ROLE OF SOME BIOLOGICALLY IMPORTANT COMPOUNDS ON THE CORROSION OF MILD STEEL AND COPPER IN SODIUM CHLORIDE SOLUTIONS

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ABSTRACT

The performance of amino acids and carboxylic acids of biological importance on the corrosion of mild steel and copper in sodium chloride solutions was investigated. Manyof the amino acids are inhibitive. Aspartic acid, cysteine, cystine, threonine and histidine enhance the corrosion of mild steel. For copper, however, all the compounds except 4-amino n-butyric acid and hippuric acid, promote corrosion. The specific influence of the benzoyl group in hippuric acid is brought out.

Of the carboxylic acids investigated propionate, oxalate, succinate and α-ketoglutarate bring about considerable inhibition for mild steel. For copper all the anions, except formate, acetate and propionate, increase corrosion and thioglycollate ions are highly aggressive. With a view to study the antimicrobial properties, the effects of papaverine, brucine, strychnine, ephedrine and cinchonidine were also examined. Papaverine is inhibitive for mild steel while brucine, strychnine and cinchonidine are inhibitive for copper. The results are presented in the light of their structural relationships.

Key Words: Corrosion of Steel & Copper, Role of biological compounds

INTRODUCTION
Microbiological Corrosion

Microbes are widely distributed. Bacteria are known to be useful in leaching of low-grade ores of metals [1-5], power generation and extraction of gold from gold mines. Microbiological corrosion, is a subject of much practical and economic importance and therefore, detailed studies and suitable remedial measures become imperative. The microflora of soils and natural waters may be mainly algae, bacteria and fungi. Corrosion by algae which are aerobic and photolithotrophic, is due to the production of a depolarizer namely the oxygen, formed in the photosynthetic reaction.

The bacteria are differentiated as aerobic and anaerobic members depending upon their oxygen requirements. The corrosion of metals by obligate aerobes of the genus thiobacillus (chemo-lithotrophs) is due to the production of sulphuric acid. Corrosion of steel in Waxman's medium was observed in the presence of thiobacillus thiooxidans cultures [6]. An increased heterogeneity of the surface was observed [7] during the corrosion of low carbon steel under the metabolic influences of a number of sulphur oxidizing and sulphate reducing bacteria. Corrosion of steel components at the Ontario hydronuclear power plant occurred as a result of bacterial infestations [8]. Loss of passivation of copper base alloys in sea water was attributed to the bacterial contamination with the species of pseudomonas, micrococcus and corynebacterium [9]. Heat exchanger tubes of stainless steel 304 L of nuclear reactor systems suffered corrosion losses due to the action of bacteria producing sulphides, organic acids and slimy layers [10]. The influence of the growth of aerobic bacteria viz. bacillus megaterium, pseudomonas, fluorescens liquefaciens and bacillus mycoides during the cathodic polarization of steel in sea water was investigated. Bacillus mycoides showed a greater corrosive effect [11]. Corrosive effects of some aerobic bacteria on passivating and non-passivating steels and alloys in sea water

were studied and the decrease in corrosion of metals was attributed to the absorption of oxygen from the medium [12, 13]. A shift in potential to more negative values was observed when some saprophytic bacteria contacted stainless steel plates immersed in sea water [14]. It is to be noted that during the course of studies on microbial corrosion of steel in sea water an increase in pH and a lowering of corrosion were observed upon sterilization of the medium [15]. This is obviously due to the absence of microbial activity in the system.

Bacteria which proliferate under anaerobic conditions viz. desulphovibrio desulphuricans sp. a gram-negative nonsporing mesophile, cause the liberation of a corrosive species, sulphide. Some organisms (e.g. clostridium aceticum, methanobacterium omelianskii) having the hydrogenase activity bring about depolarization by removing the hydrogen from the metal surface. The mechanism of anaerobic corrosion has been the subject of much discussion and the significance of sulphide in the corrosion process was reported [16]. However, supporting evidence for the formation of a product containing phosphorus, and causing corrosion, is also augmented [17]. Corrosion of petroleum well equipment [18] and the diesel oil storage steel tanks [19] was brought about by the action of desulphovibrio desulphuricans sp. These organisms are thus a potential source of metal deterioration and their influence on the cathodic protection of copper and brass [20] and carbon steel [20a] in sea water has been investigated. Besides, during the course of studies on passivity of steel it was reported [21] that these sulphate reducing microorganisms destroy the passive films on metal surfaces.

Corrosion of metals by fungi which are nonchlorophyllous and chemoorganotrophic is due to the production of organic acids and the corresponding anions functioning as anodic depolarizers in corrosion reactions. The corrosive influence of aspergillus fumigatus on supersonic aircraft aluminium alloy [22], and the corrosion of aircraft fuel

tanks by the fungus cladosporium resinae [23–25] which utilizes the hydrocarbons present in aviation kerosene, were attributed to the action of the metabolic products of the organisms. The influence of aspergillus niger on the corrosion of copper, iron and aluminium was investigated [26] and a four-fold increase was observed. A comparative study was made of the action of aspergillus niger and Trichoderma viride cultures on the corrosion of aluminium, Pb-alloys and steel, and it was reported [27] that A. niger was more corrosive than T. viride.

OBJECTIVE

During the course of microbial metabolism under aerobic and anaerobic environments a number of amino acids [28] and carboxylic acids [29] are formed and they come into contact with the system influencing the corrosion of metals. To alleviate the corrosive effects it is required to employ antimicrobial agents having no adverse reactions of their own with the metal. Keeping these in view the effects of a number of alkaloids of plant origin, amino acids and carboxylic acids on the corrosion of heat exchanger materials namely mild steel and copper in sodium chloride solutions have been investigated and the results are reported in this paper.

EXPERIMENTAL

Mild steel (C 0.1–0.2, Mn 0.4–0.5, P 0.3–0.8 and S 0.02–0.3) and copper (electrolytic) coupons of size 2 cm × 1/16″ were employed for the corrosion experiments. Sodium chloride used was of AR grade and all the other organic compounds were of laboratory reagent grade. The solutions were prepared with distilled water. Mild steel and copper specimens were polished and degreased with trichloroethylene. Triplicate specimens of each metal were weighed and suspended by means of glass hooks in 430 ml of the test solutions taken in 500 ml beakers for a duration of 30 days. At the end of the experiment the specimens were removed, washed and cleaned according to the standard procedures [30], dried and weighed. The values of inhibition efficiency data were obtained by finding out the percentage reduction in weight losses in the presence of the organic compounds. All the experiments were conducted at 28 ± 2°C.

RESULTS AND DISCUSSION

Alkaloids

The data on the performance of five alkaloids on the corrosion of mild steel and copper in 100 ppm sodium chloride solutions are shown in Table I.

Table I: Influence of some alkaloids on the corrosion of mild steel and copper in sodium chloride solutions (100 ppm, pH 8)
Duration of experiments, 30 days;   Temp. 28 ± 2°C
Conc. of alkaloid, 4.8 × 10⁻³M or (Satd) as indicated. The figures indicate the values of inhibition efficiency (%).

Alkaloid	Mild steel	Copper
Papaverine	90.5	− 188.2
Brucine (Satd)	− 5.9	85.3
Strychnine (Satd)	− 3.9	67.6
Ephedrine	− 8.9	− 41.2
Cinchonidine (Satd)	− 8.3	94.0

It is interesting to note that for mild steel only papaverine, an opium alkaloid, is effective with an efficiency of 90% and all the other four alkaloids viz brucine, strychnine, ephedrine and cinchonidine are not inhibitive and give negative values of efficiency. However, for copper papaverine and ephedrine only accelerate corrosion. It is further seen that brucine, strychnine (nux vomica) and cinchonidine (cinchona bark)

bring about considerable inhibition. Cinchonidine gives the best performance with an efficiency of 94%. Ephedrine (ephedrasinica) is corrosive both to mild steel and copper. These alkaloids have been taken up in this study with a view to examining their antimicrobial activity (Fig. 1) and
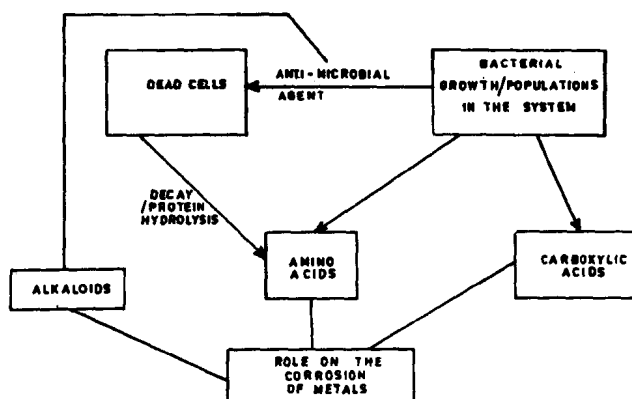

Fig. 1. Diagram showing the relevance of the compounds for the study

their performance in the presence of various metal ions. In the case of brucine, strychnine and cinchonidine a concentration of 4.8 × 10⁻³ M could not be prepared in view of the apparent insolubilities of the compounds and hence their saturated solutions containing 100 ppm sodium chloride were employed for the experiments.

Amino acids⁎

The results on the performance of twenty two amino acids on the corrosion of mild steel and copper in 100 ppm sodium chloride solutions, a composition representative of cooling waters in heat exchangers, are presented in Table III. These compounds are glycine, L (+) alanine, 4-amino n-butyric acid, DL-serine, L (−) proline, L (+) ornithine, L aspartic acid, L (+) glutamic acid, L (+) valine, L (−) threonine, L (+) cysteine, L — leucine, asparagine, L (−) methionine, L (+) histidine, DL-phenylalanine, L (+) arginine, hippuric acid, L-tyrosine, L-lysine, DL-tryptophane, and L (−) cystine. Most of these compounds of biochemical significance are derived from the hydrolysis of proteins (Fig. 1) and have an amino group attached to the α-carbon atom of the molecule. Comparing the values of inhibition efficiency data with molecular weights of the amino acids it is clear that there exists no uniformity in behaviour. The corrosion of mild steel and copper in the presence of these amino acids is uniform. For mild steel, though the values of inhibition efficiency are low, in some cases it is noted that many of the compounds are only inhibitive and however, with histidine, aspartic acid, cysteine, cystine and threonine there is an enhancement of corrosion in NaCl solutions. Hippuric acid is very effective with an inhibition efficiency of 95%. For copper many of these compounds are corrosive and some are highly corrosive. 4-amino n-butyric acid and hippuric acid are inhibitive. However, it is interesting to compare the relative performances of glycine, the simplest of the amino acids, and hippuric acid which is benzoyl glycine, on the corrosion of mild steel and copper in sodium chloride solutions. It is clearly evident that the introduction of benzoyl group (C₆H₅.CO−) into the glycine molecule has a significant effect. For mild steel with hippuric acid, the value of inhibition efficiency brought about by glycine (14%) is considerably increased to 95%. Again for copper it is clearly obvious that the highly corrosive nature of glycine is changed and a value of 100% inhibition efficiency is obtained with its benzoyl derivative. It is seen from the results of glycine and 4-amino n-butyric acid the proximity of the amino group with the −COOH group also has an influence on the performance of the compounds. If the amino group is far removed from the −COOH group the extent of inhibition increases indicating its specific role. Comparing the inhibition efficiency data of glycine with tryptophane it is further evi-

dent that substitutions in the α-carbon atom of the amino acid, probably a reactive center with the metal atoms, have an effect on the performance of the molecules. In the case of tryptophane the inhibition efficiency is increased for mild steel, and for copper it is less corrosive compared with glycine. However, this does not seem to be applicable uniformly. In addition it may be mentioned that the organisms which are indole positive (i.e. a characteristic trait for escherichia coli, proteus vulgaris and many others) may attack the tryptophane molecule whereby the products become probably corrosive or the efficiencies may be low as in the case of simpler molecules for mild steel. The effects brought about by tyrosine and phenylalanine may now be compared. Tyrosine is more inhibitive for mild steel and for copper its aggressiveness is also lower. Tyrosine contains an additional hydroxyl group in the phenyl ring compared to the phenylalanine molecule. Greater inhibition or lesser aggressiveness of tyrosine may be attributed probably to its low solubility which favours greater adsorption on the metal surface. It may be noted that these are only the general remarks and that the inhibition or acceleration of corrosion is a net result when the nature of the charge on the metal with respect to the corrosive solution computed from the values of zero charge potentials, adsorption in the double layer and complex forming tendencies of the organic molecules collectively or individually play their own roles under the experimental conditions.

As aspartic acid and histidine increased corrosion and papaverine brought about considerable inhibition for mild steel in sodium chloride solutions it was thought that a combination of papaverine with the corrosive amino acids may be having a beneficial effect and the experiments were carried out accordingly. However, the presence of papaverine did not bring about the changes as expected. In a similar way the effect of cinchonidine, a corrosion inhibitor for copper was also studied on the effects of glycine and phenylalanine. It was observed that the presence of cinchonidine in the amino acid contained solutions actually enhanced the corrosion of copper specimens.

In the case of alanine, serine and cysteine, the effects of a methyl group, and the hydroxyl and thiol substitutions in methyl group of the α-carbon atom of the glycine molecule may be followed. For mild steel though there is an increase in the efficiency of alanine compared with glycine, the other substitutions namely $HO.CH_2-$, $HS.CH_2-$ and $C_6H_5.CH_2-$ groups present in serine, cysteine and phenylalanine respectively do not improve the performance. The influence of the presence of π-electrons in phenyl ring of phenylalanine molecule is not specifically brought out owing probably to its preferred orientation in the electrical double layer. Phenyl substitution is alanine lessens its aggressiveness for copper though glycine and alanine are corrosive almost to the same extent. Comparing alanine, serine and cysteine it is noted that for mild steel, —OH substitution lowers the inhibition efficiency and the —SH group is much more deleterious and there is actually an enhancement of corrosion in the case of cysteine. With serine and cysteine for copper, as the efficiency values do not vary significantly it is indicated that the —OH and —SH groups present in the compounds cause only minor differences with respect to each other. The presence of an electron rich atom or group adjacent to the metal in the compact double layer would favour dissolution thereby bringing down the efficiency of the organic molecules to inhibit the corrosion of metals.

Cysteine, methionine and cystine are the sulphur containing amino acids taken up in this study and it is known that the organic sulphides by virtue of their low solubility and high available electron density over the sulphur atom are better corrosion inhibitors for metals in acid media [31]. In the case of cysteine and cystine as they are apparently insoluble compounds at the selected concentration the clear saturated solutions containing the specified concentration of sodium chloride were employed for the experiments. Of these amino acids only methionine is inhibitive for steel and its similar performance was also reported in the sulphuric acid medium [32]. For copper however all these three amino acids are only aggressive.

Proline is a ring amino acid whereas histidine and tryptophane molecules have clear heterocyclic substitutions in the β-carbon atom of

the amino acid. Histidine, as it increases the corrosion of mild steel and also copper there may be depolarization in the overall corrosion reactions and this applies equally well in other cases too. All these three amino acids enhance the corrosion of copper in sodium chloride solutions and histidine is the most aggressive one.

Lysine and ornithine have two amino groups besides the former having an additional methylene group. Although there is no significant difference in the values of inhibition efficiency data obtained with mild steel for these compounds the aggressiveness of lysine for copper is considerably less compared with ornithine. The effects of glycine, ornithine and lysine are not gradational. In the case of aspartic acid, glutamic acid and cystine it may be noted that the substituents of the amino carbon atom too contain a carboxyl group. However, with cystine the effects must also be related to the presence of the sulphur atoms in its molecule. These three amino acids are only corrosive to copper and mild steel in NaCl solutions, and only a low level of inhibition is shown by glutamic acid for mild steel as an exception.

Arginine, having four nitrogen atoms in its molecule is the most corrosive for copper of all the amino acids. During the course of corrosion of copper it is interesting to note that many of these amino acids form blue coloured (Table II) solutions, an observation probably having an application in the colorimetric analysis of the metal ions.

Table II: Influence of some amino acids on the corrosion of mild steel and copper in 100 ppm sodium chloride solutions (pH, 8).
Duration of experiments, 30 days; Temp 28 ± 2 °C
Conc of amino acid, 1.9×10^{-2} M or (satd) as indicated. The figures indicate the values of inhibition efficiency (%).

Amino acid	Mild steel	Copper	Colours developed during corrosion of copper
Glycine	14.2	−2328	Blue
L(+) Alanine	30.9	−2347	Blue
4-Amino n-butyric acid	36.6	56	Colourless
DL-Serine	14.1	− 892	Blue
L(−) Proline	33.0	−1496	Blue
L(+) Valine	32.1	−2137	Blue
L(−) Threonine	−13.7	−1272	Blue
L(+) Cysteine (Satd)	−33.3	− 846	Yellow/amber
L. Leucine	45.1	− 439	Blue
Asparagine	8.2	− 967	Blue
L(+) Ornithine	24.4	−2668	Blue
L. Aspartic acid	−25.4	− 798	Blue
L(+) Glutamic acid	9.1	− 955	Blue
L(−) Methionine	28.9	−1761	Blue
L(+) Histidine	−50.4	−1592	Green
DL. Phenylalanine	18.4	−1024	Blue/dull
L(+) Arginine	29.6	−2786	Blue
Hippuric acid	95.1	100	Colourless
L — Tyrosine (Satd)	30.5	− 116	Light green (dull)
L — Lysine	19.5	−1109	Blue
DL — Tryptophane (Satd)	45.6	− 273	Yellow
L (−) Cystine (Satd)	− 5.4	− 511	Yellow/amber

Organic anions

The data on the effects of ten organic acids on the corrosion of mild steel and copper in sodium chloride solutions are brought out in Table III.

Table III: Influence of some organic acids on the corrosion of mild steel and copper in sodium chloride solutions (100 ppm, pH 8)
Duration of experiment, 30 days; Temp 28 ± 2°C
Conc of organic acid, 0.11 M

These compounds are formed during the course of microbial metabolism and exist as the corresponding anions under the cell

The figure indicate the values of inhibition efficiency (%)

Organic acid	Mild steel	Copper
Formic acid	2.5	94.9
Acetic acid	75.4	51.3
Propionic acid	97.8	100
Glycollic acid	−22.5	−776
Thioglycollic acid	−39.0	−8418
Lactic acid	13.2	− 496
Oxalic acid	99.2	−1480
Succinic acid	92.3	− 110
K-Ketoglutaric acid	100	−1481
Maleic acid	−27.4	− 372
Citric acid	−297	−4521

(biological) pH conditions. For comparison thioglycollic acid is also included in this study. Comparing acetate and glycollate ions the presence of a hydroxyl group in the latter seems to enhance corrosion. This is also reflected in the behaviors of propionate and its hydroxy derivative namely lactate ions. The inhibition efficiency in the case of lactate is considerably brought down. Propionate is effectively inhibitive both for mild steel and copper. The presence of a thiol (—SH) group promotes corrosion both in the case of amino acids and organic anions. It is seen that as in the case of glycollate ions, thioglycollate by forming a sulphide is corrosive to mild steel, and for copper it is even more aggressive owing probably to the formation of a soluble complex. In the case of ions of dicarboxylic acids, oxalate, succinate, and -ketoglutarate the inhibition efficiency values are considerably higher for mild steel. Maleate, which has unsaturation at 2, 3 carbon atoms is corrosive whereas a good degree of inhibition is obtained in the case of succinate, its saturated analogue. This may be due to depolarization facilitated in the presence of a double bond probably involved in the formation of a soluble metal compound. It may be pointed out that the di-carboxylic acids are more corrosive if their anions do not form any protective films and in the case of citrate having three carboxyl groups and a hydroxyl group in addition is much more corrosive both for mild steel and copper. It would be interesting to carry out the studies on the structure of the electrical double layer at metal/solution interfaces in the presence of these organic anions and the work is being taken up on these lines.

CONCLUSION

Of the many amino acids and carboxylic acids investigated in this study some compounds accelerate the corrosion of mild steel and copper in 100 ppm sodium chloride solutions. All of the metabolic products are not corrosive. Papaverine is inhibitive for mild steel and for copper brucine, strychnine and cinchonidine are corrosion inhibitors in NaCl solutions. It is evident from the effects of alkaloids that the corrosion of the metals is not inhibited even after the incorporation of the particular inhibitive compounds (e.g. papaverine and cinchonidine) into the system containing the amino acids which accelerate corrosion. The best information on biological corrosion of metals would be obtained only when the experiments are carried out with the pure cultures of microbes, as the nature of the metabolic products is definitely very complex in the presence of a variety of microbial populations thriving in any practical environment and also involving a number of enzyme systems to directly affect the rates of electrochemical reactions (e.g. in leaching operations of low grade ores of metals). However, the structures of the organic compounds and also the nature of the substituent groups have a precise role to promote or inhibit the corrosion of mild steel and copper in NaCl solutions.

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