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EVALUATION OF THE SYNERGY EFFECT OF SOME HALIDE IONS IN THE INHIBITION OF COPPER CORROSION IN A HNO_3 ENVIRONMENT IN THE PRESENCE OF PIROXICAM.

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ABSTRACT

The objective of this work is to study the effect of synergy between halide ions (Cl^-, Br^- and I^-) and piroxicam which is a drug molecule with anti-inflammatory properties proposed as a corrosion inhibitor copper in nitric acid medium using the gravimetric method. The experimental results show that the inhibitory efficiency increases considerably with the addition of halide ions on piroxicam. The observed inhibitory efficiency reaches more than 94 % in nitric acid medium (1 M) with the addition of iodide ions to piroxicam at 323 K. The presence of I- ions considerably improves efficiency compared to Br^- and Cl^- ions. So the classification of the halide ions studied, in the sense of those which could help to improve the inhibitory efficacy of piroxicam is I^- > Br^- > Cl^-, which confirms previous studies.

KEYWORDS: synergy effect, gravimetry, corrosion inhibition, halide ions, piroxicam.

INTRODUCTION

Copper is a widely used metal, especially in the electronics and mechanical industries because of its remarkable properties [1-3]. Indeed, the corrosion of copper by corrosive media, such as nitric acid solutions, is most often unavoidable and limits its application in industry. Recently, the use of drug molecules have emerged, we can cite for example: atenolol, bisoprolol, etc., have been used as inhibitors in order to fight against the corrosion of metals in an acid medium [4-9]. Similarly, recent studies on antihypertensive, aspirin and anti-biotics have been used to combat metal corrosion in acidic environments [10-15]. Several modifications have been made in recent times with the aim of improving the effectiveness of drugs and organic molecules as metal corrosion inhibitors in an acid medium. One of these modifications is the addition of halide ions to these different molecules [16-19]. The molecule studied called piroxicam is a drug molecule used for its anti-inflammatory properties. It is used for the treatment of pain and inflammation in osteoarthritis and rheumatoid arthritis. The molecular structure of Piroxicam (C_{15} $H_{13}N_3$ O_4S)

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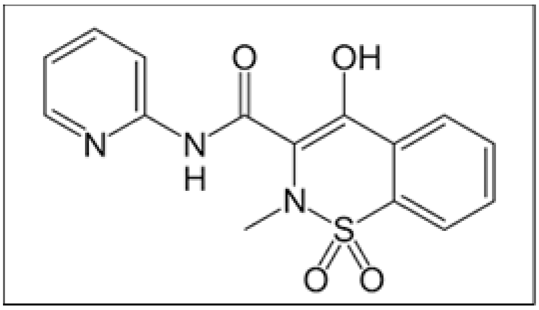

Figure 1: Molecular structure of Piroxicam

The halogenated compounds NaCl, NaBr and KI were used in the case of our study because they contain halide ions (Cl^-, Br^- and I^-), respectively.

However, the aim of this work is to study the synergistic effect of halide ions (Cl^-, Br^-, I^-) in inhibiting copper corrosion in HNO_3 (1 M) medium in the presence of piroxicam. Our aim is to test the performance of piroxicam as an inhibitor in the study medium, evaluate corrosion rates and inhibitory efficacy, determine adsorption thermodynamic quantities and assess the synergy between piroxicam and halide ions.

MATERIALS AND METHODS

Copper Specimens

The copper samples were in the form of a rod 10 mm long and 2 mm in diameter. It is a commercial copper of 99 % purity.

Solution

For the preparation of our solutions we proceeded as follows:

- Sampling of a volume of 65 % commercial nitric acid of analytical quality from Merck, which is diluted with distilled water to obtain a 1 M nitric acid solution,
- Measurement of the masses of organic molecules for different concentrations (0.01 mM; 0.05 mM; 0.1 mM and 0.5 mM),
- Addition of these masses in the same volume of prepared 1 M nitric acid solution.

Samples of the metal were immersed for one hour in different solutions:

- control solution containing one of the halide ions (10^{-3}M; 10^{-2}M)
- control solution containing piroxicam (10^{-4} M) and one of the halide ions (10^{-3} M; 10^{-2} M).

Weight loss method

The mass loss method **[20-22]** is one of the most widely used methods for evaluating corrosion inhibition of metals due to its simplicity and reliability of measurements. Mass loss measurements were made by total immersion of the pre-weighed copper sample in 100 ml capacity beakers containing 50 ml of the test solution maintained at a temperature of (298 K to 323 K). The samples were collected one hour later and rinsed thoroughly with distilled water and reweighed using a balance with a sensitivity of ±0.1 mg. The average values of the mass loss data were used to calculate parameters such as corrosion rate, inhibition efficiency and recovery rate using the following relationships:

$$W = \frac{\Delta m}{St} \quad \textbf{(1)}$$

$$EI(\%) = \frac{W_0 - W}{W_0} \times 100 \quad \textbf{(2)}$$

$$\theta = \frac{W_0 - W}{W_0} \quad \textbf{(3)}$$

Where W_0 and W are the corrosion rate in the absence and presence of the inhibitor respectively

Δm is the weight loss, S is the total surface area of the copper sample and t is the immersion time.

RESULTS AND DISCUSSION

Study of the synergistic effect of halide ions

Effect of Cl^-, Br^- and I^- ions on the corrosion rate of copper in medium HNO_3 1 M

Figures 1,2,3,4,5 and 6 give the evolution of the copper corrosion rate in 1 M HNO_3 medium in the presence of piroxicam (10^{-4} M) and one of the halide ions for different concentrations (10^{-3} M;10^{-2} M).

- **NaCl**

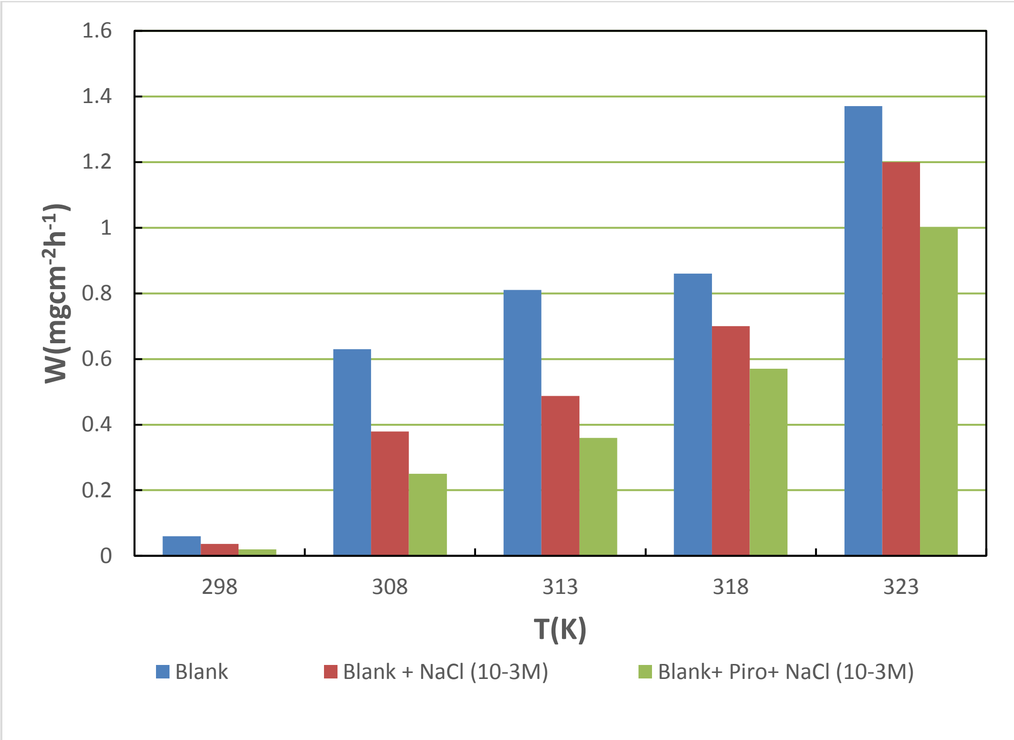

Figure 2: Copper corrosion rate in 1 M HNO_3, 10^{-3} M NaCl and 10^{-4} M piro medium.

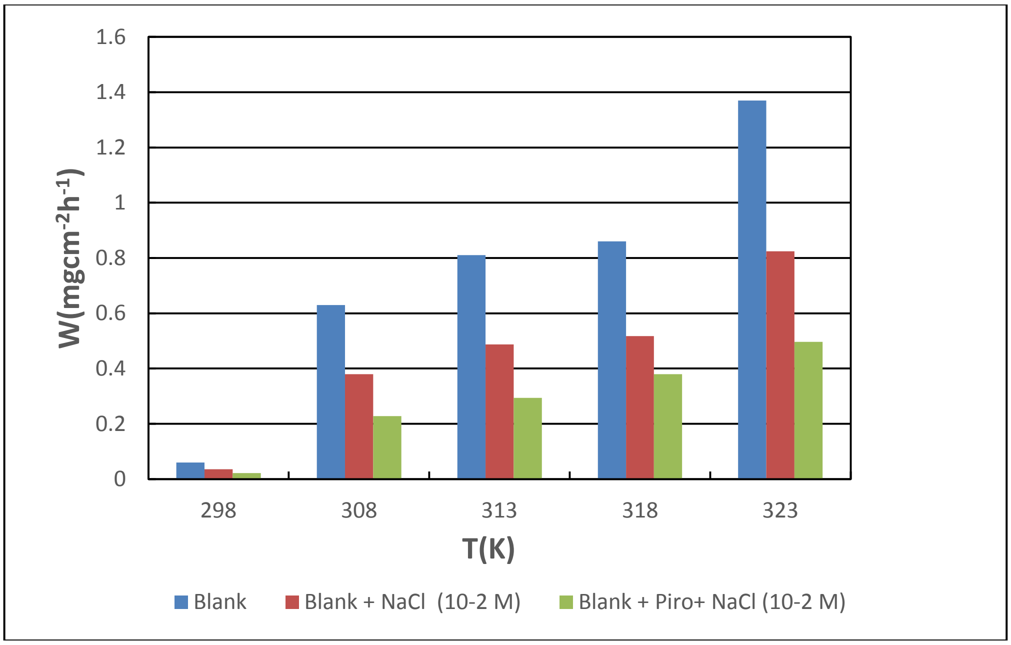

Figure 3: Copper corrosion rate in 1 M HNO_3, 10^{-2} M NaCl and 10^{-4} M piro medium.

- **NaBr**

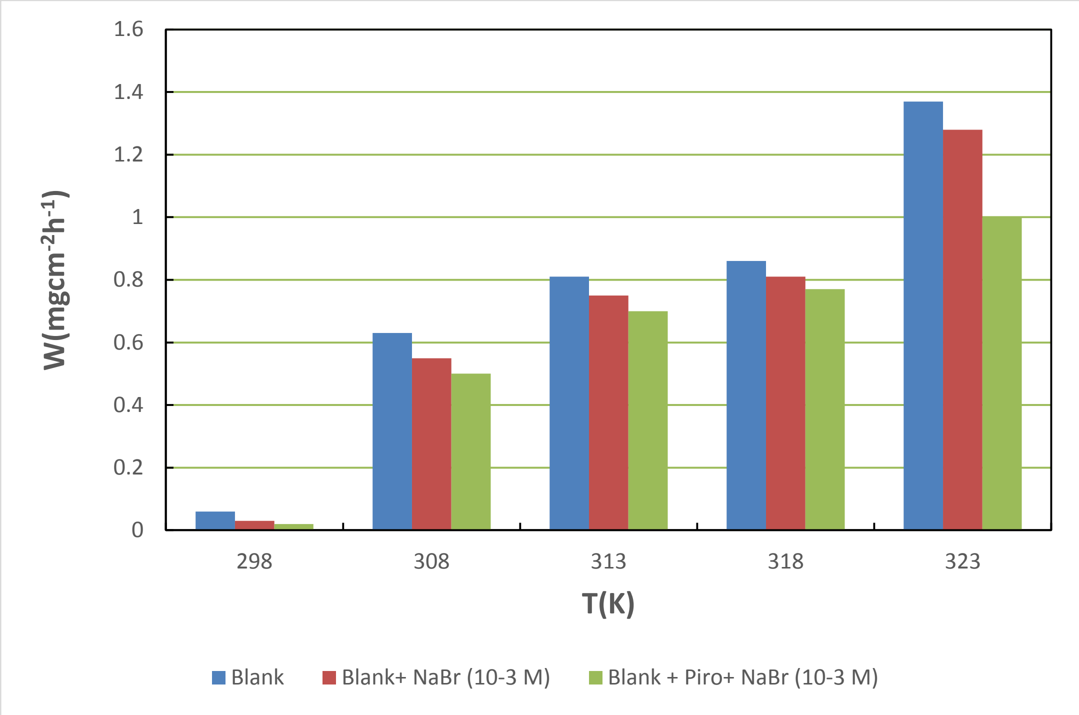

Figure 4: Copper corrosion rate in 1 M HNO_3, 10^{-3} M NaBr and 10^{-4} M piro medium.

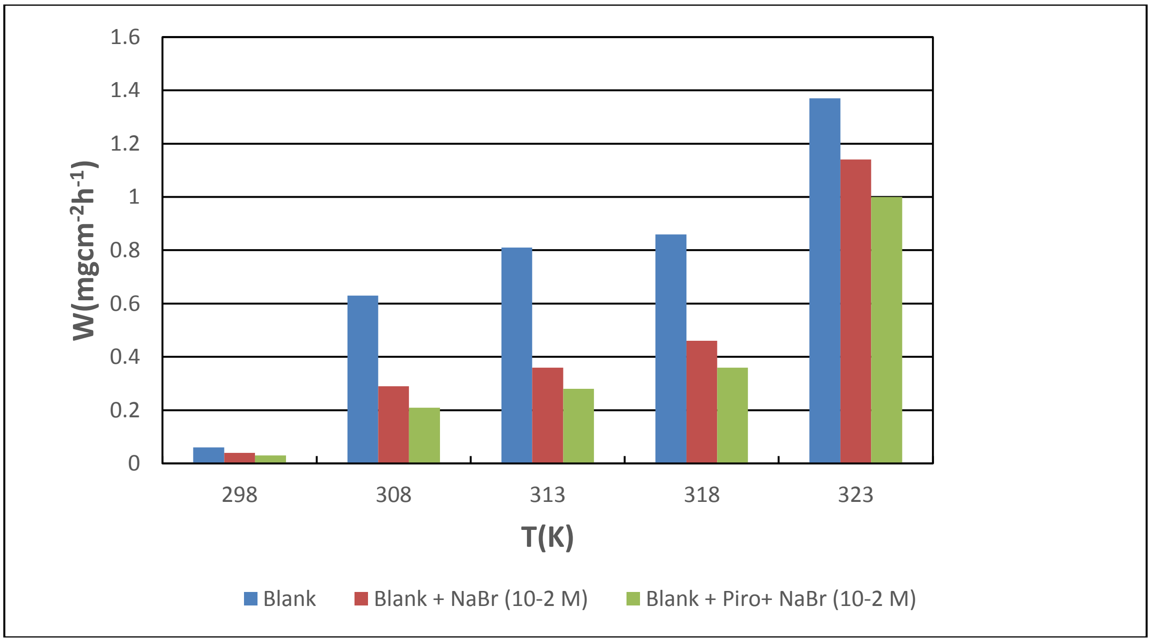

Figure 5: Copper corrosion rate in 1 M HNO_3, 10^{-2} M NaBr and 10^{-4} M piro medium.

- **KI**

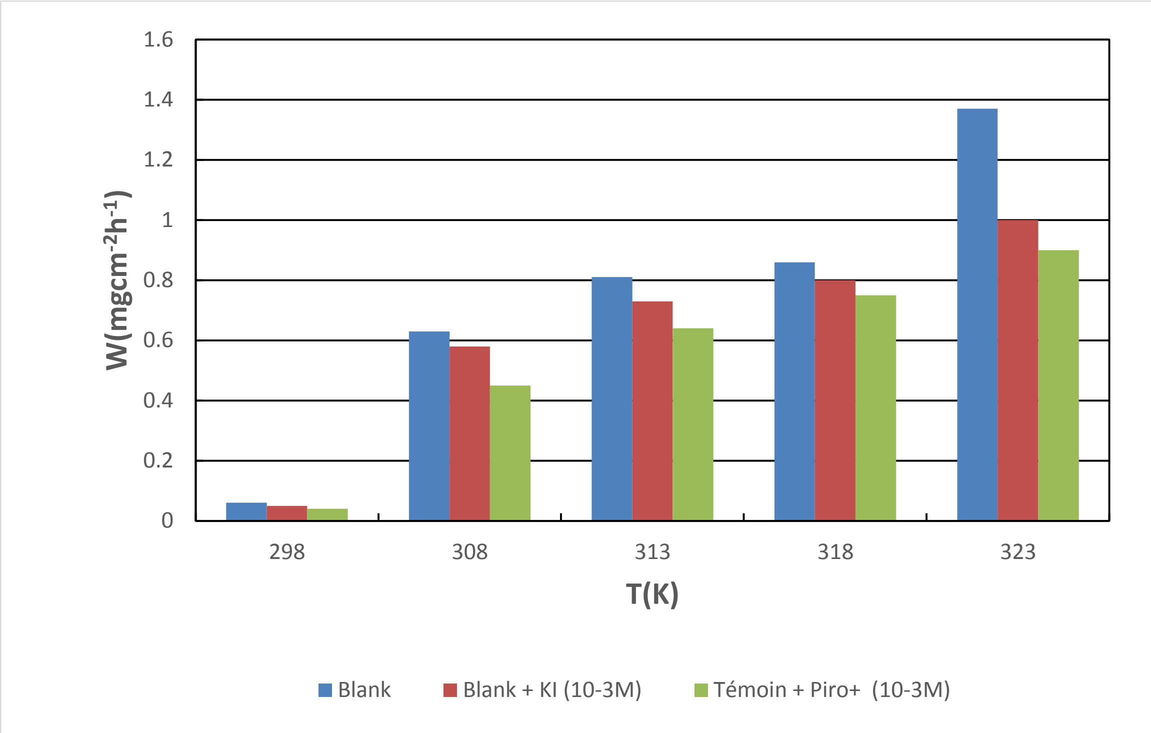

Figure 6: Copper corrosion rate in 1 M HNO_3, 10^{-3} M KI and 10^{-4} M piro medium.

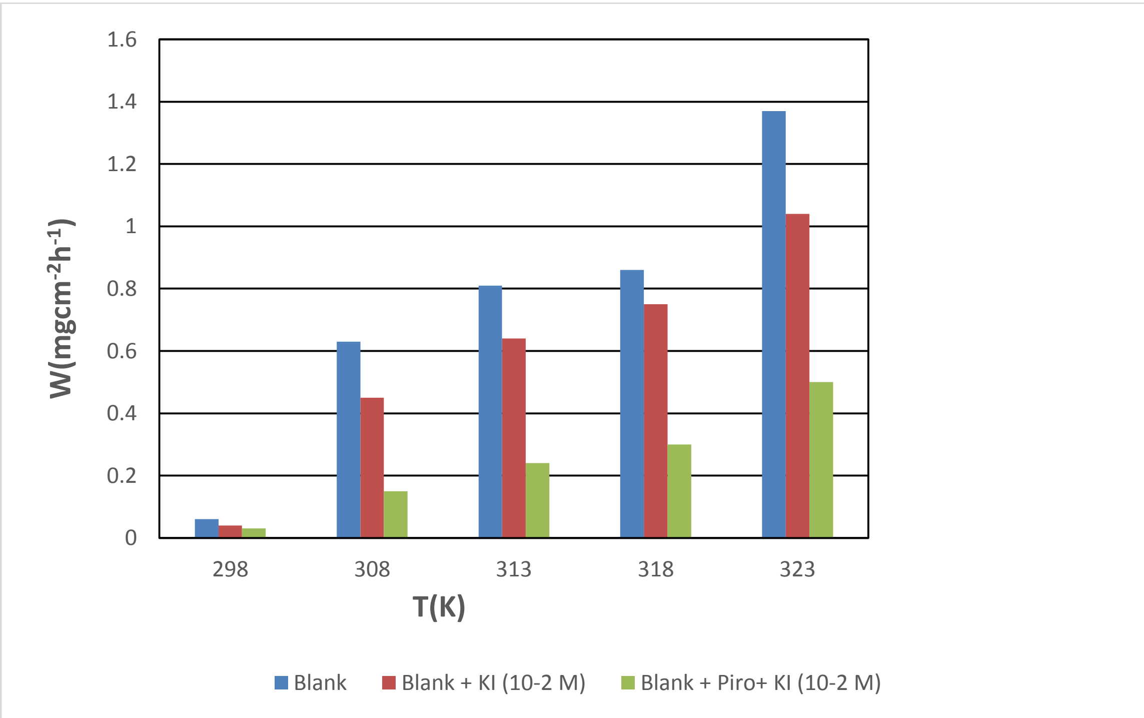

Figure 7: Copper corrosion rate in 1 M HNO_3, 10^{-2} M KI and 10^{-4} M piro medium.

The histograms above clearly illustrate the existence of a synergistic effect between the halide ions and the piroxicam molecule. However, the presence of Cl^- and Br^- and I^- ions influence the evolution of the corrosion rate in this corrosive environment.

In this study, according to the results obtained, the synergy between the iodide ions and the piroxicam is the most favorable for the inhibition of the corrosion of copper in the medium HNO_3 1 M. Indeed, the rate of corrosion of the metal in this mixture is lower than that of the mixture containing only piroxicam for the different study concentrations. It is the same as with piroxicam and the Cl^- and Br^- ions at these same concentrations. Then the classification of the halide ions studied, in the sense of those which could help to improve the inhibitory efficacy of piroxicam is $I^- > Br^- > Cl^-$, which is therefore consistent with previous studies **[23-25]**.

Effect of Cl^-, Br^- and I^- ion concentration on inhibitory efficacy

Figures 8, 9, 10, 11, 12 and 13 below represent the evolution of the inhibitory efficacy of piroxicam as a function of the concentrations of halide ions at the different study temperatures.

- **NaCl**

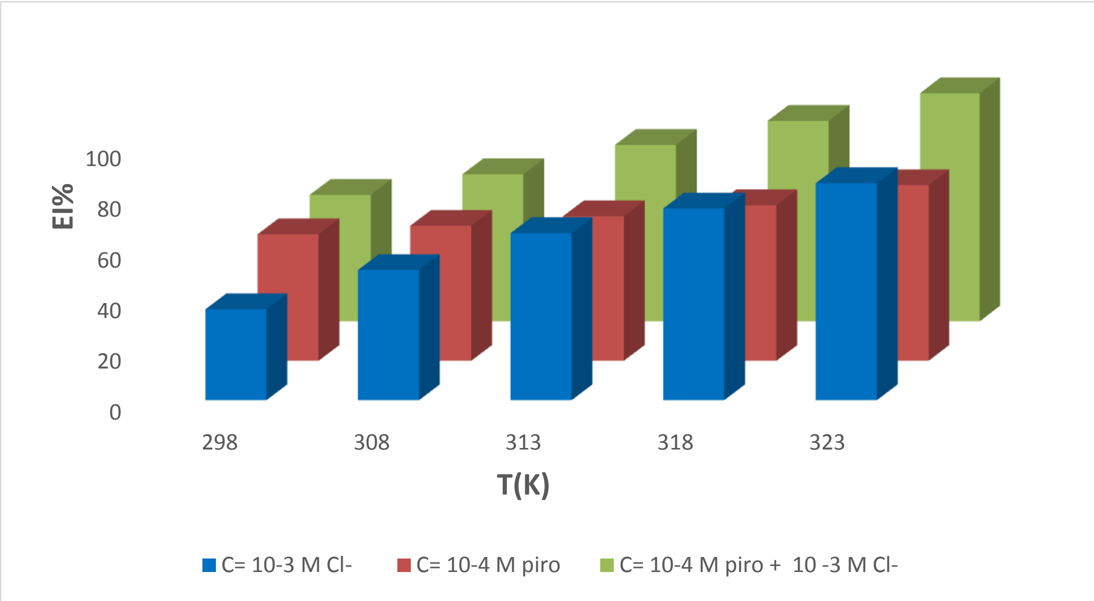

Figure 8: Inhibitory efficacy of piroxicam (10^{-4} M) and piroxicam (10^{-4} M) + Cl^- (10^{-3} M) for copper corrosion in HNO_3 (1 M).

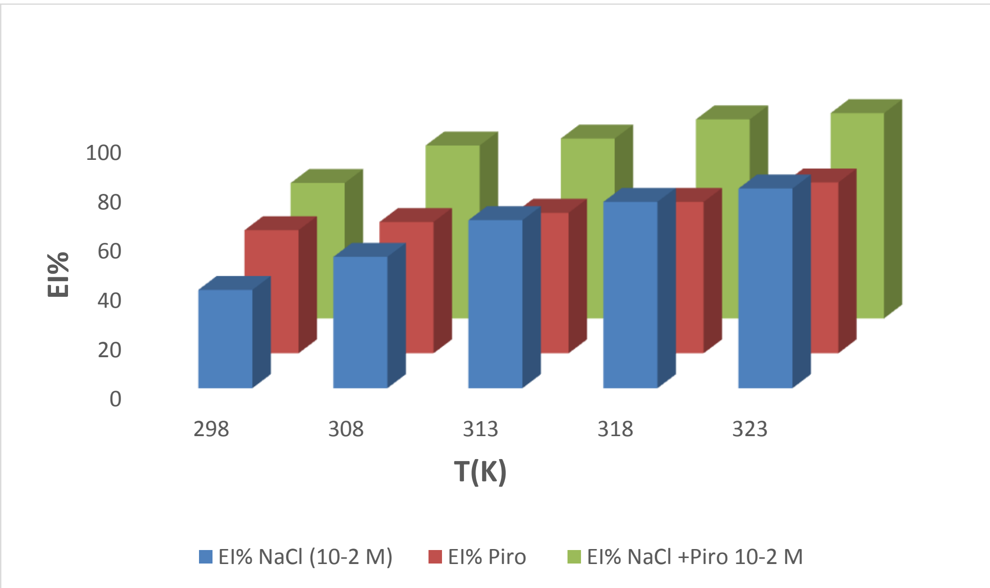

Figure 9: Inhibitory efficacy of piroxicam (10^{-4} M) and piroxicam (10^{-4} M) + Cl^- (10^{-2} M) for copper corrosion in HNO_3 (1 M).

- **NaBr**

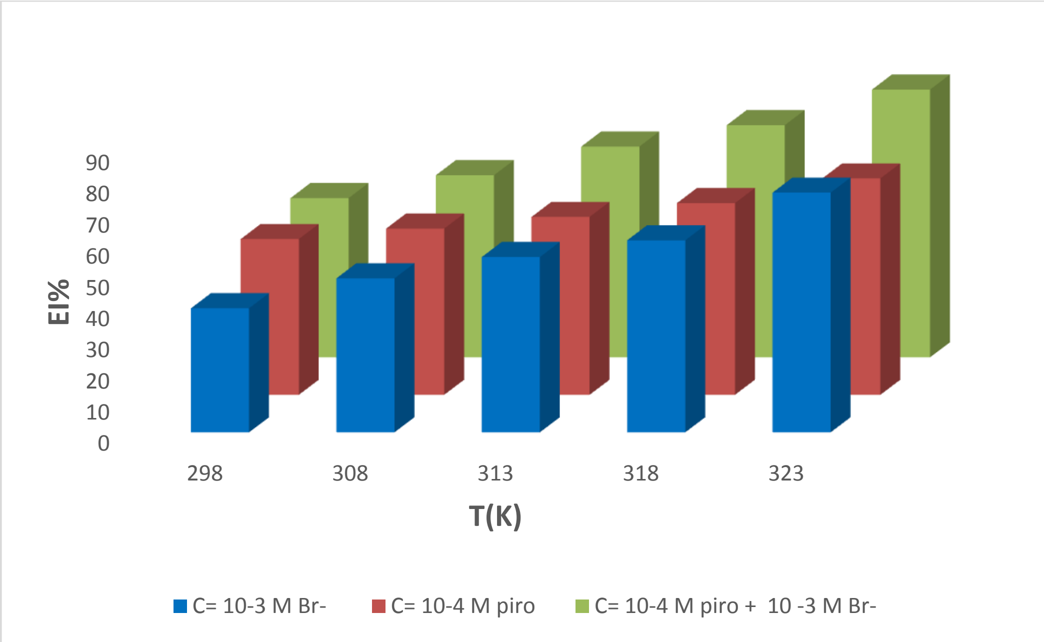

Figure 10: Inhibitory efficacy of piroxicam (10^{-4} M) and piroxicam (10^{-4} M) + Br^- (10^{-3} M) for copper corrosion in HNO_3 (1 M).

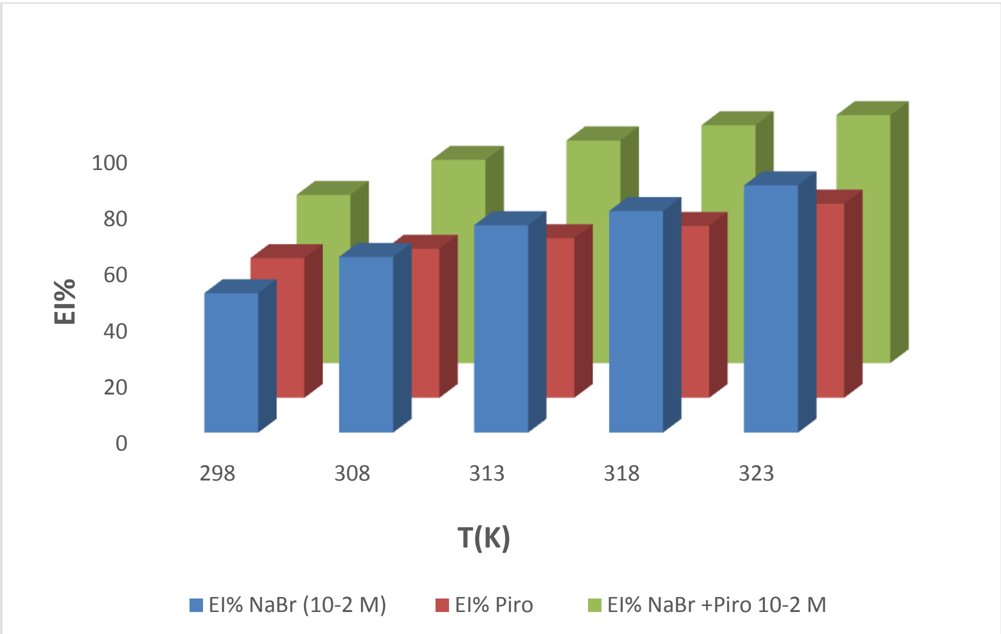

Figure 11: Inhibitory efficacy of piroxicam (10^{-4} M) and piroxicam (10^{-4} M) + Br^- (10^{-2}M) for copper corrosion in HNO_3 (1 M).

- **KI**

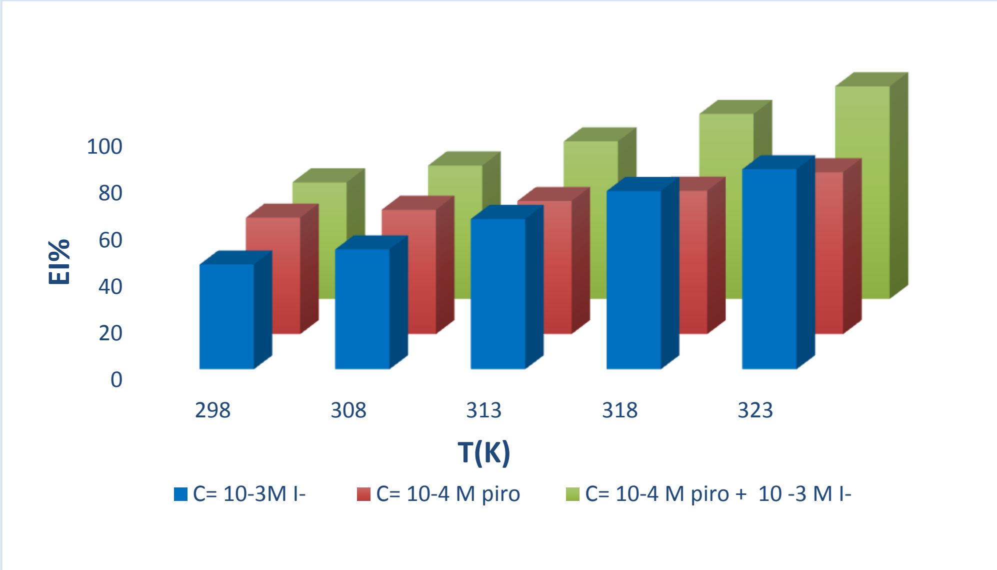

Figure 12: Inhibitory efficacy of piroxicam (10^{-4} M) and piroxicam (10^{-4} M) + I^- (10^{-3} M) for copper corrosion in HNO_3 (1 M).

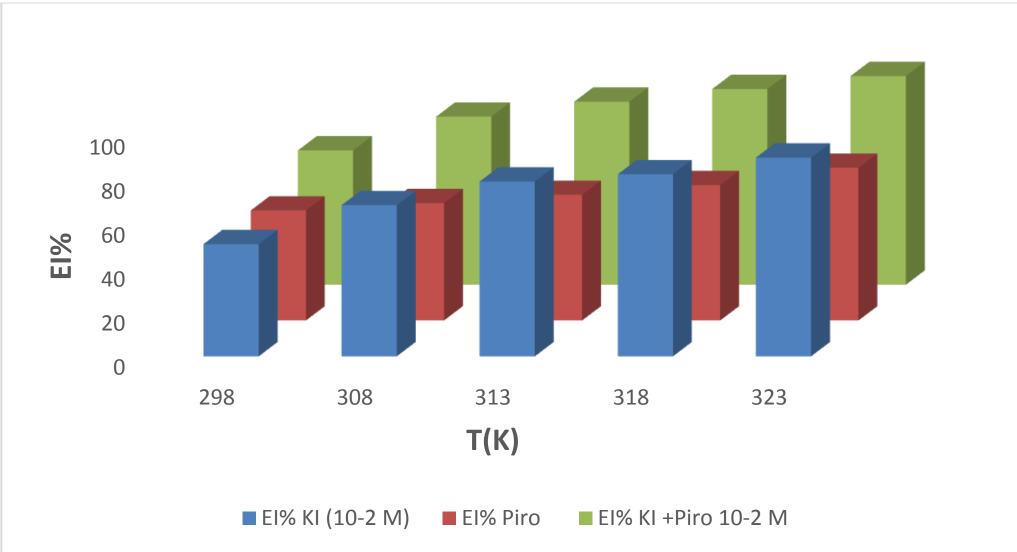

Figure 13: Inhibitory efficacy of piroxicam (10^{-4} M) and piroxicam (10^{-4} M) + I^- (10^{-2} M) for copper corrosion in HNO_3 (1 M).

We observe through these different representations above that the association of anions with piroxicam improves its inhibitory efficiency with respect to the corrosion of copper in a nitric acid medium. This improvement in inhibitory efficacy is significant with increasing concentration. The improvement in the inhibitory efficacy observed at the level of the different figures and therefore of the molecule could be due to the synergistic effects between the inhibitor and the anions thus forming Inh-anion complexes **[26-28]**. This synergistic effect is caused by an interaction between constituents of the inhibitor and one of the ions present in solution. This could facilitate co-adsorption of the anions combined with the inhibitor on the surface of the metallic structure by unbonded electron pairs of sulfur, oxygen and nitrogen atoms, as well as π electrons of rings aromatic.

From the analysis of the different figures above, it appears that the contribution of the iodide ion (I^-) is more significant than that of the chloride (Cl^-) and bromide (Br^-) ions.

Synergy Parameters

In order to better assess the synergistic effect of our compounds, the synergy parameter (S) was determined.

Tables 1, 2, 3, 4.5 and 6 below give the calculated values of the synergy parameter between the anions (Cl^-, Br^- and I^-) for concentrations of 10^{-2} M and 10^{-3} M and the piroxicam of concentration 10^{-4} M.

Table 1: Synergy factor between chloride ions (Cl^-) at 10^{-3} M and piroxicam at 10^{-4} M in copper inhibition in 1 M HNO_3 medium for different temperatures

C=10^{-3} M				
T(K)	EI % (piroxicam)	EI %(Cl^-)	EI % (piro + Cl^-)	synergy factor
298	49.85	35.80	49.85	1.73
308	53.19	51.28	57.97	1.82
313	56.91	65.82	69.54	1.78
318	62.66	75.51	79.01	1.76
323	69.19	85.5	89.9	1.72

Table 2: Synergy factor between chloride ions (Cl^-) at 10^{-2} M and piroxicam at 10^{-4} M in copper inhibition in 1 M HNO_3 medium for different temperatures

C=10^{-2} M				
T(K)	EI % (piroxicam)	EI % (Cl^-)	EI % (piro + Cl^-)	synergy factor
298	49.85	39.82	54.86	1.65
308	53.19	53.19	70.12	1.40
313	56.91	68.05	72.91	1.51
318	62.66	75.51	80.66	1.56
323	69.19	80.9	83.21	1.81

Table 3: Synergy factor between chloride ions (Br^-) at 10^{-3} M and piroxicam at 10^{-4} M in copper inhibition in 1 M HNO_3 medium for different temperatures

C=10^{-3} M				
T(K)	EI % (piroxicam)	EI % (Br^-)	EI % (piro + Br^-)	synergy Factor
298	49.85	39.82	51.85	1.74
308	53.19	49.37	54.15	1.91
313	56.91	56.16	67.31	1.69
318	62.66	61.51	74.11	1.68
323	69.19	76.72	85.5	1.71

Table 4: Synergy factor between chloride ions (Br^-) at 10^{-2} M and piroxicam at 10^{-4} M in copper inhibition in 1M HNO_3 medium for different temperatures

C=10^{-2} M				
T(K)	EI % (piroxicam)	EI % (Br^-)	EI % (piro + Br^-)	synergy Factor
298	49.85	49.85	59.88	1.67
308	53.19	62.74	72.3	1.61
313	56.91	73.99	79.2	1.66
318	62.66	79.01	84.60	1.68
323	69.19	88.14	88.21	1.79

Table 5: Synergy factor between chloride ions (I^-) at 10^{-3} M and piroxicam at 10^{-4} M in copper inhibition in 1M HNO_3 medium for different temperatures

C=10^{-3} M				
T(K)	EI % (piroxicam)	EI % (I^-)	EI % (piro + I^-)	Synergy factor
298	49.85	50.85	52.86	1.92
308	53.19	68.48	57.01	2.15
313	56.91	79.20	67.31	2.04
318	62.66	82.50	79.01	1.85
323	69.19	89.02	90.77	1.75

Table 6: Synergy factor between chloride ions (I^-) at 10^{-2} M and piroxicam at 10^{-4}M in copper inhibition in 1M HNO3 medium for different temperatures

C=10^{-2} M				
T(K)	EI % (piroxicam)	EI % (I^-)	EI % (piro + I^-)	synergy factor
298	49.85	50.85	60.86	1.67
308	53.19	68.48	76.12	1.61
313	56.91	79.2	82.91	1.03
318	62.66	82.5	88.66	1.64
323	69.19	90.02	94.53	2.70

The tables above indicate that the synergy factor is greater than 1 (S > 1) for all temperatures at different concentrations. This arrangement clearly shows that the inhibition of copper corrosion provided by the molecule and the anions are synergistic in nature.
It can therefore be concluded that there is a cooperative effect between the inhibitor molecule and the anions.
This means that the piroxicam molecule chemisorbs onto the copper surface while the anions in turn adsorb onto the piroxicam **[29]**.

CONCLUSION

The aim was to evaluate the synergistic effect of piroxicam and the halide ions I^-, Cl^-, Br^-. The results obtained showed that the corrosion rate was significantly lower in the presence of the iodide ion and piroxicam than with the other Cl^- and Br^- ions. Furthermore, inhibitory efficacy increases considerably with the addition of halide ions to the molecule. There is thus a cooperative effect between the inhibitor molecule and the anions. The piroxicam molecule chemisorbs onto the copper surface, while the anions in turn adsorb onto it. In this study, the presence of I^- ions improved efficacy compared with Br^- and Cl^- ions.

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