



Influence of Polyvinyl Acetate on the Corrosion Inhibition of Mild Steel in Sulphuric Acidic Environment

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ABSTRACT

The impact of polyvinyl acetate (PVAc) in controlling the induced corrosion of mild steel in 0.5 M H₂SO₄ solution was investigated using experimental and theoretical approach respectively. The experimental approach used includes weight loss measurement, potentiodynamic polarization technique whereas chemical quantum computation was the theoretical approach used. It is observed that PVAc inhibited the dissolution of mild steel in 0.5 M H₂SO₄ acid solution effectively, with inhibition efficiency of up to 85.67% according to weight loss results. Furthermore, PVAc was found to exhibit the characteristic features of mixed-type inhibition from polarization results. Adsorption of PVA on the mild steel surface followed the trend of Langmuir adsorption isotherm. The proposition of chemical adsorption for the inhibition mechanism was dependent on the calculated values of energy of activation, heat of adsorption and rise in temperature with in inhibition efficiency. Chemical quantum computations revealed adsorption capability of PVAc repeat unit and PVAc molecules clusters on the mild steel surface. Finally, the theoretical computation results were in conformity with the experimental findings.

Key words: Polyvinyl acetate, dissolution, adsorption, experimental approach, mild steel and chemical quantum computations

INTRODUCTION

Polymer, a macromolecule [1-4], is obtained from re-occurrence of smaller molecules (repeat units) that are covalently bonded together. Polymers can either be sourced from synthetic (e.g petroleum products) or natural (e.g animal and vegetable products) background respectively. Natural polymers have been in existence with man from time immemorial and they are part basis of human life. Synthetic polymers are available due to relationship existing between polymer structures and properties, availability of repeat units, new processing techniques, etc. Today, it is possible to develop new synthetic polymers with different and better characteristic features from the already existing ones by modifications of the physical and chemical properties of the existing ones. Generally, polymeric materials exist either in solid, liquid and powder form with endless and fascinating applications. The usage and production of polymeric materials will continue to increase without restriction due to development in the new processing techniques [4] and quest to solve our domestic and industrial problems.

The degradation or deterioration of properties of materials (metals, alloys, etc) as a result of reactions with the surrounding environment is regarded as corrosion [5]. Corrosion causes material damage, economic loss, environmental and human health related problems, so there is need to checkmate the menace of corrosion of metals. Many researchers have reported [6-29] the use of polymers from natural and synthetic sources in retarding the dissolution of metals in aggressive service environment in the scientific literature. This is possible because these polymers are non-toxic, biodegradable, abundant and renewable, capable of reacting with other molecules, etc. In addition, these polymers are effective in retarding the corrosion process of metals in aggressive environment because of presence of functional groups, cyclic and aromatic ring structure within the polymer structure. Hence, these give the polymers ability to either donate or accept of electrons from the charge on the metal surface. The activities of polymer molecule in controlling corrosion may occur via one or combination of the mechanisms proposed (formation of passive layer and galvanic method) [30-33] for corrosion control at any time. The passive layer mechanism occurs due to

reactions between polymer molecule and surface charge of the metal, and the resultant effect is adsorption of the layer on the metal surface. This mechanism requires that oxidation potential of polymer should be has higher than that of metal. It functions by either reducing the available corrosion sites on the metal surface or altering energy barrier of the electrochemical corrosion process. The simple galvanic mechanism requires that polymer possess lower oxidation potential than the metal for polymer to be preferentially corroded during the process.

Polyvinyl acetate (PVAc) is water soluble, non-toxic, biodegradable and synthetic polymer synthesized by polymerizing vinyl acetate monomer. It is widely used as a binder in adhesives production, water-based paints (latex) as the film-forming ingredient and other household products. It possesses the desirable and characteristic features of a good corrosion inhibitor from the molecular point of view due to presence of vinyl group and acetate group. Presently, to the best of our knowledge, there is no reported experimental work in scientific literature on inhibitive effect of PVAc on corrosion of mild steel in hydrochloric and sulphuric acid solutions. Therefore, we find it necessary to study the influence of PVAc on the corrosion inhibition of mild steel in sulphuric acidic environment.

MATERIALS AND METHODS

Sample Preparation

Mild steel coupons with percentage composition of C = 0.06%, Si = 0.03%, Mn = 0.04%, Cu = 0.06%, Cr = 0.06%, Remainder = Fe were used in this study. The metal coupons used were mechanically cut, polished with abrasive paper (finer grade), degreased in absolute ethanol, dried in acetone and weighed. The polyvinyl acetate (PVAc) used was product of Sigma-Aldrich Fluka analytical, Germany. Sulphuric acids used were BDH AR grade. 0.5 M H₂SO₄ acid solution used as blank solution was prepared with double distilled water whereas the inhibitor solutions used ranged from 0.2g/L – 0.8g/L concentration

Weight Loss Measurement

Pre-cleaned and weighed mild steel coupons (3cm x 4cm x 0.2cm) were immersed in 200ml of test solutions in a glass beaker with aid of hook and glass, and kept at room temperature of 30 ± 1^o C . Weight loss was determined by retrieving the coupons at 24 h interval progressively for 5 days, via washing, drying and reweighing. The weight loss was determined as the difference between the initial weight and final weight at a given time interval. This process was repeated in triplicate and average values were recorded. The value of corrosion rate was determined using Equation 1 stated below:

$$CR \text{ (mm/yr)} = \left[\frac{87,600\Delta B}{\rho At} \right] \quad (1)$$

where, ΔB = weight loss in gram (g), ρ = density of the mild steel coupons (g/cm³), A = exposed surface area of the coupons (cm²) and t = time of exposure (h)

The percentage inhibition efficiency (I.E %) was calculated according to Equation 2 stated as follows:

$$I.E \% = \left[1 - \frac{CR_p}{CR_A} \right] \times 100 \quad (2)$$

where, CR_p = corrosion rate in the presence of inhibitor and CR_A = corrosion rate in absence of inhibitor.

Electrochemical Measurement

Electrochemical measurement was performed in cylindrical glass electrolytic cell containing test solution and three conventional electrodes (graphite rod was used a counter electrode (CE), saturated calomel electrode (SCE) as the reference electrode (RE) and metal coupon (as the working electrode). The working electrode (1cm² surface area) was immersed in the test solution and allowed to corrode freely for 30 min during which its open circuit potential (OCP) was recorded as a function of time. After establishing a steady state potential, the electrochemical measurements were performed in a computer controlled electrochemical workstation (PARC- 263 model). The potentiodynamic polarization curves were obtained in the potential range of ± 250mV versus corrosion potential using linear sweep technique at a scan rate of 0.333mV/s. Power suite software was used to extrapolate the data. Each test was run in triplicates to verify the reproducibility of the system.

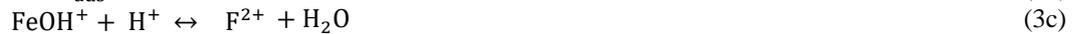
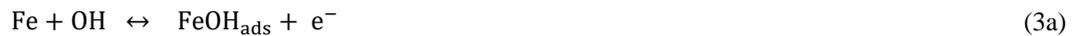
Chemical Quantum Computations

All chemical quantum calculations were performed to investigate the correlation between the inhibitive performance of PVAc and its electron molecular structure. This was done with Material Studio 7.0 Software (Accelry Inc) via density functional theory (DFT) electronic structure DMol³ program and Forcite quench molecular dynamics program.

RESULTS AND DISCUSSION

Effect of Inhibitor Concentration and Time Variation on Corrosion rate and Inhibition Efficiency Corrosion Rate: Anodic and cathodic reactions are the two electrochemical processes that manifest during corrosion of metals. At the anodic site dissolution of metal occurs via anodic reaction whereas cathodic reaction gives the hydrogen gas evolution. During the anodic dissolution of iron in the presence of hydrate ion the reaction processes [34-35] that

occur are as shown in Equation 3a-3c below:



The resultant effect of these reaction processes does not guarantee the safety of the economy, materials, human health and environment. Table 1 illustrates the calculated values of corrosion rates of mild steel in 0.5 M H₂SO₄ in the absence and presence of different concentrations of PVAc at different days. It is observed that corrosion impact manifests more in the blank solution compared to inhibited solutions from the results obtained and there is no passivation behaviour exhibited by mild steel in the test solutions. In addition, the rate of corrosion and material loss was reduced in the presence of PVAc. This result is more pronounced with increase in the concentration of inhibitor, thus signifying that inhibition effectiveness is dependent on amount of inhibitor present in the acidic solution. Furthermore, we observed that corrosion rate of mild steel in acid solution decreases with time. Hence, we suggested that decline in the diffusion rate of corrosive agent into the corroding metal surface or the formation of stable corroded product may be responsible for the depression of the actions of corrosive agent.

Inhibition efficiency (IE %): This is ability of inhibitor to reduce corrosion damage or dissolution of metal surface exposed to aggressive environment. According to Oguzie, Onuoha and Onuchukwu, 2005 [36] inhibitors of organic background inhibit corrosion process by displacing water molecules on the metal surface and adsorption of complex layer (formed from interaction between the surface charges on the metal and organic inhibitor) on the metal surface. Hence, the rate at which the corrosive agent diffuses into the metal surface is deactivated by complex layer with resultant suppression of the dissolution of metal. Fig. 1 illustrates the plots of inhibition efficiency against inhibitor concentration for mild steel corrosion in 0.5 M H₂SO₄ at different days. It is seen from the plots that inhibition effectiveness increased with increasing concentration of PVAc and this result is concentration dependent. The maximum inhibition efficiency observed is 85.62% at the highest inhibition concentration (0.8g/L).

Effect of Temperature Variations on Corrosion rate and Inhibition Efficiency

Temperature effect on the corrosion and inhibition process of mild steel in 0.5 M H₂SO₄ in the absence and presence of PVAc was studied using weight loss measurement at different temperatures. The objective of this study was to underscore the nature of adsorption mechanism of PVAc on to the mild steel surface. The experiments were performed at 10 K intervals in the temperature range 303–333 K for 6 h immersion and results obtained are presented in Table 2.

It is observed from the result data that corrosion rate in both blank and inhibited solutions increased with rise in temperature but the effect manifests more in the blank solution. In addition, inhibition potency of PVAc increased with rise in temperature (Fig. 2), thus suggesting that chemical adsorption mechanism [37] is the mode through which PVAc adsorbed on the mild steel surface. The comparison between inhibition efficiency value at maximum PVAc concentration for a 6 h immersion period at 333 K (89.16%) and that obtained after 24 h of immersion at room temperature (85.67%) is evidence of enhanced molecular effect at higher temperature, and also slow dissolution and diffusion process of some polymers especially at room temperature due to large size of polymer molecules.

Table -1 Calculated values of Corrosion rate, C_R (mm/yr), Inhibition Efficiency (IE %) for Mild Steel in 0.5 M H₂SO₄ in the Absence and Presence of PVAc from Weight Loss Measurement at Different Days

| System | Corrosion Rate (mm/yr) | | | | | Inhibition Efficiency (%) | | | | |
|--------|------------------------|-------|-------|------|-------|---------------------------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| Blank | 42.35 | 30.32 | 20.71 | 15.7 | 12.70 | – | – | – | – | – |
| 0.2g/L | 7.23 | 6.75 | 5.55 | 5.08 | 5.03 | 82.93 | 77.74 | 73.20 | 67.66 | 60.39 |
| 0.4g/L | 6.93 | 6.40 | 5.33 | 4.83 | 4.68 | 83.64 | 78.89 | 74.26 | 69.26 | 63.15 |
| 0.6g/L | 6.51 | 6.11 | 5.17 | 4.61 | 4.45 | 84.63 | 79.85 | 75.04 | 70.66 | 64.96 |
| 0.8g/L | 6.07 | 5.83 | 4.98 | 4.49 | 4.33 | 85.67 | 80.77 | 75.95 | 71.42 | 65.91 |

Table -2 Calculated Values of Corrosion Rate, Inhibition Efficiency, Activation Energy and Heat of Adsorption for Mild Steel in 0.5 M H₂SO₄ in the Absence and Presence of PVAc from Weight Loss Measurement at 303 –333K

| Conc | Corrosion rate (mm/yr) | | | | Inhibition efficiency (%) | | | | E _a (KJ/mol) | Q _{ads} (KJ/mol) |
|--------|------------------------|-------|--------|--------|---------------------------|-------|-------|-------|----------------------------|------------------------------|
| | 303K | 313K | 323K | 333K | 303K | 313K | 323K | 333K | | |
| Blank | 62.61 | 89.82 | 150.22 | 204.80 | – | – | – | – | 33.13 | – |
| 0.2g/L | 9.23 | 11.29 | 16.05 | 21.34 | 85.26 | 87.43 | 89.32 | 89.58 | 23.44 | 12.94 |
| 0.8g/L | 6.79 | 7.69 | 10.70 | 13.06 | 89.16 | 91.44 | 92.88 | 93.62 | 18.30 | 18.48 |

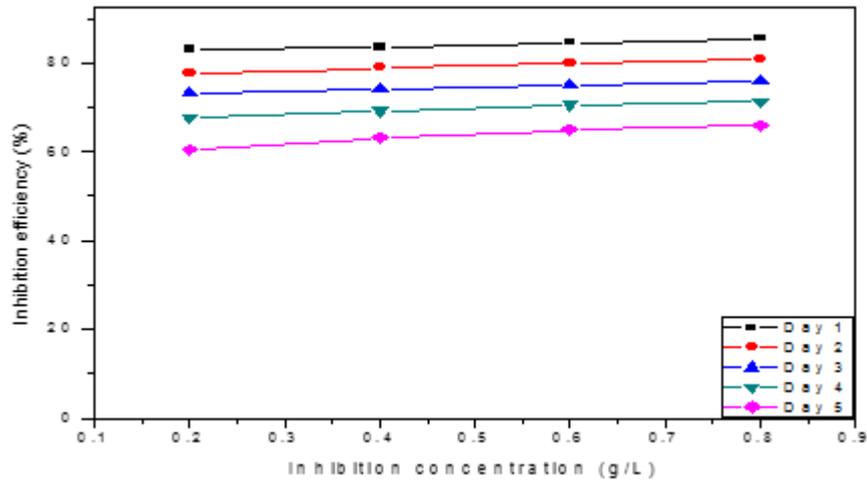


Fig.1 Plots of inhibition efficiency against inhibitor concentration mild steel corrosion in 0.5 M H₂SO₄ at different days

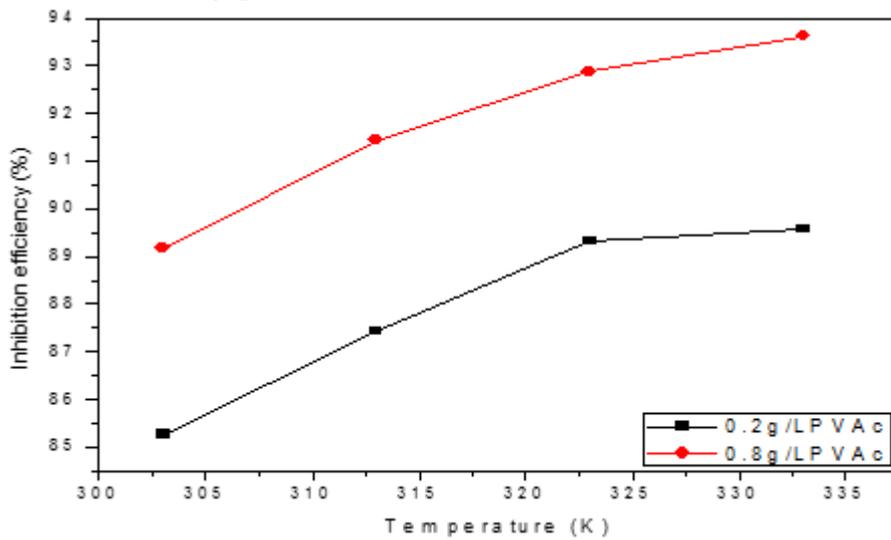


Fig. 2 Plot of inhibition efficiency against temperature for mild steel corrosion in 0.5 M H₂SO₄ PVAc

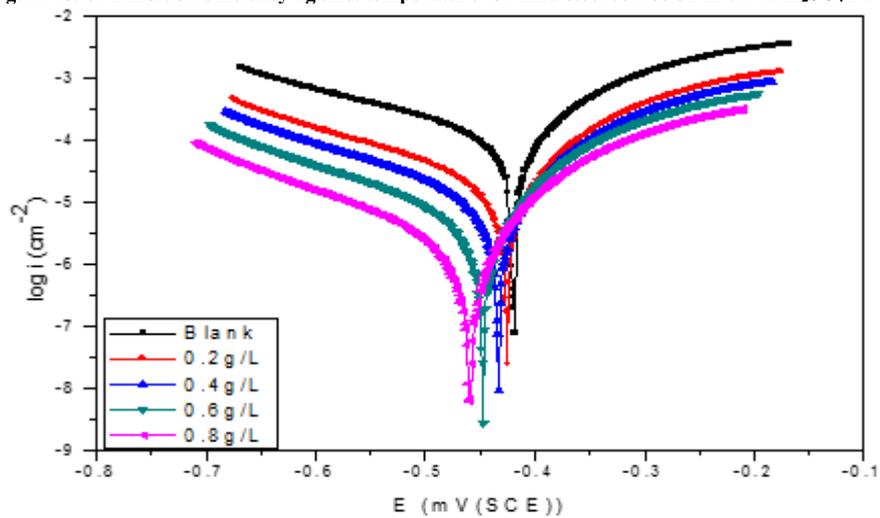


Fig. 3 Plot of $\log i$ (cm^{-2}) against E (mV(SCE)) mild steel corrosion in 0.5 M H₂SO₄ in the absence and presence of PVAc

Table -3 Calculated Polarization Parameters for Mild Steel Corrosion in 0.5 M H₂SO₄ in the Absence and Presence of Polyvinyl Acetate

| System | E_{corr} (mV(SCE)) | I_{corr} (μAcm^{-2}) | b_c (mVdec ⁻¹) | b_a (mVdec ⁻¹) | IE(%) |
|---|-----------------------------|--|------------------------------|------------------------------|-------|
| Blank (H ₂ SO ₄) | -410.56 | 772.09 | 163.45 | 108.45 | — |
| 0.2g/LPVAc | -423.62 | 175.74 | 113.45 | 89.09 | 77.24 |
| 0.4g/LPVAc | -430.58 | 152.42 | 87.68 | 63.65 | 80.26 |
| 0.6g/LPVAc | -445.32 | 135.02 | 72.09 | 48.87 | 82.51 |
| 0.8g/LPVAc | -460.76 | 100.04 | 59.78 | 37.09 | 87.04 |

Potentiodynamic Polarization Measurements

The polarization technique was used to measure anodic and cathodic kinetic reactions of mild steel in 0.5 M H₂SO₄ solution in the absence and presence of PVAc. The results data of Table-3 confirmed that cathodic and anodic current values decreased more in the inhibited solutions compared to blank solution, thus suggesting that PVAc depressed both the anodic dissolution of mild steel and cathodic hydrogen gas evolution [38]. In addition, the data of Table 3 revealed that corrosion process of mild steel followed Tafel's law and E_{corr} of the inhibited solutions shifted towards negative potential with slight increasing effect as inhibitor concentrations increase (Fig. 3). Hence, this displacement trend manifested by E_{corr} is evident of modification of both anodic and cathodic reaction processes respectively by PVAc, though cathodic reaction was predominantly controlled. Nevertheless, the retardation of cathodic and anodic corrosion current observed is an indication that PVAc is a good inhibitor for mild steel corrosion in H₂SO₄ acidic medium. It has reported that E_{corr} displacement value of 85mV between the blank and inhibited solution is the basis for classifying inhibitor as either mixed-type inhibitor, cathodic or anodic [39]. Hence, the E_{corr} displacement values obtained range from 13.06mV to 50.20mV, thus signifying that PVAc manifested mixed-type features of inhibition. The inhibition efficiency was calculated from the Equation 4 stated as follows:

$$I. E_{\text{corr}}(\%) = \left[1 - \left(\frac{I_{\text{corr}}^{\text{P}}}{I_{\text{corr}}^{\text{A}}} \right) \right] \times 100 \quad (4)$$

where I_{corr}^P is the corrosion current in the presence of inhibitor whereas I_{corr}^A is the corrosion current in the absence of inhibitor.

Adsorption Considerations

Inhibitors displace water molecules on the metal surface by substitution reaction [36] and form complex by interacting with surface charges on the metal. Then, the complex adsorbs on the metal surface in form of a layer or film and protects the corroding metal surface by intercepting the movement of corrosive agents into the surface. More corroding metal surface can be protected against the corrosion attack by either increasing the amount of inhibitor concentration or introducing synergistic additives into the aggressive system to strengthen the inhibition efficiency of the inhibitor. The use of classical adsorption isotherms is essential tool needed to work out the mode of adsorption (single layer, double layer or their combination) of inhibitors on the corroding metal surface. In this regard, degree of surface coverage, $\theta = IE\%100$ (experimental data) from weight loss measurement was fitted into some classical isotherms in order to investigate the adsorption process of PVAc on the mild steel surface. Co-efficient of linear correlation (R²) was used to determine the best fit and the proximity of R² to unity indicates the best results. Langmuir adsorption isotherm incidentally gave best fit with the experimental data. The Langmuir adsorption isotherm is deduced from the Equation 5 stated below:

$$\frac{C}{\theta} = \frac{1}{K_C} + C \quad (5)$$

where C, K_C and θ is the inhibitor concentration, adsorption equilibrium constant and surface coverage respectively.

Plot of C/θ versus C for PVAc adsorption on mild steel in 0.5 M H₂SO₄ solution is shown in Fig. 4. Linear plot was obtained with slope = 1.14 and R² = 0.9998. This indicates good fit of the experimental data with Langmuir adsorption isotherm and also confirms validity of the assumptions associated with the isotherm [40]. The value of slope obtained which is unity authenticates the mechanism of physical adsorption. The value of K_C (71.428) was calculated from the intercept of the linear plot and the positive value reflects the adsorption capability of PVAc on the surface of metal.

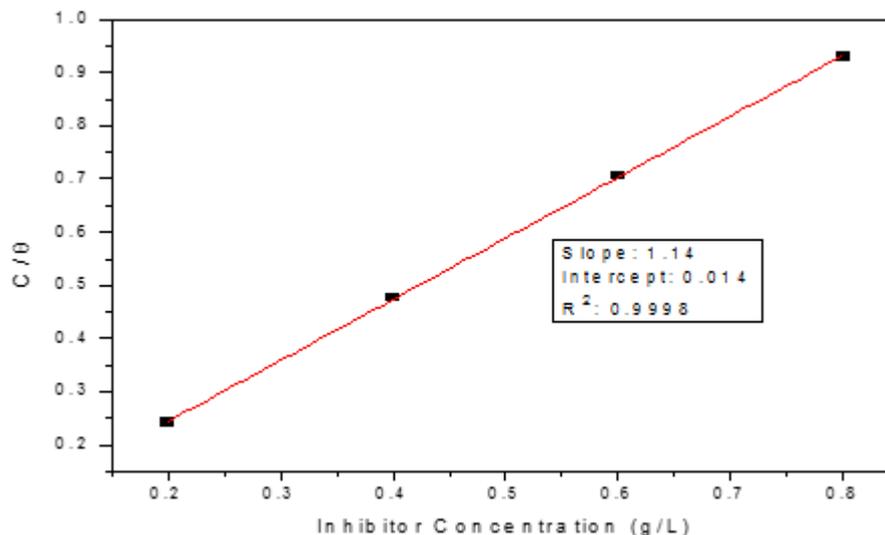


Fig. 4 Plot of Langmuir adsorption isotherm for inhibition of mild steel in 0.5 M H₂SO₄ by PVAc

Thermodynamic Studies

The thermodynamic properties investigated in this work include: Apparent activation energy (E_a): The apparent activation energy (E_a) for the corrosion process was deduced from the relationship between the activation energy (E_a) and corrosion rate in the presence temperature according to Arrhenius Equation 6 stated below:

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (6)$$

where E_a , CR_1 , CR_2 , R = apparent activation energy, corrosion rate at temperature T_1 , corrosion rate at temperature T_2 and universal gas constant (8.3142KJ/mol) respectively. Calculated values of apparent activation energy (E_a) are illustrated in Table 2. Data on Table 2 revealed that activation energy values in the presence of PVAc are lower than those of blank solution. This indicates that energy of activation of sulphate ions (corrosive agent) together with rate of dissolution of mild steel is reduced by PVAc. The mechanism (physical or chemical) of inhibitor adsorption is determined from the difference between value of energy of activation between blank and inhibited solution [31]. Hence, from the results we obtained inhibition adsorption exhibits the characteristic features of chemical mechanism Heat of adsorption, Q_{ads} : The estimated heat of adsorption, Q_{ads} occurred in the absence and presence of PVAc during the corrosion process was deduced from the relationship between temperature and degree of surface coverage (θ) according to Equation 7 stated below:

$$Q_{ads} = 2.303R \left[\log \left(\frac{\theta_2}{1-\theta_2} \right) - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right] \times \frac{T_1 T_2}{T_2 - T_1} \quad (7)$$

where θ_1 , θ_2 = degree of surface coverage at temperature T_1 and θ_2 is the degree of surface coverage at temperature T_2 respectively. Table -2 illustrates the calculated heat of adsorption values for the corrosion process. Data on Table 2 confirmed that positive heat of adsorption, Q_{ads} values was obtained, thus showing that degree of surface coverage and temperature increased correspondingly. This suggested that adsorption process is endothermic and confirmed the adsorption mechanism (chemical) [37] proposed earlier.

CHEMICAL QUANTUM COMPUTATIONS

Molecular Reactivity

The impact of theoretical simulations in the study of reaction processes during corrosion and adsorption of inhibitor on to the metal surface at the molecular level is on the increase due to development in the software modelling tools. For instance, density functional theory (DFT) of material studio software has proved to be vital tool in this regard due its capability to deduce the effectiveness of inhibitor from the molecular electronic structure of the inhibitor and also predict the chemical reactivity of inhibitor at a molecular level. In the course of performing the simulation, the electronic molecular structure of PVAc was geometrically optimized by means of DFT electronic structure DMol³ program and spin polarization was restricted using DND basis set, Perdew Wang (PW) correlation density functional and NVE ensemble (with a time step of 1 fs and simulation time of 5 ps at 298K). The molecular electronic structure of inhibitor is correlated with the effectiveness of inhibitor according to frontier molecular orbitals (FMO) which include [41-44]. The frontier molecular orbitals evaluated are energy of highest occupied molecular orbital (E_{HOMO}) and energy of lowest unoccupied molecular orbital (E_{LUMO}).

In addition, energy gap (ΔE) between the E_{HOMO} and E_{LUMO} is also another important parameter that assesses the inhibitive performance of inhibitor at the molecular level. It acts as function in the reactivity of inhibitor molecule and its adsorption on the metal surface [45]. The decrease in energy gap increases both the reactivity potential of inhibitor and inhibition efficiency. Hence, low energy gap, ΔE value offers good inhibition efficiency since the energy required to remove an electron from the last occupied orbital will be reduced. Furthermore, chemical reactivity of the inhibitor was assessed in terms of electrophilic and nucleophilic attack using Fukui function. Electrophilic attack is associated with the propensity of inhibitor to release electrons whereas nucleophilic attack corresponds with the tendency of the inhibitor to attract electrons. The geometry optimized structure, HOMO and LUMO orbitals, total electron density, electrophilic (f^-) attack and nucleophilic (f^+) attack of the PVAc repeat unit obtained from the simulation are illustrated in Fig. 5.

E_{HOMO} is linked to the electron donation ability of inhibitor whereas E_{LUMO} is associated with electron accepting capability of inhibitor. High E_{HOMO} values indicate the capability of inhibitor to donate electron(s) to an appropriate acceptor with vacant molecular orbitals whereas low E_{HOMO} values designate the disposition of inhibitor to accept electron(s) from an appropriate donator. The computed E_{LUMO} and E_{HOMO} values are -0.0866eV and -6.2463eV respectively while the energy gap, ΔE value obtained is 6.1597eV . These results are in conformity with the proposition made earlier that PVAc will offer good inhibition performance from the molecular point of view.

The electron density is saturated all around the PVAc repeat unit whereas HOMO and LUMO orbitals spread over the acetate group as seen in Fig 5(b-d), thus indicating the expectation of a flat-lying adsorption orientation. It is clearly seen from our results that f^- sites are correlated with the HOMO locations and the f^+ sites are correlated with the LUMO locations; indicating the regions through which the PVAc repeat unit would likely interact with the surface charges on mild steel.

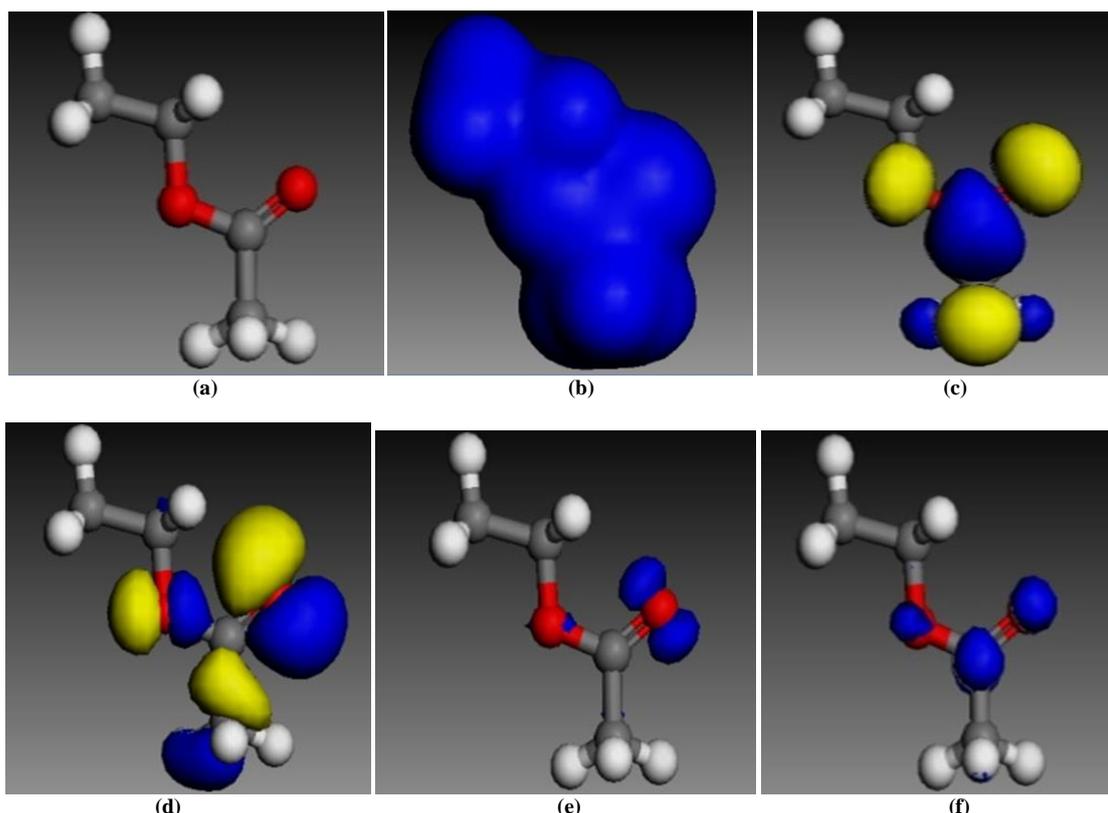


Fig. 5 Electronic properties of PVAc repeat unit: (a) Optimized structure, (b) Total electron density (c) HOMO orbital, (d) LUMO orbital, (e) Electrophilic attack (f^-), (f) Nucleophilic attack (f^+). (Atom legend: where H, C and O = white, gray and red respectively). The electron density difference is shown by blue and yellow isosurfaces; the yellow regions indicate electron loss whereas blue regions indicate electron accumulation

MOLECULAR DYNAMICS (MD) SIMULATION

This was performed using Material Studio 7.0 Software (Accelry Inc) via Forcite quench molecular dynamics program. The simulation illustrates the different low energy of adsorption of a PVAc repeat unit on the Fe surface at a molecular level. In course of performing the simulation, a density packed Fe crystal surface was cleaved along the (110) plane (most stabilized position) and structure of the PVAc and Fe was optimized using 10×8 supercell, COMPASS force field and Smart algorithm with NVE (microcanonical) ensemble with a time step of 1 fs and simulation time of 5 ps at 298K, constrained surface atoms, 5000 number of steps and 250 quench every steps. Fig. 6 presents the top view of the lowest energy adsorption interaction between PVAc repeat unit and Fe (110) surface from our simulations. The PVAc repeat unit is seen to maintain a flat-lying adsorption orientation on the Fe (110) surface due to the delocalization of electron clusters all around the PVAc repeat unit. This adsorption orientation improves contact or interaction between PVAc repeat unit and surface charges on the steel and, also enhances the degree of surface coverage.

In order to estimate quantitatively the adsorption energy utilized during the interaction between PVAc repeat unit and the Fe surface, binding energy ($E_{\text{Binding Energy}}$) a very important parameter used in characterizing the adsorption interaction between PVAc repeat unit and Fe surface was determined according to Equation 8 stated below:

$$E_{\text{Binding Energy}} = E_{\text{Total}} - (E_{\text{PVAc}} + E_{\text{Fe}}) \quad (8)$$

where E_{PVAc} , E_{Fe} , and E_{Total} = energy of PVAc repeat unit, energy of Fe surface without adsorption, and total energy of the system containing PVAc repeat unit and Fe surface respectively. The value of binding energy of adsorption obtained between the interaction of PVAc repeat unit and Fe surface is $-112.8556 \text{Kcal/mol}$. This value was determined by calculating the average of energies of five structures of lowest energy or five most stable representative adsorption configurations. The large negative value of binding energy of adsorption obtained is an indication of strong stable adsorption interaction between PVAc repeat unit and Fe surface.

To gain an insight into the actual adsorption interaction between cluster of PVAc molecules and Fe surface, molecular dynamic simulation was utilized. This presents better adsorption interaction characteristics between cluster of PVAc molecules and Fe surface. In doing the simulation, the cluster of PVAc molecules was generated from the vinyl acetate molecule (repeat unit) using the Polymer Builder (MS Studio 7.0). The conformational structure of

polymer obtained which is rather impracticable was modified using the geometrical optimization. This generates the polymer chains (backbone chains containing sequences of vinyl groups and side chains containing acetate groups) obtained to resemble those found in ideal solutions or actual melts (Fig. 7a). Similar simulation procedure and parameters used in estimating adsorption interaction between PVAc repeat unit and Fe (110) surface were followed. Finally, the quantitative estimate of binding energy ($E_{\text{Binding Energy}}$) of adsorption interaction between cluster of PVAc molecules and the Fe surface was calculated using Equation 9 as follows:

$$E_{\text{Binding Energy}} = E_{\text{Total}} - (E_{\text{Polymer}} + E_{\text{Fe}}) \quad (9)$$

where E_{Total} = energy of the polymer and Fe, E_{Fe} = energy of the Fe surface without the polymer, E_{polymer} = energy of the polymer without the Fe surface and the binding energy ($E_{\text{Binding Energy}}$) obtained is -1251.130Kcal/mol . Fig. 7b shows the molecular dynamic simulation of top view of the lowest energy adsorption interaction between cluster of PVAc molecules and Fe (110) surface. It was observed that binding energy of adsorption interaction was enhanced with increase in the number of polymer molecules on the Fe surface, thus indicating that cluster of PVAc molecules interacts more strongly with the Fe (110) surface than PVAc repeat unit. This could be linked to trend of rapid increase in inhibition efficiency with increase in PVAc concentration observed and possibly accounts for the high inhibition efficiency of PVAc as observed experimentally.

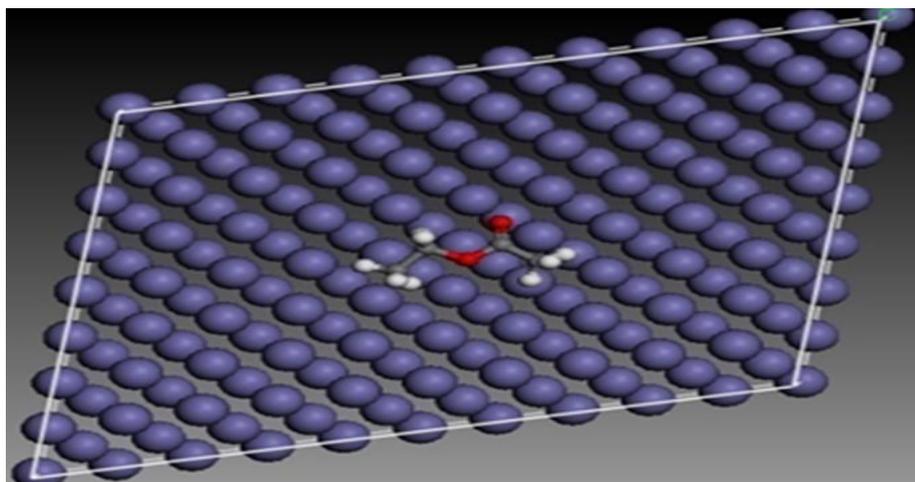


Fig. 6 Molecular dynamics model of top view of the lowest energy adsorption interaction between PVAc repeat unit and Fe (110) surface

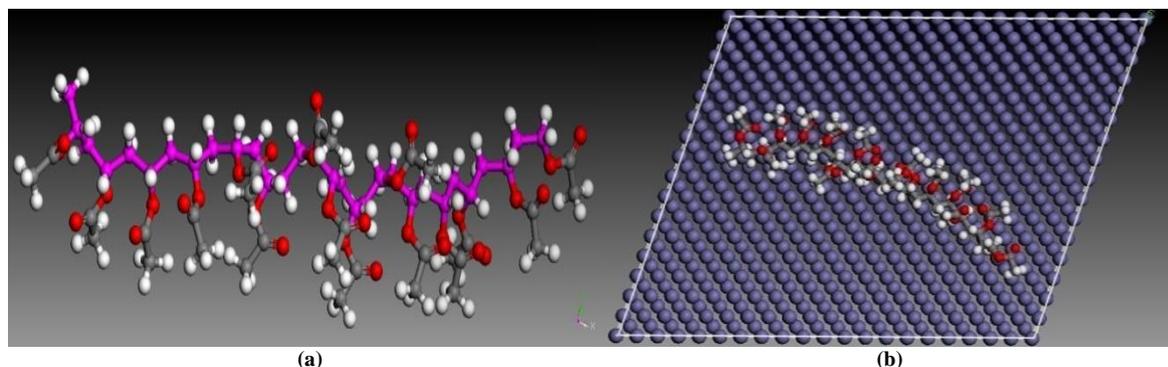


Fig. 7(a) Geometrically optimized structure of cluster of PVAc molecules; (b) Molecular dynamic simulation of top view of the lowest energy adsorption interaction between cluster of PVAc molecules and Fe (110) surface. Atom legend: H, C and O = white, gray and red respectively)

CONCLUSIONS

The combination of experimental and theoretical approaches has made the investigation of inhibitive performance of PVAc on the corrosion of mild steel in 0.5 M H_2SO_4 acid solution successful. The experimental approach revealed the effect of inhibitor concentration, time and temperature variations on the corrosion rate, inhibition efficiency of PVAc and electrochemical reaction process of mild steel. It revealed that PVAc inhibited the dissolution of mild steel in 0.5 M H_2SO_4 acid solution effectively at room temperature, with inhibition efficiency of up to 85.67% and also established that PVAc exhibited characteristic features of mixed-type inhibition. Inhibition adsorption behaviour was best modelled by the Langmuir adsorption isotherm while the proposed adsorption mechanism was based on the effect of temperature on inhibition efficiency, trend of activation energy and heat of adsorption values respectively. The theoretical approach confirmed the possible reactive regions on PVAc repeat unit, revealed the correlation between the inhibitive performance of PVAc and its electronic molecular structure, substantiate the adsorption potential of PVAc repeat unit and cluster of PVAc molecules.

Acknowledgement

The support received from the Nigeria Tertiary Education Trust Fund (TET Fund); under 2011/2012 TET Fund Research Allocation for the Federal University of Technology Owerri was highly acknowledged.

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