Chapter – 6

Inhibition Effects of Organic Compounds against Acidic Corrosion on Brass of Industrial Importance
Inhibition effects of organic compounds against acidic corrosion on brass of industrial importance

The man's knowledge of retrieving copper from its ore and concept of alloying with other elements dates back to medieval periods. The fossilized extraction of civilized societies of yester years such as Harappa and Mohenzudaro leaves strong imprints of man's close intimacy with copper and copper based alloys.

Ever since man gained acquaintance with the element copper, the consumption of copper and copper based alloys by the civic societies has kept on growing beyond leaps and bounds. Today's industrial society has become so much dependent on the copper that every act of it does involve copper in one form or the other and unlimited usage is attributed to good corrosion resistance of the latter in variety of environments coupled with high electrical, thermal conductivity followed by attractive mechanical properties at low, normal and moderately elevated temperatures. The table inserted below contains the engineering properties of some of the copper and copper based alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Density</th>
<th>Melting point</th>
<th>Coeff exp</th>
<th>Elecrkl conde</th>
<th>Thermal conde</th>
<th>Tensile strgth</th>
<th>Elonga%</th>
<th>Vickers hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Admiralty Brass</td>
<td>8.91</td>
<td>1150°C</td>
<td>16x10^5</td>
<td>10%I.A.C.S</td>
<td>50w/m°K</td>
<td>310-620</td>
<td>8-55%</td>
<td>90-200</td>
</tr>
</tbody>
</table>

The metal copper in its purest form which has been refined through zone refining will have highest electrical conductivity. Some of the requirements of electrical applications demand purity greater than 99.94%. The de oxidized copper is consumed in large quantity by electrical equipment manufacturing industries.
The brasses are basically alloys of copper with zinc whose percentage varies from 10 to 45. Along with the prime components the brass also contains additional elements to small extent only to fine tune mechanical properties. The other varieties of copper based alloys prominently used in industries are bronzes and silvers.

Copper belongs to group 3 B in the periodic table with an electronic configuration of 2,8,18,1. The existence of lone electron in the outer most shell is likely to be lost while forming Cu$^+$ ion. Cu$^+$ ion further oxidizes to produce Cu$^{+2}$ ion.

The chemical inertness exhibited by copper and its position in the electrochemical series makes the evolution of hydrogen gas from the acid solution a difficult proposition. As such the corrosion rate observed with copper is minimum and likely to get arrested after some time due to formation of non-pervious film of corrosion product on the surface. As is the case with many inhibitor film protected corrosion rate retardation. Any punctured site in the film can aggravate the corrosion in the underneath surface.

Alloys of copper with other elements make it better resistant to corrosion than copper alone. This is attributed to synergised behavioral pattern of the alloying element. These either help in forming protective film or the alloy element may be more resistant to corrosion. On the contrary the alloy of copper with zinc can suffer severely from the phenomena of dezincification due to dissolution of zinc in acidic medium.

The final selection of metal or any of its alloy will have to be done meticulously through thorough understanding of the environment and mechanical stresses that may invariably go in to design. The cited references related to corrosion behavior of copper and its alloys shed more light in to the problem. The
behavior of the copper in electrified interfaces in various solutions under aerated conditions has been discussed in considerable detail by Gatty and spooner.

The on load performances of chemical transportation pipings for corrosion damage in the environs of reasonably aggressive medias will be practically monitored through linear polarisation of active surface against standard non polarisable electrode. The out come of such an observation will shed light on the progress of corrosion in the metal surface. The polarisation studies of copper electrodes in mediums of varying pHs under constant current conditions have been carried out by Hickling and Taylor\(^ {142}\).

The stages that appear during the anodic polarisation include

a) Charging of double layer followed by

b) The formation of film of cuprous oxide which gets oxidized to cupric oxide instantly.

In an alkaline pH, the O\(_2\) evolution begins after sufficient layers of film develops on the electrode surface, while in acidic pH's the corrosion product film never builds as it gets washed away from the surface. Other workers have also studied the anodic polarisation behavior of copper and its alloy in alkaline and acidic medium\(^ {143,144}\).

**Atmosphere induced corrosion in copper**

Copper has very high degree of resistance to corrosion induced by atmosphere and this is due to an impervious corrosion product that forms on the surface. The nature of the corrosion products developed on the surface due to atmospheric exposure has been considerably investigated by Vernon and whiteby.\(^ {145}\)

It is evident from the works described and other investigations\(^ {146}\) that copper and most of the copper alloys are highly resistant to atmospheric corrosion. The
instances of rapid corrosion in copper exposed to atmosphere could be attributed to the following reasons

a) Extremely local pollution by products of combustion.
b) Bad design or construction or existence of dead pockets that does not drain out completely.
c) Constant dripping of rainwater polluted with atmospheric pollutants or organic acids from lichens.
d) Corrosion fatigue due to inadequate allowance for expansion and contraction with consequent buckling as temperature fluctuates.

De Zincification of brasses

The concept of dezincification is bound to damage the structure as leaching of zinc leaves porous body. Though the external appearance does not reveal any deformity the discontinuity created within the body destroys mechanical strength. The incorporation of arsenic element to an extent of 0.04% will prevent dezincification in brasses as evidenced through the reviews cited(147,148). An interesting observation made in cited reference in regards the effect of impurities on inhibitive properties of arsenic element on dezincification was made with magnesium element and was found to diminish the inhibitive qualities of arsenic(149).

The alloy copper in the environs of hydrogen sulphides is prone for corrosion as scales of hydrogen sulphides are non protective and let alone offering any sort of protection it appears to stimulate more corrosion in copper.

Electrode potential relationships

Three different electrode reactions can be visualized at the interface involving copper and aqueous phase,
Chapter 6

1) \( \text{Cu}^{2+} + 2e = \text{Cu} \) (Reversible).

2) \( \text{Cu}^+ + e = \text{Cu} \) (Reversible).

3) \( \text{Cu}^{2+} + e = \text{Cu}^+ \)

The standard potentials for the above electrode reactions are +0.34 V, +0.52 V and +0.17 V respectively.

For the equilibrium \( 2\text{Cu}^+ = \text{Cu}^{2+} + \text{Cu} \), the K value, \( a_{\text{Cu}^{2+}}/( a_{\text{Cu}^+})^2 \), is around \( 1 \times 10^6 \) at 298 K, indicate that the at equilibrium the concentrations of cupric ions will predominate and the conversion of cuprous ions to cupric ion is energetically favorable.

The destability in cupric state can be happening only when the concentration of cuprous ions becomes very low through processes such as saturation precipitation or through complexation with cyanide anions or ammonia molecules. The Pourbaix diagram constructed for copper in aqueous phase reveals different zones of stability for the protective oxide film. The proton reduction curve traced over different hydrogen activity and oxygen reduction curve traced like wise over different activity zones yields two parallel curves of slope 0.059 as per the equation,

\[
E = 0.0 - 0.059p^H + 0.03\log p^H \]

for the reaction \( 2\text{H}^+ + 2e = \text{H}_2 \),

While for the reaction \( \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e = 2\text{OH}^- \),

\[
E = 1.23 - 0.059p^H + 0.15 \log p^{\text{O}_2}.\]

The Pourbaix diagram constructed for the Cu H2O system reveals the nobility of the Cu towards oxidation and curve originates from a point where the proton reduction curve tracing begins. The trajectory begins to slope down at basic \( p^H \) indicating the formation of cuprous ions.

The thermal conductivity of copper and its alloys being high the use of copper based alloys in heat exchangers for recovering waste heat in power plants is on the
rise. The condenser tubes mounted below low pressure turbine extracts all the latent heat of steam and condenses it to water at decreased pressure. The rate of production of steam and the rate at which it is condensed will be enormously high in power stations that are operating at very high pressure. Any imbalance in the rates of the two processes can throw the power station off gear.

The heat exchanging ability of copper based alloy tubes can suffer under the instances of an insulative film developing on any of two exposed surfaces. Also the heat exchanging can decrease drastically if alloy matrix looses any of the constituents through corrosion processes. Copper based alloys do frequently loose alloying component through, for instance, dezincification process. The other factor that can lead to the decreased heat exchanging efficiency is deposition of non conductive scales which could be salts thrown out from saturated solutions or even the gritty corrosion debris lodging on the heat exchange area.

The corrosion in condenser tubes was a problem of great magnitude in the first quarter of the century. This intriguing problem has been thoroughly investigated and widely practiced remedial methods are to be attributed to painstaking research carried out by Bengough et al\(^\text{[150, 151]}\)

The occasional failure of condenser tubes can be due to factors listed below,

1) Localised attack or pitting in badly contaminated waters.
2) Pitting under decaying barnacles, shell fishes or other deposits.
3) Impingement attack due to high local water velocities.
4) Erosion due to sand or other abrasive particles suspended in water
5) Use of tubes of wrong alloy or incorrect composition containing manufacturing defects.
The industrially practiced methods of retrieving the heat exchanging surface involve cleaning the affected areas physically through wire brushing or through bullet cleaning and if the surface couldn’t be recovered by the processes mentioned, as a last resort, the surfaces will be acid pickled in presence of suitable inhibitor to protect the pristine bare metal.

As the aphorism says the precaution is better than the prevention a good water chemistry, meticulous alloy selection, corrosion protection supplements viz anodizing or cathodising, and frequent on line monitoring can save not only unnecessary plant shut downs but also prolong the life expectancy of the plant.

The microbial induced corrosion in copper and allied tubes is quite expected in contaminated waters. The cooling water flown through shell and tube heat exchanger made out of copper alloy tubes deposits microbial spores on the tube surface. The spore grows in to colony and appear as blister. The surface under neath the blister gets pitted leading to material failure at a later date.

The presence of H₂S gas in water should indicate the presence of sulpha vibrio bacteria. A thoroughly disinfected cooling water does not harbor any sort of organic life. This would help in maintaining clean heat exchanging surface. The reference cited will shed more light on the microbial menace and its control.

The problem of corrosion in condenser tubes has been found to eat huge exchequer from national earnings of Japan and research work cited in the reference briefs about the electrochemical methods adopted during one of the pioneering works carried out.

The corrosion prevention in tube plates and tube ends with base metal structure totally insulated through rubberized paintings becomes very much essential.
The designs of the condensers in the past would have exposed less noble body metal facilitating the anodic protection.

The designs in vogue necessitates application of negative potential or mounting sacrificial anodes in the form of iron studs to mitigate corrosion in copper structures. Apart from the physical methods of preventing corrosion it requires to protect the system while it is under load.

The food and beverage industry where in copper and its alloys find preference by the virtue of chemical resistance will have to be protected against the fermentation acids such as formic and acetic acid induced corrosion.

The use of system compatible media miscible chemical formulations whether organic or inorganic in nature to offer insitu protection against the corrosion is being widely practiced nowadays. With the availability of formulations which can be safely incorporated even in food and beverage industry are presently available in the market. The use of extracts of vegetative origin as corrosion inhibitors are explicitly investigated by researchers for devising an eco friendly formulations to combat corrosion.

Although the ability of copper to withstand corrosion induced by acid is well known the presence of dissolved oxygen or carbon dioxide or ammonia gas renders it susceptible for corrosion.

Not withstanding the vulnerability of copper and copper based alloys towards corrosion in environs that contain gaseous pollutants as mentioned in the concluded paragraph, copper and its alloys have been successfully used to handle hydrofluoric acid, sulphuric acid, phosphoric acid and other fatty acids.

The inhibitors are the compounds finding maximum use now days as a solution to corrosion prevention under insitu conditions. The inhibitors since time of
their invention have gone a sea change in terms of the formulations, effectiveness, versatality and most significantly they have become more eco friendly. The organic formulations have been found to successfully inhibit corrosion in many substrate surfaces and variety of environments.

The requirement of a supposed inhibitor compound, as explored through researches, must possess in the molecule matrix, groups which can extend the valency through coordination such as oxygen atom of aldehyde alcohols, nitrogen of amides amine or Sulphur of thiols or thiophenes or even the sites of unsaturation.

The requisites of the inhibitor could all be satisfied through single compounds or synthesized through means to incorporate all in one compound.

The condensation reaction effected between aldehyde group and amine group yields aldoxime with imine linkages.

The use of condensation products as corrosion inhibitor on steel, copper and its alloy in acidic environment, the use of amino acids, amides, and triazoles as corrosion inhibitors in acidic environments have been the focus of many investigations in the field. The schiffs bases, as condensation products are otherwise also called as, form the basis of the investigations carried out in this project as inhibitors against organic acid induced corrosion in admiralty brass. The potential of using compound with hetero atoms as corrosion inhibitors in acidic medium on variety of metal substrates have been documented.

As an attempt to synergise the inhibitive performances of known ligand groups which are part of separate molecules in to one compound and exploit their possible inhibitive efficiency against acid induced corrosion in brass, schiffs bases were synthesized in accordance with first principles of organic chemistry using
aldehyde, amine amino acids and hydrazine. The resulting aldoximes and hydrazides were used as inhibitors in acetic acid medium on brass metal coupons.

The performances were evaluated through mainly electrochemical studies and weight loss in un-stirred corroding acetic acid medium. Elevated temperature performances were part of the investigation. The surface morphology of the inhibitor film developed by the virtue of adsorption on the metal substrate was evaluated through electron probing.
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Hydrazides as corrosion inhibitors on admiralty brass in 2N acetic acid

Hydrazine sulphate reacts with aldehyde under room temperatures in presence of liquor ammonia to form hydrazides. With both reactive amine groups participating in the reaction the azine link will be established at both ends. The triazoles have known history of corrosion inhibiting quality on copper and its alloys in variety of environment. This is attributed to the presence of heteroatoms in the form of oxygen and nitrogen with whose lone pair of electrons the inhibitor molecule binds on to the metal substrate.

The azides which can partly satisfy the pre requisites of inhibitor molecule through the presence of N atoms and conjugated unsaturation have been evaluated as corrosion inhibitor in steel in acid medium. The possibility of azides performing as inhibitors on copper and its alloys in organic acid medium forms the crux of the present investigation.

The copper exhibits lower dissolution tendency in acids by the virtue of nobility and as such the threat of acid leaching the substrate metal surface is less but still the alloy component being less nobler than copper de alloying can set in. The de-alloyed copper will be having lower mechanical strength and porous matrix leading to structure failure.

The solubility of corrosion product plays a significant role in mitigating the overall corrosion rate. In the present case the solubility of cupric acetate being less the corrosion debris can lodge on the metal surface and prevent further acid attack on the metal. The coarseness and the porosity of the debri can stimulate further corrosion through differential oxygenation.
The Hydrazides FFMH, FMH that were synthesized and investigated for corrosion inhibition efficiency on corten steel in acidic medias as covered in chapter 4 and 5 formed the part of investigation of performance as inhibitor against acetic acid induced corrosion on brass substrate.

The practical procedures involved in synthesizing compound, product purification, compound structure and the corresponding IR graphs have been given in chapter 4.1 through 4.3. The practical problem encountered during product dissolution in aqueous corroding media and the necessity of having polar solvent combination has been highlighted in previous chapters. The corroding media in the present investigation part has been selected as 2N Acetic acid and admiralty brass as substrate.

The performance of the inhibitor in acetic acid medium on admirality brass coupons were evaluated through weight loss technique, galvano static polarisation technique, and elevated temperature performance at optimized concentration were carried out to know the thermodynamic parameters.

The surface morphology of inhibitor film developed on the brass coupons were mapped using scanning electron microscope at high resolution.

6.1.1 Results and Discussions
6.1.1.1 Galvano static polarization method

The performance of azide inhibitors on brass coupons in acetic acid medium was evaluated galvano statically by polarizing the working electrode against non polarisable platinum electrode. The chemical reactions initiated at the inseparable anode and cathode centres at the instance of polarisation can create sufficient turbulence so as to dislodge the adhered corrosion product. The artificial creation of
polarity leads to creation of driving force which would attract the electro active species and harbor reactions. The existence of concentration gradient between the electrode surface and the bulk of the solution introduces diffusion-based transportation.

The presence of too many forces acting at the solution electrode interface does not provide unequivocal comparison of with weight loss data. The weight loss data was generated by observing weight loss in corrosion coupon by immersing in un-stirred corroding medium. The driving force under unstirred conditions is merely diffusion and ion transportation to metal surface takes place by the virtue of concentration gradient only. The situations existing at and near the metal surface during weight loss observations offer a conducive situation to promote insulative film growth in presence of dissolved oxygen.

During polarisation studies the surfaces of corrosion coupons were prepared as per the procedure suggested in chapter 3 and to minimize the area to be polarized insulating varnish was applied on all sides except $1cm^2$ area at the bottom of one face.

The paraphernalia required for galvano static polarisation method for evaluating the inhibitor compound, procedures adopted while preparing the media as well as the corrosion coupons and strategy evolved during the evaluation have all been identical to the one practiced in previous chapters.

The tafel curve was constructed by plotting polarized voltage against dc current. The corrosion parameters such as tafel slopes, equivalent corrosion current and equivalent corrosion potential were arrived through graphical interpretation. The inserted graphs are the tafel curves constructed for the inhibitor FMH and FFMH azides over different concentrations in corroding medium.
Fig. 6.1.1.1 polarisation curve of FMH

Fig. 6.1.1.2 polarisation curve of FFMH
The inserted table 6.1.1.1 contains the corrosion parameters as arrived through method of intercept.

**Table 6.1.1.1 Corrosion parameters generated via Galvano static polarisation method in 2N HAc media at 303K**

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration</th>
<th>$i_{corr}$ ($\mu$A cm$^{-2}$)</th>
<th>Corrosion rate gpy</th>
<th>%IE</th>
<th>$b_a$ (mv)</th>
<th>$b_c$ (mv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%Wt</td>
<td>ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FMH</td>
<td>0.00</td>
<td>-</td>
<td>44.66</td>
<td>0.9201</td>
<td>-</td>
<td>15.00</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>200</td>
<td>14.08</td>
<td>0.2900</td>
<td>68</td>
<td>46.10</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>400</td>
<td>12.02</td>
<td>0.2476</td>
<td>73</td>
<td>43.24</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>600</td>
<td>6.92</td>
<td>0.1425</td>
<td>85</td>
<td>40.00</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>800</td>
<td>4.86</td>
<td>0.1000</td>
<td>89</td>
<td>40.00</td>
</tr>
<tr>
<td>FFMH</td>
<td>0.00</td>
<td>-</td>
<td>44.66</td>
<td>0.9201</td>
<td>-</td>
<td>15.00</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>200</td>
<td>24.90</td>
<td>0.5131</td>
<td>44</td>
<td>0857</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>400</td>
<td>22.38</td>
<td>0.4620</td>
<td>50</td>
<td>1212</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>600</td>
<td>18.75</td>
<td>0.3825</td>
<td>58</td>
<td>0640</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>800</td>
<td>17.37</td>
<td>0.3578</td>
<td>61</td>
<td>0500</td>
</tr>
</tbody>
</table>

The tafel curves constructed with different inhibitor concentration for brass in acetic acid medium appears to trace an identical profile with multiple inflection points.

The cathodic tafel curves are characterized by three different zones namely the charging of double layer of the capacitor which proceeds flat to the current axis. The portion of the curve after first inflection traces almost linear profile with respect to the applied current. The last part of the curve could be due to the initiation of water...
molecule reduction curve or it could also be due to continuous charging of some electrically conductive corrosion debri which is preventing the access of acid to bare metal with simultaneous introduction of over voltage. The overall corrosion rate in brass coupon immersed in corroding medium sans inhibitor compounds decreased with the increased time of immersion.

The profile after the first inflection point represents the inhibitor film build up stage and with more current admitted the curve should have started tracing line parallel to ordinate axis (Y-axis) as is the case with limiting current marking the commencement of hydrogen evolution. This could have been seen at the electrode solution interface if the adsorbed film is electrically stable enough to add over voltage to electrode reaction. The profile instead appears to slope down indicating capacitative nature of the adsorbed film.

The anodic polarisation curve characterized by gradual raise in the voltage with the applied current. indicating metal dissolution. The flattened profile of anodic polarisation curve could also be due to unlimited capacitance of the corrosion debri lodging on the electrode surface.

The shift in open circuit potential to more positive side than the standard reduction potential can be attributed partly to the presence of zinc in the alloy composition. The tendency of zinc, a less noble element in the matrix, to oxidize easily in aerated acid media could influence the open circuit potential (OCP). Mere line polarity could be triggering dissolution in the alloy.

The compound FMH appears to reduce corrosion rate in brass coupon with the increase in concentration. The anodic dissolution obstructs the interpretation of the possible shifts in equivalent corrosion potential the inhibitor compounds can bring in.
Like wise the tafel slope for anodic half of the polarisation curve whose overall profile runs almost parallel to ordinate axis could not be inferred from the graph.

The tafel slope for the cathodic polarisation curve for the inhibitor FMH reflects the slowing down of the polarisation process across the working electrode before the profile reaches second inflection point. This indicates that the charging of capacitor at metal solution interface now has to penetrate sufficient depth created by adsorption of inhibitor molecules before the bulk of the solution is reached. Also it is a fact that the composition of the capacitor has changed from the one that does not contain the inhibitor compound. The decreased cathodic tafel slope observed at different concentration would only substantiate the arguments submitted.

The compound FFMH was found to decrease in overall the corrosion rate with the increase in inhibitor concentration. The overall profile of the tafel curves does not appear to change much. The cathodic tafel halves of the compound criss crosses one another at and near inflection points there by necessitating the construction of tafel curves for individual concentrations. The decrease in cathodic tafel slopes over different concentrations would only imply the formation and growth of adsorption layers deep in to the bulk of the solution. The effectiveness of the inhibitor FFMH as compared against FMH is less pronounced this could perhaps be attributed to the size related hindrances coming in to play.

Both the compounds do satisfy the requisites of an inhibitor such as possessing conjugated double bonds and hetero atoms for coordination.

The order of inhibiting efficiency can be arranged in the way given below,

FMH > FFMH.
6.1.1.2. Adsorption isotherms

The molecules with hetero atoms in their structure subscribe to a special ability to bind on to recipient surfaces through act of chemisorption or physisorption. The hetero atoms with unpaired electrons at their disposal can extend the valency with metals having vacant d orbital.

In the course of adsorption the molecules will be establishing a physical barrier between metal and surrounding medium. The inhibitive ability of some of the classes of organic compound is attributed in essence to the phenomena of adsorption. The extent of inhibition offered depends on the magnitude of the surface coverage. The rate of adsorption and rate of desorption reaches out equilibrium and the constant of which bears a definite relation with extent of surface coverage.

Different adsorption models with each one specifically suiting to one mode of adsorption pattern are defined in terms of mathematical models called in the honour of scientists who proposed them.

To correlate the extent of surface coverage and the concentration of inhibitor many mathematical models are in vogue such as Flory Huggins, Langmuir, Tempkin Frumkin and BDM to name a few. The mathematical expressions for different isotherms are presented in chapter 4.

The adsorption isotherm that exactly fits the experimental data has to be ascertained through the curve fitting. The extent of inhibition offered by the inhibitor molecules can directly be related to the surface coverage and hence the corrosion rate.

The table inserted below contains different parameters required for tracing isotherms using different mathematical equations.
Table 6.1.1.2 Data of FMH for graphical fits of adsorption isotherms

<table>
<thead>
<tr>
<th>Concentration ppm</th>
<th>Conc Moles/lttr.</th>
<th>lnC</th>
<th>Surface coverage ( \theta )</th>
<th>ln((\theta/1-\theta))</th>
<th>ln[(C(1-\theta))]</th>
<th>(\theta^{3/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>3.57x10^-3</td>
<td>-5.635</td>
<td>0.68</td>
<td>0.7759</td>
<td>-6.410</td>
<td>0.57</td>
</tr>
<tr>
<td>400</td>
<td>7.14x10^-3</td>
<td>-4.942</td>
<td>0.73</td>
<td>0.9986</td>
<td>-5.941</td>
<td>0.62</td>
</tr>
<tr>
<td>600</td>
<td>0.0107</td>
<td>-4.537</td>
<td>0.85</td>
<td>1.6966</td>
<td>-6.234</td>
<td>0.78</td>
</tr>
<tr>
<td>800</td>
<td>0.0142</td>
<td>-4.248</td>
<td>0.89</td>
<td>2.1040</td>
<td>-6.352</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Fig 6.1.1.3 Tempkin fit of FMH/HAc Cu
The interaction parameter \( f \) interpreted as slope of the graph has a value 6.52 indicating there is inter molecular attraction and the value of adsorption desorption equilibrium, \( K \), interpreted through the intercept, has a value, 21,587. The drop in free energy for the adsorption of FMH molecules on the brass surface is of the magnitude \(-35.25 \) K joule/mole. The compound FMH appears to follow with approximation Tempkin type adsorption model. The data table contains different ordinate and abscissa parameters used during model fitting.

**Table 6.1.1.3 Data the FFMH for graphical fits of adsorption isotherms**

<table>
<thead>
<tr>
<th>Conc(^a) ppm</th>
<th>Conc Moles/ltr</th>
<th>lnC</th>
<th>Surface coverage ( \theta )</th>
<th>ln ((\theta/1-\theta))</th>
<th>ln ([C(1-\theta/\theta)])</th>
<th>( \theta )(^m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.063x10(^{-3})</td>
<td>-6.85</td>
<td>0.44</td>
<td>0.4519</td>
<td>-7.30</td>
<td>0.48</td>
</tr>
<tr>
<td>400</td>
<td>2.127x10(^{-3})</td>
<td>-6.15</td>
<td>0.50</td>
<td>-0.0088</td>
<td>-6.14</td>
<td>0.35</td>
</tr>
<tr>
<td>600</td>
<td>3.191x10(^{-3})</td>
<td>-5.75</td>
<td>0.58</td>
<td>0.3400</td>
<td>-6.08</td>
<td>0.45</td>
</tr>
<tr>
<td>800</td>
<td>4.255x10(^{-3})</td>
<td>-5.46</td>
<td>0.61</td>
<td>0.4519</td>
<td>-5.91</td>
<td>0.48</td>
</tr>
</tbody>
</table>

The compound FFMH appears to follow Tempkin type adsorption while adsorbing on brass substrate coupon in acetic acid medium. The interaction parameter, which is a measures, inter molecular interaction, is positive with a value 8.34. The value of adsorption desorption equilibrium turns out to be 37254 while the drop in free energy is around \(-36.63 \) K joules/mole. The inserted table contains the data used for ascertaining the adsorption kind.
6.1.1.3 Elevated temperature studies and Arrhenius plots.

To know the performance of inhibitors at elevated temperature and to find out the thermodynamic parameters such as $\Delta H$, $\Delta S$ and $\Delta G$ inhibition studies were conducted at optimized concentrations of inhibitor and at temperatures of $30^0\text{C}$, $40^0\text{C}$ and $50^0\text{C}$. All standard practices that guarantee clean polished surfaces on working electrodes were followed to eliminate the errors. The required experimental set up and the preparation of test medium containing FMH, FFMH were imitated in lines with the methodology as followed in chapter 4.3 excepting that acetic acid replaced other acids.

The specimen brass coupon preparation, its alignment inside the three compartment polarisation cell and polarisation data accumulation were followed as per the practices suggested in concluded chapters.
The tafel graphs were constructed for the data collected and graphs were interpreted through the method of intersection. The corrosion rate was calculated applying faraday conversion factor on the equivalent corrosion current data.

Yet another set of experiment identical in all respects excepting that the corroding medium does not contain any of the inhibitors was also performed with specimen coupons. The tafel curves were constructed to find out the corrosion rate in plain corroding medium.

The Arrhenius plots were constructed by plotting \( \ln \left(\frac{\theta}{1-\theta}\right) \) versus reciprocal temperature expressed in absolute scale yielding a straight line whose slope corresponds to the enthalpy change occurring during the course of adsorption. Here \( \theta \) corresponds to the surface coverage and the ration signifies the equilibrium constant.

The thermodynamic parameter \( \Delta G \) was arrived through the relation

\[
\Delta G = RT \ln 55.5^\circ K
\]

where terms have usual meanings.

The entropy change occurring during the adsorption process has been arrived through mathematical relation \( \Delta G = \Delta H - T\Delta S \).

<table>
<thead>
<tr>
<th>( \frac{1}{T \times 10^3 K} )</th>
<th>( \ln \left(\frac{\theta}{1-\theta}\right) )</th>
<th>( \theta )</th>
<th>( \ln \left(\frac{\theta}{1-\theta}\right) )</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FFMH</td>
<td>FFMH</td>
<td>FMH</td>
<td>FMH</td>
</tr>
<tr>
<td>3.3</td>
<td>-0.2318</td>
<td>0.44</td>
<td>0.7759</td>
<td>0.68</td>
</tr>
<tr>
<td>3.1948</td>
<td>-0.3792</td>
<td>0.41</td>
<td>0.1603</td>
<td>0.54</td>
</tr>
<tr>
<td>3.0959</td>
<td>-0.5356</td>
<td>0.37</td>
<td>0.0000</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Table 6.1.1.5 Elevated temperature Corrosion parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>i₀ ma/cm²</th>
<th>C</th>
<th>Rate</th>
<th>%η</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain 2N HAc</td>
<td>303K</td>
<td>0.0447</td>
<td>0.9201</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>313K</td>
<td>0.0772</td>
<td>1.5898</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>323K</td>
<td>0.0891</td>
<td>1.8360</td>
<td>-</td>
</tr>
<tr>
<td>0.02% FMH</td>
<td>303K</td>
<td>0.0141</td>
<td>0.2901</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>313K</td>
<td>0.0355</td>
<td>0.7309</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>323K</td>
<td>0.0447</td>
<td>0.9202</td>
<td>50</td>
</tr>
<tr>
<td>0.02%FFMH</td>
<td>303K</td>
<td>0.0249</td>
<td>0.5131</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>313K</td>
<td>0.0458</td>
<td>0.9438</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>323K</td>
<td>0.0562</td>
<td>1.1580</td>
<td>37</td>
</tr>
</tbody>
</table>

Fig 6.1.1.5 Arrhenius plot of FMH
Fig 6.1.1.6 Arrhenius plot of FFMH
From the table inserted below it can be seen that the thermodynamic parameter entropy decreases in both the investigated compounds. Also the rate of corrosion increased with the increase in temperature with respect to compounds FMH and FFMH.

Table 6.1.1.6 Thermodynamic parameters data table

<table>
<thead>
<tr>
<th>Comp&lt;sup&gt;ad&lt;/sup&gt;</th>
<th>Conc ppm</th>
<th>Interaction Parameter f.</th>
<th>Rate constant K</th>
<th>Free energy change ΔG KJ/mole</th>
<th>Enthalpy change ΔH KJ/mole</th>
<th>Entropy change ΔS J/mole</th>
<th>Adsorption type</th>
</tr>
</thead>
<tbody>
<tr>
<td>FMH</td>
<td>200</td>
<td>6.52</td>
<td>21,587</td>
<td>-35.25</td>
<td>-31.66</td>
<td>11.84</td>
<td>Tempkin</td>
</tr>
<tr>
<td>FFMH</td>
<td>200</td>
<td>8.34</td>
<td>37,254</td>
<td>-36.63</td>
<td>-12.31</td>
<td>80.26</td>
<td>Tempkin</td>
</tr>
</tbody>
</table>

6.1.1.4 Scanning Electron Microscope probing

The practical procedures involved while preparing SEM designate sample strips, inhibitor solution preparation, methodology for developing adsorption film, intact preserving of the inhibitor film on the surface of brass coupon till contour mapping using SEM have all been followed as per the scheme adopted in chapter 4.1. The inserted figures are the SEM images of the inhibitor deposited on substrate brass surface.
Fig 6.1.1.7a SEM image of Plain brass coupon and its negative aspect

Fig 6.1.1.7b SEM image of corroded Plain brass coupon in 2N HAc
Fig 6.1.1.7c SEM image of brass coupon in HAc with FMH.

Fig 6.1.1.7d SEM image of brass coupon in HAc with FFMH.
The aberrations in the surface preparation due to soft nature could be seen in the SEM picturisation. The comparison of SEM images and its negative version placed beside one another exposes the spots at which deposition of corrosion debris has taken place. Also it reveals the pitting corrosion that was taking place beneath the surface of the debris. The presence of whitish spots on the developed image indicates the spots of active corrosion.

The fig 6.1.1.7a corresponds to the SEM image and its negative version of plain brass surface. The dark spots in the positive version are merely the surface dents and the shadow seen in the negative version indicates some dust on the coupon.

The fig 6.1.1.7b corresponds to the SEM image and its shadow version of the brass surface immersed in the acetic acid. It can be seen from the morphology that acid induced pitting causes blister like perforations on the metal surface. Also the pitting density being less as well as taking the weight loss data into cognizance it can be inferred that the net corrosion rate in brass coupon in 2N acetic acid is less. The lack of presence of residual corrosion product on the surface implies that the debris adhesion is weak.

The fig 6.1.1.7c stands for the SEM image and its negative version of brass coupon immersed in acetic acid with inhibitor compound FMH. The zoomed version of the negative image displays few pittings and otherwise its performance is reasonably good.

The fig 6.1.1.7d stands for the SEM image of the inhibitor film formed on brass substrate in acetic acid medium containing FFMH. The zoomed up version of the negative image of film grown on the substrate brass coupon by the inhibitor FFMH reveals formation of pits at few locations. The film growth is otherwise
uniform. The pit density as compared to bare metal corrosion in acid medium appears to be less.

6.1.1.5 Weight loss observations.

Due to passive corrosion that was observed in admiralty brass specimen coupons when immersed in 2N acetic acid over extended times of immersion, the study of weight loss in brass coupons in presence of inhibitor compounds at different levels of concentration were restricted to two hour duration.

An identical metal preparation method was adopted during the evaluation and cleaning metal surfaces as per the methodology described in chapter 3 were strictly complied with only to eliminate the errors that could creep because of metal surface aberrations.

Weight loss observations were made on corrosion test coupons made out of admiralty brass of composition Cu 97% Zn 2% and Ni 1%. The mirror finish in corrosion coupons could not be obtained as even fine emery abrasion leaves uneven surface. This is quite expected, as the element is mechanically soft.

The corrosion test coupons measured linear dimensions of 7.6cmx1.28cmx0.2cm and corrosion studies were made by immersing in 200 ml of unstirred 2N HAc solution with and without solubilised inhibitor for fixed immersion time periods of 2 hours with increments in concentrations of the inhibitor.

During the evaluation the concentration of the inhibitors were varied from 200 ppm to 800 ppm a level well within the concentration of inhibitor used during acid cleaning of water side of condenser tubes and other associated heat exchangers.

During profiling of the admiralty brass coupons for corrosion rate as a function of different time periods of immersion under unstirred conditions in different acids it was observed that the corrosion rate, in addition being low, also decreased
with the increase in time of immersion. The inserted table contains the corrosion rate in admiralty brass in plain 2N acetic acid with 25 ml solvent mixture.

**Table 6.1.1.7 Corrosion rate data of Admiralty brass in 2N HAc.**

<table>
<thead>
<tr>
<th>Admiralty brass.</th>
<th>2 hours</th>
<th>4 hours</th>
<th>6 hours</th>
<th>8 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion rate in gpy</td>
<td>1.25</td>
<td>0.540</td>
<td>0.490</td>
<td>0.345</td>
</tr>
</tbody>
</table>

One of the expected corrosion product with HAc is cupric acetate whose solubility in water is low. Perhaps the extended time periods of immersion facilitate adhesion of the corrosion debris on metal surface. The access for the acid or inhibitor molecule on to the metal surface, quite possibly, is restricted if not totally denied. This is a valid proposition, as oxide film growth in acidic medium does not take place.

Also it is essential that the inhibitor molecule should bind on to the substrate surface through act of coordination and any factor that intervenes with the act is bound to be reflected across the overall inhibitive efficiency.

The weight loss observations having been carried out in the static condition the dislodging of the debris from the surface does not take place effectively. The observations made with respect to the inhibitor compounds appear to reflect the possible influence of the corrosion debris. The compounds studied show decreased symptoms of corrosion inhibition irrespective of the concentrations of the inhibitor compound.

On the other hand polarisation experiments creates fresh surface by the virtue of vigorous microscopic level activity harbored at working electrode irrespective of the cycle of polarisation.
Conclusions

- Admiralty brass does not appear to suffer severely from the acid induced corrosion.
- Hydrazides perform well as corrosion inhibitors on brass surface in acetic acid medium.
- Amongst the hydrazides the compound FMH out performs the compound FFMH.
- The order of inhibitive efficiencies presented above gets able support through the SEM findings.
- The adsorption of inhibitors on to the brass surface proceed through coordination bonding.
- The compound FMH obeys Tempkin isotherm during adsorption.
- The compound FFMH obeys Tempkin isotherm during adsorption.
- The adsorption of inhibitor molecules on to the surface of metal proceeds with liberation of heat energy.
- The adsorption of molecules on to the surface leads to overall decrease in entropy.
- The free energy decreases sufficiently during the adsorption of inhibitor compounds.
- The increase in temperature decreases the overall inhibitive efficiency of the compounds.
- The solubility of azides in water media is very low and commands solubilisation using polar solvent mixtures.
- The anodic dissolution of the metal during anodic polarisation renders tafel slope low in magnitude.
- The cathodic tafel curve shows two inflection points marking commencement of two cathodic processes such as hydroxide reduction and hydrogen evolution.
Chapter 6.2

Aromatic Hydrazides as corrosion inhibitors on admiralty brass in 2N acetic acid medium

In retrieving the lost heat exchange surface of water wall side of admiralty brass tube in thermal power station routinely practiced procedure involve pickling tubes across water side with mild acids such as citric acid accompanying with the inhibitor. Hydrochloric acid has also been used in occasions to remove carbonaceous scales. To enhance the effectiveness of the process the temperature of the acid bath will be raised to 60 to 80°C.

In the course of pickling the threat of leaching of base metal looms large necessitating the use of system compatible inhibitor compounds that can selectively block the substrate metal. Owing to extensive research in the recent past there are now plethora of proprietary controlled formulations available in the market which can be used as an insitu inhibitor during the acid cleaning of the dirt laden cooling tubes.

The triazoles have known history of corrosion inhibiting quality on copper and its alloys in variety of environment as such the derivatives of triazoles have been extensively investigated for corrosion inhibition properties on copper based alloys. The inhibitive properties, from first principles of corrosion inhibition chemistry, are attributed to presence of atoms or groups which can extend their valency through coordination.

The ability of Hydrazine sulphate to react at two free ends to form azines has been extensively used in commercial applications as well as academic purposes to derive end products with various end uses. Thus hydrazine reacts with aldehyde under room temperature conditions in presence of liquor ammonia to form hydrazides. The presence of ammonia ensures removal of sulphuric acid which otherwise would have
thwarted reaction. As the reaction extends to both amine groups the reaction yields di
azides as end product.

The azides which can partly satisfy the pre requisites of inhibitor molecule
through the presence of N atoms and conjugated unsaturation have been evaluated as
corrosion inhibitor in steel in acid medium. The possibility of azides performing as
inhibitors on copper and its alloys in organic acid medium forms the crux of the
present investigation.

To have the synergised inhibitory performance of both hydrazine and
aldehydes, simple aromatic aldehydes and their homologues were taken for evaluation
purpose\textsuperscript{(16)}.\n
The hydrazides, NDBH and DBMH, which were evaluated for performance
on corten steel surface in corroding acid medium in the preceding chapters were again
considered for the performance evaluation in acetic acid medium on brass substrate.
The procedures followed while synthesizing the afore said inhibitors have been given
in chapter 4.3. The structures of the compounds and the IR spectras are presented as
inserts in the chapter 4.3.

The solubility associated problem in respect to the referred hydrazides and the
necessity of polar solvent mixture have been highlighted in the chapter 4.3. The
methods of evaluating the inhibitory performance of the compounds and the relevant
preliminary coupon preparation, solution preparation strategy discussed in previous
chapters have been adopted in the present investigation.

The copper, in the absence of dissolved oxygen, exhibits lower dissolution
tendency in acids by the virtue of nobility and as such the threat of acid leaching the
substrate metal surface is less but still the alloy component being less nobler than
copper de alloying can set in. The de-alloyed copper will be having lower mechanical
strength and porous matrix leading to structure failure. The presence of dissolved oxygen and anions that can form soluble complexes, enhance copper leaching.

The solubility of corrosion product plays a significant role in mitigating or enhancing the overall corrosion rate. In the present case the solubility of cupric acetate being less the corrosion debris can lodge on the metal surface and prevent further acid attack on the metal. The coarse ness and the porosity of the debri can stimulate further corrosion through differential oxygenation.

The performance of the inhibitor in acetic acid medium on admiralty brass coupons were evaluated through weight loss technique, galvano static polarisation technique, and elevated temperature performance at optimized concentration were carried out to know the thermodynamic parameters.

The surface morphology of inhibitor film developed on the brass coupons were mapped using scanning electron microscope at high resolution.

6.2.1 Results and Discussions

6.2.1.1 Galvano static polarisation method

The performance of azide inhibitors on brass coupons in acetic acid medium was evaluated galvano statically by polarizing the working electrode against non polarisable platinum electrode. The voltage generated at specimen electrode was monitored against a standard calomel electrode.

The instant the electrodes are polarized, attractive forces of sufficient magnitude comes in to fore and electrode designated chemical reactions start taking place. The driving forces such as electrostatic and concentration fluxes across different layers of the test solution sustains the reaction. The chemical reactions so initiated at the inseparable anode and cathode centres can create reasonable turbulence
as to peel off the corrosion debris from the surface. The presence of too many forces acting at the solution electrode interface does not provide unequivocal comparison of with weight loss data. The weight loss data was generated by observing weight loss in corrosion coupon by immersing in un stirred corroding medium. The driving force under unstirred conditions is merely diffusion and ion transportation to metal surface takes place by the virtue of concentration gradient only. The situations existing at and near the metal surface during weight loss observations offer a conducive situation to promote insulative film growth in presence of dissolved oxygen.

During polarisation studies the surfaces of corrosion coupons were prepared as per the standard procedure and to minimize the area to be polarized insulating varnish was applied on all sides keeping $1\text{cm}^2$ area at one face blocked by flex tape. The practical procedures adopted in galvanostatic polarisation studies covered in previous chapters were followed in totality while generating experimental data involving referred inhibitors in acetic acid medium.

The tafel curve was constructed by plotting polarized voltage against DC current. The corrosion parameters such as tafel slopes, equivalent corrosion current and equivalent corrosion potential were arrived through graphical interpretation.

The inserted figures are the tafel curves constructed for the inhibitor NDBH and DBMH azides over different concentrations in corroding medium. An identical polarisation experiment was conducted on admiralty brass coupon in corroding medium with all ingredients san inhibitors.
Fig 6.2.1.1 Polarisation curve of NDBH

Fig 6.2.1.2 Polarisation curve of DBMH
The inserted table contains the corrosion parameters arrived through curve extrapolation and other graphical interpretations.

Table 6.2.1.1 Corrosion parameters generated via Galvano static polarisation method in 2N HAc media at 303K

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration</th>
<th>( i_{corr} ) ( \mu \text{Acm}^{-2} )</th>
<th>Corrosion rate, gpy</th>
<th>%IE</th>
<th>( b_a ) mv</th>
<th>( b_c ) mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDBH</td>
<td>0.00</td>
<td>44.66</td>
<td>0.9201</td>
<td>-</td>
<td>15.00</td>
<td>2171</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>39.80</td>
<td>0.8198</td>
<td>11</td>
<td>46.10</td>
<td>1312</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>33.10</td>
<td>0.6819</td>
<td>26</td>
<td>43.24</td>
<td>1198</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>29.85</td>
<td>0.6142</td>
<td>33</td>
<td>40.00</td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>25.10</td>
<td>0.5171</td>
<td>44</td>
<td>40.00</td>
<td>1312</td>
</tr>
<tr>
<td>DBMH</td>
<td>0.00</td>
<td>44.66</td>
<td>0.9201</td>
<td>-</td>
<td>15.00</td>
<td>2171</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>18.62</td>
<td>0.3835</td>
<td>58</td>
<td>959</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>20.41</td>
<td>0.4204</td>
<td>54</td>
<td>1014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>27.22</td>
<td>0.5607</td>
<td>39</td>
<td>1256</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>28.84</td>
<td>0.5941</td>
<td>35</td>
<td>1268</td>
<td></td>
</tr>
</tbody>
</table>

The tafel curves constructed with different inhibitor concentration for brass in acetic acid medium appears to trace an identical profile with multiple inflection points.

The cathodic tafel half of the polarisation curves constructed for plain acid appears to originate at less negative open circuit potential than compared to the open circuit potential of the inhibited polarisation curves. The shift in potential in OCP
could be interpreted as over voltage introduced due to the affinity driven orientation of the inhibitor molecules towards the base metal substrate.

The anodic half of the tafel curve irrespective of inhibited or un inhibited appears to originate at potentials around close to zero in the tafel curve.

This could be due to unprovoked dissolution of the some components of the alloy at the very slightest temptations such as the polarity reversals at source \(^{(169-170)}\). The external short-circuiting could be sufficient cause for dissolution. The presence of inhibitors does not appear to arrest the dissolution tendency either. The insignificant magnitude of change seen in anodic tafel slopes testify the dissolution process taking place.

The shifting of open circuit potential to more negative side by the inhibitors and subsequent changes in the general profile of the cathodic tafel curve indicate the cathodic protecting nature of the inhibitor be it is NDBH or DBMH. The reactions that are normally promoted at the cathodes do encounter resistance in the form of over voltage when the inhibitors are incorporated in the corroding medium.

The cathode specific reactions such as cupric ion reduction, water molecule reduction or even the proton reduction which appear at specific voltages at the electrode surface suffer kinetically as inhibitor layer builds around the surface.

The cathodic tafel curve was found to have two significant inflection points with one commencing immediately after the capacitor charging regime and the other originating from aborted limiting current curve. The down ward sloping nature of the current voltage curve beyond limiting current curve abortion indicates the continuous build up of potential which may be attributed to the formation of hydroxides. The insoluble cupric hydroxides could in all probability forming second insulative layer around the substrate. The view and the argument presented were ably supported by
the observations made during weight loss studies. The overall corrosion rate decreased with the increased time of immersion during weight loss observations.

The compound NDBH was found to inhibit more effectively as concentration is increased and though the compound possess all requisite quality of an supposed inhibitor the increased concentration could in all probability add sufficient concentration flux to pierce the debri layer and establish itself on the substrate. The clipping of SEM image presented later in the chapter does indicate the presence of pot holes underneath the corrosion debri which in all likely hood get filled up at higher concentrations.

In the molecular structure presented in the beginning of the chapter reveals the presence of extended conjugation hetero atoms in the form of nitrogen and topping them all is the planarity of the molecule. The SEM picture stands testimony for the theoretically predicted surface morphology of the inhibitor film.

The inhibitor compound DBMH was found to offer less protection as concentration was increased. The compound in general was found to be cathodic inhibitor. The polarisation curve traced an identical profile as that of plain acid polarisation curve excepting that it differed at OCP and origin of second inflection point. The truncation of limiting current profile starts at less negative voltage than seen with the inhibitor NDBH. This could possibly be interpreted based on the better proton accommodating nature of the molecule.

The molecule structure presented elsewhere in the chapter indicates the presence of doubly alkylated nitrogen, which could electromerically, enhance the electron density around nitrogen atom. The protonation of nitrogen atom under this electron surplus situation becomes kinetically easy as well as gets strongly bound
also. The lack of sufficient free protons truncates the limiting current. The subsequent water reduction to hydroxide ions begins to be traced by the polarisation curve.

The decreased inhibitory performance of the compound DBMH with the increase in concentration may probably be due to the steric factors associated with the molecule. The presence of di substitution on the molecule could turn out to be a kinetic bottle neck while guided diffusion is taking place.

The anodic polarisation curve characterized by gradual raise in the voltage with the applied current, indicating metal dissolution. The shift in open circuit potential to more positive side than the standard reduction potential can be attributed partly to the presence of zinc in the alloy composition. The tendency of zinc, a less noble element in the matrix, to oxidize easily in aerated acid media could influence the OCP. Mere line polarity could be triggering dissolution in the alloy.

6.2.1.2. Adsorption isotherms

The molecules with heteroatoms in their structure subscribe to a special ability to bind on to recipient surfaces through act of chemisorption or physisorption. The heteroatoms with un paired electrons at their disposal can extend the valency with metals having vacant d orbital. In the course of adsorption the molecules will be establishing a physical barrier between metal and surrounding medium. The inhibitive ability of some of the classes of organic compound is attributed in essence to the phenomena of adsorption. The extent of inhibition offered depends on the magnitude of the surface coverage. To correlate the extent of surface coverage and the concentration of inhibitor many mathematical models are in vogue such as Flory Huggins, Langmuir, Tempkin Frumkin and BDM to name a few. The mathematical expressions for different isotherms are presented in the previous chapter.
The adsorption isotherm for the experimentally observed data points has been ascertained by the method of best fit. The extent of inhibition offered by the inhibitor molecules can directly be related to the surface coverage, \( \theta \) and hence the corrosion rate.

The inserted table gives the parameters required for fitting adsorption curves for the compounds NDBH and DBMH.

**Table 6.2.1.2 NDBH data for adsorption model fitting.**

<table>
<thead>
<tr>
<th>Conc( ^a ) ppm</th>
<th>Conc moles/ltr.</th>
<th>( \ln C )</th>
<th>Surface coverage ( \theta )</th>
<th>( \ln (\theta/1-\theta) )</th>
<th>( \ln [C(1-\theta/\theta)] )</th>
<th>( \theta^{3/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.9615( \times )10(^{-3} )</td>
<td>-6.947</td>
<td>0.11</td>
<td>-2.090</td>
<td>-9.037</td>
<td>0.037</td>
</tr>
<tr>
<td>400</td>
<td>1.923( \times )10(^{-3} )</td>
<td>-6.253</td>
<td>0.26</td>
<td>-1.052</td>
<td>-7.305</td>
<td>0.13</td>
</tr>
<tr>
<td>600</td>
<td>2.884( \times )10(^{-3} )</td>
<td>-5.849</td>
<td>0.33</td>
<td>-0.697</td>
<td>-6.546</td>
<td>0.19</td>
</tr>
<tr>
<td>800</td>
<td>3.846( \times )10(^{-3} )</td>
<td>-5.560</td>
<td>0.44</td>
<td>-0.249</td>
<td>-5.810</td>
<td>0.29</td>
</tr>
</tbody>
</table>

**Table 6.2.1.3 DBMH data for adsorption model fitting.**

<table>
<thead>
<tr>
<th>Conc( ^a ) ppm</th>
<th>Conc moles/ltr.</th>
<th>( \ln C )</th>
<th>Surface coverage ( \theta )</th>
<th>( \ln (\theta/1-\theta) )</th>
<th>( \ln C(1-\theta/\theta) )</th>
<th>( \theta^{3/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.6756( \times )10(^{-3} )</td>
<td>-7.300</td>
<td>0.58</td>
<td>0.335</td>
<td>-6.9648</td>
<td>0.45</td>
</tr>
<tr>
<td>400</td>
<td>1.351( \times )10(^{-3} )</td>
<td>-6.606</td>
<td>0.55</td>
<td>0.180</td>
<td>-6.4264</td>
<td>0.40</td>
</tr>
<tr>
<td>600</td>
<td>2.027( \times )10(^{-3} )</td>
<td>-6.201</td>
<td>0.39</td>
<td>-0.446</td>
<td>-6.6468</td>
<td>0.24</td>
</tr>
<tr>
<td>800</td>
<td>2.702( \times )10(^{-3} )</td>
<td>-5.913</td>
<td>0.35</td>
<td>-0.600</td>
<td>-6.5144</td>
<td>0.21</td>
</tr>
</tbody>
</table>

The compounds were found to trace Tempkin type isotherms.

The interaction parameter, \( f \), which stands for inter molecular interaction indicates the existence of reasonably strong cohesive forces. The thermodynamic
parameters such as adsorption desorption constant and the free energy change that occurs during adsorption process was calculated from the slope and the intercept values.

The order of inhibiting efficiencies of the compounds can be arranged the way given below,

\[ \text{NDBH} > \text{DBMH}. \]

6.2.1.3. Arrhenius plot and elevated temperature studies.

Any chemical reaction irrespective of whether it is microscopic or macroscopic will strongly depend on the reaction temperature and its rate will approximately double for every 10 degree rise in the temperature. On similar grounds even the corrosion rate increases significantly with the temperature.

The adsorption of any components on the active surfaces will, in general, liberate heat energy and any slight rise in temperature will severely dampen the adsorption of the molecules.

The inhibition offered by the organic compounds on to the metal surfaces in corrosive conditions does behave similarly and their inhibition efficiencies are bound to suffer at elevated temperatures.

In the case of adsorption of inhibitor molecules on to the base metal substrate the bonds of the nature covalent or coordinate will be established and hence the quantum of energy exchanged between the participating groups will be reasonably high.

To evaluate the performances of the inhibitor compounds at elevated temperature polarisation experiments were conducted on the substrate coupon as per the practical method adopted in previous chapters.
The corrosion parameters were interpreted through tafel graphs and inhibiting efficiencies were calculated by noting the corrosion current densities. The Arrhenius plots were constructed to find out the enthalpy of adsorption which was measured as slope of the plot between corrosion rate versus reciprocal temperature. The thermodynamic parameter such as entropy was calculated using the parameters ΔG and ΔH. The inserted table contains the Arrhenius plot details.

Table 6.2.1.4 Arrhenius plot data of NDBH

<table>
<thead>
<tr>
<th>1/Tx10^3K</th>
<th>ln(θ/1-θ)</th>
<th>θ</th>
<th>ln(θ/1-θ)</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDBH</td>
<td>NDBH</td>
<td>DBMH</td>
<td>DBMH</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>-2.09</td>
<td>0.11</td>
<td>0.335</td>
<td>0.58</td>
</tr>
<tr>
<td>3.1948</td>
<td>-1.32</td>
<td>0.21</td>
<td>-0.659</td>
<td>0.34</td>
</tr>
<tr>
<td>3.0959</td>
<td>-1.47</td>
<td>0.19</td>
<td>-1.045</td>
<td>0.26</td>
</tr>
</tbody>
</table>
### Table 6.2.1.5 Corrosion rate and temperature data of NDMH, DBMH in acetic acid medium on brass surface

<table>
<thead>
<tr>
<th>Compound</th>
<th>$i_0$ ma/cm$^2$</th>
<th>C Rate</th>
<th>%$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain 2N HAc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303K</td>
<td>0.044</td>
<td>0.92</td>
<td>-</td>
</tr>
<tr>
<td>313K</td>
<td>0.077</td>
<td>1.59</td>
<td>-</td>
</tr>
<tr>
<td>323K</td>
<td>0.089</td>
<td>1.84</td>
<td>-</td>
</tr>
<tr>
<td>0.02% NDBH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313K</td>
<td>0.061</td>
<td>1.26</td>
<td>21</td>
</tr>
<tr>
<td>323K</td>
<td>0.072</td>
<td>1.49</td>
<td>19</td>
</tr>
<tr>
<td>0.02%DBMH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303K</td>
<td>0.019</td>
<td>0.38</td>
<td>58</td>
</tr>
<tr>
<td>313K</td>
<td>0.051</td>
<td>1.05</td>
<td>34</td>
</tr>
<tr>
<td>323K</td>
<td>0.066</td>
<td>1.36</td>
<td>26</td>
</tr>
</tbody>
</table>

![Arrhenius plot NDBH](image)

**Fig 6.2.1.3 Arrhenius plot NDBH**
Table 6.2.1.6 Thermodynamic parameters of NDBH and DBMH on Cu in HAc

<table>
<thead>
<tr>
<th>Comp\textsuperscript{nd}</th>
<th>Conc\textsuperscript{a} ppm</th>
<th>Interaction Parameter f.</th>
<th>Rate constant K</th>
<th>Free energy change $\Delta G$ KJ/mol</th>
<th>Enthalpy change $\Delta H$ KJ/mole</th>
<th>Entropy change $\Delta S$ J/mole</th>
<th>Adsorption type</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDBH</td>
<td>200</td>
<td>10.13</td>
<td>$2.311 \times 10^4$</td>
<td>-35.43</td>
<td>-13.81</td>
<td>71.35</td>
<td>Tempkin.</td>
</tr>
<tr>
<td>DBMH</td>
<td>200</td>
<td>-5.705</td>
<td>46.24</td>
<td>-19.78</td>
<td>-56.23</td>
<td>-120.3</td>
<td>Tempkin</td>
</tr>
</tbody>
</table>

It can be seen from the table the thermodynamic parameter, $\Delta H$, is reasonably exothermic indicating strong chemisorption, while drop in free energy is sufficiently negative to promote adsorption smoothly. Another thermodynamic entity the entropy...
is found to decrease in respect to compound DBMH while it remained positive with respect the compound NDBH.

6.2.1.3. Scanning Electron Microscope Probing Studies

The arrangement of the inhibitor molecules and their packing in the film built around the base metal substrate was evaluated using powerful electron microscope. The resolution ability being extremely high around 1 by 50 trillionth of a meter all surface deformations can be effectively mapped. The reflected, scattered and secondary electrons generated were all retrieved by the field lens and overall surface contour was generated.

The coupons meant for SEM scanning were taken through all preliminary surface preparation procedures and hung in corroding medium containing 0.02% of inhibitor. SEM mapping of the surface of brass coupon corroded in the acidic medium without containing the inhibitor was also done as to make comparisons more realistic.

The SEM designated plates were subjected to both pre immersion and post immersion surface preparation and surface protection operations before they are finally mapped by SEM for contour profile. The media preparation required during SEM film growth was done as per the methodology described in the previous chapters.

The plates 6.2.1.5a and b presented below depict the presence of some pits which are to be attributed to the artefaction of machining of soft natured substrate surface. The corrosion debris if at all any appear as white spots in the image. The negative version of the image plate does reveal the locations where in the dents caused underneath the corrosion debris appear as deep holes.
The acetic acid induced corrosion in on brass coupon appears as blister deformations seen at few locations on the surface. The negative version of the SEM identifies the corrosion spots as scattered pits of varying depths.

The compound NDBH as an inhibitor to brass coupon in acetic acid medium has been found to offer better protection as revealed by the absence of corrosion deformations and formation appears to be neat and orderly one.

The plate 6.2.1.5b, representing the contour of DBMH film grown around the brass coupon reveals scale type deposition although the negative version does not disclose any abnormality in the substrate structure. Nevertheless the overall appearance of the SEM image with respect to DBMH is not neat and smooth.
Fig 6.2.1.5a SEM image of brass coupon in HAc with NDBH and its negative aspect

Fig 6.2.1.5b SEM image of brass coupon in HAc with DBMH
Conclusions

- Under situations that prevailed during experimentations admiralty brass does not appear to suffer severely from acetic acid induced corrosion.
- Hydrazides of aromatics and their homologues under perform as corrosion inhibitors on brass surface in acetic acid medium.
- Amongst the hydrazides, the compound NDBH turns out as copybook type inhibitor with efficiency increasing with the concentration, while the compound DBMH follows opposite pattern.
- The order of inhibitive efficiencies presented above gets able support through the SEM findings.
- The adsorption of inhibitors on to the brass surface proceed through coordination bonding.
- The compound NDBH obeys Tempkin isotherm during adsorption.
- The compound DBMH obeys Tempkin isotherm during adsorption.
- The adsorption of inhibitor molecules on to the surface of metal proceeds with liberation of heat energy.
- The free energy decreases sufficiently during the adsorption of inhibitor compounds.
- The increase in temperature decreases the overall inhibitive efficiency of the compounds.
- The solubility of azides in water media is very low and commands solubilisation using polar solvent mixtures.
- The anodic dissolution of the metal during anodic polarisation renders tafel slope low in magnitude.
- The cathodic tafel curve shows two inflection points marking commencement of two cathodic processes such as hydroxide reduction and hydrogen evolution.
- The investigated azides are cathodic inhibitors.
Formyl Chloro quinilines and its schiff bases with amino acids as corrosion inhibitors on brass in acetic acid medium

The condensation products are the class of compounds that can be obtained by reacting compounds with aldehyde functional groups with compounds having amine functional groups. Acid catalyzed condensation reaction under reasonably vigorous reflux conditions promote coupling across two functional groups leading to formation of compounds with imine linkages.

The first principles of corrosion inhibition and umpteen researches carried world over\(^\text{171-172}\) have been able to establish and lay down with authenticity the mandatory requirements of supposed inhibitor compound. Accordingly the supposed inhibitor must possess groups of atoms or functional groups which can extend the atom valency by sharing surplus electrons without loosing the very own identity.

Thus atoms such as Nitrogen, Oxygen, Sulphur, aromatic rings, incorporated in to organic molecules have been found to inhibit corrosion in metals. The class of compounds containing hetero atoms in fused rings such as triazoles have been the heartthrob of many research activities pertaining to inhibition studies especially on copper based substrates\(^\text{173-177}\).

With growing concern to protect and propagate the healthy environment through strict pollution norms imposed the Government agencies world over are ensuring to phase out those chemicals that endanger the human race as well as the other inhabitants of the mother earth.

The eco friendly, the most chanted hymn of the contemporary world, have forced the entrepreneurs to rethink the use of chemicals that have well established
history of carcinogenicity. For instance the Benzo triazoles have been already voted out due to carcinogenicity$^{(178-182)}$.

The use of system compatible, eco friendly and nevertheless effective in the end use has become the motto of many business entrepreneurs marketing corrosion inhibitors.

Thus a rapid stride could be seen in the research activity aiming to fuse synergistically the inhibiting qualities of some of the eco friendly compounds which stands true to the cardinals laid down by the first principles of the corrosion inhibition theory.

Thus amino acids as such and their condensation reaction products with aldehydes are actively pursued compounds for exploring their potentiality as corrosion inhibitors evidenced through cited research programmes.$^{(183-188)}$

Quinolines are known to civic society since time immemorial for its ability to control anaphelese menace which once threatened to wipe out human race from the earth. The biocidal effect of the quinolines and their miscibility with the human physiology have been the grounds for possible application of the compounds in the field of affecting inhibition against corrosion on metals using bio degradable chemicals.

Substituted quinolines with incorporation of groups and atoms that have potential to either extend the valency through reactions or spare the surplus electrons for complexation are the source of many investigations in the past as corrosion inhibitors on metal surfaces in variety of environment conditions.$^{(189-192)}$.

In the present investigation a substituted quinoline with formylation at number three position and amino acids with terminal amine groups have been condensed to get compounds with imine linkage at the centre. The use of the derived condensation
products as corrosion inhibitors on admiralty brass in the environs of organic acids forms the basis of this investigation(193).

The use of copper and copper based alloys in the variety of applications have surged to astronomical heights which is to be solely attributed to the special qualities the alloy possess crowned along with immense chemical resistance.

The concept of heat recovery and accompanying economisation of fuel usage have forced many of the thermal power stations to strive hard to achieve the goal. Of the late the concern of global warming have still further tightened the noose around the managements of TPS.

The heat recovery from all sources to maximum extent has been possible nowadays because of use of efficient heat exchangers. Copper and copper based alloys are amongst the front-runners in the final materials to be used in heat exchanger designing. The improper conditioning of two heat exchanging medias around any heat exchanger will drastically affect the overall performance of the heat exchanger.

The heat exchange ability can suffer due to non conductive scales that get deposited at one side of the heat exchanger.

The retrieval of lost heat surface area of heat exchanger tubes in thermal power stations will normally involve pickling the affected area with acids such as citric acid, hydrochloric acid etc. The threat of virgin metal being eaten away by scale removing acids are effectively countered through use of system compatible organic inhibitors such as rhodine which can competitively block virgin metal from marauding acid.

In the present investigation condensation products derived from reacting 2-chloro-3-formyl-quinoline with amino acids containing hetero atoms such as N O and
S as briefed in the chapter 3 for getting FQAA, FQHA and FQBA was considered for inhibitory performance evaluation in acetic acid medium against brass surface.

The synthesizing of afore said inhibitor compounds were attempted as per the standard method described in chapter 3. The structure of the condensation products have been presented as tabular inserts in chapter 4.1 while IR graphs of the inhibitor compounds are given as figure inserts.

The solubility of corrosion product plays a significant role in mitigating or enhancing the overall corrosion rate. In the present case the solubility of cupric acetate being less the corrosion debris can lodge on the metal surface and prevent further acid attack on the metal. The coarseness and the porosity of the debris can stimulate further corrosion through differential oxygenation.

The performance of the inhibitor in acetic acid medium on admiralty brass coupons were evaluated through weight loss technique, galvano static polarisation technique, and elevated temperature performance at optimized concentration were carried out to know the thermodynamic parameters.

The surface morphology of inhibitor film developed on the brass coupons were mapped using scanning electron microscope at high resolution.

6.3.1 Results and Discussions

6.3.1.1 Galvano static polarisation method

The performance of condensation products as inhibitors on brass coupons in acetic acid medium was evaluated galvano statically by polarizing the working electrode against non polarisable platinum electrode. The chemical reactions initiated at the inseparable anode and cathode centres at the instance of polarisation can create sufficient turbulence so as to dislodge the adhered corrosion product. The artificial
creation of polarity leads to creation of driving force which would attract the electroactive species and harbor reactions. The existence of concentration gradient between the electrode surface and the bulk of the solution introduces diffusion-based transportation.

During polarisation studies the surfaces of corrosion coupons were prepared as per the standard procedure and to minimize the area to be polarized insulating varnish was applied on all sides keeping 1cm$^2$ area at one face blocked by flex tape.

All precautions to be exercised at the time of preparing specimen coupons for weight loss as well as polarisation studies as given in dedicated chapter 3 were followed in total while experiments were planned. The electrical connections between three different electrodes comprising the polarisation cell were established as per the circuit provided in chapter 1.

The tafel curve was constructed by plotting polarized voltage against DC current. The corrosion parameters such as tafel slopes, equivalent corrosion current and equivalent corrosion potential were arrived through graphical interpretation.

The inserted graphs are the tafel curves constructed for the inhibitors FQAA, FQHA and FQBA at different concentrations in corroding medium maintained by acetic acid. The solubility of the compounds in corroding medium have been enhanced through dissolution in polar solvent phase whose necessity has been described in chapter 3.
The polarisation of admiralty brass coupon in corroding medium containing acetic acid and solvent mixture was also conducted on identical lines to ascertain the
extent of corrosion in the absence of inhibitors. The corrosion parameters as interpreted through the tafel curves through method of extrapolation and anodic and cathodic slopes measured at the inflection points of the polarisation curve are tabulated in the table 6.3.1.1 inserted below,

**Table 6.3.1.1 Corrosion data of condensation products as inhibitors on brass in acetic acid medium.**

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration</th>
<th>( i_{corr} ) (( \mu \text{Acm}^-2 ))</th>
<th>Corrosion rate gpy</th>
<th>%IE</th>
<th>( b_a ) mv</th>
<th>( b_c ) mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>FQAA</td>
<td>%Wt</td>
<td>ppm</td>
<td>44.66</td>
<td>0.92</td>
<td>-</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>-</td>
<td>44.66</td>
<td>0.92</td>
<td>-</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>200</td>
<td>19.05</td>
<td>0.39</td>
<td>57</td>
<td>78.0</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>400</td>
<td>16.60</td>
<td>0.34</td>
<td>63</td>
<td>110.0</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>600</td>
<td>16.03</td>
<td>0.33</td>
<td>64</td>
<td>89.0</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>800</td>
<td>14.45</td>
<td>0.30</td>
<td>68</td>
<td>78.0</td>
</tr>
<tr>
<td>FQHA</td>
<td>%Wt</td>
<td>ppm</td>
<td>44.66</td>
<td>0.92</td>
<td>-</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>-</td>
<td>44.66</td>
<td>0.92</td>
<td>-</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>200</td>
<td>18.26</td>
<td>0.37</td>
<td>59</td>
<td>0822</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>400</td>
<td>16.59</td>
<td>0.34</td>
<td>63</td>
<td>1192</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>600</td>
<td>15.66</td>
<td>0.32</td>
<td>65</td>
<td>1111</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>800</td>
<td>11.35</td>
<td>0.23</td>
<td>75</td>
<td>0723</td>
</tr>
<tr>
<td>FQBA</td>
<td>%Wt</td>
<td>ppm</td>
<td>44.66</td>
<td>0.92</td>
<td>-</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>-</td>
<td>44.66</td>
<td>0.92</td>
<td>-</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>200</td>
<td>13.70</td>
<td>0.28</td>
<td>69</td>
<td>43.80</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>400</td>
<td>07.52</td>
<td>0.15</td>
<td>83</td>
<td>42.60</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>600</td>
<td>08.39</td>
<td>0.17</td>
<td>81</td>
<td>35.50</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>800</td>
<td>07.07</td>
<td>0.15</td>
<td>84</td>
<td>39.50</td>
</tr>
</tbody>
</table>
The comparison of open circuit potential of the brass coupon during each cycle of polarisation was found to shift to negative side during cathodic while it shifted to more positive during anodic cycle.

The introduction of over voltage could be attributed to the possible adsorption of the inhibitor molecules on to the metal surface through electrostatic forces. The presence of ligand moieties on the molecule could in all possibility align around substrate surface with such an stereo chemistry as to promote insulation.

Interestingly the anodic half of the polarisation curve appears to originate at potentials close to zero as compared to SCE. The alloy composition being rich in respect to a nobler element and lean in baser element, the dissolution of zinc at the instance of anodisation through external DC source can be taking place with absolute ease. The anodic polarisation and subsequent application of steps of DC current could be sufficient to trigger dissolution in the brass coupon.

The shift in equivalent corrosion potential as arrived through graphical interpretation though could not be accurately determined due to non merging nature of the cathodic and anodic tafel halves, definitely the OCP shift alone can be taken as the slide rule for assessing the inhibitors behavior.

The tafel curves for the compounds shows up multiple inflection points especially in the cathodic tafel half indicating the possibility of too many cathode specific reactions taking place as over voltage crosses some thresh hold values.

The over all shape of the tafel curves, be it is anodic or cathodic, does not change with inhibitors in the corroding medium as compared against the tafel curve constructed for the plain acid medium. The conclusion can be drawn here that the inhibitors does only block the reactive surface and does not alter the reaction mechanism.
The supposed cathode reactions such as the reduction of proton, the reduction of water molecules or the reduction of cupric ions proceed with kinetic ease and reaction begins at the cost of some enhanced over voltage.

The cathodic tafel curve was found to have two significant inflection points with one commencing immediately after the capacitor charging regime and the other originating from aborted limiting current curve. Also it was noted that while comparing the heights of the linear zones between two inflection points it appeared to differ significantly in all the investigated compounds.

In compound FQAA the profile of the linear zone almost replicates that of the limiting current profile, while it is shortened in linear dimension and appears to loose the demarcations phases between inflection points for the compounds FQHA and FQBA as well.

The abortion of limiting current curve and its premature transition at lower over voltage to last phase of the polarisation curve all reflect on the ability of FQHA and FQBA compounds to effectively decrease the hydrogen ion concentration at the electrode surface.

The capacitor-charging regime characterized by the phenomena of accommodating the impressed charge by the adsorbed inhibitor molecules till the OHP and the IHP layers attain saturation limits will only polarize electrode surface leading to the initiation of un hindered corrosion. This corrosion reaction appears to proceed smoothly till it is encountered with kinetically sluggish reduction of some form of hydroxide ions. Beyond this point the corrosion in the substrate surface appears to cease.

The weight loss observations made on specimen coupons in corroding medium with inhibitors at known concentrations indicate the formation of some sort of
corrosion debris layer around the metal surface which blocks the inhibitor from accessing the surface of the specimen coupon. Thus effective cementation of the surface does not take place.

The compound FQAA offers enhanced inhibition with the increase in concentration with only solubility and solution retention factor preventing the studies at still higher concentrations. The compound turns out to be a cathodic inhibitor. The N atom in the chemical structure can accommodate hydrogen ions sufficient enough to make its availability in the vicinity of electrode surface very minimum. Thus the hydrogen ion reduction to yield hydrogen gas suffers significantly. The truncation of polarisation curve mid way by the formation of hydroxide layer as advocated earlier will also consume hydrogen ions in the process of layer consolidation.

The cathodic tafel slope was found to decrease as compared to the plain corroding media polarisation curve. The slight flattening as reflected by the inclination towards the ordinate axis could be attributed to hydrogen ions which has been depleted by the virtue of protonation of the inhibitor molecules.

The compound FQHA was found to offer better inhibition to brass coupon in acetic acid medium and whose inhibition efficiency increased with the increase in the concentration. The inhibitor turned out to be a cathodic inhibitor. The cathodic tafel slope as measured from the curves shows significant decrease in the value as compared against the plain acid media curve. This shall indicate the flattened profile of the curve between two inflection points.

The molecular structure of the compound FQHA presented else where in the chapter indicate the presence of ligand sites which can be sued to effect coordination with base metal atom or can be protonated in acidic media. Also the increased end to
end linear dimension and flexible intervening linkage help the inhibitor molecule in insulating the substrate metal surface.

The compound FQBA was found to be more effective than the rest of the investigated compounds in preventing corrosion in brass coupon in acetic acid medium. Also the inhibition efficiency was found to increase with the increase in concentration of the inhibitor. The inhibitor FQBA turned out to be a cathodic inhibitor with OCP shifting to more negative side than the plain acid corrosion.

The ability of the inhibitor molecule FQBA to hinder kinetically the hydrogen evolution reaction was very much evident from the profile of cathodic half of the tafel curve. It was found that the profile between two inflection points in the tafel curve sloped down significantly indicating the sluggish behavior of electrode reaction which is to be inferred as the retardation of the hydrogen evolution process.

The presence of too many ligand moieties in the molecule structure facilitate establishing of coordination bonds by the molecule with substrate brass surface at many locations. The ability of copper to form hexa dentate ligand with elements such as chloride and nitrogen is well known chemistry.

The arrangement of inhibitor compounds based on the performances can be put down as follows,

FQBA > FQHA > FQAA

6.3.1.2. Adsorption isotherms

The ability of some of the surface rich compounds to trap reversibly gaseous molecules and surface viability for regeneration has been known to human kind since time immemorial. The huge surface area offered by activated charcoal is industrially exploited for recovering or refining some dissolved gaseous components and as such
the use of surface active agents in chemical process industry of diversified activities has crossed leaps and bounds.

The adsorption and subsequent desorption of chemical components from the surface of the traps through thermal interference merely indicate the nature of binding force behind the adsorption of molecules on the trap.

The binding forces between adsorbent and adsorbate can be any thing from purely physical to chemical in nature while the traps in the form of metal surfaces though do not offer rich surface area can still retain ions through virtual chemical bonding whose enthalpy of adsorption will be greater than gaseous molecule adsorption by several orders.

The molecules with heteroatom in their structure subscribe to a special ability to bind on to recipient surfaces through act of chemisorption or physisorption. The heteroatom with un paired electrons at their disposal can extend the valency with metals having vacant d orbital. The nature of bonding in such instances could be any thing from covalent to coordinative to purely vandervaals with consequent enthalpy of adsorption varying from fraction of kilo joules to several kilojoules.

The inhibitive ability of some of the classes of organic compound is attributed to the phenomena of adsorption. The extent of inhibition offered depends on the magnitude of the surface coverage. The rate of adsorption and rate of desorption reaches out equilibrium and the constant of which bears a definite relation with extent of surface coverage.

To correlate the extent of surface coverage and the concentration of inhibitor many mathematical models are in vogue such as Flory Huggins, Langmuir, Tempkin Frumkin and BDM to name a few.
The adsorption of molecules on to the substrate surface proceed in a definite fashion with the extent of surface coverage and concentration of the adsorbent following a mathematical equation defined under the names mentioned above. The experimental data points and the fitting on to mathematical models will yield different curves. The extent of surface coverage and the corresponding concentration for various inhibitors as included in table 6.3.1.1 were used for adsorption model fitting. The inserted table below contains the data required for ascertaining the adsorption model for FQAA, FQHA and FQBA.

**Table 6.3.1.2 FQAA data for adsorption model fitting**

<table>
<thead>
<tr>
<th>Concentration ppm</th>
<th>Conc moles/ltr x10^-3</th>
<th>lnC</th>
<th>Surface coverage θ</th>
<th>ln (θ/(1-θ))</th>
<th>ln C(1-θ/θ)</th>
<th>θ</th>
<th>θ^3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.8064</td>
<td>-7.123</td>
<td>0.57</td>
<td>0.2953</td>
<td>-7.418</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>1.6129</td>
<td>-6.429</td>
<td>0.63</td>
<td>0.5253</td>
<td>-6.955</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>2.4190</td>
<td>-6.024</td>
<td>0.64</td>
<td>0.5753</td>
<td>-6.599</td>
<td>0.51</td>
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</tr>
<tr>
<td>800</td>
<td>3.2250</td>
<td>-5.737</td>
<td>0.68</td>
<td>0.7368</td>
<td>-6.474</td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.3.1.3 FQHA data for adsorption model fitting.

<table>
<thead>
<tr>
<th>Concentration ppm</th>
<th>Conc Moles/ltr x10^3</th>
<th>lnC</th>
<th>Surface coverage θ</th>
<th>ln (θ/1-θ)</th>
<th>ln C(1-θ/θ)</th>
<th>θ^3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>FQHA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.4184</td>
<td>-7.779</td>
<td>0.59</td>
<td>0.3639</td>
<td>-8.143</td>
<td>0.45</td>
</tr>
<tr>
<td>400</td>
<td>0.8368</td>
<td>-7.085</td>
<td>0.63</td>
<td>0.5236</td>
<td>-7.609</td>
<td>0.50</td>
</tr>
<tr>
<td>600</td>
<td>1.2552</td>
<td>-6.680</td>
<td>0.65</td>
<td>0.6155</td>
<td>-7.296</td>
<td>0.52</td>
</tr>
<tr>
<td>800</td>
<td>1.6736</td>
<td>-6.392</td>
<td>0.75</td>
<td>1.0763</td>
<td>-7.469</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 6.3.1.4 FQBA data for adsorption model fitting.

<table>
<thead>
<tr>
<th>Concentration ppm</th>
<th>Conc Moles/ltr x10^3</th>
<th>lnC</th>
<th>Surface coverage θ</th>
<th>ln (θ/1-θ)</th>
<th>ln [C(1-θ/θ)]</th>
<th>θ^3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>FQBA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.341</td>
<td>-7.983</td>
<td>0.69</td>
<td>0.81418</td>
<td>-8.7978</td>
<td>0.58</td>
</tr>
<tr>
<td>400</td>
<td>0.682</td>
<td>-7.29</td>
<td>0.83</td>
<td>1.5856</td>
<td>-8.876</td>
<td>0.76</td>
</tr>
<tr>
<td>600</td>
<td>1.0238</td>
<td>-6.884</td>
<td>0.81</td>
<td>1.463</td>
<td>-8.347</td>
<td>0.73</td>
</tr>
<tr>
<td>800</td>
<td>1.365</td>
<td>-6.596</td>
<td>0.84</td>
<td>1.658</td>
<td>-8.2548</td>
<td>0.77</td>
</tr>
</tbody>
</table>
The inserted graphs are the adsorption isotherms fitted for investigated inhibitors.

**Fig 6.3.1.4 Tempkin fit FQAA**

**Fig 6.3.1.5 Tempkin fit FQHA**
The compound FQAA was found to fit well with Tempkin type isotherm with inter molecular interaction parameter $f$ having positive value. The parameter $f$ denotes the drop in free energy with the increase in the surface coverage. The inserted table 6.3.1.5 contains thermodynamic parameters derived out of adsorption curves.

The compound FQHA was found to fit reasonably well with Tempkin type adsorption model. The surface coverage data and the corresponding concentration as included in table 6.3.1.1 were used while constructing isotherms.

The compound FQBA followed Tempkin type isotherm when table contents of 6.3.1.1 were plotted against concentration terms.
### Table 6.3.1.5. Thermodynamic parameters of condensation compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc ppm</th>
<th>Interaction Parameter f.</th>
<th>Rate constant K</th>
<th>Free energy change ΔG KJ/mole</th>
<th>Enthalpy change ΔH KJ/mole</th>
<th>Entropy change ΔS J/mole</th>
<th>Adsorption type</th>
</tr>
</thead>
<tbody>
<tr>
<td>FQAA</td>
<td>200</td>
<td>14.35</td>
<td>4.71*10⁶</td>
<td>-48.82</td>
<td>-153.53</td>
<td>-348.82</td>
<td>Tempkin</td>
</tr>
<tr>
<td>FQHA</td>
<td>200</td>
<td>10.19</td>
<td>8.44*10⁵</td>
<td>-44.49</td>
<td>-93.35</td>
<td>-186.27</td>
<td>Tempkin</td>
</tr>
<tr>
<td>FQBA</td>
<td>200</td>
<td>9.927</td>
<td>3.50*10⁶</td>
<td>-48.07</td>
<td>-</td>
<td>-</td>
<td>Tempkin</td>
</tr>
</tbody>
</table>

#### 6.3.1.3. Elevated temperature studies and Arrhenius plots.

The adsorption being a surface phenomenon will always proceed with the drop in free energy. The overall enthalpy change of such a reaction is always negative leading to the liberation of surplus energy in the form of heat energy.

The inhibition offered by the organic compounds on to the metal surfaces in corrosive conditions does exhibit dependency on temperature and accordingly their inhibition efficiencies are bound to suffer at elevated temperatures.

The nature of interactive forces operating between the adsorbing sites and adsorbing molecules will decide the magnitude of energy exchanged with the surrounding.
In the case of adsorption of inhibitor molecules on to the base metal substrate the bonds of the nature covalent or coordinate will be established and hence the quantum of energy exchanged between the participating groups will be reasonably high.

The relevant experiments to construct Arrhenius plot and subsequent graphical evaluation of thermodynamic parameter, galvano static polarisation of brass coupons in acetic acid medium were conducted in line with the practical procedure described in chapter 3.

The media and material preparations and precautions while performing polarisation assessment were duly complied as per the procedures described and practiced during each experiment. The corrosion parameters were interpreted through tafel curves.

The thermodynamic parameter such as entropy was calculated using the parameters $\Delta G$ and $\Delta H$.

The inserted table contains the parameters used during construction of Arrhenius plots.

<table>
<thead>
<tr>
<th>$1/T \times 10^{-3} K$</th>
<th>FQHA $\ln(\theta/1-\theta)$</th>
<th>$\theta$</th>
<th>FQAA $\ln(\theta/1-\theta)$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>1.03</td>
<td>0.74</td>
<td>0.2953</td>
<td>0.57</td>
</tr>
<tr>
<td>3.1948</td>
<td>-2.10</td>
<td>0.11</td>
<td>-1.509</td>
<td>0.18</td>
</tr>
<tr>
<td>3.0959</td>
<td>-2.73</td>
<td>0.06</td>
<td>-1.9924</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The inserted graphs are the Arrhenius fits for the investigated compounds. It could be noted that the inhibition efficiency drops down with the rise in the
temperature of the corroding medium. The adsorption being strongly surface phenomena any factor that energizes the molecules present at and near the interface will promote desorption leading to the decreased inhibition.

6.3.1.4. Scanning Electron Microscope probing Studies

The arrangement of the inhibitor molecules and their packing in the film built around the base metal substrate was evaluated using powerful electron microscope. The resolution ability being extremely high around 1 by 50 trillionth of a meter all surface deformations can be effectively mapped. The reflected, scattered and secondary electrons generated were all retrieved by the field lens and overall surface contour was generated.

The coupons meant for SEM scanning were taken through all preliminary surface preparation procedures and hung in corroding medium containing 0.02% of inhibitor. SEM mapping of the surface of brass coupon corroded in the acidic medium without containing the inhibitor was also done as to make comparisons more realistic.

The plates presented below depict the presence of some pits which are to be attributed to the artefact of machining of soft natured substrate surface. The corrosion debris if at all any appear as white spots in the image. The negative version of the image plate does reveal the locations where in the dents caused underneath the corrosion debris appear as deep holes.

The acetic acid induced corrosion in on brass coupon appears as blistery deformations seen at few locations on the surface. The negative version of the SEM identifies the corrosion spots as scattered pits of varying depths. The inserted plates are the SEM images of the inhibitor film developed on the brass surface in acetic acid medium. The negative version of the film has also been provided for flaw less location of corrosion debri deposit.
Fig 6.3.1.7a SEM image of brass coupon in HAc with FQAA and its negative aspect

Fig 6.3.1.7b SEM image of brass coupon in HAc with FQHA

Fig 6.3.1.7c SEM image of brass coupon in HAc with FQBA
The fig 6.1.1.7b representing the plain acid corroded brass coupon depict the etching of surface in the form of blisters with varying indentation depths.

The fig 6.3.1.7a (plate id 3001) representing the inhibitor FQAA protected brass coupon depicts reasonably well protected surface excepting the surface preparation aberrations. The corrosion pattern as seen in the plain acid corroded coupon could not be seen in the plates representing FQAA inhibition.

The fig 6.3.1.7b (plate id 2998) representing the inhibitor film due to the compound FQHA appears to be totally free from the corrosion as it reveals corrosion dents at very few locations.

The fig 6.3.1.7c (plate id 2999) presented for the inhibitor film FQBA developed on brass coupon appears to form a neat film. The blister appearance on the surface cannot be attributed to that of pitting caused by acid as the very nature of acid induced pitting appears totally in a different way than the pittings seen in the film FQBA. This could perhaps be due to the release of some gaseous products while the film consolidation was in progress.

The overall view presented by the SEM contour tracing and the experimental observations made through polarisation studies appears to complement one another in evaluating the performances of the inhibitor compounds.

The hierarchy presented for the performances of the inhibitor compounds thus stands justified.

The weight loss observations in unstirred conditions for admiralty brass coupons in presence of the investigated compounds in acetic acid medium were not tracing the generally expected trend and further evaluations were not attempted.
Conclusions

- Under situations that prevailed during experimentations admiralty brass does not appear to suffer severely from acetic acid induced corrosion.

- The condensation products obtained by reacting substituted quinolines and amino acids perform reasonably well as corrosion inhibitors on brass surface in acetic acid medium.

- Amongst the condensation products FQBA out performs the rest inhibitors in terms of offering protection to brass coupon in corroding medium.

- The order of inhibitive efficiencies presented above gets able support through the SEM findings.

- The adsorption of inhibitors on to the brass surface proceed through coordination bonding.

- The investigated compound obey Tempkin isotherm during adsorption.

- The adsorption of inhibitor molecules on to the surface of metal proceeds with liberation of heat energy.

- The free energy decreases sufficiently during the adsorption of inhibitor compounds.

- The increase in temperature decreases the overall inhibitive efficiency of the compounds.

- The solubility of condensation products in water media is very low and commands solubilisation using polar solvent mixtures.

- The anodic dissolution of the metal during anodic polarisation renders tafel slope low in magnitude.
The cathodic tafel curve shows two inflection points marking commencement of two cathodic processes such as hydroxide reduction and hydrogen evolution.

The investigated condensation products are cathodic inhibitors.

The low quantity of less noble element in the pool of more nobler alloy component trigger leaching of the former at slightest temptation.

The condensation products having been synthesized through bio compatible chemicals does not pose threat to biotic life.