

Effect of temperature on the corrosion inhibition of iron base metallic glass alloy in neutral solutions

S.T. Arab^a and K.M. Emran^{b,*}

^aDepartment of Chemistry, Girls' College of Education, P.O. Box (55002), Jeddah 21413, SAUDI ARABIA

^bDepartment of Chemistry, Girls' College of Education, Al-Madinah Al-Monawarah, SAUDI ARABIA

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Abstract

Electrochemical measurements have been used to study the influence of temperature on corrosion and inhibitive effects of 4-methyl acetophenone thiosemicarbazone and 4-methoxy acetophenone thiosemicarbazone on the corrosion of Fe₇₈B₁₃Si₉ metallic glass in 0.2 M Na₂SO₄ between 293 and 333K. A good agreement between the data obtained by polarization and impedance measurements was found. A rise in temperature associated with an increase in i_{corr} and $1/R_{ct}$ values and decrease in the inhibition efficiency suggest a physical adsorption model for the corrosion processes. The results show that these compounds almost inhibit the iron-based glassy alloy corrosion at elevated temperatures. The difference in the inhibition behavior of the two compounds is explained in terms of the difference in the electron densities on the centers of adsorption in the thiosemicarbazone molecules. Thermodynamic parameters, ΔE_{app} , ΔH^* and ΔS^* , have been calculated and are discussed.

Keywords: Metallic glass; Iron-base glassy alloy; Corrosion; Acetophenone thiosemicarbazone; Physisorption

Introduction

During the last three decades a great deal of effort has been expended in the characterization and understanding of the general corrosion behavior of metal–metalloid metallic glasses [1,2]. It is known that glassy alloys based on iron, nickel and cobalt (with no other metallic elements such as chromium) show poor corrosion resistance in different media [3–5].

Improvement in the corrosion resistance of metallic glasses by the alloying elements has been considerably studied, but very little attention has been paid to the use of inhibitors to decrease the severity of the corrosive attack. However, some attempts have been made to inhibit the iron base glassy alloys corrosion by certain organic compounds [6–12].

The inhibiting action of thiosemicarbazide on mild steel corrosion in HCl solution was studied at different temperatures. The protective effect increased with both inhibitor concentration and the temperature of the corrosion medium (293–333K). The low values of the apparent activation energy (E_{app}) of the corrosion process in the presence of the inhibitors was proof for the chemisorption of the inhibitors [13].

Gad Allah *et al.* [14] investigated the inhibition of corrosion of Helwan mild steel in 1.0 M HCl by carbamide, urea and thiocarbamide derivatives, and thiosemicarbazide at temperatures between 323 and 358K.

The corrosion rate was found to depend on the solution temperature, inhibitor type and concentration. The rate of corrosion at temperatures < 358K decreased with increasing urea concentration and the trend reversed at higher temperatures.

On the other hand, the inhibition efficiency at all temperatures increased with the concentration of thiourea up to a critical concentration above which it decreased, the extent of which depending on the inhibitor concentration and solution temperature. Pang *et al.* [15] have studied the corrosion rates of Fe_{50-x}Cr₁₆Mo₁₆C₁₈B_x ($x = 4, 6, 8$ at.%) glassy alloys in 1.0, 6.0 and 12.0 N HCl at 298K.

The present work is a systematic study on the effect of temperature on the corrosion and protection of Fe₇₈B₁₃Si₉ amorphous alloy in neutral solutions. It includes the effect of substitution on thiosemicarbazone's benzene ring as well as of the addition of Cl⁻ or Br⁻.

Experimental

Inhibitors

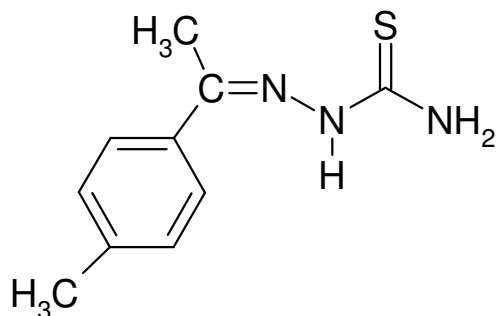
Thiosemicarbazone derivatives employed in this investigation (Fig. 1) were prepared by condensation of a suitable carbonyl compound with thiosemicarbazide (Aldrich) in the presence of an acid catalyst [16].

Specimens and test solutions

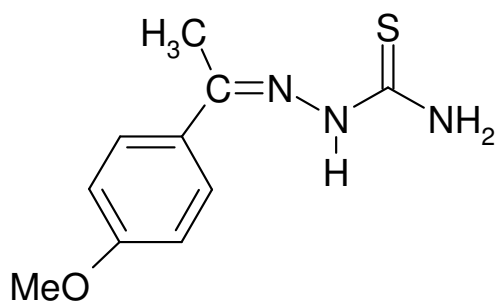
Fe₇₈B₁₃Si₉ glassy alloy used was supplied by Goodfellow. Rounded specimens were cut from a foil (50 mm wide, 0.025 mm thickness) with a working area of 30

*Author for correspondence
Email: k_imran2000sa@yahoo.co.uk

mm² in all the experiments. The specimens were used without mechanical polishing. Electrochemical measurements were made on the bright face of the working electrode.



(A) 4-methyl acetophenone thiosemicarbazone
(MeActhioSCAzn)



(B) 4-methoxy acetophenone thiosemicarbazone
(MEActhioSCAzn)

Fig. 1. Symbols and structures of the inhibitors.

Each experiment was carried out with a new strip. The electrodes were degreased with alcohol and rinsed several times with double distilled water and finally cleaned in an ultrasonic bath (Model LF2003, 50160Hz, Dal Trozzo, Italy). The electrode was connected to a copper specimen holder and immersed in the test solution without drying. The chemicals (Na₂SO₄, NaCl and NaBr) used were from BDH, while methanol was from Hyman. Solutions were prepared by using double distilled water. All tests were performed in range 293–333K±0.01K.

Electrochemical studies

Electrochemical measurements were made by connecting the electrochemical cell to ACM Gill AC and to a Samsung computer (Bridge DVD ASUS 8X max). Potentiodynamic polarization curves were recorded at scan rate of 60 mV.min⁻¹. Electrode potentials were measured with respect to a silver/silver chloride reference electrode with a Luggin capillary bridge and a platinum wire counter electrode. Kinetic data were obtained directly from the potentiodynamic measurements analyzed on the basis of

the Tafel extrapolation method.

The percentage reduction in the corrosion current (*I.E.*%) was calculated from equation (1):

$$I.E.\% = (i_{corr}^* - i_{corr} / i_{corr}^*) \times 100 \quad (1)$$

where i_{corr}^* and i_{corr} denote the corrosion current densities in the absence and presence of 10⁻⁴ M of the inhibitor (A or B) at each studied temperature, respectively.

Impedance data (R_{ct} , $1/R_{ct}$ and C_{dl}) were obtained in the frequency range 0.5 Hz – 10 KHz. The impedance data are presented as Nyquist plots. The capacitance of the double layer was calculated from the following expression [2,16]:

$$C_{dl} = 1 / 2\pi f (-Z_{max}^{\prime}) R_{ct} \quad (2)$$

where f is the frequency at the maximum height of the semicircle on the imaginary axis and R_{ct} is the charge transfer resistance. The inhibition percentage efficiencies (Inh. R_{ct} %) and (Inh. C_{dl} %) of the corrosion rate in the presence of the thiosemicarbazone derivatives (A or B) were calculated as follows [16]:

$$\text{Inh.}R_{ct}\% = (R_{cto}^{-1} - R_{ct}^{-1} / R_{cto}^{-1}) \times 100 \quad (3)$$

$$\text{Inh.}C_{dl}\% = (C_{dlo} - C_{dl} / C_{dlo}) \times 100 \quad (4)$$

where R_{cto}^{-1} and R_{ct}^{-1} are the reciprocals of charge transfer resistance and C_{dlo} and C_{dl} are the double layer capacitance of glassy alloy in absence and the presence of 10⁻⁴ M of the inhibitor A or B at each studied temperature, respectively.

Results and Discussion

Effect of temperature on corrosion

Cathodic and anodic potentiodynamic polarization curves for Fe₇₈B₁₃Si₉ glassy alloy in a 0.2 M Na₂SO₄ solution containing 10% MeOH at 293, 303, 313, 323 and 333K are shown in Fig. 2a. The corresponding data obtained are given in Table I.

The corrosion current density (i_{corr}) values are directly proportional to the temperature. The E_{corr} values shifted to more anodic potentials in an irregular manner. At the lower temperatures (293–313K) the anodic polarization curves show two transient passivity regions, first in the range from –700 to –780 mV and another in the range from –550 to 680 mV.

The Nyquist plots in Fig. 2b enable the calculation of the temperature effect on the electrochemical impedance parameters (Table I). It can be seen that $1/R_{ct}$ and C_{dl} values increase in temperature. The Nyquist plots show approximately semicircle-type behavior, which indicates that the corrosion of Fe₇₈B₁₃Si₉ glassy alloy is mainly controlled by the charge transfer process.

Table I

Electrochemical polarization parameters for $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass in a 0.2 M Na_2SO_4 solution containing 10% MeOH at different temperatures.

Temperature (K)	$-E_{corr}$ (V)	i_{corr} ($\text{mA}\cdot\text{cm}^{-2}$)	b_a (V dec^{-1})	$-b_c$ (V dec^{-1})	C_{dl} (μF)	R_{ct} ($\Omega\cdot\text{cm}^2$)	$1/R_{ct}$ ($\Omega^{-1}\cdot\text{cm}^{-2}$)
293	0.907	0.670	0.086	0.084	32.92	1055	9.48×10^{-4}
303	0.877	0.952	0.086	0.090	48.03	654.2	1.53×10^{-3}
313	0.846	1.252	0.063	0.068	65.18	498.0	2.01×10^{-3}
323	0.843	1.382	0.066	0.077	70.60	441.2	2.27×10^{-3}
333	0.877	1.937	0.069	0.065	105.20	322.7	3.10×10^{-3}

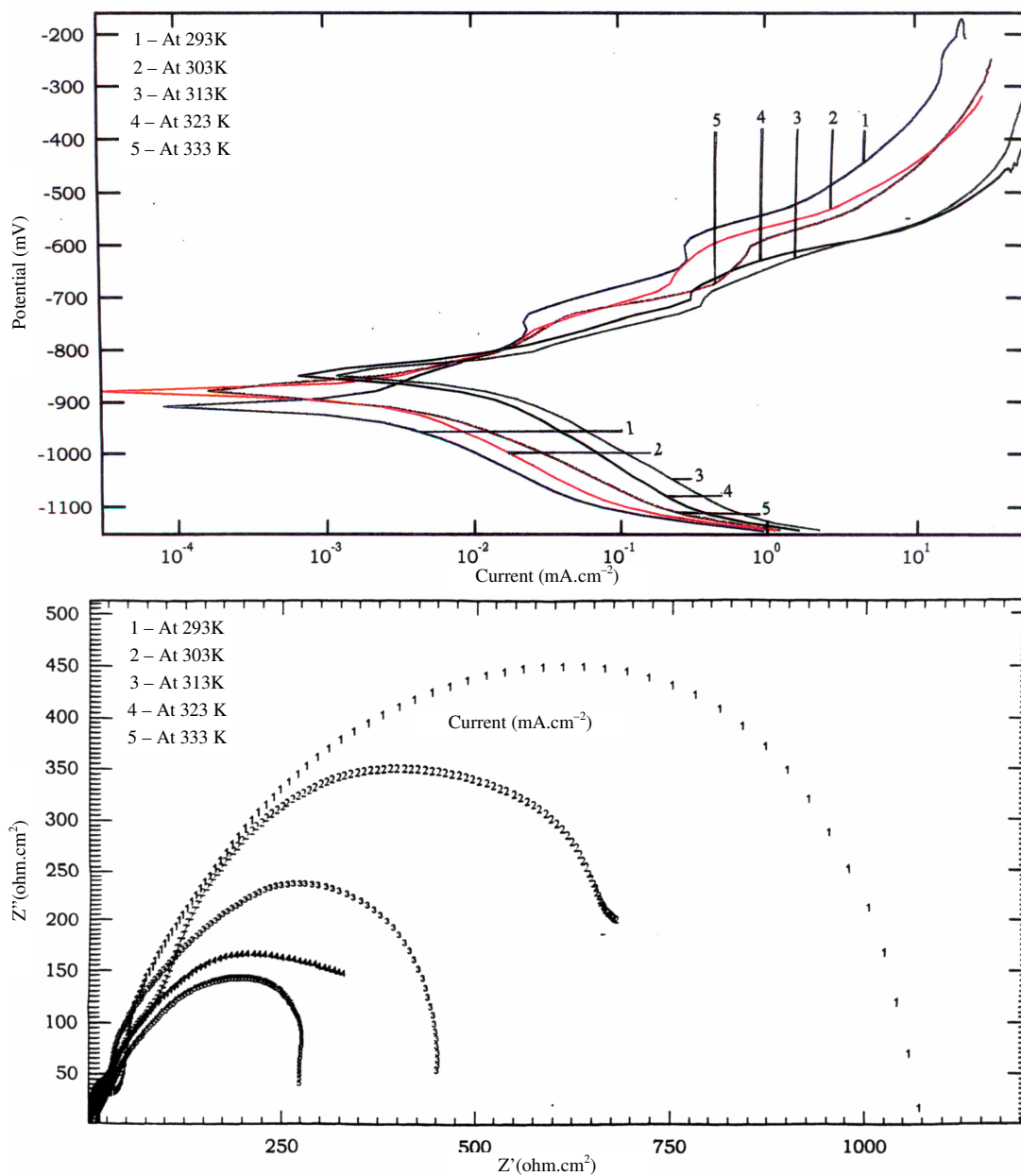


Fig. 2 (a) Polarization curves of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass in a 0.2 M Na_2SO_4 solution containing 10% MeOH at different temperatures; and (b) Nyquist diagrams for the corrosion of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass in a 0.2 M Na_2SO_4 solution containing 10% MeOH at different temperatures.

The Arrhenius activation energy (apparent activation energy E_{app}) was calculated from polarization [17] and impedance [18] data by the following relationships, respectively:

$$\log i_{corr} = \log A - (-\Delta E_{app} / 2.303RT) \quad (5)$$

$$\log 1/R_{ct} = \log A - (\Delta E_{app} / 2.303RT) \quad (6)$$

where i_{corr} is the corrosion current density, R_{ct} the charge transfer resistance, A is the Arrhenius pre-exponential constant, R is the universal gas constant and T is the absolute temperature.

A plot of $\log i_{corr}$ or $\log 1/R_{ct}$ against $1/T$ Figs. 3a and 4a gives a straight line with a slope of $-\Delta E_{app}/2.303R$. The calculated values of ΔE_{app} are 20.30 and 22.55 kJ.mol⁻¹, respectively, and are in good agreement.

Values of enthalpy ΔH^* and entropy ΔS^* for the corrosion of Fe₇₈B₁₃Si₉ glassy alloy in the test solution were calculated from transition state eqns. [19]:

$$\log (i_{corr}/T) = \log (R/Nh + \Delta S^*/2.303R) - \Delta H^*/2.303RT \quad (7)$$

$$\log (1/R_{ct}/T) = \log (R/Nh + \Delta S^*/2.303R) - \Delta H^*/2.303RT \quad (8)$$

where h is the Plank's constant and N is the Avogadro's number.

A plot of $\log (i_{corr}/T)$ or $\log (1/R_{ct}/T)$ against $1/T$ gives a straight line with a slope of $-\Delta H^*/2.303R$, Figs. 3b and 4b, and the intercept is $(\log R/Nh + \Delta S^*/2.303R)$ from which the values of ΔH^* and ΔS^* were deduced. The calculated values of ΔH^* are 17.71 and 19.93 kJ.mol⁻¹, respectively, which are in good agreement. The more negative value of ΔS^* indicates a random system.

Temperature effect on corrosion inhibition

Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur or oxygen, each of them being an adsorption center. The protection properties of such compounds depend on the electron density around the adsorption center: the higher the electron density at the center, the more effective is the inhibitor.

It is also well known that the sulphur atom of thio compounds is the reaction center for adsorption on to metal surfaces. Therefore, the electron density on the center (C = S in the case of thiosemicarbazone) would determine the effectiveness of this type of inhibitor. Temperature can modify the interaction between the amorphous alloy and the electrolyte in the presence of acetophenone thiosemicarbazone compounds.

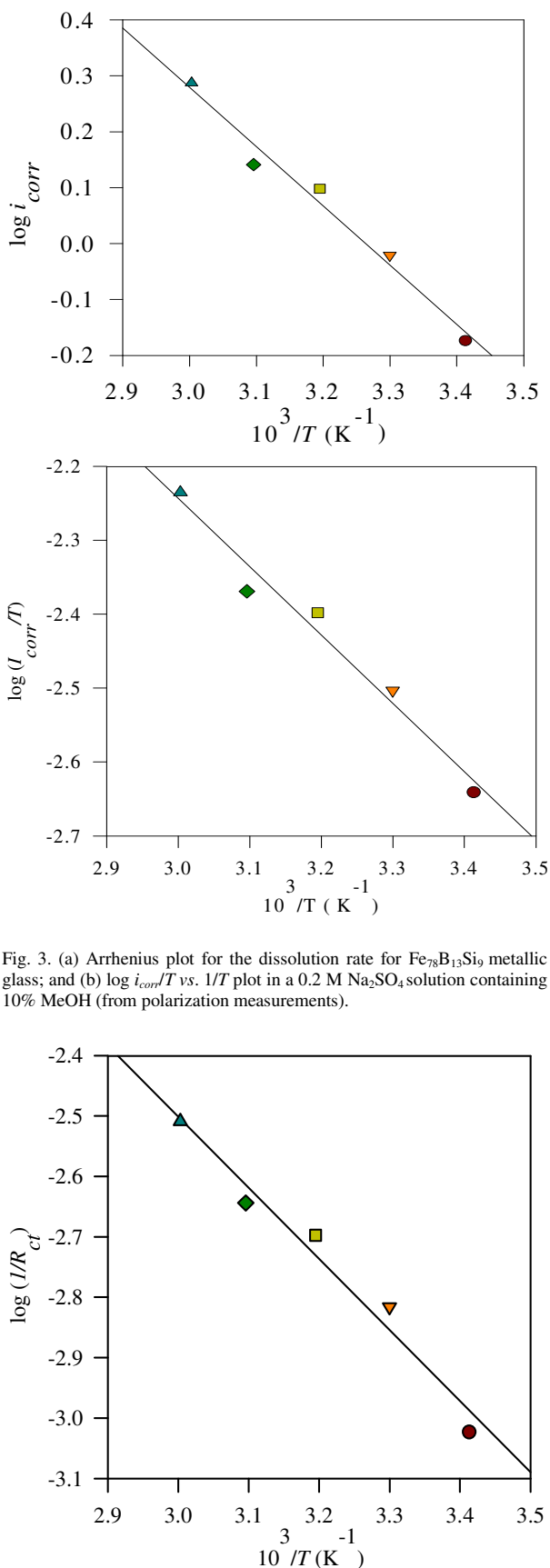


Fig. 3. (a) Arrhenius plot for the dissolution rate for Fe₇₈B₁₃Si₉ metallic glass; and (b) $\log i_{corr}/T$ vs. $1/T$ plot in a 0.2 M Na₂SO₄ solution containing 10% MeOH (from polarization measurements).

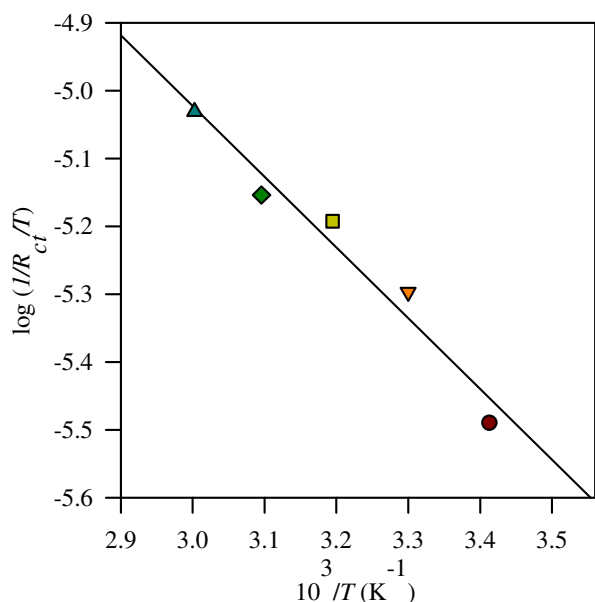


Fig. 4. (a) Arrhenius plot for the dissolution rate for $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass; and (b) a plot of $\log 1/R_{ct}/T$ vs. $1/T$ in a 0.2 M Na_2SO_4 solution containing 10% MeOH (from impedance measurements).

The effect of temperature on the inhibition efficiency was determined in a 0.2 M Na_2SO_4 solution containing 10% MeOH in the presence 10^{-4} M 4-methyl acetophenone thiosemicarbazone (A) or 4-methoxy acetophenone thiosemicarbazone (B) at temperatures between 293 and 333K. The temperature effect on the Tafel lines of the iron-based metallic glass is given in Table II.

It can be seen that both inhibitors at different temperatures act as mixed inhibitors. A rise in temperature is associated with an increase in i_{corr} values in the presence of a fixed concentration of the acetophenone thiosemicarbazones derivatives.

Figure 5 gives typical impedance diagrams for the corrosion of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ glassy alloy in the presence of inhibitors. Nyquist plots for inhibitor A at 293K has a long tail in the low-frequency region. This behavior indicates the formation of a film on the amorphous surface where ions diffusion can take place.

Upon addition of the inhibitors and with a protective film on metal surface, the pore size in the film controls the diffusion of ions through the film [20]. This behavior is also found at 293 and 303K for inhibitor B, while its other Nyquist plots give a diffusion tail. All the other Nyquist plots for inhibitor A show approximately a semi-circle, indicating that the corrosion process is mainly a charge transfer process and that a rise in the temperature in the range 303–333K does not change the mechanism of dissolution of the amorphous alloy.

The depression of semicircle connected with certain increase in heterogeneity could be a result of surface metal

roughening. The latter may be caused by enhanced dissolution of the metal, which takes place at high temperatures [18]. An increase in temperature leads to a decrease in the R_{ct} values and an increase in the C_{dl} values. This is associated with an increase in the corrosion rate.

The corrosion inhibition efficiency given in Table II decreases with increasing temperature, indicating a higher dissolution of the alloy. The dependence of inhibition efficiency ($I.E.\%$, $\text{Inh.}R_{ct}\%$ and $\text{Inh.}C_{dl}\%$) on temperature suggests a good agreement between polarization and impedance studies.

A comparison of the inhibition efficiency shows that compound B has higher protection properties at all temperatures compared with compound A. This may be due to a better electron-donating property of the MeO group than that of the CH_3 group in the benzene ring. Hence an increased electron density around the active site explains why B is more active than A. The results obtained in this study are in agreement with the observation of El-Naby *et al.* [21].

The decrease in the inhibition efficiency of these inhibitors indicates that both the compounds are physically adsorbed on the amorphous surface [22], and may be explained as due to the time between the process of adsorption and desorption of the inhibitor molecules over the metal surface, which becomes shorter at higher temperatures. Hence, the metal surface remains exposed to the aggressive environment for a longer period, thereby increasing the rate of corrosion at higher temperatures. Therefore, the inhibition efficiency falls [23].

The nature of adsorption process as being either a physical or chemical process may be elucidated from the magnitude of the heat of adsorption (Q). Barrow [24] distinguished between the two types of adsorption processes. He stated that the heat of adsorption for physisorption was less than about 40 kJ.mol^{-1} , while it was greater than 80 kJ.mol^{-1} for chemisorption. Heat of adsorption was estimated by the Langmuir isotherm (eq. 9):

$$\log \Theta/1-\Theta = \log A + \log C - Q/2.303RT \quad (9)$$

where Θ is the surface coverage, and other abbreviation are the same as in eq.(5).

The slope of the linear portion of plot $\log \Theta/1-\Theta$ against $1/T$ (Fig. 6) are equal to $(-Q/2.303R)$, from which the average heat of adsorption Q was calculated [23,25]. The values obtained are given in Table III. The values of Q are negative, reflecting the exothermic behavior of the thiosemicarbazone adsorption on the amorphous alloy surface [26]. It can be seen from Table III that B (MEActhioSCAzn) is more strongly adsorbed than A (MeActhioSCAzn).

Table II

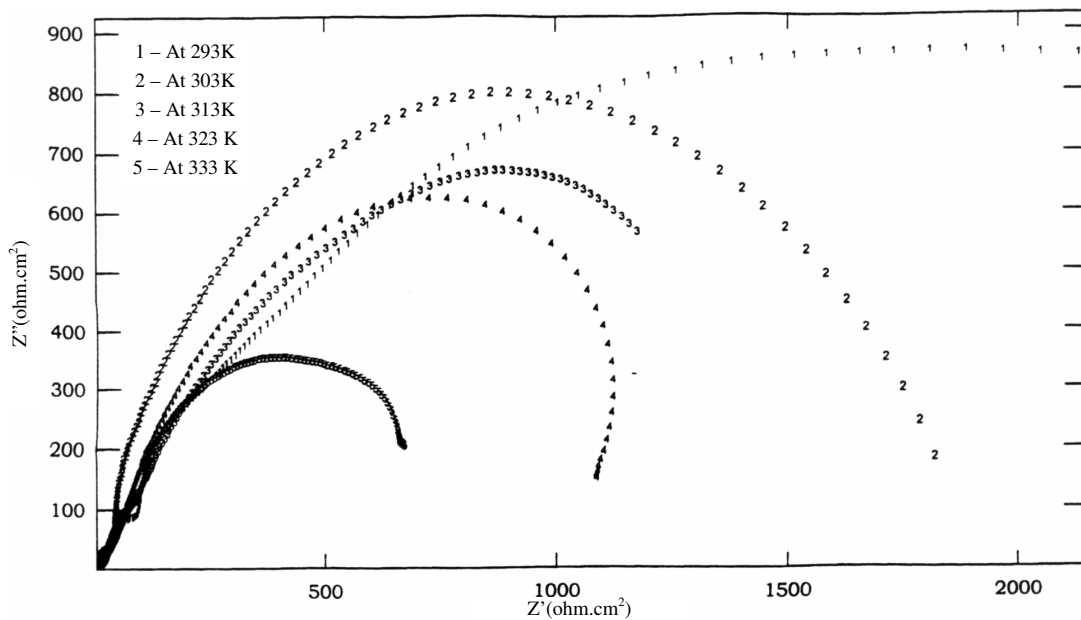
Electrochemical polarization parameters and percentage inhibition for $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass in a 0.2 M Na_2SO_4 solution containing 10% MeOH in presence of 10^{-4} M of inhibitors A and B at different temperatures.

Temperature (K)	$-E_{corr}$ (V)	i_{corr} ($\text{mA}\cdot\text{cm}^{-2}$)	$I.E.$ (%)	R_{ct} ($\Omega\cdot\text{cm}^2$)	C_{dl} (μF)	Inh. R_{ct} (%)	Inh. C_{dl} (%)
Inhibitor A							
293	0.904	0.222	66.87	3040	12.53	65.30	61.94
303	0.906	0.316	66.81	1852	18.59	64.68	61.39
313	0.807	0.491	60.78	1401	25.53	64.45	60.83
323	0.892	0.612	55.72	1088	29.04	59.45	58.87
333	0.877	0.925	52.25	663.4	44.77	51.36	57.44
Inhibitor B							
293	0.884	0.068	89.85	11200	02.12	90.58	93.96
303	0.904	0.102	89.29	6905	03.12	90.53	93.50
313	0.878	0.254	79.71	1769	15.38	71.85	76.40
323	0.876	0.482	65.12	1268	27.18	64.50	61.50
333	0.863	0.696	64.07	816.2	41.46	60.46	60.59

Table III

Heat of adsorption and thermodynamic parameters for the corrosion of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass in a 0.2 M Na_2SO_4 solution containing 10% MeOH in the absence and presence of 10^{-4} M of the inhibitors (from polarization and impedance measurements).

Compound symbol	Heat of adsorption Q ($\text{kJ}\cdot\text{mol}^{-1}$)	Polarization			Impedance		
		ΔE_{app} ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔH^* ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS^* ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	ΔE_{app} ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔH^* ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS^* ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
Blank	–	20.30	17.71	–187.37	22.55	19.93	–233.98
A	–13.907	28.54	25.98	–168.73	28.98	26.42	–174.05
B	–38.05	44.19	41.58	–124.28	56.46	53.98	v



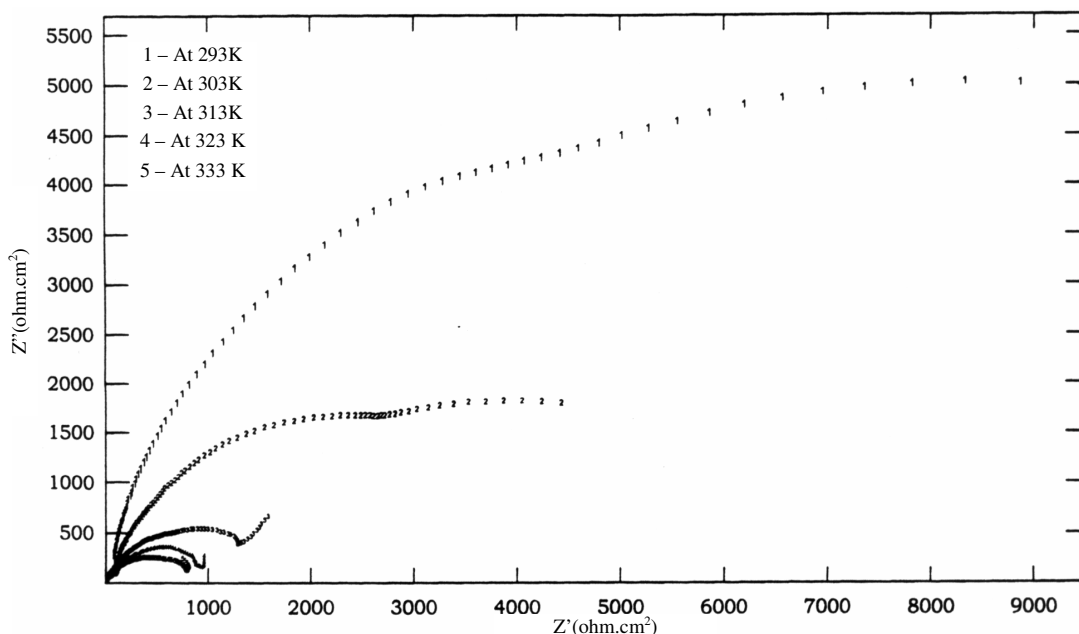


Fig. 5. Nyquist plots for the corrosion of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass in a 0.2 M Na_2SO_4 solution containing 10% MeOH in the presence of 10^{-4} M of the inhibitors at different temperatures.

The Arrhenius activation energy (apparent activation energy) E_{app} calculated from polarization and impedance data using eqns. (5) and (6), respectively, are presented in Table III. It can be noted that the apparent activation energy calculated for the inhibited solutions in the study is relatively higher than that obtained in the uninhibited solution. This result can be explained that the use of inhibitors to protect metals from corrosion is involving the formation of a physical barrier (resulting from physical adsorption) between the metal and the inhibitor molecules [22]. Also the higher values of ΔE_{app} in the presence of the inhibitors than that for the uninhibited solution indicated a strong adsorption of the inhibitors at the metal surface, which leads to an increase in the energy barrier for the corrosion process [27].

However, the highest values of the activation energy is associated with the most efficient inhibitor. The degree of increase in the activation energy in the present work is in good agreement with the above mentioned order of the inhibitors. Values of enthalpy ΔH^* and entropy ΔS^* for the inhibition of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ glassy alloy in the presence of a fixed concentration of the compounds were calculated from eqns. (7) and (8) from the polarization and impedance studies, respectively. It is clear that the values of ΔS^* for each of the inhibitor-containing solution has a less negative value than that for the uninhibited solution ($-187.36 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

According Grigorev [20] the presence of inhibitors leads the corrosion system to pass from a less random to a more ordered arrangement, and hence a less negative value of entropy is observed. From Table III, it is clear that ΔE_{app}

and ΔH^* for the inhibition processes of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ glassy alloy in the test solutions with the inhibitors are nearly the same and higher than those in the uninhibited solution, indicating that the corrosion reactions are affected without changing the mechanism [19].

Effect of Temperature on corrosion in solutions containing Cl^- or Br^-

The effect of temperature in the range 293–333K on the corrosion of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ glassy alloy in 0.2 M Na_2SO_4 solution containing 10% MeOH in the presence of 0.01 M Cl^- is shown in Fig. 7a and 7b. As expected, the corrosion current density increases and the diameter of the capacitive loops decreases more rapidly with increasing temperature. E_{corr} values are shifted to more negative values as the temperature increases. The distorted semi-circles in the Nyquist plots may be due to a charge transfer controlled process besides a frequency dispersion [16,29]. The small capacitive loop appearing at high frequencies at 293K may be explained as due to some sort of film on the alloy surface.

Table IV represents the inhibition efficiency calculated from both the polarization and impedance data in the presence of Cl^- and Br^- ions. The negative inhibition efficiency indicates a corrosion accelerating effect by Cl^- , which increases with temperature (from 293 to 333K). Using the polarization measurements, ΔE_{app} for the dissolution of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ glassy alloy was determined from the Arrhenius equation. As can be noted, that ΔE_{app} value in Cl^- solution is lower ($19.91 \text{ kJ}\cdot\text{mol}^{-1}$) than that in the blank solution.

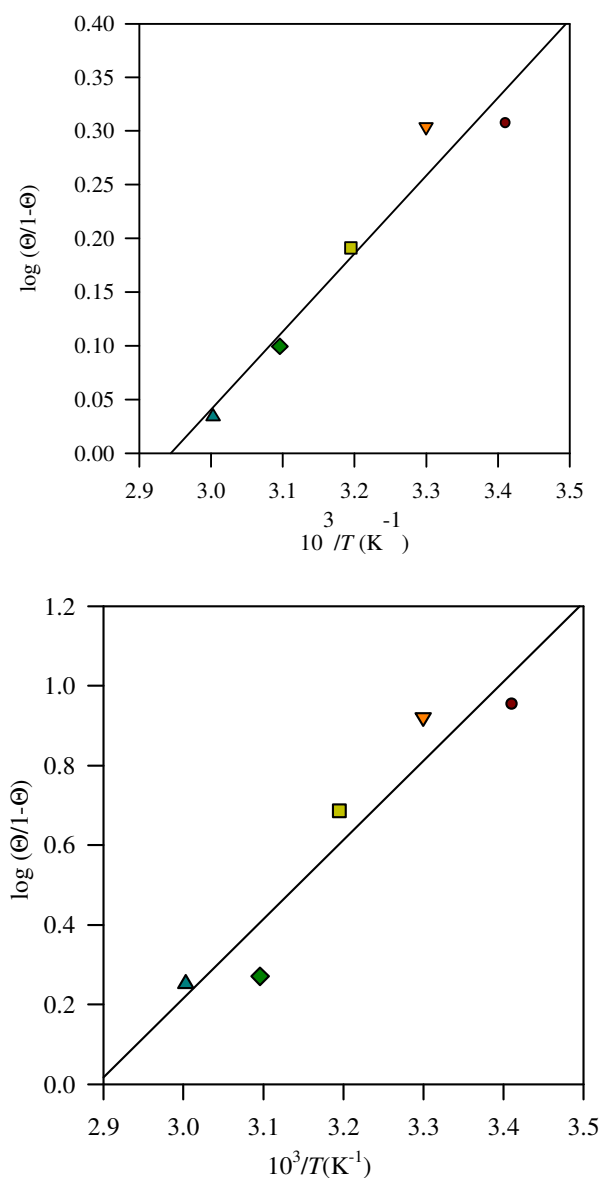


Fig. 6. Variation of logarithm($\Theta/1 - \Theta$) vs. $1/T$ for $Fe_{78}B_{13}Si_9$ metallic glass in a 0.2 M Na_2SO_4 solution containing 10% MeOH in the presence of 10^{-4} M of the inhibitors.

The reduction of the apparent activation energy in presence 0.01 M Cl^- may be explained as a reduction in the energy barrier for the corrosion process, which means an increase the corrosion rate. The values of ΔH^* and ΔS^* , calculated from transition state equation from polarization and impedance, are 24.61, 39.83 $kJ.mol^{-1}$ and -163.30 , $-165.60 J.mol^{-1}k^{-1}$, respectively.

In the presence of 0.01 M Br^- , E_{corr} values are irregular and shift to the anodic side and i_{corr} values in test solutions increase progressively with increase in temperature. Transient passivity regions present in anodic polarization curves at low temperatures (293–313K), may be due to adsorption of Br^- on the alloy surface.

The impedance diagrams for the corrosion of $Fe_{78}B_{13}Si_9$ glassy alloy in the presence of 0.01 M Br^- approximately have semi-circle-type behavior at all temperatures employed, indicating that the corrosion process is controlled by a charge transfer process. The distortion in the Nyquist plots may be due to frequency dispersion [16,29]. Values of inhibition efficiency calculated from both studies are given in Table IV, which show good agreement. The decrease in inhibition efficiency with rise in temperature indicates physical adsorption of Br^- on the amorphous alloy.

Values of ΔE_{app} in the presence of Br^- from the polarization and impedance measurements are 32.93 and 39.25 $kJ.mol^{-1}$, respectively. The high value of ΔE_{app} in the presence of Br^- supports the inhibition behavior of Br^- in the tested solutions. Also, ΔH^* values are 30.25 and 36.76 $kJ.mol^{-1}$ from the polarization and impedance measurements, respectively. The good agreement between ΔE_{app} and ΔH^* values indicate that addition of Br^- in the test solution does not change the mechanism of corrosion [19]. ΔS^* values are -152.20 and $-184.56 J.mol^{-1}.K^{-1}$, respectively. The less negative values of ΔS^* in the presence Br^- in Na_2SO_4 solution indicate that the corrosion system becomes more ordered.

Effect of Temperature on corrosion at fixed concentrations of the inhibitors and Cl

Potentiodynamic polarization scans were made in the presence of 0.01M Cl^- and 10^{-4} M of the inhibitors (A or B) at different temperatures (293–333K). The various electrochemical parameters calculated from the Tafel plots reveal that an increase in the temperature result in an irregular shift in the corrosion potential. This suggests that these compounds are mixed inhibitors. i_{corr} values increase with an increase in temperature, which may due to a desorption process of the adsorbed organic molecules at high temperatures.

Figure 8 shows the Nyquist plots at 293K for inhibitor A, and at 293 and 303K for inhibitor B. They have a semicircular shape with a long tail at the low-frequency region, indicating that the film on the metal is formed by adsorption of both the inhibitor and Cl^- or Br^- . Therefore, the diffusion processes take place on the amorphous surface after the addition of both the inhibitor and the halide ion [20]. The other plots with these inhibitors has approximately a semi-circle-type behavior, indicating that the corrosion of the alloy is controlled mainly by a charge transfer process.

As can be seen from Table V, the inhibitor efficiency decreases with increasing temperature. Both techniques give values which are in good agreement. These results confirm that the compounds act as efficient corrosion inhibitors in the range of temperatures studied, particularly the inhibitor A for which the inhibition efficiency decreases after 323K.

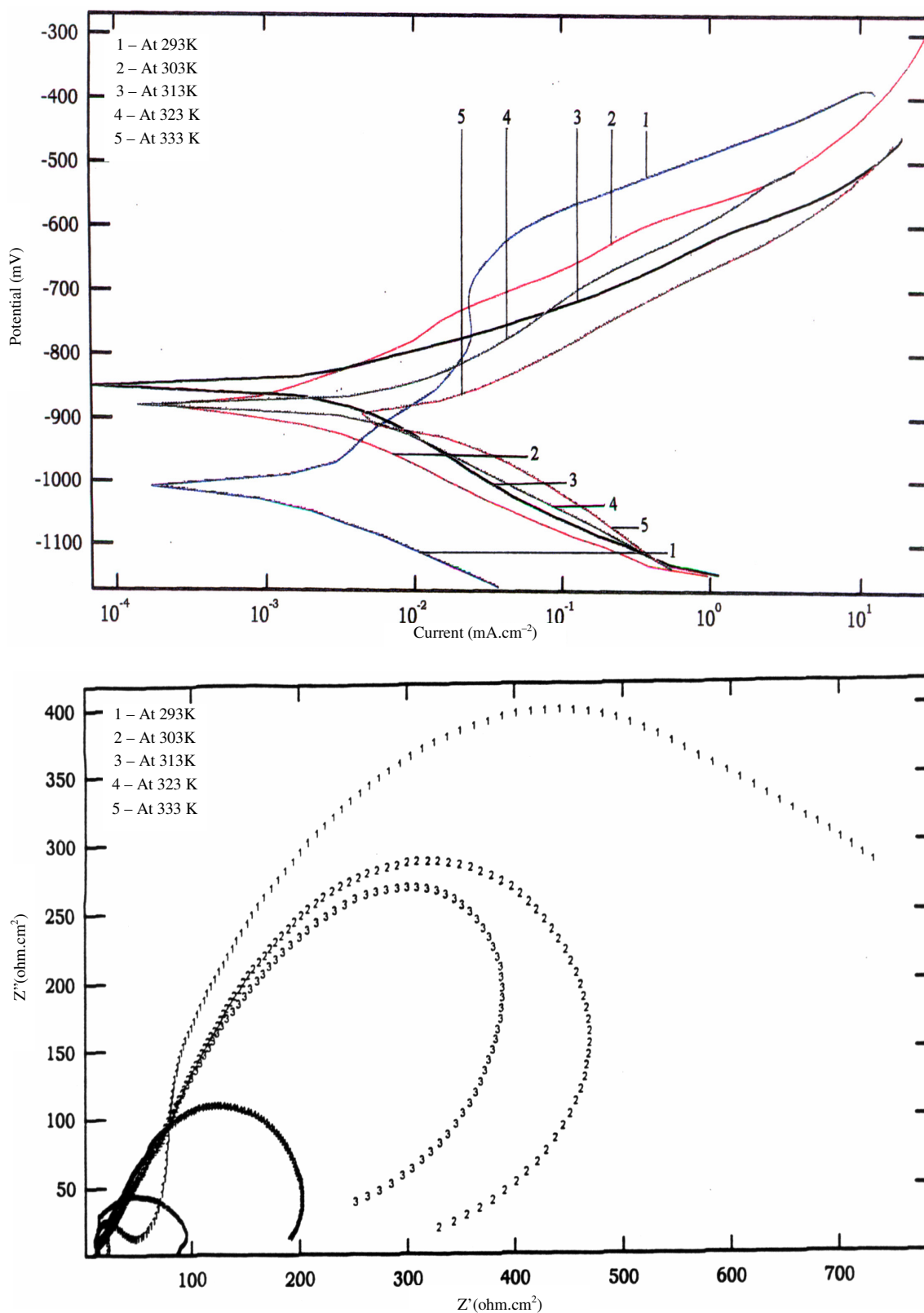


Fig. 7 (a) Polarization curves of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass in a $0.2\text{ M Na}_2\text{SO}_4$ solution containing 10% MeOH in the presence of 0.01 M Cl^- at different temperatures; and (b) Nyquist plots for the corrosion of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass in a $0.2\text{ M Na}_2\text{SO}_4$ solution containing 10% MeOH in the presence of 0.01 M Cl^- at different temperatures.

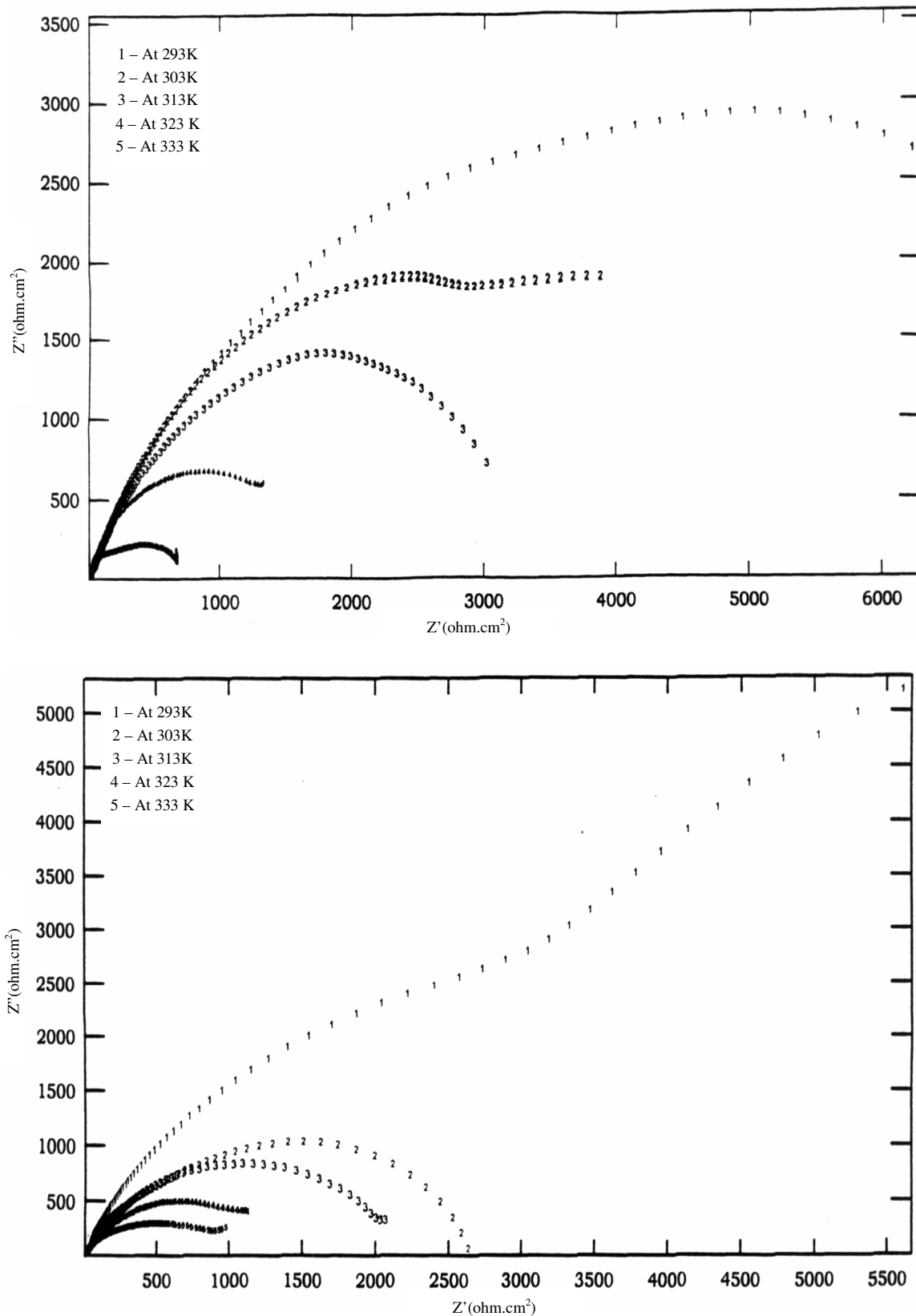


Fig. 8. Nyquist plots for the corrosion of $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$ metallic glass in a 0.2 M Na_2SO_4 solution containing 10% MeOH in the presence of 10^{-4}M of the inhibitors and 0.01 M Cl^- at different temperatures.

Table IV

Electrochemical polarization and impedance parameters, and percentage inhibition for the corrosion of Fe₇₈B₁₃Si₉ metallic glass in a 0.2 M Na₂SO₄ solution containing 10% MeOH in the presence of 0.01 M Cl⁻ and Br⁻ at different temperatures.

Temperature (K)	$-E_{corr}$ (V)	i_{corr} (mA.cm ⁻²)	$I.E.$ (%)	R_{ct} (Ω.cm ²)	C_{dl} (μF)	Inh. R_{ct} (%)	Inh. C_{dl} (%)
In Cl ⁻ Ions							
293	1.012	0.815	-21.64	837.4	41.02	-24.61	-25.99
303	0.881	1.179	-23.84	514.2	59.94	-24.80	-27.23
313	0.849	1.693	-35.22	383.8	82.48	-26.54	-29.76
323	0.868	2.017	-45.95	200.5	128.70	-82.29	-
333	0.892	3.290	-69.85	96.58	277.5	-	-
In Br ⁻ Ions							
293	0.921	0.289	56.87	2722	11.83	61.24	64.06
303	0.899	0.417	56.20	1530	17.61	57.24	63.34
313	0.832	0.602	51.92	881.9	29.58	43.53	54.62
323	0.866	0.940	31.98	554.2	47.99	20.39	32.03
333	0.877	1.467	24.26	402.3	74.84	19.79	28.86

Table V

Electrochemical polarization and impedance parameters, and percentage inhibition for the corrosion of Fe₇₈B₁₃Si₉ metallic glass in a 0.2 M Na₂SO₄ solution containing 10% MeOH in the presence of 10⁻⁴ M of the inhibitors and 0.01 M Cl⁻ at different temperatures.

Temperature (K)	$-E_{corr}$ (V)	i_{corr} (mA.cm ⁻²)	$I.E.$ (%)	R_{ct} (Ω.cm ²)	C_{dl} (μF)	Inh. R_{ct} (%)	Inh. C_{dl} (%)
Inhibitor A							
293	0.878	0.106	84.18	9258	02.66	88.60	91.92
303	0.917	0.152	84.03	5647	04.09	88.41	91.48
313	0.865	0.202	83.87	3584	07.85	86.10	87.96
323	0.811	0.252	81.77	1626	20.41	72.87	71.09
333	0.874	0.793	59.06	732.3	37.32	55.93	35.48
Inhibitor B							
293	0.878	0.135	79.85	5459	07.60	80.67	76.91
303	0.902	0.227	76.15	2699	12.66	75.76	73.64
313	0.909	0.302	75.88	2042	18.52	75.61	71.59
323	0.874	0.448	67.58	1437	20.10	69.30	71.53
333	0.879	0.636	67.17	1039	30.10	68.94	70.52

Comparing ΔE_{app} values shown in Table VI with the value of ΔE_{app} in blank solution or in solutions with only Cl⁻, it is seen that with the addition of Cl⁻ to the corrosive medium containing the inhibitors, the apparent activation energy ΔE_{app} increases. This can be interpreted as due to a physical or columbic type of adsorption. The higher value of ΔE_{app} in the presence of both 0.01 Cl⁻ and inhibitor A indicates an increase in the inhibition efficiency, while a

lower value of ΔE_{app} in the case of inhibitor B is due to a low inhibitive effect.

Values of ΔE_{app} and ΔH^* of the corrosion processes give a similar indication that no change has happened in the mechanism of corrosion [19]. Also, the corrosion system passes from a less random to an orderly arrangement, and hence a less negative entropy ΔS^* is observed.

Effect of temperature on corrosion at fixed concentrations of the inhibitors and Br⁻

Effect of temperature on polarization of Fe₇₈B₁₃Si₉ glassy alloy in a 0.2 M Na₂SO₄ solution containing 10% MeOH in the presence of 0.01 M Br⁻ and 10⁻⁴ M of thiosemicarbazones (A or B) indicates that the inhibitors act as mixed type inhibitors without changing the dissolution mechanism. A rise in temperature from 293 to 333K is associated by an increase in the corrosion current (*i_{corr}*). Desorption at the higher temperature may be responsible for the increase in the corrosion rate, since the surface alloy becomes less covered. Again, there is good

agreements between the results obtained with the two techniques (Table VII).

As can be noted in Table VIII, ΔE_{app} values are relatively higher than that obtained in the blank solution (20.30 kJ.mol⁻¹). This shows that the protection of the alloy in the presence of Br⁻ and the inhibitor include a physical adsorption by both on the alloy surface. As mentioned earlier, the nearly equal values of ΔE_{app} and ΔH^* means that no change on the corrosion mechanism occurs [19]. Moreover, the corrosion system seems to become more ordered in the presence of Br⁻ and inhibitors (A or B), as suggested by the value of entropy ΔS^* .

Table VI

Thermodynamic parameters for the corrosion of Fe₇₈B₁₃Si₉ metallic glass in a 0.2M Na₂SO₄ solution containing 10% MeOH in the absence and presence of 10⁻⁴ M of the inhibitors and in the presence of 0.01 M of Cl⁻ (from polarization and impedance measurements).

Symbol	Polarization measurements			Impedance measurements		
	ΔE_{app} (kJ.mol ⁻¹)	ΔH^* (kJ.mol ⁻¹)	ΔS^* (J.mol ⁻¹ .K ⁻¹)	ΔE_{app} (kJ.mol ⁻¹)	ΔH^* (kJ.mol ⁻¹)	ΔS^* (J.mol ⁻¹ .K ⁻¹)
No Inh.	19.91	24.61	-163.30	-	39.83	-165.60
A	36.38	33.70	-149.38	50.93	48.44	-156.79
B	30.25	27.76	-166.56	32.17	29.68	-176.13

Table VII

Electrochemical polarization and impedance parameters, and percentage inhibition for the corrosion of Fe₇₈B₁₃Si₉ metallic glass in a 0.2 M Na₂SO₄ solution containing 10% MeOH in the presence of 10⁻⁴ M of the inhibitors and in the presence of 0.01 M Br⁻ at different temperatures.

Temperature (K)	$-E_{corr}$ (V)	i_{corr} (mA.cm ⁻²)	<i>I.E.</i> (%)	<i>R_{ct}</i> (Ω .cm ²)	<i>C_{dl}</i> (μ F)	Inh. <i>R_{ct}</i> (%)	Inh. <i>C_{dl}</i> (%)
Inhibitor A							
293	0.889	0.192	71.34	4545	10.56	76.79	67.92
303	0.874	0.293	69.22	2617	15.93	75.09	66.83
313	0.877	0.432	65.50	1989	21.74	74.96	66.65
323	0.878	0.489	64.62	1429	24.66	69.13	65.07
333	0.879	0.759	60.82	836.0	38.20	61.40	63.69
Inhibitor B							
293	0.914	0.109	83.73	7276	04.23	85.50	87.15
303	0.922	0.158	83.40	4466	07.64	85.35	84.09
313	0.904	0.287	77.08	2018	12.93	75.32	80.16
323	0.881	0.390	71.78	1505	17.33	70.68	75.45
333	0.898	0.729	62.36	725.4	38.95	55.51	62.98

Table VIII

Thermodynamic parameters for the corrosion of Fe₇₈B₁₃Si₉ metallic glass in a 0.2M Na₂SO₄ solution containing 10% MeOH in the absence and presence of 10⁻⁴ M of the inhibitors and in the presence of 0.01 M of Br⁻ (from polarization and impedance measurements).

Symbol	Polarization measurements			Impedance measurements		
	ΔE_{app} (kJ.mol ⁻¹)	ΔH^* (kJ.mol ⁻¹)	ΔS^* (J.mol ⁻¹ .K ⁻¹)	ΔE_{app} (kJ.mol ⁻¹)	ΔH^* (kJ.mol ⁻¹)	ΔS^* (J.mol ⁻¹ .K ⁻¹)
No Inh.	32.93	30.25	-152.20	39.25	36.76	-184.56
A	26.50	23.93	-176.71	32.36	29.68	-213.03
B	38.10	35.42	-142.63	46.14	43.46	-170.20

Conclusions

It can be concluded that:

- The corrosion rate of Fe₇₈B₁₃Si₉ metallic glass in 0.2 M Na₂SO₄ is directly proportional to an increase in temperature.
- The compounds, 4-methyl acetophenone thiosemicarbazone and 4-methoxy acetophenone thiosemicarbazone, inhibit the corrosion of the metallic glass by adsorption on the amorphous surface, although a better performance is observed with 4-methoxy acetophenone thiosemicarbazone.
- The negative sign for inhibition in the presence of Cl⁻ indicates an acceleration effect of this ion, which increases with rise in temperature from 293 to 333K. The opposite behavior is observed with the Br⁻ ion.
- Halide ions in the corrosive medium containing acetophenone thiosemicarbazone compounds inhibit the corrosion of iron-based glassy alloy.
- On the basis of the heat of adsorption, activation energy and the experimentally observed increase in inhibition at low temperatures, a physisorption process is proposed for both the acetophenone thiosemicarbazone compounds and halide ions under the conditions of the experiments.

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