CHAPTER VI

Metal Tetrasulphophthalocyanine As Corrosion Inhibitors

6.1 Introduction

Corrosion is the deterioration of metals by electrochemical or direct chemical reactions and in that sense it is an industry in reverse. Corrosion rate is influenced by factors such as nature of the metal, the corrodent, nature of the corrosion product temperature, electrical potential between two metals and the relative velocity of the corrodent with respect to the metal. The relationship among these factors determines the type of corrosion.

All metals except gold are thermodynamically unstable with respect to their oxides. Corrosion represents the tendency of pure metals and alloys to return to thermodynamically stable compounds. The fundamental process of corrosion is the anodic dissolution of the metal to form its ions.

\[ \text{M} \rightarrow \text{M}^{n+} + n\text{e}^- \]  

The ions may be carried away into the bulk of the solution in contact with the metal or may for insoluble compounds which adhere on the metal surface. A layer of oxide or hydroxide may be formed on the surface and this is sometimes further converted to a higher oxide. Such layers may be porous allowing further corrosion (as with iron), or they may be compact and nonporous, forming a protective layer blocking further corrosion (as with aluminium).

When an isolated piece of metal is communicating with a corrosive medium the corrosion reaction represented by equation (1) cannot proceed unless another process takes place at the same rate to carry away the electrons accumulated in the metal. In most cases, spontaneous corrosion is accompanied by hydrogen evolution or oxygen reduction, although other cathodic reactions may serve the same purpose of consuming the electrons released in the anodic dissolution of the metal.

Corrosion will be either accelerated or retarded by an applied electric potential by changing the chemical activity of metals relative to each other and to hydrogen. In general, if an applied potential lowers the activity of metal below to each other and to hydrogen, corrosion is retarded or stopped and the metal is said to be cathodically protected. Cathodic protection can also be secured by using an external electrode that is more active than the metal being protected.

Active metals such as aluminium, titanium and high chromium (stainless) steel owe their good corrosion resistance under oxidising conditions to surface oxide film that is adherent and impervious, though of non oxidizing conditions. When this passive layer is not formed these metals may corrode quite rapidly. The acidity of the corroding medium and whether or not it is aerated also can affect the formation of passive layer.

In the case of spontaneous corrosion, when steady state is reached, the metal attains a constant potential, \( E_{\text{corr}} \) which is termed the mixed potential or corrosion potential. At this potential there is an anodic overpotential,

\[ \eta_a = E_{\text{corr}} - E_{\text{r,a}} \]

and a cathodic overpotential \( \eta_c = E_{\text{corr}} - E_{\text{r,c}} \) driving the
The value of these overpotentials and hence the corrosion potential \( E_{corr} \) are determined by the condition that the anodic and cathodic process must occur at exactly the same rate. \( E_{corr} \) is determined by the reversible potentials of the two processes taking place as well as their exchange-current densities and the Tafel slopes, i.e. by both thermodynamic and kinetic factors.

When the corroding metal is connected to a source of current or potential and polarized anodically or cathodically with respect to its \( E_{corr} \) and if the anodic and cathodic processes are assumed to be linear in the Tafel region of \( E_{corr} \)

\[
i_{corr} = i_{oa} \exp \left( \frac{E_{oa} - E_{oa}}{b_a} \right) / ba = \exp \left( - \frac{E_{oa} - E_{oa}}{b_c} \right) / bc
\]

[2]

Where the subscripts a and c refer to the anodic and cathodic process respectively. The current which flows is given by

\[
i = i_{oa} \exp \left( \frac{E_{oa}}{b'a} \right) - i_{oc} \exp \left( - \frac{E_{oc}}{b'c} \right)
\]

[3]


\[
i = i_{corr} \left[ \exp \left( \frac{E - E_{corr}}{ba} \right) - \exp \left( - \frac{E - E_{corr}}{bc} \right) \right]
\]

The equation permits the electrochemical determination of the corrosion rate \( i_{corr} \) by extrapolation of the \( E \) vs \( \log i \) plot from high values of \( E - E_{corr} \) on either the anodic or cathodic side to the corrosion potential, or by measuring \( i \) as a function of \( E \) in the vicinity of \( E_{corr} \).

The anodic and the cathodic reactions occur on different parts of the metal, which may be termed anodic and cathodic areas. These are determined by the structure and composition of the metal, mechanical strain (highly strained areas tend to be more anodic) partial contact with the corrosive medium (through fault coating), variation in the composition of the medium etc. Under steady state corrosion, the total anodic and cathodic currents must be equal, while the current densities may differ substantially depending on the relative magnitude of the anodic and cathodic areas.

**CORROSION PREVENTION**

The methods of corrosion prevention are many and varied. Cathodic protection, anodic protection and inhibition are the electrochemical methods generally applied to prevent corrosion.

### 6.1.2 Protective films

During corrosion reactions, thicker films may also be formed on metals. However, the corroding condition determines whether these films are protective or not. In petroleum refineries ferrous sulfide corrosion will be protective if organic foulants are co-deposited as they are formed; whereas when formed alone, under clean conditions, it may turn to be non-protective.

The electronic conductor transports electrons released by anodic dissolution from the corroding surface to the cathodic surface where the electrons reduce the corroding agent. In aqueous
solutions the electron acceptor is usually dissolved $O_2$. Ionic conduction through the medium completes the circuit to the corroding surface. Because such a corrosion cell is a closed circuit, the overall rate of corrosion is limited to that of its slowest step, which may occur at the anode, or at the cathode.

6.1.3 At the Anode

For metal atoms to undergo anodic dissolution from bulk metallic phase to mobile ion, a thorough transformation is necessary. An atom, for example an iron atom must leave its tiny body-centred cubic form, pick up six coordinating ligands and lose two electrons.

\[ \text{Fe} = \text{Fe}^{2+} + 2e^- \]  

[1]

The net reaction involves more steps in between. The most significant aspects of this anodic dissolution are absorption, desorption and electron transfer as shown below

\[ \text{Fe} + \text{OH}^- \xrightarrow{\text{ads}} \text{FeOH} \]  

[2]

\[ \text{FeOH} \xrightarrow{\text{des}} \text{FeOH} + e^- \]  

[3]

\[ \text{FeOH} \xrightarrow{\text{ads}} \text{FeOH}^+ + e^- \]  

[4]

\[ \text{FeOH}^+ \xrightarrow{\text{des}} \text{FeOH}^+ \]  

[5]

Underlining in these equations indicates species that are adsorbed on the metal surface.

The adsorption-desorption steps (2) and (5) are obviously susceptible to environmental influences and thus to inhibition. Competitive adsorption from electrolyte constituents, such as chloride and benzoate or even neutral molecules, can either retard corrosion by repression step (2) or accelerate it by promoting step (5).

In anodic control of corrosion, passivation which is by far the most important phenomenon, and inhibitors can greatly broaden the range over which passivity can be obtained.

Anodic protection can be used successfully only in certain well defined cases which occur commonly in the chemical industry and in the storage of certain corrosive chemicals. The structure to be protected is made the anode, and its potential is set in the passive region.

6.1.4 At the Cathode

A cathodic process of corrosive reduction is the necessary complement of every anodic reaction. Only one of the two corrosives is involved in a great majority of practical corrosion problems—dissolved dioxygen or hydrogen ion. The overall reactions for the cathodic reduction of these two are:

\[ O_2 + 2H_2O + 4e^- \xleftrightarrow{\text{kin}} 4OH^- \]  

[7]

\[ 2H^+ + 2e^- \xleftrightarrow{\text{kin}} H_2 \]  

[8]

In the case of oxygen caused corrosion, the mass transfer of oxygen is usually rate-determining due to its low solubility.

In an acid-caused corrosion, when a hydrogen ion arrives at the cathodic interface it is adsorbed and reduced to adsorbed atomic hydrogen, as:
At this point, two alternative paths appear to be well established. Either hydrogen gas is formed by the combination of adsorbed hydrogen atoms,

\[
\begin{align*}
2H & \rightleftharpoons H_2 \\
\text{or hydrogen gas is formed by reaction between an adsorbed hydrogen atom and a hydrogen ion plus an electron} & \\
H + H^+ + e^- & \rightleftharpoons H_2
\end{align*}
\]

In either case, desorption of the hydrogen molecule completes the process.

In the case of cathodic protection an external net cathodic current is allowed to pass through the metal so that the corrosion rate can be brought to the desired level. An active metal, generally zinc is used as a "sacrificial" anode in contact with the corroding metal, and no external power source is required. The zinc serves as the anode and is slowly dissolved while the other metal is cathodically protected by the current passed.

6.1.5 Corrosion Inhibitors

Any electrochemical poison which retards either the cathodic or the anodic reaction involved in the spontaneous corrosion process, can retard the process itself. The corrosion inhibitors can be broadly classified into three groups viz., corrosive deactivators, adsorptive inhibitors and passivators, and corrosion product-barrier formers.

6.1.6 Corrosive Deactivators

This approach is used to combat corrosion in boilers through removal of oxygen by chemical reaction with sulfite, or possibly with hydrazine. In a similar manner, acid corrosion can be stopped by neutralization with ammonia or other bases. This approach represents a direct frontal assault on the corrosion process; removes the corrodent and stops corrosion.

6.1.7 Adsorptive Inhibitors

In deaerated aqueous solutions, the corrosion is controlled mainly by the cathodic hydrogen evolution reaction. Since the rate limiting steps in cathodic reduction of hydrogen ion occur on the cathode surface, the adsorption characteristics of this surface determine the overall cathodic reaction rate to a large degree. Chemical factors affecting adsorption are (1) the inherent properties of the cathode material (2) the presence or absence of competing species.

Many compounds which are known to poison cathodic hydrogen evolution reaction (e.g. As_2O_3, pyridine, piperidine, some nitrogen-containing alkaloids) are found to be effective corrosion inhibitors. The action of such inhibitors is two fold. They are adsorbed on the surface of the metal (upto a monolayer or less) and physically block the sites on the surface at which hydrogen is evolved. The structure of the double layer is altered by adsorbing the inhibitor. Thus the specific electron
transfer rate constants for both the anodic and cathodic reactions may be changed even on sites which are not directly blocked by the adsorbed inhibitor.

6.1.8 Passive and corrosion product barrier formers

These act to varying degrees on both the anodic and cathodic reactions. In anodic reactions, the effects of these inhibitors are of suppressing nature, whereas on cathodic reaction their effects are opposite. Thus, a passivator may increase potential cathodic-current density to exceed the critical anodic current density for spontaneous passivation, whereas a corrosion-product barrier may limit the cathodic reaction.

Applications

Corrosion by strong acids (HCl and H₂SO₄) are usually inhibited by adsorption type inhibitors. With concentrated solutions, combinations of acetylenic alcohols and polar nitrogen compounds are most commonly used. Weak acids (H₂S and CO₂) can usually be effectively inhibited by nonacetylenic, adsorption type inhibitors.

6.1.9 Some general considerations

1. Effect of inhibitor on corrosion rate: minimum concentration exists below which it is not effective
2. Relation to surface area of metal: initial consumption in coating surface or reaction with existing scale.
3. Effectiveness as a function of time.
4. Tendency to be consumed by a reaction with ingredients of the medium.
5. Effectiveness under varied conditions, such as temperature, concentration of corrodent etc.
6. Effectiveness on already corroded metal.
7. Adverse effects on quality of product from the process.
8. Adverse effects on process, as for example, emulsification, impaired heat transfer etc.
9. Effect on other metals or on bimetallic couples that may be present.

6.2 INHIBITION OF CORROSION OF ALUMINIUM IN HYDROCHLORIC ACID BY METAL TETRASULPHOPHTHALOCYANINES

Metal phthalocyanines (MPcs) have a variety of electrochemical and surface adsorption properties by virtue of their molecular structure. The phthalocyanine moiety is planar and the electronegative groups are located at the centre. They have a strong tendency to be adsorbed on metal surface. The favourable characteristics of MPcs can be exploited for inhibiting corrosion if they are rendered soluble in aqueous medium.

Metal tetrasulphophthalocyanines (MTSP) form a class of unique water soluble pigments stable in acid and alkaline media. MTSPs withstand optical radiations and are not degraded by dioxygen even in strong alkali. The stability of MTSPs in a wide variety of environments and their electrochemical and adsorptive properties make them potential corrosion inhibitors.

In an uninhibited media the following electron transfer reactions which lead to the corrosion of aluminium take place:

\[
\begin{align*}
\text{Al} & \quad \rightarrow \quad \text{Al}^{3+} + 3e^- \\
\text{O}_2 + 2\text{H}^+ + 4e^- & \quad \rightarrow \quad 2\text{OH}^-
\end{align*}
\]
This reaction can be further enhanced by the presence of species which break the protective oxide layer on aluminium. CoTSP is known to catalyse dioxygen reduction and has a tendency to be adsorbed on metal surface, whereas CuTSP is isostructural but its catalytic activity towards \( \text{O}_2 \) reduction is less. Which one of these conflicting properties does dominate can be ascertained by evaluating the corrosion inhibition efficiency of these two MTSPS. Advantageous solubility characteristics are found in MTSP and it is worthwhile to investigate the effect of metal phthalocyanines on the inhibition of aluminium dissolution in HCl medium. Inhibition activity has been measured by weight loss, thermometry, gas evolution and polarization methods and the thermodynamic parameters are reported.

6.2.2 EXPERIMENTAL

Aluminium strips (Indal 2S of the constitution, Si -0.3%, Fe - 0.5%, Ti -0.01%, B -0.05%, Ga - 0.02% and the rest Al) were used for the studies. The test pieces were polished with 4/0 grade emery paper, degreased with alkaline solution (15g/l \( \text{Na}_2\text{CO}_3 \) + 15g/l \( \text{Na}_3\text{PO}_4 \)) and washed with a copious amount of distilled water. They were washed with reagent grade acetone and dried by pressing between filter paper folds. A fresh test piece was used for each measurement. CoTSP and CuTSP were prepared and purified by the procedure of Weber and Busch. \text{\textit{J}}\text{\textit{J}}\text{} solutions of different concentrations were prepared from a \( 10^{-2} \text{M} \) stock solution in water.

6.2.3 THERMOMETRIC METHOD

The test pieces of aluminium were bent to U shape and put in a reaction vessel which was insulated with foamed polystyrene to prevent heat loss. The temperature of the system was measured using a sensitive mercury thermometer, lower end of which rested on the dome of the metal specimen.

The dissolution of aluminium in hydrochloric acid is considerable at concentrations > 1.5M. Hence 2M HCl containing varying amounts of CoTSP was used as the medium.

6.2.4 WEIGHT LOSS METHOD

The test pieces were prepared as above, weighed, and immersed in 50 ml of test solution at room temperature for a period of 15 minutes. They were then washed with distilled water, dried and weighed.

6.2.5 GASOMETRIC METHOD

The dissolution of aluminium in 2M HCl with and without the inhibitor was studied by the hydrogen evolution method in the temperature range 25° to 45° C. The test pieces were prepared as above. A gasometric reaction vessel of the type shown in fig. 6.1 described by Hassan et al was used. Temperature was controlled at 0.1°C by circulating thermostated water around the reaction vessel.

6.2.6 POLARIZATION STUDIES

Aluminium sheet of size 50X25X0.5 mm was used as the electrode. This was polished, cleaned and dried as described above. A coating of wax was applied on the specimen using a mask, thus exposing only a defined area (2 cm²) to the medium. A platinum sheet was used as auxiliary electrode and saturated calomel was used as the reference electrode. Measurements were done in
Fig. 6.1: Gasometric Reaction Vessel
the test solution (75 ml.) in an undivided cell. A scanning potentiostat/galvanostat (EG & G PAR Model 362) was used for the polarization studies. The test solutions were flushed with nitrogen for 30 minutes. Both anodic and cathodic polarization measurements were made.

6.3.3 RESULTS AND DISCUSSION

The inhibitor efficiency, I, is calculated from the weight loss method using the relation,

\[ \%I = \frac{\text{Wt. loss}_{\text{pure}} - \text{Wt. loss}_{\text{inh}}}{\text{Wt. loss}_{\text{inh}}} \times 100 \]

Fig.62 & 6.10 shows that the weight loss-time relationship for different concentrations of CoTSP and CuTSP also in their absence. The dissolution is markedly inhibited by the presence of MTSPs. The induction period is enhanced in presence of MTSP. This may be due to the protection of the oxide layer against dissolution by MTSP molecules adsorbed on the surface.

Thermometric method was used to evaluate the reaction number and percentage inhibition \[219,220\]. The reaction number is defined as

\[ \text{RN} = \frac{T_m - T_i}{T} \text{ °C min}^{-1} \]

where, \( T_m \) & \( T_i \) are the maximum and initial temperatures respectively in °C and ‘t’ is the time in minutes taken to reach \( T_m \). The percentage inhibition is calculated from the relation;

\[ \%I = \frac{\text{RN}_{\text{pure}} - \text{RN}_{\text{inh}}}{\text{RN}_{\text{pure}}} \times 100 \]

In Fig. 6.3 & 6.11 the variation of temperature with time for different concentrations of MTSP is shown. It is seen that the effectiveness of CoTSP and CuTSP inhibitors is distinct only in concentration exceeding \( 10^{-5} \) M. Below this concentration, the inhibition efficiency sharply falls. The reaction number vs log C plot (Fig.6.4 & 6.2) also shows that RN is low upto \( 10^{-5} \) M CoTSP.

At concentrations below this RN increases rapidly (Table II). This is in agreement with the temperature - time plot and the gravimetric results.

The inhibition efficiency is expressed by the percentage reduction in reaction rate as measured by gasometry according to the relation,

\[ \% \text{ reduction in RR} = \frac{R_{\text{free}} - R_{\text{inh}}}{R_{\text{free}}} \times 100 \]

where \( R_{\text{free}} \) and \( R_{\text{inh}} \) are rates of aluminium dissolution in the absence and in the presence of the added reagent respectively, both being measured for the same reaction time.

The rate of hydrogen evolution was determined at 25, 35, 40 and 45° C at different concentrations of MTSP in 2M HCl. Typical results are given in Fig.6.5 and 6.13.

The plot of volume of hydrogen evolved vs time at different temperatures shows that the rate increases slowly during the initial period. Thermometric method also shows an incubation period for dissolution. This incubation corresponds to the breakdown of the oxide film present on the metal surface \[211\] by its dissolution in acid which does not involve hydrogen evolution. The post-incubation reaction of aluminium is linearly related to reaction time and this behaviour is characteristic of zero order reaction may be written in the form, \( x = kt \) where \( x \) is the fraction of aluminium converted into
Fig. 6.2: Weight loss-time plot for the dissolution of aluminium in presence and absence of CoTSP; medium 2M HCl.

- HCl: 
- $10^{-4}$ M: 
- $10^{-6}$ M: 
- $10^{-8}$ M: 
- $10^{-6}$ M: 
- $2 \times 10^{-4}$ M:
Fig. 6.3: Temperature-time plots for the dissolution of aluminium at different concentrations of CoTSP in 2M HCl

- HCl;
- $10^{-1}$M;
- $10^{-4}$M;
- $10^{-3}$M;
- $2 \times 10^{-3}$M
Fig. 6.4: Plot of log $C_{\text{CrTS}}$ versus reaction number for the dissolution of aluminium in 2M HCl
Fig. 6.5: Volume of hydrogen evolved- time curves obtained at various temperatures in 2M HCl Only.

- 45°C;  ▲  40°C;  ○  35°C;  △  25°C
Fig. 6.6: Volume of hydrogen evolved-time curves obtained at various temperatures in the presence of $2 \times 10^{-4}$ M CoTSP. Medium 2M HCl.

- $45^\circ$C;   - $40^\circ$C;   - $35^\circ$C;   - $25^\circ$C
Fig. 6.7: Log k-1/T plot at different concentrations of CoTSP.
- o HCl;
- △ 10⁻⁷M;
- □ 10⁻⁶M;
- ● 10⁻⁴M;
- △ 2 x 10⁻⁴M
Fig. 6.4: Dependence of $\log(\theta / (1 - \theta))$ on the concentration of CoTSPP.
Fig. 6.9: Polarization curves obtained at different concentrations of CoTSP. Medium 2HCl.

- $\bullet$ HCl
- $\triangle$ $10^{-7}$M
- $\Delta$ $10^{-5}$M
- $\times$ $10^{-5}$M
- $\times 2 \times 10^{-4}$M
Fig. 6.10: Weight loss-time plot for the dissolution of aluminium in presence and absence of CuTSP; medium 2M HCl.

- $10^{-5}$ M
- $10^{-7}$ M
- $10^{-9}$ M
- $10^{-4}$ M
- $2 \times 10^{-4}$ M
Fig 6.11: Temperature - time plots for the dissolution of aluminium at different concentrations of CuTSP in 2M HCl

- $10^{-4}$M
- $10^{-5}$M
- $2 \times 10^{-5}$M
- $10^{-7}$M
Fig. 6.12: Plot of $\log C_{\text{CuTSP}}$ versus reaction number for the dissolution of aluminium.
Fig. 6.13: Volume of hydrogen evolved vs time curves obtained at various temperatures in the presence of $2 \times 10^{-4}$ M CuTSP. Medium 2M HCl

- ○ 45°C;
- ● 40°C;
- △ 35°C;
- ▲ 25°C
Fig. 6.14: Polarization curves obtained at different concentrations of CuTSP Medium 2M HCl.

- ● HCl;  
- △ $10^{-7}$M;  
- ▲ $10^{-6}$M;  
- ○ $10^{-5}$M;  
- × $10^{-4}$M;  
- ✠ $2 \times 10^{-4}$M
products at time \( t \), which in turn is directly proportional to volume of hydrogen evolved at time \( t \) and \( k \) is the rate constant of the reaction. The value of \( k \) can be calculated from the \( x \)-\( t \) curve at any given temperature (table 4). The value of \( k \) increases with increase in temperature and decreases with increase in inhibitor concentration.

The activation energy \( E_a \) is calculated from Arrhenius relationship, 
\[
E_a = \frac{k}{A e^{-E_a / RT}}
\]
where \( k \) is the rate constant and \( A \) is the pre-exponential factor. From the plot of \( \log k \) vs \( 1/T \) (Fig.6.7) the value of \( E_a \) is evaluated and given in Table 5.

The activation energy for aluminium dissolution increases with increasing inhibitor concentration. Increase in activation energy is due to increased adsorption of the inhibitor on the metal surface.

Surface coverage \( \theta \) of the inhibitor on the metal surface was determined using the relation,
\[
\theta = 1 - \frac{U_i}{U}
\]
where \( U_i \) and \( U \) are the corrosion rates in solution with and without inhibitor respectively.

The isothermal variation of \( \theta \) with concentration confirmed to the Langmuir adsorption isotherm which may be written in the form,
\[
\log \frac{\theta}{1 - \theta} = \log BC - \frac{G}{2.303} \frac{RT}{G}
\]
where \( B \) is the adsorption equilibrium constant and \( G \) is the free energy of adsorption. Fig.6.8 is the plot of \( \log \theta / 1 - \theta \) vs \( \log C \). The slope of this straight line is free energy of adsorption \( \Delta G_{ads} \) and is found to be \(-38.9 \text{ kJ mol}^{-1}\) for CoTSP. This is in agreement with the fact that stronger the adsorption greater will be the free energy of adsorption and the inhibition efficiency. The negative value indicate the spontaneous absorption of the inhibitor on aluminium.

The effect of inhibitor on the anodic and cathodic reactions can be determined using the relation,
\[
I_a = 1 - \frac{i}{i_{corr}}
\]
\[
I_c = 1 - \frac{j}{j_{corr}}
\]

where \( I_a \) and \( I_c \) are the efficiency of anodic and cathodic reactions, \( i_{corr} \) is the corrosion current density without inhibitor, \( i \) and \( j \) were obtained from the log (current density) vs potential plot. The polarization curves clearly indicate that the inhibitor shows down the hydrogen evolution. Table 5 gives the tafel slope and percentage inhibition from polarization data.

It is seen that catalysing effect of CoTSP for dioxygen reduction does not interfere with its corrosion inhibition efficiency. The nonconducting aluminium oxide layer on which CoTSP is absorbed inhibits the CoTSP-mediated electron transfer from aluminium to dioxygen. CuTSP is also effective but to a lesser extent.

The inhibition efficiency of CoTSP and CuTSP in HCl medium is superior to that of \( \beta \)-diketo compounds and phenylazo derivatives. The surface coverage of CoTSP on aluminium surface is 0.85 and for CuTSP it is 0.76 which are much higher than the values for similar inhibitors. The activation energy for corrosion is also high. CoTSP exhibits its inhibiting property in concentrations as low as \( 1.0 \times 10^{-7} \text{ M} \) and the inhibition efficiency reaches saturation at concentrations exceeding...
about $2.0 \times 10^{-4}$ M. In the case of CuTSP of lowest concentration at which it displays corrosion efficiency is $1.0 \times 10^{-6}$ M. Even at lower concentrations it does not accelerate corrosion. Moreover phthalocyanines are non-toxic and well tolerated in living systems\textsuperscript{282}.
### Table 1

**INHIBITOR EFFICIENCY FOR THE DISSOLUTION OF ALUMINIUM 2S IN 2M HCl AT VARIOUS CONCENTRATIONS OF CoTSP AND CuTSP**

<table>
<thead>
<tr>
<th>Conc./M</th>
<th>% Inhibition after 30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoTSP</td>
<td></td>
</tr>
<tr>
<td>$2.0 \times 10^{-4}$</td>
<td>84.6</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>78.6</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>73.6</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>67.9</td>
</tr>
<tr>
<td>$1.0 \times 10^{-7}$</td>
<td>60.7</td>
</tr>
<tr>
<td>$1.0 \times 10^{-8}$</td>
<td>35.7</td>
</tr>
<tr>
<td>CuTSP</td>
<td></td>
</tr>
<tr>
<td>$2.0 \times 10^{-4}$</td>
<td>71.78</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>68.57</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>63.57</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>57.50</td>
</tr>
</tbody>
</table>

### Table 2

**DEPENDENCE OF REACTION NUMBER AND PERCENTAGE INHIBITION ON THE CONCENTRATION OF CoTSP & CuTSP; MEDIUM 2M HCl**

<table>
<thead>
<tr>
<th>Conc. MTSP</th>
<th>Tinitial/ °C</th>
<th>Tmax/ °C</th>
<th>Time/minute</th>
<th>RN</th>
<th>%I</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M HCl</td>
<td>31.0</td>
<td>68.3</td>
<td>31</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>CoTSP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2.0 \times 10^{-4}$</td>
<td>31.0</td>
<td>50.4</td>
<td>78</td>
<td>0.25</td>
<td>79</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>31.0</td>
<td>53.8</td>
<td>60</td>
<td>0.38</td>
<td>68</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>31.0</td>
<td>58.6</td>
<td>65</td>
<td>0.41</td>
<td>60</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>31.0</td>
<td>59.2</td>
<td>48</td>
<td>0.58</td>
<td>51</td>
</tr>
<tr>
<td>$1.0 \times 10^{-7}$</td>
<td>31.0</td>
<td>63.1</td>
<td>35</td>
<td>0.93</td>
<td>23</td>
</tr>
<tr>
<td>CuTSP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2.0 \times 10^{-4}$</td>
<td>31.0</td>
<td>51.2</td>
<td>74</td>
<td>0.30</td>
<td>67.22</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>31.0</td>
<td>54.6</td>
<td>62</td>
<td>0.38</td>
<td>68.02</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>31.0</td>
<td>59.3</td>
<td>59</td>
<td>0.48</td>
<td>56.36</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>31.0</td>
<td>60.4</td>
<td>44</td>
<td>0.67</td>
<td>44.45</td>
</tr>
</tbody>
</table>
Table 3

PERCENTAGE REDUCTION IN RR AT VARIOUS CONCENTRATIONS OF MTSP; MEDIUM 2M HCl

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Time/Min</th>
<th>% Reduction in RR Concentration of MTSP/M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2.0 X 10^-4</td>
</tr>
<tr>
<td>CoTSP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>40</td>
<td>75.8</td>
</tr>
<tr>
<td>35.0</td>
<td>40</td>
<td>68.3</td>
</tr>
<tr>
<td>40.0</td>
<td>25</td>
<td>65.4</td>
</tr>
<tr>
<td>45.0</td>
<td>25</td>
<td>54.7</td>
</tr>
<tr>
<td>CuTSP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>40</td>
<td>70.30</td>
</tr>
<tr>
<td>35.0</td>
<td>40</td>
<td>62.42</td>
</tr>
<tr>
<td>40.0</td>
<td>25</td>
<td>55.75</td>
</tr>
<tr>
<td>45.0</td>
<td>25</td>
<td>47.27</td>
</tr>
</tbody>
</table>

Table 4

RATE CONSTANT, SURFACE COVERAGE, ACTIVATION ENERGY AND HEAT OF ADSORPTION FOR THE DISSOLUTION OF ALUMINIUM IN 2M HCl AT DIFFERENT CONCENTRATIONS OF MTSP

<table>
<thead>
<tr>
<th>Conc. of MTSP</th>
<th>Rate Constant, k</th>
<th>Surface Coverage</th>
<th>Activation Energy, E_a</th>
<th>Heat of Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C 35°C 40°C 45°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nil</td>
<td>0.42 0.67 1.25 4.23</td>
<td>—</td>
<td>17.9</td>
<td>—</td>
</tr>
<tr>
<td>CoTSP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 X 10^-4M</td>
<td>0.1 0.21 0.44 1.88</td>
<td>0.85</td>
<td>69.3</td>
<td>12.9</td>
</tr>
<tr>
<td>1.0 X 10^-5M</td>
<td>0.16 0.28 0.66 2.28</td>
<td>0.79</td>
<td>62.7</td>
<td>21.3</td>
</tr>
<tr>
<td>1.0 X 10^-4M</td>
<td>0.18 0.42 0.88 2.82</td>
<td>0.68</td>
<td>37.7</td>
<td>30.4</td>
</tr>
<tr>
<td>1.0 X 10^-7M</td>
<td>0.24 0.49 1.56 3.56</td>
<td>0.61</td>
<td>34.7</td>
<td>29.10</td>
</tr>
<tr>
<td>CuTSP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 X 10^-4M</td>
<td>0.12 0.21 0.56 1.99</td>
<td>0.76</td>
<td>61.8</td>
<td>14.5</td>
</tr>
<tr>
<td>1.0 X 10^-4M</td>
<td>0.16 0.30 0.69 2.39</td>
<td>0.72</td>
<td>56.4</td>
<td>24.3</td>
</tr>
<tr>
<td>1.0 X 10^-3M</td>
<td>0.18 0.38 0.92 3.28</td>
<td>0.69</td>
<td>35.2</td>
<td>32.7</td>
</tr>
<tr>
<td>1.0 X 10^-6M</td>
<td>0.22 0.37 0.97 3.29</td>
<td>0.64</td>
<td>34.0</td>
<td>28.3</td>
</tr>
<tr>
<td>Conc. of MTSP/M</td>
<td>( i_e ), mA cm(^2)</td>
<td>TAFEL Slope/mV</td>
<td>% Inhibition</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------</td>
<td>----------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>Nil</td>
<td>18.0 =( i_0 )</td>
<td>353</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>CoTSP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2 \times 10^4 )</td>
<td>0.36</td>
<td>313</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>( 1.0 \times 10^5 )</td>
<td>0.45</td>
<td>301</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>( 1.0 \times 10^6 )</td>
<td>0.66</td>
<td>314</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>( 1.0 \times 10^7 )</td>
<td>5.3</td>
<td>352</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>CuTSP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2 \times 10^4 )</td>
<td>0.58</td>
<td>318</td>
<td>96.7</td>
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</tr>
<tr>
<td>( 1.0 \times 10^5 )</td>
<td>0.94</td>
<td>321</td>
<td>94.7</td>
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</tr>
<tr>
<td>( 1.0 \times 10^6 )</td>
<td>3.31</td>
<td>325</td>
<td>81.6</td>
<td></td>
</tr>
<tr>
<td>( 1.0 \times 10^7 )</td>
<td>6.8</td>
<td>334</td>
<td>62.22</td>
<td></td>
</tr>
</tbody>
</table>