyl ring in addition to 3-methyl substituent on decalin ring.

The introduction of a methyl group in the 3rd position in decalin ring increased the rate of oxidation of ketones, because of the combined effects of inductive as well as steric and was discussed above. But, further introduction of methyl group on 1st position that is, on N atom of heterocyclic ring has showed some influence on the rate of oxidation. The rate of oxidation of 1, 3-dimethyl-2-phenyl-trans-decahydroquinolin-4-one (9) (presence of methyl group at both 1 and 3 positions) was found to be high when compared with the rate of oxidation of compound (1), having no methyl group in position 3 but was showed less rate of oxidation compared to compound 5 (having methyl group at position 3). Further the rate of oxidation of 2-$o$-chlorophenyl-trans-decahydroquinolin-4-one was expected to be low, but was found to be high when compared with the rates of oxidation of compounds 1 to 3 and is almost similar to the rate constant of compound 8. This type of higher rate constant of $o$-chloro compound was already reported in oxidation of the same compounds with thallium (II) and lead (IV) metal ions (Table 2) but has not gained proper reason.

The oxidation kinetics of 2-aryl-trans-decahydroquinolin-4-ones has also been carried out in different compositions of acetic acid and the relevant data was given in Table 3. The concentration of sulphuric acid was maintained constant at 6.0 N in all these studies and the temperature was maintained at 30°C. Increase in the percentage of acetic acid of the medium increases the rate of oxidation. Further increase in concentration of sulphuric acid also increased the rate of oxidation of the said compounds and the data was given in Table 4. This observation was quite consistent with Cr(VI) reagents where the oxidation potential of this type of reagents increases with increase in concentration of acid in the reaction medium. The oxidation studies were also carried out at different temperatures (Table 5).
Table 5. Effect of temperature on the oxidation of 2-Phenyl-4-one by CTADC.

<table>
<thead>
<tr>
<th>Name of the Compound</th>
<th>Variation in temperature ( (10^2 \times k_2 \text{ dm}^3 \text{ mol}^{-1} \text{sec}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Phenyl-4-one</td>
<td>07.53 ± 0.12</td>
</tr>
</tbody>
</table>

\([H^+] = 4.0 \text{ N}, \text{ Solvent} = 50 \% \text{ AcOH.}\)

In product analysis, the completion of the reaction was confirmed by comparison of Thin layer chromatography (TLC) of starting material with reaction mixture. A preliminary examination was carried out in order to identify the product. A spectral study was carried out to establish the compound present in the crude product in the workup of the reaction mixture. An examination of the IR spectrum (Figure 3) of the product mixture revealed that they are quite different from the spectrum of the original compounds taken.

A broad peak \( (3452 \text{ cm}^{-1}) \) in the region of 3300 to 3460 cm\(^{-1}\) indicated the presence of –OH of a carboxylic group or an -N-H group in the mixture. The sharp peaks at 2918 and 2850 cm\(^{-1}\) indicated the presence of aromatic system. Further, on spraying ninhydrin reagent on TLC of the product mixture gave spots of purple color. These spots might be due to presence of nitrogen atom in the crude product.

The earlier reports in respect of oxidation of the present type of systems indicated that the product is an amino acid (Meenal and Roopakalyani 1988a, Dhar and Vardarajan 1991; Satyanarayana et al., 2010, 2013b). However, the earlier authors have not conclusively confirmed the formation of amino acid. This prompted the present authors to isolate the product from the oxidation of compound (3) through reverse phase HPLC and was successfully isolated the products. The products were analyzed through \(^1\)H NMR (Figure 4) and mass spectroscopy (Figure 5), which gave surprising results.

The \(^1\)H NMR spectrum of this compound revealed that one of the products was \( p \)-methoxy benzamide and this was further confirmed by the mass spectrum of the product obtained \((m/z=152.2)\). These observations prompted us to suggest that probably the carbon-nitrogen bond of alicyclic ring and piperidine ring might have been broken to form an amide, when the alicyclic ring was found to be completely broken from the heterocyclic ring. The other product is likely to be cyclohexane derivative which could not be identified and it needs further investigation. A reasonable scheme for the formation of the product is given in Scheme 1.

**Conclusions**

A kinetic study was carried out for the substituted 2-aryl-
trans-decahydroquinolin-4-ones system using spectrophotometric approach. Substituent effects on the rate of oxidation of 2-aryl-trans-decahydroquinolin-4-ones were also studied. The presence of electron releasing groups on aryl group at C-2 position and methyl group at C-3 position increased the rate of oxidation of the
compounds with CTADC. The products obtained during the oxidation were established.

Conflict of Interest

The author(s) have not declared any conflict of interests.

ACKNOWLEDGEMENTS

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REFERENCES


Kinetics of the corrosion of mild steel in petroleum-water mixture using ethyl ester of lard as inhibitor

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Ethyl Esters of Pork Oil (EEL) has been investigated as a mild steel corrosion inhibitor in petroleum-water mixture by weight-loss tests at different concentrations (0.1l, 0.2, 0.3, 0.4 and 0.5g/L) of inhibitor, and at temperatures of 303, 313, 323 and 333K. 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 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 min, temperature of 75°C, content of catalyst of 1% and alcoholic content of 72 cm³.

Key words: Corrosion inhibitor, ethyl ester, pork oil, 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

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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 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
countries have eliminated the use of lard (pork oil) 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 oil 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, pork oil 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 (Equation (1)) and the Arrhenius
equation (Equation (2)) can be used to estimate
activation parameters for some systems (Khadom et al.,
2009):

\[ r = \frac{(RT/Nh)}{C} \times \exp\left(-\frac{\Delta H}{RT}\right) \times \exp\left(\frac{\Delta S}{R}\right) \]  \hspace{1cm} (1)

\[ r = A \exp\left[-\left(\frac{E}{RT}\right)\right] \]  \hspace{1cm} (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:

\[ r = k \exp(BC) \]  \hspace{1cm} (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:

\[ r = k C^n. \]  \hspace{1cm} (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 Equations (1) to (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 x 2.0 x 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
Table 1. Parameters used in Equations (1) to (4).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r )</td>
<td>Corrosion rate</td>
</tr>
<tr>
<td>( A )</td>
<td>Pre-exponential factor</td>
</tr>
<tr>
<td>( E )</td>
<td>Activation energy (J/mol)</td>
</tr>
<tr>
<td>( R )</td>
<td>Gas constant (8.314 J/mol K)</td>
</tr>
<tr>
<td>( T )</td>
<td>Absolute temperature (K)</td>
</tr>
<tr>
<td>( H )</td>
<td>Enthalpy of activation</td>
</tr>
<tr>
<td>( S )</td>
<td>Entropy of activation</td>
</tr>
<tr>
<td>( N )</td>
<td>Avogadro's Number ((6.022 \times 10^{23}))</td>
</tr>
<tr>
<td>( h )</td>
<td>Planck's constant ((6.626 \times 10^{-34}))</td>
</tr>
<tr>
<td>( C )</td>
<td>Inhibitor concentration</td>
</tr>
<tr>
<td>( B )</td>
<td>Constant for reaction studies</td>
</tr>
<tr>
<td>( K )</td>
<td>Reaction rate constant</td>
</tr>
<tr>
<td>( N )</td>
<td>Order of reaction</td>
</tr>
</tbody>
</table>

**Figure 1.** Influence of temperature and reaction time on conversion.

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 inhibitor: 0.1 g/l, 0.2 g/l, 0.3 g/l, 0.4 g/l, 0.5 g/l.

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 L of water. The pork 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). 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 oil will result in production of an unusable soap, while a deficit ratio of KOH to oil 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 min, temperature of 75°C, content of catalyst of 1% and alcoholic content of 72 cm³. Figures 1 and 2 show
Table 2. Effect of temperature and inhibitor concentration on the corrosion rate of mild steel.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Conc. (g/L)</th>
<th>303K</th>
<th></th>
<th>313K</th>
<th></th>
<th>323K</th>
<th></th>
<th>333K</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CR (g/cm³h) x10⁶</td>
<td>IE%</td>
<td>CR (g/cm³h) x10⁶</td>
<td>IE%</td>
<td>CR (g/cm³h) x10⁶</td>
<td>IE%</td>
<td>CR (g/cm³h) x10⁶</td>
<td>IE%</td>
</tr>
<tr>
<td>1</td>
<td>Blank</td>
<td>15.19</td>
<td>-</td>
<td>28.21</td>
<td>-</td>
<td>33.42</td>
<td>-</td>
<td>36.89</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.825</td>
<td>94.50</td>
<td>1.645</td>
<td>94.12</td>
<td>2.395</td>
<td>92.84</td>
<td>13.68</td>
<td>62.92</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>0.608</td>
<td>95.89</td>
<td>1.302</td>
<td>95.44</td>
<td>2.322</td>
<td>93.05</td>
<td>13.58</td>
<td>63.19</td>
</tr>
<tr>
<td>4</td>
<td>0.3</td>
<td>0.434</td>
<td>97.01</td>
<td>0.955</td>
<td>96.55</td>
<td>2.261</td>
<td>93.23</td>
<td>13.06</td>
<td>63.53</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>0.284</td>
<td>98.05</td>
<td>0.651</td>
<td>97.70</td>
<td>2.101</td>
<td>93.72</td>
<td>12.35</td>
<td>66.53</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>0.255</td>
<td>98.32</td>
<td>0.556</td>
<td>98.03</td>
<td>1.971</td>
<td>94.10</td>
<td>12.12</td>
<td>67.15</td>
</tr>
</tbody>
</table>

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

Table 2 shows the corrosion rate of mild steel in petroleum-water mixture in the absence and presence of different concentrations of the inhibitor at different temperatures. As shown in Table 2, corrosion rate of mild steel increases with an increase in temperature but reduces with increase in inhibitor concentration.

**Activation energy and frequency factor**

The average values of activation energies and frequency factors are evaluated using Equation (2) by plotting \( \ln(\tau) \) against \( 1/T \) as shown in Figure 3. These values are shown in Table 3. 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 EEPO 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 \( S \), Equation (1) was rearranged to give a straight line equation. The rearranged equation is:

\[
\ln(\tau/T) = \ln[R(Nh)] + \Delta S/R - \Delta H/(RT). \tag{5}
\]

Graphs of \( \ln(\tau/T) \) against \( 1/T \) are plotted as shown in Figure 4 and used to evaluate the values of \( H \) and \( S \).
Figure 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.

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

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Values of $A$ (day) E13</th>
<th>Values of $E$ (kJ/ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>7.3</td>
<td>13.50</td>
</tr>
<tr>
<td>0.1</td>
<td>25.43</td>
<td>67.43</td>
</tr>
<tr>
<td>0.2</td>
<td>38.56</td>
<td>75.10</td>
</tr>
<tr>
<td>0.3</td>
<td>59.33</td>
<td>83.70</td>
</tr>
<tr>
<td>0.4</td>
<td>76.35</td>
<td>94.32</td>
</tr>
<tr>
<td>0.5</td>
<td>89.78</td>
<td>97.85</td>
</tr>
</tbody>
</table>

Figure 4. Transition state plot for mild steel corrosion in petroleum-water mixture in the absence and presence of different concentrations of ethyl ester of Pork Oil, EEPO.
Table 4. Values of $H$ and $S$ from Equation (5).

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>$H$ (kJ/mol)</th>
<th>$S$ (kJ/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>37.87</td>
<td>-231.87</td>
</tr>
<tr>
<td>0.1</td>
<td>57.87</td>
<td>-167.21</td>
</tr>
<tr>
<td>0.2</td>
<td>68.95</td>
<td>-157.43</td>
</tr>
<tr>
<td>0.3</td>
<td>73.76</td>
<td>-132.11</td>
</tr>
<tr>
<td>0.4</td>
<td>86.11</td>
<td>-120.99</td>
</tr>
<tr>
<td>0.5</td>
<td>94.47</td>
<td>-105.84</td>
</tr>
</tbody>
</table>

Figure 5. Relationship between $\ln(r)$ and $C$.

These are shown in Table 4 for all concentrations.

As shown in 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 EEPO 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. Umore 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).

Table 5. Kinetic parameter values.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>$B$ (g/cm$^2$day)</th>
<th>$K$ (g/cm$^2$day)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.145</td>
<td>0.253</td>
<td>1.54</td>
</tr>
<tr>
<td>0.1</td>
<td>0.457</td>
<td>0.167</td>
<td>1.34</td>
</tr>
<tr>
<td>0.2</td>
<td>0.576</td>
<td>0.148</td>
<td>1.23</td>
</tr>
<tr>
<td>0.3</td>
<td>0.621</td>
<td>0.146</td>
<td>1.31</td>
</tr>
<tr>
<td>0.4</td>
<td>0.698</td>
<td>0.121</td>
<td>1.22</td>
</tr>
<tr>
<td>0.5</td>
<td>0.856</td>
<td>0.109</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Figure 6. Graph of $\ln(r)$ versus $\ln(C)$.

Rate constant and reaction constants

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

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

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

By plotting $\ln(r)$ versus $C$ (Figure 5) and $\ln(r)$ versus $\ln(C)$ (Figure 6), respectively, average 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. 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
Figure 7. Relationship between -log(W) and time at 303 K.

![Figure 7](image)

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

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (day$^{-1}$)</td>
</tr>
<tr>
<td>Blank</td>
<td>0.22</td>
</tr>
<tr>
<td>0.1</td>
<td>0.16</td>
</tr>
<tr>
<td>0.2</td>
<td>0.14</td>
</tr>
<tr>
<td>0.3</td>
<td>0.14</td>
</tr>
<tr>
<td>0.4</td>
<td>0.12</td>
</tr>
<tr>
<td>0.5</td>
<td>0.11</td>
</tr>
</tbody>
</table>

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. 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 ($\theta$) according to the equation (Eddy and Odoemelam, 2008):

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

where $k$ is the equilibrium constant of adsorption. Taking logarithm of both sides of the equation gives:

$$\log(C/\theta) = \log(C) - \log(k). \quad (11)$$

By plotting values of $\log(C/\theta)$ versus values of $\log(C)$, straight line graphs were obtained as shown in Figure 8. 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. 2008).

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 h of immersion time. Figure 9 shows the variation of protection efficiency with the drying time.

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

**Conclusion**

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

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

**Conflict of Interest**

The author(s) have not declared any conflict of interests.

**REFERENCES**
