



THERMODYNAMIC AND ADSORPTION STUDIES OF CORROSION CONTROL OF MILD STEEL IN HYDROCHLORIC ACID USING IONIC LIQUID (1-BUTYL-1-METHYLPYROLIDINIUM TETRAFLUOROBORATE) AS A VIABLE INHIBITOR

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Abstract - The goal of this work is to limit mild steel corrosion in an HCl solution by employing an ionic liquid (1-butyl-1-methylpyrolidinium tetrafluoroborate) as an inhibitor. To determine the molecular components and functional groups, the ionic liquids of 1-butyl-1-methylpyrolidinium tetrafluoroborate were produced and described. The quantization method was used to synthesize the ionic liquid. The thermometric method was used to determine the inhibitors' reaction counts and associated efficiencies. Examined were the effects of corrosion control variables on the inhibitory power of ionic liquid. Thermodynamic and adsorption characteristics were assessed in the corrosion control procedure. The C = O stretch, C = C stretch, C-H stretch, O-H stretch, N-H bend, and =C–O–C symmetric and asymmetric stretch were identified as the major functional groups of 1-butyl-1-methylpyrolidinium tetrafluoroborate. Nitrogen and oxygen heteroatoms can be found in both ionic liquids. Thermometric data demonstrated that the number of reactions dropped with an increase in the concentration of the inhibitor. Thermodynamic values demonstrated the physical adsorption and exothermic nature of the corrosion inhibition mechanism. The correlation between inhibition efficacy and the variables of temperature, time, and inhibitor concentration was well-explained. It can be deduced that 1-butyl-1-methylpyrolidinium tetrafluoroborate should be applied in corrosion control practice.

Keywords: Ionic Liquid, Corrosion Inhibitor, 1-butyl-1-methylpyrolidinium tetrafluoroborate, mild steel

1.1 Introduction

Ionic liquids (ILs) are molten salts composed of various anions and organic cations (Shukla et al., 2011, Ferguson et al., 2012). They are defined as organic cations combined with inorganic anions to form low-lattice-energy crystalline structures. In terms of phase, they are found in the liquid state at or near room temperature. ILs can be used in solvent-functions such as chemical, catalytic and biological reactions in place of traditional organic molecules. In chemical research and engineering, ILs act as solvents, catalysts, and catalytic support materials (Rajni, 2014). Its

synthesis has evolved from scholarly laboratory work to the industrial sector, where its practical uses have spawned a host of sustainable innovations. The ability to alter design in order to change attributes allows a researchers to create an ionic liquid that best suits their needs. There are a ton of opportunities to investigate in the realm of ionic liquid production and application, particularly with regard to metal corrosion control. It can be used to mitigate mild steel deterioration.

Mild steel is a useful metal with a resilient tensile capability, but it is prone to rusting. It is

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widely available and simple to make for industrial use. Its application spans numerous industries as a result (Singh et al, 2014; Popova et al, 2015; Verma et al., 2016). Its industrial usefulness is hindered by the possibility of the mild steel structure to deteriorate because of corrosion. Enormity of the corrosion is influenced by factors such as temperature, time and aggressive medium. In most circumstances, mild steel corrodes severely when exposed to acid solutions in the course of acid cleaning, acid shipping, acid de-scaling, acid storage, and other chemical operations (Fouda et al, 2021).

The degradation of materials brought on by an electrochemical reaction with the surrounding media is known as corrosion. Numerous detrimental consequences of corrosion exist, many of which are more dangerous than the substantial loss of metal (Uwiringiyimana et al., 2019; Mahgoub et al., 2019; Yang et al., 2021). Corrosion is detrimental to the chemical, oil and metallurgical industries. As a result, metal corrosion continues to be a global scientific concern. Studies on corrosion processes and control are currently being conducted by researchers from a range of industrial sectors (Azeez et al, 2018; Deyab, 2020). Corrosion will develop as unstable oxides are formed during these many industrial processes. As a result, certain chemicals known as corrosion inhibitors were required for these processes. These additives provide a protective layer over the metallic surface, keep metals isolated from their surroundings, and prevent corrosive degradation (Verma et al., 2017). Inhibitors can be used to regulate the corrosion of metals (Omotioma and Onukwuli, 2017; Jadhav et al, 2019). Today's stringent environmental regulations and increased global ecological consciousness forbid the production and use of traditional volatile corrosion inhibitors that pose a risk to human health. Improvements in synthetic and engineering chemistry are therefore desperately needed, whether through the use of environmentally benign starting materials or careful planning for synthesis employing unconventional energy

sources like microwave and ultrasonic heating. Ionic solutions should be used as a corrosion inhibitor. Ionic liquids may dissolve a broad range of organic and inorganic compounds and have low volatility (low vapor pressure), excellent gas solubility, and a broad range of stability over pH and temperature fluctuations. The assessment of 1-butyl-1-methylpyrrolidinium tetrafluoroborate as a potential inhibitor for reducing mild steel corrosion in a hydrochloric acid media was the main goal of this work.

2.1 Materials and Method

2.1.1 Mild Steel Preparation

The 3cmx3cm coupons of mild steel were utilized in this investigation. The coupons were first cleaned with distilled water, and then their surfaces were prepared using various grades of emery paper. As a solvent, acetone was then used to remove any remaining grease.

2.1.2 Syntheses of the IL

For the 1-butyl-1-methylpyrrolidinium tetrafluoroborate (IL) synthesis, the standard technique was adopted. In a 2-liter flask with two necks and a reflux condenser, newly distilled methylpyrrolidine (250 g) was gradually mixed with 30 g of n-bromohutane. The addition was made at a rate that prevented the mixture's temperature from rising above 40 °C. After that, this mixture was agitated for a day at room temperature using a magnetic stirrer. In this period, a solid yellow substance appeared. After filtering and washing with 10 milliliters of diethylether, this solid was vacuum-dried. After that, deionized water was used to dissolve the yellow solid. One hundred milliliters, after adding 3 g of decolorizing charcoal to the mixture, was heated to 65° C for a whole day. After cooling to normal temperature, the mixture was filtered.

2.2 Characterization of 1-butyl-1-methylpyrrolidinium tetrafluoroborate

2.2.1 Determination of chemical constituents of 1-butyl-1-methylpyrrolidinium tetrafluoroborate

The molecules of the IL were identified using an Agilent Technologies model 7890A and 5977B MSD gas chromatography-mass

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spectrophotometer in conformity with the report of Suleiman et al (2020). The apparatus employed a joint technique of GC (gas chromatography) and MS (mass spectrometry) to classify different compounds present in the ionic liquid sample. The GC's use of heat caused the ionic liquid to separate into its constituent chemical elements. The chemical components were then passed through the column using an inert gas. They departed from the column and flew into the MS, the ionic liquid's constituents were classified according to the mass of the determined molecules.

2.2.2 Functional groups determination of 1-butyl-1-methylpyrrolidinium tetrafluoroborate

The Fourier transform infrared (FTIR) spectrophotometer (Cary 630 from Agilent Technologies USA) aided in the identification of the IL's functional groups. High spectral resolution data are required to be obtained with a spectrophotometer (Suleiman et al, 2017). The Fourier transform, a mathematical process, was then applied to translate IL's raw data into the factual spectrum. Analysis of the several FTIR-generated peaks (in the transmittance against wavelength design) was done in functional groups' identification.

2.3 Thermometric routine of the corrosion control experiment

This experimental procedure used the thermometric routine that Onukwuli and Omotioma (2016) advocated. In it, a water bath with a thermostat (set to 30.0 degrees celcius) was used for the experiment. As soon as a constant temperature was found, the temperature of the beaker holding the mild steel coupon and the acid medium was noted. Eq. (1) was used to get the reaction number, while Eq. (2) was used to determine the inhibitor efficiency:

$$RN = \frac{[(T)_m - T_i]}{t} \quad (1)$$

$$IE = \left(1 - \frac{RN_{add}}{RN_{free}}\right) \times 100 \quad (2)$$

For equation (1): RN = reaction number, T_m = mean reaction temperature, T_i = initial reaction temperature, t= reaction time

For equation (2): IE% = percentage inhibition efficiency, where RN_{free} and RN_{add} are the reaction numbers for the mild steel dissolution in uninhibited and inhibited HCl media respectively.

2.4 Weight loss experimental routine

This study used the weight reduction (gravimetric) approach that Omotioma and Onukwuli (2017) used. In 1M HCl medium, weight loss changed over time at different temperatures and with different inhibitor concentrations present or absent. When the time came, the mild steel samples were removed, submerged in acetone, scrubbed with a bristle brush under running water, dried, and then weighed once more. The difference between the starting weight and the weight after corrosion was used to compute the weight loss. The weight loss, inhibition efficiency (IE), surface covered (Θ) and corrosion rate (CR) were obtained using Eqs. 3, 4, 5, and 6 respectively.

$$\Delta w = w_i - w_f \quad (3)$$

$$IE\% = (\omega_o - \omega_1/\omega_o) \times 100 \quad (4)$$

$$\theta = (\omega_o - \omega_1)/\omega \quad (5)$$

$$CR = (w_i - w_f)/At \quad (6)$$

Where w_i and w_f are the initial and final weight of mild steel samples respectively; ω_1 and ω_o are the weight loss values in the presence and absence of inhibitor, respectively. A is the total area of the mild steel sample, Θ is the degree of surface coverage, and t is the time of immersion.

2.4.1 Effects of Control Variables Determination

The relationships between corrosion control parameters (inhibitor concentration, temperature, and time) and weight loss, corrosion rate, and inhibition effectiveness were examined using response surface methodology (RSM).

2.4.2 Determination of thermodynamic parameters

a) Activation energy determination

Using the linear form of the Arrhenius (Eq 7), the activation energy of the corrosion control mechanism was calculated (Idris et al, 2013).

$$\ln CR = \ln A - \left(\frac{E_a}{R}\right) \times \left(\frac{1}{T}\right) \quad (7)$$

b) Heat of adsorption determination

Equation (8) was used to calculate the heat of adsorption Q_{ads} (kJmol⁻¹) (Onukwuli and Omotioma, 2016).

$$Q_{ads} = 2.303R \left\{ \log \left(\frac{\theta_2}{1-\theta_2} \right) - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right\} \times (T_2 \cdot T_1 / T_2 - T_1) \quad (8)$$

Where θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively.

Also, where CR is the corrosion rate of the mild steel, A is the frequency or pre-exponential factor, E_a is the activation energy, and R is the universal gas constant.

2.2.8 Consideration of the adsorption isotherms

Langmuir and Temkin adsorption isotherms were tested in line with the routine procedure (Onukwuli and Omotioma, 2016).

For Langmuir isotherm;

$$\frac{\log c}{\log \theta} = \log C - \log K \quad (9)$$

For Temkin isotherm;

$$\theta = -\left(\frac{2.303 \log K}{2a}\right) - \left(\frac{2.303 \log C}{2a}\right) \quad (10)$$

3.1 Characteristics of the Ionic Liquid

3.1.1 Chemical Constituents of the Ionic Liquid
Chromatogram of the 1-butyl-1-methylpyrrolidinium tetrafluoroborate is presented in Figure 1. The peaks of the chromatogram represent the chemical constituent of the ionic liquid. The chemical constituents with corresponding peaks and retention time contain 1H-Imidazole, 1'-carbonyldiimidazole, 1H-pyrazole, and methyl

tetradecanoate. It also comprises heterocyclic molecules with branches, which revealed it is suitable for corrosion inhibition (Suleiman et al, 2017).

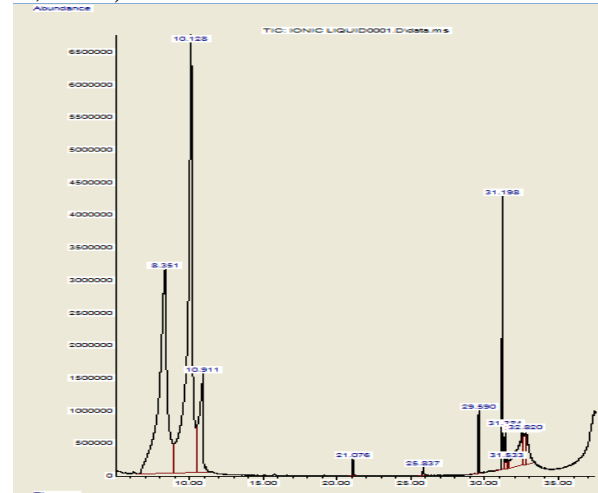


Figure 1: Chromatogram of Ionic Liquid (1-butyl-1-methylpyrrolidinium tetrafluoroborate)

3.1.2 Functional groups of the IL

The functional groups of the ionic liquid are identified using Figure 2's FTIR spectra. The =C–O–C symmetric and asymmetric stretch, C–H stretch, O–H stretch, C–C stretch, N–H bend, and C=O stretch were found to be the main functional groups of the ionic liquid. The ionic liquid (1-butyl -methylpyrrolidinium tetrafluoroborate) contains heteroatoms of nitrogen and oxygen. There is also the presence of double bonds. These features suggest that they possess suitable corrosion-inhibitive properties (Suleiman et al, 2020).

Figure 2: Functional groups of the Ionic Liquid

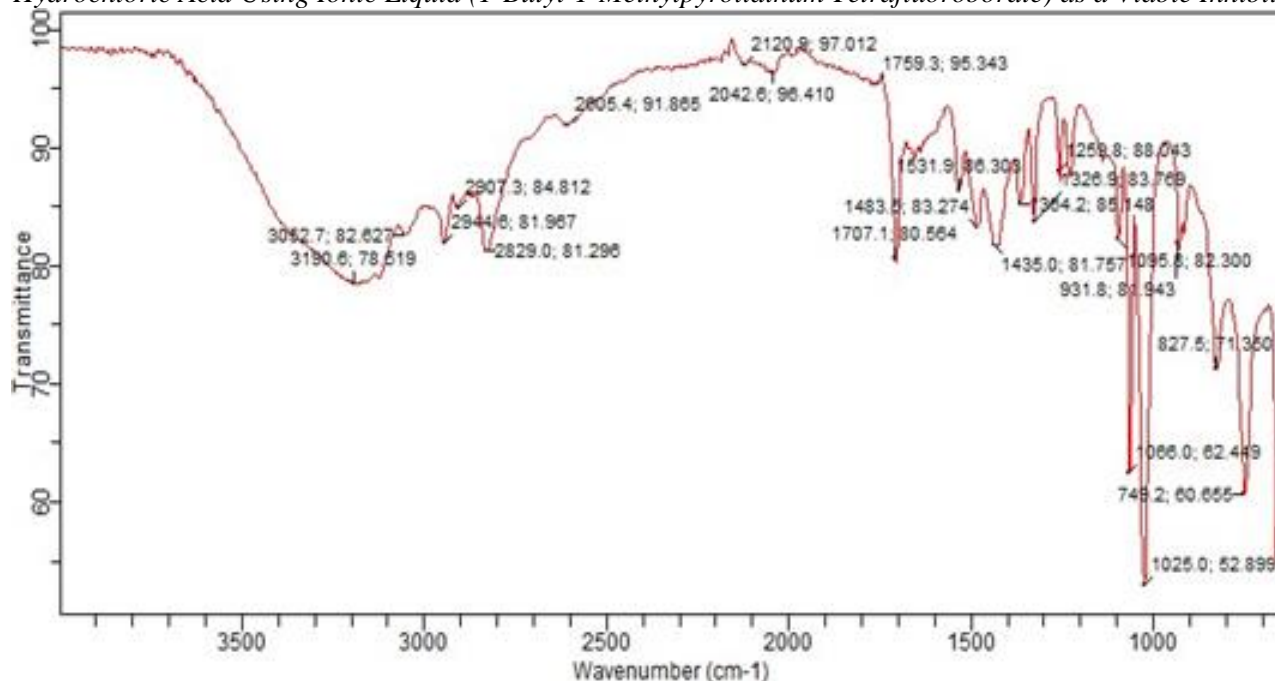


Figure 2: Functional groups of the Ionic Liquid

3.2 Thermometric Results

Table 1 shows the effects of inhibitor concentration on the reactivity number (RN) and inhibition efficiency (IE) of mild steel in HCl solution. There is an inverse correlation between the inhibition efficiency (IE) and the reaction number. The value of the reaction number was computed as a function of the ratio of temperature change to the maximum time obtained. The number of reactions dropped as the inhibitor's concentration increased. As the inhibitor concentration rose in both situations, inhibition energy (IE) increased until it peaked at 0.7 g/L hydrochloric acid solution.

Table 1: Effect of concentration on the efficiency as determined by thermometric routine

| Conc., g/L | RN (°C/min.) | IE (%) |
|------------|--------------|--------|
| 0.0 | 0.4172 | |
| 0.1 | 0.1947 | 53.33 |
| 0.3 | 0.1392 | 66.63 |
| 0.5 | 0.099 | 76.26 |
| 0.7 | 0.0128 | 96.92 |
| 0.9 | 0.0213 | 94.89 |

3.3 Effects of control variables on IL's effectiveness

This result is consistent with Onukwuli and Omotioma's (2016) report. With a higher inhibitory efficiency of 96.72%, the ionic liquid excels. This could be a result of the ionic liquid molecules' increased affinity for the mild steel surface.

The effects of time, temperature, and concentration on the effectiveness of 1-butyl-1-methylpyrrolidinium tetrafluoroborate (IL) are shown in Tables 2 to 5. Table 2 demonstrates that both weight loss and corrosion rate increased with time. Over three hours, the level of inhibition efficiency and surface coverage peaked. After peaking, the efficiency decreased from 96.05% to 92.59%. A reduction in the force of attraction between the ionic liquid molecules and the mild steel surface can account for this. Table 3 shows that the weight loss and corrosion rate decrease with increasing inhibitor concentration. These discoveries arose from an increase in electrostatic attraction (Jadhav et al., 2019; Omotioma and Onukwuli, 2019). Table 4 shows that a temperature increase reduces the ionic liquid's ability to block.

Table 2: Effect of time on the effectiveness of IL

| t (hr) | Δw_0 (g) | CR_0 (mg/cm ² hr) | ΔW_1 (g) | CR_1 | I.E.(%) | Θ |
|--------|------------------|--------------------------------|------------------|--------|---------|----------|
| 1 | 0.11 | 12.222 | 0.01 | 1.111 | 90.91 | 0.9091 |
| 2 | 0.24 | 13.333 | 0.02 | 1.111 | 91.67 | 0.9167 |
| 3 | 0.76 | 28.148 | 0.03 | 1.111 | 96.05 | 0.9605 |
| 4 | 0.79 | 21.944 | 0.05 | 1.389 | 93.67 | 0.9367 |
| 5 | 0.81 | 18.000 | 0.06 | 1.333 | 92.59 | 0.9259 |

Table 3: Effect of concentration on the effectiveness of IL at 313K

| Conc. (g/L) | ΔW_0 (g) | C.R ₀ (mg/hr.cm ²) | ΔW_1 (g) | CR ₁ (mg/hr.cm ²) | IE (%) | Θ |
|-------------|------------------|---|------------------|--|--------|----------|
| 0.0 | 0.76 | 28.148 | | | | |
| 0.1 | | | 0.27 | 10.00 | 64.47 | 0.6447 |
| 0.3 | | | 0.22 | 8.148 | 71.05 | 0.7105 |
| 0.5 | | | 0.11 | 4.074 | 85.53 | 0.8553 |
| 0.7 | | | 0.03 | 1.111 | 96.05 | 0.9605 |
| 0.9 | | | 0.04 | 1.481 | 94.74 | 0.9474 |

Table 4: Effect of temperature on the effectiveness of IL

| Temp. (K) | Δw_0 (g) | CR ₀ (mg/hr.cm ²) | $\Delta \hat{w}_1$ (g) | C.R ₁ (mg/hr.cm ²) | I.E (%) | Θ |
|-----------|------------------|--|------------------------|---|---------|----------|
| 303 | 0.74 | 27.407 | 0.05 | 1.852 | 93.24 | 0.9324 |
| 313 | 0.76 | 28.148 | 0.03 | 1.111 | 96.05 | 0.9605 |
| 323 | 0.79 | 29.259 | 0.10 | 3.704 | 87.34 | 0.8734 |
| 333 | 0.81 | 30.000 | 0.13 | 4.815 | 83.95 | 0.8395 |
| 343 | 0.83 | 30.741 | 0.16 | 5.926 | 80.72 | 0.8072 |

Table 5: Effect of concentration on the effectiveness of IL at 323K

| Inh. Conc. (g/L) | Δw_0 (g) | CR ₀ (mg/hr.cm ²) | ΔW_1 (g) | CR ₁ (mg/hr.cm ²) | I.E. (%) | Θ |
|------------------|------------------|--|------------------|--|----------|----------|
| 0.0 | 0.79 | 29.259 | | | | |
| 0.1 | | | 0.34 | 12.59 | 56.96 | 0.5696 |
| 0.3 | | | 0.31 | 11.48 | 60.76 | 0.6076 |
| 0.5 | | | 0.25 | 9.259 | 68.35 | 0.6835 |
| 0.7 | | | 0.10 | 3.704 | 87.34 | 0.8734 |
| 0.9 | | | 0.13 | 4.815 | 83.54 | 0.8354 |

3.4 Activation energy result

The activation energy statistics for the inhibition of mild steel corrosion are shown in Table 6. Figure 3, on the other hand, shows the graph of the Ea criterion. In both cases, the activation energy values were below the 80 kJ/mol standard. This suggests that the inhibitory process is mediated by a physical adsorption mechanism (Idris et al, 2013; Omotioma and Onukwuli, 2017).

Table 6: Activation energy result

| T(K) | 1-butyl-1-methylpyrolidinium tetrafluoroborate CR (mg/cm ² hr) | E _a (kJ/mol) |
|------|--|-------------------------|
| 303 | 1.852 | 32.60 |
| 313 | 1.111 | |
| 323 | 3.704 | |
| 333 | 4.815 | |
| 343 | 5.926 | |

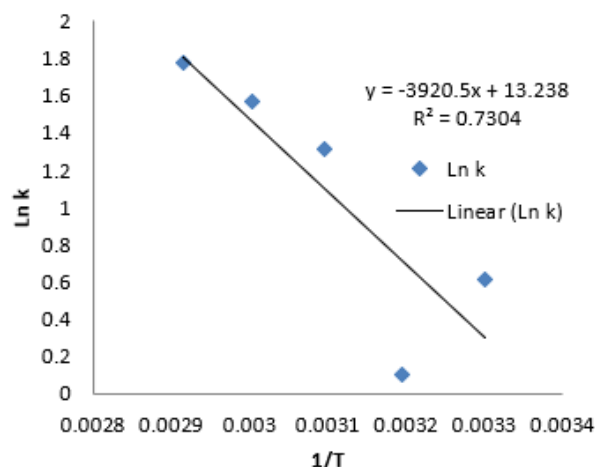


Figure 3: Graph for the determination of activation energy

3.5 Heat of Adsorption

The adsorption heat values for the inhibitor's mild steel corrosion control in HCl are shown in Table 7. It shows negative heat of adsorption, indicating an exothermic mechanism for the inhibitor's adsorption on the mild steel surface. It agrees with the assertions of Onukwuli and Omotioma (2016) and Idris et al (2013).

Table 7: Heat of adsorption values

| Concentration (g/L) | Q_{ads} (J/mol) (1-butyl-1-methylpyrrolidinium tetrafluoroborate) |
|---------------------|---|
| 0.1 | -26532.4 |
| 0.3 | -38720.3 |
| 0.5 | -84647.8 |
| 0.6 | -105909 |
| 0.9 | -106483 |

3.6 Adsorption Parameters for the Corrosion Control

The graph of the Langmuir adsorption isotherm for $\log(C/\theta)$ versus $\log(C)$ is displayed in Figure 4. Substituting linear graph plots, the correlation of determination (R^2) was almost one (1). There is a strong adherence to the Langmuir adsorption isotherm. This aligns with the findings of Charitha et al (2017). Figure 5 displays plots of θ vs. $\log C$ on the Temkin isotherm. Each of them also generated a linear graph that showed that they followed the Temkin adsorption isotherm. Nevertheless, considering their R^2 values, it was discovered that the Langmuir isotherm, whose R^2 is nearer to one (1), better fit the data.

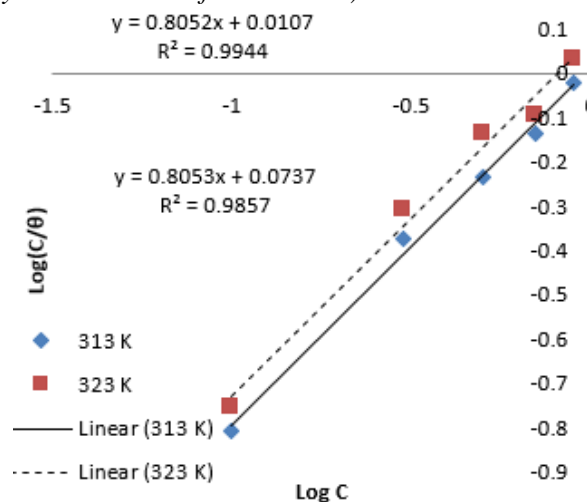


Figure 4: Langmuir isotherm plot for 1-butyl-1-methylpyrrolidinium tetrafluoroborate

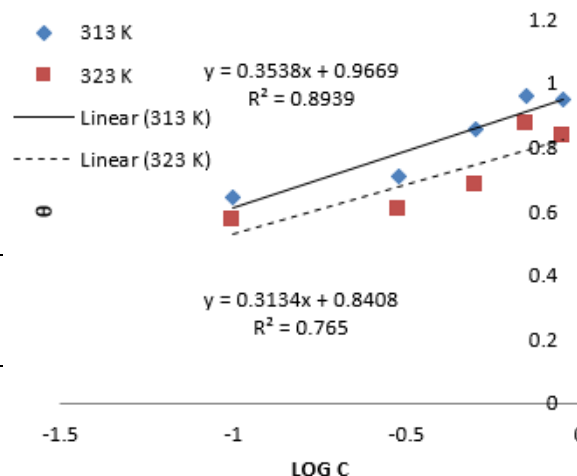


Figure 5: Temkin isotherm plot for 1-butyl-1-methylpyrrolidinium tetrafluoroborate

4.1 Conclusion

The following deductions were made from the evaluation of the experimental results: The thermodynamic study revealed that the corrosion inhibition process is spontaneous and exothermic, indicating that ionic liquids can effectively stabilize the metal surface. Conversely, computational models were used to investigate the adsorption behavior of ionic liquid (IL) on the mild steel surface. The IL (1-butyl-1-methylpyrrolidinium tetrafluoroborate) contains 1H-imidazole, 1'-carbonyldiimidazole, 1H-pyrazole, and methyl tetradecanoate. Heterocyclic molecules with

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branches are also present in the ionic liquid, indicating that it is appropriate for inhibiting corrosion. The main functional groups of 1-butyl -methylpyrrolidinium tetrafluoroborate were found to be the C-H stretch, O-H stretch, C C stretch, N-H ben, C = O stretch, C = C stretch, and =C–O–C symmetric and asymmetric stretch. The number of reactions decreased as the inhibitor's concentration rose, according to thermometric measurements. Conversely, the efficiency of inhibition increased with the inhibitor's concentration and peaked at 0.7 g/L. One possible explanation for the high inhibitory efficacy (96.92%) of 1-butyl -methylpyrrolidinium tetrafluoroborate could be that the ionic liquid molecules' increased affinity for the mild steel surface. The effectiveness of ionic liquids' inhibition was influenced by temperature, immersion duration, and inhibitor concentration. As the inhibitor's concentration and duration increased, so did its efficiency of inhibition; however, as the temperature climbed, this efficiency decreased. The physical adsorption and exothermic character of the corrosion inhibition mechanism were shown by thermodynamic experiments. The quadratic model provided a satisfactory explanation for the relationship between the variables of temperature, time, and inhibitor concentration and the effectiveness of inhibition. 95.37% was reported to be the best inhibitory efficiency for 1-butyl -methylpyrrolidinium tetrafluoroborate. Since the Langmuir isotherm's R^2 is closer to one.

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