

The kinetics of steel dissolution in the presence of some thiouracil derivatives

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A COMPARATIVE study of the efficiency of thiouracil derivatives (TUr) as inhibitors of the corrosion of steel in sulphuric acid solutions was undertaken using gasometry and potentiometry. Both techniques gave the same order of inhibition. The efficiency of the TUr can be improved by the introduction of a bromine atom in position five of the heterocyclic ring. In all acid solutions tested, the most efficient compound proved to be 6-methyl-5-bromo-2-thiouracil. Moreover, potentiodynamic polarization curves indicated that the compounds which do not contain a bromine atom act as cathodic-type inhibitors, whereas the bromo-compounds act as mixed-type inhibitors. The kinetic relationship of the corrosion reaction in the presence of TUr derivatives is in the form: $R = kC^B$, where B is the order of the reaction and varies between -1.18 and -0.19 for the most efficient compound. All data were compared and fitted to the kinetic-thermodynamic model in terms of an active site occupancy parameter, γ , and a binding constant, K, of the inhibitor. The experimental findings also fit well to the Temkin adsorption isotherm in terms of the lateral interaction and the binding constant between the inhibitor molecules and the surface of the metal. The mode of adsorption of the organic molecules according to their structure is discussed in detail.

Introduction

The significance of the use of acid solutions arises from their wide applications in numerous manufacturing processes in various industries, such as acid cleaning, acid descaling, and oil-well acidification. The practice of inhibition is commonly used to reduce the corrosive attack suffered by metallic materials in such applications. The corrosion of iron in acid solutions takes place with hydrogen depolarization[1]. The neutralization of H^+ and H_2 diffusion is usually the slowest among all possible stages of the cathodic process (transport, H^+ discharge, adsorption and absorption of hydrogen atoms and their recombination, electrochemical desorption, etc.). Thus, it is interesting to study the kinetics of corrosion in the presence of inhibitors.

Three different types of inhibition mechanisms have been proposed for organic inhibitors: the indifferent coverage (blocking) mecha-

nism, the de-activating coverage mechanism, and the reactive coverage mechanism[2]. In the case of indifferent coverage, the electrode reaction does not take place at the covered area, which is relatively large ($\theta = 1$). In the case of de-activating coverage, the inhibitor particles are preferentially blocking the active sites of the electrode surface and therefore $\theta \ll 1$ for comparable efficiencies. Reactive coverage arises when the primary adsorbed inhibitor species itself undergoes a chemical or electrochemical reaction or when the basic electrode reaction takes place at the covered electrode surface[3]. The degree of coverage is usually large, i.e. $\theta = 1$.

Thiouracil derivatives have been selected due to both the high electron density of their two nitrogen and one sulphur atoms and their heterocyclic ring. The purpose of the present work is evaluating the effect of such thiouracil inhibitors on the corrosion kinetics of steel. Additionally, the adsorption behaviour is analysed in order to choose the appropriate adsorp-

Table 1.
Chemical
composition
of steel.

Element	Fe	C	Si	P	Mn	S	Cr
Amount in %	98.53	0.09	0.037	0.064	1.13	0.10	0.04

tion isotherm and determine the free energy of adsorption.

Experimental

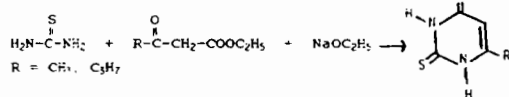
The experiments were performed with steel rods having a cross-sectional area of 0.92cm² and a chemical composition given in Table 1. The influence of inhibitor additives on the dissolution process of the specimens in sulphuric acid was monitored chemically and electrochemically. In the chemical method, steel samples were placed in a simple vessel containing test solution. The vessel had the form [4] which allowed the volume of hydrogen evolved to be measured as a function of time. In the electrochemical part of the study, the polarization measurements were recorded using an *ACM Potentiostan*. The scanning rate employed in this study was 0.02Vmin⁻¹. All experiments were carried out in de-aerated media using purified nitrogen at 25 ± 0.1°C.

Before measurements the samples were mechanically polished with a series of emery papers starting with a coarse one and proceeding in steps to finer grades using a polisher. They were washed with doubly-distilled water then ultrasonically degreased with CCl₄ (AR) for 5min.

Inhibitors

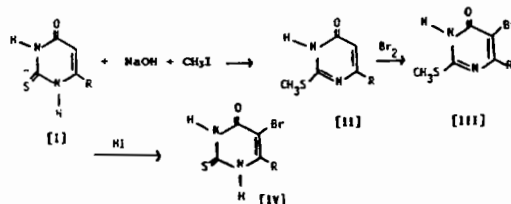
The following inhibitors were employed in the present investigation: 6-n-propyl-2-thiouracil (PTUr), 6-n-propyl-5-bromo-2-thiouracil (PBTUr), 6-methyl-2-thiouracil (MTUr), 6-methyl-5-bromo-2-thiouracil (MBTUr), and 6-methyl-2-thiouracil (MTUr).

Synthesis of 6-alkyl-2-thiouracil:



Thiourea (0.05mol) and the appropriate β-keto ester (0.05mol) were added simultaneously to a solution of sodium ethoxide (0.1mol) in absolute ethanol (70ml). The mixture was refluxed for 8hr and the ethanol was removed by distillation under vacuum. The residue was dissolved in water (50ml) and acidified to pH3 with

Synthesis of 6-alkyl-5-bromo-2-thiouracil:



HCl. The precipitate was filtered, washed with water and recrystallized from aqueous ethanol.

Intermediate [II] was prepared by the addition of methyl iodide (2.2ml) to the 6-alkyl-2-thiouracil [I] (0.03mol) in the presence of NaOH (0.03mol). It was then brominated with bromine (3ml) in the presence of glacial acetic acid containing 5% acetic anhydride (40ml) to get 5-bromo-6-alkyl-2-methyl thiouracil [III]. The methyl group was removed by HI (7ml of 66%) and the 5-bromo-6-alkyl-2-thiouracil [IV] isolated and crystallized out of dilute alcohol.

All test solutions contained 10 vol % of methanol to keep the inhibitor completely soluble.

Results and discussion

Adsorption of the inhibitors on steel electrodes

The corrosion of mild steel in acid solutions containing small amounts of 6-n-propyl-2-thiouracil (PTUr), 6-n-propyl-5-bromo-2-thiouracil (PBTUr), 6-methyl-2-thiouracil (MTUr), and 6-methyl-5-bromo-2-thiouracil (MBTUr), was studied using the gasometry method.

Fig.1 shows the volume of evolved hydrogen gas against time when test pieces of steel were immersed in 2.0M H₂SO₄/10% methanol in presence and absence of different concentrations of 6-n-propyl-2-thiouracil. The dissolution of steel is characterized by a linear increase of the volume of evolved hydrogen with time. The protection efficiency, P, of the inhibitor was calculated by applying the following relationship:

$$P = \left(1 - \frac{R \cdot R_{inh}}{R \cdot R_c} \right) \times 100 \quad (1)$$

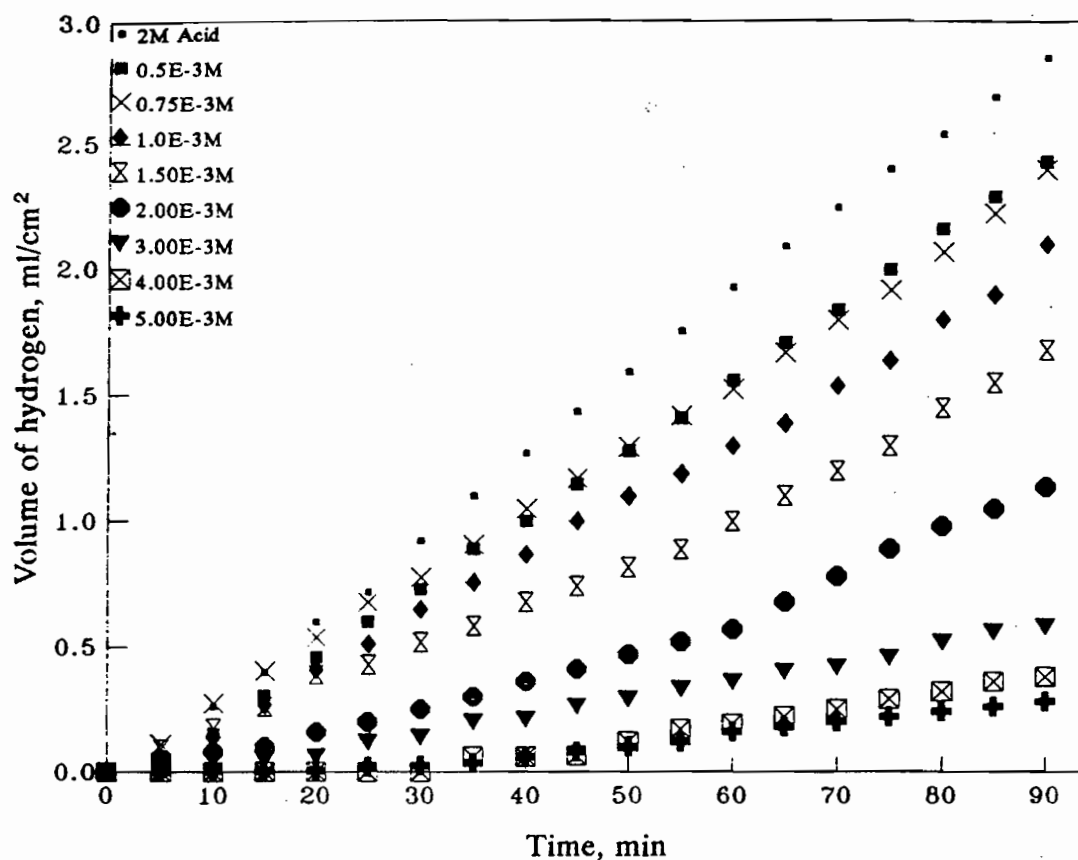


Fig.1.
Relation
between the
hydrogen
evolution and
exposure time
of steel in 2M
 H_2SO_4 in
different
concentrations
of PTUr.

where $R.R_0$ and $R.R_{inh}$ are the reaction rates (slope of the straight lines in the gasometry plot) in absence and presence respectively of a certain concentration of the inhibitor.

Figs 2a and 2b show the variation of the protection efficiency calculated from gasometry with the concentration of (PTUr, PBTUr) and (MTUr, MBTUr) respectively. The data show that the corrosion rate of steel in acid medium depends on the concentration and the type of the inhibitor present. The investigated compounds could be classified into two groups dependent on their molecular structure: group I contains PTUr and PBTUr, and group II contains MTUr and MBTUr. The curves of group I consist of an initial linear portion which changes to a region of constancy, an indication of completion of a mono-layer of the adsorbate. Also, these curves are invariably sigmoid in nature whereas, for the second group, the curves exhibit a second rise in the protection efficiency, leading to the formation of multilayers.

The protection efficiency increases in the following order:

$$PBTUr > PTUr \text{ and } MBTUr > MTUr$$

This behaviour may be attributed to the difference in the molecular structure, since PBTUr and MBTUr contain an extra bromine atom in position 5 of the heterocyclic ring which

increases the electron density on the molecule moiety as a whole.

The kinetic relationship of the corrosion reaction in the presence of the inhibitors may be deduced by examining the reaction data obtained from gasometry as a log rate with log molar concentration. Figs 3a and 3b illustrate the mechanism of steel dissolution in acid medium in presence of PTUr, PBTUr, MTUr and MBTUr. A linear relationship of the type:

$$R = kC^B \quad (2)$$

describes the experimental data, where R is the overall reaction rate, k is the specific rate constant, B is a further constant for the reaction studied, and C is the concentration of the inhibitor used. In the same figure, lines with slopes of -1.18, -0.46, -0.65, and -0.19 for PTUr, PBTUr, MTUr and MBTUr respectively are reported. These empirical values reflect the order of the reaction and indicate that MBTUr is more efficient than MTUr, and PBTUr is more efficient than PTUr by a factor of 2.6 and 3.4 respectively. This could be explained on the basis of the side chain in MTUr being attached to a methyl group, whereas in PTUr it is connected to an n-propyl group.

The presence of an n-propyl group enhances the steric hindrance and decreases the chance for

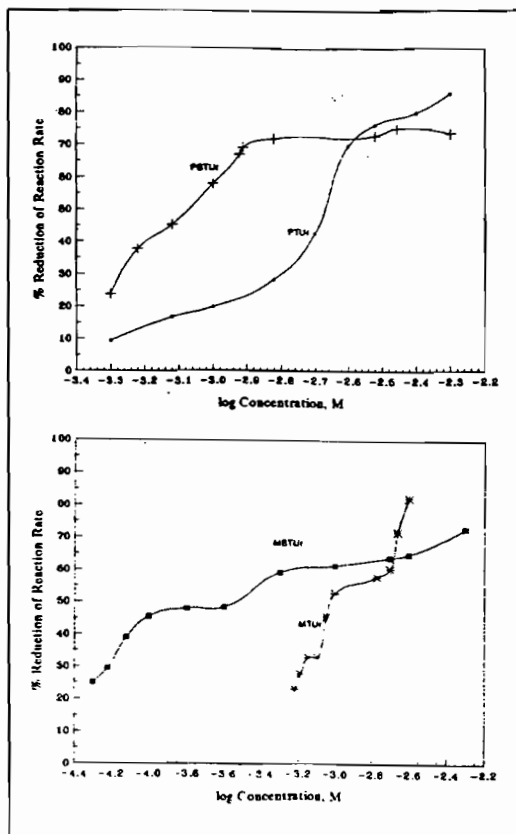


Fig.2. (a) - top: Adsorption isotherms of PTUr and PBTUr calculated from gasometry measurements. (b) - bottom: Adsorption isotherms of MTUr and MBTUr calculated from gasometry measurements.

the thio group to be free for the adsorption process, thus lowering the efficiency of that inhibitor compared to MTUr.

Determination of the adsorption isotherm

In order to understand the role of organic inhibitors in the inhibition mechanism of corrosion, the adsorption behaviour of the organic adsorbates on the electrode surface must be known. The experimental data obtained from the adsorption of PTUr, PBTUr, MTUr, and MBTUr from aqueous acid solutions on steel electrodes follow one of two adsorption isotherms[5-8,9]. In the first case, the molecular interaction (a), which depends on the molecular interaction in the adsorption layer and on the degree of heterogeneity of the sample, is included. In the latter, the number of water molecules replaced by one molecule of organic adsorbate (x), is included[10].

Recently, a kinetic model has been developed[11,12]. The corrosion process is taking place via the occupation by a given inhibitor molecule of a number, 1/y, of surface-active sites according to:

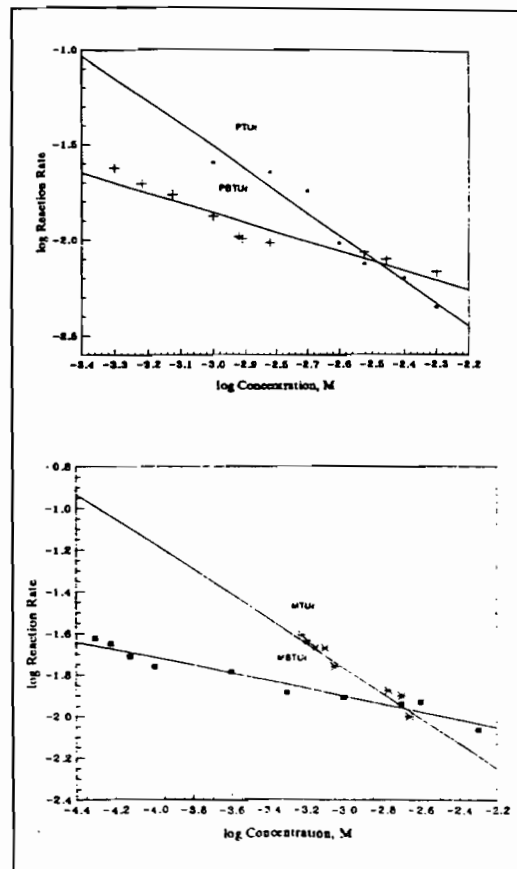


Fig.3. (a) - top: Log reaction rate as a function of log concentration of PTUr and PBTUr. (b) - bottom: Log reaction rate as a function of log concentration of MTUr and MBTUr.

$$S + yI = SI_y \tag{3}$$

where y is the number of inhibitor molecules occupying one active site. This leads to the relationship:

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K' + x \log C \tag{4}$$

where C is the inhibitor concentration in the bulk of the solution and θ is the degree of coverage. The binding constant K is given by:

$$K = K'^{(1/y)} \tag{5}$$

A specially-written computer program is employed in this study to fit the experimental data with the proper adsorption isotherm equations mentioned above.

For the inhibitor compounds used in this study, it is found that the kinetic-thermodynamic model and the Temkin adsorption isotherm fit the experimental data, with a correlation coefficient of 0.98. The Temkin isotherm is

given below:

$$a\theta = \ln KC \quad (6)$$

where (a) is a molecular interaction parameter depending on the molecular interactions in the adsorption layer and on the degree of heterogeneity of the surface. It can have both positive and negative values and is a measure of the steepness of the adsorption isotherm. The more positive the value of (a), the steeper is the adsorption isotherm. This has been interpreted [13] to imply that the interactions between molecules with positive values for (a) cause an increase in the adsorption energy with the increase of θ . The equilibrium constant of the adsorption process, K, is related to the standard free energy of adsorption, ΔG_{ads}° , by the following equation:

$$K = \frac{1}{55.5} \exp \left[\frac{-\Delta G_{ads}^{\circ}}{RT} \right] \quad (7)$$

the value 55.5 in the above equation being the concentration of water in the solution in mol/li.

Figs 4a and 4b represent the kinetic model for (PTUr, PBTUr) and (MTUr, MBTUr) respectively. A plot of $\log [\theta/(1-\theta)]$ versus $\log C$ gave a straight line with a slope of y and intercept $\log K'$. The Temkin adsorption isotherms are plotted for the inhibitors and illustrated in Figs 5a and 5b. A straight line was invariably obtained indicating the validity of the isotherms. The reciprocal of the lateral interaction coefficient (a) is given by the slope of the straight line, whereas the intercept is $(1/a) \ln K$. The values of a, K, ΔG_{ads}° and y calculated from the kinetic model and Temkin adsorption isotherm are exhibited in Table 2. Large values of K mean better inhibition efficiency of a given compound, i.e. stronger electrical interaction between the double layer existing at the phase boundary and the adsorbing molecules. The values of K obtained from the kinetic model and Temkin isotherm are incompatible. The lack of the compatibility may be attributed to the fact that the Temkin isotherm is only applicable to cases where one active site per inhibitor molecule is occupied. The lateral interaction parameter was introduced to treat deviations from Langmuir-ideal behaviour, whereas the kinetic model uses the parameter of size. The values of the lateral interaction parameter were found to be positive and enhanced with increasing surface coverage. The large negative values of the standard free energy of adsorption, ΔG_{ads}° , indicate that the reaction is proceeding spontaneously and is accompanied by a high efficient adsorption for such a compound. The number of centres of the active sites increases

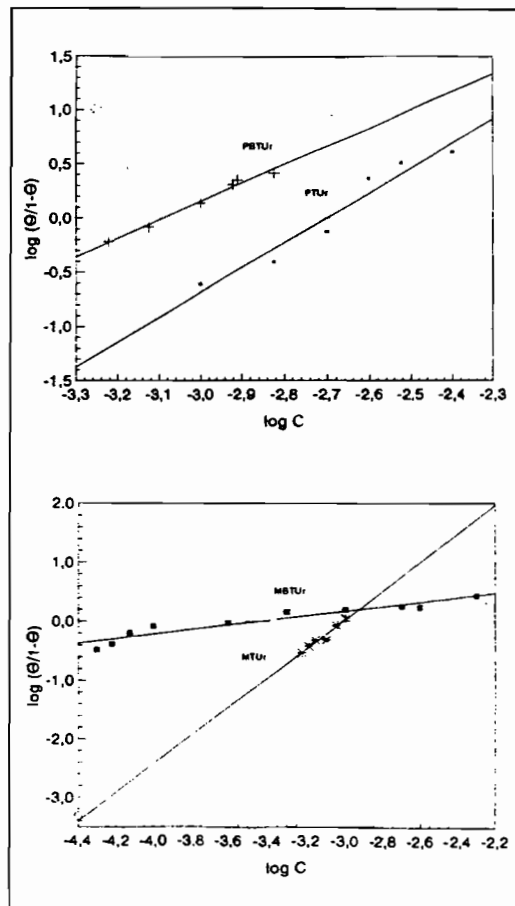


Fig.4. (a) - top:
Application of
the Kinetic
model for PTUr
and PBTUr in
acid solutions.

(b) - bottom:
Application of
the Kinetic
model for MTUr
and MBTUr in
acid solutions.

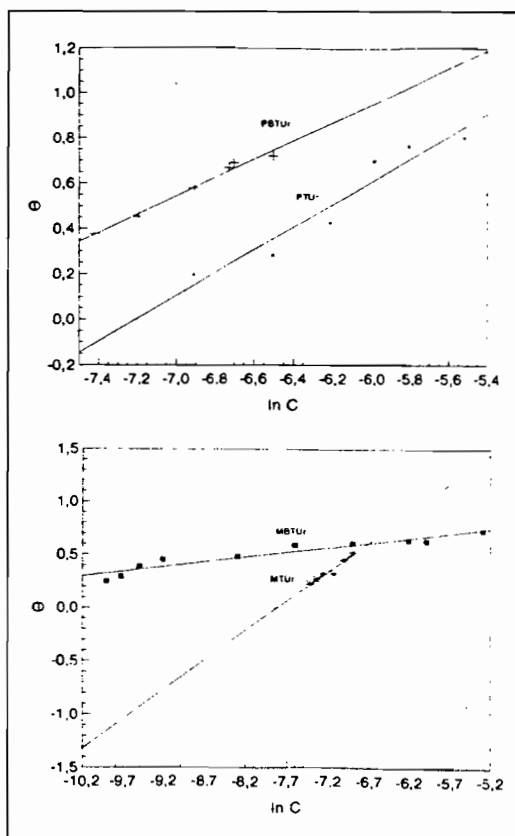


Fig.5. (a) - top:
Application of
the Temkin
adsorption
isotherm for
PTUr and
PBTUr in
acid
solutions.

(b) - bottom:
Application of
the Temkin
adsorption
isotherm for
MTUr and
MBTUr in
acid
solutions.

Compound	Kinetic Model			Temkin Isotherm		
	γ	K	$-\Delta G^0$ kJ/mol	a	K	$-\Delta G^0$ kJ/mol
PTUr	0.4	450	24.9	2.0	1352	27.4
PBTUr	0.6	1226	28.0	2.5	4207	31.1
MTUr	0.4	1020	27.6	1.8	2496	29.8
MBTur	2.6	2803	30.1	11.2	762726	44.3

Table 2. Lateral interaction, binding constant, number of active sites, and free energy change values obtained from the Temkin isotherm and the thermodynamics-kinetic model.

with increasing efficiency of the compounds. Values of γ less than unity mean that a given inhibitor molecule will occupy more than one active site, whereas values of γ greater than unity imply the formation of multilayers of the inhibitor on the surface of the metal as in case of MBTur.

Potentiodynamic polarization behaviour

Anodic and cathodic polarization curves were measured in 0.1M H₂SO₄/10% methanol in the

absence and presence of different concentrations of the inhibitors. Fig.6 represents the potentiodynamic polarization in presence of MBTur. The presence of the inhibitor induced an increase in both cathodic and anodic overvoltages. Thus, the compound influences both cathodic and anodic processes and inhibits hydrogen-evolution and anodic dissolution processes, i.e. the inhibitor acts as a mixed-type inhibitor. Because of the presence of a degree of non-linearity in the Tafel-slope part of the polarization curves, the Tafel constants and subse-

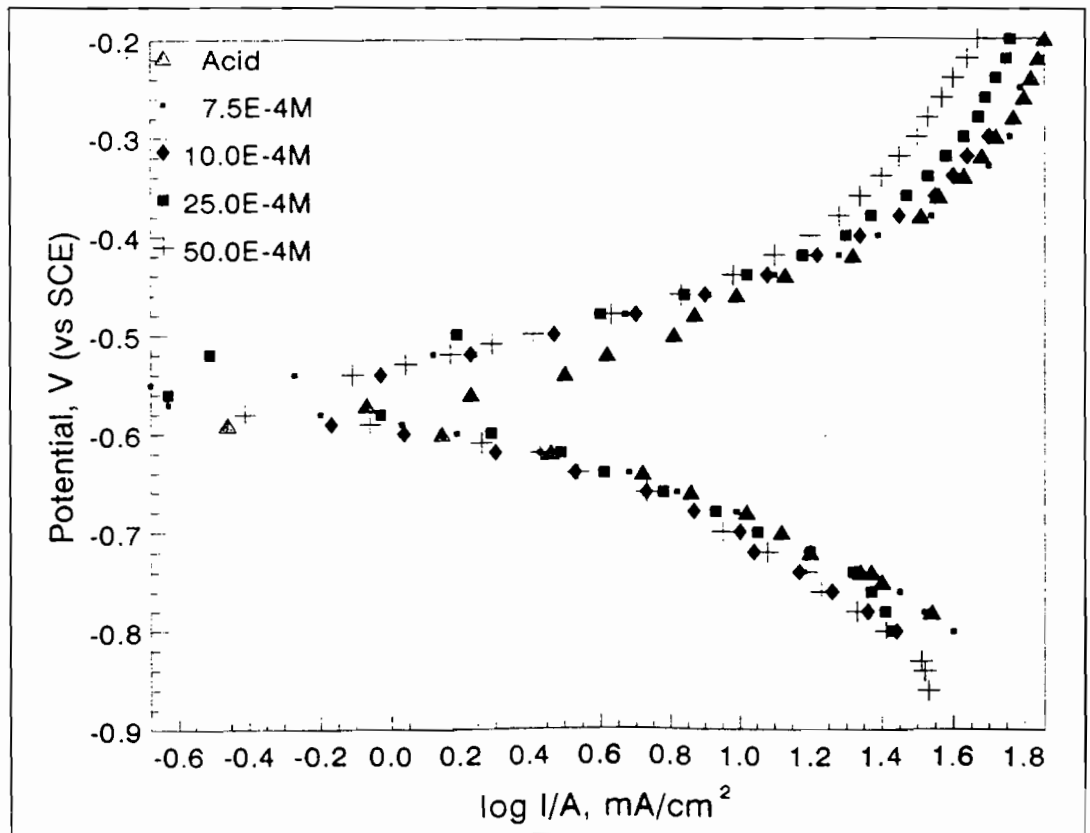


Fig.6. Potentiodynamic polarization curves for mild steel in 0.1M H₂SO₄/10% methanol in different concentrations of MBTur.

Conc. $\times 10^{-4}$ M	$-E_{\text{corr}}$ V	β_a V/decade	$-\beta_c$ V/decade	i_{corr} $\mu\text{A}/\text{cm}^2$	% i_{corr}
Acid	0.58	0.14	0.13	1226	--
7.5	0.56	0.10	0.11	891	27.3
10.0	0.55	0.09	0.11	562	54.1
25.0	0.55	0.09	0.09	487	60.3
50.0	0.55	0.09	0.09	446	63.6

Table 3.
Electrochemical
parameters
obtained from
potentio-
dynamic
polarization
measurements
of different
concentrations
of MBTUr in
0.1M H_2SO_4 /
10% methanol.

quently the corrosion currents were calculated as a slope of the points after E_{corr} by $\pm 50\text{mV}$.

Table 3 reveals the electrochemical parameters for the dissolution of steel in the presence of MBTUr. The data illustrate that the corrosion potential of the iron electrode shifts slightly to the anodic direction with increasing concentration of the inhibitor, and thus the presence of the compound in the acidic solution influences the anodic process.

Anodic and cathodic Tafel constants did not change significantly with the increase in the

inhibitor concentration, i.e. the inhibitor affects both the cathodic and anodic overpotentials and shifts the position of the Tafel lines in parallel in both directions, indicating that the presence of the inhibitor does not alter the reaction mechanism. Fig.7 shows that the presence of MTUr does not alter the anodic polarization curves, but affects only the cathodic curves and acts as a cathodic-type inhibitor. This behaviour could be attributed to the presence of the large-size bromine atom which can adsorb on the anodic area of the metal electrode. Thus, compounds con-

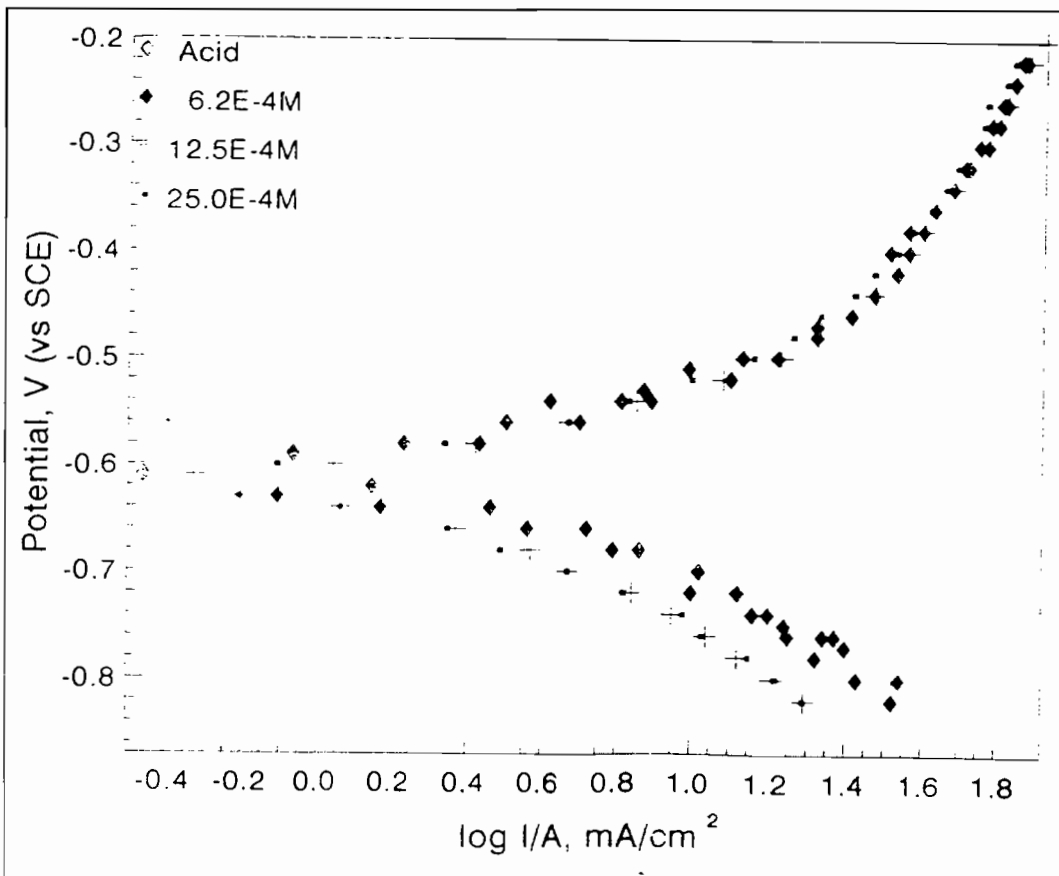


Fig.7.
Potentiodynamic
polarization
curves for mild
steel in 0.1M
 H_2SO_4 /10%
methanol in
different
concentrations
of MBTUr.

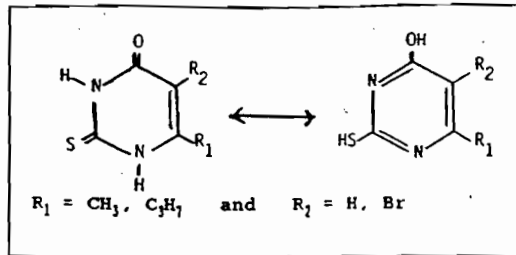


Fig.8. Tautomerism of the thiouracil derivatives.

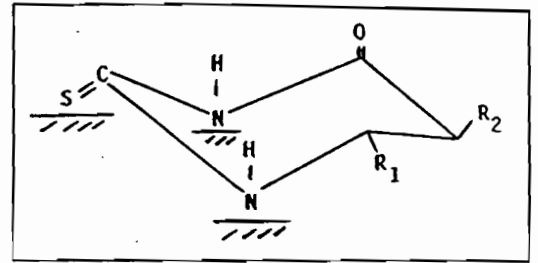


Fig.9. Skeletal diagram for thiouracil derivatives.

taining the bromine atom (PBTUr and MBTUr) act as mixed-type inhibitors.

Chemical structure and corrosion inhibition

Fig.8 illustrates a tautomerism that can exist in the inhibitor molecules employed. The polar effect of R_1 and R_2 substituents on the aromatic nucleus of the heterocyclic moiety will be transmitted to the whole conjugate system through π -bonds.

Vertical adsorption of the additive molecules on the iron oxide surface is proposed. The skeletal representation of the mode of adsorption of the inhibitor compounds is shown by Fig.9.

Adsorption most probably takes place through the two secondary amine and the thio groups present in the heterocyclic ring. The transfer of a lone pair of electrons on the nitrogen and/or sulphur atoms to the surface, forming a coordinate bond, is favoured. Inhibition of the anodic and/or cathodic reactions would depend on the degree of coverage of the metal with the adsorbate.

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