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SYNERGISTIC ACTION OF SOME THIOSEMICARBAZONE DERIVATIVES WITH CHLORIDE ION ON THE CORROSION INHIBITION OF IRON BASE METALLIC GLASS

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ABSTRACT

An example of a new class of $Fe_{78}B_{13}Si_9$ alloy corrosion inhibitors, namely, thiosemicarbazone derivatives were synthesized and their inhibition action on the corrosion of iron – base glassy alloy in 0.2 M Na_2SO_4 at 30°C was investigated by electrochemical and morphological study. The addition of chloride ions to sulphate solution accelerate the corrosion process. Presence of both thiosemicarbazone derivatives and chloride may increase or decrease the corrosion rate. The increase in surface coverage value in the presence of chloride ions indicates that thiosemicarbazone derivatives formed an insoluble complex by undergoing joint (specific) adsorption. The synergism parameters (S_θ) is defined and calculated by surface coverage values. The parameter in the case of thiosemicarbazone derivatives may be found to be more than unity, indicating that the enhanced inhibition efficiency caused by the addition of chloride ions is only due to synergism and there is a definite contribution from the inhibitor molecule .

KEYWORDS: Metallic glasses, iron -base alloy, thiosemicarbazones, corrosion, inhibition, chloride ion, electrochemical methods and synergism.

INTRODUCTION

Some aqueous solutions containing aggressive ions particularly Cl^-, Br^- or I^- can cause pitting corrosion , localized attack or stimulating the corrosion process resulting in metal destruction[1]. Various metals (e.g. Al , Fe , Mg , Zn , Cu and Co) and their alloys are susceptible to pitting corrosion [2-4]. Based on many previous studies, a general order of halogen aggressivity can be written as:

$$Cl^- > Br^- > I^-$$

The stable passivity of $Fe_{75}B_{25-x}Si_x$ with $x > 12$ breaks down easily in chloride – containing solution and appear very susceptible to pitting at only 10^{-4} M [5]. Seshu et.al.[6] have found weak passivation of five $Fe_{68}Ni_{14-x}Mo_xSi_2B_{16}$ glasses with x=0,1,2,3 and 4 in more aggressive 1.0 M HCl and not in relatively mild H_2SO_4 solutions. This has been explained in terms that Cl^- ions promote the formation of passive film while SO_4^{2-} ions do not favor such film formation.

The corrosion behavior of $Fe_{80-x}Co_xB_{10}Si_{10}$ (x = 0, 15, 30, 55, 70, 80) glassy alloys has been investigated in sulphate and chloride containing solutions [7]. Results indicated that the sulphate containing solution were more aggressive than the chloride containing ones. Furthermore, the most dominant anodic reaction of $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ and $Fe_{70.5}Si_{16}B_8Nb_{4.5}Cu_1$ amorphous alloys in fluoride media was the formation of sodium fluorosilicate . In chloride media, amorphous $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ alloys shows uniform dissolution, while $Fe_{70.5}Si_{16}B_8Nb_{4.5}Cu_1$ shows transient passivity at low chloride concentrations and the surface shows localized attack which is consistent with the observation of passivation.

The resistance of metallic glasses to the corrosive attacks in electrolytic solutions is mainly related to their easy formation of a stable condition, favored by the high reactivity of amorphous state .Their novel structure promise and , in many cases, do deliver novel properties , or rather the combination of properties , which make them attractive for applications[8].

Therefore, the study of corrosion processes of these alloys in various environments and the development of proper inhibiting substances is of interest.

Accordingly , ***the aim of this work is to study***: (1) the action of chloride ion at different concentration on the corrosion of $Fe_{78}B_{13}Si_9$ metallic glass. (2) the effect of chloride ion on corrosion inhibition of $Fe_{78}B_{13}Si_9$ glassy alloy in 0.2 M Na_2SO_4 solution in the presence of fixed concentration of thiosemicarbazone derivatives.

2.EXPERIMENTAL DETAILS

The experiments were performed on $Fe_{78}B_{13}Si_9$ glassy alloy supplied by Goodfellow. The bright face electrode with working area (30 mm^2) was degreased with alcohol and rinsed several times with bi-distilled water and finally cleaned in an ultrasonic bath (Model LF2003, 50160Hz , Dal Trozzo) made in Italy.

Experiments were carried out in 0.2 M Na_2SO_4 solution in the absence and presence of thiosemicarbazone derivatives [Fig. (1)]. The chemicals (Na_2SO_4, NaCl and NaBr) used were of BDH and methanol were of Hyman. Solutions were prepared by using bi-distilled water . All tests were performed at 30 °C ± 0.01.

Electrochemical measurements have been achieved by connecting the electrochemical cell to ACM Gill AC and to a Samsung computer (Bridge DVD ASUS 8X max) . Potentiodynamic polarization curves were performed with scan rate of 60 mV/min. Electrode potentials were measured with respect to a silver / silver chloride reference electrode with a Luggin capillary bridge and a platinum wire counter electrode. Impedance data was obtained in the frequency range 0.5Hz – 10kHz. For morphological studies, the samples were prepared and treated as described before and immersed in the test solution for 45 minutes, then SEM analysis was carried out using Leitz METALLUX 3 scanning microscope (WETZLAR, Germany), with magnification (500x).

3-RESULTS AND DISCUSSION

3-1 *Effect of chloride ion on corrosion of $Fe_{78}B_{13}Si_9$ glassy alloy in 0.2 M Na_2SO_4 solution:*

Chloride ion is the most aggressive corrosion agent and the most thoroughly studied because of its wide distribution in nature. The effect of chloride ion addition on the anodic and cathodic potentiodynamic polarization curves and the impedance spectra of $Fe_{78}B_{13}Si_9$ glassy alloy corrosion in 0.2 M Na_2SO_4 solution containing 10% MeOH in presence of increasing Cl^- concentration in the aggressive medium is shown in Figs.(2a & 2b).

The charge transfer resistance, R_{ct} (limiting zero frequency value of the real part of the complex impedance), values are calculated from the difference in the impedance at lower and higher frequencies. To obtain the double layer capacitance, C_{dl}, the frequency at which the imaginary component is maximum ($-Z'_{max}$) is found and C_{dl} values are obtained from the following equation:

$$C_{dl} = 1 / 2\pi f(-Z'_{max})\, R_{ct} \qquad (1)$$

The inhibition efficiency can be calculated on the basis of the data from the electrochemical experiments from equations :

$$Inh._p\% = (i^{\circ}_{corr} - i_{corr} / i^{\circ}_{corr}) \text{ x } 100 \qquad (2)$$

$$Inh._{Rct}\% = (R^{-1}_{cto} - R^{-1}_{ct} / R^{-1}_{cto}) \text{ x } 100 \qquad (3)$$

where i°_{corr} and i_{corr} denote corrosion current densities and R^{-1}_{cto} and R^{-1}_{ct} are the reciprocals of charge transfer resistance in the absence and presence of Cl^- respectively .

Table (1) indicates that dissolution current density along the active region increases with Cl^- concentration increase this is in agreement with that reported before [7,9,10].

It can also be seen from the table that b_a values are more enhanced than b_c values which changed to lower values in the presence of different concentrations of Cl^-, these data indicated that the addition of chloride ion enhances the anodic dissolution reaction of the glassy alloy.

The values of R_{ct} and C_{dl} in solution containing increasing Cl^- concentrations are reflecting
the stimulating nature of this ion towards dissolution of studied iron-base glassy alloy in the Na_2SO_4 solution.

The inhibition efficiency as being associated to these data have a negative sign which donates the acceleration effect on the corrosion of the studied alloy in Cl^- solutions.

The impedance spectra obtained for the corrosion of $Fe_{78}B_{13}Si_9$ glassy alloy in test solution consist of a depressed capacitive loops. The impedance diagrams have a semicircle appearance, which indicates that the corrosion of studied alloy in Cl^- solutions is controlled by the charge transfer process and Cl^- addition does not alter mechanism of the alloy dissolution. The distortion semicircles behavior of Nyquist diagrams may be due to charge transfer control process beside to frequency dispersion [11-13].

The dissolution mechanism of iron in chloride ion solution seems to be even more complicated since the chloride ion participates in the dissolution process. The specific adsorption of negatively charged species on metal surface lowers the potential of the inner Helmholtz plane and this in turn assists anodic electron-transfer processes through the electrical double layer. In this case, the suggested mechanism may be written be as [14]:

$$\begin{array}{rcl}
Fe + X^-_{(aq)} & \longleftrightarrow & (FeX^-)_{(ad)} \\
(FeX^-)_{(ads)} + H_2O & \longleftrightarrow & (FeOH^-)_{(ads)} + H^+ + X^- \\
(FeOH^-)_{(ads)} & \longrightarrow & (FeOH)_{(ads)} + e \\
(FeOH)_{(ads)} & \longrightarrow & (FeOH^+) + e \\
(FeOH^+) & \longleftrightarrow & Fe^{2+}_{(aq)} + OH^- \\
OH^- + H^+ & \longleftrightarrow & H_2O
\end{array}$$

where (ads) refers to an adsorbed species on the surface. The overall reaction rate depends mainly upon the rate of the first step.

3-2 Effect of chloride ion on corrosion inhibition of $Fe_{78}B_{13}Si_9$ glassy alloy in 0.2 M Na_2SO_4 solution in the presence of fixed concentration of the inhibitor:

Polarization study of $Fe_{78}B_{13}Si_9$ glassy alloy were performed in 0.2 M Na_2SO_4 solution containing 10% MeOH in the absence and presence of 10^{-4} M of each inhibitors containing different amount of Cl^- (0.01 - 0.04 M) are presented in Figs.(3a & 3b).

Data recorded in table (2) for studied inhibitors shows the corrosion parameters at different concentrations of Cl^- in the presence of different compounds of thiosemicarbazones. Tafel slopes (b_a&b_c) decreased, but cathodic Tafel slopes were more affected with inhibitors (MeActhioSCAzn), (BndthioSCAzn) and (MEBndthioSCAzn) (*cathodic control*) while anodic Tafel slopes were more affected with inhibitors (MEActhioSCAzn), (EtBndthioSCAzn) and (BrBndthioSCAzn) (*anodic control*).

The values of i_{corr} increase in the presence of inhibitors (MeActhioSCAzn), (BndthioSCAzn), (MEBndthioSCAzn), and (BrBndthioSCAzn), but it decrease in presence of inhibitors (MEActhioSCAzn) and (EtBndthioSCAzn). E_{corr} values are shifted to negative side, but the shift does not show a regular trend .

Figures (4a & 4b) show the Nyquist plots in the presence of 10^{-4} M of studied inhibitors containing increasing concentrations (0.01-0.04 M) of Cl^- . R_{ct} and C_{dl} have been calculated and recorded in table (3).

In these figures (4a & 4b) the Nyquist plots in the presence of 10^{-4} M of (MeActhioSCAzn) and (MEBndthioSCAzn) and 0.01 and 0.02 M Cl^-, also at 0.04 M of Cl^- in presence of inhibitor (MEActhioSCAzn), consist of a depressed semicircle with a long tail at the low frequency region. This behavior indicates that the diffusion process of ions takes place on the alloy after the addition of both inhibitor and Cl^- and the existence of a protective porous film on metal surface, in which the diameters of the pores control the diffusion ions through the film [15].

Figures (5 and 6) give a schematic diagrams of the metal surface covered by porous films and the simplified equivalent circuit model or the previous system respectively.

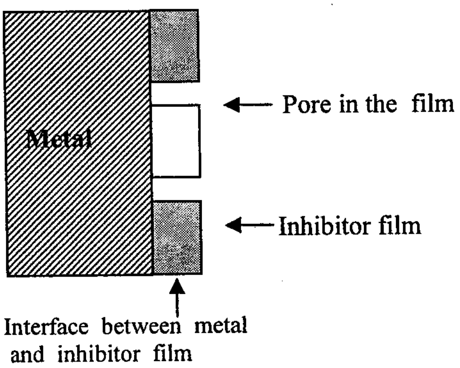


Fig.(5): A schematic diagram of the metal covered by porous inhibitor films.

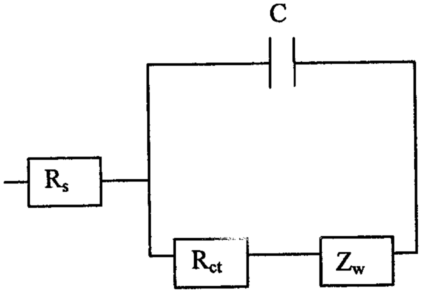


Fig.(6): Equivalent circuit model for the metal covered by porous inhibitor films, R_s, solution resistance, R_{ct}, charge transfer resistance, Z_w, Warburg impedance.

The remain impedance diagrams has a semicircle appearance, which indicates that the corrosion of $Fe_{78}B_{13}Si_9$ glassy alloy is mainly controlled by charge transfer process, and there is no change in the mechanism of the dissolution of the alloy in presence of additives. Whereas in presence of inhibitor (BndthioSCAzn), all impedance plots have a semicircle appearance at all concentrations of Cl^-, except at 0.02 M and 0.03 M Cl^-, the diffusion tail is observed. The values of b_f ($b_f = -\sigma\omega^{-1/2}$) corresponding the low frequency decrease with Cl^- concentration increase, this fact implies that the inhibitor film adsorbed on the alloy surface became more porous with Cl^- concentration increase and lead to increase of the corrosion rate (decrease in R_{ct} values)[15]. This phenomenon is observed at 0.01 M Cl^- in presence EtBndthioSCAzn.

At low frequencies, the capacitive component (C) no longer affects the total impedance value and the total impedance Z_t can be presented as [15]:

$$Z_t = R_s + R_{ct} + Z_w \qquad (4)$$

The Warburg impedance (Z_w) can be given by the following equation [15]:

$$Zw = \sigma\omega^{-1/2} - \sigma\omega^{-1/2}\,j \qquad (5)$$

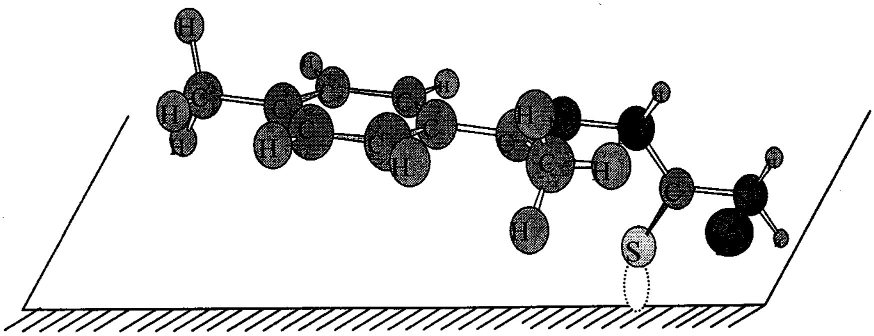
where σ is Warburg coefficient (Ω cm^2 $s^{-1/2}$) and $\omega=2\pi f$ (rad s^{-1}). From equation (5), the imaginary part, ($-\sigma\omega^{-1/2}j$), represents the information of diffusion process. Therefore, in Nyquist plot at low frequency, where the diffusion tail shows up the value of Imag-axis presents the item of $\sigma\omega^{-1/2}$, so that Warburg impedance can be obtained by the value of Imag-axis at low frequency.

The diameter of the capacitive loop obtained in sulphate solution in presence of 10^{-4} M of inhibitors MEActhioSCAzn and EtBndthioSCAzn containing increasing concentrations of Cl^- is increased. The data corresponding for these two inhibitor clearly seen that the R_{ct} increase with Cl^- concentration increase, C_{dl} values decrease in the same time indicating an adsorption process occur on the alloy surface.

Finally the impedance results show a good agreements with polarization results. A closer inspection of these data show that the presence of Cl^- with the 10^{-4} M of each inhibitor may enhance the inhibition efficiency or decrease it , this shows that the inhibition efficiency depends on the concentration of Cl^- in test solution.

As can be seen from table (4) that the inhibition efficiency show that these compounds can be divided into two groups:

First group, an increase the inhibition was found by addition of 0.01 M of Cl^- , then by increasing Cl^- concentration a decrease is produced. This group include inhibitors (MeActhioSCAzn, BndthioSCAzn, MEBndthioSCAzn and BrBndthioSCAzn). The decrease of inhibition was sharp only with unsubstituted inhibitor (BndthioSCAzn) while in another inhibitors it was gradual. The behavior of the first group may explained as to be a joint (specific) adsorption of Cl^- with inhibitor molecules [14], or by ionic or physical overlap [16] adsorption of Cl^- over the thiosemicarbazone molecules as described by the following scheme;



Charged iron base glassy alloy

Inhibitor molecules adsorption through their adsorption center $(>C = S)$ which also have (NH_3^+) group , in the presence of Cl^- this leads it to attract to positive charge causing great inhibition., so it may be assumed that the adsorption of these inhibitor molecules with (0.01 M) Cl^- is ionic in nature and it's an overlap type .The presence of diffusion tail at LF region in the case of inhibitors BndthioSCAzn and BrBndthioSCAzn indicated that the adsorbed layer on the metal is less protective. The decreasing in inhibition efficiency by increasing Cl^- concentrations may due to starting the dissolve the adsorbed layer as mentioned by Khamis et.al.[16]. The decrease in inhibition efficiency by the addition of Cl^- in the presence of the inhibitors may be due to Cl^- adsorption on the metal surface, so a replacement of some inhibitors molecules by Cl^- may occur, this leaves less space for organic molecules to get adsorbed [17].

Second group , in which the addition of 0.01 M Cl^- produced a decrease in inhibition comparing with the inhibitor alone then by increasing Cl^- concentration , an increase of inhibition is found , these are included inhibitors (MEActhioSCAzn & EtBndthioSCAzn).

Nyquist plots show clearly that the corrosion of $Fe_{78}B_{13}Si_9$ glassy alloy is mainly controlled by charge transfer process , and as Cl^- concentration increase the efficiency of inhibition is increased may be due to a joint adsorption (insoluble film) of both Cl^- and inhibitor molecules. This phenomenon is clearly found in inhibitor EtBndthioSCAzn and to less extended with inhibitor MEActhioSCAzn.

The synergism parameter (S_θ) was calculated using the relationship given by Aramaki and Hackermann[19].

$$S_\theta = \frac{(1 - \theta_{1+2})}{(1 - \theta'_{1+2})}$$

where

$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$

θ_1 = surface coverage by anion .

θ_2 = surface coverage by cation.

θ'_{1+2} = measured surface coverage by both anion and cation .

Table (5) give the values of S_θ calculated for various concentration of Cl^-. The S_θ values are more than unity and this suggests that the enhanced inhibition efficiency caused by the addition of chloride ions to thiosemicarbazone is only due to a synergistic effect. The synergistic effect is increased by increasing Cl^- concentration in the case of MEActhioSCAzn and EtBndthioSCAzn and decreased in presence of other inhibitors

3-3 Scanning electron microscopy of $Fe_{78}B_{13}Si_9$ glassy alloy in Na_2SO_4 solution in the presence chloride ion with and without the inhibitor:

To establish that inhibition is due to the formation of an organic film on the metal surface, scanning electron micrographs were taken . The clean surface of the sample before immersion in test solution is shown in Fig.(7a). As can be seen from the picture , the surface contains only trace produced during the parallel flow casting of the material from the liquid to solid state. Examination of micrograph Fig.(7b) for $Fe_{78}B_{13}Si_9$ glassy alloy specimen immersed in 0.2 M Na_2SO_4 solution containing 10 % MeOH at 30°C after 45 mint revealed a general corrosion with large shallow pits may caused by SO_4^{2-} ions at the amorphous alloy surface. An evidence of a severely attack of the alloy by Na_2SO_4 was occurred.

An acceleration of corrosion was observed in Fig.(7c) in presence of 0.01M Cl^- in Na_2SO_4 solution without any inhibitors. Where there are many deep and irregular pits on amorphous surface .

The presence of both 10^{-4}M of MeActhioSCAzn and 0.01M Cl^- in test solution improve the inhibition action as seen in Fig.(7d) , due to the presence of the adsorbed coating film on amorphous surface giving large coverage . But presence of 10^{-4}M of MEActhioSCAzn in the same conditions gives less inhibition ,Fig.(7e) .

Micrograph Fig.(7g) exhibits the effect of addition of 0.01M Cl^- to test solution in presence of 10^{-4}M of inhibitor MEActhioSCAzn on the corrosion of glassy $Fe_{78}B_{13}Si_9$ alloy. From the picture , it is observed that the corrosion is inhibited in test solution to a large extent, which is due to coating films formation on amorphous surface .

There is evidence for general corrosion in presence of 10^{-4} M of inhibitor EtBndthioSCAzn, Fig.(7h). This may due to presence of porous film on amorphous surface .

Corrosion is inhibited by presence of both Cl^- and BndthioSCAzn and BrBndthioSCAzn, Figs.(7f & 7i), respectively in test solution. The improvement of inhibition may due to the formation of an adsorbed layer of both Cl^- and inhibitors on amorphous sample.

CONCLUSION

i. Negative sign of inhibition efficiency in the presence of Cl^- indicates the acceleration effect of this ion on the alloy corrosion, and a mechanism is suggested for this process.

ii. Electrochemical data show that the presence of Cl^- with the 10^{-4} M of each inhibitor may enhanced the inhibition efficiency or decrease it, this shows that the inhibition efficiency depends on the concentration of Cl^- in test solution.

iii. The results show a good agreements between polarization and impedance data.

iv. Optical micrograph studies of $Fe_{78}B_{13}Si_9$ in the absence and presence of the inhibitors significantly reduces the reactions between the test solution and amorphous surface. The specimens immersed in test solution containing both Cl^- and organic compounds were covered with a film due to *joint adsorption*.

v. Among the four studied compounds, EtBndthioSCAzn was the most effective inhibitor.

DEMİR ESASLI METALİK CAMIN KOROZYONUNUN ÖNLENMESİNDE BAZI TİYOSEMİKARBON TÜREVLERİNİN KLORÜR İYONUYLA SİNERJİSTİK ETKİSİ

ÖZET

$Fe_{78}B_{13}Si_9$ alaşımının korozyon inhibitörlerinden yeni bir sınıfın bir örneği tiyosemikarbazon türevleri sentezlendi ve demir-esaslı camsı alaşımın korozyonu üzerinde inhibisyon etkileri elektrokimyasal ve morfolojik çalışmayla 30°C ‘de 0.2 M Na_2SO_4 çözeltisinde araştırıldı. Tiyosemikarbazon türevlerinin ve klorürün varlığı, korozyon hızını artırabilir veya azaltabilir. Klorür iyonları varlığında yüzey kaplama değerindeki artış, tiyosemikarbazon türevlerinin, spesifik adsorpsiyon ile çözünmeyen bir kompleks oluşturduğunu göstermektedir. Sinerji parametreleri (S_θ) yüzey kaplama değerlerinden hesaplandı ve belirlendi. Tiyosemikarbazon türevleri durumunda parametre bütünlükten daha fazla bulunabilmektedir. Bu da klorür iyonlarının eklenmesiyle artan inhibisyon etkinliğinin sadece sinerji nedeniyle olduğunu gösterir ve inhibitör molekülden kesin bir katkısı vardır.

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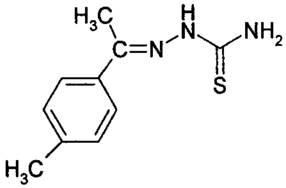
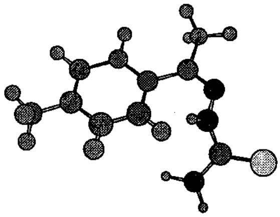
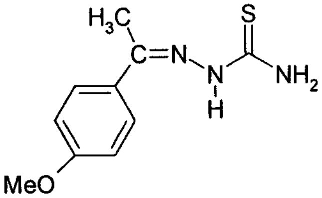


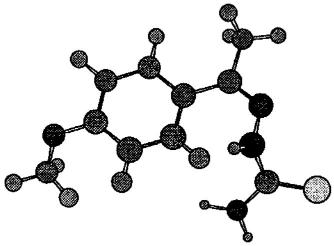
4-methyl acetophenone thiosemicarbazone



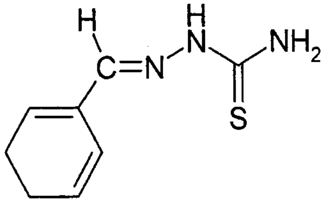
(MeActhioSCAzn)



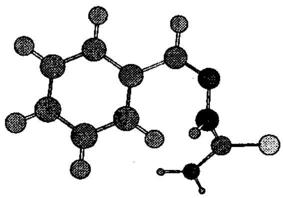
4-methoxy acetophenone thiosemicarbazone



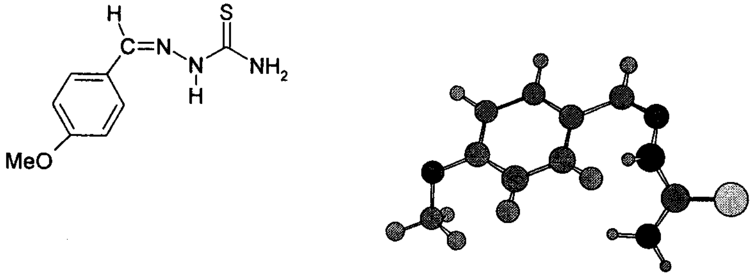
(MEActhioSCAzn)



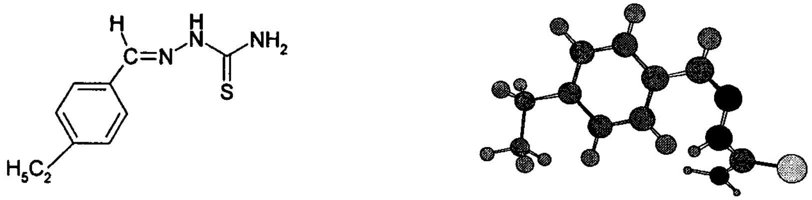
Benzaldehyde thiosemicarbazone



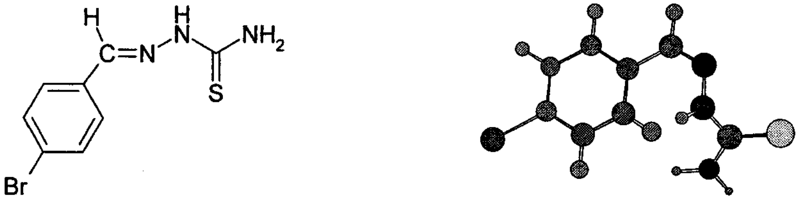
(BndthioSCAzn)



4-methoxy benzaldehyde thiosemicarbazone (MEBndthioSCAzn)



4-ethyl benzaldehyde thiosemicarbazone (EtBndthioSCAzn)



4-bromo benzaldehyde thiosemicarbazone (BrBndthioSCAzn)

Fig.(1): Molecular structure of the compounds studied.

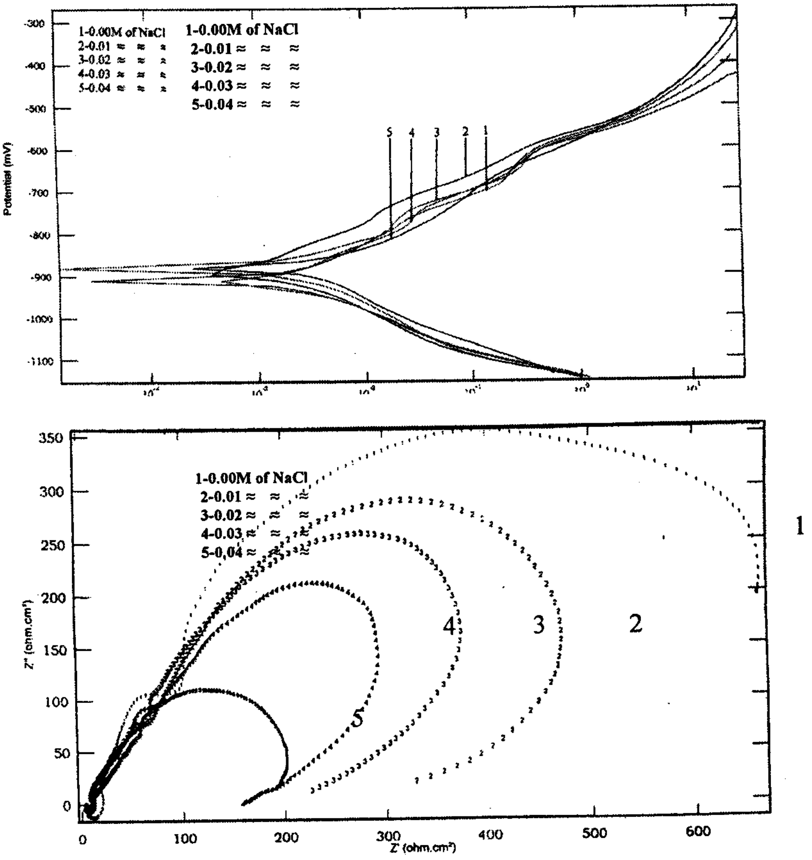


Fig.(2): Polarization and Nyquist curves of $Fe_{78}B_{13}Si_9$ metallic glass corrosion in 0.2 M Na_2SO_4 solution containing 10% MeOH in the absence and presence of various Cl^- concentrations at 30°C.

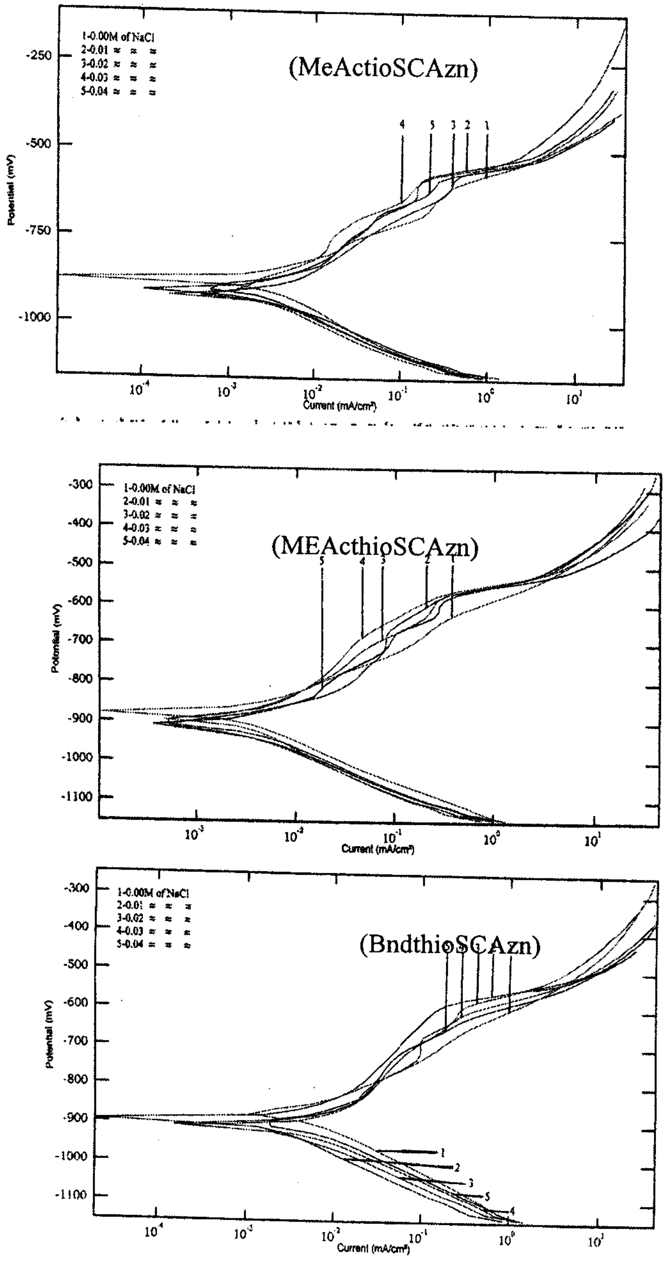


Fig.(3a): Polarization curves for $Fe_{78}B_{13}Si_9$ metallic glass corrosion in 0.2M Na_2SO_4 containing 10% MeOH in absence and presence of 10^{-4} M MeActhioSCAzn, MEActhioSCAzn and BndthioSCAzn for various Cl^- concentrations at 30°C.

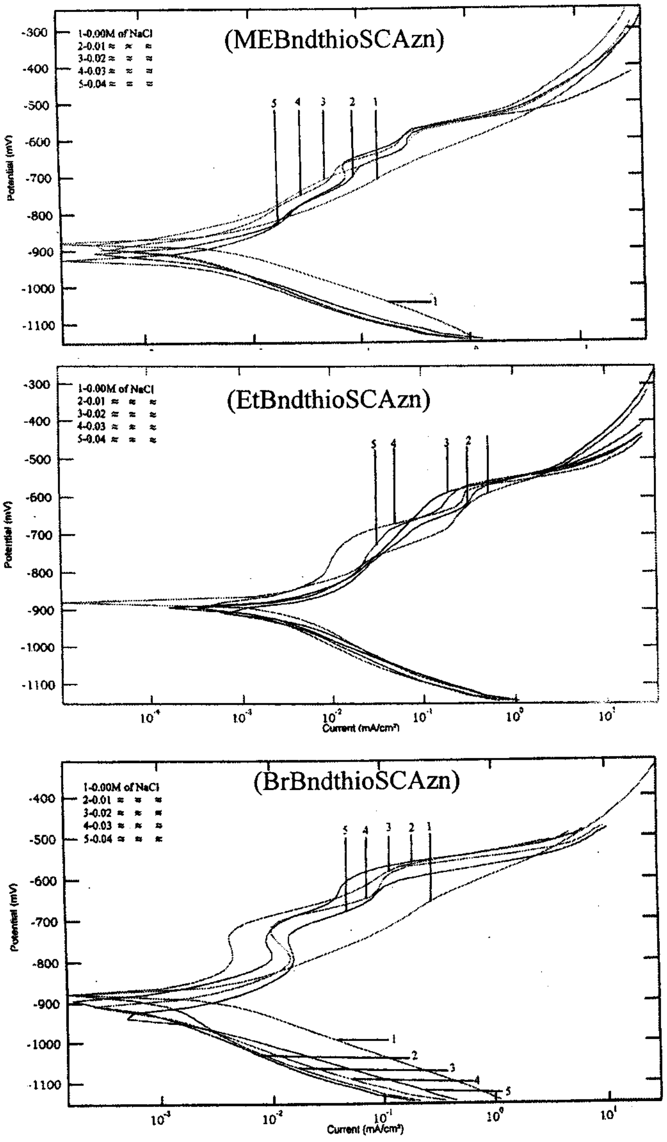


Fig.(3b): Polarization curves for $Fe_{78}B_{13}Si_9$ metallic glass corrosion in 0.2M Na_2SO_4 containing 10% MeOH in absence and presence of 10^{-4} M MEBndthioSCAzn, EtBndthioSCAzn and BrBndthioSCAzn for various Cl^- concentrations at 30°C.

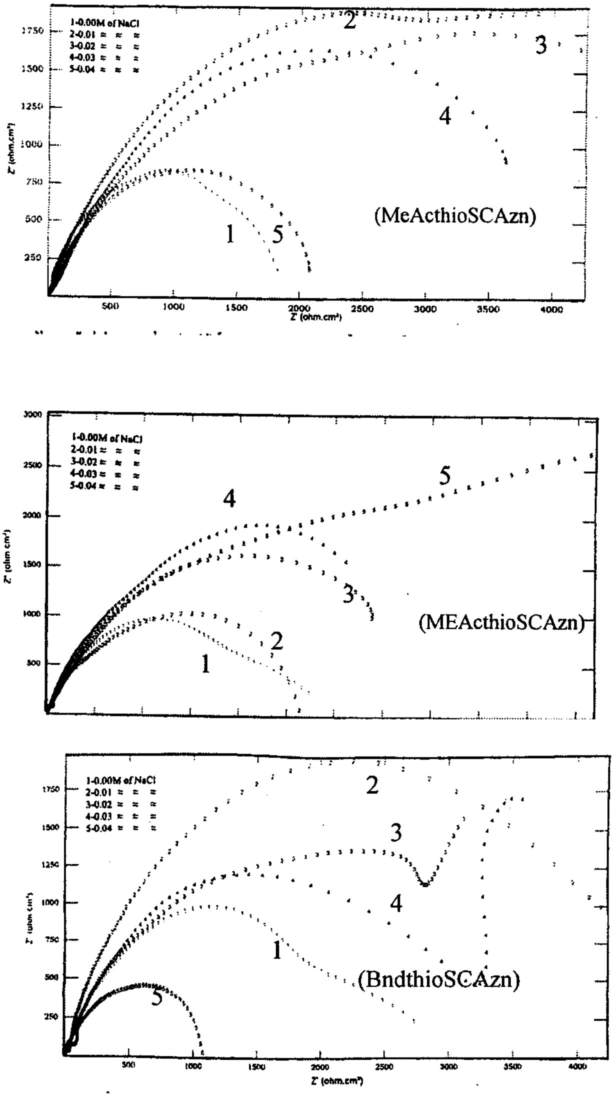


Fig.(4a): Nyquist diagrams for $Fe_{78}B_{13}Si_9$ metallic glass corrosion in 0.2 M Na_2SO_4 solution containing 10%MeOH in absence and presence of 10^{-4} M MeActhioSCAzn, MEActhioSCAzn and BndthioSCAzn for various Cl^- concentrations at 30°C.

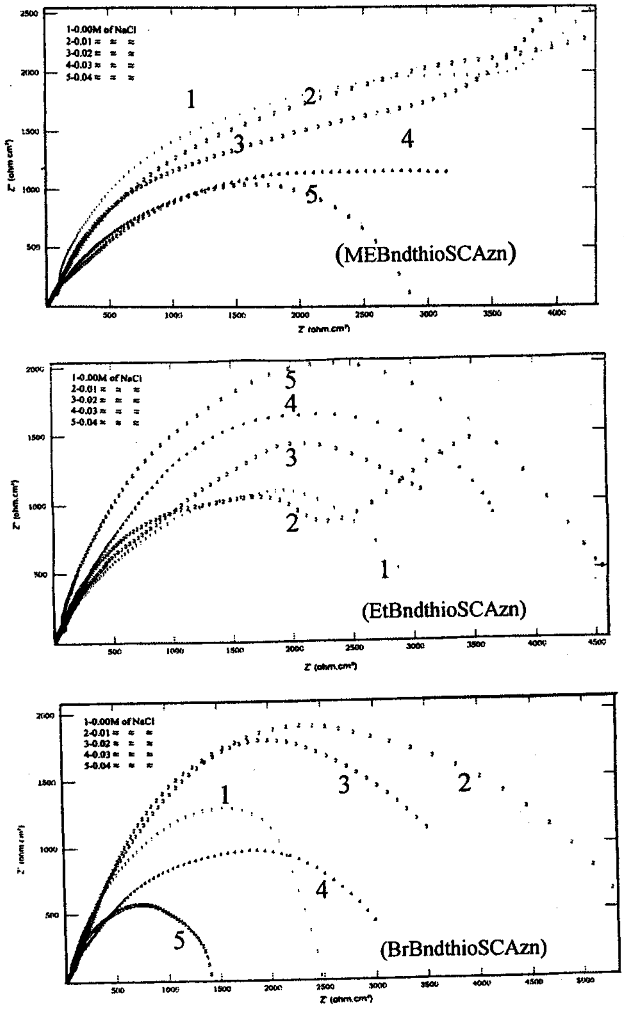


Fig.(4b): Nyquist diagrams for $Fe_{78}B_{13}Si_9$ metallic glass corrosion in 0.2 M Na_2SO_4 solution containing 10%MeOH in absence and presence of 10^{-4} M MEBndthioSCAzn, EtBndthioSCAzn and BrBndthioSCAznfor various Cl^- concentrations at 30°C.

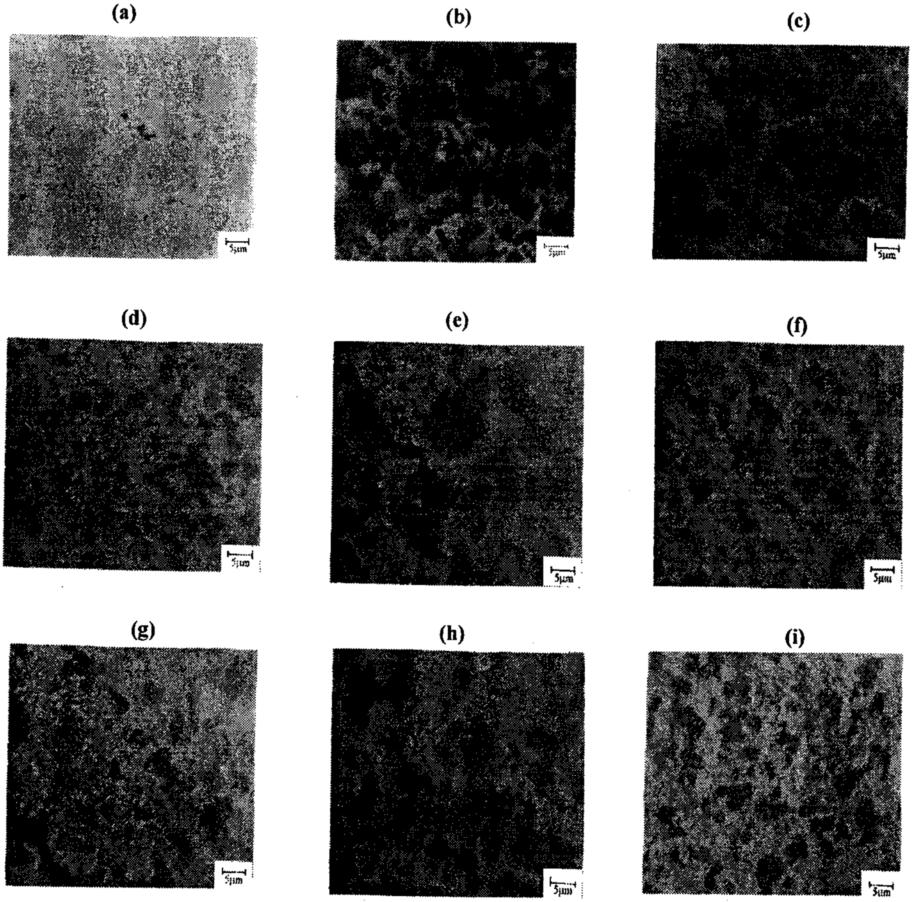


Fig.(7): (a) Optical micrographs (500X) of as-received surface of $Fe_{78}B_{13}Si_9$ glassy alloy,
(b) Optical micrographs (500X) of $Fe_{78}B_{13}Si_9$ glassy alloy after 45 min immersion in 0.2 M Na_2SO_4 solution containing 10 % MeOH at 30°C,
(c) 0.2 M Na_2SO_4 + 0.01 M Cl^-,
(d) 0.2 M Na_2SO_4 + 0.01 M Cl^- + 10^{-4} M of Inh. MeActhioSCAzn,
(e) 0.2 M Na_2SO_4 + 0.01 M Cl^- + 10^{-4} M of Inh. MEActhioSCAzn,
(f) 0.2 M Na_2SO_4 + 0.01 M Cl^- + 10^{-4} M of Inh. BndthioSCAzn,
(g) 0.2 M Na_2SO_4 + 0.01 M Cl^- + 10^{-4} M of Inh.MEBndthioSCAzn,
(h) 0.2 M Na_2SO_4 + 0.01 M Cl^- + 10^{-4} M of Inh. EtBndthioSCAzn and
(i) 0.2 M Na_2SO_4 + 0.01 M Cl^- + 10^{-4} M of Inh. BrBndthioSCAzn.

Table(1): Impedance and polarization parameters and inhibition percentages for $Fe_{78}B_{13}Si_9$ metallic glass corrosion in 0.2 M Na_2SO_4 solution containing 10% MeOH in absence and presence different concentration of Cl^- at 30°C.

C_{Cl^-} (M)	$-E_{corr}$ V	i_{corr} mA/cm^2	b_a ($V\,dec^{-1}$)	$-b_c$ ($V\,dec^{-1}$)	R_{ct} (Ωcm^2)	C_{dl} (μF)	Inh.p %	Inh.R_{ct} %
0.00	0.877	0.952	0.086	0.090	654.2	48.03	-	-
0.01	0.881	1.179	0.106	0.081	514.2	59.94	-23.84	-27.22
0.02	0.900	1.294	0.079	0.086	415.7	73.31	-35.92	-57.37
0.03	0.915	1.355	0.124	0.084	398.8	76.94	-42.33	-64.40
0.04	0.875	1.429	0.078	0.098	217.9	81.22	-50.11	-

Table(2): Electrochemical parameters of $Fe_{78}B_{13}Si_9$ metallic glass corrosion in 0.2 M Na_2SO_4 solution containing 10 %MeOH in absence and presence of 10^{-4} M thiosemicarbazones at different concentration of Cl^- at 30oC.

C_{Cl^-} (M)	MeActhioSCAzn				MEActhioSCAzn)(				BndthioSCAzn			
	$-E_{corr}$ V	i_{corr} mA/cm2	b_a ($V\,dec^{-1}$)	$-b_c$ (V dec-1)	$-E_{corr}$ V	i_{corr} mA/cm2	b_a ($V\,dec^{-1}$)	$-b_c$ ($V\,dec^{-1}$)	$-E_{corr}$ V	i_{corr} mA/cm2	b_a ($V\,dec^{-1}$)	$-b_c$ ($V\,dec^{-1}$)
0.00	0.877	0.952	0.086	0.090	0.877	0.952	0.086	0.090	0.877	0.952	0.086	0.090
0.01	0.917	0.152	0.085	0.080	0.902	0.227	0.061	0.065	0.891	0.152	0.064	0.052
0.02	0.898	0.159	0.071	0.089	0.894	0.148	0.060	0.064	0.915	0.185	0.065	0.054
0.03	0.914	0.179	0.085	0.055	0.893	0.139	0.060	0.059	0.921	0.212	0.060	0.044
0.04	0.906	0.265	0.066	0.062	0.906	0.094	0.059	0.047	0.909	0.576	0.060	0.060

C_{Cl^-} (M)	MEBndthioSCAzn				EtBndthioSCAzn				BrBndthioSCAzn			
	$-E_{corr}$ *V*	i_{corr} *mA/cm2*	b_a (*V dec*$^{-1}$)	$-b_c$ (V dec^{-1})	$-E_{corr}$ *V*	i_{corr} *mA/cm2*	b_a (*V dec*$^{-1}$)	$-b_c$ (V dec^{-1})	$-E_{corr}$ *V*	i_{corr} *mA/cm2*	b_a (*V dec*$^{-1}$)	$-b_c$ (V dec^{-1})
0.00	0.877	0.952	0.086	0.090	0.877	0.952	0.086	0.090	0.877	0.952	0.086	0.090
0.01	0.903	0.106	0.076	0.055	0.897	0.266	0.056	0.066	0.898	0.103	0.049	0.072
0.02	0.897	0.139	0.075	0.044	0.890	0.149	0.041	0.041	0.876	0.187	0.056	0.098
0.03	0.891	0.178	0.074	0.054	0.885	0.129	0.049	0.069	0.909	0.219	0.049	0.068
0.04	0.923	0.197	0.075	0.055	0.895	0.111	0.040	0.053	0.939	0.287	0.052	0.048

Table(3): Impedance parameters for $Fe_{78}B_{13}Si_9$ metallic glass corrosion in 0.2 M Na_2SO_4 solution containing 10% MeOH in absence and presence of 10^{-4} M of studied compound at different concentrations of Cl^- at 30°C.

	MeActhioSCAzn		MEActhioSCAzn		BndthioSCAzn		MEBndthioSCAzn		EtBndthioSCAzn		BrBndthioSCAzn	
C_{Cl^-} (M)	R_{ct} (Ωcm^2)	C_{dl} (μF)	R_{ct} (Ωcm^2)	C_{dl} (μF)	R_{ct} (Ωcm^2)	C_{dl} (μF)	R_{ct} (Ωcm^2)	C_{dl} (μF)	R_{ct} (Ωcm^2)	C_{dl} (μF)	R_{ct} (Ωcm^2)	C_{dl} (μF)
0.00	654.2	48.03	654.2	48.03	654.2	48.03	654.2	48.03	654.2	48.03	654.2	48.03
0.01	5647	04.09	2699	12.66	4553	10.76	6219	09.95	3225	16.32	5564	08.12
0.02	5107	04.22	4024	09.97	3869	13.05	4568	11.14	3959	12.05	4028	10.39
0.03	3734	07.72	4186	08.94	3509	14.53	4089	12.81	4111	11.97	3363	10.97
0.04	2185	10.51	7191	03.98	1064	33.10	2974	15.19	4657	10.27	1443	26.16

Table(4): Inhibition percentages for $Fe_{78}B_{13}Si_9$ metallic glass corrosion in 0.2 M Na_2SO_4 solution containing 10% MeOH in absence and presence of 10^{-4}M of studied compounds at different concentrations of Cl^- at 30C.

compound	$Inh._p$ %	$Inh.R_{ct}$ %	$Inh._p$%	$Inh.R_{ct}$ %	$Inh._p$%	$Inh.R_{ct}$ %	$Inh._p$%	$Inh.R_{ct}$ %	$Inh._p$%	$Inh.R_{ct}$ %
	0.00M		$0.01M_{(Cl^-)}$		$0.02M_{(Cl^-)}$		$0.03M_{(Cl^-)}$		$0.04M_{(Cl^-)}$	
MeActhioSCAzn	66.81	64.68	84.03	88.41	83.30	87.19	81.20	82.48	72.16	70.06
MEActhioSCAzn	89.29	90.53	76.15	75.76	84.51	83.74	85.40	84.37	90.13	90.96
BndthioSCAzn	79.18	77.08	84.03	85.63	80.57	83.09	77.73	81.36	39.50	38.52
MEBndthioSCAzn	83.82	89.65	88.87	89.48	85.40	85.68	81.30	84.00	79.31	78.00
EtBndthioSCAzn	81.35	80.44	72.06	79.71	84.35	83.48	86.45	84.09	88.34	85.95
BrBndthioSCAzn	76.26	73.30	89.18	88.24	80.36	83.76	77.00	80.55	69.85	54.66

Table(5): Synergism parameters S_θ for various concentrations of Cl^-.

C_{Cl^-} (M)	MeActhioSCAzn	MEActhioSCAzn	BndthioSCAzn	MEBndthioSCAzn	EtBndthioSCAzn	BrBndthioSCAzn
	S_θ	S_θ	S_θ	S_θ	S_θ	S_θ
0.01	2.57	0.56	1.61	1.80	0.82	2.71
0.02	2.70	0.94	1.46	1.51	1.61	1.64
0.03	2.51	1.04	0.75	1.23	1.95	1.46
0.04	1.79	1.63	0.52	1.17	2.39	1.18