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Impedance investigation of corrosion inhibition of armco iron by thiourea

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The inhibitive action of thiourea on the corrosive behaviour of ARMCO iron was investigated in deaerated 0.5 M H_2SO_4 solution, by means of electrochemical impedance spectroscopy. The inhibitor effectiveness increases with concentration, reaches a maximum (at about 1 mM) and then decreases. The adsorptive behaviour of thiourea on the electrode surface up to its peak follows a Frumkin-type isotherm with lateral repulsion, where the molecules are vertically adsorbed on the iron surface via the sulfur atom. Thiourea acts as a mixed inhibitor up to the critical concentration. It decreases the dissolution of iron and the hydrogen evolution reaction by blocking the electrode surface. The free energy of adsorption $\Delta G^{ad} = -39\,\mathrm{kJ\,mol^{-1}}$ and the attraction constant $a = -4.4$.

List of symbols

a	attraction constant
b	Tafel slope (mV)
C	capacitance ($\mathrm{F\,cm^{-2}}$)
c	concentration ($\mathrm{mol\,dm^{-3}}$)
E	electrode potential (mV)
E^*	activation energy ($\mathrm{kJ\,mol^{-1}}$)
f	frequency (Hz)
$\mathcal{R}$	gas constant
T	temperature (K)
Z	electrode impedance ($\Omega\,\mathrm{cm^2}$)
j	current density ($\mathrm{mA\,cm^{-2}}$)
K	adsorption constant ($\mathrm{dm^3\,mol^{-1}}$)
R	resistance ($\Omega\,\mathrm{cm^2}$)

Greek letters

α	transfer coefficient
Θ	inhibition efficiency (%)
ω	angular velocity ($\mathrm{rad\,s^{-1}}$)
ν	scan rate ($\mathrm{mV\,s^{-1}}$)

Subscripts and superscripts

a	anodic
c	cathodic
corr	corrosion
ct	charge transfer
p	polarization

1. Introduction

It is well known that thiourea (TU) is strongly adsorbed on many metal surfaces and may be of technological interest. TU is interesting for studying adsorption for several reasons. It is often employed in metal electrodeposition, such as copper [1, 2] or silver [3], to influence such properties as deposit smoothness, deposit brightness and grain refinement. TU is also known to influence the electrochemical evolution of hydrogen on many electrodes. For example it accelerates the hydrogen evolution reaction (HER) at the silver electrode in neutral solutions, while retarding it in acid media [4]. Inhibition of the HER may be one of the reasons why TU inhibits corrosion of many metals.

Thiourea and its derivatives have been studied for acidic corrosion of iron [5–18] and steel [19, 20] over a long period by using d.c. polarization measurements, and there are many conflicting reports on its inhibitory mechanism. Unlike many other inhibitors, thiourea shows a maximum in the concentration-efficiency curves [6–10, 18]. Beyond this maximum, thiourea progressively loses its efficiency and eventually becomes a corrosion promoter. Controversies exist as to the value of inhibitor concentration corresponding to maximum protection efficiency and the mechanisms underlying the resulting loss of efficiency at higher concentrations.

The results of our d.c. study of TU adsorption on ARMCO iron in 0.5 M H_2SO_4 solution at 30 °C [18] can be summarized as follows:

(i) The addition of TU in concentration up to 1 mM induced a decrease in both cathodic and anodic currents, but had insignificant effect on the corrosion potential. The presence of TU did not affect cathodic Tafel slopes ($b_c \approx -120\,\mathrm{mV}$), while it caused an increase in the anodic Tafel slope (from approx. 75 mV in a free solution up to 135 mV at $c(\mathrm{TU}) = 1\,\mathrm{mM}$). Further increase in inhibitor concentration produced an opposite effect.

(ii) The protection efficiency, calculated from corrosion currents, increased with increasing TU concentration, and at $c(\mathrm{TU}) = 1\,\mathrm{mM}$ it was around 70%. Approximately the same result was obtained by using the HER exchange current densities.

(iii) The above facts indicated that thiourea did not influence the mechanism of the cathodic reaction. It blocked a fraction of the electrode surface, reducing the surface area available for hydrogen evolution.

The aim of this work was to investigate the thiourea inhibitory mechanism on ARMCO iron corrosion in 0.5 M H_2SO_4 by using electrochemical impedance spectroscopy, and to compare the results with those obtained from d.c. measurements.

2. Experimental details

Measurements were carried out on Armco iron wire moulded in polyester, one end of which was immersed in the solution. The electrode surface was abraded with emery paper to an 800 metallographic finish, degreased in trichloroethylene and rinsed with triply distilled water. The tests were performed in a standard electrochemical cell with a separate compartment for the reference electrode, connected with the main compartment via a Luggin capillary. The counter electrode was a platinum gauze and the reference electrode was a saturated calomel electrode (SCE). All potentials are referred to the SCE. The cell was a water-jacketed version, connected to a constant temperature circulator. Experiments were performed at 20, 30, 40 and 50 °C.

The test solution was 0.5 M H_2SO_4 solution alone, and in the presence of various concentrations of thiourea. All solutions were deaerated by argon and bubbling was maintained during measurements.

Impedance measurements were performed at E_{corr} with the a.c. voltage amplitude ±5 mV in the frequency range 30 mHz to 100 kHz.

All measurements were carried out by a PAR potentiostat (model 273A) and a PAR lock-in amplifier (model 5315A) with an IBM PS/2 computer.

3. Results and discussion

Impedance measurements on the Armco iron electrode in a 0.5 M H_2SO_4 alone and in the presence of various concentrations of inhibitor were performed at the open circuit potential over the whole temperature range.

Fig. 1 represents the influence of TU concentration on impedance spectra presented as 3D Nyquist and the Bode plots at 30 °C. The influence of temperature on the impedance spectra of iron electrode in a pure 0.5 M sulfuric acid solution and in the presence of 1 mmol dm^{-3} TU are represented in the Nyquist and the Bode plots in Figs 2 and 3, respectively.

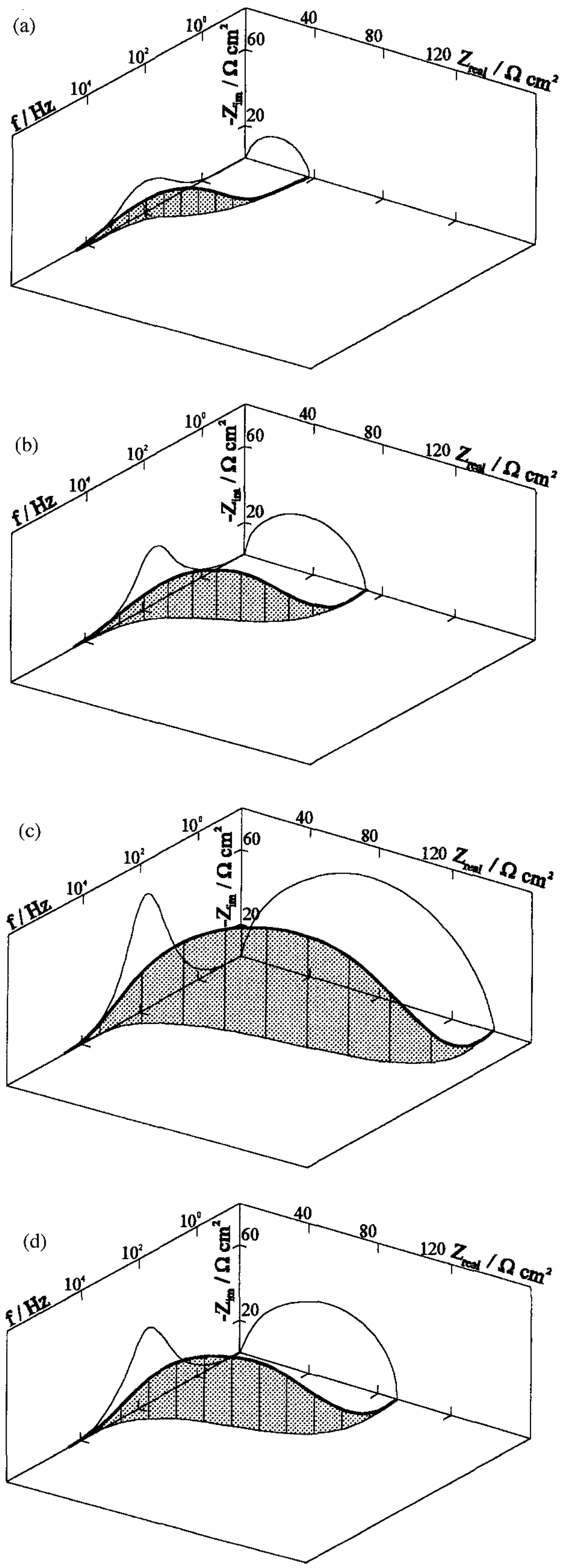


Fig. 1. 3D Nyquist and Bode plots for an iron electrode in 0.5 M H_2SO_4 without (a) and in the presence of TU: (b) 0.1, (c) 1.0 and (d) 10.0 mM at 30 °C.

In all cases the Nyquist plot shows that the

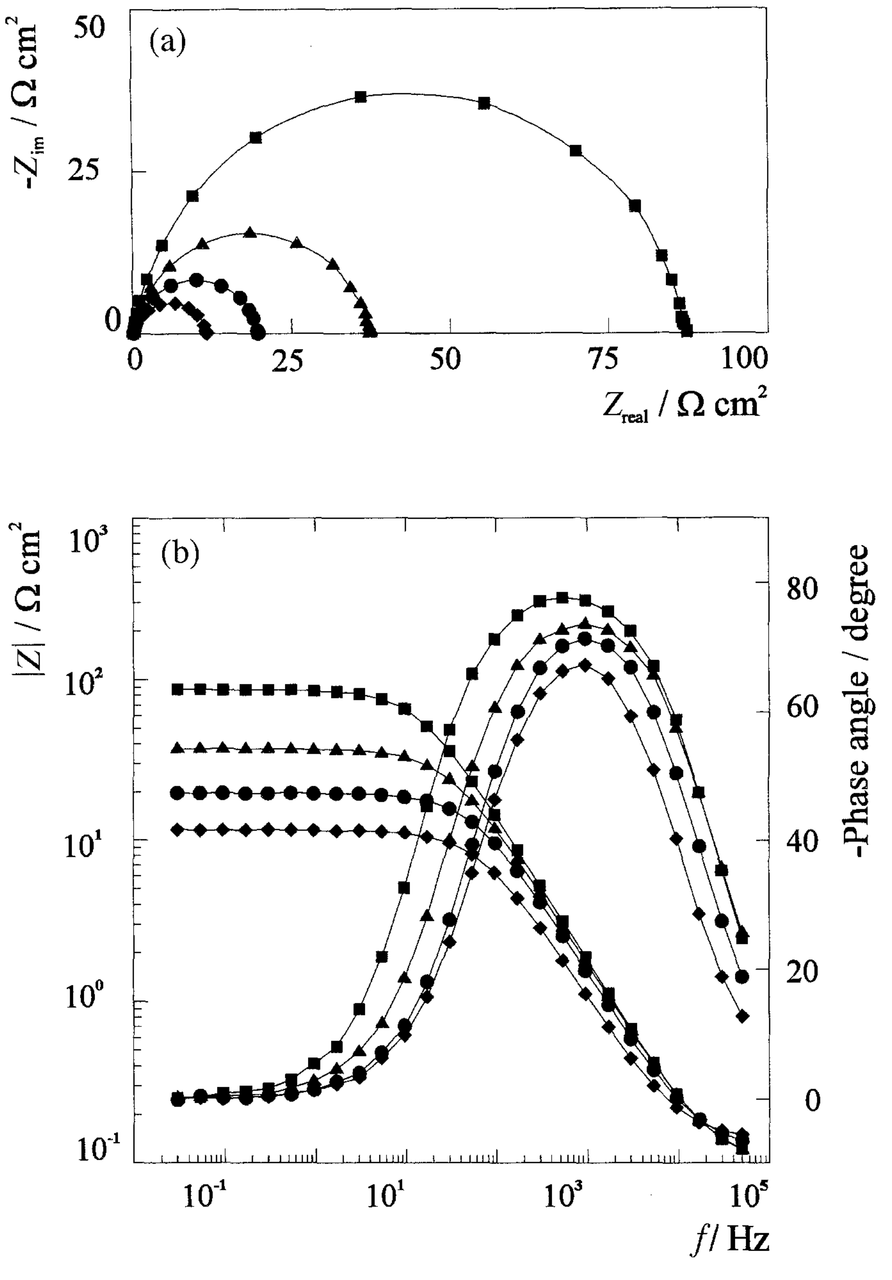


Fig. 2. (a) Nyquist plots and (b) Bode plots for an iron electrode in 0.5 M H_2SO_4 at: (■) 20, (▲) 30, (●) 40 and (◆) 50 °C.

semicircles obtained are depressed, while in the Bode plot the slopes of the log Z against log f curves are not -1. Deviations of this kind, often referred to as frequency dispersion, have been attributed to inhomogeneities of the solid surfaces. A practical way to represent distributed processes such as corrosion of a rough and inhomogeneous electrode is possible with the element following its distribution. The constant phase element (CPE) meets that requirement. The impedance of CPE takes the form [21]:

$$Z_{CPE} = (Q(j\omega)^n)^{-1} \tag{1}$$

where the coefficient Q is a combination of properties related to both the surface and the electroactive species. The exponent n has values between -1 and 1. A value -1 is characteristic of an inductance, a value of 1 corresponds to a capacitor, a value of 0 corresponds to a resistor and a value of 0.5 can be assigned to diffusion phenomena.

The polarization resistance can be determined from the impedance data by using the equation [22]:

$$R_p = \lim_{\omega \to 0} Re\{Z_f\} \tag{2}$$

where $Re\, Z_f$ denotes the real part of the complex faradaic impedance Z_f and ω corresponds to the frequency of the a.c. signal ($\omega = 2\pi f$).

The equivalent circuit used to fit the experimental data consisted of resistor R_{el} (electrolyte resistance) in series with the parallel combination of CPE (Q) and R_p (polarization resistance). For each set of experimental data the parameters R_{el}, Q and R_p were evaluated using a nonlinear least square fit procedure (Table 1). The data were found to be sufficiently well fitted by the transfer function of a given equivalent circuit within the limits of experimental error. The data show that increase in inhibitor concentration up to 1 mM caused a decrease in Q and an increase in R_p. In addition the surface coverage calculated from R_p data are in a good agreement with those obtained from d.c. polarization measurements [18].

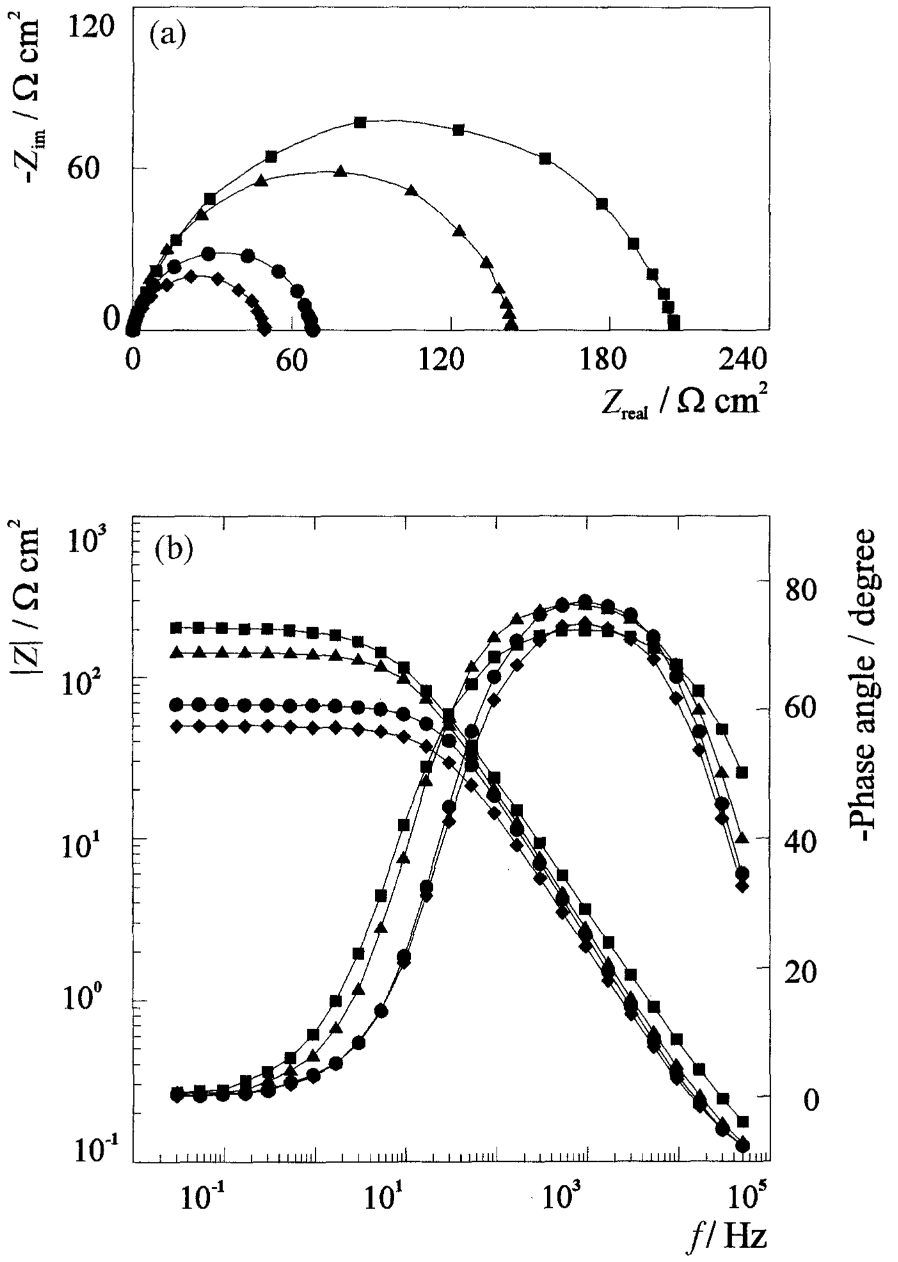
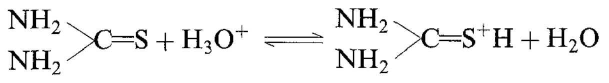


Fig. 3. (a) Nyquist plots and (b) Bode plots for an iron electrode in 0.5 M H_2SO_4 containing 1 mmol dm^{-3} TU at: (■) 20, (▲) 30, (●) 40 and (◆) 50 °C.

Thiourea in acid solution can be presented both as molecular and protonated species:



$$(NH_2)_2C{=}S + H_3O^+ \rightleftharpoons (NH_2)_2C{=}S^+H + H_2O \quad (3)$$

An equilibrium between these two forms is characterized by the equilibrium constant, reported [23] as 0.1. Therefore, in 0.5 M H_2SO_4, used as the electrolyte in our measurements, only about 5% of thiourea was protonated.

Consequently, it is possible that the inhibitory effect of TU is more likely due to a specific adsorption of the molecular species (i.e., blocking effect) than to a specific adsorption of protonated species. The polarization behaviour of the system investigated, as well as the results of impedance measurements, are in support of this statement as follows:

(i) The presence of inhibitor does not change the cathodic polarization behaviour; the Tafel straight lines are quite parallel, giving a value of b_c from 120 to 123 mV, thus suggesting that the HER follows the Volmer mechanism on the Fe electrode [24]. That is also in agreement with the fact that the electrolyte was a rather concentrated solution of a strong acid and that the zeta potential is small. The values of anodic Tafel slope in the presence of TU can be regarded in terms of the dissolution mechanism in the presence of the molecular species, although the b_a value at higher concentration of TU seems rather high [9] and,

(ii) The corrosion reaction can be regarded as a rate process, the rate of which is given by

$$j_{corr} = A \exp(-E^*/\mathcal{R}T) \quad (4)$$

where E^* is the activation energy of corrosion. Taking the logarithm of Equation 4 and substituting j_{corr} from the well known Stern–Geary equation: $j_{corr} = b_a b_c / 2.3(b_a + b_c)R_p$, where $b_a = 2.3\mathcal{R}T/\alpha_a F$

Table 1. Impedance parameters, corrosion currents and inhibition efficiencies of 0.05, 0.1, 0.5, 1.0 and 10.0 mM TU for an iron electrode in 0.5 M H_2SO_4 at 20, 30, 40 and 50 °C

t /°C	c /mM	$Q \times 10^6$ /Ω^{-1} cm^{-2}	n	R_p /Ω cm^2	j_{corr} /mA cm^{-2}	θ /%
20	0.00	206	0.905	87	0.145	–
	0.05	201	0.870	96	0.131	9
	0.10	146	0.908	137	0.092	36
	0.50	160	0.891	199	0.063	56
	1.00	206	0.827	205	0.061	58
	10.00	312	0.819	143	0.088	39
30	0.00	270	0.881	37	0.352	–
	0.05	198	0.898	63	0.207	41
	0.10	199	0.889	70	0.186	47
	0.50	204	0.867	117	0.112	68
	1.00	174	0.879	143	0.091	74
	10.00	202	0.864	92	0.142	59
40	0.00	285	0.889	20	0.674	–
	0.05	282	0.897	26	0.518	25
	0.10	198	0.904	34	0.396	43
	0.50	208	0.867	61	0.221	68
	1.00	160	0.899	67	0.201	71
	10.00	358	0.816	45	0.300	57
50	0.00	446	0.878	12	1.159	–
	0.05	355	0.883	17	0.818	34
	0.10	314	0.879	19	0.732	39
	0.50	241	0.870	41	0.339	72
	1.00	252	0.865	50	0.278	77
	10.00	486	0.786	32	0.435	65

* $R_{el} = 0.10 \pm 0.03\,\Omega\,cm^2$.

and $b_c = 2.3\mathscr{R}T/\alpha_c F$, it follows that

$$\ln R_p/T = E^*/\mathscr{R}T + \text{constant} \qquad (5)$$

where the constant includes A, R, F, α_a and α_c.

Therefore, a plot of $\ln R_p/T$ against $1/T$ gives a straight line from the slope of which E^* can be calculated. Fig. 4 illustrates such a plot for various concentrations of thiourea. Table 2 lists the values of E^* obtained with various inhibitor concentrations. It can be seen that E^* decreases slightly with increasing concentration. It is evident from Fig. 4 and Table 2 that none of the used thiourea concentrations increases E^*, and hence the mechanism of their inhibition must be via blocking effects [25].

Table 2. Activation energies of corrosion process of an iron electrode in 0.5 M H_2SO_4 without and in the presence of TU

c/mM	0.00	0.05	0.10	0.50	1.00
E^*/kJ mol^{-1}	54.3	50.4	54.9	45.0	41.8

Adsorption of thiourea molecules can occur through the Fe–S interaction by replacement of the adsorbed water from the iron surface:

$$(NH_2)CS_{(aq)} + xH_2O_{(ad)} \longleftrightarrow (NH_2)CS_{(ad)} + xH_2O_{(ad)} \qquad (6)$$

where x is the number of water molecules replaced by one molecule of thiourea.

Basic information on interaction between thiourea molecules and an iron surface and their geometric configuration can be provided from the adsorption isotherm. Fig. 5 shows that the experimental data can be well described by the Frumkin adsorption isotherm:

$$\ln \theta/c(1-\theta) = \ln K + 2a\theta \qquad (7)$$

where K is the constant of the adsorption equilibrium including the adsorption energy, and a is the attraction constant characterizing the lateral interaction between the molecules in the adsorption layer. Equation 7 is valid only when one adsorbed molecule displaces one H_2O molecule from the surface ($x = 1$). Negative value for a indicates that mutual repulsion predominates in the adsorption layer. These facts

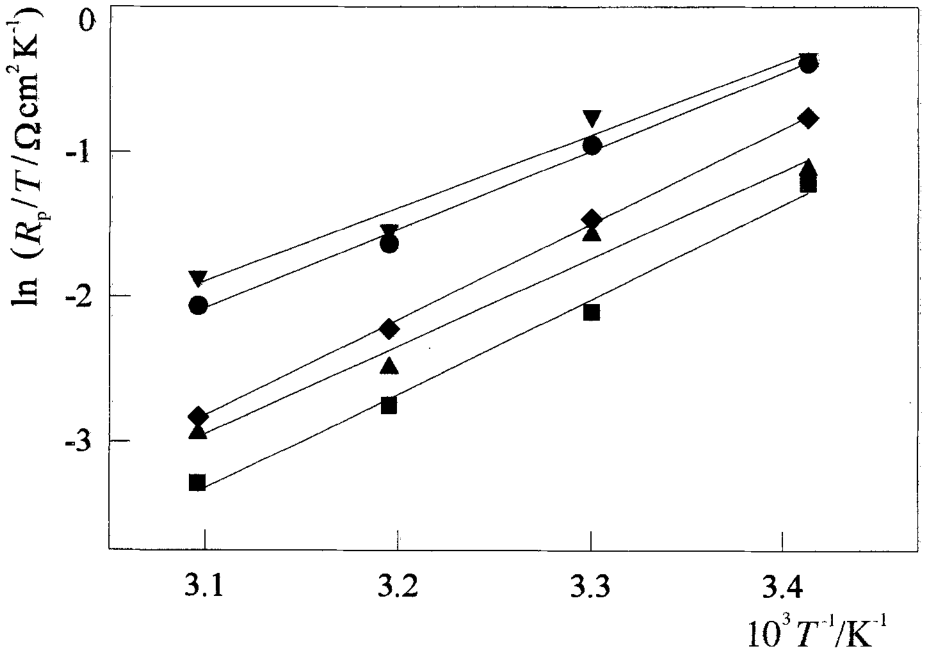


Fig. 4. Arrhenius plot of an iron electrode in 0.5 M H_2SO_4 containing various concentration of TU: (■) 0.05 (▲) 0.1, (●) 1.0 and (◆) 10.0 mM.

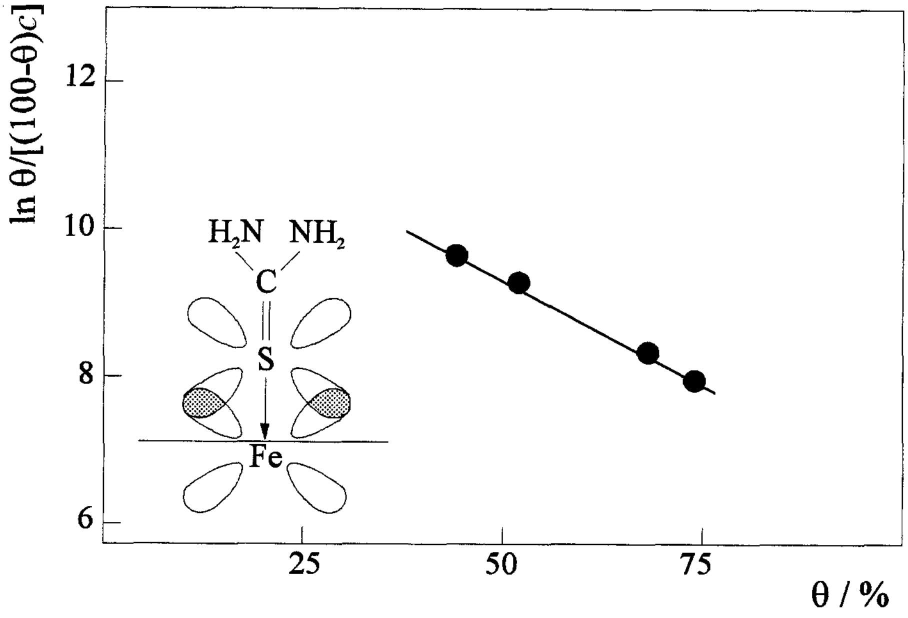


Fig. 5. Frumkin's adsorption isotherm on an iron electrode in a solution of TU in 0.5 M H_2SO_4 at 30 °C.

($a = -4.4$ and $x = 1$) are compatible with vertical adsorption (perpendicular orientation) of thiourea on the electrode surface. The dipole moment of thiourea is in the direction of the C=S bond and the lateral repulsion appears when the molecules are adsorbed vertically. This is not manifested when the molecules are adsorbed horizontally, since then the dipole moment is parallel to the surface.

The free energy of adsorption obtained from the Frumkin isotherm at 30 °C, $\Delta G^{ad} = -39\,\mathrm{kJ\,mol^{-1}}$ indicates a strong adsorption, which is actually chemisorption. The comparable value for free energy of thiourea adsorption on a mild steel electrode surface was reported by Ateya *et al.* [11] $\Delta G^{ad} = -41\,\mathrm{kJ\,mol^{-1}}$. The bond responsible for chemisorption is the formation of a dative link between metal and the organic molecule. The bond could be formed by sharing a pair of electrons, from the inhibitor, with iron. Because sulfur is less electronegative than nitrogen and has two electron pairs available for coordination, the bonding between the thiourea molecule and the iron surface probably occurs via a sulfur atom.

The decrease in inhibitor effectiveness at higher concentration which, according to the literature, can be caused by various factors, such as inhibitor protonation [8, 9], cathodic decomposition [10, 11], is still under the study.

4. Conclusions

(i) The influence of *c*(TU) on ARMCO iron corrosion at 20, 30, 40 and 50 °C was investigated in deaerated 0.5 M H_2SO_4 solution, by means of electrochemical impedance spectroscopy.

(ii) The inhibitor efficiency presents a maximum value for thiourea concentration of about 1 mM. The results show that the addition of thiourea up to the critical concentration increases polarization resistance.

(iii) Electrochemical parameters obtained from impedance and from d.c. measurements are in good agreement, and the a.c. technique can be conveniently used to study the effect of thiourea on the corrosion of iron in sulfuric acid solution.

(iv) The adsorptive behaviour of thiourea on the electrode surface up to the critical concentration follows a Frumkin-type isotherm with lateral repulsion, where the molecules are vertically adsorbed on the electrode surface. $\Delta G^{ad} = -39\,\mathrm{kJ\,mol^{-1}}$ and $a = -4.4$.

(v) On the basis of the study it can be assumed that, up to the critical concentration, thiourea is a mixed type inhibitor. It blocks the iron surface and thus decreases iron dissolution and hydrogen evolution.

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