



Studying the Effect of Paracetamol Drug on the Conductivity of 0.5M Hydrochloric Acid Solution at Different Temperatures

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Abstract:

In this study paracetamol drug is used to reduce the conductivity of 0.5M hydrochloric acid at different concentrations for each one of them at different temperatures ranged (30-60)°C. Generally , increasing of the concentration of the inhibitor leads to reducing in conductivity of the acid at constant temperature. On the other hand, at constant concentration of inhibitor, the conductivity is reduced as temperature increased i.e., paracetamol can adsorbed chemically on the metal or alloy. Furthermore the kinetic study of the molar conductance process reveal that in presence of paracetamol the activation energy and enthalpy of activation are negative compared with their values in absence of paracetamol where they are negative because the reducing the conductivity in presence of paracetamol where the non spontaneous property for the conductance of acid is increased as the paracetamol concentration increased in addition to increasing the negative value of entropy in presence of paracetamol that indicate to restrict for the mobility of hydrogen and chloride ions which correspond to 90.47% as efficiency of reducing the conductance of acid by paracetamol. On the other hand thermodynamic study is achieved which explained the adsorption of paracetamol obey to Freundlich model.

Keywords: molar conductance, adsorption isotherms, paracetamol, corrosion Inhibitors, Hydrochloric acid.



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1. Introduction:

Acid pickling baths are employed to remove undesirable scale from the surface of the metals. Once the scale is removed, the acid is then free for further attack on the metal surface. Hence, several organic compounds containing N, O and S have been studied as corrosion inhibitors by several authors [1,2]. The use of organic compounds with hetero atoms based corrosion inhibitors is often associated with chemical and/or physical adsorption, involving a variation in the charge of adsorbed substance and a transfer of charge from one phase to the other [3]. Special attention was paid to the effect of electron donating atom and electron

With drawing groups which are responsible for adsorption and hence on the performance [4]. Furthermore, it has been observed that the adsorption mainly depends on steric factor, aromaticity and structural properties of the organic compounds, which induce greater adsorption of the inhibitor molecules onto the surface of the metal [5,6]. Synergistic corrosion inhibitor plays an important role both in theoretical and practical research [7,9]. Synergistic inhibition effects of organic inhibitor/metallic ion mixture and organic inhibitors/organic inhibitor mixture on the corrosion metal in acid media have also been reported[10-12]. Evaluation of corrosion inhibitors for mild steel in acidic media is important for both theoretical as well as industrial point of views. Acid solutions are generally used for the removal of rust and scale in industrial processes. Hydrochloric acid is widely used in the pickling, cleaning and descaling of steel and ferrous alloys[13]. Thus, mineral acid solutions such as hydrochloric acid are widely used for various treatments of materials in industry[14,15]. The corrosion of metallic materials in acidic solution causes considerable costs. In order to reduce the corrosion of metals, several techniques have been applied. The use of inhibitors during acid pickling procedure is one of the most practical methods for protection against corrosion in acidic media[16]. Hence, inhibitors are used to reduce the rate of dissolution of metals by using compounds containing N, S, and O atoms have been reported as excellent inhibitors[17]. Conductivity measurements are widely used in industry. Some important applications are described like water treatment, Raw water as it comes from a lake, river, or the tap is rarely suitable for industrial use. The water contains contaminants, largely ionic, that if not removed will cause scaling and corrosion in plant equipment, particularly in heat exchangers, cooling towers, and boilers[18]. Conductivity is typically measured in aqueous solutions of electrolytes. Electrolytes are substances containing ions, i.e. solutions of ionic salts or of compounds that ionize in solution. The ions formed in solution are responsible for carrying the electric current. Electrolytes include acids, bases and salts and can be either strong or weak. Most conductive solutions measured are aqueous solutions, as water has the capability of stabilizing the ions formed by a process called solvation. As a result, the concentration of ions in solution is proportional to the concentration of the electrolyte added. They include ionic solids and strong acids, for example HCl. Solutions of strong electrolytes conduct electricity because the positive and negative ions can migrate largely independently under the influence of an electric field[19]. Paracetamol (acetaminophen) is commonly used as an analgesic and antipyretic drug in pharmaceutical formulations solely or in the mixtures with a few contaminants, typically caffeine, acetylsalicylic acid and some others. It is extensively used in the treatment of mild to moderate pain and fever and available without a prescription. Overdose of paracetamol can lead to hepatic necrosis or renal failure[20].

In this study the paracetamol drug at different concentrations i.e., (10-50)ppm were prepared as inhibitor for the conductivity of 0.50M HCl at constant temperature. On the other hand, the effect of temperature on the inhibition effect of paracetamol against the conductivity of the 0.50M HCl at constant concentration was studied at range (30-60) °C in order to evaluate the paracetamol as a corrosion inhibitor for steel or other alloy or metals depending on the reducing of the conductivity of the corrosive environment like acid i.e., 0.50M HCl. Thus, the molar conductivity is used in this study because the concentration of electrolyte (corrosive environment) is taken into account.

2. Experimental part:

After the extraction of additives from a paracetamol by using a methanol as solvent, a stock solution of purified Paracetamol (1000 ppm) was prepared by dissolving 1g of paracetamol in 1L of 0.50M HCl as a solvent then, a different concentrations of paracetamol is prepared (10-50)ppm by using 0.50M HCl as a solvent to study their role on the molar conductance of 0.5M hydrochloric acid in addition to study the effect of temperature on the molar conductance of hydrochloric acid in presence and absence of paracetamol. The structure of paracetamol(*N*-(4-hydroxyphenyl) acetamide) is show below in Figure 1:

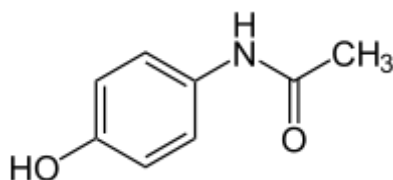


Figure 1: Structure of Paracetamol (*N*-(4-hydroxyphenyl)acetamide).

Then the conductivity of 0.50M HCl is measured in the absence and presence of different concentration of paracetamol i.e., (10-50) ppm at different temperatures where, the conductivity of distilled water at the temperatures ranged (30-60) °C is subtracted from the conductivity of 0.50M HCl solutions whether in presence or absence of paracetamol. On the other hand, the cell constant values of the conductance cell is measured experimentally by using 0.1M KCl solution at different temperatures ranged (30-60) °C as shown in Table 1:

**Table1: The cell constant relative to 0.10M potassium chloride solution at different temperatures:**

Cell constant.cm ⁻¹	Temperature (°C)
0.91	30
0.85	40
0.80	50
0.71	60

Thus, the study of the effect of concentrations of paracetamol on the molar conductance of the mentioned acid at constant temperature and the reverse can be explained as in results below:

3. Results and Discussions:

1. Study the effect of concentration of paracetamol on the molar conductance of 0.50M HCl at constant temperatures:

The conductivity of the 0.5M hydrochloric acid is measured in absence and presence of paracetamol relative to the conductivity of the distilled water according to the following equation:

$$G_{\text{solute}} = G_{\text{solution}} - G_{\text{solvent}} \quad \dots\dots\dots 1$$

Where G is the conductivity in Ω^{-1} , G_{solute} , G_{solution} and G_{solvent} are the conductivity in Ω^{-1} (Semens) for the 0.50 M HCl, the conductivity for the solution and the conductivity for the solvent respectively. On the other hand the specific conductance for the hydrochloric acid solution is measured according to the following equation:

$$\kappa_{\text{solute}} = A \times G_{\text{solute}} \quad \dots\dots\dots 2$$

Where κ is the specific conductance of the solute in $\Omega^{-1}.\text{cm}^{-1}$. Hence, the molar conductance is calculated according to the following equation:

$$\Lambda_{\text{molar}} = \frac{10^3 \times \kappa}{C} \quad \dots\dots\dots 3$$

Where Λ_{molar} is the molar conductance in $\Omega^{-1}.\text{mol}^{-1}.\text{cm}^2$ and C is the concentration of the hydrochloric acid respectively where C = 0.50M thus, the concentrations of paracetamol is used to study the effect of paracetamol on the conductivity of hydrochloric acid. In fact, the study of the molar conductance is used due to it express to the real conductivity for electrolyte i.e., hydrochloric acid because, it take into account the concentration of the electrolyte. Thus, the reducing in molar conductivity of the acid can be calculated according to the following equation :

$$\text{Eff}\% = \frac{\Lambda_{\text{Blank}} - \Lambda_{\text{Inhibitor}}}{\Lambda_{\text{Blank}}} \times 100 \quad \dots\dots\dots 4$$

Where efficiency% is the efficiency of paracetamol to reduce the molar conductance of hydrochloric acid, Λ_{Blank} and $\Lambda_{\text{Inhibitor}}$ are the molar conductance of hydrochloric acid in absence and presence of paracetamol as inhibitor respectively. On the other hand, the ionic mobility can be calculated for the hydrochloric acid according to the following equations:

$$U = \frac{\Lambda}{F} \quad \dots\dots\dots 5$$

Where U is the ionic mobility $\text{m}^2.\text{s}^{-1}.\text{V}^{-1}$ for hydrochloric acid and F is Faraday's constant ($96500 \text{ Coloumb}.\text{mol}^{-1}$). Hence the efficiency and the ionic mobility can be listed as in Tables (2-5) as below:

Table 2 : The molar conductance of 0.50M HCl in presence of different concentrations of paracetamol compared with hydrochloric acid alone at 30°C.

Compound	Conc.(ppm)	$\Lambda / \Omega^{-1} \text{ mol}^{-1}.\text{cm}^2$	$U / \text{m}^2 \text{ s}^{-1}.\text{V}^{-1} \times 10^{-4}$	Eff%
Hydrochloric acid	18250	388.8	40.29	-
paracetamol	10	72.8	7.54	81.21
paracetamol	20	69.2	7.17	82.14
paracetamol	30	63.8	6.61	83.53
paracetamol	40	60.0	6.23	84.50
paracetamol	50	56.40	5.84	85.43

**Table 3: The molar conductance of 0.50M HCl in presence of different concentrations of paracetamol compared with hydrochloric acid alone at 40°C.**

Compound	Conc.(ppm)	$\Lambda / \Omega^{-1} \text{ mol}^{-1} \cdot \text{cm}^2$	$U / \text{m}^2 \text{ s}^{-1} \cdot \text{V}^{-1} \times 10^{-4}$	Eff%
Hydrochloric acid	18250	438.9	45.48	-
paracetamol	10	71.4	7.40	83.79
paracetamol	20	66.4	6.88	84.93
paracetamol	30	61.2	6.34	86.12
paracetamol	40	57.8	5.99	86.89
paracetamol	50	54.4	5.64	87.67

Table 4: The molar conductance of 0.50M HCl in presence of different concentrations of paracetamol compared with hydrochloric acid alone at 50°C.

Compound	Conc.(ppm)	$\Lambda / \Omega^{-1} \text{ mol}^{-1} \cdot \text{cm}^2$	$U / \text{m}^2 \text{ s}^{-1} \cdot \text{V}^{-1} \times 10^{-4}$	Eff%
Hydrochloric acid	18250	484.4	50.20	-
paracetamol	10	68.8	7.13	85.61
paracetamol	20	64.0	6.63	86.60
paracetamol	30	60.8	6.30	87.26
paracetamol	40	57.6	5.97	87.92
paracetamol	50	52.6	5.45	89.38

Table 5: The molar conductance of 0.50M HCl in presence of different concentrations of paracetamol compared with hydrochloric acid alone at 60°C.

Compound	Conc.(ppm)	$\Lambda / \Omega^{-1} \text{ mol}^{-1} \cdot \text{cm}^2$	$U / \text{m}^2 \text{ s}^{-1} \cdot \text{V}^{-1} \times 10^{-4}$	Eff%
Hydrochloric acid	18250	533.4	55.27	-
paracetamol	10	63.8	6.61	87.82
paracetamol	20	59.4	6.16	88.64
paracetamol	30	55.2	5.72	89.42
paracetamol	40	53.8	5.58	89.68
paracetamol	50	49.6	5.14	90.47

From the above tables the ionic mobility of the acid is reduced as the concentration of paracetamol is increased which leads to reduce in its molar conductivity this can be attributed to the increasing the ability of paracetamol as its concentration is increased to retard the mobility of the hydrogen and chloride ions for hydrochloric acid toward the their oppose electrodes where the increasing of inhibition efficiency of paracetamol is increased as its concentration is increased hence, paracetamol can be evaluated as corrosion inhibitor for a certain metal or alloy due to its ability to reduce the ionic mobility of hydrochloric acid i.e., reducing the evolution of hydrogen gas on the cathode or on the metal surface if immersed in HCl solution i.e., reduce in molar conductance of hydrochloric acid. Thus, the results of the maximum inhibition efficiency about 90.47% which approximately correspond with another study for using a paracetamol as corrosion inhibitor for mild steel alloy in sulfuric acid where, the maximum efficiency for a paracetamol is 85% [21]. The relation between efficiency and concentration of paracetamol can be shown as in Figures (2-5) below:

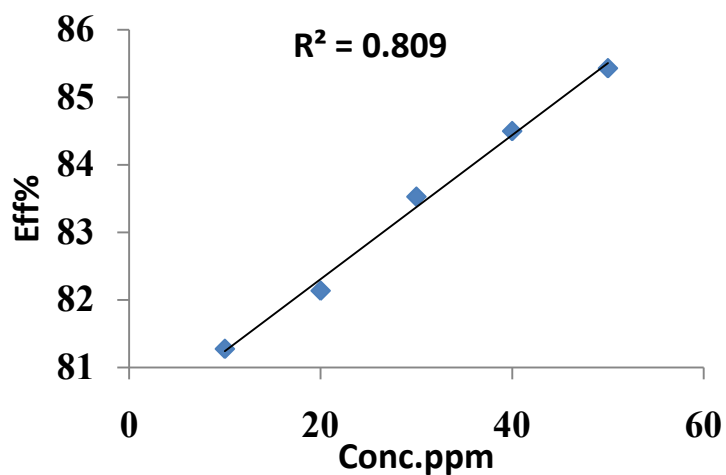


Figure 2: The relation between inhibition efficiency of Paracetamol and its concentrations against the molar conductance of 0.5M HCl at 30°C.

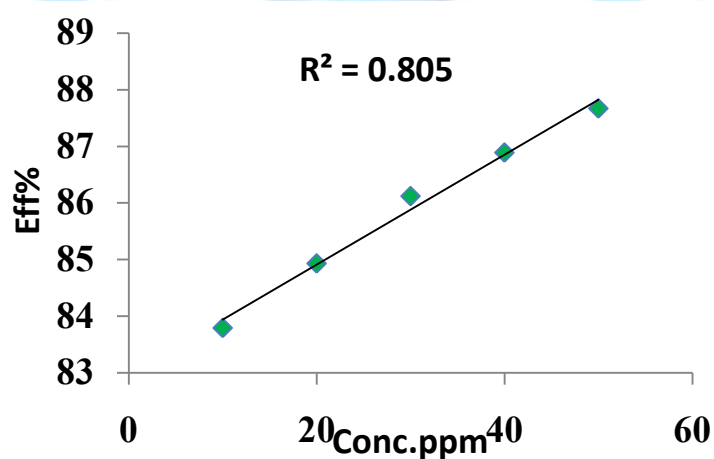


Figure 3: The relation between inhibition efficiency of Paracetamol and its concentrations against the molar conductance of 0.5M HCl at 40°C.

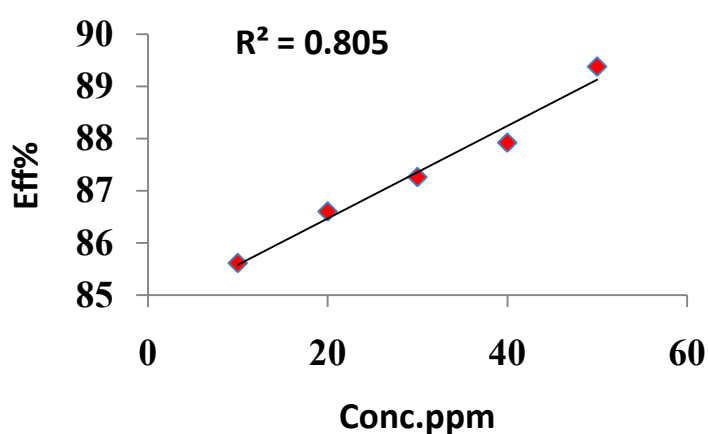


Figure 5: The relation between inhibition efficiency of Paracetamol and its concentrations against the molar conductance of 0.5M HCl at 50°C.

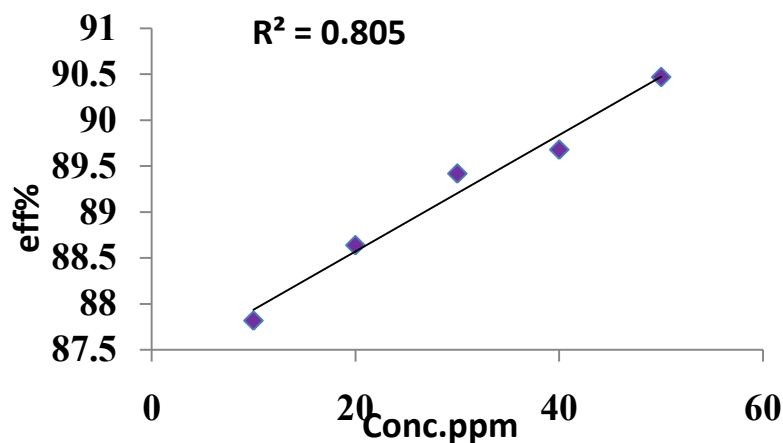


Figure 6: The relation between inhibition efficiency of Paracetamol and its concentrations against the molar conductance of 0.5M HCl at 60°C.

The relation between efficiency and concentration of paracetamol at different temperatures can be summarized as in Figure 7:

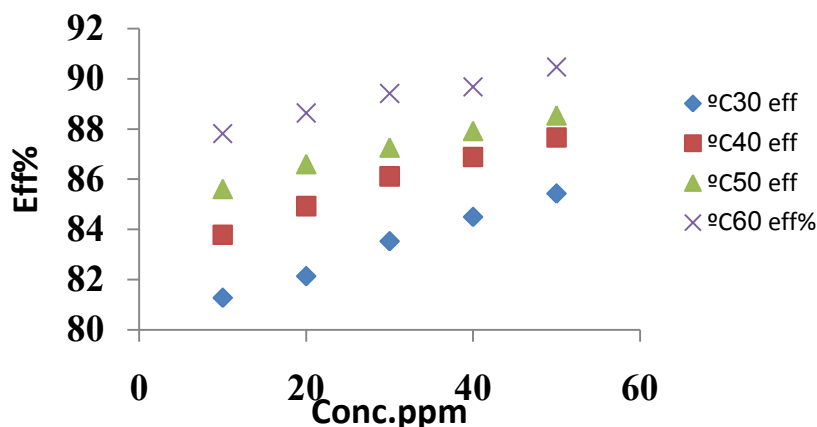


Figure 7: The relation between inhibition efficiency of Paracetamol and its concentrations against the molar conductance of 0.5M HCl at different temperatures.

On the other hand, the relation between ionic mobility of hydrochloric acid in presence of different concentration of paracetamol at different temperatures can be shown in Figure 8 where the zero concentration of paracetamol means presence of acid only without paracetamol.

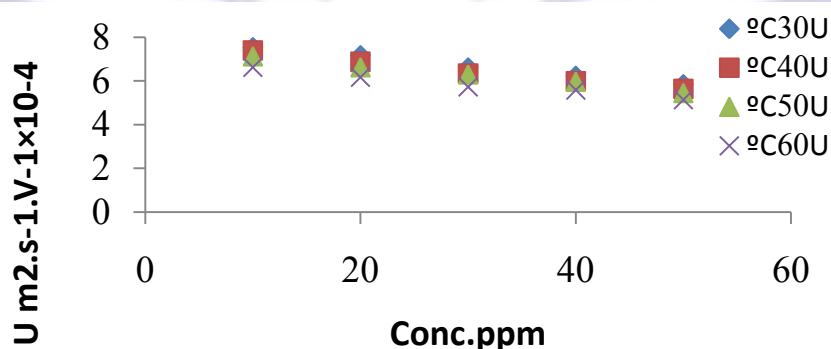


Figure 8: variation of the ionic mobility for 0.5M HCl at different concentrations of Paracetamol at different temperatures.

As in Figure 8 above generally, the ionic mobility of hydrochloric acid is reduced as the concentration of paracetamol is increased at different temperatures ranged (30-60) °C especially at 60 °C this can be attributed to reducing the activation energy of paracetamol to inhibit the mobility of hydrogen and chloride ions toward the opposite electrodes thus, the



reducing in molar conductance for hydrochloric acid as increasing the concentration of paracetamol will be occurred at the above range of temperatures corresponding to the case of ionic mobility as shown in Figure 9 below:

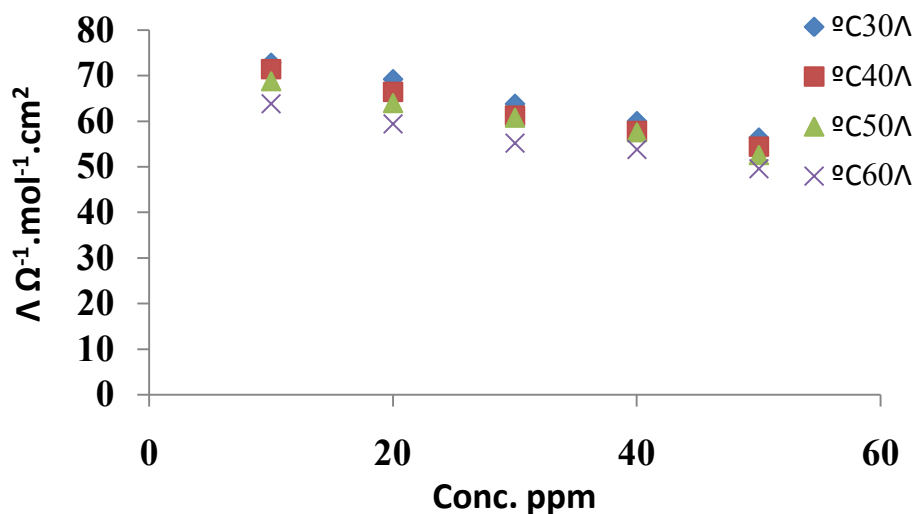


Figure 9: variation of Molar conductance for 0.5M HCl at different concentrations of Paracetamol a different temperatures.

2. Study the effect of temperature on the molar conductance of 0.50M HCl at constant concentration of paracetamol:

The effect of temperature on the molar conductance for 0.5M HCl in the presence and absence of paracetamol was studied which can be summarized in Tables (6-11) as below:

Table 6: The effect of temperature on molar conductance of 0.50 M (18250ppm) HCl in absence of paracetamol:

Compound	Temp. (°C)	$\Lambda / \Omega^{-1} \text{mol}^{-1} \cdot \text{cm}^2$	$U / \text{m}^2 \text{s}^{-1} \cdot \text{V}^{-1} \times 10^{-4}$	Eff%
Hydrochloric acid	30	388.8	40.29	-
Hydrochloric acid	40	438.9	45.48	-
Hydrochloric acid	50	484.4	50.20	-
Hydrochloric acid	60	533.4	55.27	-

Table 7: The effect of temperature on molar conductance of 0.50 M (18250ppm) HCl in presence of 10ppm of paracetamol:

Compound	Temp. (°C)	$\Lambda / \Omega^{-1} \text{mol}^{-1} \cdot \text{cm}^2$	$U / \text{m}^2 \text{s}^{-1} \cdot \text{V}^{-1} \times 10^{-4}$	Eff%
paracetamol	30	72.8	7.54	81.21
paracetamol	40	71.4	7.40	83.79
paracetamol	50	68.8	7.13	85.61
paracetamol	60	63.8	6.61	87.82

Table 8: The effect of temperature on molar conductance of 0.50 M (18250ppm) HCl in presence of 20ppm of paracetamol:

Compound	Temp. (°C)	$\Lambda / \Omega^{-1} \text{mol}^{-1} \cdot \text{cm}^2$	$U / \text{m}^2 \text{s}^{-1} \cdot \text{V}^{-1} \times 10^{-4}$	Eff%
paracetamol	30	69.2	7.17	82.14
paracetamol	40	66.4	6.88	84.93
paracetamol	50	64.0	6.63	86.60
paracetamol	60	59.4	6.16	88.64

**Table 9: The effect of temperature on molar conductance of 0.50 M (18250ppm) HCl in presence of 30ppm of paracetamol:**

Compound	Temp. (°C)	$\Lambda / \Omega^{-1} \text{ mol}^{-1} \cdot \text{cm}^2$	$U / \text{m}^2 \text{ s}^{-1} \cdot \text{V}^{-1} \times 10^{-4}$	Eff%
paracetamol	30	63.8	6.61	83.53
paracetamol	40	61.2	6.34	86.12
paracetamol	50	60.8	6.30	87.26
paracetamol	60	55.2	5.72	89.42

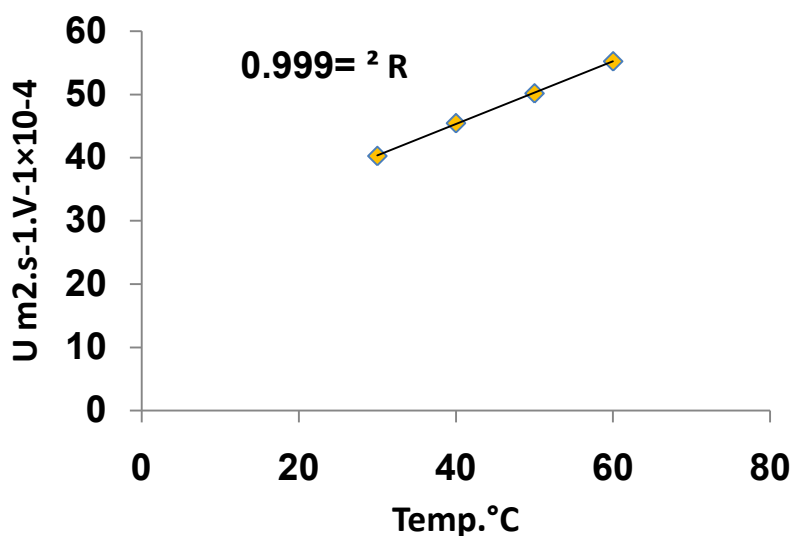
Table 10 : The effect of temperature on molar conductance of 0.50 M (18250ppm) HCl in presence of 40ppm of paracetamol:

Compound	Temp. (°C)	$\Lambda / \Omega^{-1} \text{ mol}^{-1} \cdot \text{cm}^2$	$U / \text{m}^2 \text{ s}^{-1} \cdot \text{V}^{-1} \times 10^{-4}$	Eff%
paracetamol	30	60.0	6.23	84.50
paracetamol	40	57.8	5.99	86.89
paracetamol	50	57.6	5.97	87.92
paracetamol	60	53.8	5.58	89.68

Table 11: The effect of temperature on molar conductance of 0.50 M (18250ppm) HCl in presence of 50ppm of paracetamol:

Compound	Temp. (°C)	$\Lambda / \Omega^{-1} \text{ mol}^{-1} \cdot \text{cm}^2$	$U / \text{m}^2 \text{ s}^{-1} \cdot \text{V}^{-1} \times 10^{-4}$	Eff%
paracetamol	30	56.40	5.84	85.43
paracetamol	40	54.4	5.64	87.67
paracetamol	50	52.6	5.45	89.38
paracetamol	60	49.6	5.14	90.47

As shown from the above tables the molar conductance of acid is increased as temperature increased due to the ionic mobility for acid ions is increased as in Table 6 but, when a paracetamol is added at different concentrations i.e., (10-50)ppm Tables (7-11), each one of the mentioned concentrations reduced the molar conductance of acid because, the ionic mobility of acid is reduced in presence of paracetamol where the efficiency of inhibition of conductivity is increased. Furthermore, the highest concentration of paracetamol has the higher ability to reduce the molar conductance of acid compared with lowest concentration as in Tables (7-11). The relation between ionic mobility of acid and temperatures can be shown as in Figures (10-15) below:

**Figure 10: Variation of ionic mobility of 0.5M HCl with temperature in absence of paracetamol.**

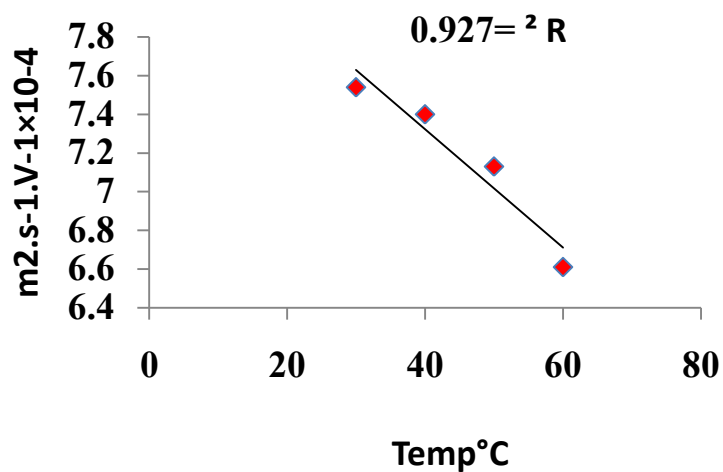


Figure 11: Variation of ionic mobility of 0.5M HCl with temperature in presence of 10 ppm paracetamol.

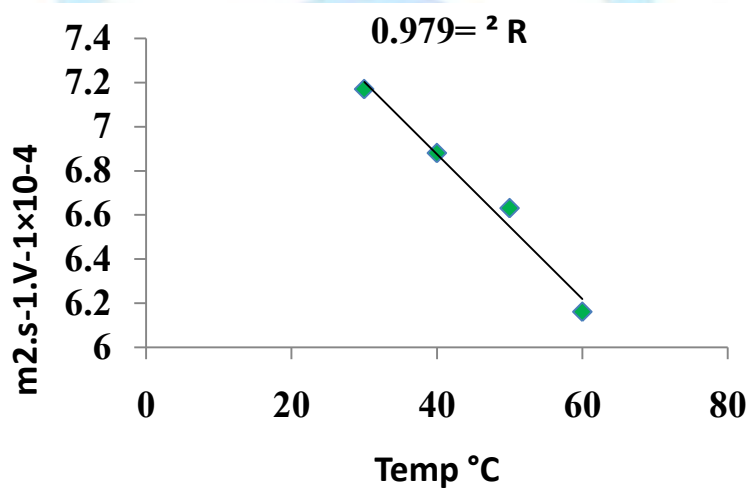


Figure 12: Variation of ionic mobility of 0.5M HCl with temperature in presence of 20 ppm paracetamol.

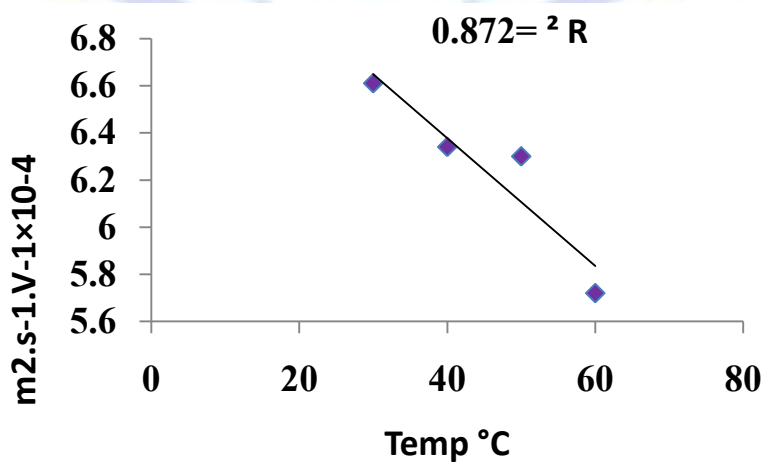


Figure 13: Variation of ionic mobility of 0.5M HCl with temperature in presence of 30 ppm paracetamol.

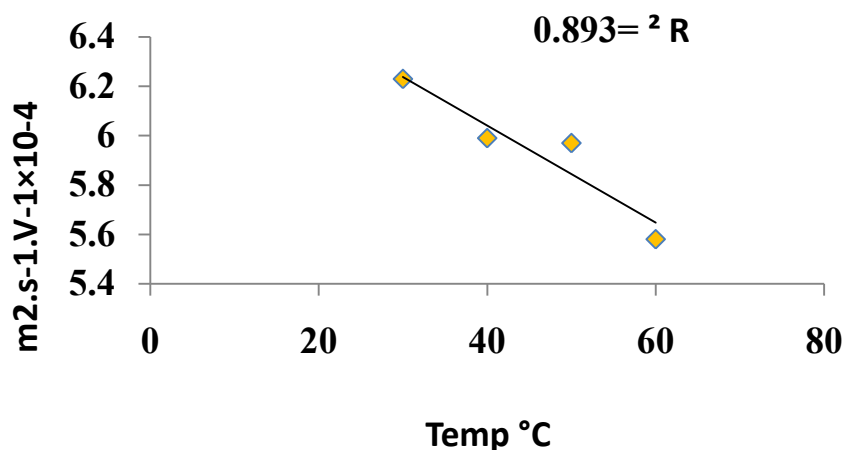


Figure 14: Variation of ionic mobility of 0.5M HCl with temperature in presence of 40 ppm paracetamol.

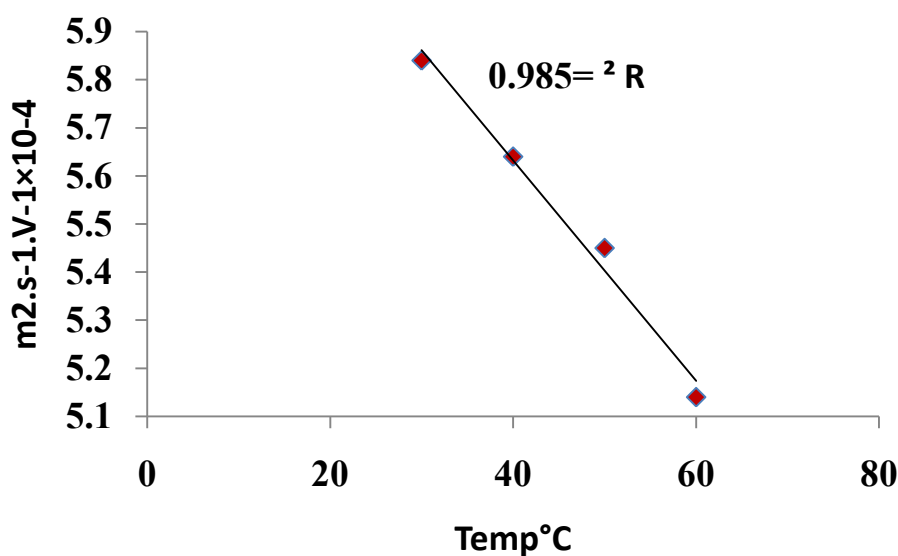


Figure 15: Variation of ionic mobility of 0.5M HCl with temperature in presence of 50 ppm paracetamol.

On the other hand, the increasing of inhibition efficiency with temperatures is predominant at all concentrations of paracetamol especially at higher concentration i.e., decreasing the activation energy that needed for paracetamol as temperature increase to reduce the molar conductance of acid hence, increasing the concentration of paracetamol make it has more strong ability to reduce the conductance of acid in other words increasing temperature leads increase the activation energy for acid ions to transport toward the oppose electrode in the conductance cell. The relation between inhibition efficiency and temperature is shown in Figures (16-20) below:

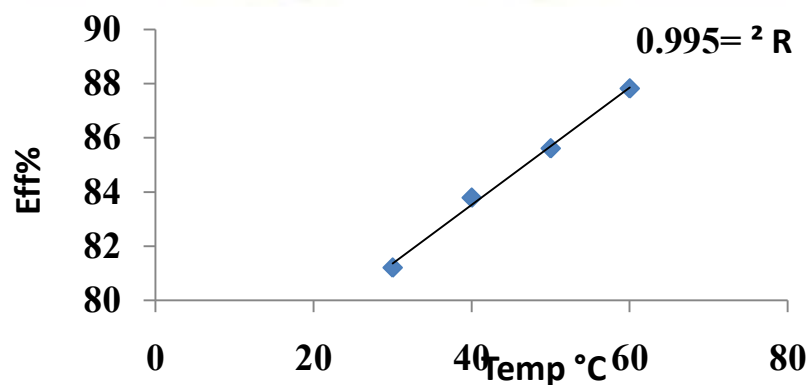


Figure 16: Variation of inhibition efficiency of 10 ppm paracetamol against the molar conductance for 0.5M HCl with temperature .

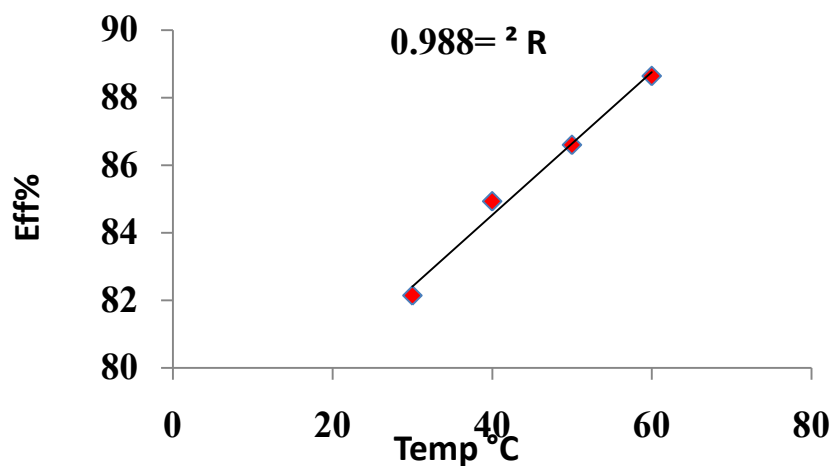


Figure 17: Variation of inhibition efficiency of 20 ppm paracetamol against the molar conductance for 0.5M HCl with temperature .

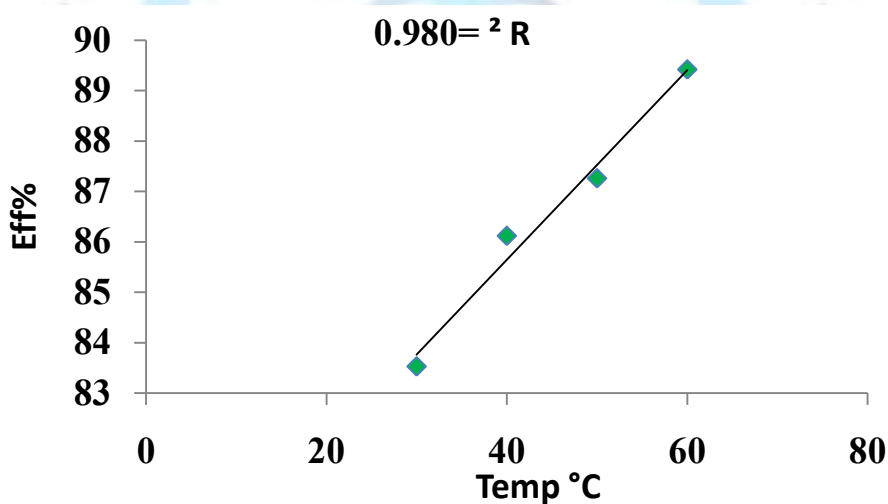


Figure 18: Variation of inhibition efficiency of 30 ppm paracetamol against the molar conductance for 0.5M HCl with temperature .

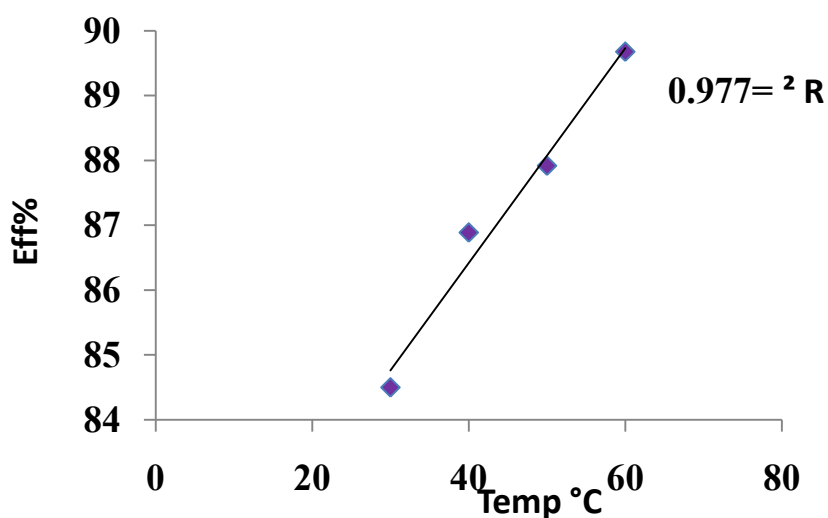


Figure 19: Variation of inhibition efficiency of 40 ppm paracetamol against the molar conductance for 0.5M HCl with temperature

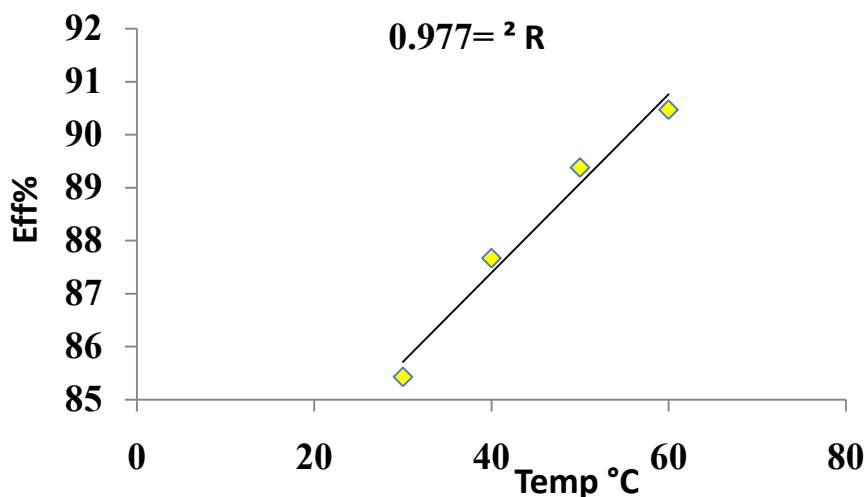


Figure 20: Variation of inhibition efficiency of 50 ppm paracetamol against the molar conductance for 0.5M HCl with temperature .

3. Kinetic study:

The molar conductance for hydrochloric acid in presence and absence of paracetamol can be studied kinetically at temperatures ranged (30-60) °C where, activation energy, enthalpy of activation, free energy of activation and entropy of activation are functions will be studied according to the particular equations i.e., Arrhenius equation is used to calculate the activation energy for hydrochloric acid in presence and absence of paracetamol where the molar conductance of the acid can be considered as a function of activation energy[22]:

$$\Lambda = \Lambda^{\circ} e^{\frac{-E_a}{RT}} \dots\dots\dots 6$$

Where Λ is the molar conductance, Λ° is the infinite molar conductance as Arrhenius constant, E_a is an activation energy in kJ.mol⁻¹, R is Molar gas constant (8.314 J k⁻¹.mol⁻¹) and T is the absolute Temperature in K. Thus, Arrhenius equation is converted into natural logarithm for as below:

$$\ln \Lambda = \ln \Lambda^{\circ} - \frac{E_a}{RT} \dots\dots\dots 7$$

When the relation between $\ln(\Lambda)$ against inverse of absolute temperature, the yielded slope is an activation energy and the intercept is the Arrhenius constant. . Figures (21-26) explain the relation between $\ln \Lambda$ and the inverse of absolute temperature (Arrhenius equation) for 0.50M HCl in presence and absence of different concentrations from the Paracetamol respectively:

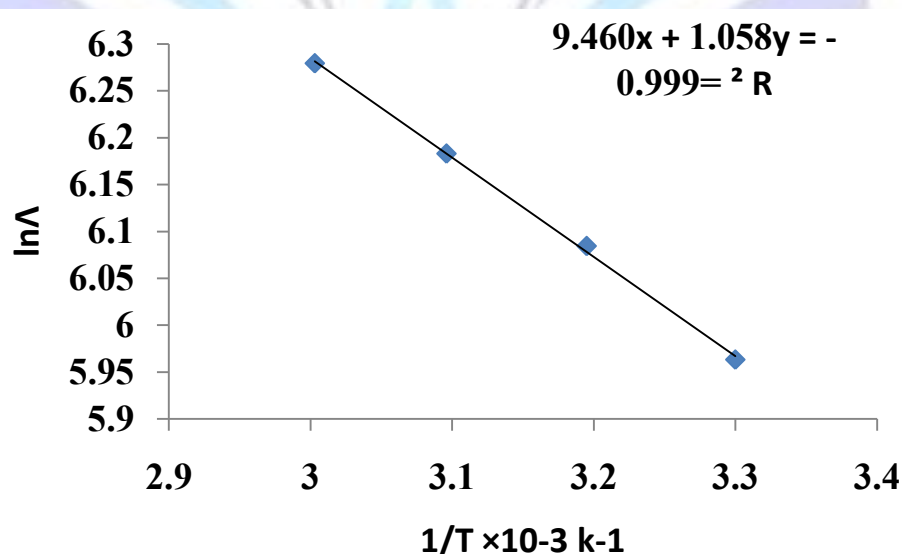


Figure 21: Arrhenius relationship for the molar conductance of 0.50M HCl in absence of Paracetamol.

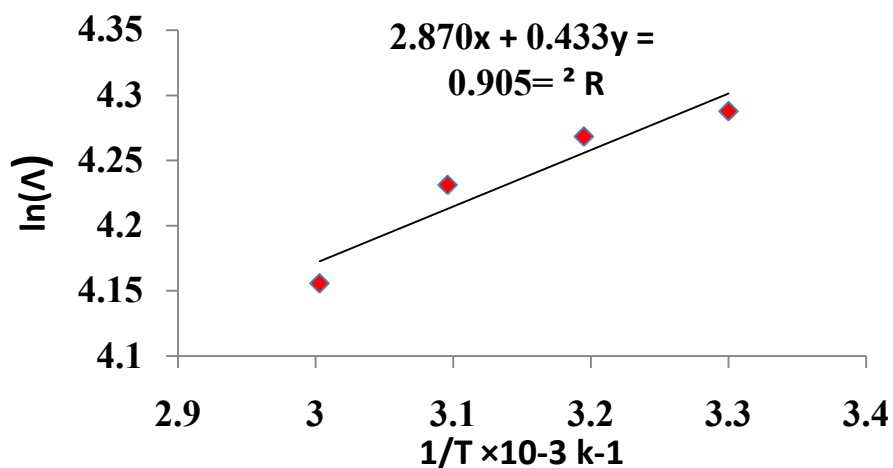


Figure 22: Arrhenius relationship for the molar conductance of 0.50M HCl in presence of 10ppm Paracetamol.

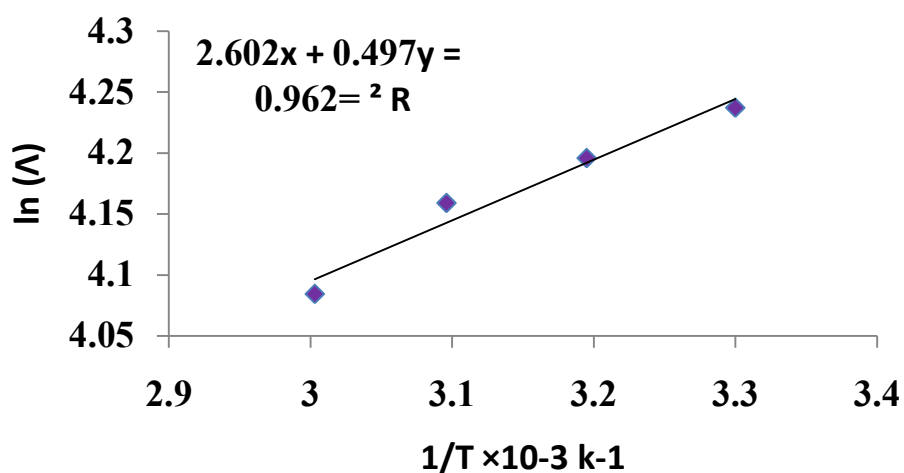


Figure 23: Arrhenius relationship for the molar conductance of 0.50M HCl in presence of 20ppm Paracetamol.

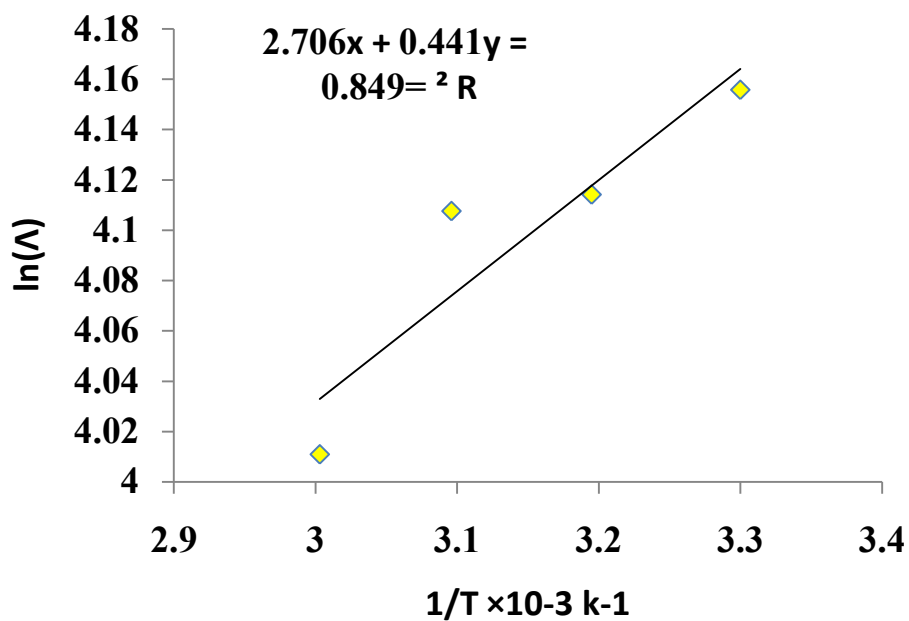


Figure 24: Arrhenius relationship for the molar conductance of 0.50M HCl in presence of 30ppm Paracetamol.

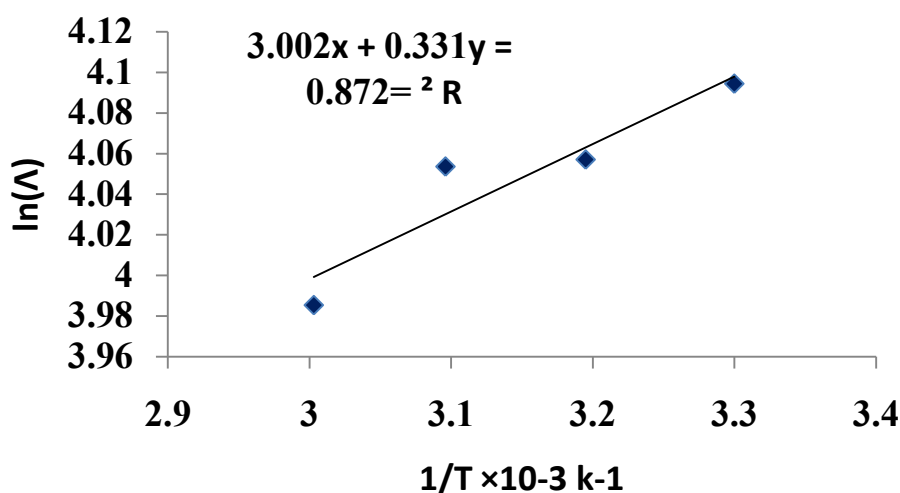


Figure 25: Arrhenius relationship for the molar conductance of 0.50M HCl in presence of 40ppm Paracetamol.

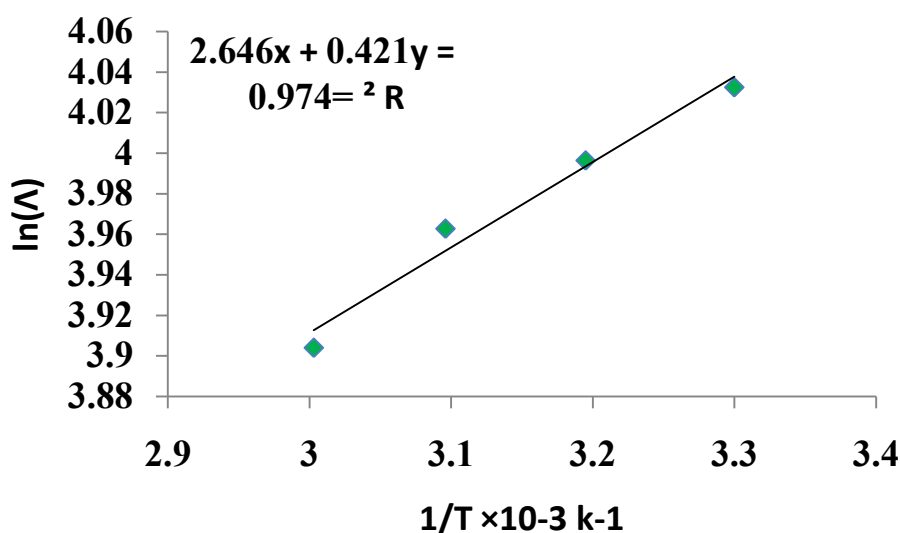


Figure 26: Arrhenius relationship for the molar conductance of 0.50M HCl in presence of 50ppm Paracetamol.

Thus, enthalpy of activation is calculated according to the following equation which superimposed to Eyrlying equation:

$$\ln \frac{U}{T} = \ln \frac{k}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \dots \dots \dots 8$$

Where ΔH^* and ΔS^* are the enthalpy and entropy of activation in kJ/mol and J.k⁻¹.mol⁻¹ respectively, k is a Boltzmann constant and U is the ionic mobility of hydrochloric acid. Furthermore, the free energy of activation ΔG^* is calculated according to the following equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \dots \dots \dots 9$$

Where ΔG^* is the free energy of activation in kJ/mol. The calculation of enthalpy, entropy and free energy of activation can be explained in Figures (27-32) as below :

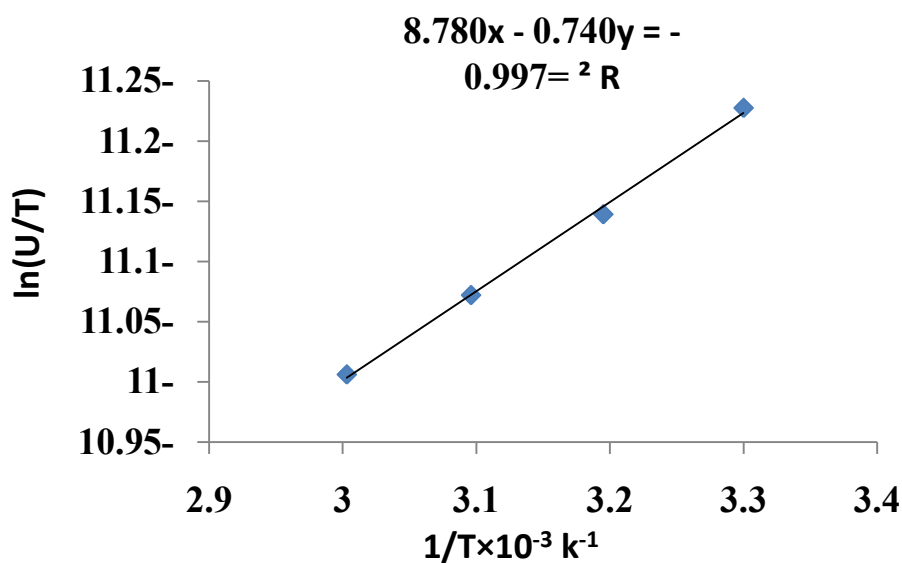


Figure 27: Calculation the activation parameters for 0.5 HCl in absence of paracetamol.

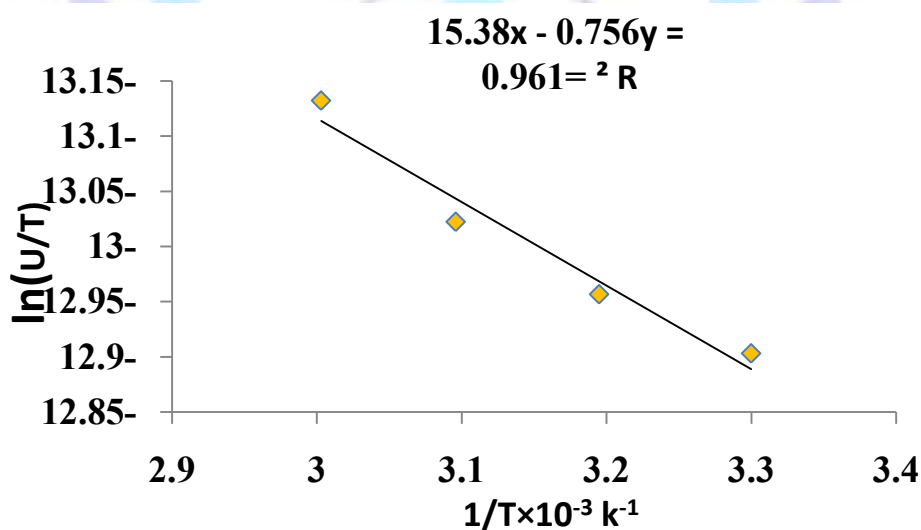


Figure 28: Calculation the activation parameters for 0.50M HCl in presence of 10 ppm paracetamol.

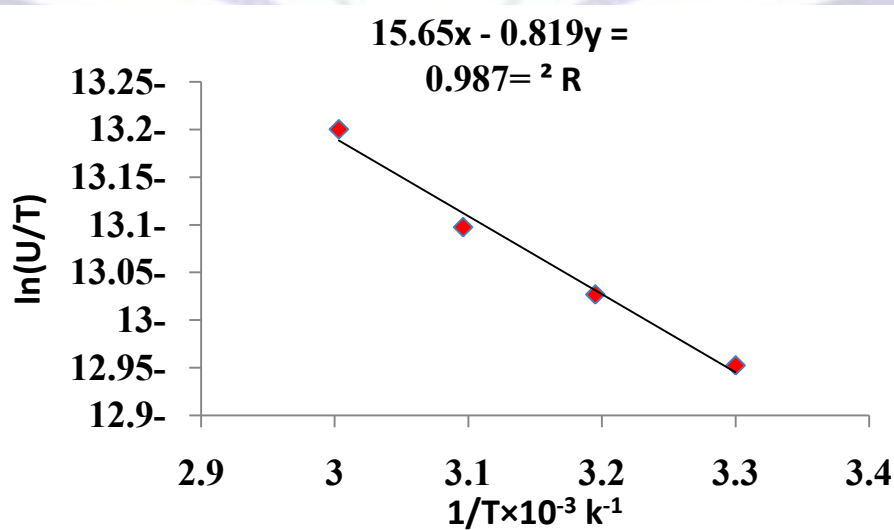


Figure 29: Calculation the activation parameters for 0.50M HCl in presence of 20 ppm paracetamol.

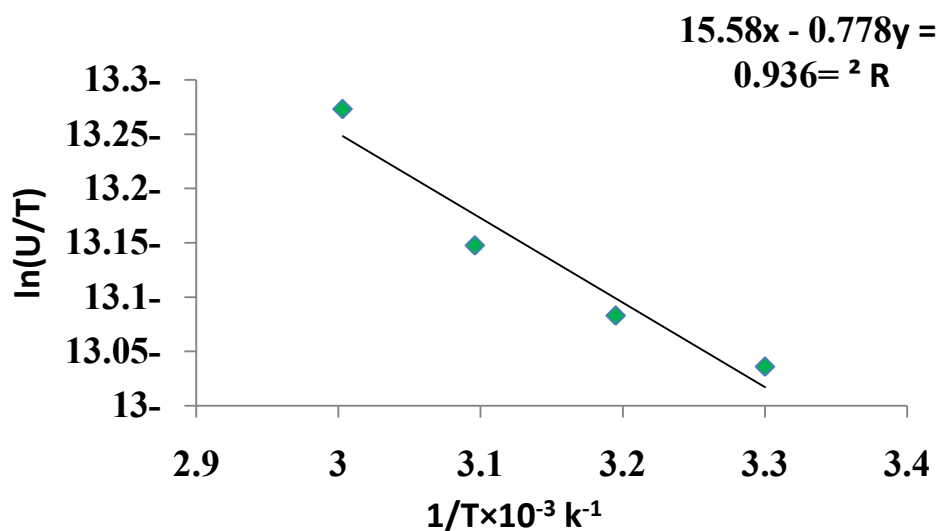


Figure 30: Calculation the activation parameters for 0.50M HCl in presence of 30 ppm paracetamol.

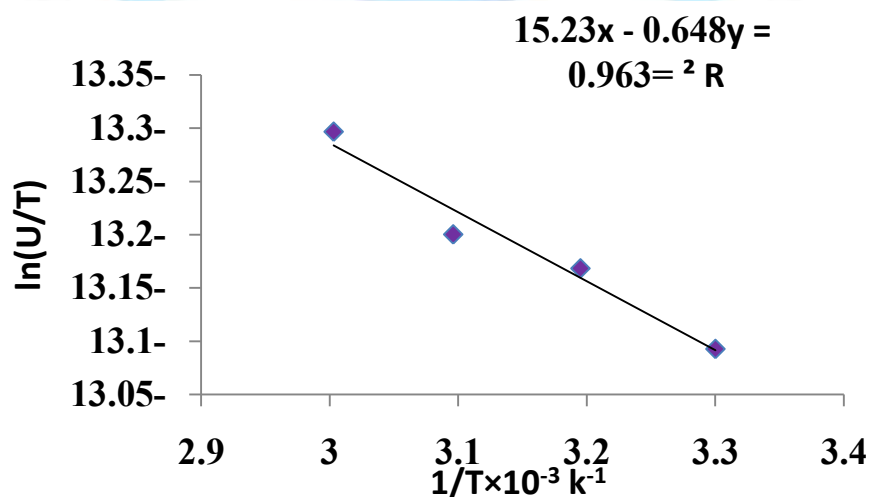


Figure 31: Calculation the activation parameters for 0.50M HCl in presence of 40 ppm paracetamol.

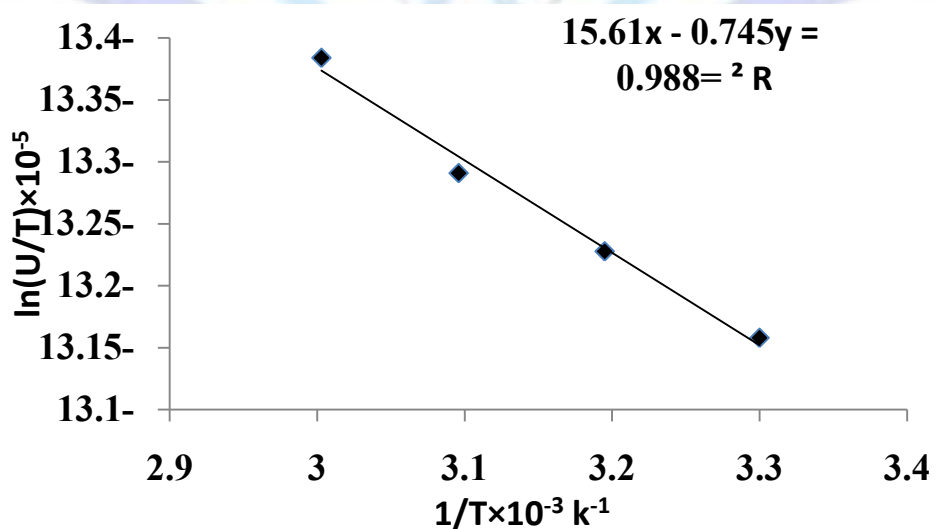


Figure 32: Calculation the activation parameters for 0.50M HCl in presence of 50 ppm paracetamol.



The kinetic activation functions is summarized in Table 12:

Table 12: Kinetic parameters for the conductance of 0.50M HCl in presence and absence of different concentration of paracetamol.

Compound	Conc. (ppm)	E _a (kJ.mol ⁻¹)	ln(Λ°)	Λ° Ω ⁻¹ mol ⁻¹ .cm ²	ΔH [*] (kJ.mol ⁻¹)	ΔS [*] (J.mol ⁻¹)	ΔG [*] (kJ.mol ⁻¹)
HCl	18250	8.769	9.460	12835.88	6.152	-270.538	88.125
paracetamol	10	-3.600	2.870	17.637	-6.285	-325.410	92.314
paracetamol	20	-4.132	2.602	13.491	-6.809	-327.655	92.470
paracetamol	30	-3.666	2.706	14.969	-6.468	-327.073	92.635
paracetamol	40	-2.752	3.002	20.126	-5.387	-324.163	92.834
paracetamol	50	-3.500	2.646	14.098	-6.193	-327.322	92.986

Table 12 reveal that all functions of activation like energy of activation. Enthalpy of activation and energy of activation are positive i.e., endothermic and non-spontaneous process that corresponding with the highly value of infinite molar conductance (Λ°) in the mentioned table. When the paracetamol is present, the activation energy will become negative that means the molar conductance process is reduced in presence of paracetamol and this process is reduced as the concentration of paracetamol is increased which can be indicated by reducing in (Λ°) values i.e., the molar conductance of acid decreases with increase in temperature in presence of all concentrations for paracetamol this corresponding to negative values for enthalpy of activation in presence of different concentration of paracetamol that can be attributed to the heat of adsorption for paracetamol becomes larger than the activation energy of the intrinsic kinetic for the molar conductance for the hydrochloric acid i.e., The negative apparent electrochemical enthalpy of activation can be explained by a sufficiently negative enthalpy for the preceding adsorption equilibrium, which can lead to a negative apparent electrochemical enthalpy of activation for the overall process[22]. On the other hand, the free energy of activation for the molar conductance of hydrochloric acid in presence of paracetamol will become more non-spontaneous which meant reducing the molar conductance in presence of . On the other hand, the negative values of entropy of activation is increased as concentration of paracetamol increased insist that the mobility of both chloride and hydrogen ions toward the oppose electrodes in conduction cell is retarded by the paracetamol[17].

4. Thermodynamic studies:

In this paragraph, thermodynamic functions like enthalpy of adsorption ΔH_{ads}, free energy of adsorption ΔG_{ads} and entropy of Adsorption ΔS_{ads} will be calculated related to the isotherms of adsorption as below:

Basic information on the interaction between the inhibitor and the alloy surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the fractional coverage values θ as a function of inhibitor concentration must be obtained. It well known that θ can be obtained from the corrosion current via [23]:

$$\theta = \frac{\Lambda_{Blank} - \Lambda_{Inhibitor}}{\Lambda_{Blank}} \dots\dots\dots 10$$

Where θ is the value of retardation of hydrogen and chloride ions in hydrochloric acid to mobile toward the oppose electrode by paracetamol

The θ values obtained in this way are shown in Table 13.

Attempts were made to fit these θ values to various isotherms including Frumkin, Langmuir, Temkin, and Freundlich. Many adsorption isotherms were plotted for the paracetamol and the best isotherm for each one of them was selected according to the R² that has value near to unity value, According to θ is related to equilibrium adsorption constant(K and concentration of inhibitor morality C via

$$\theta = \left(\frac{-1}{2f}\right) \times \left[\ln(C) - \left(\ln\left[\frac{\theta}{1-\theta}\right] + \left(\frac{-1}{2f}\right) \ln K_{ads}\right) \dots\dots\dots 11$$

(Frumkin adsorption isotherm) where f factor of energetic inhomogeneity

$$\theta = K_{ads} \times C \dots\dots\dots 12 \text{ (Freundlich adsorption isotherm)}$$



$$\theta = \left(\frac{-1}{f}\right) \times \ln K_{ads} + \left(\frac{-1}{f}\right) \times \ln(C) \dots \dots \dots 13$$

Timken adsorption isotherm, where f factor of energetic inhomogeneity.

$$\log \theta = n \log C + \log K_{ads} \dots \dots \dots 14$$

Langmuir adsorption isotherm . From the above equations, the equilibrium constant of adsorption can be calculated, then the standard energy of adsorption, ΔG°_{ads} by [24]:

$$K = \frac{1}{55.5} \times \exp \frac{(-\Delta G^\circ_{ads})}{RT} \dots \dots \dots 15$$

where the value 55.5 is the concentration of water in the solution in mol.dm⁻³, K is the equilibrium constant of adsorption, C is the concentration in molarity.

Table 13. Concentration dependence of the surface coverage (θ) values at different concentrations for paracetamol inhibitor in 0.50M HCl solution at different temperatures.

Conc .mol/l $\times 10^{-5}$	30 °C	40 °C	50 °C	60 °C
6.623	0.8121	0.8379	0.8561	0.8782
13.246	0.8214	0.8493	0.8660	0.8864
19.869	0.8353	0.8612	0.8726	0.8942
26.492	0.8450	0.8689	0.8792	0.8968
33.115	0.8543	0.8767	0.8839	0.9047

The adsorption isotherms can be shown in Figures (33-36) below:

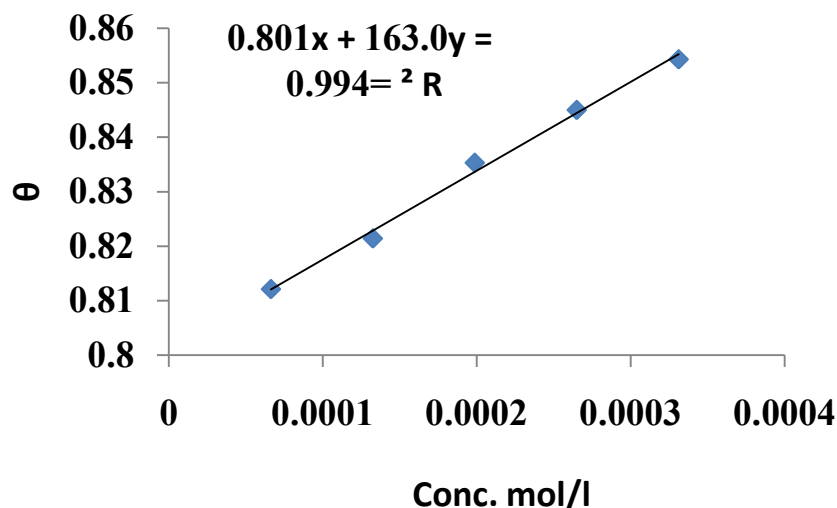


Figure 33: Freundlich adsorption isotherm for paracetamol as inhibitor against the molar conductance of 0.50M HCl solution at 30°C.

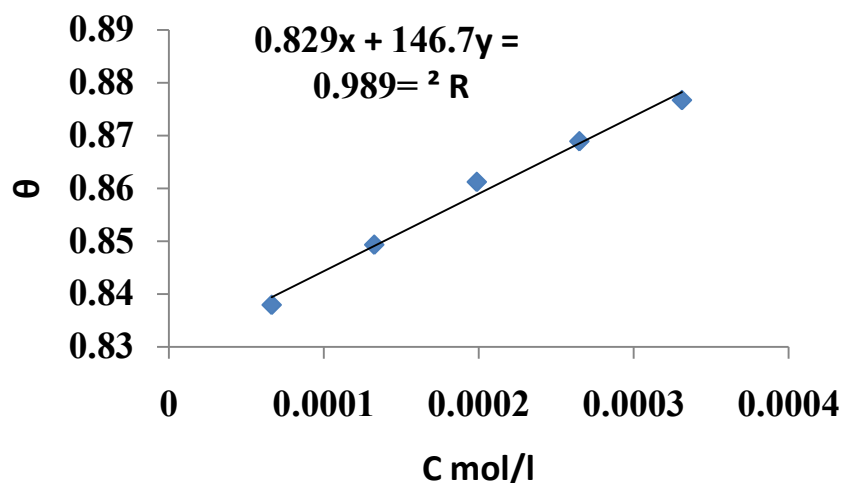


Figure 34: Freundlich adsorption isotherm for paracetamol as inhibitor against the molar conductance of 0.50M HCl solution at 40°C.

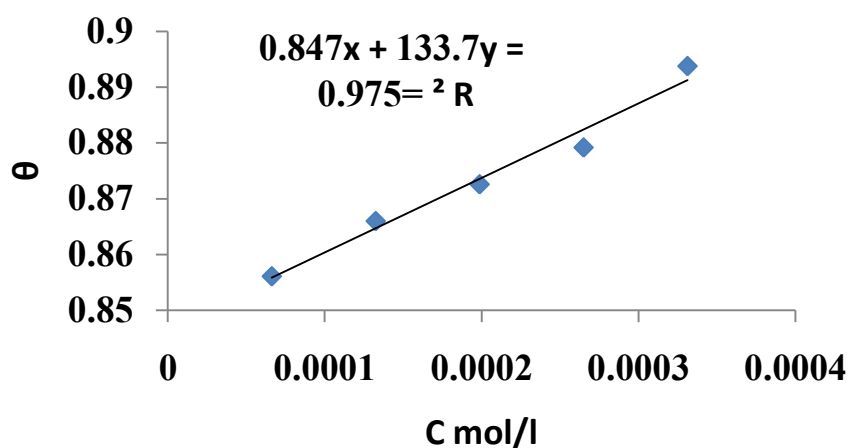


Figure 35: Freundlich adsorption isotherm for paracetamol as inhibitor against the molar conductance of 0.50M HCl solution at 50°C.

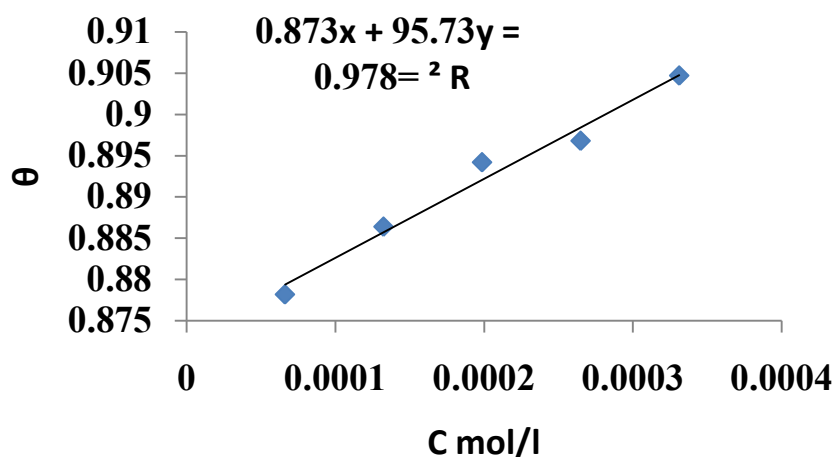


Figure 36: Freundlich adsorption isotherm for paracetamol as inhibitor against the molar conductance of 0.50M HCl solution at 60°C.

Figures (33-36) show the type of adsorption isotherm for Paracetamol as inhibitor in 0.50M HCl at temperature ranged (30-60) °C. The data are fitted to the Frumkin, Freundlich Timken and Langmuir adsorption isotherms by using regression



methods then K and $\Delta G_{\text{ads}}^{\circ}$ can be obtained. Generally, at all temperatures paracetamol obey to Freundlich isotherm of adsorption as shown above. The correlation coefficient (R^2) was used to choose the isotherm that best fit experimental data for each one of the temperatures in this study[25]. Hence, the equilibrium constant, free energy of adsorption $\Delta G_{\text{ads}}^{\circ}$, enthalpy of adsorption $\Delta H_{\text{ads}}^{\circ}$ and entropy of adsorption $\Delta S_{\text{ads}}^{\circ}$ where, the following equation can be used to calculate a thermodynamic functions:

$$\frac{\Delta G_{\text{ads}}^{\circ}}{T} = \frac{\Delta H_{\text{ads}}^{\circ}}{T} + k \dots \dots \dots 16$$

The variation of $\Delta G_{\text{ads}}^{\circ}/T$ with $1/T$ gives a straight line with a slope that equals $\Delta H_{\text{ads}}^{\circ}$ (Figure 37). It can be viewed from the Figure that $\Delta G_{\text{ads}}^{\circ}/T$ decreases with $1/T$ in a linear manner. The calculated values are shown in Table 14. The adsorption heat could be approximately regarded as the standard adsorption heat under experimental conditions. The negative sign of $\Delta H_{\text{ads}}^{\circ}$ in HCl solution indicates that the adsorption of inhibitor molecule is an exothermic process[24].

Table 14: Thermodynamic parameters for the adsorption of paracetamol in 0.50 M HCl at different temperatures.

Temp .k	K	$\Delta G_{\text{ads}}^{\circ}$ (kJ.mol ⁻¹)	$\Delta H_{\text{ads}}^{\circ}$ (kJ.mol ⁻¹)	$\Delta S_{\text{ads}}^{\circ}$ (J.mol ⁻¹)
303	163.000	-22.950	-14.07	29.307
313	146.700	-23.433	-14.07	29.914
323	133.700	-23.932	-14.07	30.533
333	95.73	-23.748	-14.07	29.063

On the other hand, enthalpy of adsorption is calculated according to equation 16 as shown in Figure 37 below:

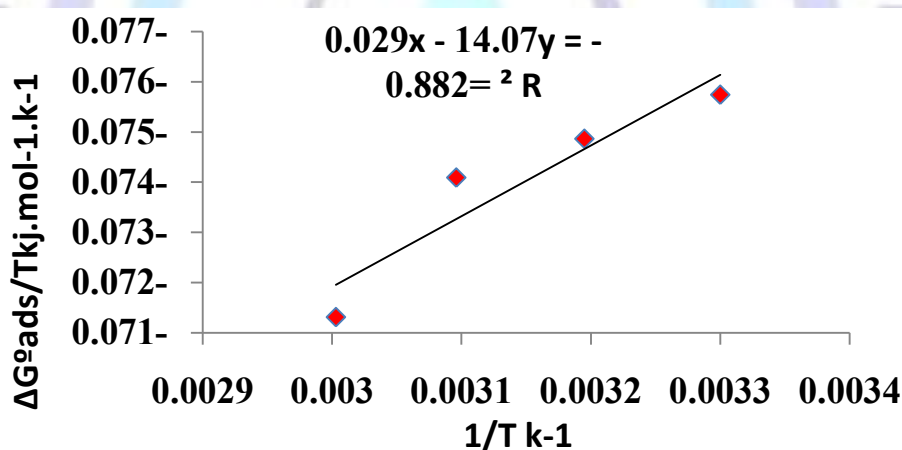


Figure 37. Adsorption isotherm plot for $\Delta G_{\text{ads}}/T$ vs. $1/T$.

Then the standard adsorption entropy $\Delta S_{\text{ads}}^{\circ}$ was obtained using the thermodynamic basic equation:

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads}}^{\circ} - T\Delta S_{\text{ads}}^{\circ} \dots \dots \dots 17$$

The negative values of free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) indicate that the adsorption process is spontaneous and the adsorbed layer on paracetamol surface is stable [26,27]. On the other hand, exothermic adsorption reaction data are obtained in addition to $\Delta S_{\text{ads}}^{\circ}$ values in the presence of paracetamol are positive, meaning a disordering in presence of inhibitor is increased in order to the inhibitor is adsorbed on the metal surface. On the other hand, when the data in Table 14 is compared with the inhibition efficiency in Tables 6-11 indicate that increasing in efficiency as temperature increased which is attributed to chemical adsorption mode, thus, at high degree of coverage, the diffusion through the surface layer containing the inhibitor and corrosion products become the rate determining step of the metal dissolution process i.e., the adsorption mode for paracetamol is chemisorptions mode[28].

5. CONCLUSION :

There are several conclusions can be summarized as below:

1. Paracetamol acts as a good retarder for the molar conductance of 0.50M HCl at different concentration i.e., (10-50) ppm at constant temperature where as the concentration of paracetamol increased, the molar conductance of acid increased at all temperatures in this study.
2. The molar conductance of acid is reduced as temperature increased in range (30-60) °C reducing the molar conductance is 90.47% which encourage us to use the paracetamol as corrosion inhibitor for the metals or alloys in acidic media.



3. It is noticed that the activation energy for the molar conductance of acid become a negative in presence of paracetamol compared with its value in absence of paracetamol (positive) which meant the paracetamol has the strong ability to inhibit the conductance of acid which correspond with the negative values for the enthalpy of activation for the molar conductance of acid due to the heat or enthalpy of adsorption process of HCl on the paracetamol is greater than the activation process for the molar conductance of acid.
4. The free energy of activation for the molar conductance of acid is positive whether in presence or absence of paracetamol but, the non-spontaneous property is increased in presence of paracetamol at all its concentrations.
5. The entropy of activation for the molar conductance of acid is negative whether in presence or absence of paracetamol but it increased as the paracetamol is present which meant that an order for the mobility of both hydrogen and chloride ions are taken placed i.e., the mobility of both ions are restricted.
6. The adsorption of paracetamol is obey to Freundlich adsorption isotherm at all temperatures that ranged (30-60) °C where, the equilibrium constant of adsorption is reduced as temperature increased, the adsorption process become more spontaneous and an exothermic adsorption process which accompanied by the positive entropy values .

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