International Journal of Science and Research Archive

eISSN: 2582-8185

Cross Ref DOI: 10.30574/ijsra

Journal homepage: https://ijsra.net/

(RESEARCH ARTICLE)

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Corrosion inhibition behaviour of synthetic 2-(phenylsulphonamido)-3-methylbutanoic acid on mild steel in alkaline solution

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International Journal of Science and Research Archive, 2023, 09(02), 108–115

Publication history: Received on 23 May 2023; revised on 01 July 2023; accepted on 04 July 2023

Article DOI: https://doi.org/10.30574/ijsra.2023.9.2.0520

Abstract

The corrosion inhibiting behaviour of synthetic 2-(phenylsulphonamido)-3-methylbutanoic acid (PSMBA) on mild steel in the presence of 0.1 M KOH was investigated using combined gravimetric, electrochemical and theoretical simulation corrosion monitoring methods. The gravimetric data showed that the inhibitor effectively protected the metal from alkaline corrosion and that the inhibition ability depended on concentration increase and reduced gradually with prolonged immersion time. The electrochemical impedance spectroscopy results show that the charge transfer resistance increased with the addition of the inhibitor while potentiodynamic polarization results showed that the corrosion current density decreased upon the addition of the inhibitor, theoretical simulation results revealed a low and comparable energy gap between the LUMO and HOMO energies. All these showed that 2-(phenylsulphonamido)-3-methylbutanoic acid functioned as a good corrosion inhibitor for mild steel in alkaline medium.

Keywords: Corrosion; 2-(phenylsulphonamido)-3-methylbutanoic acid; Mild steel; Inhibitor; Simulation

1. Introduction

Iron materials and their alloys have found wild applications in several industries, they play important roles as a result of their rich structural and mechanical strength [1-2]. Mild steel is a low carbon ferrous alloy and it has been used extensively in many industries. It is used in space vehicles, pipe making and in cooling systems [3-4]. Metals and alloys become corroded when exposed to acids and bases in their environment. The resultant effects of corrosion attack are numerous. Metallic corrosion causes tremendous destruction to the integrity and life-span of components used in industries especially in chemical processing industries and the oil and gas sectors [5-7]. The most effective method of controlling corrosion attack is to isolate the metal from the corrosive environment [7-10]. Corrosion reaction has been effectively managed by the use of corrosion inhibitors [11-16]; their method of application is not a complex technique and as such does not require special training. Corrosion inhibitors are materials that when applied in small quantities reduce the corrosion attack [17-19]. This research reports the study of the corrosion inhibition properties of 2-(phenylsulphonamido)-3-methylbutanoic acid on mild steel in 0.1 M KOH using gravimetric, electrochemical and theoretical methods.

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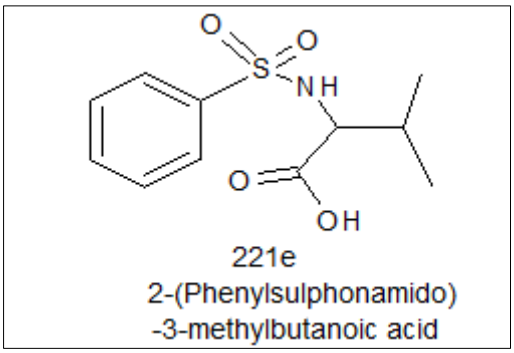

Figure 1 Chemical structure of 2-(phenylsulphonamido)-3-methylbutanoic acid

2. Material and methods

2.1. Preparation of materials

The mild steel specimen used for the experiments has the weight percentage of C = 0.05, Mn = 0.6, P = 0.36, Si = 0.3 and the balance Fe [20-21]. The corrosive solution was KOH prepared using analytical grade reagents. The stock solution that was used as the inhibitor was prepared in the organic chemistry laboratory in Imo State University Owerri (22). 2.5 g of the synthesized material was dissolved in 500 ml of 96 % ethanol to give a solution of concentration 5 g/L. Test solutions were then prepared from the stock solution in the concentration range of (0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L & 1.0 g/L)

2.2. Gravimetric Experiment

Test coupons of dimension 3 cm x 9 3 cm x 9 0.14 cm were used for the gravimetric experiments, the mild steel coupons were polish under wet condition using silicon carbide abrasive paper of grade #200-#1000 [23], then rinsed using distilled water, dried with acetone and also in warm air and kept in a desiccator. The prepared mild steel coupons were suspended in a beaker containing 300 ml of the test solution with the aid of rods and hooks. The experiments were done under unstirred and aerated conditions. The mild steel coupons were retrieved at an interval of 24-h continuously for 120-h and immersed in a solution containing 20% NaOH and 200 g/L zinc dust to momentarily halt the corrosion reaction, it was then washed while scrubbing with bristle brush, dried, re-weighed and re-immersed into the test solution. The weight loss was calculated by comparing the weight at a particular time with the initial weight of the coupon.

2.3. Electrochemical Experiment

All electrochemical experiments were conducted on mild steel coupons of dimension 1 x1 cm using a VERSASTAT 400 Complete DC Voltammetry and Corrosion System, in V3 Studio software. The mild steel coupon was encased in polytetrafluoroethylene (PTFE) rods using epoxy resin in a way that only one of its surfaces, of area 1 cm^2, was left unsealed. The exposed surface was prepared as described in the gravimetric section. The counter and reference electrode were graphite and saturated calomel electrodes (SCE) respectively. The counter electrode was connected with luggins capillary [24]. The solutions were left in an aerated and unstirred environment for 1 h and 303 K. The electrochemical impedance spectroscopy (EIS) experiments were conducted at corrosion potential (E_{corr}) with a frequency range of 100 kHz–10 mHz, and a signal amplitude perturbation of 5 mV. The potentiodynamic polarization (PDP) experiments were conducted at potential range] ±250 mV versus corrosion potential under a scan rate of 0.333 mV/s.

2.4. Theoretical Simulation

All theoretical simulations were done using the density functional theory (DFT) electronic structure programs DMol3 as contained in the Accelrys Materials Studio 7.0 software program. The theoretical simulation was performed using the density functional theory (DFT) electronic structure DMol3 program. The electronic parameters for the simulation were Mulliken population analysis, unrestricted spin polarization-DND basis set and the Perdew–Wang (PW) local correlation density functional [25-26].

3. Results and discussion

3.1. Gravimetric Results

Gravimetric experiments were conducted on mild steel coupons in 0.1 M KOH with and without different concentrations of the inhibitor at a temperature of (30 ± 1 °C) [27] in aerated and unstirred solutions. Figure 2 gives a representative plot of weight loss of the mild steel coupons versus concentration without and with the inhibitor at 30 ± 1 °C. It indicates that loss of metal material (mild steel coupon) in alkaline solution induced corrosion reduced with increase in concentration of the inhibitor. Figure 3 depicts that inhibition efficiency decreases with increase in exposure times. The results indicated that the inhibitor functioned as a good corrosion inhibitor for mild steel in alkaline solution. Inhibition efficiency was calculated from the gravimetric data with the equation below:

$$IE(\%) = \left(1 - \frac{W_1}{W_2}\right) \times 100 \text{.....(1)}$$

Where W_1 represents the weight loss of the metal in the inhibited solution while W_2 is the weight loss in the uninhibited (blank) solution.

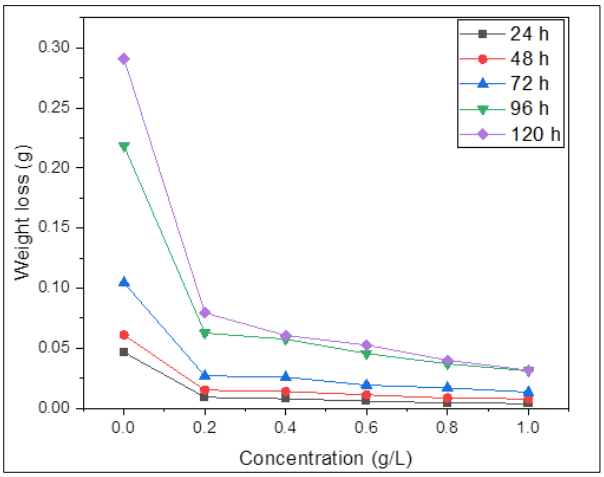

Figure 2 Variation of weight loss with concentration for mild steel corrosion without and with the inhibitor at different exposure times

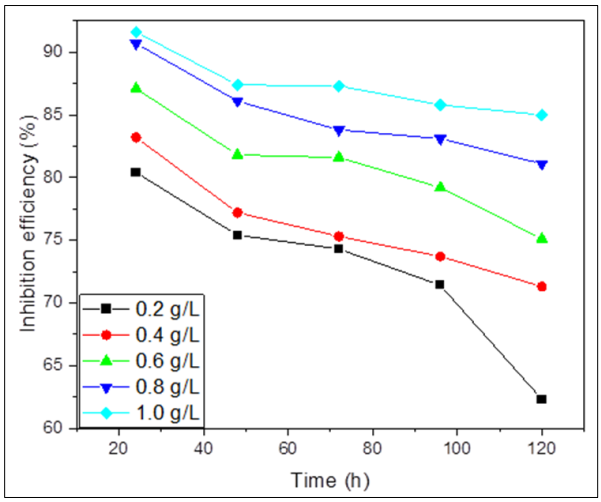

Figure 3 Variation of inhibition efficiency with time at different concentrations of the inhibitor

3.2. Electrochemistry Results

3.2.1. Electrochemical impedance spectroscopy (EIS) Results

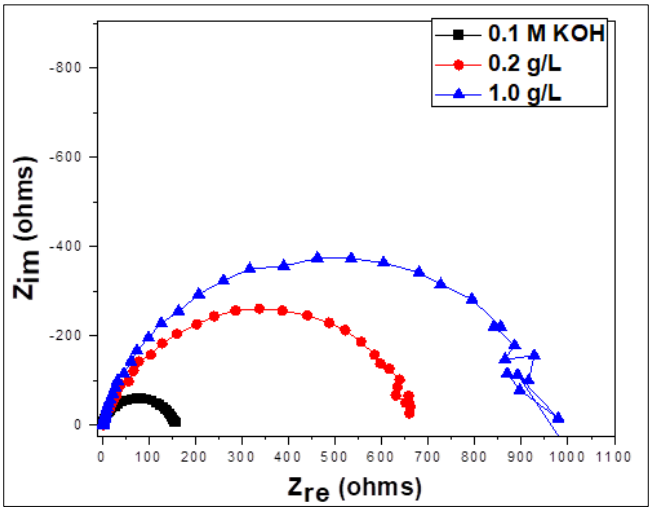

Figure 4 Electrochemical impedance spectroscopy for mild steel corrosion in 0.1 M KOH in the absence and presence of the inhibitor

The effect of the organic inhibitor on the kinetics of the reaction at the metal/alkaline interface without and with the inhibitor was ascertained using electrochemical impedance spectroscopy experiment. The result is presented in the Nyquist format in Figure 4 while the electrochemical parameters calculated from the (EIS) responses are presented in Table 1. The Nyquist plots in Figure 4 indicates a single capacitive semicircle [28] in the region of high frequency. The high frequency that intercepts with the real axis is donated as the solution resistance (R_s), similarly, the low frequency that intercepts the real axis is called the charge transfer resistance (R_{ct}). The EIS data was fitted with an equivalent circuit [$R_s(Q_{dl}R_{ct})$] [29] which has been previously used to fit impedance data. In the equivalent circuit, the solution resistance was shorted by a constant phase element (CPE) and was in parallel to the R_{ct}. The capacitor was kept with the CPE to account for deviations from dielectric behaviour. The impedance of the CPE is given below:

$$Z_{CPE} = Q_{dl}^{-1}(j\omega)^{-n}, \ldots\ldots\ldots\ldots(2)$$

Q_{dl} and n are the CPE constant and exponent respectively, j=-1 stands for an imaginary number , ω represents the angular frequency in rad s^{-1} , the value of ω is given by $2\pi f$ where f is the frequency in Hz.

Table 1 shows that the addition of the inhibitor increased the charge transfer resistance (R_{ct}) values but reduced the double layer capacitance (Q_{dl}). The increase in the value of R_{ct} corresponds to the increase in the diameter of the Nyquist semicircle and shows that the inhibitor reduced the corrosion of mild steel in the alkaline environment. The inhibition efficiency from the impedance data is given as below:

$$IE\ (\%) = \left(1 - \frac{R_{ct,bl}}{R_{ct,inh}}\right) \times 100 \ldots\ldots\ldots\ldots\ldots(3)$$

Where $R_{ct,bl}$ is the charge transfer resistance without the inhibitor while $R_{ct,inh}$ is the charge transfer resistance in the presence of the inhibitor.

3.2.2. Potentiodynamic polarization results

To investigate the effect of the inhibitor on the anodic and cathodic partial reactions, potentiodynamic polarization (PDP) experiments were performed. The polarization parameters from the PDP data are presented in Table 1 while the PDP plots in the presence and absence of the inhibitor in 0.1 M KOH are presented in Figure 5. The plots show that the inhibitor shifted the corrosion potential E_{corr} towards the positive potential, the PDP plot shows that the addition of the inhibitor deduced both the anodic and cathodic current densities and the corresponding corrosion current density (i_{corr}) showing that the inhibitor functioned as a mixed type corrosion inhibitor for mild steel in the alkaline environment studied. The inhibition efficiency was calculated from the potentiodynamic polarization data as follows:

$$IE\ (\%) = \left(1 - \frac{i_{corr,inh}}{i_{corr,bl}}\right) \times 100 \ldots\ldots\ldots\ldots(4)$$

Where $i_{corr,inh}$ represents the corrosion current density in the presence of the inhibitor while $i_{corr,bl}$ is the corresponding corrosion current density in the absence of the inhibitor.

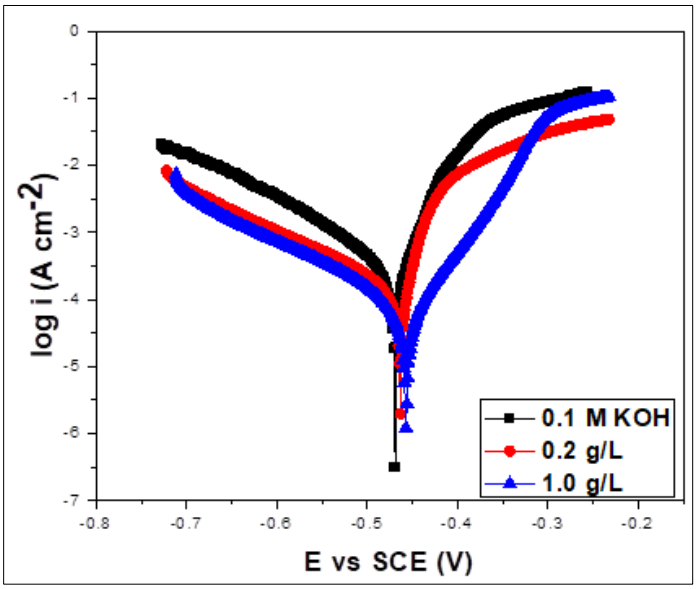

Figure 5 Potentiodynamic polarization curves of Mild steel in 0.1 M KOH in the absence and presence of the inhibitor

Table 1 Electrochemical Parameters for Mild steel in 0.1 M KOH in the Absence and Presence of PSMBA

System	E_{corr} (mVvs SCE)	i_{corr} (μA/cm²)	IE%	R_{ct}(Ωcm²)	n	I.E%
0.1 M KOH	- 463	210.3		155.2	0.88	
0.2 g/L	-456	38.9	81.5	640.9	0.88	75.8
1.0 g/L	- 449	25.8	87.7	892.5	0.89	82.6

3.3. Theoretical simulation Results

Density functional theory was used to study the correlation between the inhibition property of the inhibitor material and its molecular structure at the molecular level. This tool has been in use for accessing the inhibitive performance of an inhibitor theoretically [30] and it also serves as a guide to experiment already done. To correlate the inhibition performance of the inhibitor with its molecular structure, energies of the frontier orbitals (HOMO, LUMO and energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) were calculated. Figure 6 shows the geometrically optimized structure of the inhibitor, LUMO and HOMO orbitals and the total electron density estimated from the simulations. According to the frontier molecular orbital theory of chemical reactivity, the transfer of electron that leads to the adsorption of the inhibitor on the metal surface is as a result of the interactions that exist between it and the frontier orbitals. It has been shown that HOMO energy relates to the susceptibility of the molecule toward attack by electrophile, and this corresponds to a tendency to accept electron and is it is directly related to the ionization potential as below:

$$I = -E_{HOMO} \ldots\ldots\ldots\ldots(5)$$

Whereas LUMO energy relates to the susceptibility of the molecule towards a nucleophile attack, corresponding to a tendency of the molecule to donate electron. The LUMO energy is related to the electron affinity as below:

$$A = -E_{LUMO} \ldots\ldots\ldots\ldots(6)$$

High values of E_{HOMO} shows the ability of the specie to give out its electron to an appropriate acceptor with un-occupied orbital which enhances the adsorption process. And this shows that the specie will be a good inhibitor candidate. Similarly, low values of E_{LUMO} shows a good electron accepting property of an inhibitor. Low energy gap (ΔE)is an indication for a good inhibitor. The calculated energy properties for the inhibitor are E_{HOMO} = -5.491eV, E_{LUMO} = -1.557 eV and $\Delta E = 3.934$. Interestingly, the results obtained are of comparable values showing that the inhibitor has high tendency to adsorb on the metal surface [31].

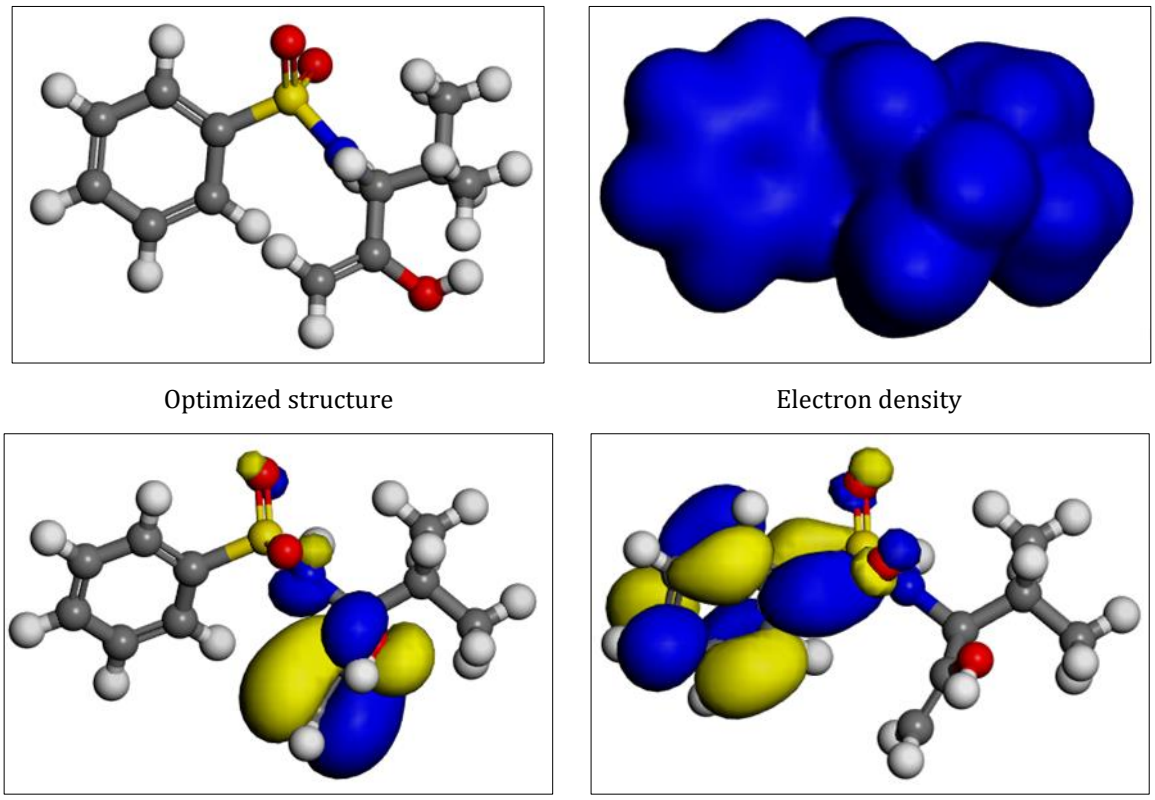

Figure 6 Electronic properties of 2-(phenylsulphonamido)-3-methylbutanoic acid (atom legend: white H, light gray C and dark gray O). The isosurfaces (larger lobes) depict the electron density difference; the darker regions show electron accumulation, whereas the lighter regions show electron loss

4. Conclusion

The corrosion inhibiting behavior of 2-(phenylsulphonamido)-3-methylbutanoic acid on mild steel in 0.1 M KOH was investigated using gravimetric, electrochemical and theoretical simulation methods. The gravimetric results showed that the inhibitor reduced the corrosion reaction and that the inhibition efficiency appreciated when the concentration of the inhibitor was increased. The electrochemistry results showed that the inhibitor reduced both the anodic and cathodic half reactions, the corrosion inhibiting ability of the 2-(phenylsulphonamido)-3-methylbutanoic acid was further confirmed by the low energy gap obtained in the theoretical simulation experiments..

Compliance with ethical standards

Acknowledgments

The author wishes to acknowledge the effort of Dr. C. B. C. Ikpa for synthesizing the 2-(phenylsulphonamido)-3-methylbutanoic acid used in this work.

Disclosure of conflict of interest

The author declares no conflict of interest.

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