CHAPTER III

INFLUENCE OF TEMPERATURE ON THE
PERFORMANCE OF INHIBITORS

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The rate of electrochemical corrosion usually increases with increase in temperature. However, the velocity of individual process, changes nonuniformly with temperature and hence, the character of control of electrochemical corrosion can vary considerably with change in temperature. The acceleration of corrosion at higher temperatures, is especially notable in media in which evolution of hydrogen accompanies corrosion(1).

The influence of temperature on the reaction between metals and acids was studied during the development of theories of heterogenous reaction kinetics. In the beginning, the studies were concentrated on the dissolution of steel and ferrous alloys, while very little attention was paid to nonferrous metals and alloys(2).

According to Putilova(2) it is of practical importance to determine the nature of the temperature relationship for the rate of dissolution of metal in media where corrosion takes place with the evolution of hydrogen, especially when inhibitors are present(2). Unfortunately, lesser attention has been paid so far to the effect of temperature on inhibited reaction than even the uninhibited reaction(3).
It was, therefore, planned to study the effect of temperature of the inhibitive action of the substances investigated for the corrosion of Al-565 in hydrochloric acid.

The corrosion process represents a closed circuit of physico-chemical and chemical reactions and purely physical processes wherein the kinetics of each can have a different activation energy i.e. a different temperature dependence(1).

Most frequently, the corrosion rate increases logarithmically with temperature. This is expressed by the Arrhenius relationship(1).

\[ U = A \cdot e^{\frac{\theta}{RT}} \]

where \( U \) is the speed of process, \( A \) and \( \theta \) are constants, \( R \) is the gas constant, \( e \) is the base of natural logarithm, and \( T \) is the absolute temperature. This equation is obeyed when the corrosion rate is principally determined by the rate of initial electrode or electrochemical reaction or diffusion process e.g. the dissolution of iron in hydrochloric acid of different concentrations(4); Sometimes, however, this equation is not obeyed due to complications arising from influence of oxygen(1).

An increase in temperature, has a strong accelerating effect on the corrosion of aluminium(5). However, at temperatures above 40°C the pitting of aluminium in water is reduced(5).
Mears and Brown (6) studied the influence of temperature on the pitting probability of aluminium in chloride solutions. With increase in temperature, the density and probability of pitting increased, while the pitting rate decreased. Porter (7) also observed that pitting of aluminium in water is temperature dependent. Similar observations were made by Godard (8), and Rowe (9).

Streicher (10) studied the dissolution of aluminium in hydrochloric acid and reported that the energy of activation of rate controlling process is 13.7 K.Cal/mole in hydrochloric acid. Sekerka (11) reported that the activation energy of aluminium in 0.05-1.0 N hydrochloric acid ranges between 1.4 and 10.2 K.Cal/mole. He observed that above 0.5 N concentration of hydrochloric acid rate of discharge of hydrogen ion is the rate determining factor. Similar observations have been made by Vogel (12) and Akimov (13) who found that corrosion rate of aluminium alloys in acid solution increases with increase in temperature. Khitrov (14,15) found that the plot of the corrosion rate against 1/T is linear up to 40°C for the corrosion of aluminium in hydrochloric acid.

Gardner (16) stated that if the temperature coefficient for a 10°C change is 1.3 to 1.5, the process is diffusion controlled and if it is 1.8 to 4.1, the process is activation controlled. Jablczynski (17) observed that the dissolution of aluminium in hydrochloric acid is unaffected by diffusion, the temperature coefficient being 2.36. Streicher (10)
reports that the dissolution rate of aluminium in hydrochloric acid approximately doubles with an increase of 10°C and this is generally considered to be true for homogenous chemical reaction. Ramachar(18,19,20) reported that temperature coefficient of different aluminium alloys is 2.34, 2.61 and 5.3, the corresponding activation energy being 23.8, 23.8 and 40.8 K.Cal/mole; for pure aluminium, 98.8% aluminium and aluminium-zinc alloy respectively.

Putilova(2) observed that the relationship \( \log \varphi = f(1/T) \) (where \( \varphi \) = corrosion rate) is quite frequently, although not always, linear in the presence of inhibitor. The effect of temperature on action of inhibitor can broadly be divided into three different types which can be represented by the diagram below(2). In Fig. 7, A, the activation energy in presence of inhibitor is more than that in its absence. Such inhibitors can be compared with unstable catalyst poisons. Their adsorption falls appreciably with increasing temperature, thus exposing greater area to the action of acid, consequently increasing the corrosion rate(2).

In the second case (Fig. 7, B), the energy of activation in the absence and presence of inhibitor is nearly identical(2). Such inhibitors can be compared with stable catalytic poison.
According to Putilova(2), the third class of inhibitors (Fig.7.C) is of practical interest. The action of such inhibitors is characterised by a lower value of activation energy in the presence of inhibitor than in its absence. Such substances, like the catalysts which do not change the temperature coefficient of reaction are firmly held on the metal surface, probably because they are bound to the surface by specific adsorption or chemisorption giving rise to a surface film. The fall in value of activation energy is probably accounted for by the increase in surface area of the metal covered by inhibitor molecules as the temperature rises(3). Machu(21) has also pointed out that with powerful inhibitors the activation energy is lowered for inhibited
rather than uninhibited reaction. This type of behaviour which means that the inhibitor becomes more effective as the temperature rises, is also explained by Riggs(3) in a different way. According to him at high coverages, the extent of adsorption is no longer rate determining.

Desai(22) et al investigated the effect of temperature on the performance of the following inhibitors for the corrosion of Al-2S and Al-57S in 1.0N hydrochloric acid. Methylamine, Dimethylamine, Trimethylamine, Ethylamine, Diethylamine, Triethylamine, Aniline, Methylaniline, Dimethylaniline, Ethylaniline, Diethylaniline, 2-butaneone, 2-4-pentanedione, o-anisidine, Cyclohexanol, Cyclohexanone, Methylcyclohexanone, Cyclohexylamine. Ethylenediamine is the best inhibitor which protects both the aluminium alloys completely upto 3 hours in the temperature range 35-55°C. In methylamines, the secondary amine is most effective whereas in ethylamines, the tertiary amine is the most effective inhibitor. Ortho substituent in aniline is not very beneficial to inhibitive action but N substitution is highly beneficial. In alicyclic compounds investigated, the order of substituents is ketone > alcohol > amine.

The plots of corrosion rate (mg/dm²/hour) against reciprocal of absolute temperature in the presence and absence of inhibitors are given in Fig.3.4 to 3.1. Activation energies calculated are given in Table 3.2. From this
table it can be seen that for methylamine, trimethylamine, diethylamine, triethylamine, ethylenediamine, diethylene triamine, triethylenetetramine, tetraethylenepentamine, aniline, morpholine, o-anisidine, and m-toluidine, the activation energies are less in the presence of inhibitor than that in uninhibited hydrochloric acid.

This shows that most of the compounds belong to the class C, of Fig.7. P. 237

Lower activation energy in the presence of inhibitors has been explained by Riggs(3) in the following way:

The corrosion rate of metal, according to Riggs(3), is expressed by the following equation:

$$\frac{-d(Me)}{dt} = k_1(1 - \Theta) + k_2\Theta$$

where $\Theta$ is the fraction of the surface covered by the adsorbed inhibitor, $k_1$ is the rate constant for the uninhibited reaction, $k_2$ the rate constant for corrosion of the completely covered surface, and $M =$ metal.

Although in many systems $k_2$ may be so small as to make $k_2\Theta$ negligible, it is not likely to be zero. It is easily seen also that as $\Theta$ becomes quite large (say $> 0.99$), then very small increases in $\Theta$ cause the term $k_1 (1 - \Theta)$ to decrease markedly, so that it would take a very large ratio of $k_1/k_2$ to make the term $k_2\Theta$ negligible at high coverages.
It is probably safe to assume then, that there are many inhibited systems for which corrosion rates at high coverages do not reflect simply the extent of adsorption, but rather a new rate expression i.e. simply $k_2 \theta$. In such cases, the term $k_1(1 - \theta)$ will be negligible small and the corrosion mechanism probably involves direct reaction of the species "metal atom adsorbed inhibitor molecules". There is thus every reason to expect that activation energy involved in the rate constant $k_2 = Ae^{-\frac{E_2}{RT}}$ will be quite different from that involved in the uninhibited rate constant $k_1$.

It is, therefore, not surprising that the activation energy of inhibitor reaction at high coverages can be either larger or smaller than that of the uninhibited reaction(3). Thus, the decrease in activation energy at higher levels of inhibitor arises from a shift of the net corrosion reaction from that on the uncovered surface to one involving the adsorbed side directly. For the better inhibitors, this decrease is likely to be sufficiently strong to carry the temperature coefficient from positive (at low concentration) to negative, in agreement with isolated report of such behaviour in the literature(3).
REFERENCES


8. Vide Reference 5, p. 66.


22. Influence of Temperature on the Behaviour of Corrosion Inhibitors for Aluminium in Hydrochloric Acid,
M.N. Desai, Y.B. Desai, C.B. Shah, M.H. Gandhi,
Third Symposium on Corrosion Inhibitors,
Ferrara, 1970.
TABLE 3

EFFECT OF TEMPERATURE ON THE CORROSION LOSS OF ALUMINIUM 56S IN 1.0 N HYDROCHLORIC ACID IN THE PRESENCE OF AMINES
(VALUES IN THE BRACKETS SHOW % EFFICIENCY) DURATION: 30 MINUTES

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<th>Inhibitor</th>
<th>Nil</th>
<th>Methylamine (43.5 ml/1)</th>
<th>Dimethylamine (43.5 ml/1)</th>
<th>Trimethylamine (43.5 ml/1)</th>
<th>Diethylamine (43.5 ml/1)</th>
<th>Ethylamine (43.5 ml/1)</th>
<th>Diethanolamine (43.5 ml/1)</th>
<th>Triethanolamine (43.5 ml/1)</th>
<th>Ethanolamine (43.5 ml/1)</th>
<th>Diethylene triamine (43.5 ml/1)</th>
<th>Triethylene tetramine (43.5 ml/1)</th>
<th>Tetraethylene penta-amine (43.5 ml/1)</th>
<th>Aniline (43.5 ml/1)</th>
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<td>40° + 0.2°C</td>
<td>45° + 0.2°C</td>
<td>50° + 0.2°C</td>
<td>55° + 0.2°C</td>
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