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Corrosion Inhibition and Adsorption Behavior of Some Thioamides on Mild Steel in Sulfuric Acid

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The objective of this work was to evalulate the effect of changing functional and structural groups on the protection efficiency imparted by the various inhibitor molecules. It was found that the molecules which include a thiocarbonyl group *e.g.* thiourea (TU), thioacetamide (TA), and thiosemicarbazide (TSC) exhibited much higher protection efficiencies than the corresponding compounds which do not *e.g.* semicarbazide, guanidine, and aminoguanidine. Furthermore, it made only little difference whether the thiocarbonyl group was attached to two amino groups as in thiourea, an amino and a methyl group as in thioacetamide or an amino and a methyl group as in thioacetamide above certain concentrations both TU and TA lose their efficiency and eventually become corrosion promotors. The adsorption behavior of TU and TA was quist complicated whereas that of TSC points towards complete coverage at high concentrations. The differences in behaviour between TSC, TU, and TA have been explained on the basis of delocalization or resonance stabilization energy.

The use of organic compounds as inhibitors for the aqueous corrosion of metals dates back several hundred years. A large number of such compounds has been developed to suit various applications. The diversity of these compounds and their applications, as well as the sheer volume of the pertinent literature, are quite evident in a classical review in the corrosion handbook[1)] which was published in 1947.

This area is still attracting considerable attention in efforts to obtain more efficient inhibitors and to further the understanding of the mechanisms involved in the corrosion and inhibition processes. The work published in the last thirty years is quite extensive and is directed more towards understanding the effect of inhibitors on the kinetics of the half-cell reactions. Some of this work has already been reviewed.[2–4)]

The relationship between the structure of the inhibitor molecule and its efficiency has been the subject of several investigations.[5–16)] On the other hand, much less attention has been paid to the dependence of the protection efficiency on the size and the electronic distribution in the inhibitor molecule. This is an important question especially for sulfur-containing compounds *e. g.* thioamides (–CS–NH_2), many of which have been found to be good inhibitors. In this connection, several questions may be asked, for example; what is the effect on the protection efficiency of replacing the amino group of thiourea by a methyl group ? or upon replacing the thiocarbamoyl group $>C=S$ by either a carbonyl or carbonimidoyl group $>C=NH$? What is the effect of the above changes on the degree of surface converage and the mechanism of adsorption? The objective of this work is to answer some of the above questions by experimental measurements.

Experimental

The system chosen for this study is the acid corrosion of mild steel. Several organic compounds have been chosen for the purpose of this work. Table 1 lists these compounds. The main criterion for their selection was to provide a number of variables *e. g.* effect of a $>C=S$ as against $>C=NH$ or $>C=O$ substitution of an –NH_2 by a –CH_3 group or by the hydra zino group –NH·NH_2.

Table 1. Molecular structures and abbreviations of the inhibitors used

Compound	Abbreviation	Molecular formula
Thiourea	TU	$H_2\ddot{N}-\overset{S}{\overset{\|}{C}}-\ddot{N}H_2$
Thioacetamide	TA	$CH_3-\overset{S}{\overset{\|}{C}}-\ddot{N}H_2$
Thiosemiearbazide	TSC	$\ddot{N}H_2-\ddot{N}H-\overset{S}{\overset{\|}{C}}-\ddot{N}H_2$
Semicarbazide	SC	$\ddot{N}H_2-\ddot{N}H-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$
Urea	U	$H_2\ddot{N}-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$
Guanidine	G	$H_2\ddot{N}-\overset{\ddot{N}H}{\overset{\|}{C}}-\ddot{N}H_2$
Aminoguanidine	AG	$H_2\ddot{N}-\ddot{N}H-\overset{\ddot{N}H}{\overset{\|}{C}}-\ddot{N}H_2$

The experimental approach taken here was to evaluate the effect of the inhibitors on the overall corrosion rate, and on the rate of the hydrogen evolution reaction (h.e.r.) at different inhibitor concentrations. This was done using the steady state galvanostatic technique. From these results, the protection efficiency of the inhibitor and the degree of coverage of the metal surface was calculated. Details of the experimental procedure, cell design, electrode preparation, pre-electrolysis....*etc.* were given elsewhere.[17)] The composition of the mild steel electrode was 0.08% C, 0.44% Mn, and trace amounts of both S and P. The temperature was adjusted to 30±0.1 °C using an air thermostat. The electrolyte was 1.0 mol dm^{-3} H_2SO_4. The compounds used as inhibitors were of the highest purity available.

Results and Discussion

Effect of Inhibitor Concentration. Figures 1a, 1b, and 1c show the effect of the concentrations of TSC,

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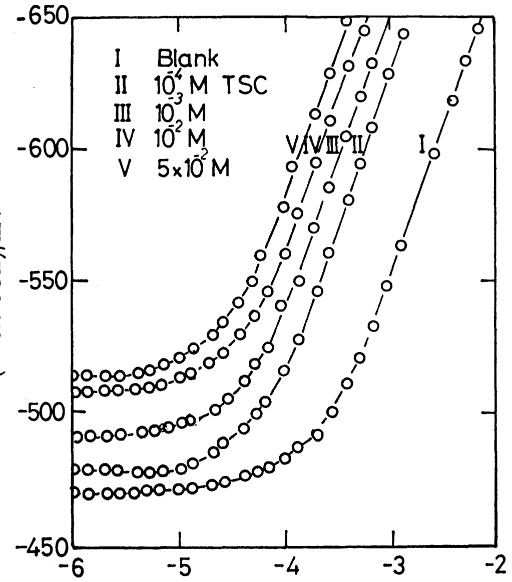


Fig. 1a. Effect of the concentration of thiosemicarbazide on the cathodic polarization curves of mild steel in 10 mol dm^{-3} H_2SO_4 at 30 °C.

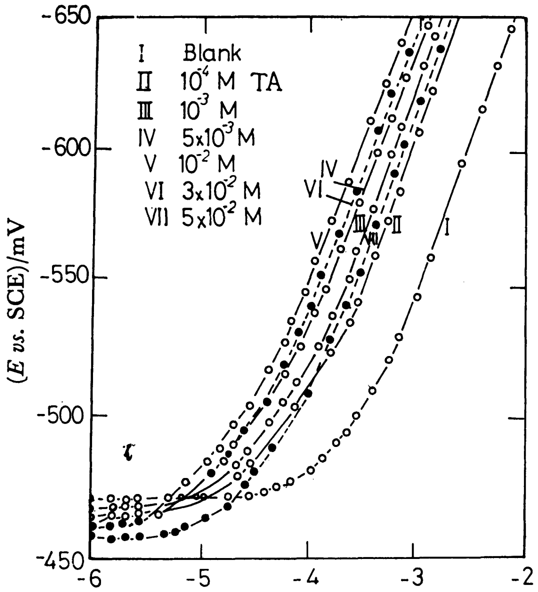


Fig. 1c. Effect of the concentration of thioacetamide on the cathodic polarization curves of mild steel in 1.0 mol dm^{-3} H_2SO_4 at 30 °C.

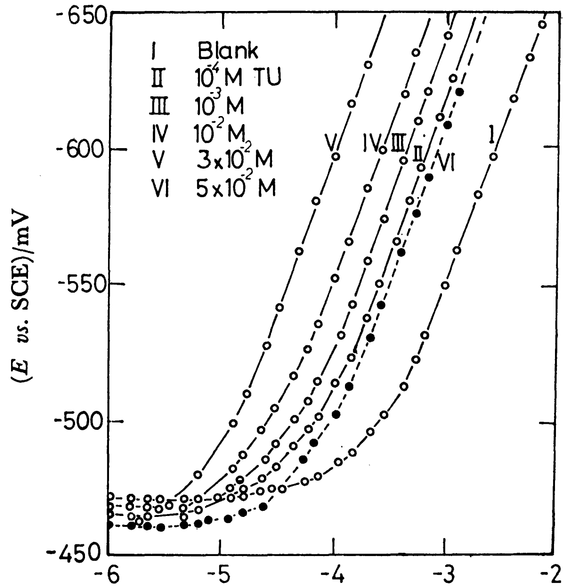


Fig. 1b. Effect of the concentration of thiourea on the cathodic polarization curves of mild steel in 1.0 mol dm^{-3} H_2SO_4 at 30 °C.

TU, and TA on the current-potential relations of hydrogen evolution on mild steel in 1.0 mol dm^{-3} H_2SO_4 at 30 °C. Clearly the concentrations of TSC, TU, and TA have a strong effect on the current-potential relations. Thus as their concentrations increase, it is seen that:

1) In case of TSC, the electrode potential at low current densities and the corrosion potential were shifted in the cathodic direction by about 10 to 40 mV, while in the cases of both TU and TA, the shifts were smaller in magnitude and in the anodic direction.

2) They caused large bodily shifts of the Tafel lines in the cathodic direction. In the case of TSC, the Tafel lines were shifted by 70 to 140 mV depending on the TSC concentration over the entire range. In the case of TU and TA, the magnitude of this shift also depended on their concentrations, only up to a critical value above which TU and TA became much less efficient (see below).

3) The Tafel slopes were approximately constant independent of inhibitor concentration.

The above two effects (2 and 3) indicate that TSC, TU, and TA have significant inhibiting effects on the hydrogen evolution reaction. From the Tafel slope, the transfer coefficient of the hydrogen evolution reaction is calculated to be $\beta=0.51$ which agrees with the generally accepted values.[18,19] The constancy of the cathodic transfer coefficient β in the presence and in the absence of the inhibitors indicates that their adsorption in the double layer does not change the mechanism of the hydrogen evolution reaction even though they significantly reduce its rate. This suggests that these inhibitors operate *via* a blocking adsorption mechanism.

It is recognized that the inhibitors which shift the entire current-potential curves in the cathodic direction are cathodic inhibitors, while those which shift them in the anodic direction are anodic inhibitors.[20] On the other hand, the inhibitors of the type of the mixed control shift the cathodic Tafel lines towards more cathodic potentials and the current-potential curves near the free corrosion potential towards less cathodic potentials. On the basis, TSC is characterized as a purely cathodic inhibitor while TU and TA exhibit dual inhibiting action, *i. e.* they inhibit both the cathodic and the anodic reactions, although to varying degrees.

Adsorption Behavior. The degree of surface coverage can be calculated from the currents obtained at constant potential in presence (i_2) and in absence (i_1) of inhibitor.[21,22] Thus

$$\theta = 1 - i_2/i_1. \qquad (1)$$

Alternatively, the degree of coverage can be obtained at constant current.[23,24] Thus

$$\theta = 1\exp(\beta\Delta\varepsilon/b), \qquad (2)$$

where B is the transfer coefficient, $\Delta E = E_{\text{inh}} - E_{\text{blank}}$ is the difference between the electrode potential in the inhibited solution and that in the blank solution, and $b = RT/F$. Under the present conditions, Eqs. 1 and 2 gave virtually identical results.

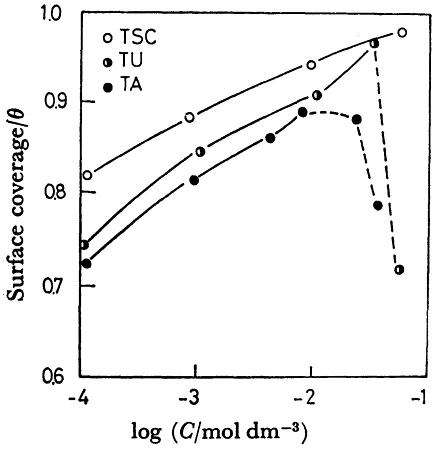


Fig. 2. Effect of inhibitor concentration on the surface coverage at 30 °C for mild steel in 1.0 mol dm^{-3} H_2SO_4.

Figure 2 shows the effect of inhibitor concentrations on coverage of the electrode surface. TSC is the only compound which displays a simple behavior over the tested concentration range. Its behavior points to the tendency to form a monolayer of adsorbed TSC. Both TU and TA undergo an apparent loss in the degree of surface coverage above certain concentrations. It is evident that at a certain inhibitor concentration, the tendency for adsorption is in the order TSC>TU>TA (see below).

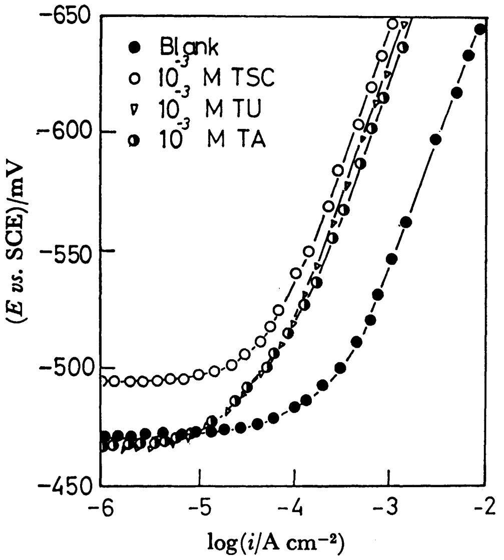


Fig. 3. Effect of the structure of molecules on the cathodic polarization curves of mild steel in 1.0 mol dm^{-3} H_2SO_4.

Effect of the Structure of the Inhibitor Molecule. Figure 3 shows a comparison of the cathodic polarization relations in the presence of TSC, TU, and TA at a concentration of 10^{-3} mol dm^{-3}. Clearly the differences among these compounds are not too large. The inhibiting effect of these compounds on the h.e.r. is in the order TSC>TU>TA as evident by the extent of the shift in Tafel lines in the cathodic direction. Alternatively, Fig. 4 shows the effect of the functional group on the current-potential relations for TSC, SC, and AG at a concentration of 10^{-2} mol dm^{-3}. Clearly aminoguanindine (AG) is a slightly better inhibitor than SC but TSC is far more efficient than both. The above evidence indicates that the inhibiting action of the compounds is mainly imparted by the thiocarbonyl group.

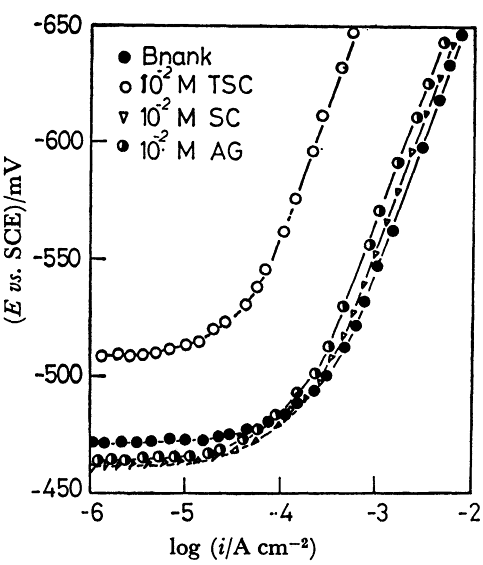


Fig. 4. Effect of TSC and AG molecules on the cathodic polarization curves of mild steel in 1.0 mol dm^{-3} H_2SO_4.

Table 2 shows the effect of TSC, TU, and TA concentrations on the exchange current density of hydrogen evolution i_0, corrosion current density i_{corr}, the protection efficiency, P, the degree of surface coverage θ and the polarization resistance R_p (see below). The protection efficiency is the parcent of relative decrease in the corrosion rate, given by

$$P(i_{\text{corr}}) = 100\left(1 - \frac{i_{\text{corr}}(\text{inhibited})}{i_{\text{corr}}(\text{blank})}\right). \qquad (3)$$

The percent of relative decrease in the exchange current density is defined similarly.

The efficiency of a corrosion inhibitor may also be evaluated by measuring its effect on the polarization resistance which is defined by

$$R_p = \mathrm{d}(E - E_{\text{corr}})/\mathrm{d}i \quad \Omega\,\text{cm}^2, \qquad (4)$$

where E and E_{corr} are in V and i in A cm^{-1}. Thus a plot of $(E - E_{\text{corr}})$ in the low polarization region, when $|E - E_{\text{corr}}| < 20$ mV, *vs.* current density i should give a straight line passing by the origin with a slope equal to the polarization resistance. Figure 5 shows such a

Table 2. Effect of the inhibitor concentration on: corrosion potential, tafel slope, exchange and corrosion current densities, and percentage decrease in each, degree of surface coverage, and polarization resistance for mild steel in 1.0 mol dm^{-3} H_2SO_4 at 30 °C

Inhibitor Concn 1	E_{corr} vs. SCE / mV	b / mV	i_0	$p(i_0)$	i_{corr} / μA cm^{-2}	$p(i_{corr})$	θ	R_p/Ω cm^2
Thiosemicarbazide TSC								
0	−471	−116	5.2	—	220	—	—	83.0
10^{-4}	−480	−119	1.1	78.8	68	73.6	0.82	300.0
10^{-3}	−495	−118	0.93	82.1	48	78.2	0.89	366.7
10^{-2}	−510	−119	0.59	88.7	38	82.7	0.94	500.0
5×10^{-2}	−515	−118	0.4	92.3	32	85.4	0.96	666.7
Thiourea TU								
0	−472	−116	5.2	—	220	—	—	83
10^{-4}	−470	−117	2.0	61.5	71	67.8	0.72	530
10^{-3}	−467	−117	1.3	75.0	40	81.8	0.82	870
5×10^{-3}	−465	−117	0.98	81.2	32	85.5	0.87	1430
10^{-2}	−463	−117	0.8	84.6	24	89.1	0.90	2150
3×10^{-2}	−461	−117	0.89	82.9	22	90.0	0.79	909
5×10^{-2}	−451	−115	1.4	73.1	39	81.9	0.79	830
Thioacetamide TA								
0	−472	−116	5.2	—	22	—	—	83
10^{-4}	−469	−116	2.0	61.5	53	75.9	0.74	370
10^{-3}	−467	−116	1.0	80.8	28	87.3	0.85	630
10^{-2}	−465	−114	0.6	87.9	16	92.7	0.91	870
3×10^{-2}	−463	−114	0.1	96.3	60	97.3	0.97	2220
5×10^{-2}	−462	−116	1.9	63.5	56	79.1	0.72	350

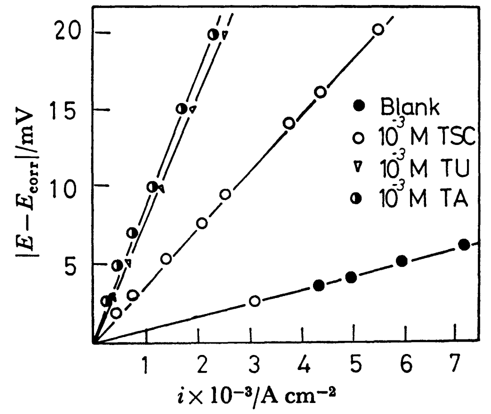


Fig. 5. The relationship between $|E-E_{corr}|$ and current density at low cathodoc polarization for mild steel in the presence of 10^3 mol dm^{-3} of each TSC, TU, and TA at 30 °C.

plot for TSC, TU, and TA at a concentration of 10^{-3} mol dm^{-3} of each. Similar straight lines were obtained at various concentrations of each inhibitor (see Table 2).

Figure 6 shows a comparison between $P(i_{corr})$ and $P(i_0)$ for TSC, TU, and TA. It is seen that for TSC $p(i_0)>p(i_{corr})$ whereas for TU and TA $P(i_{corr})>P(i_0)$ over the entire concentration range. This indicates that for TU and TA the percentage decrease in corrosion rate is greater than the percentage decrease in the rate of the h.e.r. This can be true if the anodic reaction is also partially inhibited which supports the conclusions reached above, *viz.* that TU and TA are inhibitors of dual action.

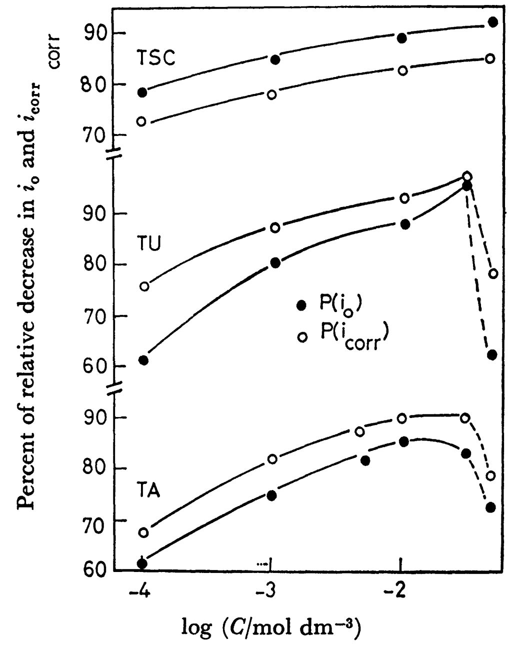


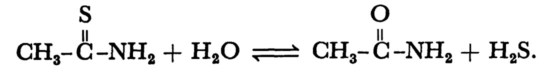
Fig. 6. Effect of inhibitor concentrations on the percent of relative decrease in i_0 and i_{corr}.

From R_p calculations, as shown in Table 2, it is seen that for TSC the polarization resistance increases with inhibitor concentration over the indicated range. In the cases of TU and TA the polarization resistance increases with inhibitor or concentration up to a critical value above which TU and TA lose their inhibiting efficiency and eventually stimulate, rather than inhibit, corrosion. The value of this critical concentration at 30 °C is about 10^{-2} mol dm^{-3} in the case of TU and about 3×10^{-2} mol dm^{-3} in the case of TA. Such a behaviour has not been observed with TSC up to a concentration of 5×10^{-2} mol dm^{-3}. Preliminary results suggest that this critical concentration is temperature dependent.

The reason for this behaviour of TU and TA is still in question. Thus whereas some workers[25,26] attribute it to the hydrolysis of TU to produce corrosion promoting species *e. g.* HS^- and S^{2-}, others[27,28] reported the disappearance of TU from the solution. The loss of TU in HNO_3 has been recently explained[2] by a scheme which involves its oxidation in solution followed by reduction at the metal surface. This scheme obviously cannot be applied in non-oxidizing acids *e. g.* HCl and H_2SO_4. On the other hand, the hydrolysis scheme cannot, as yet, be totally accepted since it is not clear why hydrolysis occurs to such an extent only in concentrated solutions and not in dilute ones. Determination of the equilibrium constant for such a reaction is required before a final judgement can be made with respect to this scheme.

Consideration of the Molecular Structure. The above results indicate that the order of the stability of the above thiocompounds in solution and the extent of their tendency to adsorb on, and hence protect, the iron surface are as follows: $\mathrm{TSC} > \mathrm{TU} > \mathrm{TA} \gg$ nonsulfur compounds. A qualitative explanation of this sequence may be found from a consideration of the electronic structure of these compounds (see Table 1). These are all similar on one side of the thiocarbonyl group and different on the other. The lone pairs of electrons on the nitrogen and sulfur atoms are delocalized and hence produce delocalization or resonance stabilization energy which stabilizes the compound.[29] There is reason to believe that the larger the number of delocalized electrons, the more stable is the structure and the more is the charge density on the "anchoring" atom (in this case S) and hence the larger is the extent of adsorption *i. e.* the larger is θ.

Therefore, where as the methyl group of TA has no delocalized electrons, the amino group of TU has one lone pair of such electrons and the hydrazine group of TSC has two such pairs. This explains the above sequence. In fact in 1.0 mol dm^{-3} H_2SO_4 medium, TA readily undergoes hydrolysis in presence of acid:



$$\mathrm{CH_3\text{-}\overset{\overset{S}{\|}}{C}\text{-}NH_2 + H_2O \rightleftharpoons CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2 + H_2S}. \tag{5}$$

The decomposition of TU does not go to the same extent. On the other hand, the results we obtained on TSC do not point towards measurable degree of decomposition or hydrolysis of the compound over the tested concentration range. The resulting H_2S or HS^- are known to be promotors of hydrogen discharge, hydrogen embrittlement and general acid corrosion.[30,31] Therefore, as the concentration of TA increases, the equilibrium of Eq. 5 shifts towards the right producing more H_2S which promotes the h.e.r. and hence the overall corrosion reaction. Similar considerations apply to the case of TU although obviously to a lesser extent.

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