

## Corrosion Inhibition of Delta 37 Steel in Acid Pickling Solution by Heterocyclic Thiourea Derivatives†

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Galvanostatic cathodic behaviour of Delta-37 Steel in 1 N-H<sub>2</sub>SO<sub>4</sub> pickling bath solutions containing different concentrations of the heterocyclic thiourea derivative. 1-(3-Amino-4-phenylazopyrazol-5-yl)-3-benzoylthiourea [A.P.T.U.] was studied. The study shows that this compound acts as a good corrosion inhibitor for this steel in H<sub>2</sub>SO<sub>4</sub> bath and with an efficiency which reaches 94% at 50°C. The inhibitory action of this compound seems to be due to its adsorption on the metal surface, hence blocking the available area for hydrogen evolution reaction without any change in the mechanism. At low concentration less than  $5 \times 10^{-5}$  M, the additive acts as corrosion accelerator because its concentration is insufficient to block all the anodic sites. The heat of adsorption, Q, was found to be 30.51 K. J./deg. mole. The adsorption of the additive molecule on the metal surface was appeared to be through the sulphur atom. The adsorption process follow the simplified Temkin isotherm. The results show that the surface coverage,  $\theta$  and the inhibition efficiency increases with the rise of temperature.

### INTRODUCTION

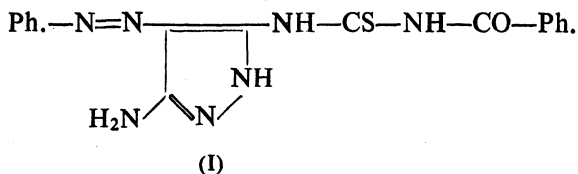
In spite of the great number of materials which have been reported as inhibitors for corrosion of iron and steels, yet researches are directed for highly efficient inhibitors to be used for specific applications, e.g. acid pickling bath of fine articles and in acid cleaning of thermal electric power plants boilers and tubes<sup>1,2</sup>. For this purpose thiourea derivatives which have been repeatedly recommended<sup>3</sup> as sulphur containing inhibitors, have been tested in the present work in a heterocyclic structure where specific features could arise. This is not surprising as much as the behaviour of thiourea derivatives as corrosion inhibitors present a number of interesting features for which controversy does not cease<sup>4-7</sup>. Moreover the action exerted by a given derivative depends on its structure as well as the composition of solution.

In this investigation, a heterocyclic thiourea derivative, viz., 1-(3-amino-4-phenylazopyrazol-5-yl)-3-benzoylthiourea (A.P.T.U.). (I) has been tested as corrosion inhibitor for acid pickling bath of low carbon steel Delta 37

†A product of Delta Steel Mill Company, Mostorod-Cairo (low carbon steel).

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before the cold drawing process. Generally the overall rate of corrosion of iron and steel is controlled by the hydrogen evolution reaction<sup>5</sup>; hence estimation of the rate of either reactions is rewarding.

### EXPERIMENTAL

The techniques employed here are essentially those employed previously<sup>8,9</sup> and stress has been made to achieve the necessary precautions for the study of the hydrogen evolution reaction. The organic additive was prepared, purified and identified following the recommended methods.<sup>10</sup> Delta 37 Steel has been tested. It has the following composition; 0.08% C, 0.03% S, 0.40% Mn, 0.02% P, 0.16% Si and the remaining is iron.

Specimens of steel were used in the form of rods having a cross sectional area of 0.189 cm<sup>2</sup>. The exposed surface area of the specimen was mechanically polished with successive finer grades of metallographic emery papers until it appears free from scratches, then degreased in acetone and finally rinsed by a stream of distilled water. The other chemicals are chemically pure grade reagents. In galvanostatic cathodic polarization measurements the steady state potentials were attained within one minute after each current increment. The potentials were measured against a saturated Ag/AgCl electrode. The solutions were saturated with nitrogen gas 30 minutes prior to immersion. All experiments were carried in air thermostat adjusted at the required temperature with  $\pm 0.1^\circ\text{C}$ .

### RESULTS AND DISCUSSIONS

Steady state potential  $E_{\text{corr}}$  were recorded after 2 hrs. immersion followed by galvanostatic polarization measurements. The galvanostatic polarization curves obtained for Delta 37 steel electrode in 1 N-H<sub>2</sub>SO<sub>4</sub> solution containing various additions of (A.P.T.U.) at different temperatures, viz. 30°, 40° and 50°C. The results are shown in Figs. 1-3 respectively. In presence of this additive, the linear portions of the curves are shifted towards the more cathodic direction, with increasing concentration of the additive. At one and same temperature, the gradients of the linear portion (Tafel slope) do not change significantly with the additive concentration. For the same solution the Tafel slope increases with temperature by 0.5 mV/°C. The slope bc at 30°, 40°, and 50°C in 1 N-H<sub>2</sub>SO<sub>4</sub> amounts to -112, -114 and -120 mV/decade of current respectively,

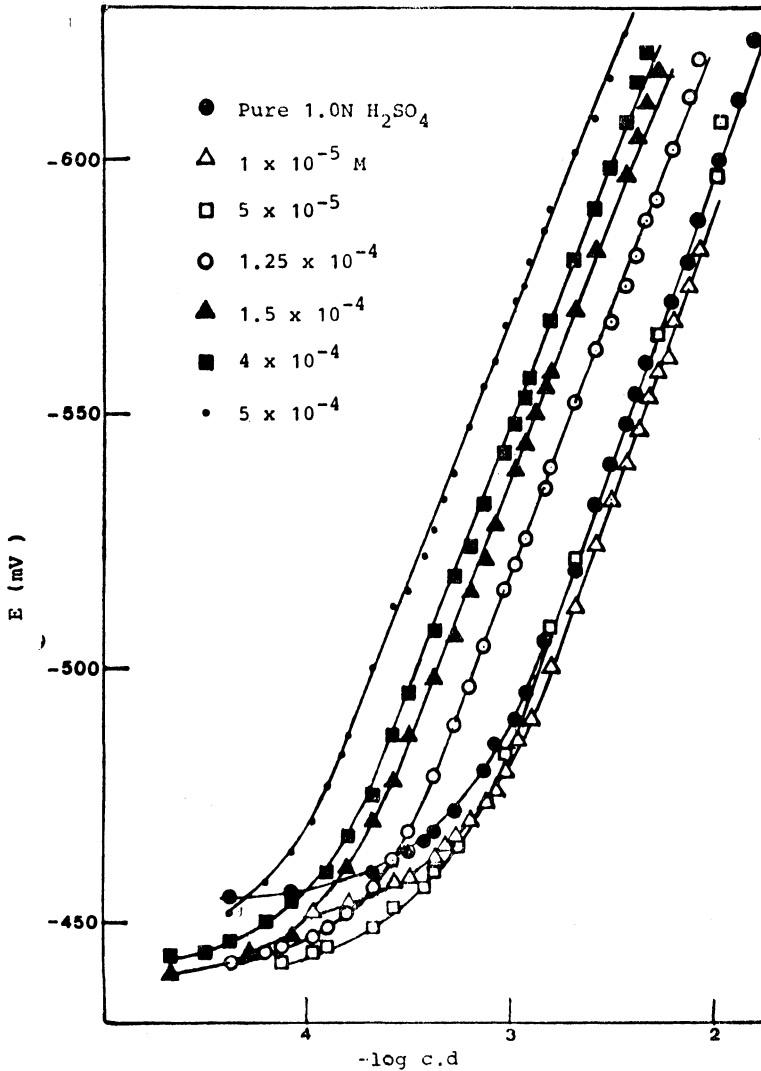


Fig. 1. Effect of additive concentration on the polarization of Delta 37 steel in 1.0 N-H<sub>2</sub>SO<sub>4</sub> at 30°C.

these values for the slope is comparable with that obtained by Selim *et al.*<sup>5</sup> and by Ateya *et al.*<sup>6</sup>. Values of  $bc$  and  $E_{corr}$ . at different additive concentrations are given in Table 1.

At the lowest concentration of (A.P.T.U.) ( $10^{-5}$  M), the potential shifts towards the anodic direction with respect to that of pure H<sub>2</sub>SO<sub>4</sub>; this shift is detectable also in other concentrations for the non-linear portion of the curves, Fig. 1 (3). This occurs whenever the additive is

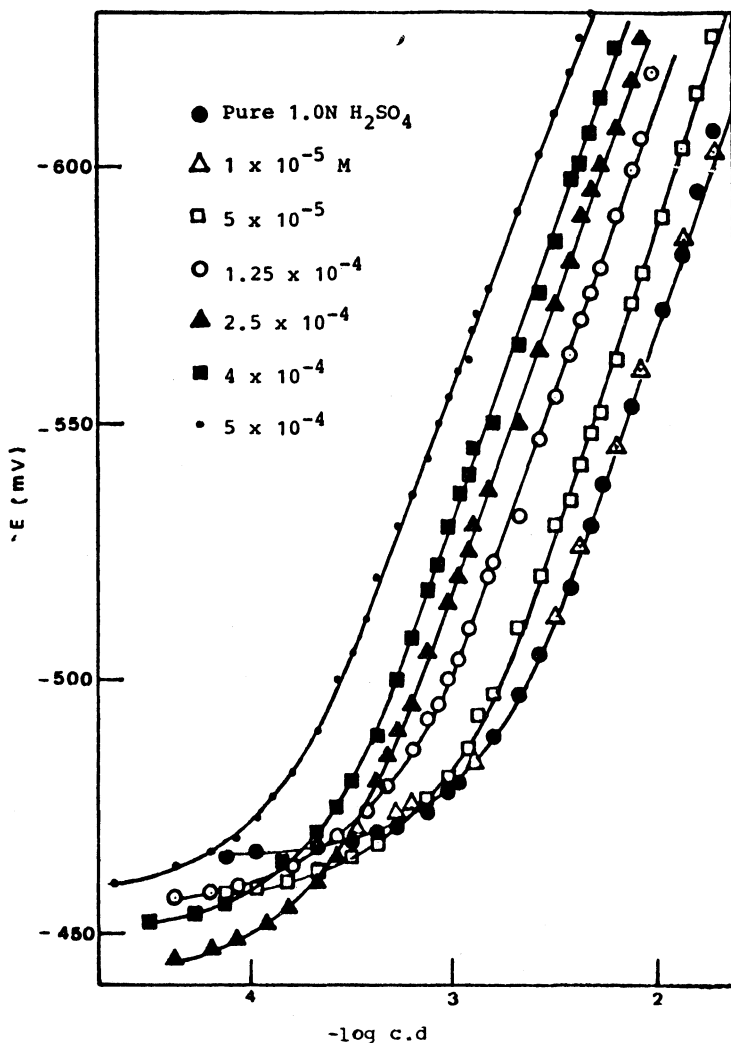


Fig. 2. Effect of additive concentration on the polarization of Delta 37 steel in 1.0 N-H<sub>2</sub>SO<sub>4</sub> at 40°.

adsorbed first on the anodic sites, such behaviour gives rise to acceleration of corrosion at low additive concentration as long as it is insufficient to block all the anodic sites, so it accelerates the corrosion process by formation of local galvanic cells. Upon further increase of the additive concentration, it blocks the anodic sites and then the cathodic ones. Under this condition the linear portion of the cathodic polarization curves is shifted significantly towards the cathodic direction and it acts as an inhibitor. So it seems that (A.P.T.U.) acts as mixed inhibitor as indicated below.

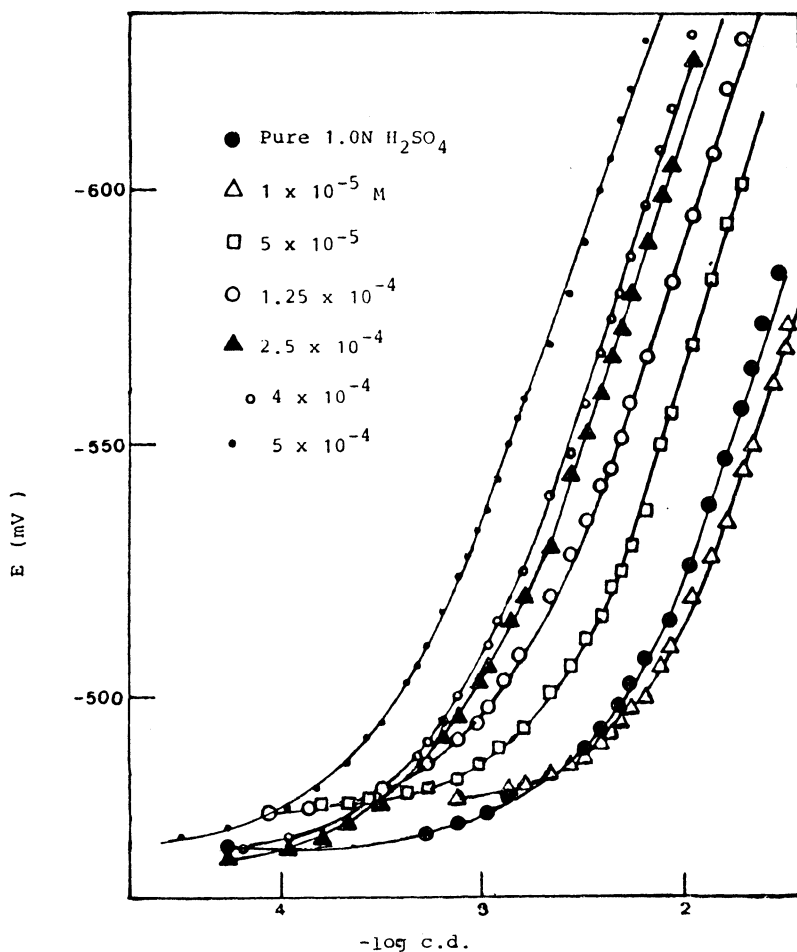


Fig. 3. Effect of additive concentration on the polarization of Delta 37 steel in 1.0 N-H<sub>2</sub>SO<sub>4</sub> 50°C.

The corrosion current,  $I_{\text{corr}}$ , was obtained by extrapolating the cathodic Tafel line to the experimentally measured open circuit corrosion potential<sup>11</sup> ( $E_{\text{corr}}$ ). The values of  $I_{\text{corr}}$ , as a function of temperature and additive concentration are shown in Fig. (4). The inhibiting efficiency of (A.P.T.U.)  $P_I$  was calculated as the percent change in  $I_{\text{corr}}$ . From the following relationship.

$$P_I = \frac{I_{\text{corr. pure}} - I_{\text{corr. add.}}}{I_{\text{corr. pure}}} \times 100$$

values of  $P_I$  are given in Table (1). The inhibitory action of this additive

TABLE 1

THE EFFECT OF TEMPERATURE AND CONCENTRATION ON THE CORROSION POTENTIAL,  $E_{cor}$ , CATHODIC TAFEL SLOPE  $bc$ , EXCHANGE CURRENT DENSITIES  $i_0$ , POLARIZATION RESISTANCE  $R$ , PER CENT CHANGE IN EACH, SURFACE COVERAGE  $\theta$ , AND THE RATIO  $r$  [-VE VALUES OF  $P_i$ ,  $P_{i_0}$ ,  $P_R$  MEANS ACCELERATION OF THE CORROSION RATE]

Temp.	Conc. of (A.P.T.U.) mole	$-E_{cor}$ mV	$-bc$ mV/dec.	$I_{corr.}$ $A/cm^2 \times 10^{-4}$	$i_0$ $A/cm^2 \times 10^{-6}$	$R$ ohm. $cm^2$	$\theta$	$P_i$	$P_{i_0}$	$P_R$	$r$
30°C	zero	454	112	5.62	7.94	30	—	—	—	—	—
	$1 \times 10^{-5}$	450	114	5.96	10.59	30	—	-0.60	-32.7	zero	—
	$5 \times 10^{-5}$	441	114	3.98	8.41	50	—	29.20	-5.9	40	—
	$1.25 \times 10^{-4}$	440	104	1.78	2.66	90	0.47	68.38	66.5	66.66	0.97
	$2.5 \times 10^{-4}$	437	102	1.08	1.59	170	0.65	80.72	80.1	82.35	0.99
	$4 \times 10^{-4}$	442	102	0.94	1.26	190	0.72	83.21	48.15	84.21	1.01
	$4 \times 10^{-4}$	447	102	0.63	0.53	290	0.82	88.78	92.32	89.65	1.05
40°C	zero	464	114	12.59	15.85	16.5	—	—	—	—	—
	$1 \times 10^{-5}$	466	117	12.97	18.84	15	—	-3.04	-18.85	-10.0	—
	$5 \times 10^{-5}$	456	120	7.94	14.13	30	—	36.77	10.88	45	0.29
	$1.25 \times 10^{-4}$	456	112	3.76	5.31	50	0.60	70.0	66.5	67	0.86
	$2.5 \times 10^{-4}$	442	113	2.11	3.76	95	0.72	83.21	76.29	82.63	0.92
	$4 \times 10^{-4}$	451	110	1.88	2.66	100	0.79	85.04	83.21	83.5	0.98
	$5 \times 10^{-4}$	460	103	1.12	1.06	160	0.87	91.09	93.32	89.68	1.03
50°C	zero	474	120	39.81	50.12	5.5	—	—	—	—	—
	$1 \times 10^{-5}$	478	120	53.09	63.1	2.5	—	-33.3	-25.9	-120	—
	$5 \times 10^{-5}$	475	128	19.95	31.62	15	—	49.89	36.91	63.35	0.74
	$1.25 \times 10^{-4}$	475	128	11.22	18.84	20	0.72	71.82	62.42	72.5	0.87
	$2.5 \times 10^{-4}$	464	126	6.31	11.89	35	0.81	84.15	76.29	84.29	0.91
	$4 \times 10^{-4}$	468	124	5.62	9.44	40	0.84	85.87	81.16	86.29	0.95
	$5 \times 10^{-4}$	470	114	2.66	3.16	85	0.92	93.32	93.69	93.53	1.00

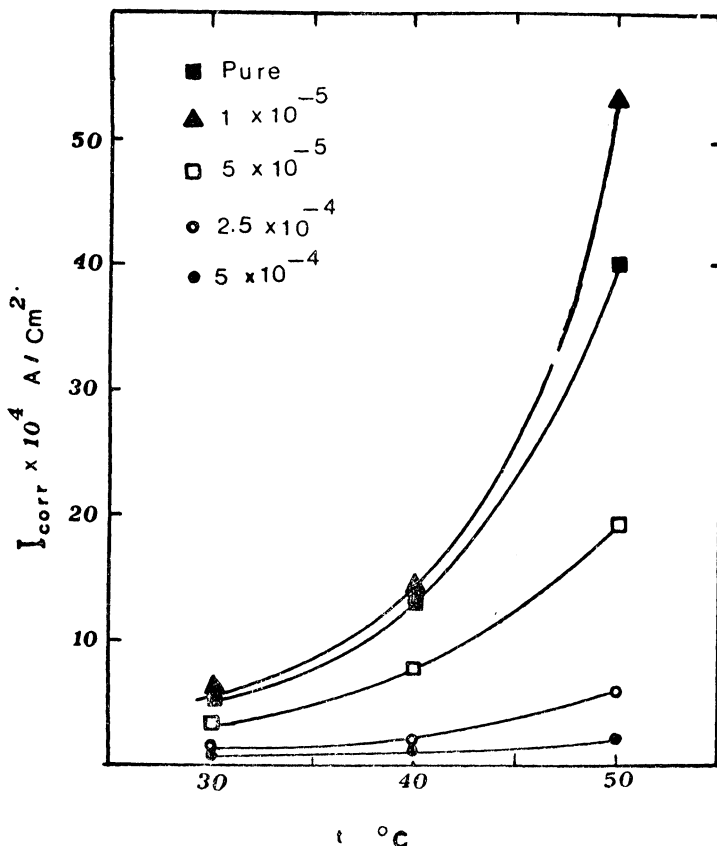


Fig. 4. Effect of temperature and additive concentration on the corrosion current of Delta 37 steel in 1.0 N-H<sub>2</sub>SO<sub>4</sub>.

increases with its concentration and solution temperature in 1 N-H<sub>2</sub>SO<sub>4</sub> (Fig. 5).

The exchange current densities of the hydrogen evolution reaction (H.E.R.)  $i_0$  were determined as the current density at the equilibrium potential of (H.E.R.)<sup>6</sup>. The efficiency of (A.P.T.U.) in reducing the rate of the hydrogen evolution reaction  $P_{i_0}$  was determined as the per cent change in  $i_0$  from the relation

$$P_{i_0} = \frac{i_0 \text{ pure} - i_0 \text{ add.}}{i_0 \text{ pure}} \times 100$$

The values of  $i_0$ ,  $P_{i_0}$  and the ratio  $r = P_{i_0}/P_I$  are given in Table 1 from which we notice that at low concentration ( $r \ll 1$ ) indicates predominance of anodic rate control<sup>6</sup>. As the concentration increases the value of ( $r$ ) increases to reach ( $r > 1$ ) which indicates cathodic rate control<sup>6</sup>. Thus one concludes that (A.P.T.U.) acts as mixed inhibitor.

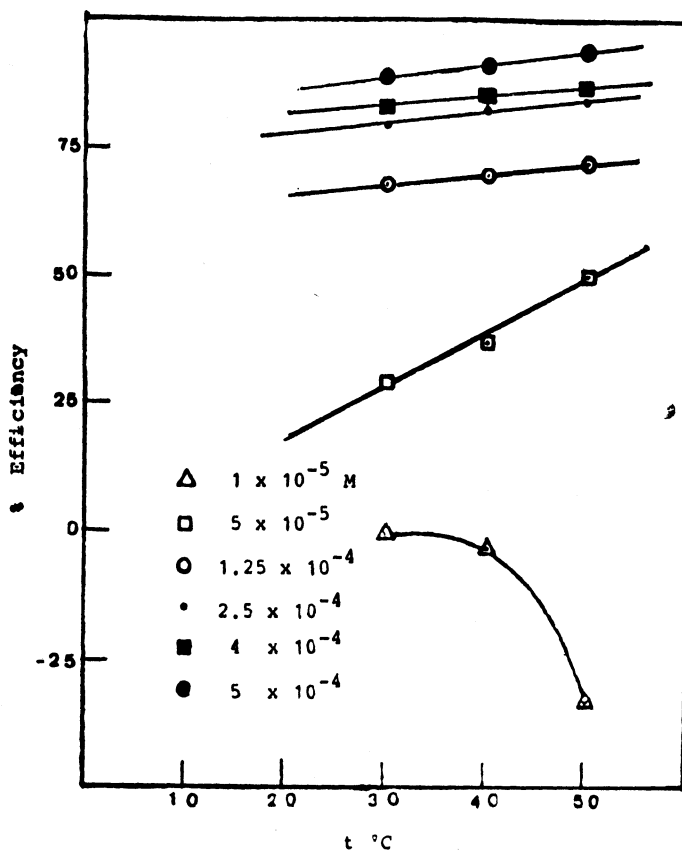


Fig. 5. Relation between additive concentration, temperature, and corrosion inhibition efficiency in 1 N-H<sub>2</sub>SO<sub>4</sub> solution.

The polarization resistance  $R$  was determined by plotting  $(E - E_{\text{corr}})$  in the low polarization region  $[(E - E_{\text{corr}}) < 20 \text{ mV}]$  vs.  $I_c$  which give straight line with a slope  $\Delta E / \Delta I$  equal to the polarization resistance  $R$  values of  $R$  are given in Table (1) which indicate that  $R$  increases with the increase of (A.P.T.U.) concentration, and decreases with rise of temperature. The efficiency of (A.P.T.U.) as an inhibitor may also be given as

$$P_R = \frac{R_{\text{add.}} - R_{\text{pur}}}{R_{\text{add.}}} \times 100$$

when there is no significant change in  $bc$ , values of  $P_R$  which given in Table (1) are closed to the values of both  $P_I$  and  $P_{I0}$  indicating that (A.P.T.U.) acts as inhibitor for Delta 37 steel corrosion in 1 N-H<sub>2</sub>SO<sub>4</sub> solution via decreasing the area available for corrosion by mechanical separation. So we can conclude that the role played by inhibitors in deceleration of rates of metallic corrosion is initiated by its adsorption in the double layer. Further reactions may then lead to the formation of



surface compounds or even a thick layer. Adsorption of the compound may affect reaction rates through enlarging the activation energy of the h.e.r. or merely decrease the effective surface area for reaction of  $H^+$  ions with the surface. From the foregoing results, one may conclude that this additive acts as an inhibitor via reduction of the rate of the h.e.r., even though the mechanism of the latter reaction does not change as shown below. In other words this inhibitor exerts its action by decreasing the effective corroding surface area, hence it belongs to the blocking adsorption type inhibitor.

To show whether the adsorbed molecule retards the h.e.r. by merely mechanical separating the reactants or providing a more hindered pathway, the apparent activation energy for the overall corrosion reaction was estimated in the presence and absence of this additive by plotting  $\log I_{\text{corr}}$  vs.  $T^{-1}$ , Fig. (6). The results indicate that there is no significant change in the apparent activation energy. It amounts to 80.26 KJ/deg.

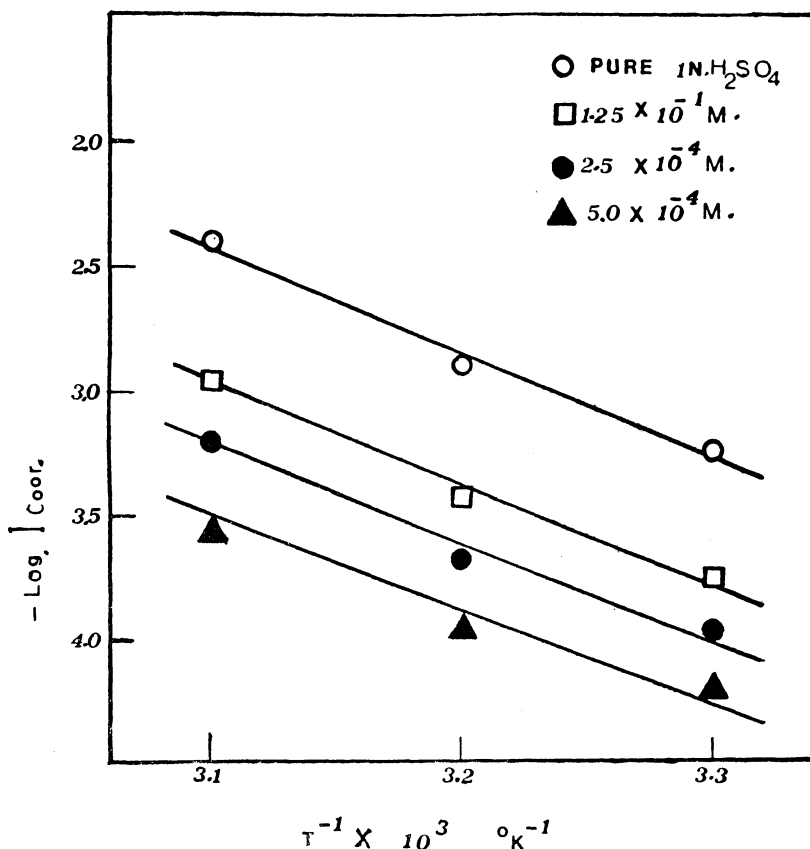


Fig. 6. Arrhenius plot;  $\log I_{\text{corr}}$  vs.  $T^{-1}$  in absence and presence of the additive in 1.0 N-H<sub>2</sub>SO<sub>4</sub>.

mole. This value is comparable with those characterizing electron transfer controlled processes<sup>12</sup>. Thus the insignificant changes in each of the Tafel slopes and in the apparent activation energy in absence and presence of the inhibitor indicate that this additive decreases the probability of interaction of  $H^+$  ions with the corroding surface. The factor of reduction of the probability amounts to 92%. This value is obtained from the relative shift in  $\log I_{\text{corr}}$  vs.  $T^{-1}$  plots, Fig. (6), at a concentration of  $5 \times 10^{-4}$  M of the additive.

The degree of surface coverage,  $\theta$  may be evaluated from the linear parallel portions of the cathodic curves at a given potential by the expression:

$$\frac{i_{c_2}}{i_{c_1}} = 1 - \theta$$

where  $i_{c_2}$  and  $i_{c_1}$  are the measured currents in presence and absence of the inhibitor respectively, at the same potential<sup>13</sup>. The degree of surface coverage  $\theta$  increases with the additive concentration and temperature. The effect of temperature is more perceptible at low concentrations, Fig. (7). Thus the supplied thermal energy activates the adsorption pro-

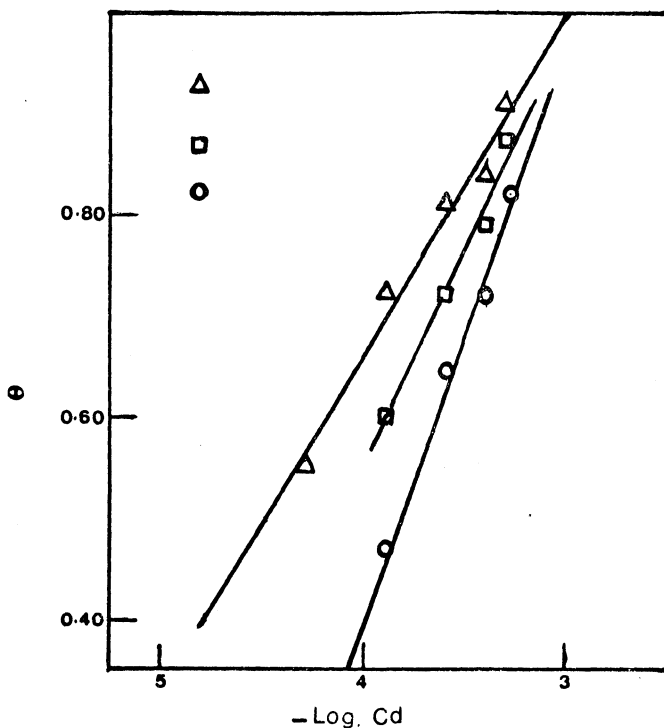


Fig. 7. Temkin adsorption isotherm for adsorption of the additive on Delta 37 steel at  $-570$  mV.

cess rather than the desorption one. It is worthwhile to mention that the degree of surface coverage  $\theta$  varies with the additive concentration  $C$  following the simplified Temkin isotherm<sup>14</sup>, according to which  $\theta$  increases linearly with  $\log C$ , as shown in Fig. 7.

The nature of this adsorption process affected by the additive, as being a physical or chemical process, may be elucidated from the magnitude of heat of adsorption,  $Q$ . The latter was estimated by the relation:

$$\left[ \frac{d \log C}{d(1/T)} \right]_{\theta, E_h} = -\frac{Q}{2.3R}$$

which has been found to be 30.51 KJ/deg. mole regardless of  $\theta$  as shown in Fig. 8.

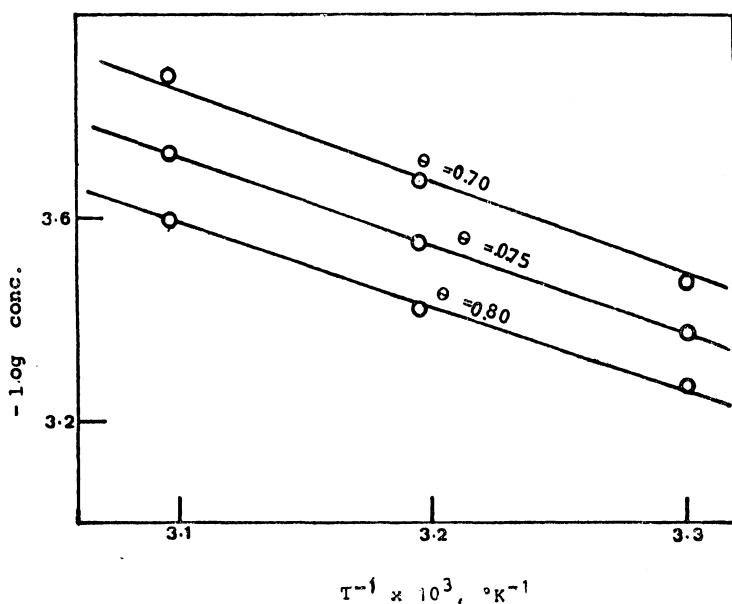


Fig. 8 Estimation of the heat of adsorption  $Q$ ; plot of  $\log C$  vs.  $T^{-1}$  at  $-570$  mV as a function of the degree of surface coverage,  $\theta$

The value for  $Q$  slightly exceeds those characterizing physical adsorption.

From the foregoing discussion one may conclude that the adsorption of the additive on the surface of steel is likely to be of chemical nature, *i.e.*, the adsorption process occurs along a specific center of the inhibitor.

This is in agreement with the suggestion proposed by Donnelly<sup>4</sup>. The adsorption of thiourea molecule takes place through the sulphur atom due to the overlap of the d-orbitals of both the sulphur and iron atoms which have d-orbitals of the symmetry compatible with each other forming

a  $\pi$ -bond. This bond is not formed with other atoms in the molecule such as oxygen and nitrogen atoms which have no d-orbitals hence incapable to form such  $\pi$ -bonding.

The value of Q was found to be independent on  $\theta$ , this means that the molecule of (A.P.T.U.) seems to be sparsely landed on the surface. This interpretation is compatible with the nature of an atomically heterogenous surface like that of steel.

### REFERENCES

1. A. K. Mindyuk, Yu S. Kost. A. D. Tkach and V. I. Soholokh *Fiz. Khim. Mekh. Mater.*, **1**, 94 (1989).
2. M. V. Uvlyuk, V. I. Ponomarenko and V. I. Malygina, *Metall. Koksokhim.*, **89**, 382 (1986).
3. I. A. Ammar and F. M. Khorafi, *Metalloberfl.*, **27**, 14 (1973).
4. B. Donnelly, T. C. Dounie, R. Crzeskowiak, H. R. Hemburg and D. Short, *Corros. Sci.*, **14**, 597 (1974).
5. M. L. Selim, A. A. Yassin and B. G. Ateya, ——— **17**, 923 (1977).
6. B. G. Ateya, B. E. El-Anadouli and F. M. El-Niazy, ——— **24**, 497 (1984).
7. A. Frignani, M. Tassinari, C. Monticelli, and G. Trabonelli, ——— **27**, 75 (1987).
8. Annual Book of A.S.T.M. Standards, Part 10, G<sub>3</sub>, pp. 794–802 (1980).
9. M. M. Abou Romia and M. M. Hefny, *J. Electronal Chem.*, **136**, 339 (1982).
10. N. S. Ibrahim, Ph.D. Thesis, Cairo University (1978).
11. G. Trabonelli and V. Carasiti, *Advances in Corrosion Science and Technology* (Eds.) M. G. Fontana and R. Staehle, Plenum Press, New York, Vol. 1, p. 47 (1970).
12. L. I. Antropy, *Theoretical Electrochemistry*, Mir Publishers, Moscow, p. 394 (1972).
13. I. A. Ammar and S. Darwish, *Corros. Sci.*, **7**, 579 (1967).
14. M. I. Temkin, *Zh. Fiz. Khim.*, **15**, 296 (1941).

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