THE EFFECT OF TEMPERATURE ON THE INHIBITION OF THE ACID CORROSION OF MILD STEEL BY SOME SULFONIUM BROMIDE DERIVATIVES

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Abstract : The effect of temperature in the range $(20 - 60)^{\circ}C$ on the performans of sulfonium bromids at a fixed concentration of each of them on mild steel corrosion in 2.0N H_2SO_4, HCl of and H_3PO_4 acids solutions using chemical methods (HEM and MLM), was carried out. It was found that in 2.0N H_2SO_4 solution the corrosion of mild steel increases with rising temperature from 20°C to 60°C for all the studied compounds except compound F who give an increase in Inh.% with rising temperature. In 2.0N HCl and 2.0N H_3PO_4 solutions it was clear that for most compounds the Inh.% or acceleration of corrosion decreases with increasing temperature. .

A decrease in the corrosion rate or an increase in Inh.% with increasing temperature is occurred only in some compounds in all the three acids, when the temperature reached 50°C. The decrease in inhibition efficiency or in acceleration of corrosion with temperature indicates that most of these compound are physically adsorbed on the mild steel surface and it also indecates that the inhibited film formed on the metal surface is less protective in nature at higher temperature. Desorption of the inhibitor molecules from the metal surface most probably occures with faster rates at high temperatures. The values of apparent activation energy ΔE_{app} of the dissolution of mild steel in 2.0N of the three acids in absence and presence of the studied compounds were calculated.

1. Introduction

The corrosion process is usually accelerated when temperature is rised, especially in media in which evolution of hydrogen accompanied corrosion, e.g., during dissolution of mild steel in acids or of zinc and aluminium in alkalies. If oxygen takes part in a cathodic reaction during corrosion, the relationship between corrosion rate and temperature becomes more complicated owing to the lower solubility of oxygen at elevated temperatures[1].

The effect of temperature in the range $(20 - 60)^{\circ}C$ on the performance of the studied sulfonium bromides at a fixed concentration of each of them on mild steel corrosion in the three inorganic acids (2.0N of H_2SO_4, HCl and H_3PO_4) will be carried out using chemical measurements (HEM and MLM). These compounds were studied before at different concentrations at 30°C[2,3].

Experimental :

The effect of the addition of sulfonium bromides on the dissolution process of commercial mild steel sample in 2.0N of H_2SO_4, HCl and H_3PO_4 was studied. The following chemical composition of the studied mild steel specimen is given in table (1).

Table (1) : Chemical composition of the mild steel specimen.

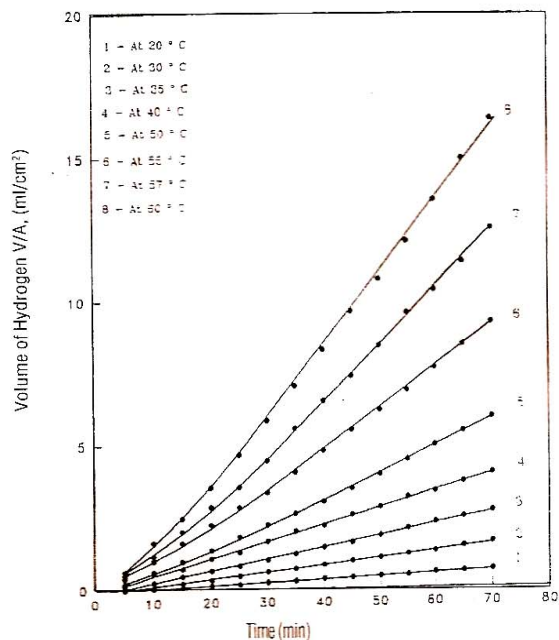| Fe	C	Mn	P	Mo	Al	Sn	V	Nb	Ni	Cu
98.86	0.17	0.57	0.011	0.002	0.011	0.005	0.004	0.007	0.027	0.043

Figure (1) : Volume of hydrogen/time curves of steel sample in 2.0N H_2SO_4 solution at different temperatures.

Table (2) : Structure, molecular wieght and melting point of studied compounds.

| Symbol	Compound Name	Structure	Molecular Weight	Melting Point(C)
A	Phenacyl dimethyl sulfonium Bromide		261.188	157.0
B	4-Methylphenacyl dimethyl sulfonium bromide.		275.300	111.0
C	4-Chlorophenacyl dimethyl sulfonium bromide.		295.500	140.0
D	4-Bromophenacyl dimethyl sulfonium bromide.		339.956	96.6
E	4-Nitrophenacyl dimethyl sulfonium bromide.		320.192	100.6
F	4-Methoxy phenacyl dimethy sulfonium bromide.		291.214	138.2
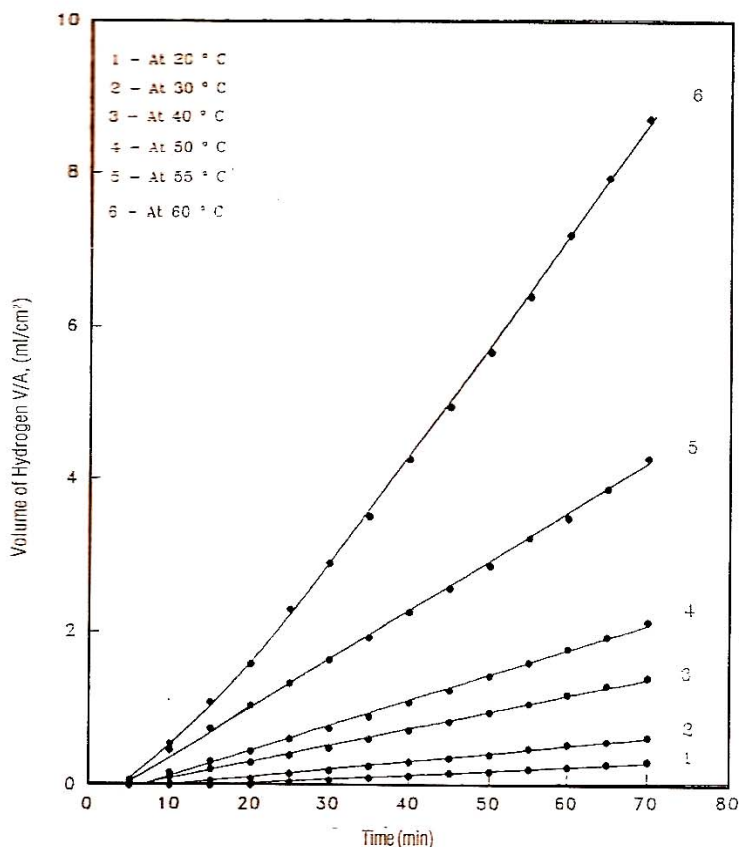
Figure (2) : Volume of hydrogen/time curves of steel sample in 2.0N HCl solution at different temperatures.

Table (3) : The inhibition percentages (Inh.$_H$%) for mild steel corrosion in 2.0N H_2SO_4 solution in presence of 1.0×10^{-3}M of studied compounds (A-F) at different temperatures from HEM.

t°C	(Inh.%)$_{HEM}$					
	A	B	C	D	E	F
30	68.22	85.51	68.60	35.59	42.74	80.04
35	-	51.51	27.39	-31.66	-	-
40	36.25	17.53	17.52	-61.40	35.88	84.49
50	20.11	6.20	-1.82	-82.89	26.52	86.10
55	11.64	28.08	15.95	-70.39	-	87.95
57	-	-	-	-	-	92.46
60	0.39	50.39	26.95	-60.41	23.05	95.47

The studied compounds were prepared as discribed before[4-6]. Table (2) gave the structure, molecular wieght and melting points of the used sulfonium compounds in the study.

Before all measurements the specimens were polished first with a series of emery papers of type (231 Qwetordry Imperical Paple aesoc), as discribed elsewhere[7-9]. All studied solutions were prepared with analytical grade reagents (A. R.). The concentration of the studied compounds was 1.0×10^{-3} M. Deionized water was used through out for the preparation of solutions. All studies were carried out using an ultrathermostat (Julabo U3 No. 8311), also in each new study the measurements of the sample area was chaked. The study was carried out using sample which has the same form as that described by Mylius[10].

Results and Discussion :

The study of corrosion and corrosion inhibition of mild steel in 2.0N of H_2SO_4, HCl and H_3PO_4 in absence and presence of phenacyl sulfonium bromide (A), and some of its p-substituted derivatives (table-2) using chemical measurements were carried out by hydrogen evolution and mass-loss methods at 30^0C in previous studies[2,3]. Figures (1- 3) show the effect of temperature on the volume of H_2 evolved in 2.0N of H_2SO_4, HCl and H_3PO_4 solutions in absence of the studied compounds and figs. (4-6) presence of 1.0×10^{-3}M of sulfonium bromide (A) in the three acids respectively. It is clear that the corrosion rate of mild steel increases with rising temperature in both uninhibited and inhibited acids, i.e., the slope of the resulting straight lines mostly increases. Similar behaviour is obtained for all studied sulfonium bromides in the three acid solutions.

The inhibition percentage was calculated from HEM (Inh.$_{HG}$) and MLM (Inh.$_M$%) measurments at any temperature using the following two equations[6-9,11-16].

$$\text{Inh.}_H\% = 100 \ (1-R/R_o) \tag{1}$$

$$\text{Inh.}_M\% = 100 \ (1-R/R_o) \tag{2}$$

where R_o and R the rates of hydrogen evolution in absence and presence of the studied compounds, respectively and R_o, R represents the rates of mass-loss in absence and presence of the studied compounds, respectively.

The variation of the Inh.% with temperature for the studied compounds in the three acids (2.0N of H_2SO_4, HCl and H_3PO_4) are recorded in tables (3-5). As it can be seen that the inhibition percentage almost decrease with the increase of temperature.

In 2.0N H_2SO_4, variation of the inhibition efficiency with temperature, table (3), showed that the Inh.% of corrosion decreases with the increase in temperature from 20^0C to 60^0C, while some times an acceleration of corrosion for all the compounds except compound F was occured. While, in case of 2.0N HCl, and 2.0N H_3PO_4, tables (4&5), it is clear that for most compounds the Inh.% of corrosion decreases with increasing temperature.

Also for some compounds in all the three acids, the Inh.% decreases with increasing temperature, untill it reaches 50^0C then a decrease in the corrosion rate or an increase in Inh.% or the acceleration increases with increasing temperature is accured, figures (7-9).
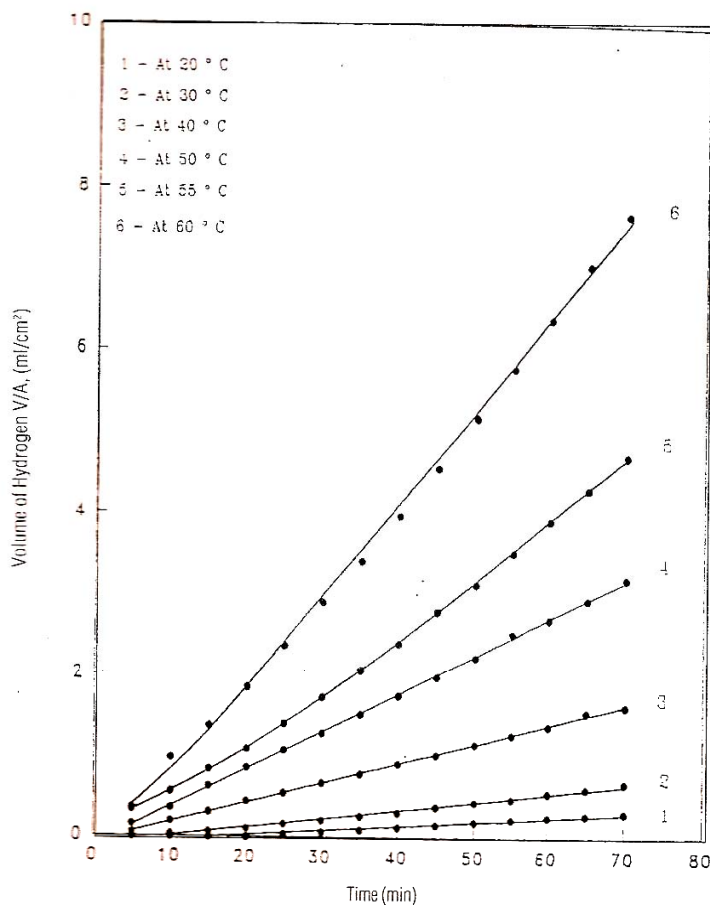
Figure (3) : Volume of hydrogen/time curves of steel sample in 2.0N
H_1PO_4 solution at different temperatures.

Table (4) : The inhibition percentages (Inh.$_H$%) for mild steel corrosion in 2.0N HCl solution in presence of 1.0 x 10^{-3}M of studied compounds (A-F) at different temperatures from HEM.

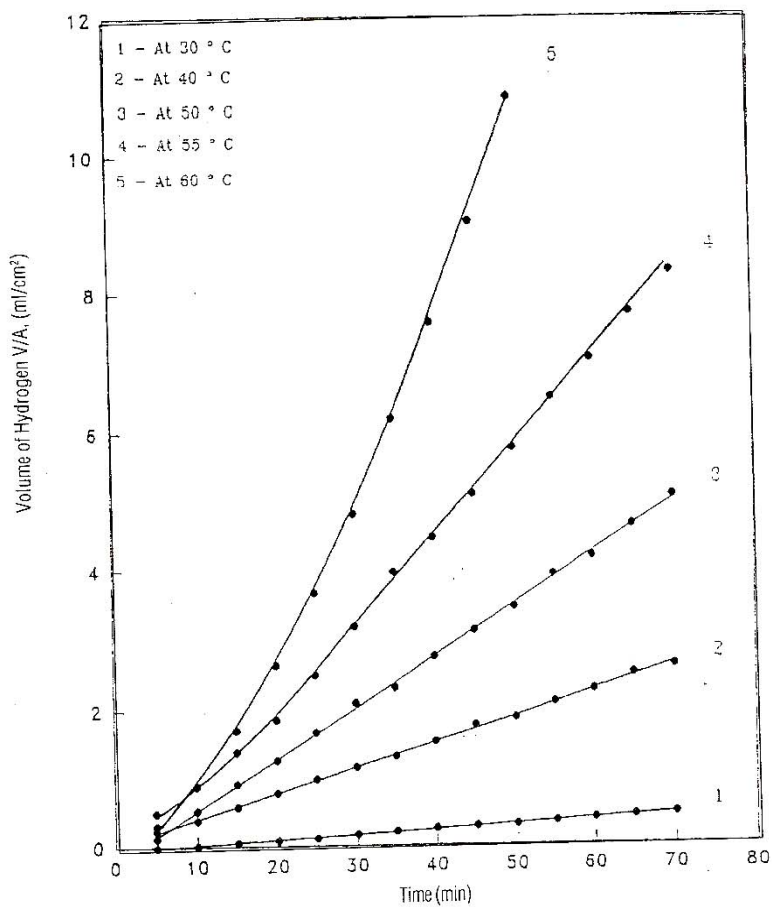| t⁰C	$(Inh.\%)_{HEM}$					
	A	B	C	D	E	F
30	53.40	52.04	50.97	32.98	41.05	72.15
40	.48.57	35.57	30.00	-75.71	33.33	40.48
50	29.72	-8.36	11.46	-88.85	16.72	27.55
55	26.96	23.36	-	-42.48	12.54	29.31
60	23.78	32.95	10.49	-39.86	11.19	33.22

Figure (4) : Volume of hydrogen/time curves of steel sample in 2.0N H_3SO_4 solution containing $1.0 \times 10^{-3}M$ inhibitor (A) at different temperatures.

Table (5) : The inhibition percentages (Inh.$_H$%) for mild steel corrosion in 2.0N H_3PO_4 solution in presence of $1.0 \times 10^{-3}M$ of studied compounds (A-F) at different temperatures from HEM.

t^{0}C	(Inh.%)$_{HEM}$					
	A	B	C	D	E	F
30	58.85	66.28	58.94	19.24	68.86	57.91
40	39.10	37.57	29.39	-64.61	30.86	49.38
50	26.77	22.06	21.41	-64.24	21.63	37.69
55	19.20	22.03	-	-	-	35.20
60	10.35	21.90	20.92	-57.78	16.90	31.03
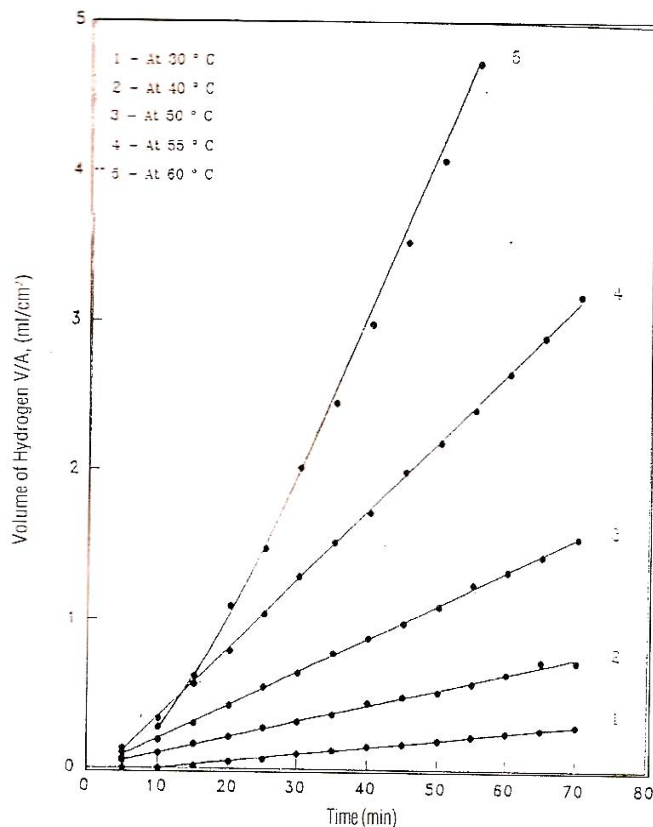
Figure (5) : Volume of hydrogen/time curves of steel sample in 2.0N HCl solution containing 1.0 x 10⁻³M inhibitor (A) at different temperatures.

Table (6) : Activation Parameters for mild steel corrosion in 2.0N H_2SO_4 solutions in absence and presence of 1.0 x 10⁻³M of the studied compounds (A-F) form HEM and MLM.

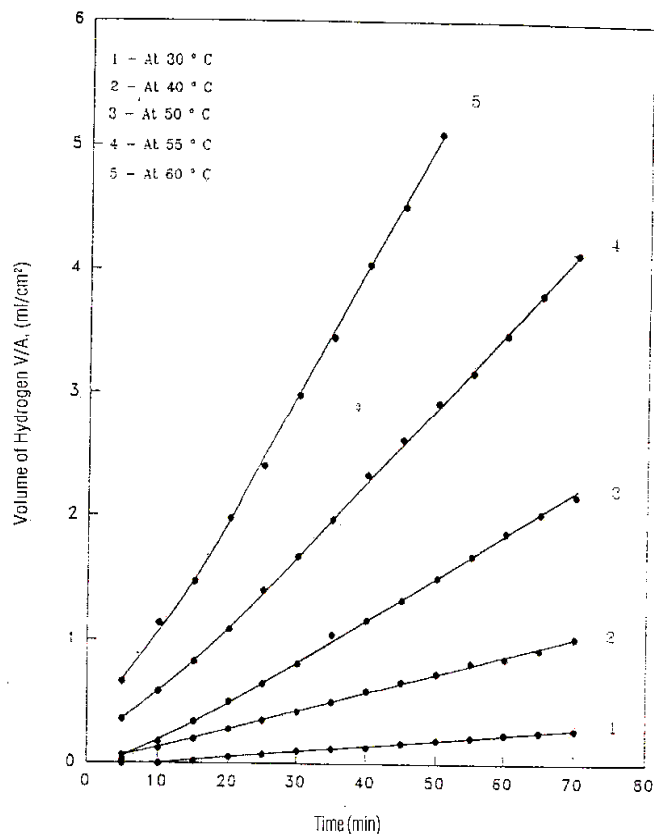| Compound Symbol	HEM			MLM		
	$\Delta E_{app.}$ (kJ.mol.⁻¹)	ΔH (kJ.mol.⁻¹)	ΔS (kJ.mol.⁻¹)	$\Delta E_{app.}$ (kJ.mol.⁻¹)	ΔH (kJ.mol.⁻¹)	ΔS (kJ.mol.⁻¹)
Blank	62.99	53.99	-278.81	58.73	59.48	-222.36
A	93.31	85.70	-258.72	90.23	106.33	-222.36
B	89.01	90.33	-258.72	93.67	73.61	-216.62
C	79.38	90.52	-252.89	85.35	61.24	-221.40
D	80.19	85.87	-251.06	83.48	70.37	-211.83
E	78.28	73.61	-266.37	73.68	73.60	-215.65
F	38.28	72.50	-280.73	47.53	45.57	-249.15

Figure (6) : Volume of hydrogen/time curves of steel sample in 2.0N H_3PO_4 solution containing
1.0 x 10^{-3}M inhibitor (A) at different temperatures.

Table (7) : Activation Parameters for mild steel corrosion in 2.0N HCl solutions in absence and
presence of 1.0 x 10^{-3}M of the studied compounds (A-F) form HEM and MLM.

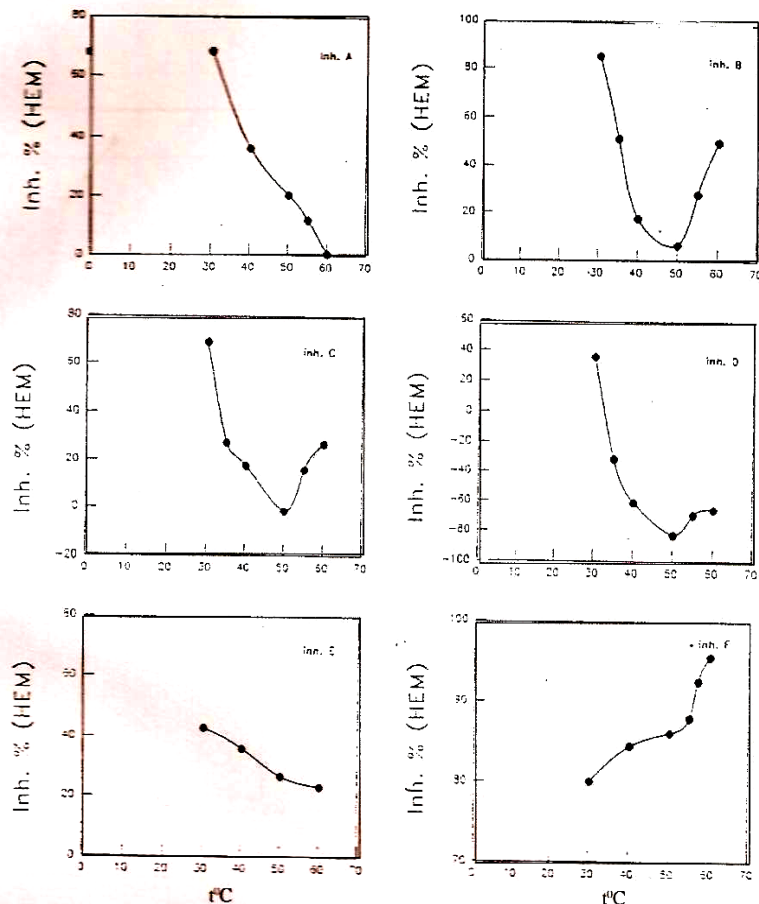| Compound Symbol	HEM			MLM		
	$\Delta E_{app.}$ (kJ.mol.$^{-1}$)	ΔH (kJ.mol.$^{-1}$)	ΔS (kJ.mol.$^{-1}$)	$\Delta E_{app.}$ (kJ.mol.$^{-1}$)	ΔH (kJ.mol.$^{-1}$)	ΔS (kJ.mol.$^{-1}$)
Blank	60.71	53.17	-285.51	57.52	53.91	-232.88
A	82.44	65.55	-275.94	71.25	68.34	-229.05
B	78.66	72.69	-274.03	73.39	76.55	-218.52
C	86.10	76.55	-271.16	76.70	76.55	-218.52
D	84.60	79.75	-264.46	88.22	70.37	-218.52
E	82.03	79.75	-269.26	72.72	70.89	-226.13
F	92.69	83.21	-269.24	86.29	85.35	-215.66

Figure (7) : The variation of inhibition efficiency (Inh. % HEM) of sulfonium bromide compounds with temperature in 2.0N H_2SO_4.

Compound Symbol	HEM			MLM		
	$\Delta E_{app.}$ (kJ.mol.$^{-1}$)	ΔH (kJ.mol.$^{-1}$)	ΔS (kJ.mol.$^{-1}$)	$\Delta E_{app.}$ (kJ.mol.$^{-1}$)	ΔH (kJ.mol.$^{-1}$)	ΔS (kJ.mol.$^{-1}$)
Blank	60.71	59.06	-279.77	60.99	59.06	-229.05
A	82.44	76.55	-270.20	79.55	71.77	-216.62
B	78.66	82.03	-268.62	84.52	79.75	-218.53
C	86.10	77.89	-269.24	81.42	72.50	-209.92
D	84.60	76.55	-264.46	80.54	71.40	-216.62
E	82.03	82.70	-268.29	98.32	80.86	-216.62
F	92.69	70.89	-275.94	73.16	76.55	-221.40

Table (8) : Activation Parameters for mild steel corrosion in 2.0N H_3PO_4 solutions in absence and presence of 1.0×10^{-3}M of the studied compounds (A-F) form HEM and MLM.
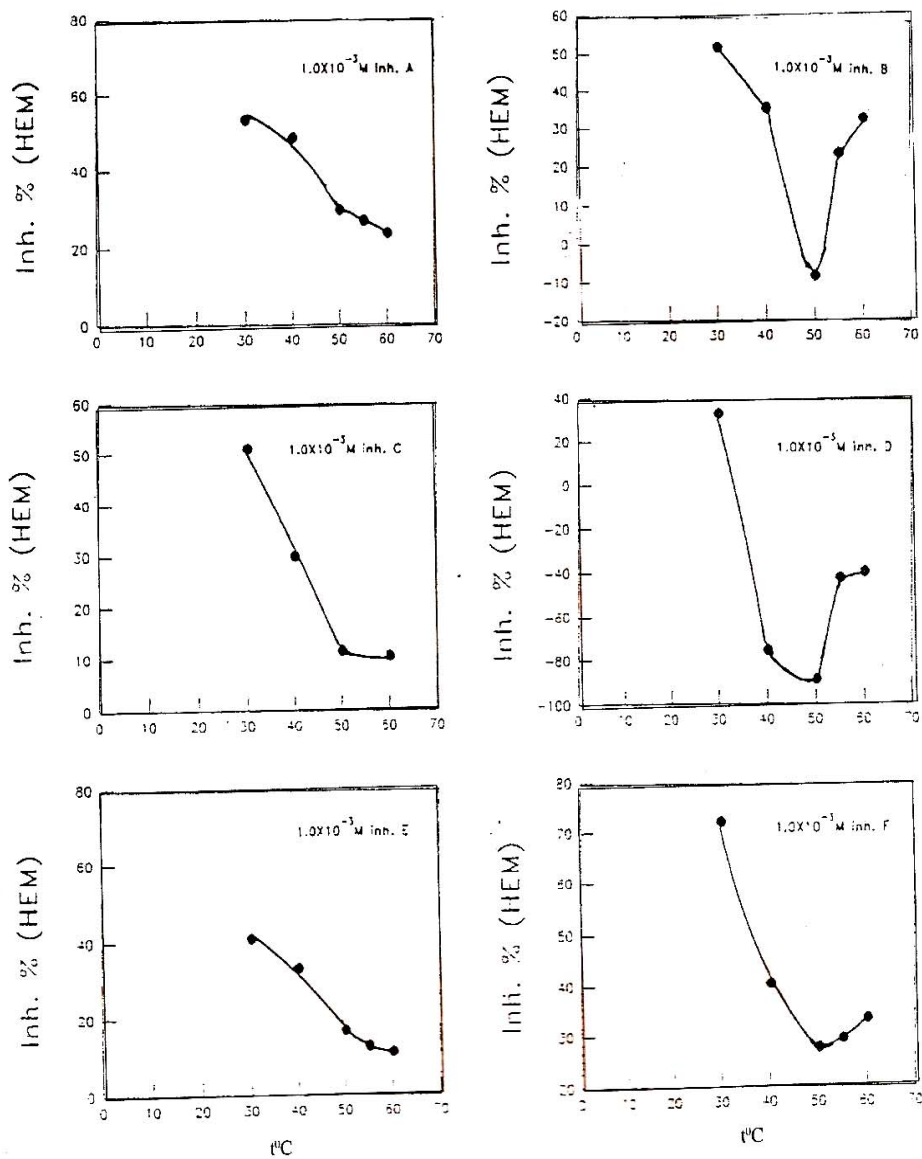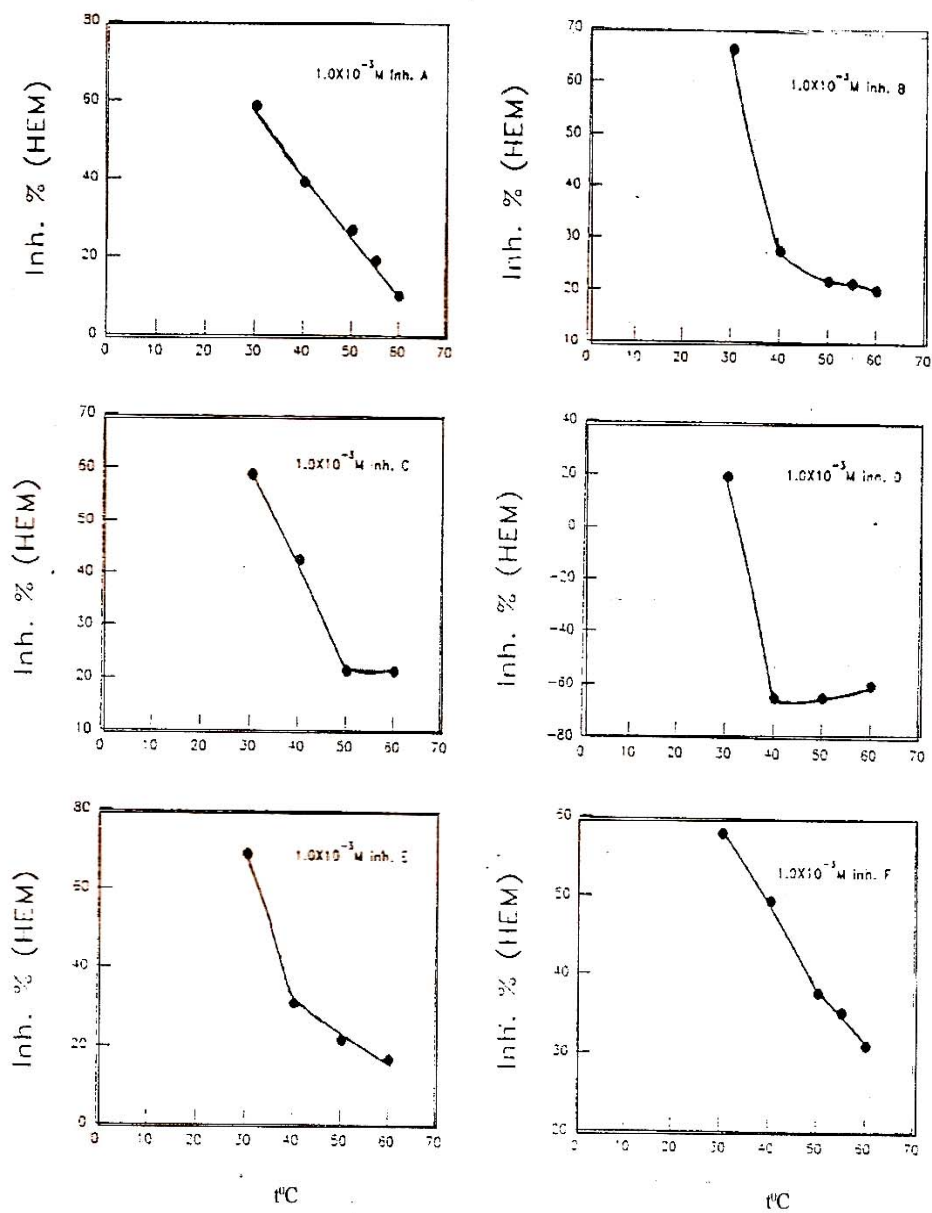
Figure (8) : The variation of inhibition efficiency (Inh. % HEM) of sulfonium bromide compounds with temperature in 2.0N HCl.

Figure (9) : The variation of inhibition efficiency (Inh. % HEM) of sulfonium bromide compounds with temperature in 2.0N H_3PO_4.
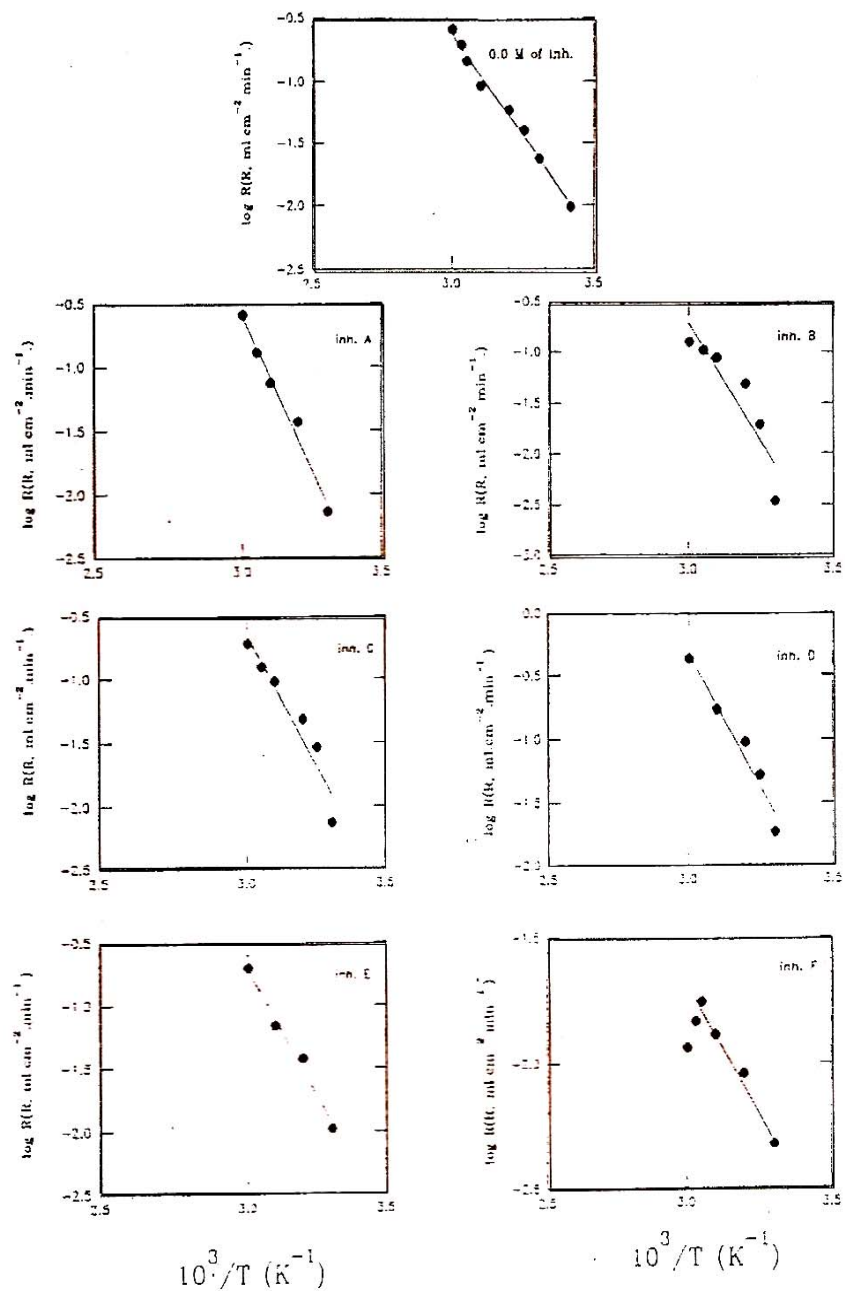
Figure (10) : Arrhenius plots for the dissolution (R) of steel sample in 2.0N H_2SO_4 in absence and presence of 1.0×10^{-3} M of sulfonium bromide compounds.

In general, the decrease in inhibition efficiency or in acceleration of corrosion with temperature indicates that most of these compounds are physically adsorbed on the mild steel surface [17] and it also indicates that the inhibited film formed on the metal surface is less protective in nature at higher temperature. Most probably desorption of the inhibitor molecules from the metal surface occurs with a faster rate at high temperatures[18].

On the other side, the decrease in inhibition action with increase in temperature may be explained as that : the time lag between the process of adsorption and desorption of inhibitor molecules over metal surface is becoming shorter with increase in temperature. Hence, the metal surface remains exposed to the acid environment for a longer period thereby increasing the rate of corrosion with increase in temperature and therefore inhibition efficiency falls for these compounds [19].

Inspection of tables (3 – 5) also show that an acceleration of corrosion is found for compound D in the three studied acids. Compound D who showed in previous studies a dual behaviour, acceleration and inhibition of corrosion at 30^0C depending on it's concentration is now found and this supported the previons suggestion to be due to it's low ability of adsorption on mild steel surface [23].

The tables also showed that compounds (B and F) have no acceleration of mild steel corrosion but it shows some decreasing of inhibition in HCl and H_3PO_4 acid solutions. In H_2SO_4 compound (B) the decreasing is followed by slow increasing in the inhibition with increasing the temperature, while in compound F slow decreasing of inhibition was obtained followed by an increasing at the higher temperatures $\geq 40^0$C. The increasing of inhibition in compounds (B and F) may explained by a chemical interaction between SO_4^{2-} and methyl group at high temperatures on mild steel surface in acid media, this interaction will prevent the mild steel dissolution. The increasing of inhibition with the increase of temperature as result of chemical reaction was reported before[20,21].

Putilova etal.[1] have pointed out that, for steel in acids, the logarithim of the corrosion rate of steel (R) can be represented as a straight line function of $1/T$ (Arrhenius equation), where T is the temperature in kelvins :

$$\log (R) = \log A - \Delta E_{app.}/2.303\,RT \tag{3a}$$

$$\log (\acute{R}) = \log A - \Delta E_{app.}/2.303\,RT \tag{3b}$$

and $\acute{R}$ is the rate of the metal dissolution reaction, $\Delta E_{app.}$ is the apparent activation energy, **R** is the universal gas constant and **A** is Arrhenius constant.

In figures (10-12) the logarithms of the corrosion rates (R and $\acute{R}$) of mild steel in the three acid solutions in the asbsecne and presence of 1.0×10^{-3} M of the studied compounds are plotted as a function of (1/T) from HEM.

Values of apparent activation energy, $\Delta E_{app.}$, calculated from the slopes of the straight lines of the figures are given in tables (6-8). In absence of inhibitor, $\Delta E_{app.}$ is equal to 62.99 kJ. mol.$^-$ $^-$ for 2.0N H_2SO_4, 60.71 kJ. mol.$^{-1}$ for 2.0N HCl and 60.71 kJ. mol.$^{-1}$ for 2.0N H_3PO_4 solutions respectively.

The results are in good agreement with that obtained by a number of authors[22-25].

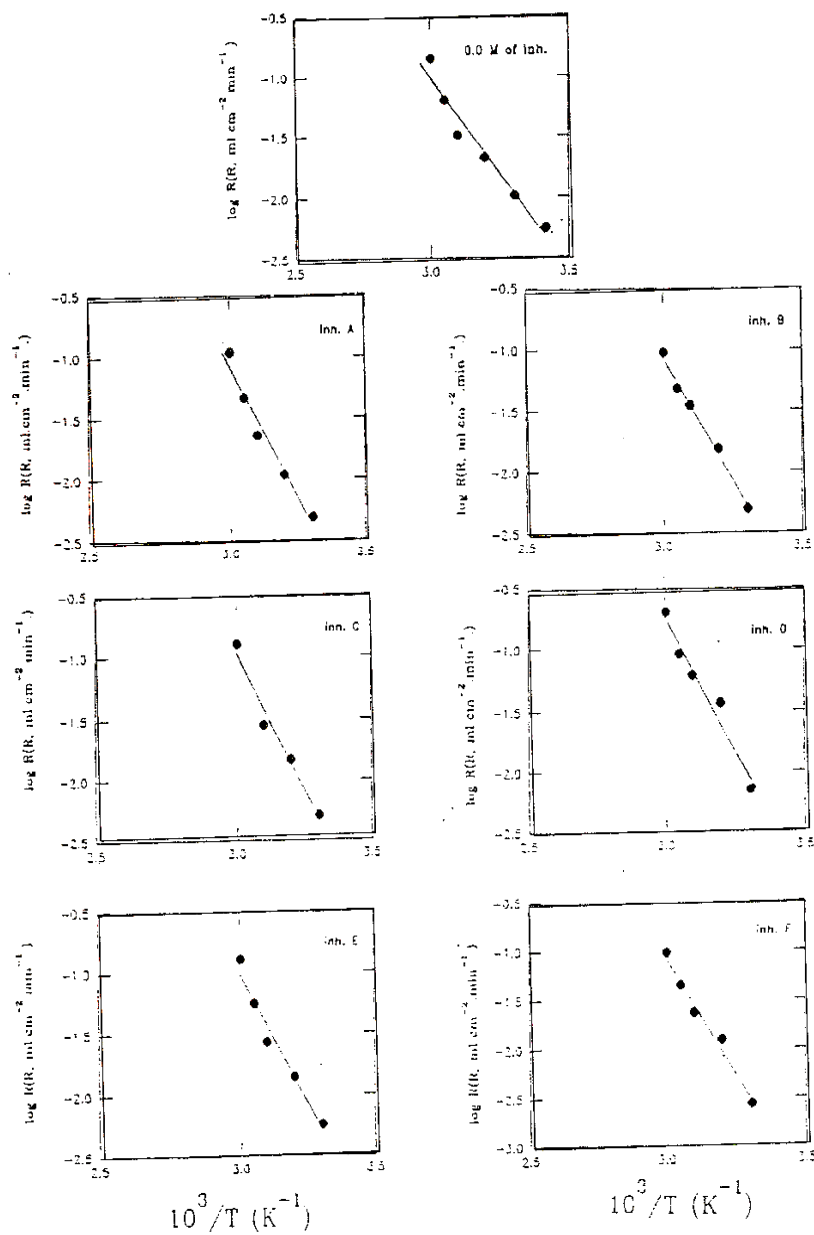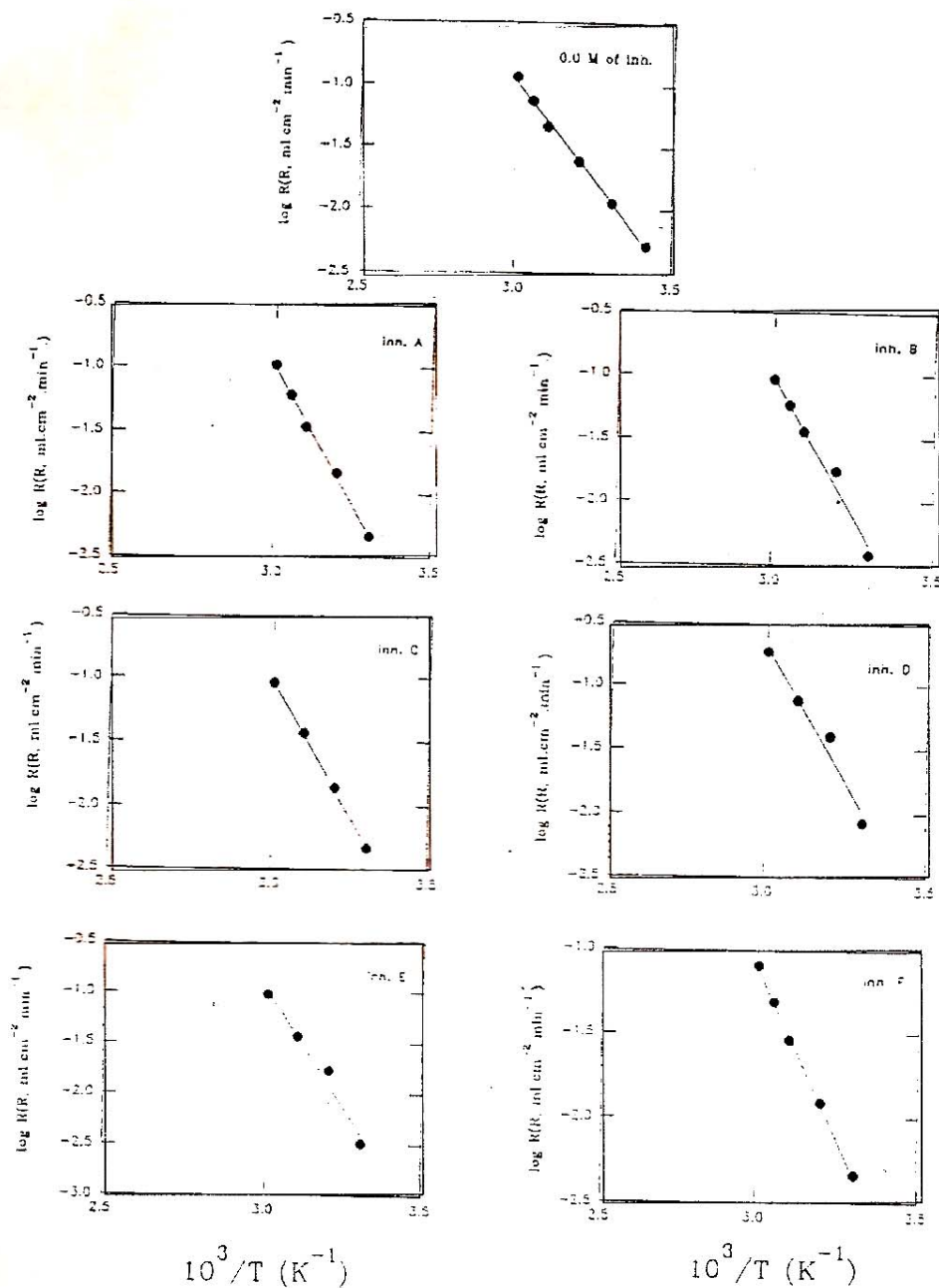**Figure (11)** : Arrhenius plots for the dissolution (R) of steel sample in 2.0N HCl in absence and presence of 1.0 x 10³ M of sulfonium bromide compounds.

Figure (12) : Arrhenius plots for the dissolution (R) of steel sample in 2.0N H_3PO_4 in absence and presence of 1.0 x 10^{-3} M of sulfonium bromide compounds.
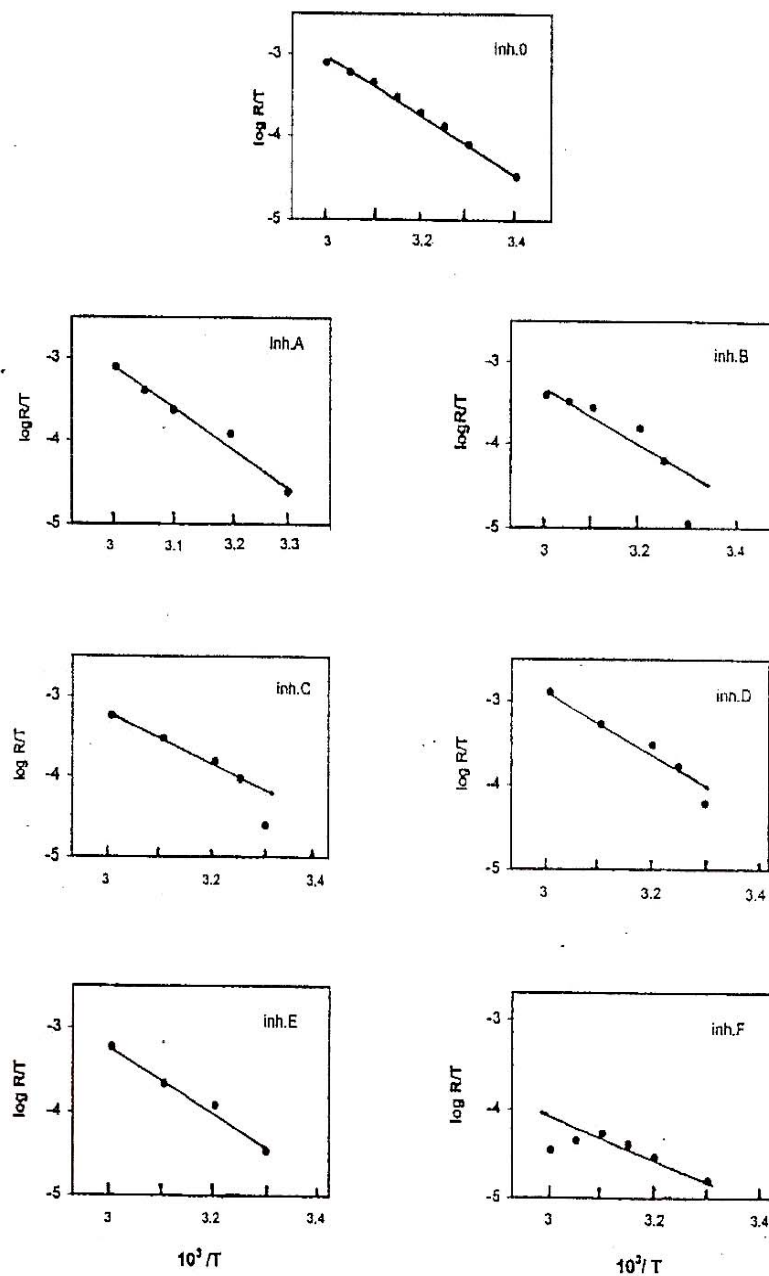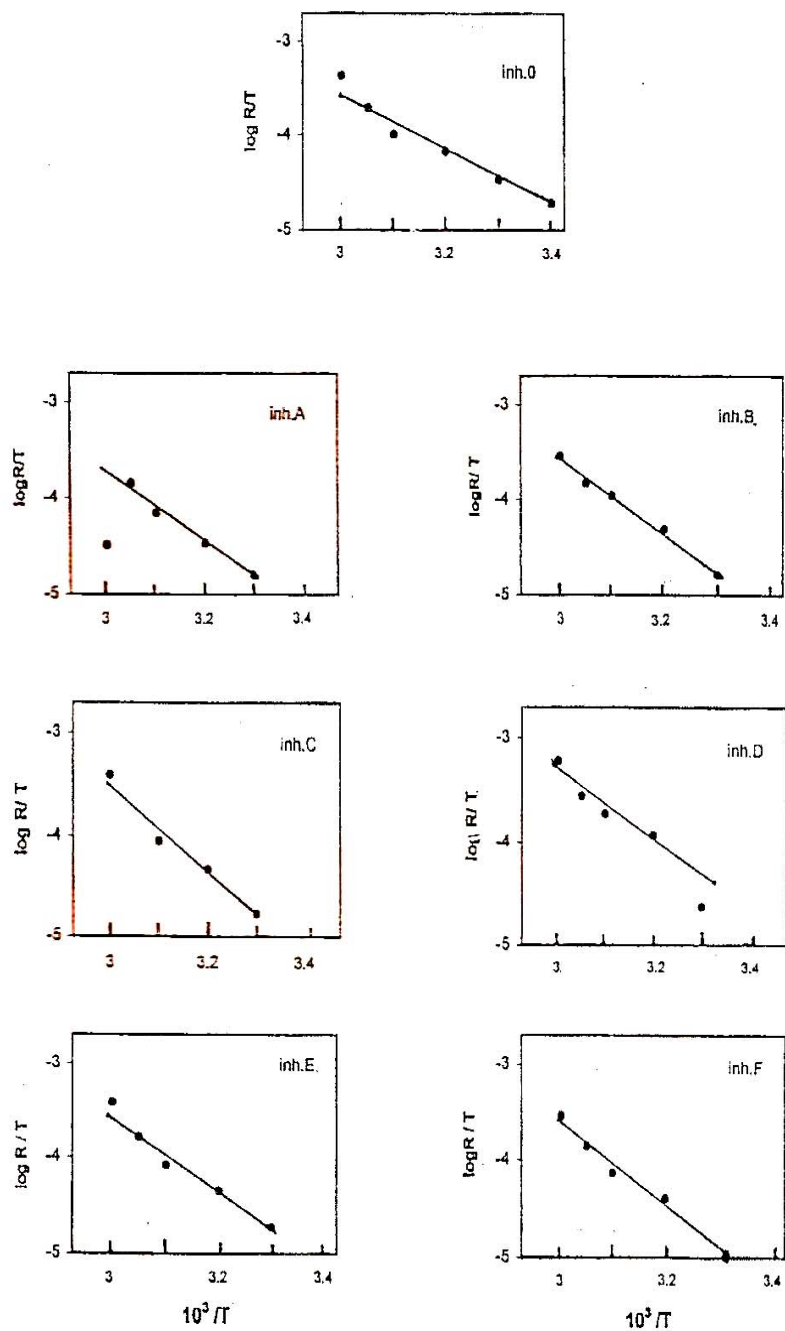
Figure (13) : Plots of log (R/T) vs. (1/T) for the corrosion of mild steel in 2.0N H$_2$SO$_4$ in absence and presence of 1.0 x 10^{-3} M of sulfonium bromide compounds.

Figure (14) : Plots of log (R/T) vs. (1/T) for the corrosion of mild steel in 2.0N HCl in absence and presence of 1.0 x 10⁻³ M of sulfonium bromide compounds.
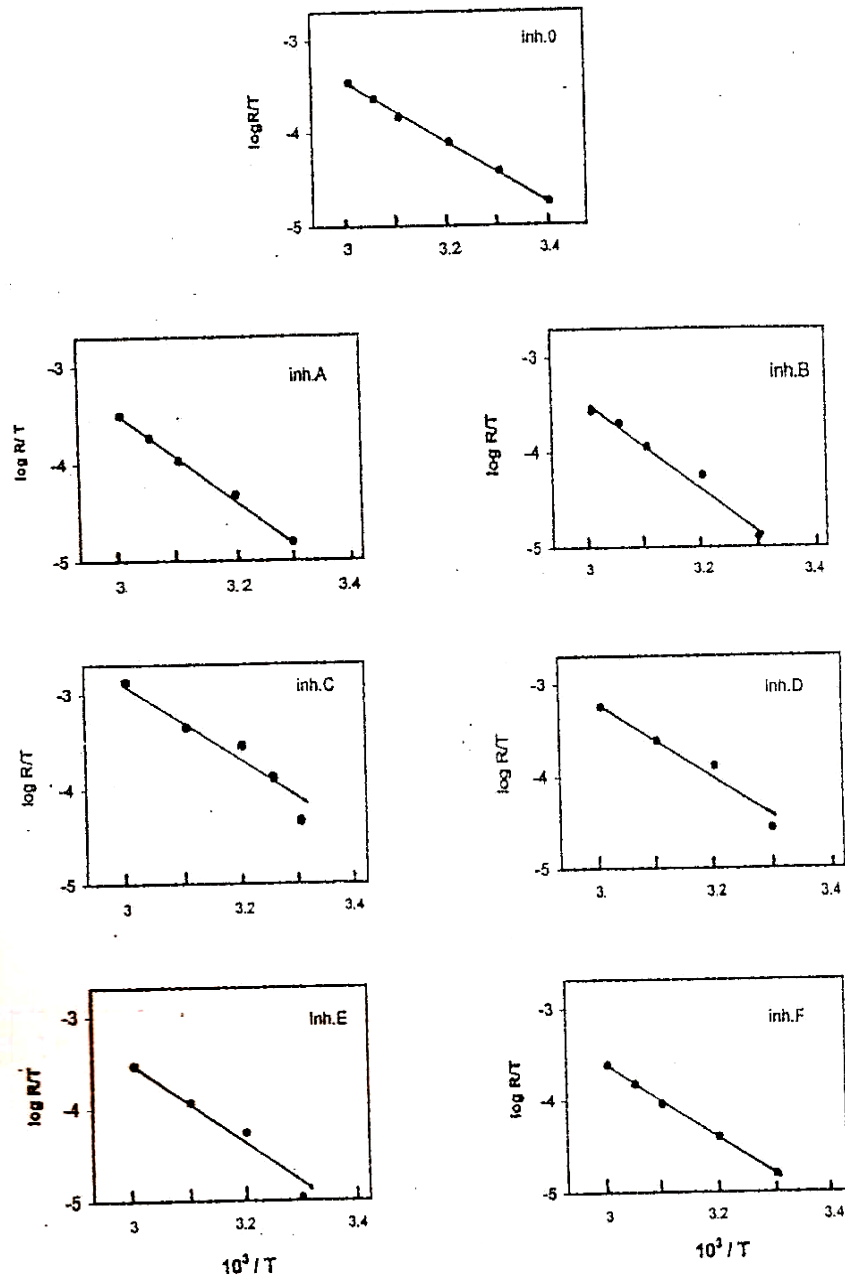
Figure (15) : Plots of log (R/T) vs. (1/T) for the corrosion of mild steel in 2.0N H_3PO_4 in absence and presence of 1.0 x 10^{-3} M of sulfonium bromide compounds.

Inspection of the data in tables (6-8) show that the apparent activation energy, $\Delta E_{app.}$, of the dissolution of mild steel in 2.0N of the three acids in presence of the studied compounds (F) except compound F are higher than that of the uninhibited acid solutions. This means that the presence of inhibitors tend to increase the value of activation energy and consequently decrease the rate of dissolution of the mild steel electrode. This finding indicates that the studied compounds act as inhibitors through increasing the activation energy of the dissolution reaction by the adsorption on the metal - solution interface making a mass barrier and charge transfer.

It is clear from table (6) that the value of $\Delta E_{app.}$ for mild steel in 2.0N H_2SO_4 in presence of compound F is less than in free acid. this means that an inhibitor becomes more effective as the temperature increases, this may be due to chemical interaction as follows [6-20,21].

$$R + SO_4^{2-} \xrightarrow{\ H^+\ } R - O - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}} - O - H$$
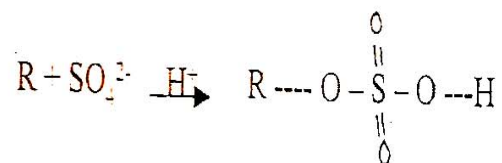
In our study R is CH_3, Cl, Br, NO_2 and OCH_3, where Cl, Br and NO_2 are electron withdrawing groups, while CH_3 and OCH_3 are electron donating group. So the previous reaction will proceeds if R is an electron donating groups, also this reaction proceeds more rapidly when methyl group is presented in methoxy (compound F) than when it is as methyl (compound B).

The formation of the complex $R - O - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}} - O - H$ will lead to an increase of the covered mild steel surface areas led to increase inhibition percentage of compound F.

An alternative form of Arrhenius equation is the transition state equation (4,6,22,26) :

$$\text{R or } \dot{R} = RT \,/\, Nh \, \exp(\Delta S^{\neq} / R) \exp(-\Delta H^{\neq} / RT) \tag{4}$$

$$\log(R / T) = \log(R / Nh) + \Delta S^{\neq} / 2.303\,R - \Delta H^{\neq}/2.303\,RT \tag{5a}$$

$$\log(\dot{R} / T) = \log(R / Nh) + \Delta S^{\neq}/2.303\,R - \Delta H^{\neq}/2.303\,RT \tag{5b}$$

where h is Plank's constant, N Avogardro's number. $\Delta S^{\neq}$ the entropy of activation and $\Delta H^{\neq}$ the enthalpy of activation. The plots of $\log(\dot{R}/T)$ vs. $1/T$ in absence and presence of the studied compounds will give straight lines ; Figures (13-15); with a slope of $-\Delta H^{\neq}/2.303R$ and an intercept of $(\log R/Nh + \Delta S^{\neq}/2.30R)$, from which the values of $-\Delta H^{\neq}$ and $-\Delta S^{\neq}$ are calculated from both HEM and MLM (tables (6-8)).

The table show that the presence of the sulfonium bromide molecules in the corrosive medium leads to a slight increase in the $\Delta H^{\neq}$ values than that of the uninhibited solutions in three acids, which means that no energy barrier for the reaction in the presence of the inhibitor is attainded, and the adsorption of the slfonium bromids occurrs through the π electron of the phenyl group as suggested before [2,3].

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