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*International Journal of Current Research*
*Vol. 7, Issue, 01, pp.11419-11425, January, 2015*

**INTERNATIONAL JOURNAL OF CURRENT RESEARCH**

**ISSN: 0975-833X**

## REVIEW ARTICLE

# ARGAN HULLS EXTRACT AS AN EFFICIENT GREEN CORROSION INHIBITOR FOR COPPER IN PHOSPHORIC ACIDIC

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**ARTICLE INFO**

*Article History:*
Received 11th October, 2014
Received in revised form
14th November, 2014
Accepted 15th December, 2014
Published online 23rd January, 2015

*Key words:*
Argan hulls extract,
Corrosion,
Inhibition,
Copper.

**ABSTRACT**

The inhibitive behaviour of Argan hulls extract (AHE) , as a type of green inhibitor, on the corrosive behaviour of copper within an aqueous solution of 2M $H_3PO_4$ containing $3.10^{-1}$M NaCl. Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and gravimetric method, was used for the measurements at 298K. A significant decrease in the corrosion rate of copper was observed in the presence of the Argan hulls extract. Inhibition efficiency increases with AHE concentration to attain 91% at 6 g/L. The potentiodynamic polarization data indicated that the inhibitor was of mixed type. Impedance measurements showed that the charge transfer resistance increased and double layer capacitance decreased with increase in the inhibitor's concentration. Also, some thermodynamic data for the activation are calculated and discussed. Results obtained from potentiodynamic polarization, impedance measurements and gravimetric method are in good agreement.



## INTRODUCTION

Copper has been one of more important materials in industry owing to its high electrical and thermal conductivities, mechanical workability and its relatively noble properties. It is widely used in many applications in electronic industries and communications as a conductor in electrical power lines, pipelines for domestic and industrial water utilities including sea water, heat conductors, heat exchangers, etc. Therefore, corrosion of copper and its inhibition in a wide variety of media, have attracted the attention of many investigators (Khaled *et al.,* 2009; El-Naggar, 2000; Woo-Jin Lee, 2003; Abd El-Maksoud *et al.,* 1995; Abd El-Waness,1994; Madkour *et al.,* 1995; Abd El-Maksoud and Hassan, 2007; Fouda *et al.,* 2006; Maayta *et al.,* 2001; Khodari *et al.,*2001). The use of inhibitors to minimize the loss of useful properties of metals or alloys due to corrosion when they attack chemically or electrochemically by its environment is one of the best known methods of corrosion protection. The structure of the inhibitor molecule is one of the major factors that influence the metal-inhibitor interaction (Trabanelli, 1991). For a metal like copper, which can form multi-bonds, inhibitor molecules containing N and S atoms are strongly recommended. Among the nitrogen-sulfur- or oxygen containing organic compounds is the heterocyclic compounds which are effective inhibitors for copper corrosion in aqueous solutions (Zucchi, 1996). Due to the currently imposed environmental requirernents for eco-friendly corrosion inhibitors,there is a growing interest in the use of natural products such as leaves, seeds or bark extracts. Sorne papers have reported the use of natural products in the development of effective green corrosion inhibitors for different metals in various environments (El-Etre, 1998; Farooqui *et al.*, 1999; El-Etre and Abdallah, 2000; El-Etre, 2001; Martinez and Štern, 2001; El-Etre, 2003; Chetouani *et al.,* 2004; Bouyanzer and Hammouti, 2004; Mabrour *et al.,* 2004; El-Etre, *et al.,* 2005; Abdel-Gaber *et al.,* 2006; Bendahou *et al.,* 2006; Oguzie *et al.,* 2006; Valek and Martinez, 2007; Abiola *et al.,* 2007; Behpour *et al.,* 2008; Okafor *et al.,* 2008; Abdel-Gaber *et al.,* 2009; de Souza and Spinelli, 2009; Mounir *et al.,* 2014; Mounir *et al.,* 2014; Mounir *et al.,* 2014; Mounir *et al.,* 2012). In the present work, inhibitive action of Argan hulls extract as

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a cheap, eco-friendly and naturally occurring substance on corrosion behavior for copper in 2M $H_3PO_4$ and NaCl 0.3 M solution.has been investigated through weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. This study aimed also to investigate the temperature effects on copper corrosion 2 M $H_3PO_4$ and NaCl 0.3 M solution in the absence and presence of various additions Argan hulls extract using a gravimetric method. The chemical composition of the hulls is characterized by high amount of ADF fiber (Valuation of the fruit of the Argan tree 2009). The Nitrogen-free hulls extract (19.5%) is quite large and probably contains several classes of secondary metabolites such as polyphenols and saponins. Our team has isolated from the hull four saponins which 2 (arganine M and N) are cited in ref. (Alaoui *et al.,* 2002). The others are also present in the fruit pulp (arganine K and Mi-saponin A). These saponins have the same aglycone as that of the meal and differ only in the saccharide portion (Fig.1).

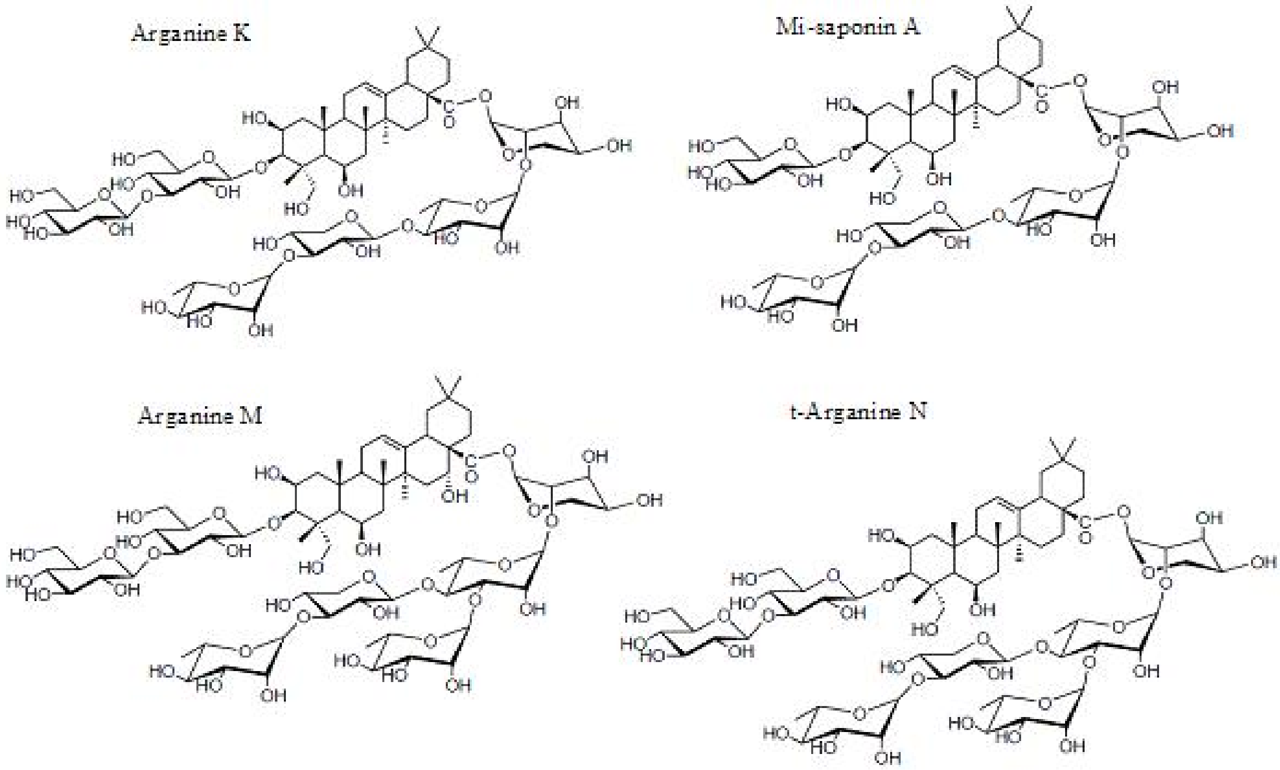


**Fig. 1. Chemical structures of Arganine K, Mi-saponin A, Arganine M and t-Arganine N**

## 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 bidistilled water before plunging the electrode in the solution. Pure copper samples (99%) were used. The experiments were carried out in 2 M $H_3PO_4$ medium containing 0.3 M of NaCl; it was prepared by dilution of Analytical Grade 84% $H_3PO_4$ with bidistilled 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 mV/SCE 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

### Polarization measurements

Fig. 2 represents the potentiodynamic polarization curves of copper in $H_3PO_4$ + $3.10^{-1}$M NaCl in the absence and presence of various concentrations of AHE. Table 1 gives the electrochemical parameters, corrosion potential ($E_{corr}$), cathodic Tafel slopes (bc), corrosion current density ($I_{corr}$), percentage inhibition efficiency (IE %) and corrosion rate. The inhibition efficiency, IE%, was calculated from polarization measurements according to following equation:

**Table 1. Electrochemical parameters of copper at various concentrations of AHE in (2M $H_3PO_4$+ 0.3M NaCl) and the corresponding inhibition efficiency**

| | x (g/l) | $E_{corr}$ (mV/SCE) | $I_{corr}$ (μA/cm²) | $b_a$ (mV/dec) | $b_c$ (mV/dec) | Ei (%) |
|---|---|---|---|---|---|---|
| | 0 | -177 | 36 | 68 | -297 | - |
| (2M $H_3PO_4$ | 0.5 | -180 | 19 | 50 | -415 | 47 |
| + | 1 | -188 | 17 | 51 | -401 | 53 |
| 0.3 NaCl) | 2 | -170 | 12 | 48 | -399 | 64 |
| + | 4 | -188 | 6 | 56 | -420 | 83 |
| xM AHE | 6 | -188 | 3 | 54 | -370 | 91 |

$$E_i(\%) = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad (1)$$

where $I_{corr}$ and $I'_{corr}$ are the uninhibited and inhibited current density, respectively. As it can be noticed, both anodic and cathodic reactions of the copper corrosion electrode were inhibited with the increase of extract concentration. This result suggests that the addition of Argan hulls extract inhibitor reduced the anodic dissolution and also retarded the cathodic reaction by blocking the copper surface.

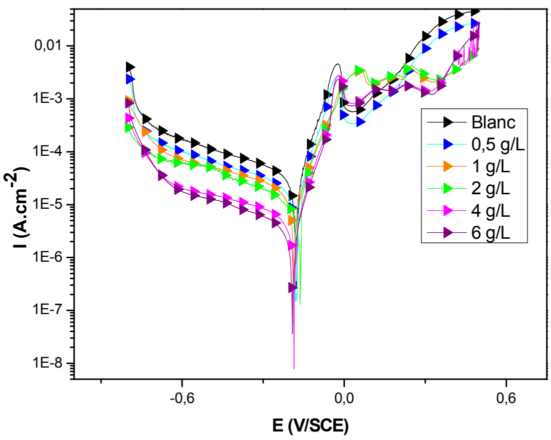


**Fig. 2. Cathodic and Anodic polarisation curves of copper in (2M $H_3PO_4$+ $3.10^{-1}$ M NaCl) at different concentrations of AHE**

We also remark that the cathodic current-potential curves give rise to Tafel lines, which indicate that hydrogen evolution reaction is activation controlled. The cathodic Tafel slope values in the presence of Argan hulls extract are different of that in its absence; we may deduce that this green inhibitor modifies the mechanism of the reduction process (Kertit and Hammouti, 1996). Additionally, From Table 1, in the presence of Artemisia plant extract the values of corrosion potential Ecorr are nearly constant; therefore, AHE could be classified as a mixed-type inhibitor. It could be noted that E% increased with increasing inhibitor concentration, reaches 91 % at 6 ml/L, AHE is a good inhibitor

### Electrochemical impedance spectroscopy

The impedance diagrams obtained after 30 min of exposure of the samples at 298K in inhibited and uninhibited 2M $H_3PO_4$ + $3.10^{-1}$ M NaCl containing various concentrations of AHE are shown in Fig. 3. The percent inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the equation:

$$E_{Rt}\,\% = \frac{(R_t - R_t^0)}{R_t} \times 100 \qquad (2)$$

Where $R_t$ and $R_t^0$ are the charge transfer resistances 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 (Ouachikh *et al.,* 2009). 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.

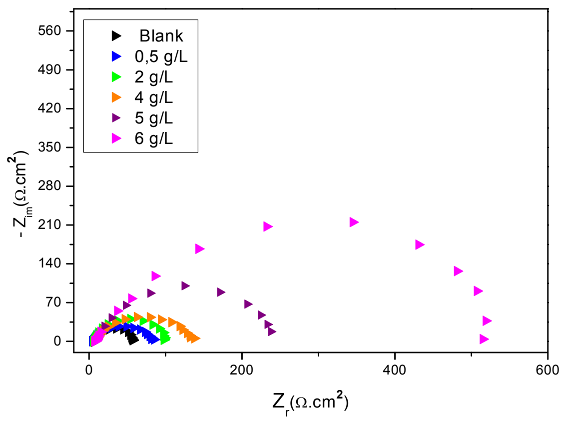


**Fig. 3. Nyquist diagrams for copper electrode in (2M $H_3PO_4$+ 0.3M NaCl) with and without AHE after 30min of immersion at $E_{corr}$**

$$C_{dl} = \frac{1}{\omega . R_t} \text{ with } \quad \omega = 2\pi f_{max} \qquad (3)$$

The impedance behavior of copper corrosion, in the form of Nyquist plots, exhibits one semicircle, which centre lies under the abscissa. These diagrams have similar shape; the shape is maintained throughout all tested concentrations, indicating that almost no change in the corrosion mechanism occurred due to the inhibitors addition. This behavior can be attributed to charge transfer of the corrosion process and the diameter of semicircle increases with increasing inhibitors concentration.

From the impedance results shown in the Table 2, the value of Rt increase with increase in the concentration of AHE inhibitor and amelioration in the protection of the surface; this indicated an increase in the corrosion inhibition efficiency. The decrease in $C_{dl}$ may be due to the adsorption of this compound on the metal surface leading to the formation of film from acidic solution (Benabdellah *et al.,* 2011; Bouklah *et al.,* 2012; Znini *et al.,* 2011; Bouklah *et al.,* 2005).

| | 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 | 0.5 | 96 | 50 | 33 | 47 |
| $H_3PO_4$ | 1 | 111 | 46 | 32 | 54 |
| + | 2 | 146 | 41 | 27 | 65 |
| 0.3 NaCl) | 4 | 255 | 30 | 22 | 80 |
| + | 6 | 510 | 14 | 21 | 90 |
| xM AHE | | | | | |

## Weight loss, corrosion rates and inhibition efficiency

The effect of addition of by Argan hulls extract tested at different concentrations on the corrosion of copper in 2 M $H_3PO_4$ + $3.10^{-1}$ M NaCl solution was studied by weight loss measurements at 298 K after 8h of immersion period. The corrosion rate (W) and inhibition efficiency Ew (%) were calculated according to the Eqs. (4) and (5) respectively:

$$W = \frac{\Delta m}{S.t} \tag{4}$$

$$E_W(\%) = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \tag{5}$$

where Δm is the specimen weight before and after immersion in the tested solution, S is the area of the copper specimen and t is the exposure time .

$W_{corr}$ 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 AHE inhibitor, respectively.

**Table 3. Copper weight loss data and inhibition efficiency of AHE in 2 M $H_3PO_4$ + 0.3 M NaCl**

| | x (g/l) | $W'_{corr}$ $(mg.j^{-1}.dm^{-2})$ | $E_w$ (%) | θ |
|---|---|---|---|---|
| | 0 | 162 | - | |
| (2M $H_3PO_4$ + 0.3 | 0.5 | 84 | 48 | 0.48 |
| NaCl) | 1 | 71 | 56 | 0.56 |
| + xM AHE | 2 | 58 | 64 | 0.64 |
| | 4 | 34 | 79 | 0.79 |
| | 6 | 15 | 91 | 0.91 |

The values of percentage inhibition efficiency Ew (%) and corrosion rate (W) obtained from weight loss method at different concentrations of AHE at 298 K are summarized in Table 3. It is very clear that the Argan hulls extract inhibits the corrosion of copper in 2 M $H_3PO_4$ + $3.10^{-1}$ M NaCl solution, at all concentrations used in this study, and the corrosion rate (W) decreases continuously with increasing additive concentration at 298 K. Indeed, Fig. 4 shown that the corrosion rate values of copper decrease when the inhibitor concentration increases while Ew (%) values of Argan hulls extract increase with the increase of the concentration reaching a maximum value of 91% at a concentration of 6 g /L.

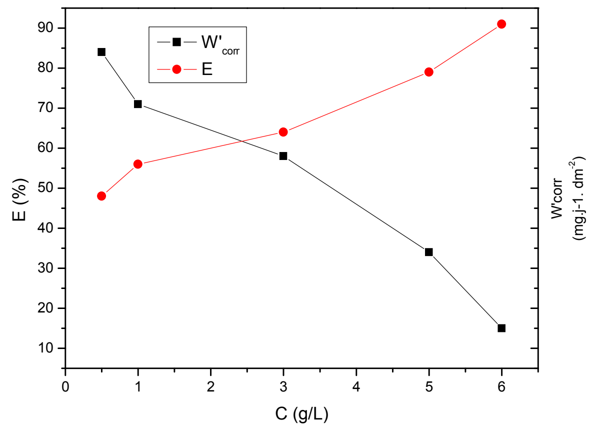


**Fig. 4. Variation of corrosion rate (W) and inhibition efficiency (Ew) of corrosion of copper in 2 M $H_3PO_4$ + $3.10^{-1}$ in the presence of AHE**

This behaviour can be attributed to the increase of the surface covered θ (Ew %/100), and that due to the components of the extract are adsorbed onto the copper surface resulting in the blocking of the reaction sites, and protection of the copper surface from the attack of the corrosion active ions in the acid medium. Consequently, we can conclude that the AHE is a good corrosion inhibitor for copper in 2 M $H_3PO_4$ + $3.10^{-1}$ solution. The results obtained from weight loss studies are in good agreement with electrochemical. A comparison may be made between inhibition efficiency E (%) values obtained by different methods (weight loss, polarization curves and EIS methods). Figure 4 shows a histogram that compares the E (%) values obtained. One can see that whatever the method used, no significant changes are observed in E (%) values. We can then conclude that there is a good correlation with the three methods used in this investigation at all tested concentrations and that Argan hulls extract is an efficient corrosion inhibitor.

## Effect of temperature

Temperature has great effect on the corrosion phenomenon. In general, the corrosion rate increases with rise in temperature. In this study, the effect of temperature on the corrosion and inhibition process of copper in 2M $H_3PO_4$ + 0.3 M NaCl in the absence and presence of optimum concentration of junipers extract after 8 h of immersion was followed at 298-323K using weight loss measurements. The results show that the inhibition efficiency (E %) is independent of temperature, showing that AHE is an efficient inhibitor in the range of temperature studied.

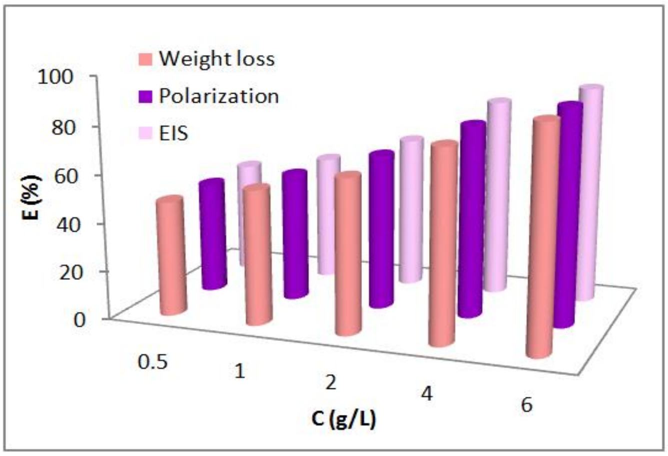


**Fig. 5. Comparison of inhibition efficiency (E %) values obtained by weight loss, polarisation and EIS methods**

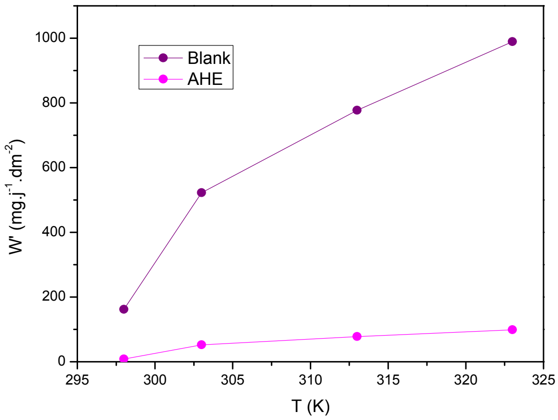


**Fig. 6. Variation of corrosion rate in 2M $H_3PO_4$ + 0.3 M NaCl on copper surface without and with of optimum concentration of extract at different temperatures**

Fig. 6 illustrates the variation of corrosion rate in the absence and of inhibitor at optimum concentration at different temperatures. The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation (Benabdellah 2011):

$$W_{corr} = k\exp(-E_a/RT)$$

where $W_{corr}$ is the corrosion rate, $E_a$ is the apparent activation energy of the copper dissolution, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor.

**Table 4. Effect of the temperature on the copper in 2M $H_3PO_4$ + 0.3 M NaCl and added of 6 g/L of AHE**

| | Temperature | W' ($mg.j^{-1}.dm^{-2}$) | $E_w$(%) |
|---|---|---|---|
| Blank | 298 | 162 | - |
| | 303 | 522 | - |
| | 313 | 777 | - |
| | 323 | 989 | - |
| AHE | 298 | 8 | 91 |
| | 303 | 52 | 90 |
| | 313 | 78 | 90 |
| | 323 | 99 | 90 |

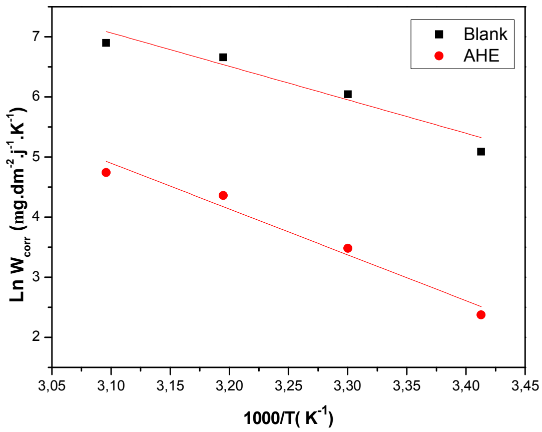


**Fig. 7. Arrhenius plots of copper in (2M $H_3PO_4$ + 0.3 M NaCl) with and without 6 g/L of AHE**

Fig.7 depicts Arrhenius plot as Ln of corrosion rate (Ln Wcorr) against the reciprocal of temperature (1/T) for copper in 2M $H_3PO_4$ + 0.3 M NaCl in the free acid solution and the acid containing different concentrations of AHE. The plots obtained are straight lines and the activation energy was evaluated from the slope of the straight line plots. The calculated values of activation energy are listed in Table 5. It can be seen in the table that $E_a$ is higher in the presence of the inhibitor than in the absence of the inhibitor. This observation further supports the proposed physical adsorption mechanism.

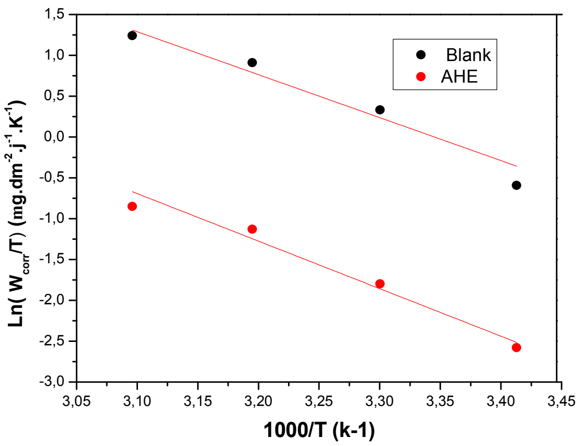


**Fig. 8. Relation between Ln($W_{orr}$/T) and 1000/T at different temperatures**

Further insight into the adsorption mechanism is offered by considering the thermodynamic functions for the copper in 2M $H_3PO_4$ + 0.3 M NaCl in the absence and presence of optimum concentration of Argan hulls extract (Fig. 8). In this regards, Transition state equation was used to evaluate the corrosion activation parameters, namely, the enthalpy of activation (ΔH*) and entropy of activation (ΔS*). Transition state equation is given by the expression (Bochris and Reddy, 1977):

$$W_{corr} = \frac{RT}{Nh}.\exp\left(\frac{\Delta S^*}{R}\right).\exp\left(-\frac{\Delta H^*}{RT}\right)$$ •

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.8 shows a plot of $\ln(W_{corr}/T)$ against 1/T for AO. 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).

**Table 5. The values of activation parameters $E_a$ , $\Delta H^*$ and ΔS* for copper in (2M $H_3PO_4$ + 0.3 M NaCl) in the absence and the presence of 6 g/L of AHE respectively**

| | $E_a$(kJ/mol) | ΔH*(kJ/mole) | ΔS*($J.mole^{-1}.k^{-1}$) |
|---|---|---|---|
| Blank | 50 | 48 | -111 |
| AHE ( 6g/L ) | 79 | 86 | -20 |

Inspection of these data revealed that the thermodynamic parameter (*ΔH) for dissolution reaction of copper in 2M $H_3PO_4$ + 0.3 M NaCl in the presence of extract is higher (86 KJ $mol^{-1}$) than that of in the absence of inhibitor (48 KJ mol $^{1}$). The positive sign of *ΔH reflect the endothermic nature of the copper dissolution process suggesting that the dissolution of copper is slow (Guan *et al.,* 2004) in the presence of inhibitor.

Large and negative value of entropie (ΔS*) imply 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 reactant to the activated complex (Soltani *et al.,* 2010; Gomma and Wahdan 1995).

## Conclusion

In this work, the inhibitive action of Argan hulls extract, an inexpensive, eco-friendly, and naturally occurring substance, on the corrosion behavior of copper in 2M $H_3PO_4$ + 0.3 M NaCl has been studied by using various methods. The results obtained are in good agreement and are given as follows:

- The Argan hulls extract provides a good inhibition of corrosion of copper in normal phosphoric acid medium.
- The inhibition efficiency increases with increased Argan hulls extract concentration to attain a maximum value of 91 % at 6 g/L.
- The inhibition efficiency of Argan hulls extract is independent of temperature.
- The values of apparent activation energy increases with the increase in the inhibitor concentration.
- Enthalpy of activation reflects the endothermic nature of copper dissolution process.
- Entropy of activation decreases with increasing inhibitor concentration; hence decrease in the disorder of the system.
- The inhibition efficiencies of the Argan hulls extract obtained from the polarization technique are in good agreement with the values obtain Argan hulls extract ed from the gravimetric measurements.

This agreement among two independent techniques proves the validity of the results.

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