Inhibition of Acid Corrosion of Steel by Some S-Alkylisothiouronium Iodides*

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ABSTRACT

Five selected S-alkylisothisothiouronium iodides have been studied as acid corrosion inhibitors at 30°C for steel in 0.5 M H_2SO_4 using gasometry, mass loss, and direct current (DC) polarization techniques. All of the data reveal that the compounds act as inhibitors in the acid environments; furthermore, polarization curves show that the compounds act as mixed-type inhibitors. It was found that the inhibition efficiency increases with the increase of the length of the additive alkyl chain. Langmuir's adsorption isotherms fit the experimental data for the studied compounds. Thermodynamic parameters were obtained from experimental data of the temperature studies of the inhibition process at five temperatures ranging from 30 to 70°C. It was observed that the activation energy is slightly increased with the increase of the additive alkyl chain. On the other hand, the sudden large increase of the inhibition behavior of S-hexylisothiouronium iodide was attributed to a different adsorption process.

KEY WORDS: acid inhibitors, inhibitors, steel

INTRODUCTION

Since aggressive acid solutions are widely used for industrial purposes, inhibitors are commonly used to reduce the corrosive attack on metallic materials.

The inhibition of steel corrosion by acids was previously studied by some sulfur- and/or nitrogen-containing compounds.[1-8]

Thiourea has been described as an inhibitor and as an accelerator of the corrosion of iron and steel in acidic solutions,[9-12] while the presence of most of its derivatives brings an appreciable inhibition.[13-18] The inhibition efficiency of those compounds was related to the properties of the polar groups and the size of the N-substituted groups.

Thiourea additives have not been investigated as corrosion inhibitors. Accordingly, this work deals with the study of the corrosion inhibition properties of a number of S-alkylisothiouronium iodides that have the general formula

where R is methyl, ethyl, n-butyl, n-pentyl, or n-hexyl. The goals of this study were to determine the efficiency of the studied compounds as inhibitors for the corrosion of steel in 0.5 M H_2SO_4 and to study the effect of chain length in these compounds on their inhibition mechanism and efficiency.

EXPERIMENTAL

Material and Specimen Preparations

The experiments were performed with steel specimen with the following composition: 99.3% Fe, 0.210% C, 0.039% Ni, 0.370% Mn, 0.020% P, 0.030% S, 0.017% Cu, 0.005% Cr, and 0.011% Mo.

Prior to each experiment, the specimen was polished with a series of emery paper of variable

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grades, starting with a coarse one and proceeding in steps to the finest grade available. Then, the specimen was washed several times with deionized water then with acetone and dried using a stream of air.

The influence of the inhibitors on the dissolution process of the specimen in 0.5 M H_2SO_4 was monitored chemically and electrochemically.

The vessel used in the chemical method is similar to that described by Mylius.[19] The specimen used was in the form of 5-cm rod with a surface area of 17.28 cm^2.

For the polarization study, a standard corrosion cell with a working steel electrode of cross section 0.5 cm was used.

Test Solutions

Solutions of 0.5 M H_2SO_4 were used as the corrosive medium. The S-alkylisothiouronium iodides, which are ionic in character,[20-22] were prepared, purified, analyzed, and kept as described elsewhere.[20-23]

In all of the preparations, reagent-grade chemicals and freshly deionized water were used.

Deaeration in the electrochemical measurement was achieved by bubbling purified nitrogen into the solution for 30 min before each polarization study.

Corrosion Rate Determination

Rates of dissolution were determined during natural immersion by gasometry and mass loss methods described elsewhere.[8] In electrochemical measurements, potentiodynamic polarization curves were produced using a potentiostat. A saturated Ag/AgCl electrode was used as a reference electrode (E° = 0.1989 V on hydrogen scale). All experiments were thermostated at 30°C ± 0.1.

In addition, gasometry and mass loss measurements were undertaken at different fixed temperatures, 30, 40, 50, 60, and 70°C, in absence and presence of 5 x 10^{-2} M of S-methyl, 3 x 10^{-2} M of S-ethyl, 1.5 x 10^{-2} M of S-n-butyl and S-n-pentyl, and finally 3 x 10^{-3} M of S-n-hexyl isothiouronium iodides. These compounds will be given the symbols A, B, C, D, and E, respectively.

The chosen concentrations of the studied compounds (from both hydrogen evolution and mass loss data) gave an inhibition percent (assumed to equal a surface coverage) of 80 to 85% at 30°C. This will allow a good comparison between the compounds used.

RESULTS AND DISCUSSION

Figure 1 represents the variation in the volume of the hydrogen evolved as a function of time when the steel test pieces were allowed to react with 0.5 M H_2SO_4 in the presence of different concentrations of compound C (0.0 – 3.5 x 10^{-2} M).

It is clear that upon increasing the concentration of compound C in the solution, the rate of hydrogen evolution (the slope of the plot) decreased. This indicates that the presence of compound C in the solution retarded the corrosion of steel by H_2SO_4 and that the extent of corrosion inhibition depends on the amount of compound C present.

The other compounds studied exhibited a similar behavior, and the inhibition efficiencies (inh.%) of the compounds were calculated by applying the following relationship.[24]

$$\text{inh.\%} = 100\ (1 - R/R_o) \qquad (1)$$

where R_o and R are respectively the steady-state corrosion rates in absence and presence of a given corrosion inhibitor.

In Figure 2, the plots of the inh.% vs the logarithmic concentration of compounds A, C, D, and E are illustrated. All of the plots have S-shaped adsorption isotherm. This suggests, but does not prove, that these compounds inhibit the acid dissolution of steel by adsorption at the steel acid solution interface. The plots also show good agreement between gasometry and mass loss results. Inspection of this figure shows that compound E has the highest inhibition efficiency, while compound A has the lowest one. This clearly indicates that the increase of the length of the hydrocarbon chain increases the inhibition of the compound.

S-alkylisothiouronium iodides offer

as a more possible adsorption center since alkyl group addition on c = s has effectively decreased the electron density on the other expected center c – s. Accordingly, the obtained results can be attributed to the following:

—The increase in the length of the hydrocarbon chain causes an increase in the bulk of the groups attached to the adsorption center

and inhibits the acid dissolution process by screening the surface from acid attack.

—The alkyl groups are electron-releasing groups. This property increases with the increase of the length

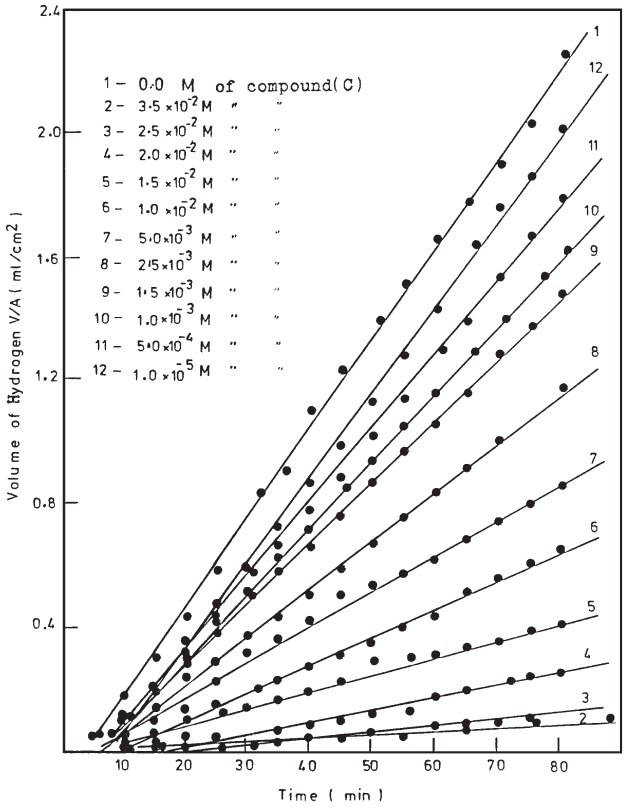

FIGURE 1. *Effect of S-n-butylisothiouronium iodide on the corrosion rate of steel in 0.5 M H_2SO_4.*

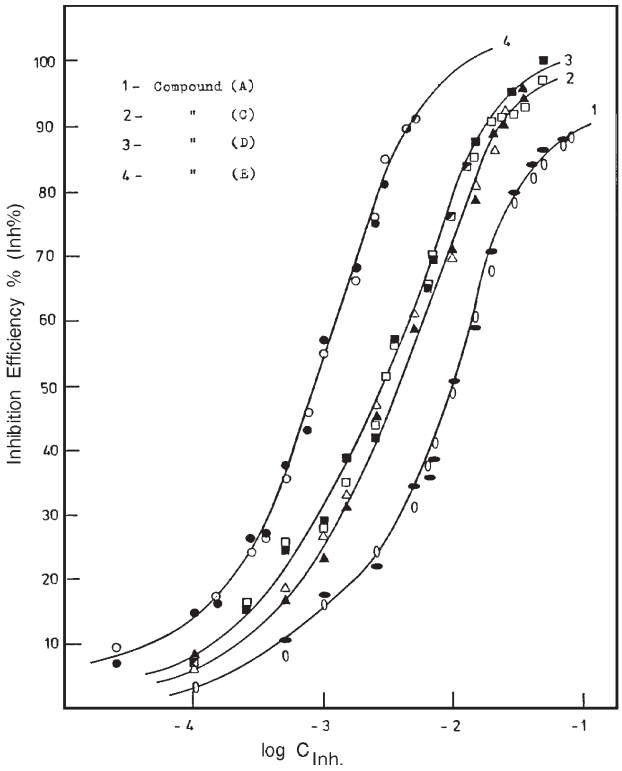

FIGURE 2. *Variation of the inhibition efficiency with the logarithm of the concentration of the S-alkylisothiouronium iodides. Inhibition from mass loss data are the black ones, while the corresponding plane ones are from hydrogen evolution data.*

of the hydrocarbon chain. Compound E has the highest electron-releasing characteristics, leading to an increase in the electron density of the adsorption center, a corresponding increase in the metal-ligand binding constant, and greater adsorption and inhibition efficiency. Thus, for the studied compounds, the following order for inhibition efficiency was obtained E > C > B > A, which is in good agreement with previous studies.[25-30]

Figure 3 shows that the inhibition efficiency of the compounds increases linearly with the increase in the number of methylene groups in the S-alkyliso-thiouronium molecule with the exception of compound E, which shows abnormal sudden increase in the inhibition efficiency. This may be attributed to the existence of two different modes of adsorption of the inhibitors. In compounds A, B, C, and D, the molecule is adsorbed to the steel surface through one amino group, while in case of compound E, the molecule may be adsorbed through both amino groups. This latter configuration gives improved inhibition by virtue of multiple bonding.

The same basis was used to explain the effect of α, w-polymethylene diamines $NH_2 – (CH_2)_n NH_2$ (n = 2 – 12) on the iron corrosion on 6.0 M HCl. It was found that the double-layer capacitance was approximately constant at 21 μF/cm² for the C_2 through C_8 diamines and alternated between 6 and 14 μF/cm² for the C_9 through C_{12} diamines. The constancy at 21 μF/cm² suggested that diamines with up to eight carbon atoms were adsorbed in the same configuration, probably the flat position. The subsequent reduction and alternation in capacitance was believed to be caused by a structuring of the adsorbate similar to that in the bulk where certain physical properties oscillate with carbon number.[31]

Based on the obtained data, it is assumed that the inhibition of the steel corrosion in 0.5 M H_2SO_4 by the inhibitors occurs by adsorption at the appropriate sites on the electrode surface. There is a correlation between the effectiveness of the inhibitor or the surface coverage (θ) or inh.% obtained from the gasometry and mass loss methods and the extent of the inhibitor concentration in the bulk solution c.

For the studied inhibitors, it was found that the experimental data fits Langmuir's adsorption isotherm, which is given by:[32]

$$\frac{\theta}{1-\theta} = K\,c \qquad (2)$$

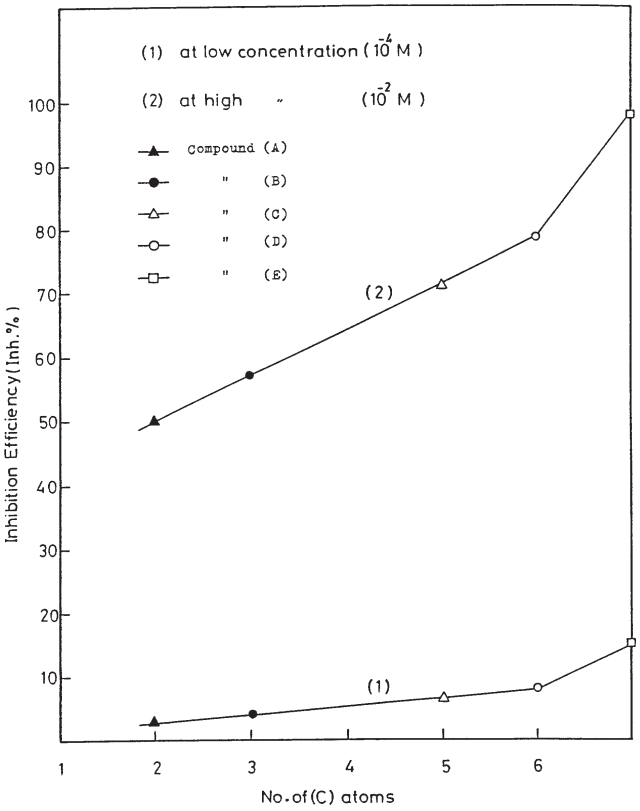

FIGURE 3. *Relation between the number of the carbon atoms in the studied compounds and the inhibition efficiency. (1) At low concentration (C = 10^{-4} M) and (2) at high concentration (C = 10^{-2}).*

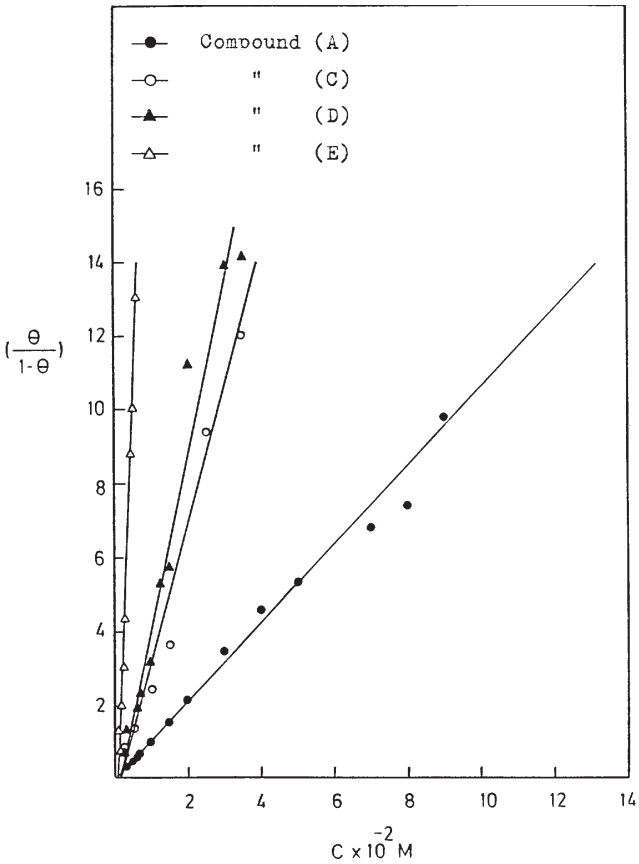

FIGURE 4. *Fitting Langmuir's adsorption isotherm for the studied compounds in 0.5 M H_2SO_4.*

where K is the equilibrium constant of the adsorption process. Figure 4 represents the Langmuir adsorption plot for the compounds. The data gave straight lines passing through the origin with a slope of K. The constant value K is related to the standard free energy of adsorption ΔG°_{ads} by:

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G^\circ_{ads}}{R\,T}\right) \qquad (3)$$

where 55.5 is the concentration of water in the solution in mol/L.

In Table 1, the thermodynamic data obtained from the adsorption isotherms are listed. It was found that the calculated standard free energies of adsorption vary from –22.0 kJ/mol for compound A to –29.89 kJ/mol for compound E, which is the strongest inhibitor of the compounds. It also appears from Table 1 that the magnitude of K is the determining factor for the inhibition efficiency. Accordingly, the order of increase in the efficiency of the studied compounds is given as: A < C < D < E. This supports the fact that the inhibition of a series of compounds increases with the increase of the chain length. This result is in agreement with previous studies of inhibition by some sulfur- and/or nitrogen-containing compounds.[5-7,25-30]

TABLE 1
Thermodynamic Data for Studied Compounds from Experimental Adsorption Isotherms

Compound	K (M^{-1})	ΔG°_{ads} (kJ mol^{-1})
A	111.67	–22.00
C	255.00	–24.08
D	480.00	–25.67
E	2566.70	–29.89

Polarization Behavior

An example of the anodic and cathodic potentiodynamic polarization curves for steel in 0.5 M H_2SO_4 alone and those containing different concentrations of compound B is represented in Figure 5. The curves show that the inhibitor causes anodic and cathodic overpotential and that the magnitude of the displacement of the Tafel plots is proportional to its concentration. This result indicates that compound B affects both the anodic and cathodic processes. Similarly, in all of the studied cases, the

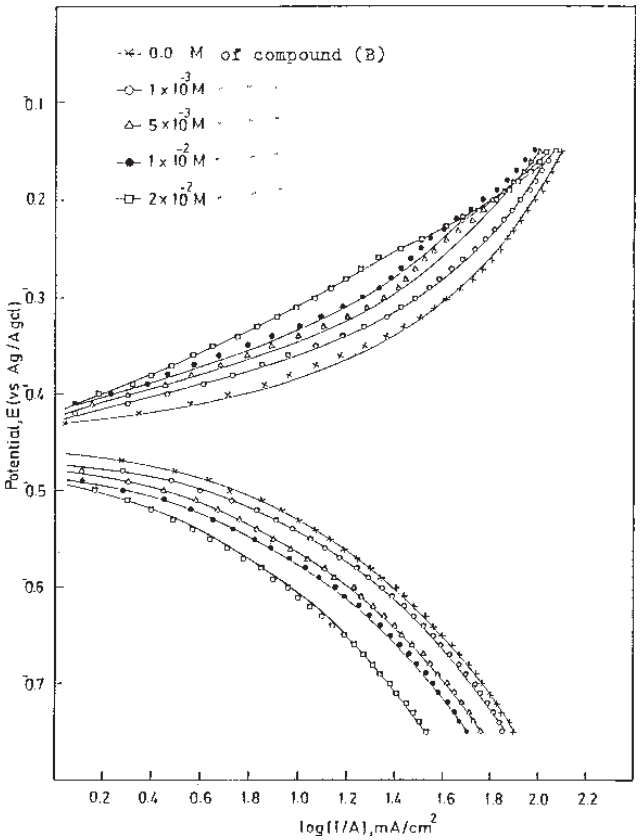

FIGURE 5. *Polarization curves of steel in 0.5 M H_2SO_4 with different concentration of compound B.*

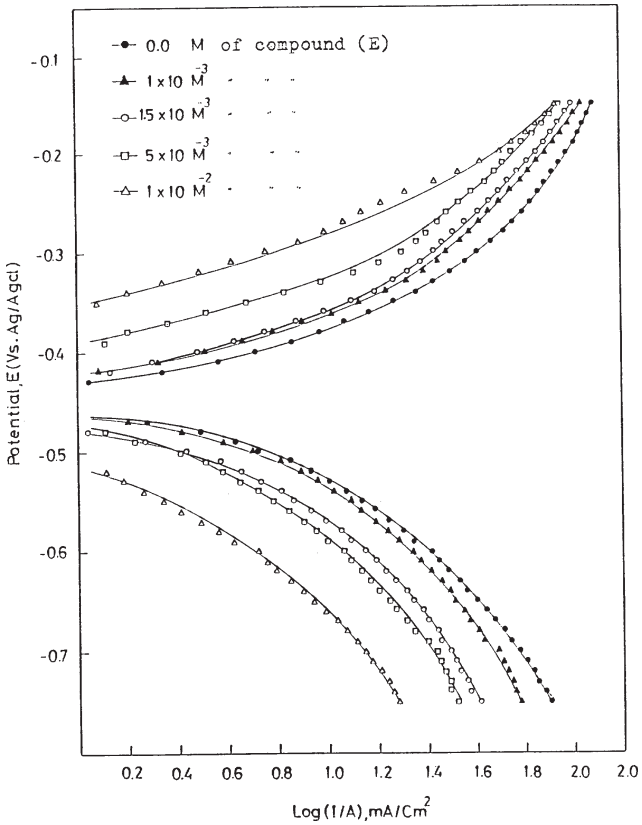

FIGURE 6. *Polarization curves of steel in 0.5 M H_2SO_4 with different concentrations of compound E.*

addition of the inhibitors induced the same behavior. With higher concentrations of compounds D and E, a larger decrease in the cathodic currents than the expected one can be observed in Figure 6.

The coadsorption of Br ion was stimulated by the adsorption of the positively charged n-alkylquaternary ammonium ions on the metal surface, and this effect increases with the length of alkyl chain.[29,30] Accordingly, the observed behavior of S-n-pentyl and S-n-hexylisothiouronium iodides is probably due to coadsorption of iodide ions.

To elucidate the influence of the change of the chain length of the studied compounds on the inhibition efficiency, the potentiodynamic polarization curves for 5 x 10^{-3} M of the inhibitors concentrations are illustrated in Figure 7. The curves show that the order of the decrease of the inhibition efficiency with respect to the change in chain length of the compounds is given as compound E > D > C > B > A. This order is the same as that obtained from gasometry and mass loss methods.

The electrochemical parameters of the steel in 0.5 M H_2SO_4 in the absence and in the presence of 5 x 10^{-3} M of the inhibitors are given in Table 2. The data show that the slopes of the anodic and cathodic Tafel lines (βa and βc) remain almost unchanged upon increasing the chain length. This behavior indicates that the first adsorbed ions of the inhibitors are attached to the most active anodic sites, usually considered to be the corners or edges of incomplete layers of atoms on the metal surface. This would interfere with the anodic reaction by hindering the escape of Fe^{+2} ions from the metal surface into the solution, and the attack on the metal would then proceed at a reduced rate from less active anodic sites. Upon increasing concentration, more ions would be adsorbed due to Van der Waals forces between the inhibitor molecules. The increasingly close-packed film thus built up would further inhibit the anodic reaction, both by steric hindrance to the escape of Fe^{+2} ions and also because of the adverse electric field from the positively charged layer of the adsorbed ions. At this stage, there is some inhibition of the cathodic reaction (Figure 6) probably due to steric hindrance of the combination of the adsorbed hydrogen atoms to form molecules. A similar mechanism was suggested for the inhibition of steel in acidic medium by 4-amino, 3-substituted, 5-mercapto

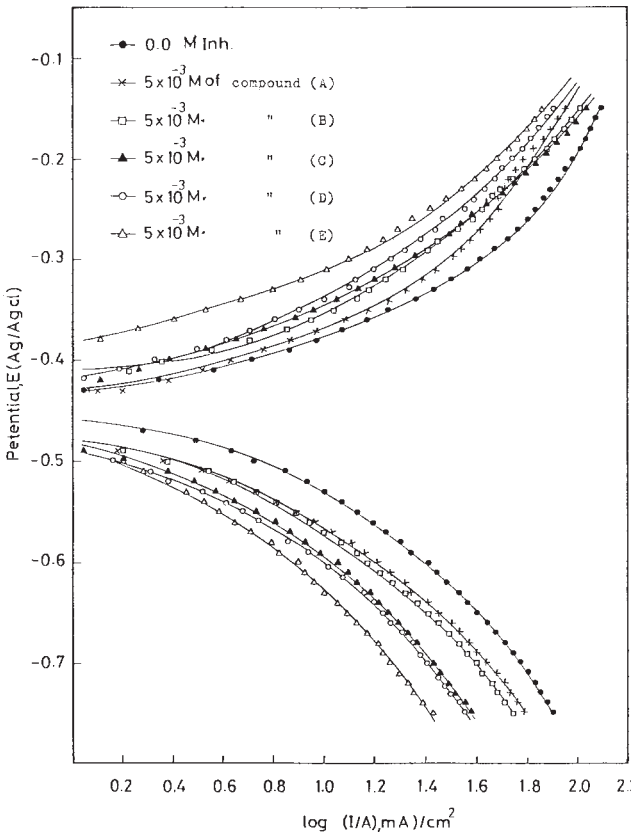

FIGURE 7. *Polarization curves of steel in 0.5 M H_2SO_4 in the absence and in the presence of 5 x 10^{-3} M of S-alkylisothiouronium iodides.*

TABLE 2

Anodic (βa) and Cathodic (βc) Tafel Constants for Steel in 0.5 M H_2SO_4 in the Absence and in the Presence of 5 x 10^{-3} M of the Compounds

Compound	βa	βc
0.0 Inh.	0.11	–0.14
5 x 10^{-3} M (A)	0.11	–0.15
5 x 10^{-3} M (B)	0.12	–0.15
5 x 10^{-3} M (C)	0.12	–0.17
5 x 10^{-3} M (D)	0.14	–0.16
5 x 10^{-3} M (E)	0.11	–0.19

1,2,4-triazoline and some related compound,[6] and also with n-alkylquaternary ammonium compounds.[29,30]

Effect of Temperature on Inhibition Characteristics of S-Alkylisothiouronium Iodides

The corrosion rates of steel in 0.5 M H_2SO_4 solution in the absence and in the presence of the inhibitors used in this work increase rapidly with the increase of temperature. In Figure 8, the variation in the volume of the hydrogen evolved as a function of time when the steel test pieces were allowed to react with 0.5 M H_2SO_4 in the presence of 3 x 10^{-3} of compound E at the different temperatures. It is clear that the corrosion rates of steel increased rapidly with the rise of temperature.

It has been pointed out by a number of authors[33] that for steel corrosion in acid solutions, the logarithm of the corrosion rate (R') is a linear function with $1/_T$ (Arrhenius equation):

$$\text{Ln } R' = -E_a/RT + A \qquad (4)$$

where E_a is the apparent effective activation energy, R is the ideal gas constant, and A is Arrhenius pre-exponential factor.

Figure 9 gives least square plots of log R' vs $1/_T$ data for the corrosion of steel in the absence and in the presence of five studied inhibitors. The values of the activation energy obtained from the slope of the lines are given in Table 3. The activation energy value for the corrosion of steel in free acid solution obtained (12.20 K cal/mol) is in agreement with that obtained elsewhere.[34-36]

It is obvious that the effective activation energy of the inhibited solutions in this study is little higher than that in the free acid solution. It is also increased by about 0.64 K cal/mol for each added (CH_2) group with the exception of compound E. This proves the previous suggestion from the chemical study that in compounds A, B, C, and D, the molecules are adsorbed to the surface of the metal in the same way[27,32] (through one amino group), while the adsorption of the molecule in compound E is different (the activation energy was lower than expected). This may be attributed to the adsorption of the molecule by both amino groups.

An alternative formulation of the Arrhenius equation is the transition state equation:

$$R' = RT/Nh \exp(\Delta S^{\#}/R) \exp \frac{-\Delta H^{\#}}{RT} \qquad (5)$$

where h is Plank's constant, N is Avogadro's number, $\Delta S^{\#}$ is the entropy of activation, and $\Delta H^{\#}$ is the enthalpy of activation.

A plot of

$$\log \frac{R}{T} \text{ vs } \frac{1}{T}$$

should give a straight line with a slope of

$$\frac{-\Delta H^{\#}}{2.303}$$

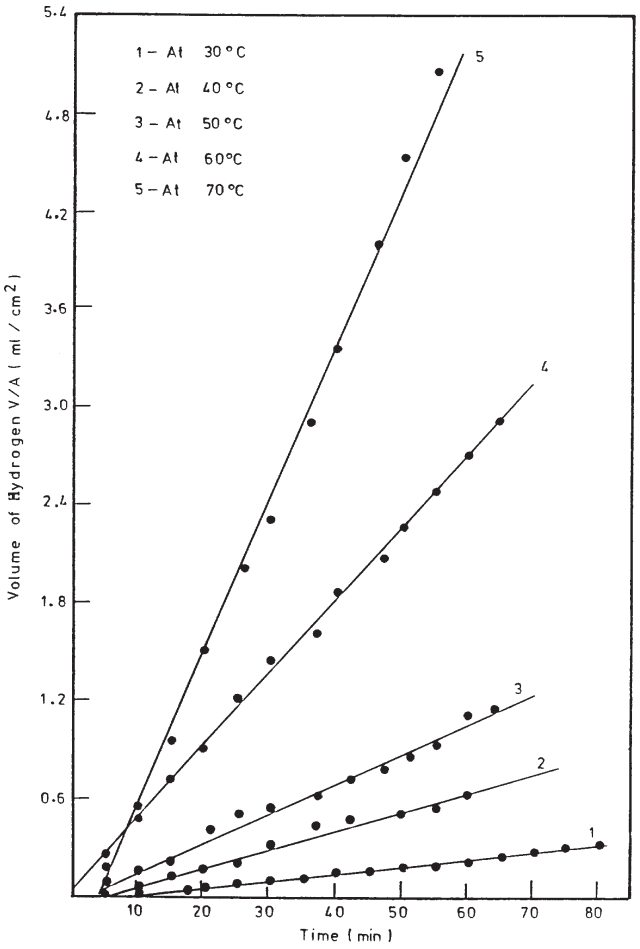

FIGURE 8. *Effect of temperatures on the corrosion rate of steel in 0.5 M H_2SO_4 + 3 x 10^{-3} M of compound E.*

TABLE 3
Activation Parameters of the Dissolution Reaction of Steel in 0.5 M Sulfuric Acid in the Absence and in the Presence of the Compounds

	E (K cal/mol)	ΔH# (KH/mol)	ΔS# (J/mol)
0.5 M H_2SO_4	12.203	47.87	–272.25
5 x 10^{-2} M of A	15.254	57.44	–277.04
2.5 x 10^{-2} M of B	16.016	57.44	–269.38
1.5 x 10^{-2} M of C	17.542	57.44	–271.29
1.5 x 10^{-2} M of D	18.304	57.44	–269.38
5 x 10^{-3} M of E	15.254	57.44	–266.51

and an intercept of

$$\left(\log \frac{R}{Nh} + \frac{-\Delta S^{\#}}{2.303\ R}\right)$$

from which the values of $\Delta H^{\#}$ and $\Delta S^{\#}$ are calculated (Table 3). The data show that the activation parameters (E, $\Delta H^{\#}$, $\Delta S^{\#}$) of the dissolution of steel in 0.5 M H_2SO_4 in the presence of the five studied inhibitors increase slightly more than those of the uninhibited solution, which means that no energy barrier for the reaction in the presence of the inhibitor is attained. These results, together with the information obtained from polarization curves, indicate that the retardation of the reactions (metal dissolution and the hydrogen evolution) are being affected without changing the mechanism.

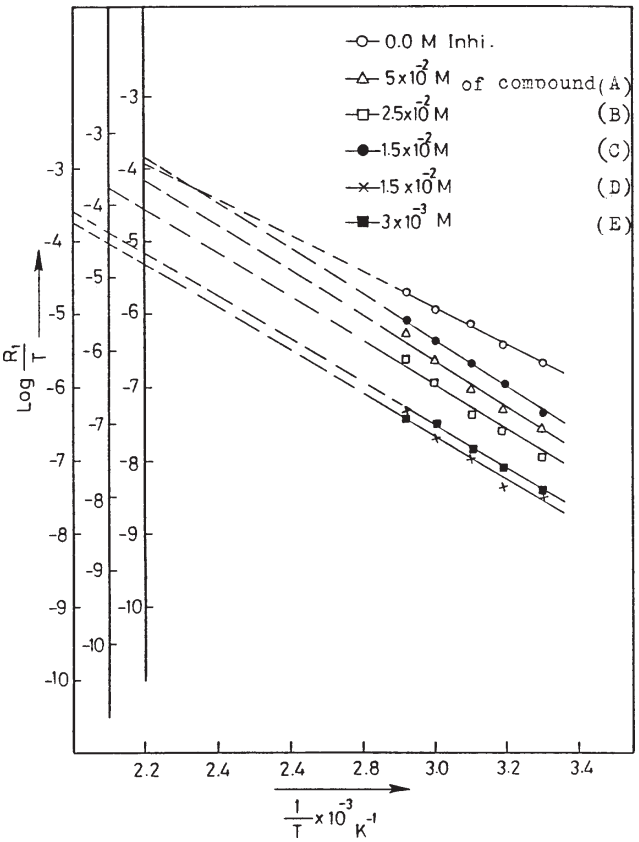

FIGURE 9. *Arrhenius plots of log R' vs # $1/_T$ for the dissolution of steel in 0.5 M H_2SO_4 in the absence and in the presence of the studied compounds.*

SUMMARY

S-alkylisothiouronium iodides were good inhibitors. The inhibition efficiency increased with the increase of inhibitor concentration and chain length. These inhibitors act as mixed-type inhibitors. They can also be used as efficient inhibitors under 50°C.

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