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# Argan Plant Extract: Green Inhibitor for Copper Corrosion in Phosphoric Acid Solution

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## ABSTRACT

*Corrosion inhibition effect of Argan plant extract (APE) on copper in 2 M $H_3PO_4$ and NaCl 0.3 M was studied using gravimetric, electrochemical polarization and impedance spectroscopy (EIS) measurements. Inhibition efficiency increases with APE concentration to attain 95% at 4 g $L^{-1}$. We note good agreement between gravimetric and electrochemical methods (potentiodynamic polarization and EIS). Effect of temperature is also made in the 298- 328 K range. Polarization measurements show also that APE act as a mixed inhibitor. The thermodynamic data of activation are determined and discussed.*

**Keywords:** Corrosion, Copper, Inhibition, Argan plant extract, Acidic solution.

## INTRODUCTION

Corrosion is one of the major problems encountered in the industrial application of materials. Millions of dollars are spent by the oil industry, for instance, on the prevention of corrosion process in metals. Among the procedures used to prevent corrosion, the use of inhibitors is the most common, given that it presents some advantages of economical and environmental nature, as well as great efficiency and high applicability. It is well known that organic molecules containing heteroatoms act efficiently as corrosion inhibitors [1-17]. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency [18–28]. But, unfortunately most of these compounds are not only expensive but also toxic to living beings.

Recently, several researcher focalize their works to use of natural products named green inhibitor, as corrosion inhibitors [29-42]. Plant extracts have attracted attention in the field of corrosion inhibition for

many decades. As natural products, they are a source of non-toxic, eco-friendly, readily available and renewable inhibitors for preventing metal corrosion [43].
The aim of the present work is to evaluate the inhibitive effect of Argan plant extract (APE) as a green corrosion inhibitor on the corrosion of copper in 2 M $H_3PO_4$ and NaCl 0.3 M solution. The assessment of the corrosion behavior was studied using weight loss, potentiodynamic polarization measurement.

## MATERIALS AND METHODS

**Weight loss measurements:** Gravimetric methods were conducted on copper test samples of a total surface of 12 $cm^2$. All experiments were carried out under total immersion in 75 ml of test solutions. Mass loss was recorded by an Analytical balance. Prior to each gravimetric or electrochemical experiment, the surface of the specimens was polished successively with emery paper up to 1200 grade, rinsed thoroughly with acetone and double distilled water before plunging the electrode in the solution. Pure copper samples (99%) were used. The experiments were carried out in 2M $H_3PO_4$ medium containing different concentration of NaCl; it was prepared by dilution of Analytical Grade 84% $H_3PO_4$ with double distilled water and pure NaCl.
**Electrochemical tests:** The current–voltage characteristics are recorded with a potentiostat PGZ100 piloted by Voltamaster soft-ware. The scan rate is 30 mV/min and the potential is ranged from catholic to anodic potentials. Before recording each curve, the working electrode is maintained with its free potential of corrosion $E_{corr}$ for 30 min. The polarisation curves are obtained from −800 to 500 mV/SCE. We used for all electrochemical tests a cell with three electrodes and double wall thermostats (Tacussel Standard CEC/TH). Saturated calomel (SCE) and platinum electrodes are used as reference and auxiliary electrodes, respectively. The working electrode is in the form of a disc from pure copper of the surface 1 $cm^2$.
The tests were carried out in a temperature range from 298 to 323 K. The electrochemical impedance spectroscopy (EIS) measurements are realised with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at $E_{corr}$ after 30 min immersion in solution. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 MHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

## RESULTS AND DISCUSSION

### Effect of concentration inhibitor

**Weight loss, corrosion rates and inhibition efficiency:** The effect of addition of APE at different concentrations on the corrosion of copper in 2M $H_3PO_4$ + $3.10^{-1}$ M NaCl solution was studied by using weight loss at 298 K. Inhibition efficiency $E_w$ (%) is calculated as follows:

$$E_W(\%) = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \qquad (1)$$

Where $W_{corr}$ and $W'_{corr}$ are the corrosion rate of copper in 2 M $H_3PO_4$ + $3.10^{-1}$ M NaCl in the absence and presence of APE inhibitor, respectively.

The weight loss results for copper in 2 M $H_3PO_4$ + $3.10^{-1}$ M NaCl with and without addition of different concentrations of APE are summarized in table 1. From Table 1 it can be seen that the extent of corrosion in 2M $H_3PO_4$ + $3.10^{-1}$ M NaCl solution containing APE decreased as the concentration of inhibitor increased. This is because the amount adsorbed and coverage of the copper surface by inhibitor increases with inhibitor concentration. The highest inhibition efficiency of 96% was obtained at 4 g $L^{-1}$ APE.

**Table 1**. Copper weight loss data and inhibition efficiency of APE in 2 M $H_3PO_4$ + 0.3 M NaCl.

| | **x ($g\ L^{-1}$)** | **$W'_{corr}$ ($mg.j^{-1}.\ dm^{-2}$)** | **$E_w$ (%)** |
|---|---|---|---|
| (2M $H_3PO_4$, 0.3 NaCl) + x($g\ L^{-1}$) APE | **0** | 162 | - |
| | **0.5** | 81 | 50 |
| | **1** | 65 | 60 |
| | **2** | 29 | 82 |
| | **4** | 06.5 | 96 |

**Polarization curves:** Potentiodynamic polarization curves for copper in 2M $H_3PO_4$ + 0.3 M in the absence and presence of APE at different concentrations at 298 K are presented in fig. 1. Corrosion data including corrosion current densities ($I_{corr}$), corrosion potential ($E_{corr}$), cathodic Tafel slope ($b_c$), anodic Tafel slope ($b_a$), and inhibition efficiency $E_i$ (%) are listed in table 2.
The inhibition efficiency was defined as:

$$E_i(\%) = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad (2)$$

Where $I_{corr}$ and $I'_{corr}$ are the uninhibited and inhibited current density, respectively.

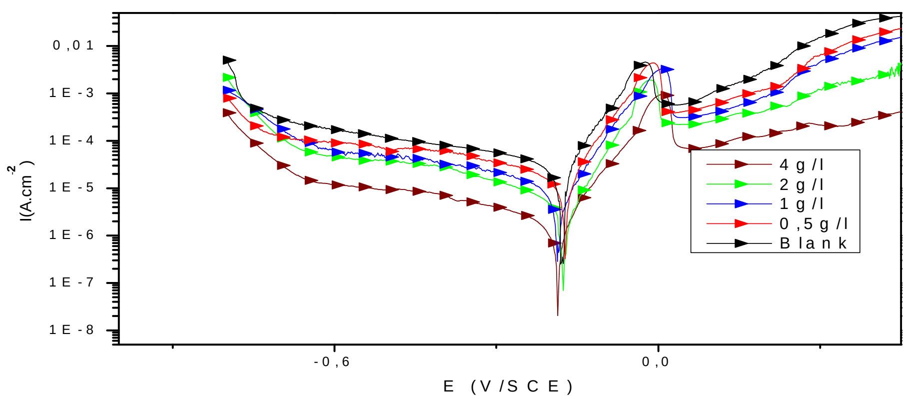


**Figure 1.** Cathodic and Anodic polarisation curves of copper in (2M $H_3PO_4$+ $3.10^{-1}$ M NaCl ) at different concentrations of APE.

**Table 2.** Electrochemical parameters of copper at various concentrations of APE in (2M $H_3PO_4$+ 0.3M NaCl) and the corresponding inhibition efficiency.

| | **x (g/L)** | **$E_{corr}$ (mV/SCE)** | **$I_{corr}$ ($\mu A/cm^2$)** | **$b_a$ (mV/dec)** | **$b_c$ (mV/dec)** | **Ei (%)** |
|---|---|---|---|---|---|---|
| 2M $H_3PO_4$ + 0.3 NaCl + x(g/L) APE | **0** | -177 | 36 | 68 | -297 | - |
| | **0.5** | -175 | 18 | 49 | -463 | 50 |
| | **1** | -189 | 11 | 60 | -447 | 69 |
| | **2** | -176 | 6 | 58 | -441 | 83 |
| | **4** | -184 | 2 | 49 | -351 | 93 |

It can be seen from the result that this inhibitor decrease $I_{corr}$ values in the concentration range of 0.5- 4g $L^{-1}$ concentrations this leads to the increase in the inhibition efficiency by increase in the inhibitor concentration. Maximum reduction of $I_{corr}$ for this inhibitor is obtained at 4g $L^{-1}$. The cathodic Tafel slope (bc) values show slight changes with the addition of APE, which suggests that the inhibiting action occurred by simple blocking of the available cathodic sites on the metal surface, which lead to a decrease in the exposed area necessary for oxygen reduction and lowered the dissolution rate with increasing APE concentration. It is also observed that $E_{corr}$ values did not change significantly in presence of inhibitor suggesting that the APE inhibitor is mixed type inhibitor [44].

**Electrochemical impedance spectroscopy measurements:** The corrosion behavior of copper in the acidic solution in the absence and presence of inhibitor was also investigated by the EIS method at 298 K. The inhibition efficiency can be calculated by the following formula:

$$E_{Rt}\% = \frac{(R_t - R_t^0)}{R_t} \times 100 \qquad (3)$$

Here $R_t$ and $R_t^0$ are the charge transfer resistance in inhibited and uninhibited solutions respectively.
The values of the charge transfer resistance were calculated by subtracting the high frequency intersection from the low frequency intersection [45]. Double layer capacitance values $C_{dl}$ were obtained at the frequency ($f_{max}$), at which the imaginary component of the Nyquist plot is maximum, and calculated using the following equation:

$$C_{dl} = \frac{1}{\omega . R_t} \quad \text{with} \quad \omega = 2\pi f_{max} \qquad (4)$$

The impedance parameters derived from this investigation are given in table 3. It is worth noting that the presence of inhibitor does not alter the profile of impedance diagrams which are almost semi-circular (Fig. 2), indicating that a charge transfer process mainly controls the corrosion of copper. In fact, the presence of inhibitor enhances the values of $R_t$ in the acidic solution. On the other hand, the values of $C_{dl}$ decreased with an increase in the inhibitor concentration. This was due to an increase in the surface coverage by this inhibitor, resulting into an increase in the inhibition efficiency. Thus, the change in $C_{dl}$ values was caused by to the gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface, decreasing the extent of metal dissolution [46].

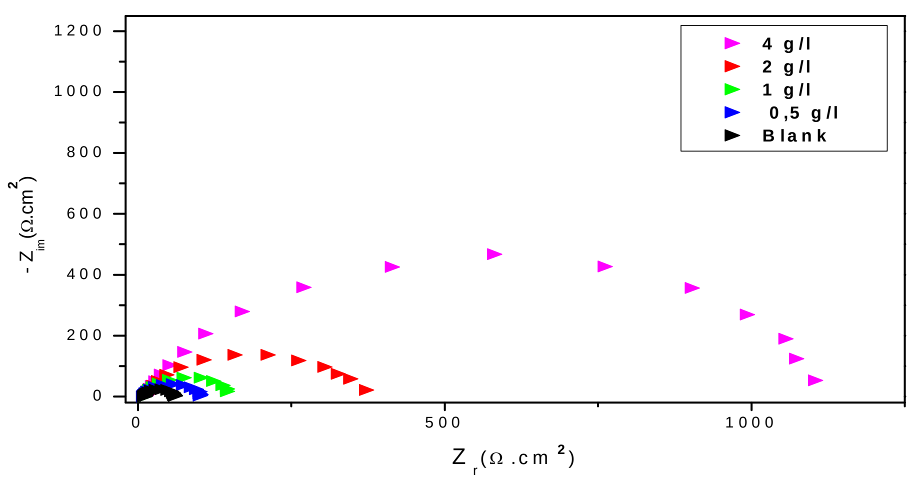


**Figure 2.** Nyquist diagrams for copper electrode in (2M $H_3PO_4$+ 0.3M NaCl) with and without APE after 30min of immersion at $E_{corr}$.

**Effect of Temperature:** The effect of temperature on the corrosion parameters of copper in free and inhibited solutions of 2M $H_3PO_4$+ $3.10^{-1}$ M NaCl was studied at a temperature range of 298-323 K. (Fig. 3 and Fig.4). Table 4 summered the electrochemical parameters deduced from the polarization curves and inhibition efficiency determined by relation (2).

The results show that the inhibition efficiency $E_i$(%) is independent of temperature, showing that Argan plant extract is an efficient inhibitor in the range of temperature studied. Such inhibitor had a practical interest where retardation of corrosion at elevated temperature is desired, for example in pickling process.

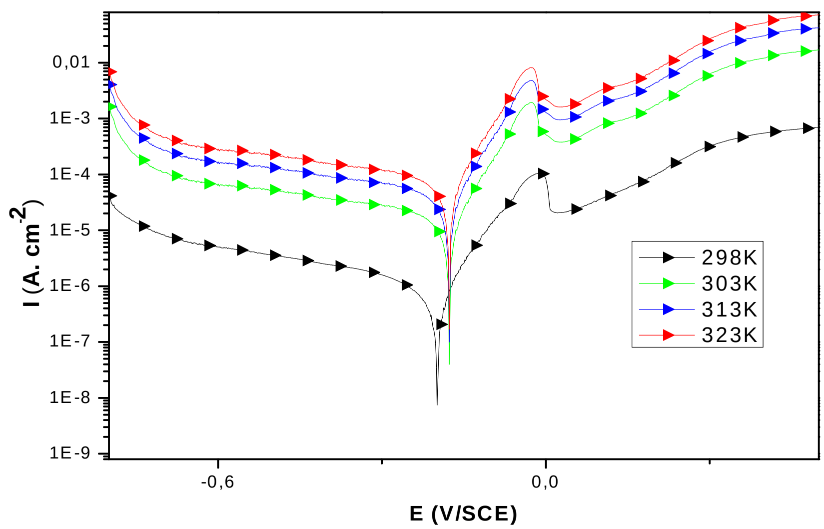


**Figure. 3** Potentiodynamic polarisation curves of copper in (2M $H_3PO_4$ + $3.10^{-1}$M NaCl) at different temperatures

**Table 3.** Impedance parameters for corrosion of copper in (2M $H_3PO_4$+ $3.10^{-1}$ M NaCl) at various concentrations of APE.

| | **Concentrations (g/L)** | **$R_t$ ($\Omega.cm^2$)** | **$f_{max}$ (Hz)** | **$C_{dl}$ ($\mu F/cm^2$)** | **$E_{Rt}$ (%)** |
|---|---|---|---|---|---|
| Blank | **0** | 50 | 63 | 49 | - |
| 2M $H_3PO_4$ + 0.3 NaCl + x**(g/L)** APE | **0.5** | 94 | 55 | 31 | 46 |
| | **1** | 142 | 40 | 28 | 64 |
| | **2** | 350 | 20 | 22 | 84 |
| | **4** | 1080 | 07 | 21 | 95 |

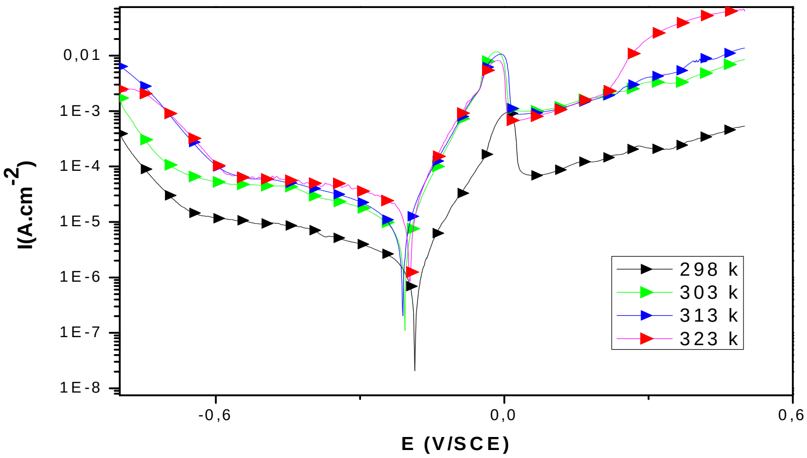


**Figure 4.** Potentiodynamic polarisation curves of copper in (2M $H_3PO_4$ + $3.10^{-1}$M NaCl) in the presence of 4g/L of APE at different temperatures.

**Table 4.** Effect of temperature on the copper in (2M $H_3PO_4$ + 0.3 M NaCl) and at 4g/L of APE.

| | **Temperature (K)** | **$E_{corr}$ (mV/SCE)** | **$I_{corr}$ ($\mu A/cm^2$)** | **$b_a$ (mV/dec)** | **$b_c$ (mV/dec)** | **$E_i$ (%)** |
|---|---|---|---|---|---|---|
| Blank | 298 | -177 | 36 | 68 | -297 | - |
| | 303 | -157 | 116 | 63 | -516 | - |
| | 313 | -136 | 174 | 54 | -504 | - |
| | 323 | -128 | 251 | 60 | -355 | - |
| APE | 298 | -184 | 02 | 59 | -351 | 93 |
| | 303 | -202 | 10 | 54 | -440 | 91 |
| | 313 | -215 | 15 | 56 | -354 | 91 |
| | 323 | -199 | 21 | 52 | -380 | 91 |

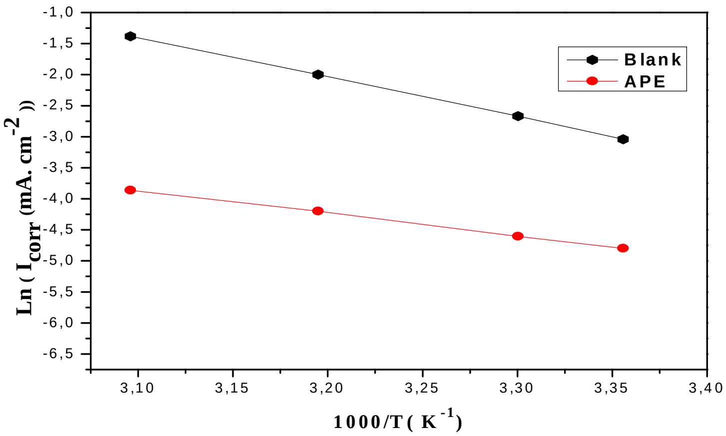


**Figure 5.** Arrhenius plots of copper in (2M $H_3PO_4$ + 0.3 M NaCl) with and without 4 g/L of APE.

Fig. 5 also shows that the corrosion reaction can be regarded as an Arrhenius-type process (Equation (5)). The activation parameters for the studied system (ΔS* and ΔH*) were estimated from the Arrhenius equation and transition state equation (Equation (6)):

$$I_{corr} = A\exp(-\frac{E_a}{R.T}) \quad (5)$$

$$I_{corr} = \frac{RT}{Nh}.\exp(\frac{\Delta S^*}{R}).\exp(-\frac{\Delta H^*}{RT}) \quad (6)$$

Where N is the Avogadro's number, h the Plank's constant, R is the perfect gas constant, ΔS* and ΔH* the entropy and enthalpy of activation, respectively.

Fig. 6 shows a plot of $\ln(I_{corr}/T)$ against 1/T for APE. Straight lines are obtained with a slope of (-ΔH*/R) and an intercept of (ln R/Nh + ΔS*/R) from which the values of ΔH* and ΔS* are calculated respectively (Table 5).

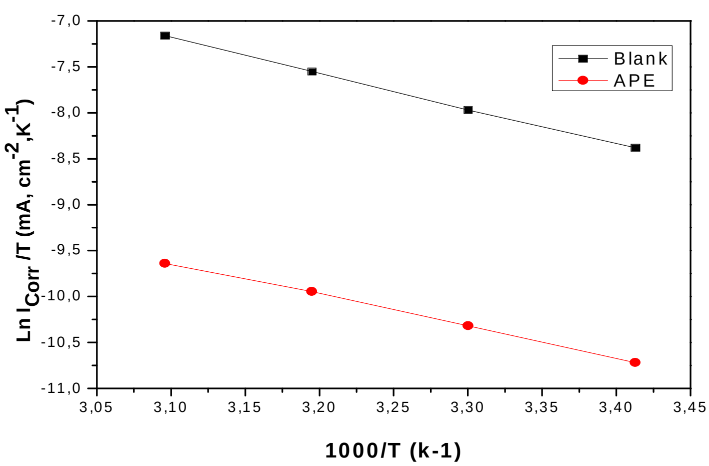


**Figure.6**: Relation between Ln ($I_{corr}$/T) and $10^3$/T at different temperatures.

**Table 5.** The values of activation parameters $E_a$ , $\Delta H^*$ and $\Delta S^*$ for copper in (2M $H_3PO_4$ + 0.3 M NaCl) in the absence and the presence of 4 g $L^{-1}$ of APE, respectively

| | $E_a$(kJ $mol^{-1}$) | ΔH*(kJ $mol^{-1}$) | ΔS*(J.$mol^{-1}$.$k^{-1}$) |
|---|---|---|---|
| **Blank** | 50 | 48 | -111 |
| **APE ( 4g $L^{-1}$ )** | 100 | 99 | -98 |

From the following results, it can be concluded that:

- The decrease in activation energy in presence of the inhibitor studied.
- The positive values of Δ*H** show that the corrosion process is an endothermic phenomenon.
- The negative values of ΔS* show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [47].

## APPLICATIONS

The results are useful to evaluate the inhibitive effect of Argan plant extract (APE) as a green corrosion inhibitor on the corrosion of copper in 2M $H_3PO_4$ and NaCl 0.3 M solution. The assessment of the corrosion behavior was studied using weight loss, potentiodynamic polarization measurement.

## CONCLUSIONS

The studied Argan plant extract (APE) shows excellent inhibition properties for the corrosion of copper in 2 M $H_3PO_4$ + $3.10^{-1}$ M NaCl at 298K, and the inhibition efficiency increases with increasing of the APE concentration. The inhibitor efficiencies determined by weight loss, Tafel polarization and EIS methods are in reasonable agreement. Based on the polarization results, the investigated Argan plant extract can be classified as mixed inhibitor. The calculated structural parameters show increase of the obtained $R_t$ values and decrease of the capacitance, $C_{dl}$, with APE concentration increase. Argan plant extract is an efficient inhibitor in the range of temperature studied.

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