

KINETICS STUDY OF THE CONDENSATION PRODUCTS OF ISATIN AS CORROSION INHIBITORS OF STEEL

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ABSTRACT

This investigation is designed to apply recent kinetic-thermodynamic model on the data obtained from acidic corrosion of steel using sulphur containing compounds. Comparison between the results obtained from the model and those using Flory-Huggins and Frumkin adsorption isotherms has been examined in details. The inhibitory effect of the condensation products of thiosemicarbazide (TSC) and aminothiophenol (ATP) with isatin (I) namely, isatin thiosemicarbazide (ITSC) and isatin aminothiophenol (IATP) was investigated. Correlation of the structural changes with the protection efficiency of ITSC and IATP with those of the parent TSC and ATP was reported. A high inhibition efficiency (> 90%) of ITSC and IATP for acidic corrosion of steel was determined at its low concentration (2×10^{-4} M) by gasometry, weight loss and polarization measurements. The experimental results indicate that the presence of adsorbed inhibitors on steel surface does not affect the mechanism of hydrogen evolution. The effect, however, was more pronounced on the cathodic rather than on the anodic process.

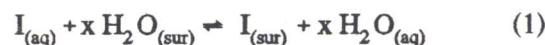
Keywords: Kinetic-thermodynamic model, Flory-Huggins, Frumkin adsorption isotherms, Corrosion inhibition, Steel.

INTRODUCTION

The action of an inhibitor in aggressive acid media is assumed to be due to its adsorption at the metal/solution interface. This phenomenon could take place via (i) electrostatic attraction between the charged metal and the charged inhibitor molecules, (ii) dipole type interaction between uncharged pairs in the inhibitor with the metal, (iii) π -interaction with the metal and (iv) a combination of all the above [1]. If the adsorption process involves charge sharing or charge transfer from the inhibitor molecules to the surface (meaning overlap of occupied ligand nonbonding orbitals with metal empty inner "d" or "f" orbitals) a coordinate type bond is formed and the process is termed chemisorption [2]. This situation can arise if the inhibitor molecule contains lone pairs of electrons; multiple bonds or conjugate π -type system [3].

Theoretically speaking the adsorption process has been regarded as a simple substitutional process, in which an inhibitor molecule in the aqueous phase

substitutes an "x" number of water molecules adsorbed on the metal surface [4] vis.



x has been termed the size ratio and is simply the number of water molecules replaced by one inhibitor molecule. Basically, all isotherm expressions are of the form: [5]

$$f(\theta, X) \exp(-a\theta) = K.C \quad (2)$$

where $f(\theta, X)$ is the configurational factor which depends essentially on the physical model and assumptions underlying derivation of the isotherm.

This work was aimed to investigate the effect of the introduction of isatin molecule to TSC and ATP to improve their inhibiting power for the corrosion of steel in acid solutions. The results obtained were

treated to obtain kinetic parameters for corrosion inhibition process using the kinetic-thermodynamic model and common adsorption isotherms.

EXPERIMENTAL

Mild steel samples used in gasometry and weight loss measurements were in 23.0 mm length and 17.0 mm diameter rods and having the following chemical composition (by percent weight): C= 0.14, Si= 0.13, Mn= 0.57, P= 0.21, S= 0.15, Cr= 0.03, Ni= 0.03, V= 0.06, Cu= 0.04, Fe to 100. Before the measurements, the samples were mechanically polished with a series of emery paper starting with a coarse one and proceeding in steps to finer grades, washed thoroughly with distilled water and dried with acetone. The steel specimens were placed in a vessel having the same form as that described by Mylius, it allowed the volume of hydrogen evolved to be measured as a function of time. All the experiments were carried out at $30 \pm 0.1^\circ\text{C}$. The reactions were done under stagnant conditions and the rates followed for a maximum of one hour to avoid drastic changes in surface characteristics.

Polarization curves recorded by Wenking Potentiostat model MP 87, on a disc electrode (0.56 cm^2 area) using an undivided cell equipped with a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference. The working electrode, consisting of the same mild steel as above within a PTFE sheath. The potential was scanned at 20 mV/min, starting corrosion potential, E_{corr} , going first in the negative direction.

Inhibitors:

Thiosemicarbazide, aminothiophenol and isatin were obtained from Alderich chemical company and were used without further purification.

Preparation of ITSC and IATP

A solution of isatin (0.01M) in ethanol (30 ml) was added to a solution of TSC or ATP (0.01M) in ethanol (30 ml). The reaction mixture was refluxed with stirring for 2 hours. Upon cooling, the precipitated products were filtered off, washed with ethanol, ether and dried *in vacuo*. The isolated products were recrystallised twice from DMF. All test solutions contained 10 vol % of

dimethylformamide to maintain complete solubility.

RESULTS AND DISCUSSION

To correlate the corrosion inhibition behaviour of the investigated compounds to their molecular structures, the compounds were divided into two categories. A simple compounds, thiosemicarbazide (TSC), aminothiophenol (ATP) and isatin (I); and the condensation products of TSC and ATP with isatin namely, isatin thiosemicarbazide (ITSC) and isatin aminothiophenol(IATP).

Figure (1) gives the variation of the volume of hydrogen gas as a function of time for mild steel immersed in 2M sulphuric acid/10% DMF in the absence and presence of different concentrations of ATP at 30°C . In all cases the rate of hydrogen evolution decreases with increasing the inhibitor concentration. This indicates that ATP retards the dissolution rate of steel in acid medium.

Relationship between the mass loss and the concentration of TSC and ATP at 30°C is presented in Figure (2). As the concentration of these compounds increases the weight loss decreases. Figure (3) gives the variation of percentage inhibition with the logarithmic concentration of these compounds. The results have the characteristics of S-shaped adsorption isotherms and is indicative of adsorption mechanisms for the inhibition processes. Inspection of these curves show that the data obtained from the gasometry are in good agreement with those obtained from weight loss measurements.

Surprisingly, isatin was found to behave as weak inhibitor yet at concentrations $> 0.01\text{M}$ even though it has a secondary nitrogen coordinating centre. This behaviour could be attributed to the presence of more than one electron withdrawing centres ($\text{C}=\text{O}$) on the isatin. In acidic media, these centres are very poorly coordinated to the metallic surface. The importance of studying isatin was to illustrate the effect of the products formed from its condensation with the other simple compounds (TSC and ATP) as corrosion inhibitors. Figure (3) also shows that ATP is more efficient than TSC. This behaviour may be attributed to the rigidity of the π -delocalized system of ATP compared to the saturated TSC molecule which exerts free rotation, thus decreasing the possibility of its attachment to the metallic surface.

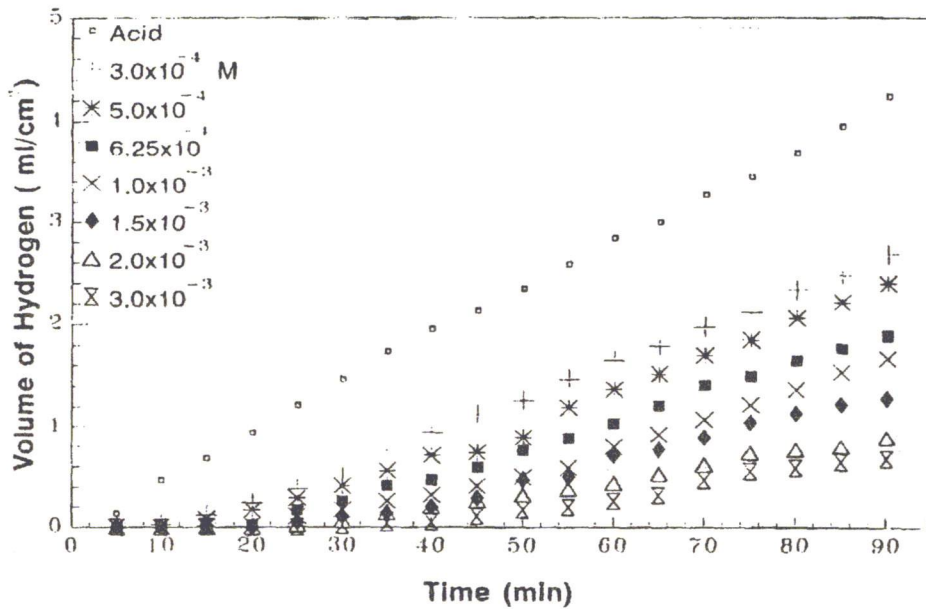


Figure 1. Variation of the volume of hydrogen gas as a function of time for mild steel immersed in 2M sulphuric acid/10% DMF in the absence and presence of different concentrations of ATP at 30°C.

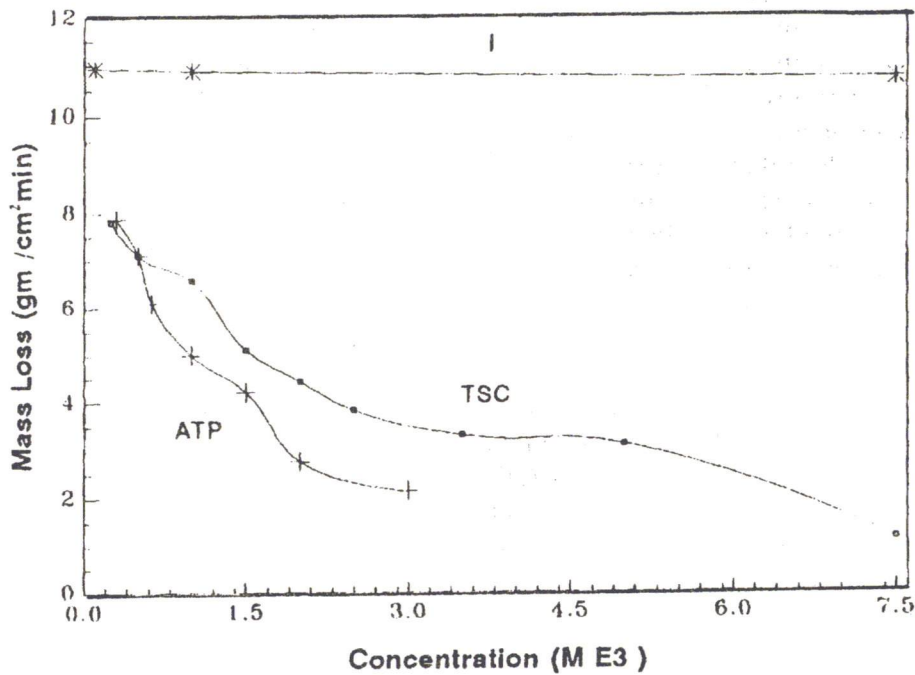


Figure 2. Relationship between the mass loss and the concentration of TSC, ATP and I at 30°C.

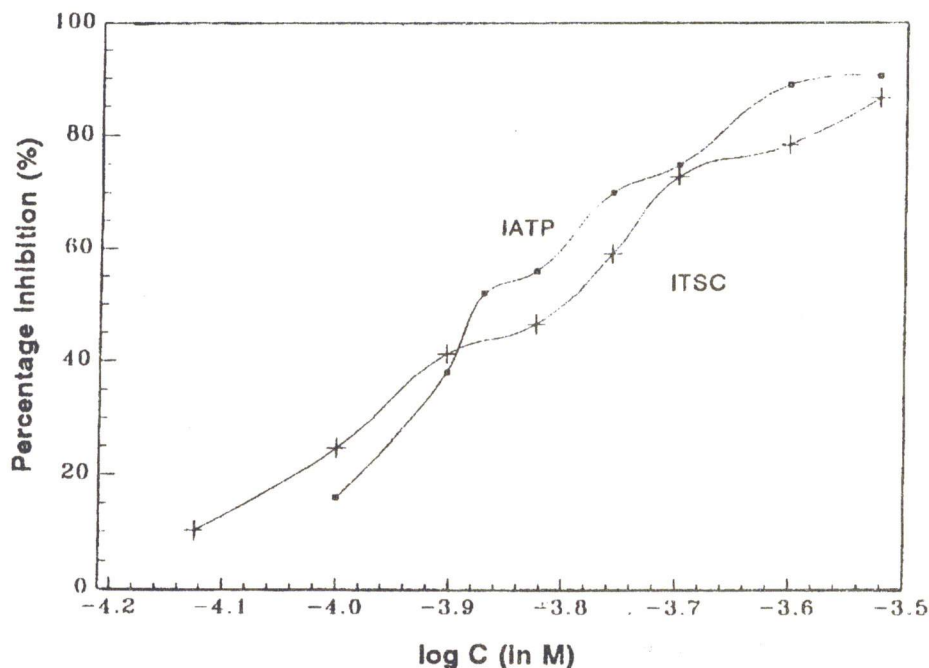


Figure 3. Variation of percentage inhibition with the logarithmic concentration of TSC and ATP.

Anodic and cathodic potentiodynamic polarization curves for steel in 2M sulphuric acid 10%/DMF in the absence and presence of 2×10^{-3} M of TSC, ATP and I (1×10^{-2} M), owing to its low reactivity) at 30°C are presented in Figure (4). The corresponding cathodic and anodic polarization curves exhibit Tafel type behaviour. It is clear that for TSC and I the anodic polarization curves are almost unaffected by the inhibitor in the medium. However, these compounds induced an increase in the cathodic overvoltage suggesting a cathodic type inhibitors. On the other hand, ATP affects both the cathodic and anodic polarization curves with a more pronounced effect on the cathodic side. This suggest that ATP acts as a mixed type inhibitor. The observed induced anodic overpotential for ATP is attributed to the benzene moiety of ATP which increases the π -electron density of the system. Thus, enhancing multilayer adsorption process. The electrochemical parameters of the simple compounds obtained from the polarization curves are presented in Table (1). These include cathodic and anodic Tafel constants (β_c , β_a), corrosion potential E_{corr} , corrosion current i_{corr} and the percentage reduction of the corrosion current $\%i_{\text{corr}}$. The data indicate

that β_c , β_a almost remain unchanged for all compounds which reveals that the inhibition of corrosion by these simple compounds has no effect on the mechanism of steel corrosion in acid medium. This suggest that the adsorbed inhibitor molecules exert their action by decreasing the effective metallic surface area by blocking the metal surface, hence, acting as blocking adsorption type inhibitors.

The above results also showed that the inhibition efficiency are not in agreement with the percentages determined by chemical measurements. This observation was earlier reported [6-8]. The disagreement between electrochemically and chemically determined rates was attributed to the operation of a separate potential-independent (chemical dissolution) process [9], which is co-existent with the electrochemical process but not measured by the polarization curve.

Variation of percentage inhibition as a function of the logarithmic concentration of ITSC and IATP at 30°C is illustrated in Figure (5). The results exhibited S-shaped adsorption isotherms.

Remarkably, the results indicated that, coupling of isatin with the simple compounds to form ITSC and IATP enhanced the protection efficiency markedly.

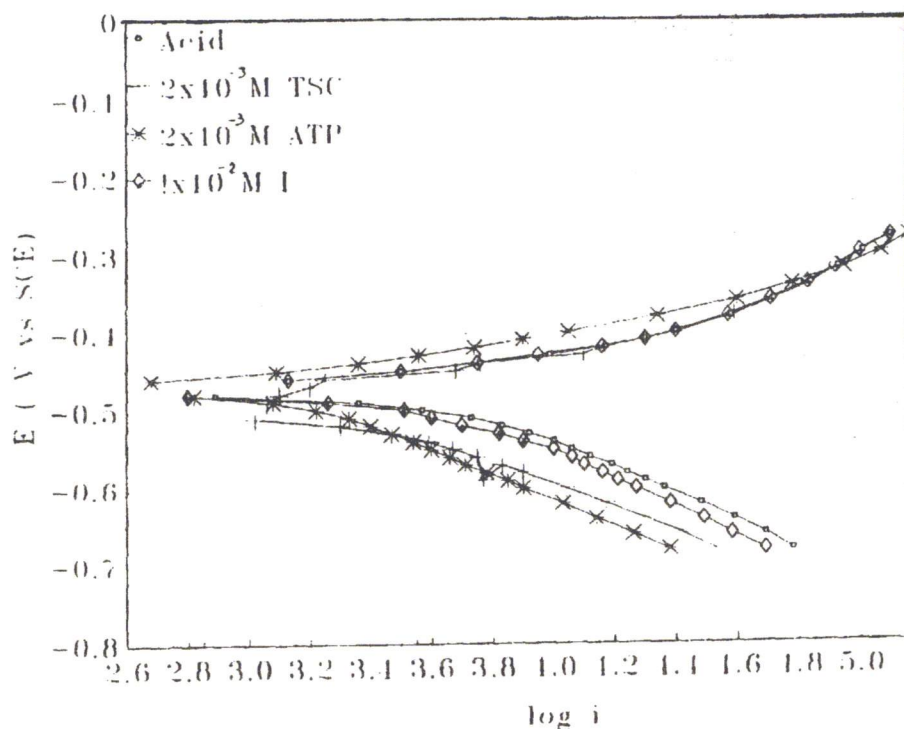


Figure 4. Anodic and cathodic potentiodynamic polarization curves for steel in 2M sulphuric acid 10%/DMF in the absence and presence of 2×10^{-3} M of TSC, ATP and I (1×10^{-2} M), owing to its low reactivity) at 30°C .

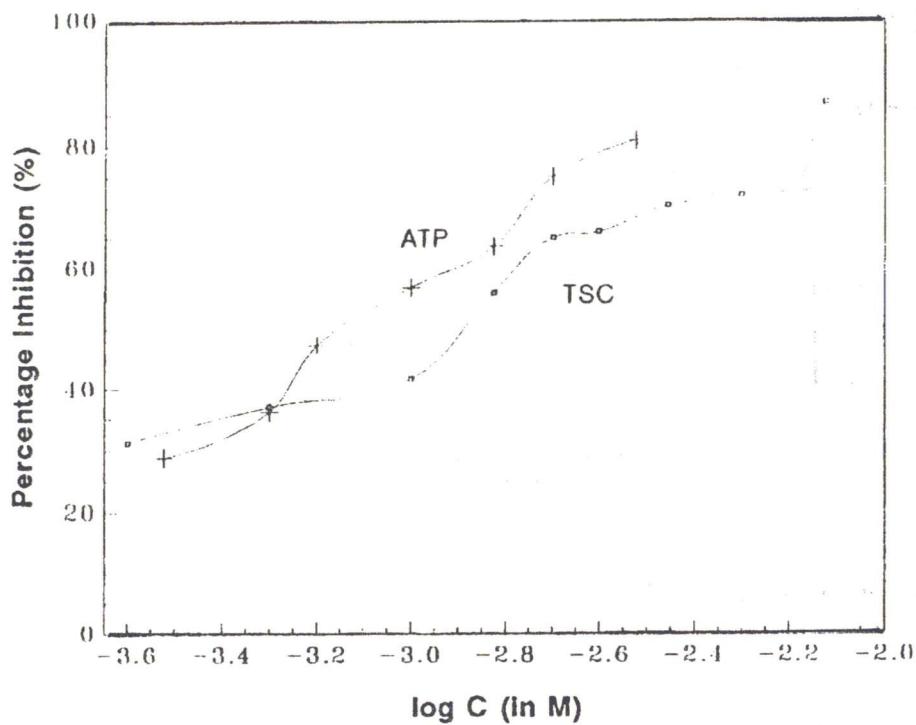


Figure 5. Variation of percentage inhibition as a function of the logarithmic concentration of ITSC and IATP at 30°C .

Moreover, it was observed that ITSC is more efficient than IATP. The terminal $-NH_2$ group and the $=NH$ group of ITSC will donate their σ electrons to the adjacent $C=S$ centre of adsorption. Thus, the electron density will increase on the ligating sulphur atom. This may explain the higher protection efficiency observed by ITSC over IATP.

Figure (6) manifested the polarization curves of steel in 2M $H_2SO_4/10\%$ DMF in the absence and presence of $3 \times 10^{-4} M$ ITSC and IATP at $30^\circ C$. Inspection of this figure shows that the ITSC and IATP affect both cathodic and anodic overvoltages with a more effect on the cathodic curves, suggesting

that these compounds act as mixed type inhibitors. In spite of TSC does not affect the anodic reaction, ITSC affect the cathodic and anodic reactions. This might b attributed to the delocalized π -system of the benzene ring of isatin moiety. The electrochemical parameters obtained from the dissolution of steel in presence of $3 \times 10^{-4} M$ ITSC and IATP are given in Table (1). Inspection of this table indicates that these compounds has no effect on the dissolution mechanism of steel in acid medium. Hence, these inhibitors exert their action by blocking the metal surface, thus reducing its effective corroding areas suggesting blocking-type inhibitors.

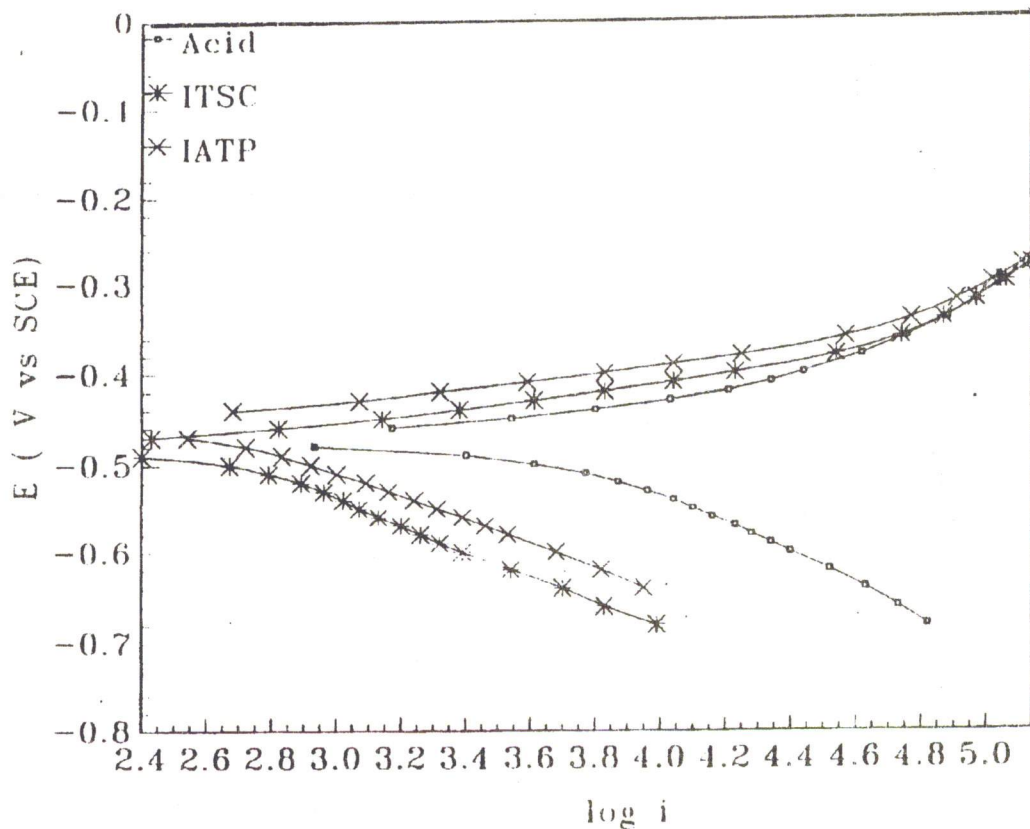


Figure 6. Polarization curves of steel in 2M $H_2SO_4/10\%$ DMF in the absence and presence of $3 \times 10^{-4} M$ ITSC and IATP at $30^\circ C$.

To evaluate the kinetic parameters and correlate them to their corrosion inhibition mechanism, it is now of value to analyze the kinetic data obtained in

the presence of the investigated inhibitors from the stand point of the generalized mechanistic scheme proposed by El-Awady et al [10,11].

Table 1. Corrosion potentials, Tafel constants, corrosion current and percentage of corrosion rate determined chemically and electrochemically for steel in 2.0 M H₂SO₄ 10% DMF at different temperatures in absence and presence of 2.0 x 10⁻³ M Thiosemicarbazide.

Compound	E _{Corr} (V)	-β _c (V/dec)	β _a (V/dec)	i _{Corr} (mA.cm ⁻²)	%i _{corr}
Acid	-0.470	0.168	0.068	2.985	-
2x10 ⁻³ M TSC	-0.485	0.162	0.067	1.400	53.0
2x10 ⁻³ M ATP	-0.470	0.166	0.070	1.258	58.8
1x10 ⁻² M I	-0.470	0.164	0.068	1.958	07.3
3x10 ⁻⁴ M ITSC	-0.485	0.156	0.048	0.421	85.0
3x10 ⁻⁴ M IATP	-0.460	0.138	0.044	0.422	85.0

The curve fitting of TSC, ATP, ITSC and IATP data to the kinetic-thermodynamic model (Eq. 3) at 30°C is given in Figure (7).

$$\frac{\theta}{(1 - \theta)} = k[I]^y \quad (3)$$

As seen, good straight line fits are given for the compounds used. Hence, the suggested model satisfactory fits the obtained experimental data. The slope of such lines is the number of inhibitor molecules occupying a single active site, y and the intercept is $\log K'$, the binding constant [3]. As mentioned, $1/y$ gives the number of active sites occupied by a single organic molecule and K'^y is the equilibrium constant for the adsorption process. Table (2) gives the values of $1/y$ and K for the studied compounds. This table shows that the number of active sites occupied by one molecule of the condensed compounds are lower than the simple compounds. The values decrease from nearly one for TSC and ATP down to about 0.3 for ITSC and IATP. This behaviour can be discussed on the basis that the TSC molecule is adsorbed through two active centres and occupy two active sites on steel surface ($1/y = 1.34$). A value of $1/y = 0.97$ for ATP suggest that adsorption process takes place by the occupation of one active site per a single inhibitor molecule. For ITSC and IATP number of active sites were found to be less than one (≈ 0.30). According to the proposed kinetic-thermodynamic model, the adsorption takes place via formation of multilayers of the inhibitor molecules on the surface

of the metal.

The findings showed that the binding constants, K , values of (ITSC/TSC) and (IATP/ATP) are seven and five times respectively. This is a convincing evidence that the condensation products of isatin with the TSC and ATP leads to a dramatic increase in their inhibition efficiency. Comparing the findings obtained from kinetic-thermodynamic model to the common adsorption isotherms. It was found that the most applicable for TSC and ATP is the Flory-Huggins isotherm, equation (4).

$$\theta/x (1 - \theta)^x = K [I] \quad (4)$$

Rearranging,

$$\log (\theta/[I]) = \log x K + x \log (1-\theta) \quad (5)$$

Figure (8) illustrates plot of $\log (\theta/[I])$ vs $\log (1-\theta)$ for TSC and ATP. The figure yield a straight lines having correlation coefficient of 0.94 with slope x and intercept $\log x K$. The values of K and x are given in table 2. Values of x show good agreement with the number of active sites calculated from the kinetic-thermodynamic model. Moreover, the nearly similar K values predicted by Flory-Huggins or kinetic-thermodynamic model for TSC and ATP gave very satisfactory agreement.

Frumkin isotherm equation (6) represents best fit for experimental data obtained from the acid corrosion inhibition using ITSC and IATP, Figure (9).

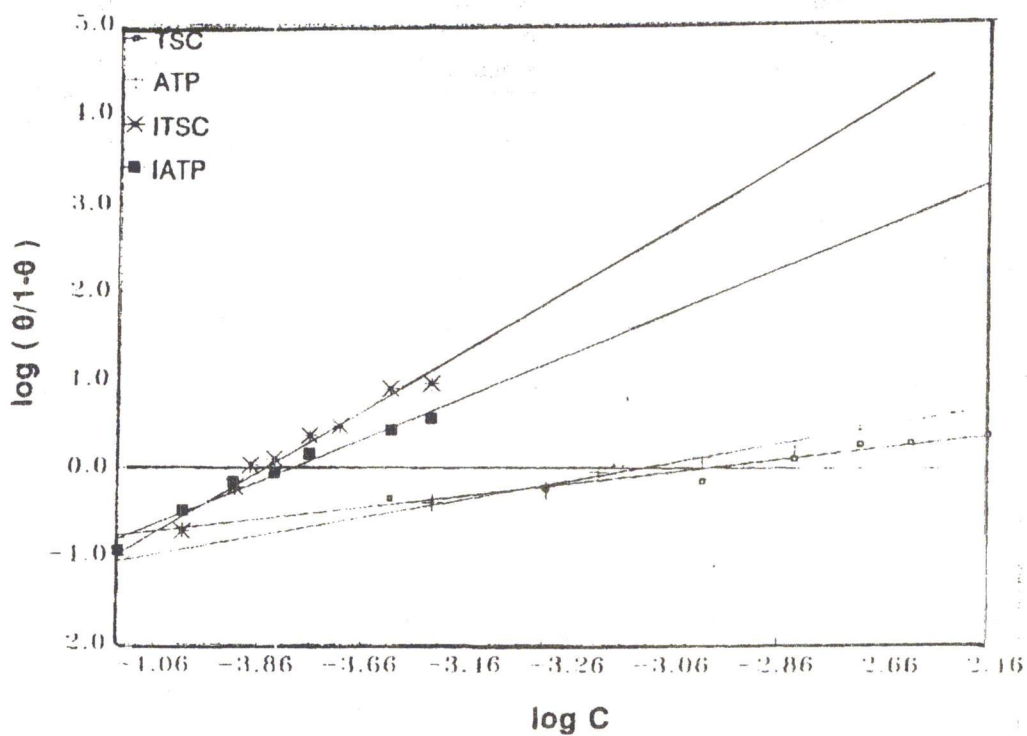


Figure 7. Application of kinetic-thermodynamic model on TSC, ATP, ITSC and IATP.

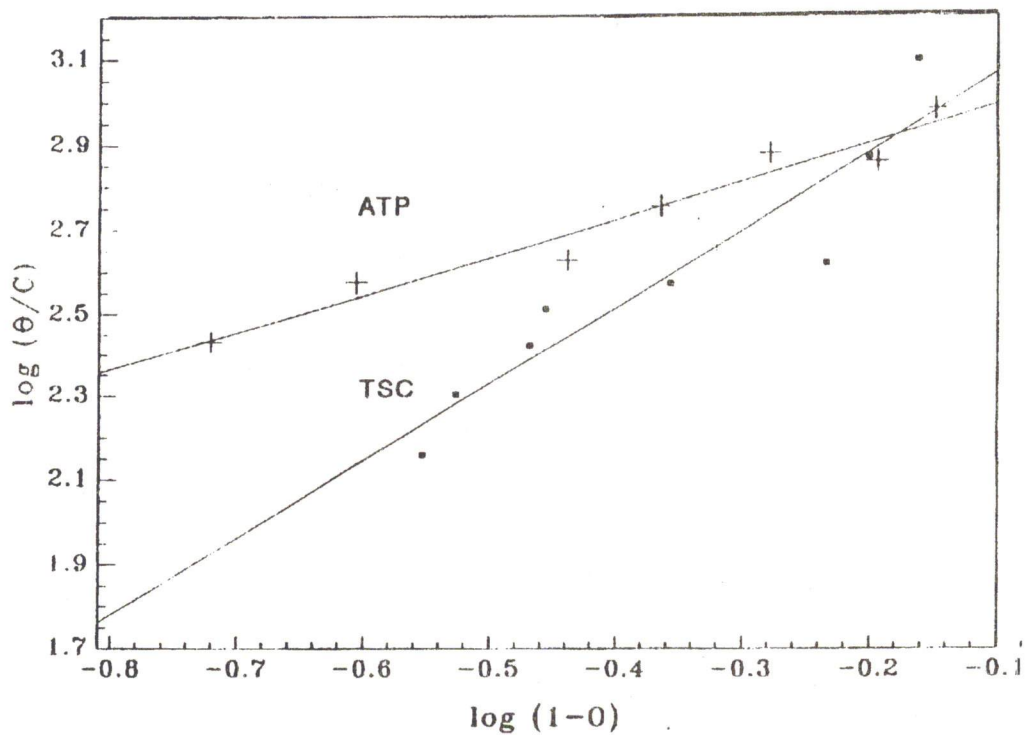


Figure 8. Application of Flory-Huggins on TSC and ATP.

Table 2. Curve fitting of TSC data to kinetic-thermodynamic model, Flory-Huggins and Frumkin isotherms for TSC, ATP, ITSC and IATP at 30°C.

Compound	Kinetic Model		Flory- Huggins		Frumkin	
	1/y	K	x	K	a	K
TSC	1.34	996.0	1.33	0905.5	-	-
ATP	0.97	1312.6	0.90	1347.2	-	-
ITSC	0.29	6936.5	-	-	-3.6	1116.3
IATP	0.35	6582.1	-	-	-3.2	1303.0

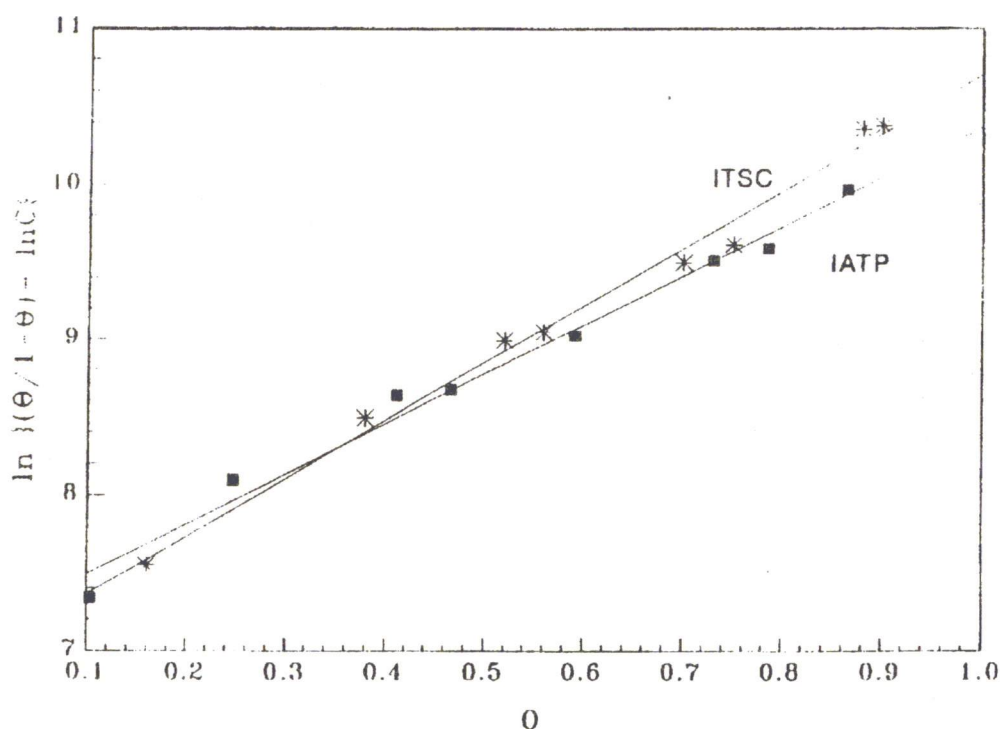


Figure 9. Application of Frumkin on ITSC and IATP.

$$\left[\frac{\theta}{1-\theta}\right] \exp[-2 a \theta] = K.C \quad (6)$$

The values of K and a are given in table 2. The lateral interaction parameter a has high negative value (≈ -3.5). This parameter is a measure of the degree of steepness of the adsorption isotherm. Whereas, the adsorption equilibrium constant (binding constant), K, calculated from Frumkin acquires a lesser values than those obtained from the

kinetic-thermodynamic model. The lack of compatibility of the calculated K values from the Frumkin and kinetic-thermodynamic model may be attributed to the fact that Frumkin 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-thermodynamic model use the size parameter.

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