

# Influence of 3-Acétyl-4-oxo-benzopyranone on inhibitive performance of bromide ions in sulfuric acid for mild steel.

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**ABSTRACT:** The influence of single bromide ions and the mixture of various concentrations of bromide ions and 0.005 M of 3-Acétyl-4-oxo-benzopyranone (AOBP) on the corrosion of mild steel in 0.5M sulfuric acid have been investigated by using weight loss method, on the range of temperature from 298 to 318 K. The study of the effects of single bromide ions and the mixture of various concentrations of bromide on the corrosion of mild steel in sulfuric acid revealed that mild steel has been more efficiently inhibited by NaBr in the presence of AOBP than single NaBr, and inhibition efficiency increases with increasing concentration of NaBr at the same temperature, but decreases with increasing temperature studied. A synergistic effect exists when AOBP and bromide ion are used together to prevent mild steel corrosion in sulfuric acid at every experimental temperature. The adsorption of NaBr and AOBP + NaBr on the mild steel surface obeys Langmuir and Freundlich adsorption isotherm respectively. Some thermodynamic parameters such as adsorption heat, adsorption entropy and adsorption free energy have been calculated by employing thermodynamic equations. Kinetic parameters such as apparent activation energy and pre-exponential factor have been calculated and discussed.

**Keywords:** mild steel, 3-Acétyl-4-oxo-benzopyranone; Bromide ions; Inhibition efficiency; Synergistic effect; Langmuir and Freundlich adsorption isotherme.

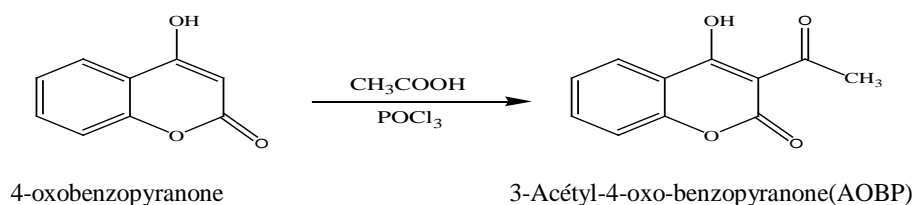
## I. INTRODUCTION

Corrosion is an afflicting problem associated with every use of metals. Acid solutions of various concentrations are extensively used in many industrial processes. Corrosion is an afflicting problem associated with every use of metals and is an important problem resulting in the production of waste with great toxicity and loss of resources and money during these applications. Mild steels undergo considerable dissolution when they are exposed to acid solutions or aggressive environments. A survey of literature reveals that the applicability of organic compounds as acidic medium are organic compound containing nitrogen, oxygen and/or sulphur corrosion inhibitors for mild steel in acidic media has been recognized for a long time [1-5]. the selection of inhibitor is controlled by its economic availability, its efficiency to inhibit the substrate material and its environmental side effects [6-11]. The protective action of an inhibitor in metal corrosion is often associated with chemical or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other. It has been observed that adsorption depends on the chemical structure of molecules, electron density at the donor atom,  $\pi$ -orbital character, the chemical composition of solutions. Synergistic effects describe the increase in the effectiveness of a corrosion inhibitor in the presence of another substance in the corrosive medium. This phenomenon has been frequently used in practice [12-15]. Furthermore, several studies have reported the synergism existing between an organic molecule and halide ions. Hence, the presence of halide ions in acidic media synergistically increases the adsorption ability of some organic compounds and the synergism is often more pronounced in the presence of iodide ions. The pronounced synergistic action is due to the larger ionic radii, high hydrophobicity, and low electronegativity of iodide ions compared to other halide ions [16-18]. In this study 3-Acétyl-4-oxo-benzopyranone have been selected to study anticorrosion on mild steel in 0.5 M sulphuric acid medium. Then, we attempted to increase the inhibition efficiency synergistically further by the bromide ions addition to the AOBP containing corrosive solution.

## II. EXPERIMENTAL PROCEDURES

### II.1. Organic Compound

The synthesis of title compound was successfully accomplished through the following steps in our laboratory , a mixture of 1 mol of 4-hydroxycoumarin, 700 ml of CH<sub>3</sub>COOH and 300 ml of POCl<sub>3</sub> is refluxed for 1 hour in an oil bath (120°C). There should be a system to trap HCl evolved. After pouring the contents of the Erlenmeyer flask into a mixture of ice water the precipitate is filtered . 0,3L by solid potassium carbonate at 10% added at the mixture. Warm gently and then filter. The filtrate is cooled and then acidified with 5N HCl. AOBP white solid, <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) :δ= 7,3-8,3 ; massif ; 4 H aromatic ; δ=2,8 ; singlet; 3 H. <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>): δ<sub>CO</sub> (ketone) = 162, 4 ppm, δ<sub>CO</sub> (lactone) = 157, 4 ppm. IR: ν<sub>CO</sub> (lactone α, β-insaturated) = 1732 cm<sup>-1</sup>, ν<sub>CO</sub> (ketone α,β-insaturated ) =1674 cm<sup>-1</sup> m.p.134°-136°C.



## II.2. Materials

Tests were performed on a mild steel electrode of the following composition, presented in table 1

TABLE 1.  
Chemical composition (wt. %) of mild steel

Element	C	Si	P	S	Mn	Al
Fe	0.21	0.38	0.09	0.05	0.05	0.05
wt.%	0.01	Balance				

## II.3. Solutions

The corrosive medium (0.5 M H<sub>2</sub>SO<sub>4</sub>) was prepared from AR grade 98% H<sub>2</sub>SO<sub>4</sub> using double-distilled water.. The desired concentrations of NaBr solutions (0.01; 0.02; 0.03; 0.04; 0.05 and 0.06M) in presence of 0.005 M inhibitor were obtained by adding a specified amount of NaBr to 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The combined inhibitor (AOBP + NaBr) solutions were prepared by adding the required amount of AOBP to NaBr -H<sub>2</sub>SO<sub>4</sub> solution. Each experiment was carried out in aerated and stagnant solutions.

## II.4. Gravimetric Technique

Gravimetric method is indeed the most simple and reliable method for the determination of inhibition efficiency. The mild steel sheets of 3,5cm ×1cm ×0.1cm were abraded with a series of emery paper (grade 320-500-800) and washed thoroughly with triple distilled water, degreased with acetone and dried using air flow at room temperature. After weighing accurately, the specimens were immersed in 30 ml beaker, which contained 30 ml sulfuric acid with and without addition of different concentrations of Oxobenzopyranone. All the aggressive acid solutions were open to air. After 6 h , the specimens were taken out, washed, dried, and weighed accurately. Experiments were carried out in triplicate. The average weight loss of three parallel mild steel sheets could be obtained. Then the tests were repeated at different temperatures and 0.5 M H<sub>2</sub>SO<sub>4</sub> concentration and mass loss was expressed in mg and corrosion rate in mg .cm<sup>-2</sup>. h<sup>-1</sup>.

## III.RESULTS AND DISCUSSION

### III.1 Weight loss and inhibition efficiency

The loss in weight of carbon steel strips in 0,5 M H<sub>2</sub>SO<sub>4</sub> solution in absence and presence of different concentrations of NaBr during 6 hours of the trials has been determined.

The protection efficiency IE(%) and the parameter (θ) that represents the weight of the metal surface covered by inhibitor molecules were calculated using the following equations (19-20):

$$IE(\%) = \left[ 1 - \frac{W_{inh}}{W_{blank}} \right] \times 100 \quad (1)$$

$$\theta = 1 - \frac{W_{inh}}{W_{blank}} \quad (2)$$

Where  $W_{inh}$  and  $W_{blank}$  are the weight losses, in milligrams, of the coupon in the presence and absence of inhibitors, respectively. The corrosion rate of the metal was determined for the immersion period from weight loss through equation (3):

$$\text{Corrosion rate} = \frac{W}{St} \quad (3)$$

Where  $W$  is the weight loss in milligrams (mg),  $A$  the coupon surface area in  $\text{cm}^2$  and  $t$  the immersion time in hours.

### III.2 Effect of concentration of NaBr on the inhibition efficiency in 0.5M $\text{H}_2\text{SO}_4$ .

The values of the corrosion rate obtained from weight loss measurements for different concentrations of NaBr inhibitor in 0.5 M  $\text{H}_2\text{SO}_4$  are given in Table 2. It is found that NaBr inhibits the corrosion of mild steel in the acid at all concentration from 0.01 to 0.06 M. The effect of temperature on inhibitor performance was studied in 0.5 M  $\text{H}_2\text{SO}_4$  between 298-318 K. These results show that the corrosion rate of mild steel in  $\text{H}_2\text{SO}_4$  increased with rise in temperature in both inhibited and uninhibited solutions. Figure 2 shows the effect of temperature at different concentration of NaBr. It was observed that increase of temperature increase the corrosion rate for all the systems studied. It is widely known that halide ions either stimulate or inhibit the corrosion of metals, depending on the concentration. Corrosion inhibiting effects of  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  ions in electrolyte solutions have been reported by several authors [21–22]. These effects were interpreted by a specific halide adsorption, which has been proved with a great precision in the case of  $\text{I}^-$  [23–26]. It is generally accepted that the presence of halide ions in acidic medium synergistically increases the inhibition efficiency of some organic compounds. It should be noted that the corrosion rate decreases more rapidly with temperature in the presence of AOBP. In the presence of NaBr and 0,005 M AOBP, the corrosion rate was observed to reduce significantly, indicating that NaBr actually inhibited the corrosion of mild steel in the acidic environment. Further reduction in corrosion rate was observed on addition of 0,005 M AOBP to NaBr. The reduction in corrosion rate of steel in the presence of AOBP when combined with iodide ions was found to be concentration dependent.

TABLE 2  
 Inhibition corrosion rate for different concentrations of NaBr without and with the addition of 0.05M AOBP in 0.5M  $\text{H}_2\text{SO}_4$  at different temperatures

NaBr (M)	AOBP (M)	corrosion rate $W(\text{g}.\text{cm}^{-2}.\text{h}^{-1})$		
		298 K	308 K	318 K
blank	-	0,0066	0,0084	0,0253
-	0,005	0,0036	0,0041	0,0084
0,01	0	0,0029	0,0037	0,0100
0,02	0	0,0021	0,0029	0,0074
0,03	0	0,0010	0,0025	0,0057
0,04	0	0,0008	0,0018	0,0048
0,05	0	0,0006	0,0013	0,0045
0,06	0	0,0002	0,0010	0,0027
0,01	0,005	0,0007	0,0009	0,0121
0,02	0,005	0,0004	0,0009	0,0086
0,03	0,005	0,0004	0,0008	0,0069
0,04	0,005	0,0004	0,0004	0,0052
0,05	0,005	0,0002	0,0004	0,0036
0,06	0,005	0,0001	0,0006	0,0024

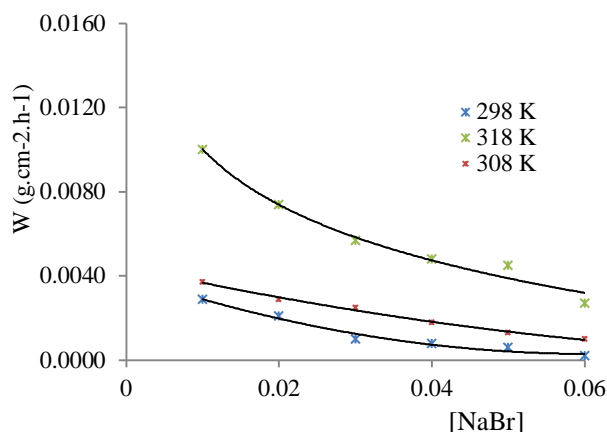


Fig 1: plot weight loss against concentration of NaBr at different temperatures.

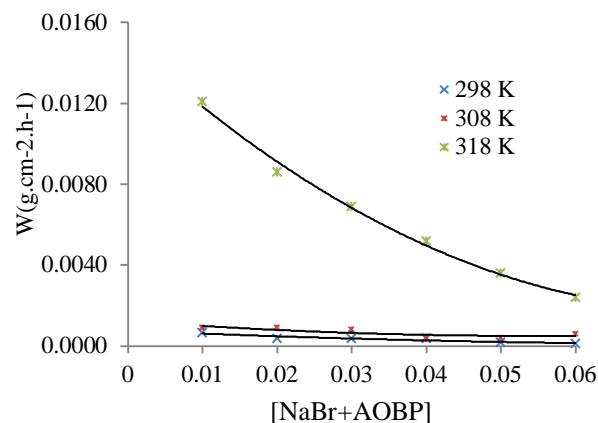


Fig 2: plot weight loss against concentration of NaBr and 0,005 AOBP at different temperatures.

### III.3 Inhibition efficiency obtained for different concentrations of AOBP with the addition of 0.02M NaBr at different temperatures

The variation of inhibition efficiency of NaBr at different concentrations, on mild steel in 0,5M H<sub>2</sub>SO<sub>4</sub>, at different temperatures revealed that the maximum efficiency in absence of AOBP ion was found to be 81.60% at 318K for 0.010 m. This result indicated that the NaBr could acts as effective corrosion inhibitor for mild steel in 0,5M H<sub>2</sub>SO<sub>4</sub>. In general, in acid media, halide ions are proven to form intermediates on a metal surface, consequently, reduce or accelerate metal dissolution by replacing OH<sup>-</sup> ions already adsorbed on metal surface during the anodic process. It has been observed that in the presence of a concentration of 0.005 M AOBP in a 0.5M sulfuric acid solution, the efficiency is approximately 88 %, which proves a very good adsorbability on the carbon-steel's surface. It can be seen from the Table 3 and Figure 4 that inhibition efficiency rapidly increases with an increase in concentration of NaBr at the same temperature. At the same concentration of NaBr however, inhibition efficiency decreases with increasing experimental temperature. This observation has been ascribed to

The inhibition of mild steel corrosion in the presence of AOBP could be attributed to the adsorption of molecules 's inhibitor onto mild steel surface , which blocks the metal and this do not permit the corrosion process to take place. AOBP contains oxygen atoms in its molecular structure having lone pair of electrons. It could be adsorbed by the interaction between the lone pair of the electrons of the oxygen atoms and mild steel surface. This process may be facilitated by the presence of d-vacant orbital of iron making the steel, as observed in the synergistic effect, which has been attributed to the formation of intermediate salt bridges by the halide (anions) between the metal surface and the positive end of the organic inhibitor [27]. The rise in temperature results in the increase in conductance of the aqueous acid medium and thereby increases the diffusion rate of hydrogen ions to the composite surface and hence the corrosion progresses faster at higher temperatures. The increase in IE(%) may be due to the blocking effect of the surface by both adsorption and film formation mechanism , the highest

**TABLE 3**  
Inhibition efficiency for different concentrations of NaBr without and with the addition of 0.005M AOBP 0.5M H<sub>2</sub>SO<sub>4</sub> at different temperatures.

protection efficiency of benzopyranone combined with bromide was attained at 298 K. As per Fouada's explanation, the decrease in the inhibition efficiency of the inhibitor with increase in temperature might be due to adsorption and

NaBr (M)	AOBP (M)	IE (%)		
		298 K	308 K	318 K
blank	-	-	-	-
-	0,005	58,0	56,1	50,0
0,01	0	53,3	52,8	45,8
0,02	0	65,6	64,2	60,3
0,03	0	82,0	70,5	66,1
0,04	0	86,9	78,9	74,6
0,05	0	89,7	84,7	76,6
0,06	0	97,5	90,1	87,2
0,01	0,05	69,5	90,9	52,2
0,02	0,05	82,7	90,9	66,0
0,03	0,05	83,6	92,5	72,8
0,04	0,05	87,1	95,4	79,4
0,05	0,05	96,3	95,4	85,7
0,06	0,05	96,5	95,6	90,6

desorption of inhibitor. Adsorption and desorption of inhibitor molecules continuously occurs at the metal surface and an equilibrium exists between these two processes at a particular temperature [28].

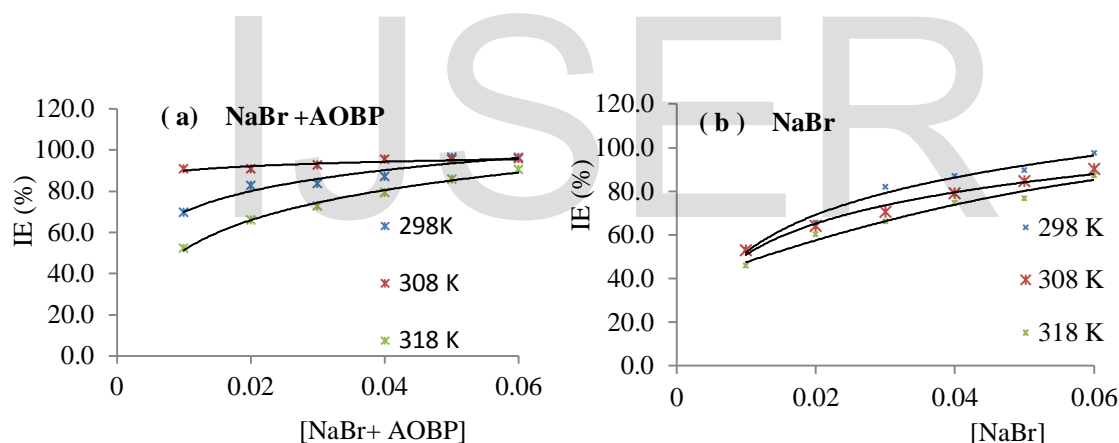


Fig 3 : Plot inhibition efficiency against concentration for mild steel corrosion in 0,5 M H<sub>2</sub>SO<sub>4</sub> in presence of (a) NaBr + 0,05 AOBP and (b) NaBr at different temperatures.

In addition to the molecular form, AOBP can be present in protonated species in acid solution. The formation of positively charged protonated species facilitates adsorption of the compound on the metal surface through electrostatic interaction between the organic molecules and the metal surface. The strong chemisorptions of bromide ions on the metal surface is responsible for the synergistic effect of bromide ions, in combination with AOBP in their cationic forms. The inhibitor are then adsorbed by coulombic attraction on the metal surface where bromide ions are already adsorbed by chemisorption. Stabilization of adsorbed bromide ions with inhibitors in cationic forms lead to greater surface coverage and thereby greater inhibition [29], [34].

#### IV. ADSORPTION STUDIES

It is generally accepted that organic molecules inhibit corrosion by adsorption at the metal/solution interface and that the adsorption process is influenced by organic compounds chemical structures: the charge distribution in molecule [35], the chemical composition of solutions, the temperature and the electrochemical potential at the metal/solution interface. Adsorption isotherms provide information about the interaction among the adsorbed molecules themselves as well as their interaction with the electrode surface. The adsorption isotherm provides insight into the mechanism of corrosion inhibition. This is determined empirically by plotting the surface area of coverage  $\Theta$  as a function of the concentration of the inhibitor. The isotherm gives the relationship between the coverage of an interface with the

adsorbed species and the concentration of species in solution. To ascertain the nature of adsorption, the surface coverage values for mixture (NaBr + AOBP) fitted into various adsorption isotherm models, and correlation coefficients ( $R^2$ ) were used to determine the best fit which was obtained with Langmuir and Freundlich adsorption isotherm, respectively. These models are expressed and presented in Equation 4 and 7.

**Langmuir adsorption isotherm:**

$$(C_{inh} / \Theta) = C_{inh} + 1/ K_{ads} \tag{4}$$

A plot of  $C_{inh}/\Theta$  with  $C$  gives a straight line indicating that the adsorption of AOBP on the mild steel surface obeys Langmuir’s adsorption isotherm (Figure 5). The regression values ( $R^2$ ) are greater than 0.99 as shown in Table 4. The data obtained in Table 4 for the mixture of NaBr+ AOBP fits well in Langmuir adsorption isotherms. Since it obeys Langmuir adsorption isotherm, it implies monolayer adsorption of inhibitor. As the slope values of Langmuir adsorption isotherm are slightly deviate from the value of unity.

TABLE 4  
 Calculated values of degree of surface coverage for mild steel corrosion in 0,5 M  $H_2SO_4$  for different systems at 298-318 K of NaBr+ AOBP from weight loss measurements.

NaBr	AOBP	Coverage		
		298 K	308 K	318 K
0,01	0,005	0,70	0,91	0,52
0,02	0,005	0,83	0,91	0,66
0,03	0,005	0,84	0,93	0,73
0,04	0,005	0,87	0,95	0,79
0,05	0,005	0,96	0,95	0,86
0,06	0,005	0,97	0,96	0,91

The deviation of the slopes from unity.can be attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation. The equilibrium constant of adsorption process  $K_{ads}$  is related to the standard Gibbs free energy of adsorption ( $\Delta G^0_{ads}$ ) by the relation [36-40]:

$$\Delta G^0_{ads} = -RT \ln ((1 / C_{solvent}) \times K_{ads}) \tag{5}$$

where  $C_{solvent}$  represents the molar concentration of the solvent (in case of water it is 55.5 mol/dm<sup>3</sup>); R universal gas constant  $R = 8.314 J.K^{-1}.mol^{-1}$ ; and T is the absolute temperature (K). The value of  $K_{ads}$  was calculated from

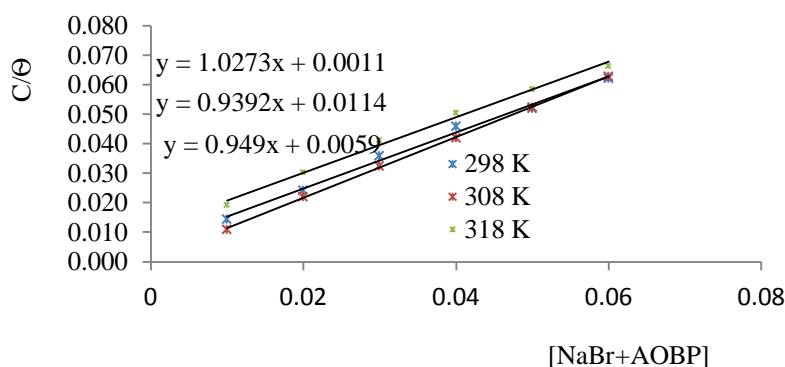


Fig 4 Langmuir adsorption isotherm of NaBr + 0,005 AOBP on carbon steel surface in 0,5 M  $H_2SO_4$ .

intercepts of straight lines  $C/\Theta$  axis and the  $\Delta G^0_{ads}$  values were calculated using Eq. (5). The  $K_{ads}$  value obtained for the system AOBP + NaBr is  $10^3 (mg.cm^{-2}.h^{-1})$  is positive is large, indicating that the inhibitor is strongly adsorbed on the mild steel surface in the presence of iodide ions. Mean while, the calculated  $\Delta G^0_{ads}$  values is around  $-28.00 kJ mol^{-1}$ . The negative values of  $\Delta G^0_{ads}$  indicate the spontaneous adsorption of the inhibitor on the mild steel mold steel surface. Generally, values of  $\Delta G^0_{ads}$  around  $-20 kJ mol^{-1}$  or lower are consistent with physisorption and those around  $-40 kJ. mol^{-1}$  or higher involve chemisorption [41-44]. However, in the present case, the value of  $\Delta G^0_{ads}$  is found around

28.00 kJ mol<sup>-1</sup>, which means that the adsorption of the combination of AOBP with NaBr on mild steel surface involves the physisorption [45].

TABLE 5  
Adsorption equilibrium constant and standard free energy of adsorption of the investigated inhibitors for carbon mild steel in 0,5 M H<sub>2</sub>SO<sub>4</sub>.

T( K)	ΔG <sub>ads</sub>	K <sub>ads</sub>	Linear regression coefficient
298	-23,08	200	0,993
308	-21,83	090	0,999
318	-28,88	1000	0,993

**Freundlich adsorption isotherm:**

$$\log \theta = \log K_{ads} + n \log C_{inh} \quad (7)$$

$$\theta < n < 1 \quad (8)$$

Where n is a constant, C is the inhibitor concentration and K<sub>ads</sub> is the equilibrium constant of adsorption process; n and K<sub>ads</sub> are temperature dependent. He observed changes in logθ are shown in Fig. 6 as a function of mixture NaBr + 0,005M AOBP in 0,5 M H<sub>2</sub>SO<sub>4</sub>. The linear plots obtained (R<sup>2</sup> > 0.95) suggest that the experimental data fit the Freundlich adsorption isotherm.

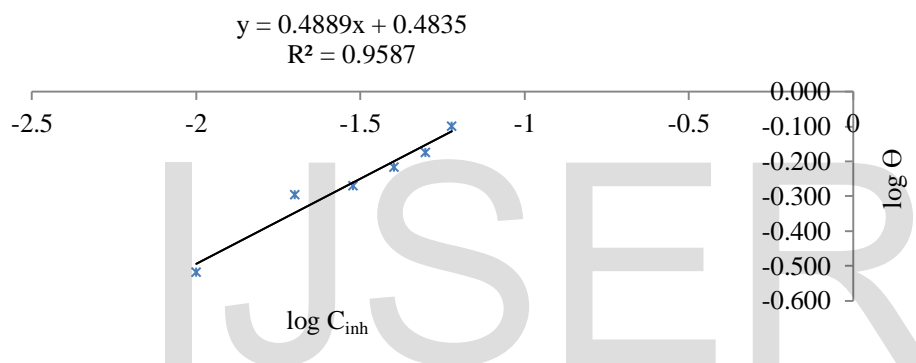


Fig 6: Curves fitting of the corrosion data of carbon steel in 0,5 M H<sub>2</sub>SO<sub>4</sub>, in the presence of NaBr + 0,005M AOBP to Freundlich isotherm.

It has been reported that the value of K<sub>ads</sub> values (100 M<sup>-1</sup>) could be attributed to a stronger and more adsorbed layer formation on the metal surface. Therefore, the large values of K<sub>ads</sub> obtained in this work mean better inhibition efficiency of the inhibitor, i.e., strong electrical interaction between the double-layer existing at the phase boundary and the adsorbing inhibitor molecules [46].

**V. KINETIC/THERMODYNAMICS CONSIDERATIONS**

Thermodynamic model is an important tool to study the mechanism of inhibitor on the corrosion of metal, a thermodynamic model for the adsorption process has been suggested. It has been known that efficient inhibitors should possess plentiful p-electrons and unshared electron pairs on either oxygen nitrogen, sulfur or phosphorus atoms of the inhibitors to the d-orbitals of iron, and by means of transference of electrons chemical adsorption may occur on the steel surface [47-54]. Theoretical fitting of the corrosion data to the kinetic - thermodynamic model was tested to show the nature of adsorption. The apparent activation energy, E<sub>a</sub>, for mild steel dissolution in 0.5M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of inhibitor (AOBP) and AOBP-halide mixtures was calculated from Arrhenius equation [55-58]:

$$\log W_{corr} = \log A - \frac{E_a^*}{2,303RT} \quad (9)$$

The regression between log W<sub>corr</sub> and 1/T was calculated by computer. Arrhenius plots of log W<sub>corr</sub> vs. 1/T for the blank and different concentrations of the mixture gives straight lines with slopes of E<sub>a</sub>\*/2,303R are shown in Figure 6. All the parameters were calculated and given in Table 6. It is clear that the value of E<sub>a</sub>\* in the presence of various AOBP concentrations+0.02 M of NaBr are higher than that in the uninhibited acid solution. These results are according with the reported studies [59]. The increase of E<sub>a</sub> in the presence of the inhibitor indicates that physical adsorption or weak chemical bonding between the mixture molecules and the steel surface might occur [60]. The activation energy rose with increasing inhibitor concentration, suggesting strong adsorption of inhibitor molecules at



the metal surface. The increase in the activation energy was due to the corrosion reaction mechanism in which charge transfer was blocked by the adsorption of AOBP + NaBr molecules on the mild steel surface. It also revealed that the whole process was controlled by the surface reaction since the energy of the activation corrosion process in both the absence and presence of AOBP + NaBr was greater than 20 kJ mol<sup>-1</sup> [61-63]. Higher Ea values in the presence of inhibitor compared to the blank solution indicates that the inhibitor will be effective at low temperatures, but efficiency will be considerably diminished at higher temperature [64]. In this study, such behavior was observed for the dependence of inhibition efficiency on temperature and further supports the proposed mechanism of physical adsorption.

TABLE 6  
activation energy and Arrhenius constant for mild steel in 0,5M H<sub>2</sub>SO<sub>4</sub> in presence of NaBr + 0,005M of AOBP

Solution	Pre-exponential factor (g.m <sup>-2</sup> .h <sup>-1</sup> )	E* <sub>a</sub> (kJ.mol <sup>-1</sup> )	Linear regression coefficient
Blank	9,3 .10 <sup>6</sup>	52,5	0,867
AOBP	2,1 .10 <sup>3</sup>	33,1	0,848
0,01NaBr+ AOBP	2,9 . 10 <sup>16</sup>	112,9	0,811
0,02 NaBr+ AOBP	7,9 . 10 <sup>17</sup>	122,2	0,928
0,03 NaBr+ AOBP	5, 4 . 10 <sup>16</sup>	115,7	0,924
0,04 NaBr+ AOBP	2,8 .10 <sup>14</sup>	103,0	0,756
0,05 NaBr + AOBP	5,2. 10 <sup>16</sup>	117,3	0,922
0,06 NaBr + AOBP	1,8. 10 <sup>16</sup>	114,8	0,999

Table 6 explores thermodynamic parameters obtained from weight loss measurements of mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> at 30°C for 6h. ΔG<sup>°</sup><sub>ads</sub> for AOBP + NaBr on mild steel showed negative indicate spontaneous adsorption of AOBP onto the mild steel surface [53] and strong interactions between inhibitor molecules and the metal surface.

$$\log \left( \frac{W_{corr}}{T} \right) = \left[ \left( \log \left( \frac{R}{hN} \right) \right) + \frac{\Delta S^*}{2.303R} \right] - \frac{\Delta H^*}{2.303RT} \quad (10)$$

The values of the entropy of activation ΔS\* in the presence of the inhibitors are large and positive, indicate an endothermic adsorption nature, and the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorderness takes place during the course of transition from reactants to the activated complex [65]. The enthalpy of activation ΔH\* is another criterion on the basis of which the mode of adsorption can be explained. The positive values of ΔH\* show that the adsorption is endothermic with a disordered phenomenon ascribed by the positive values of ΔS\*. In addition to this, the

Table 7  
Activation parameters for mild steel dissolution in 0,5 M H<sub>2</sub>SO<sub>4</sub> in the presence of mixture NaBr +0,005 M AOBP.

Solution	ΔH* (kJ.mol <sup>-1</sup> )	ΔS* (kJ.mol <sup>-1</sup> .k <sup>-1</sup> )	E* <sub>a</sub>	E <sub>a</sub> * - ΔH*	R <sup>2</sup>
blank	50,0	-120,1	52,5	2,5	0,855
AOBP	30,5	-189,9	33,1	2,6	0,827
0,01NaBr+ AOBP	110,4	61,5	112,9	2,5	0,804
0,02 NaBr+ AOBP	119,7	89,2	122,2	2,5	0,925
0,03 NaBr+ AOBP	113,1	66,8	115,7	2,6	0,921
0,04 NaBr+ AOBP	100,4	23,0	103,0	2,6	0,747
0,05 NaBr + AOBP	114,8	66,6	117,3	2,5	0,919
0,06 NaBr + AOBP	112,3	57,6	114,8	2,5	0,999

average difference in value of the E\*<sub>a</sub> - ΔH\* was found to be 2.51 kJ/mol, almost same as the value of RT (2.5 kJ/mol). This implies that the corrosion process of this metal in the acid medium is a unimolecular reaction. The higher values obtained for E\*<sub>a</sub> and ΔH\* in the presence of the studies inhibitors indicating a higher protection efficiency observed for these inhibitors.

### Synergism considerations

The extent of synergism existing between Oxobenzopyranone and bromide ions can be analyzed by the synergism parameter (S) calculated using the relationship given by Aramaki and Hackerman [66].



$$S = \frac{(1-\theta_{1+2})}{(1-\theta_1-\theta_2)} \quad (11)$$

where  $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$ ;  $\theta_1$  = surface coverage by chloride ions;  $\theta_2$  = surface coverage by cation coumarine ;  $\theta_{1+2}$  = measured surface coverage by combined inhibitor (anion + cation).  $S$  approaches unity when there are no interactions between the inhibitor compounds, while  $S > 1$  points to a synergistic effect; in the case of  $S < 1$ , the antagonistic interaction prevails.

TABLE 8  
 Synergism parameter ( $S_1$ ) for different concentration of NaBr +0,005 M AOBP.

NaBr (M)	AOBP (M)	synergism parameter S	
		Efficiency	Weight loss
0,01	0,005	2,6	0,993
0,02	0,005	2,5	0,994
0,03	0,005	2,7	0,995
0,04	0,005	2,7	0,996
0,05	0,005	2,5	0,996
0,06	0,005	2,6	0,996

The values of the synergism parameter for the various concentrations of Oxobenzopyranone studied from the gravimetric analysis are presented in Table 8. All values shown in this table are greater than unity. This is an indication that the enhanced inhibition efficiency resulting from the addition of chloride ions to Oxobenzopyranone is synergistic in nature [67]. The strong chemisorption of bromide ions on the metal surface is responsible for the synergistic effect of bromide ions, in combination with AOBP + cation, the cations of the inhibitors are absorbed by coulombic attraction on the metal surface where chloride ions are already adsorbed. Stabilization of adsorbed bromide ions with AOBP + leads to greater surface coverage and thereby greater inhibition. The synergistic effect is due to the co-adsorption of halide ions on the surface which forms oriented dipoles with their negative ends toward the solution, thus increasing adsorption of organic molecules [68]. The increase in inhibition efficiency and synergism factor show that the mechanism of synergistic action is due to the coadsorption of molecules AOBP and bromide ions. This is very similar to the observation made by El-Warraky et al [69] for the adsorption synergistic of iodide ions with the benzotriazole or thiourea and iodide ion on the corrosion of Al-bronze in acidified 4% NaBr, it is found that in the presence of halide ions, the adsorbed halide ions make the iron surface into a negatively charged one and due to electrostatic interaction, strong adsorption of the cations of the inhibitors with halide covered surface takes place. The stabilization of adsorbed halide ions by means of electrostatic interaction with inhibitor cations leads to more surface coverage and hence greater inhibition.

## VI. CONCLUSIONS

1. 3-Acetyl-4-oxo-benzopyranone effectively inhibits mild steel corrosion in sulphuric acid, the inhibition efficiency increases with inhibitor concentration at all temperatures studied and also increases with rise in temperature
2. The addition of AOBP to bromide ions enhanced the inhibition efficiency due to synergistic effect.
3. The adsorptive behavior may be approximated by Langmuir and Freundlich adsorption isotherms.
4. The negative values of the free energy of adsorption is an indication that the process was spontaneous.
5. The values of S (synergistic parameter) obtained from the method employed are greater than unity showing the corrosion inhibition brought about by AOBP in combination with halide ions is synergistic in nature.

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