



RESEARCH ARTICLE

STUDY OF THE SYNERGISTIC EFFECT OF HALIDE IONS ON THE CORROSION RATE OF ALUMINUM IN A 1 M HYDROCHLORIC ACID SOLUTION IN THE PRESENCE OF THREE METHYLXANTHINES

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ABSTRACT

The objective of this study is to investigate the synergistic effect of halide ions (I⁻, F⁻, Cl⁻) and three natural methylxanthines (caffeine, theobromine, and theophylline)—which have complementary properties and are of great interest in nutrition and pharmacology—as proposed inhibitors of aluminum corrosion in hydrochloric acid using the gravimetric method. The experimental results show a considerable increase in inhibitory efficiency with the addition of halide ions to the three methylxanthines between 298 K and 308 K. Thus, at T = 298 K and for solutions with concentrations of (10⁻² M) in iodide ions and (10⁻⁴ M) in organic molecules, the following increases in inhibitory efficacy were observed: 93.4% for caffeine, 90.47% for theobromine, and 90.07% for theophylline. Determination of the synergy factor between iodide ions and each of the inhibitors led to the identification of different temperature ranges exhibiting cooperative adsorption and competitive adsorption.

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INTRODUCTION

Corrosion is a natural phenomenon; it is an electrochemical process in which a material degrades through reaction with its surrounding environment (1). Aluminum and its alloys are generally susceptible to general corrosion and pitting corrosion, the latter of which is considered the most damaging. Indeed, the corrosion of aluminum by corrosive media, such as hydrochloric acid solutions, is often unavoidable and limits its industrial applications. Recently, the use of pharmaceutical molecules has emerged; examples include atenolol, bisoprolol, etc., have been used as inhibitors to combat metal corrosion in acidic environments (2-7). Several modifications have been made recently with the aim of improving the effectiveness of drugs and organic molecules as metal corrosion inhibitors in acidic environments. One such modification is the addition of halide ions to these various molecules (8-10). However, the objective of this study is to investigate the synergistic effect of halide ions in inhibiting aluminum corrosion in a 1 M HCl solution in the presence of three methylxanthines.

MATERIALS ET METHOD

Aluminum specimens and preparation of solutions: The aluminum specimens consist of aluminum rods with a purity of 99.6%, a density of 2.7 g/cm³ (0.1325 ± 0.0001 g), and a diameter of 0.2 cm. The corrosive solution is a 1 M hydrochloric acid (HCl) solution, obtained by diluting 37% commercial concentrated hydrochloric acid with distilled water. Another 1 M hydrochloric acid solution is prepared but without any inhibitor added (control solution). To study the synergistic effect between each inhibitor under investigation and iodide anions, a 1 M hydrochloric acid solution was prepared by adding an inhibitor at a concentration of 10⁻⁴ M and sodium iodide (a water-soluble salt with the formula NaI and a purity of ≥ 99.5%) at a concentration of 10⁻² M to the solution.

Gravimetric Method: The mass (m₁) of each sample is determined using a balance (accuracy: ± 0.1 mg) prior to immersion in 50 mL of the 1 M hydrochloric acid corrosive

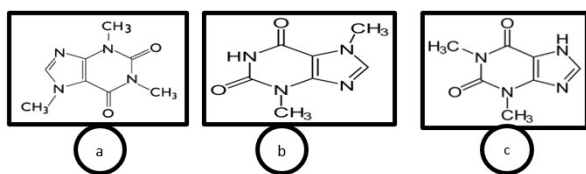


Figure 1. Structures of the molecules studied; a : Caf eine (1, 3, 7-trim ethylxanthine) b : Th eobromine (3,7-dim ethylxanthine), c : Th eophylline (1,3-dim ethylxanthine)

solution prepared with or without an inhibitor. After one hour of immersion at a constant temperature in a thermostatic bath, each sample is removed from the solution, rinsed thoroughly with distilled water, dried at 50 C, and then weighed again (m_2) on the balance to subsequently calculate the mass loss ($\Delta m = m_1 - m_2$). The various temperatures set during the experiment range from 298 K to 323 K. The average values of the mass loss data were used to calculate parameters such as corrosion rate, inhibition efficiency, and coverage rate using the following equations:

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

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

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

Where W_0 and W are the corrosion rates in the absence and presence of the inhibitor, respectively. Δm is the mass loss, S is the total surface area of the copper sample, and t is the immersion time.

RESULTS AND DISCUSSION

Effect of Cl^- , F^- , and I^- ions on the corrosion rate of aluminum in 1 M HCl: To improve the inhibitory efficacy of the organic compounds studied, an investigation was conducted into the influence of halide ions on the corrosion rate of aluminum in 1 M HCl and the synergistic effect of these ions with theobromine. Accordingly, several preparations were made. Metal samples were immersed for one hour in various solutions: control solution containing one of the halide ions (10^{-2} M); control solution containing theobromine (TB) (10^{-4} M) and one of the halide ions (10^{-2} M). Figures 2, 3, and 3 show the evolution of the corrosion rate in the presence of the different ions.

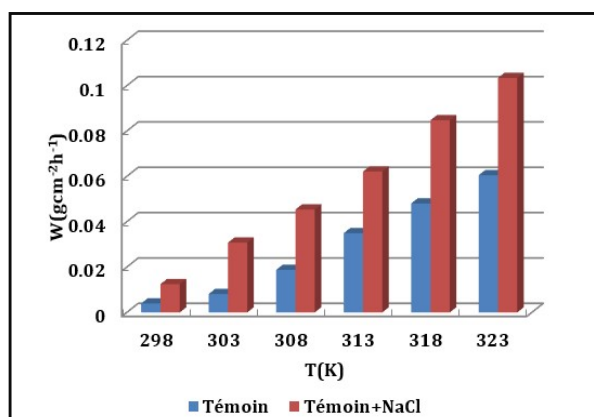


Figure 2. Corrosion rate of aluminum in a 1 M HCl and NaCl solution

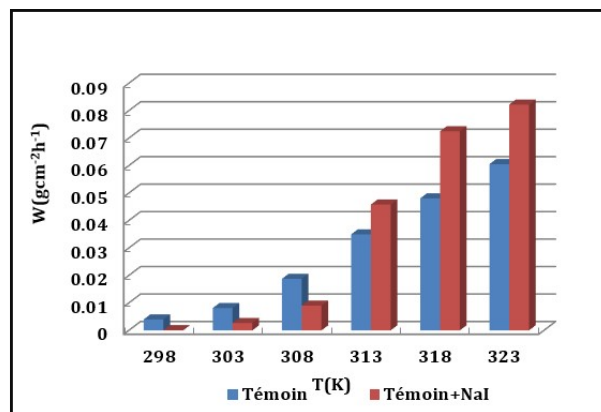


Figure 3. Corrosion rate of aluminum in a 1 M HCl and NaF solution

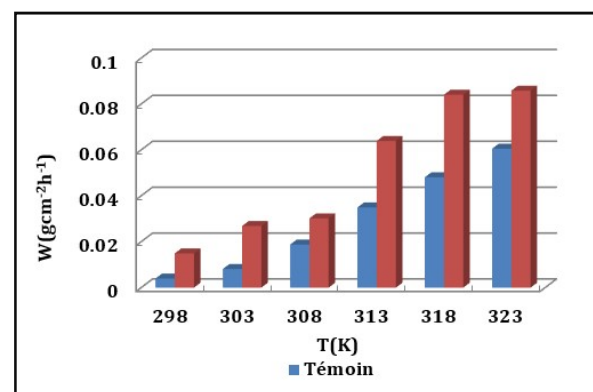


Figure 4. Corrosion rate of aluminum in 1 M HCl and NaI solutions

These three graphs show that the least corrosive of the three halides is the iodide ion. In fact, it acts as an inhibitor at temperatures ranging from 298 K to 308 K. The other two halides increase the corrosion rate to a greater extent. Figures 5, 6, and 7 show the evolution of the corrosion rate of aluminum in a 1 M HCl solution in the presence of theobromine (10^{-4} M) and one of the halide ions (10^{-2} M).

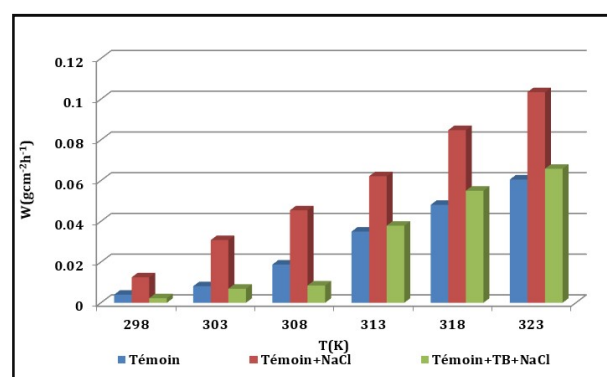


Figure 5. Corrosion rate of aluminum in 1 M HCl, 10^{-2} M NaCl, and 10^{-4} M TB solutions

The histograms clearly illustrate the existence of a synergistic effect between the halides and the inhibitor molecule. However, the presence of Cl^- and F^- ions does not reduce the corrosion rate in this corrosive environment. The results presented graphically in Figure 8 allow for a clear comparison of the effect of each ion in order to identify which one would improve the molecule's inhibitory effectiveness.

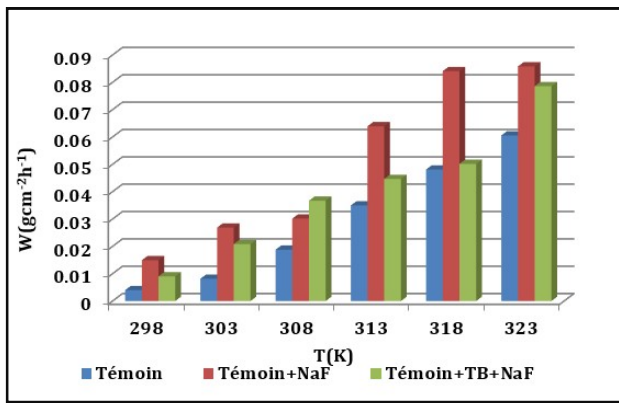


Figure 6. Corrosion rate of aluminum in 1 M HCl, 10⁻² M NaF, and 10⁻⁴ M TB solutions

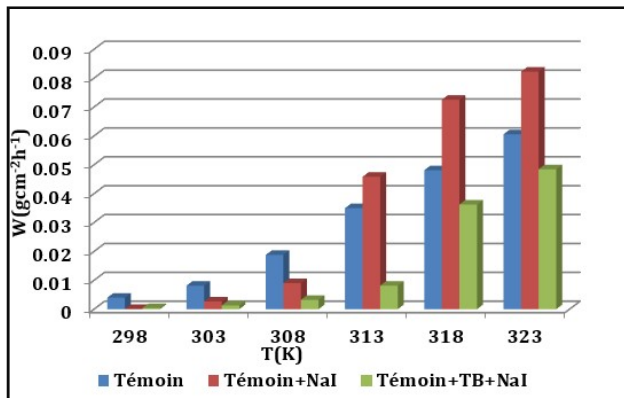


Figure 7. Corrosion rate of aluminum in a solution containing 1 M HCl, 10⁻² M NaI, and 10⁻⁴ M TB

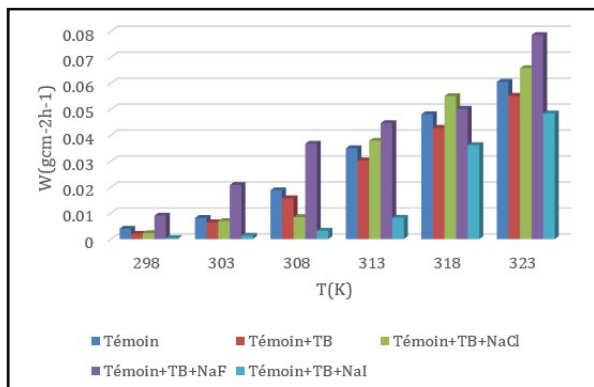


Figure 8. Comparison of the Effect of Cl⁻, F⁻, and I⁻ Ions on the Corrosion Rate of Aluminum in 1 M HCl and 10⁻⁴ M TB Solutions

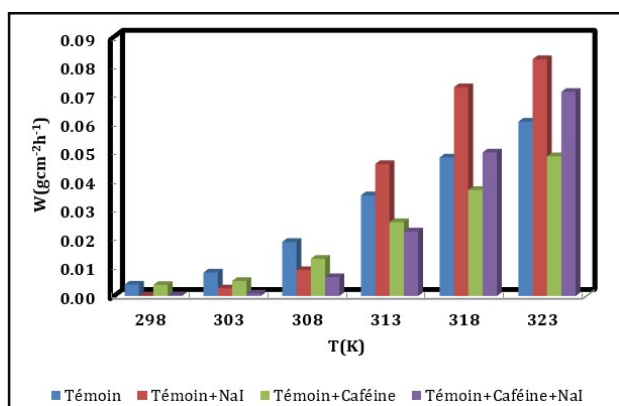


Figure 9. Corrosion rate of aluminum in a solution containing 1 M HCl, 10⁻² M I⁻, and 10⁻⁴ M caffeine

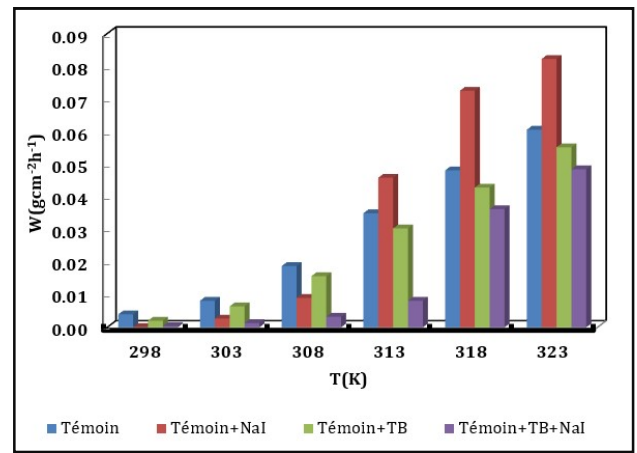


Figure 10. Corrosion rate of aluminum in a solution containing 1 M HCl, 10⁻² M I⁻, and 10⁻⁴ M TB

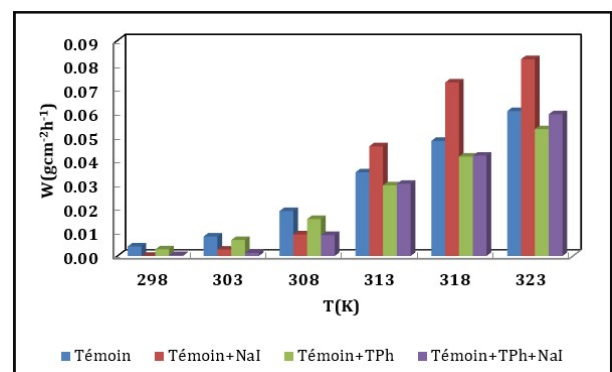


Figure 11. Corrosion rate of aluminum in a solution containing 1 M HCl, 10⁻² M I⁻, and 10⁻⁴ M TPh

In this study, based on the results obtained, the synergy between iodide ions and theobromine is most effective for inhibiting aluminum corrosion in a 1 M HCl solution. Indeed, the corrosion rate of the metal in this mixture is lower than that in the mixture containing only theobromine at temperatures ranging from 298 K to 313 K. Thus, the ranking of the halide ions studied, in terms of those that could help improve the inhibitory efficacy of theobromine, is I⁻ > Cl⁻ > F⁻, which confirms previous studies.

Effect of iodide ions on the corrosion rate of aluminum in 1 M HCl solution and in the presence of the studied methylxanthines: Having discovered that iodide ions enhance the inhibitory efficacy of theobromine by significantly reducing the corrosion rate of aluminum, the study was extended to the other two molecules (caffeine and theophylline) to verify whether the presence of these ions is also beneficial for inhibiting aluminum corrosion with these two molecules in 1 M HCl. Figures 9, 10, and 11 show the effect of iodide ions on the corrosion rate of aluminum in the presence of the studied molecules in 1 M HCl solution.

In Figures 9, 10, and 11, iodide anions reduce the corrosion rate of aluminum in 1 M HCl over the following temperature range:

- From T = 298 K to T = 313 K, when caffeine is present;
- From T = 298 K to T = 323 K, when present with theobromine;

- From $T = 298$ K to $T = 308$ K, when present with theophylline.

At low temperatures (from 298 K to 308 K), iodide anions adsorb onto the aluminum surface, thereby inhibiting metal corrosion. Above 313 K, as the temperature rises, the anti-corrosive effect of the iodide ions diminishes: likely, both types of adsorption occur, but physical adsorption predominates. Iodide anions adsorb onto the positive surface of the aluminum due to electrostatic forces that weaken as the temperature rises.

Synergy parameter: The synergistic effect of two compounds can be evaluated using the synergy parameter (S) proposed by Aramaki et Hackerman (11-15):

$$S = \frac{1-I_{1+2}}{1-I_1-I_2} \quad (4)$$

With $I_{1+2} = I_1 + I_2$; I_1 is the inhibitory potency of the halide ion, I_2 is the inhibitory potency of the inhibitor (organic compound); I_{1+2} is the inhibitory potency of the inhibitor in solution with the halide ion. The synergy between the two compounds produces either a competitive effect ($S < 1$) or a cooperative effect ($S > 1$). Tables 1, 2, and 3 show the calculated values of the synergy parameter between iodide anions and caffeine, theobromine, and theophylline, respectively.

Table 1. Synergy factor between iodide ions and caffeine in the inhibition of aluminum in 1 M HCl medium at different temperatures

T(K)	EI (caféine)	EI (NaI)	EI (NaI+CAF)	Synergy factor
298	39.7	98.1	93.4	1.48
303	35.8	67.1	89.3	1.15
308	31.2	52.0	65.1	1.28

Table 2: Synergy factor between iodide ions and TB in the inhibition of aluminum in 1 M HCl at different temperatures

T(K)	EI (TB)	EI (NaI)	EI (NaI+TB)	Synergy factor
298	48.92	98.11	90.47	1.63
303	20.86	67.13	84.05	1.05
308	16.49	52.01	82.75	0.82

Table 3. Synergy factor between iodide ions and TPh in the inhibition of aluminum in 1 M HCl solution at different temperatures

T(K)	EI (TPh)	EI (NaI)	EI (NaI+TPh)	Synergy factor
298	30.24	98.11	90.07	1.43
303	18.07	67.14	84.26	1.01
308	17.76	52.01	53.41	1.31

The synergy factor is greater than 1 ($S > 1$): from 298 K to 308 K for caffeine and theophylline, and from 298 K to 303 K for theobromine. In this case, there is a cooperative effect between the inhibitory molecule and the iodide ions: one of the compounds is chemisorbed onto the metal surface, and the other is physisorbed onto it. In this study, it is the iodide anions that are chemisorbed. Caffeine, theobromine, or theophylline are physically adsorbed onto the adsorbed iodide anions, which form intermediate bridges between the positively charged metal surface and the positive end of the organic molecule. The synergy factor is less than 1 ($S < 1$): above the temperatures mentioned above. In this case, there is a competitive effect. The inhibitor molecule and the halide ion

I^- occupy different sites. At temperatures above $T = 313$ K, corrosion is enhanced, which could be explained by the weakening of the adsorption driving force. Thus, the inhibitory efficiency of organic molecules between 298 K and 308 K is significantly improved. With a small amount of inhibitor (10^{-4} M), the inhibitory efficiency reaches 90% for a concentration of 10^{-2} M of I^- ions at 298 K.

CONCLUSION

The results obtained reveal that caffeine, theobromine, and theophylline are effective corrosion inhibitors for aluminum in a 1.0 M HCl solution. Inhibitory efficacy depends on both concentration and temperature. For each of these molecules, inhibitory efficacy increases as the inhibitor concentration increases but decreases as the temperature rises. As for the synergistic effect between iodide ions and the molecules studied, it is clear that the presence of I^- ions significantly improves the inhibitory efficacy of the molecules at certain temperatures.

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