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Scientific paper
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Corrosion behaviour of carbon steel in presence of Cu²⁺ ions and citrate ions

Corrosion behaviour of carbon steel in the presence of Cu²⁺ ions and citrate ions has been investigated by electrochemical studies such as polarization, AC impedance and cyclic voltammetry. It was found that as the concentration of Cu²⁺ ions increased, the corrosion rate of carbon steel citrate also increased. When citrate was added in the presence of Cu²⁺, corrosion rate decreased. As the concentration of increased, the corrosion rate decreased. The protective film consisted of Fe²⁺ - citrate complex formed on the anodic sites of the metal surface. In the presence of Cu²⁺ ion and citrate ion, two semicircles were observed in the AC impedance spectra.

Key words: Corrosion of carbon steel, pitting corrosion, copper ion, citrate ion, rain water(RW)

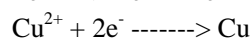
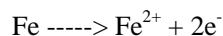
INTRODUCTION

Pitting is one of the most destructive and insidious forms of corrosion [1]. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. Pitting may be considered as the intermediate between general overall corrosion and complete corrosion resistance. Pitting corrosion of carbon steel and steel has attracted the attention of several researches [2-12]. Pitting corrosion of the stainless steel ventilation duct in a roofed swimming pool [2], corrosion protection of carbon steel by thin films of poly (3-alkyl thiophenes) in 0.5 M H₂SO₄ [3], localized corrosion susceptibility of supermartensitic stainless steel in welded joints [5], role of climatic conditions on corrosion characteristics of structural steels [6], fatigue strength of trolley bridge stringers made of ASTM A7 steel [7], corrosion behaviour of phosphoric irons in simulated concrete pore solution [8], properties of low carbon high nitrogen martensitic stainless steels [10] and localized dissolution kinetics of low carbon steel [11] have been studied in detail. The study of Sedek et al., [2] revealed in detail. The study of Sedek et al., [2] revealed that on the surface of an uptake venti-

lation duct made of austenitic stainless steel, installed in a roofed swimming pool with chlorinated water, corrosion pits appeared after two years service. Localized dissolution of low carbon steel in saturated calcium hydroxide with different amount of sodium chloride has been investigated, using a DC technique [11]. Potentiometric polarization curves indicated that pitting corrosion potentials decrease linearly with the log of chloride concentration.

The pitting corrosion of carbon steel in carbonate-formation water solution in the presence of chloride ions and the effect of addition of WO₄²⁻, MoO₄²⁻ and NO₂⁻ anions on the pitting corrosion were studied using cyclic voltammetry and potentiostatic time-current measurements and complemented by scan electron microscope and X-ray photoelectron spectroscopy investigations. Cyclic voltammograms of carbon steel in the presence of chlorion ions in carbonate -formation water solution show one anodic peak, corresponding to the formation of green rust carbonate and the two cathodic peaks. It was found that pitting inhibition of carbon steel increases in the sequence: (WO₄)²⁻ > (MoO₄)²⁻ > (NO₂)⁻ [9].

It is reported that Cu²⁺ ions are electron acceptors. They readily accept the electrons donated by iron. Cu²⁺ ions are easily reducible as follows [10].



The present work is undertaken (1) to investigate the corrosion behaviour of carbon steel in the presence of Cu²⁺ (as CuSO₄·5H₂O), (2) to study the

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influence of trisodium citrate (TSC) on the corrosion behaviour of carbon steel in the presence of Cu^{2+} (3) to carry out these studies by polarization study, AC impedance spectra and cyclic voltammetry, (4) to analyze the protective film by FTIR spectra.

EXPERIMENTAL

Preparation of the specimen

Carbon steel (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest Fe) specimen encapsulated in Teflon was polished to a mirror finish and degreased with trichloroethylene. The surface area of the exposed metal surface was 0.5 cm^2 .

Parameters of rain water (RW) collected from roof top are given in Table 1.

Table 1 - Parameters of rain water (RW) collected from roof top and stored in concrete tank

Parameters	Value
pH	8
Conductivity	122 $\mu\text{mhos/cm}$
Chloride	0 ppm
Sulphate	0 ppm
Total hardness	20 ppm
Total Dissolved Solids	55 ppm

Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, model 660A. It was provided with iR compensation facility. A three-electrode cell assembly was used. The work electrode was carbon steel. A saturated calomel electrode (SCE) was the reference electrode; platinum was the counter electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) Tafel slopes (anodic = b_a and cathodic = b_c) and linear polarization resistance (LPR) were calculated. During the polarization study, the scan rate (v/s) was 0.01; Hold time at E_f (s) was zero and quiet time (s) was 2.

Table 2 - Corrosion parameters of carbon steel immersed in various test solutions, obtained by polarization curves.

Sample	E_{corr} mV vs SCE	b_c mV	b_a mV	LPR ohm cm^2	I_{corr} $\text{A}/0.5 \text{ cm}^2$
RW(rain water)	-453	257	253	8.633×10^3	6.413×10^{-6}
RW + Cu^{2+} 25 ppm	-496	256	237	7.74×10^3	6.905×10^{-6}
RW + Cu^{2+} 50 ppm	-517	274	233	6.119×10^3	8.946×10^{-6}
RW + Cu^{2+} 25 ppm + TSC 100 ppm	-376	263	305	18.90×10^3	3.244×10^{-6}
RW + Cu^{2+} 25 ppm + TSC 300 ppm	-225	197	258	20.85×10^3	2.341×10^{-6}

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated. AC impedance spectra were recorded with initial $E(v) = 0$; High Frequency (Hz) = 1×10^5 ; Low Frequency (Hz) = 1; Amplitude (V) = 0.005 and Quiet Time (s) = 2.

Cyclic voltammetry

The instrument used for polarization study and AC impedance spectra was used for recording cyclic voltammograms also. Initial $E(v) = -1$. High $E(v) = 1$; Low $E(v) = -1$; Initial P/N = P; Scan Rate (V/s) = 0.1; Sample interval (v) = 0.001; Quiet Time (s) = 2; and Sensitivity (A/V) = 0.001.

Carbon steel specimen was immersed in rain water collected from roof top and stored in concrete tanks in the presence of Cu^{2+} ions and SPT. Polarization curves, AC impedance spectra and cyclic voltammogram were recorded.

FTIR spectra

These spectra were recorded with a Perkin-Elmer – 1600 spectrophotometer. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixed it with KBr and making the pellet.

RESULTS AND DISCUSSION

Analysis of polarization curves

The polarization curves of carbon steel immersed in various test solutions are shown in Fig 1. The corrosion parameters such as corrosion potential, E_{corr} , Tafel slopes (b_c = cathodic, b_a = anodic), linear polarization resistance (LPR) and corrosion current, I_{corr} derived from these curves are given in Table 2.

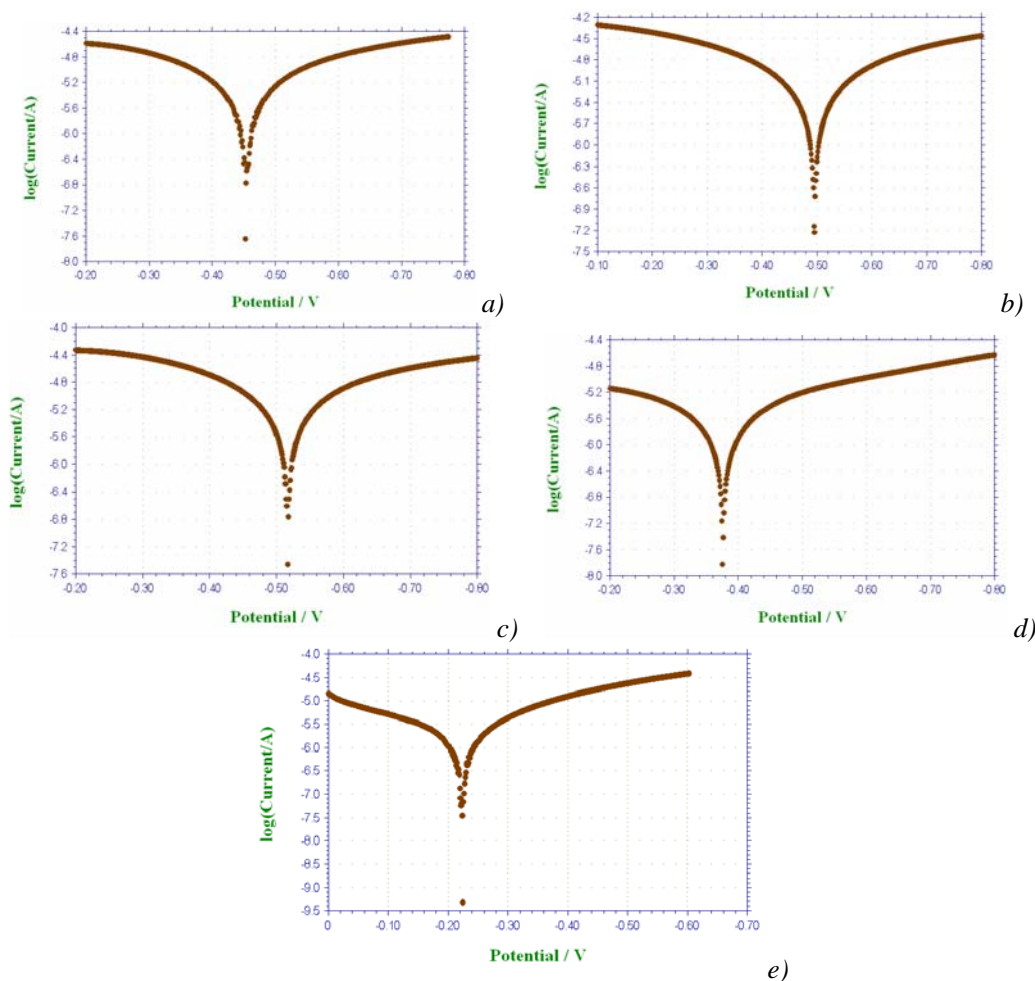


Fig. 1 - Polarization curves of carbon steel immersed in various test solutions, a)RW, b)RW + Cu^{2+} 25 ppm, c) RW + Cu^{2+} 50 ppm, d) RW + Cu^{2+} 25 ppm + TSC 100 ppm, e) RW + Cu^{2+} 25 ppm + TSC 300 ppm

When carbon steel was immersed in rain water (RW) collected from roof top, the corrosion potential was -453 mV vs SCE. When 25 ppm of Cu^{2+} (as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was added, the corrosion potential shifted to cathodic side. The metal surface has become active. That is, in presence of Cu^{2+} ions, iron becomes more active and goes into solution, by transferring electrons to Cu^{2+} ions which is an electron acceptor. In such cases pitting corrosion will take place [13]. This fact is supported by the observation that the linear polarization resistance value decreases from 8.633×10^3 to 7.74×10^3 ohm cm^2 ; further, the corrosion current increases from 6.413×10^{-6} to 6.905×10^{-6} A/ 0.5 cm^2 .

When the concentration of Cu^{2+} was increased from 25 ppm to 50 ppm, the corrosion potential was shifted to more cathodic side (-517 mV vs SCE) (Fig.1c). That is the metal surface became

more active, enhancing the dissolution rate by releasing more electrons in the presence of high concentration of electron acceptors, namely, Cu^{2+} ions. This fact is strongly supported by the evidence that the linear polarization resistance still decreased to 6.119×10^3 ohm cm^2 and the corrosion current further increased to 8.946×10^{-6} A/ 0.5 cm^2 . The flow of electron through the metal surface was facilitated and was very fast. Under these conditions more pitting corrosion of metal is expected take place.

Influence of trisodium citrate (TSC) on the pitting behaviour of iron in presence of Cu^{2+}

Influence of TSC on pitting behaviour of iron in presence of Cu^{2+} was studied. For this purpose various concentrations of TSC (100 ppm and 300 ppm) were added to a fixed concentration of Cu^{2+} (25 ppm), and the corrosion parameters were

measured (Figs. 1d,e ; Table 2).

It was interesting to note that when 100 ppm of TSC was added to 25 ppm of Cu^{2+} , the corrosion potential shifted to the anodic side (-376 mV vs SCE).

The metal surface has become more noble. The transfer of electron from Fe to Cu^{2+} was difficult. The rate of electron transfer was retarded to some extent. This fact was supported by the observation that the LPR value considerably increased from 7.74×10^3 to 18.9×10^3 ohm cm^2 ; further evidence was the considerable decrease in the value of corrosion current. It decreased from 6.905×10^{-6} to 3.244×10^{-6} A/0.5 cm^2 .

When 300 ppm of TSC was added to 25 ppm of Cu^{2+} , the corrosion potential still became more noble. (-496 to -225 mV vs SCE). The rate of electron transfer became more difficult. This fact was supported by the observation that the LPR value increased from 7.74×10^3 to 20.65×10^3 ohm cm^2 ; further the corrosion current decreased from 6.905×10^{-6} to 2.341×10^{-6} A/0.5 cm^2 .

Further, in presence of TSC, there is also possibility of formation of Fe^{2+} -TSC complex on the metal surface, thus preventing the electron transfer process and corrosion.

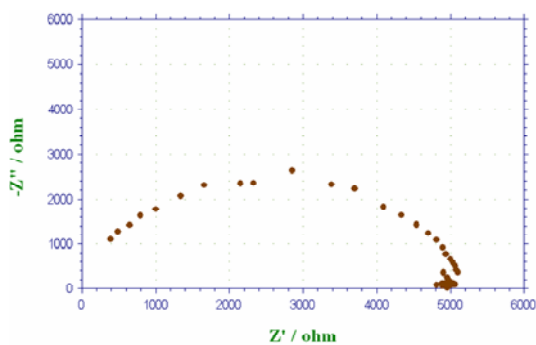
In the presence of Cu^{2+} ions, corrosion (pitting) of iron was observed. However, when TSC was added to Cu^{2+} ion, corrosion rate was reduced. This decrease in corrosion rate increased when higher concentration of TSC was added.

The rate of electron transfer from the iron surface to the bulk of the solution containing Cu^{2+} , may be prevented either by formation of a protective film on the metal surface or by enclavement of Cu^{2+} ion by the added TSC. In the latter case the availability of Cu^{2+} ion is reduced because of the formation of Cu^{2+} -TSC complex in solution.

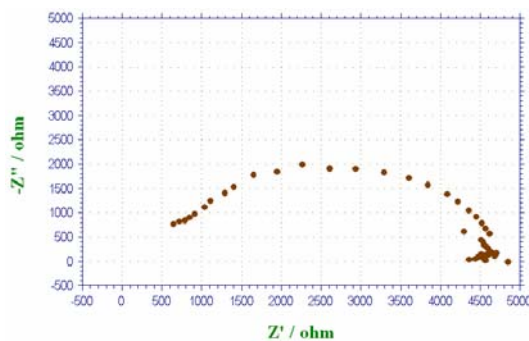
In order to investigate which concept plays a major role in controlling corrosion of carbon steel in the presence of Cu^{2+} and TSC, AC impedance spectra were recorded.

Analysis of AC impedance spectra

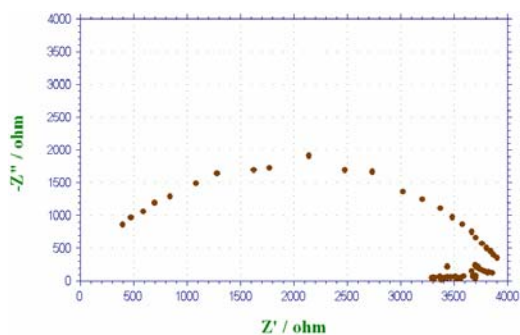
AC impedance spectra (Nyquist plots and Bode plots) of carbon steel immersed in various test solutions are shown in Fig. 2A and Fig. 2B, respectively. The impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) (derived from Nyquist plots) and impedance value, $\log(z/\text{ohm})$ derived from Bode plot are given in Table 3.



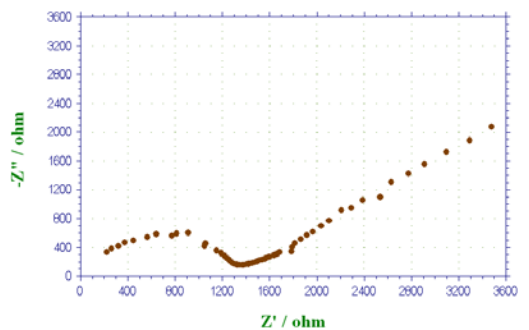
a)



b)



c)



d)

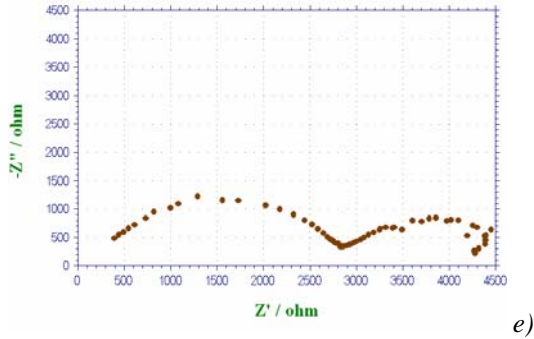


Fig. 2A - AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots), a) RW, b) RW + Cu²⁺ 25 ppm, c) RW + Cu²⁺ 50 ppm, d) RW + Cu²⁺ 25 ppm + TSC 100 ppm, e) RW + Cu²⁺ 25 ppm + TSC 300 ppm

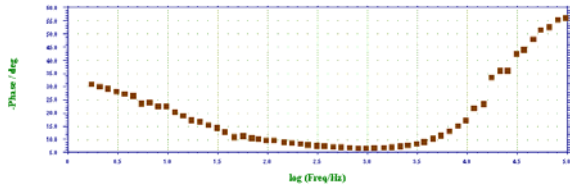
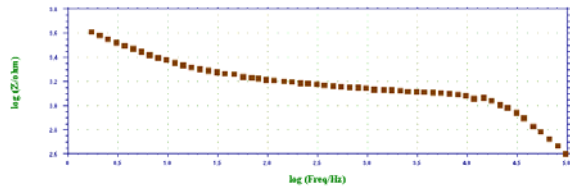
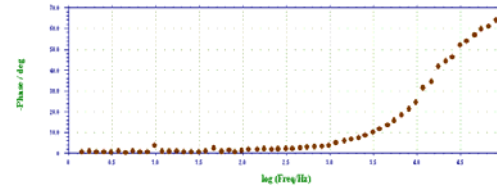
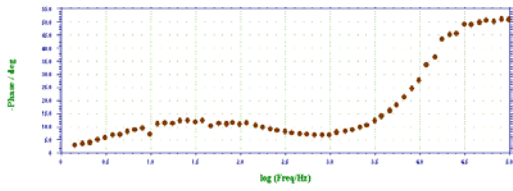
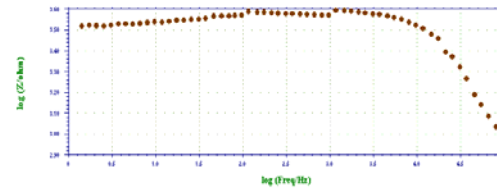
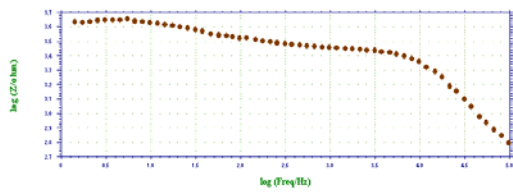
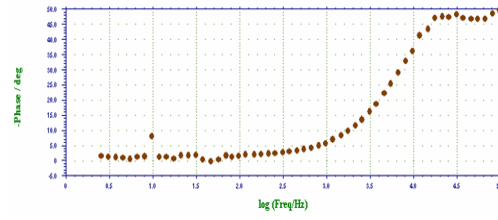
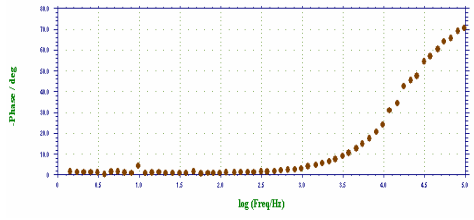
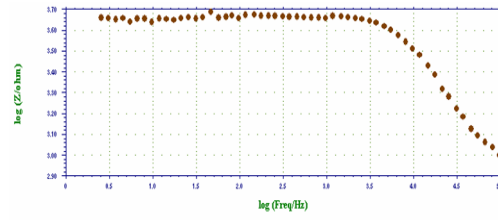
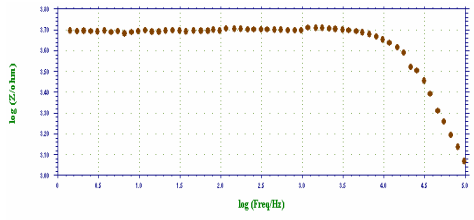
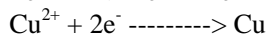
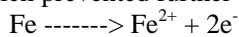


Fig. 2B - AC impedance spectra of carbon steel immersed in various test solutions (Bode plots), a) RW, b) RW + Cu²⁺ 25 ppm, c) RW + Cu²⁺ 50 ppm, d) RW + Cu²⁺ 25 ppm + TSC 100 ppm, e) RW + Cu²⁺ 25 ppm + TSC 300 ppm

Table 3 - AC impedance parameters of carbon steel immersed in various test solutions obtained from AC impedance spectra

Sample	R_t ohm cm^2		C_{dl} , $\mu F/0.5 cm^2$		Impedance log (z/ohm)
	R_{t1}	R_{t2}	C_{dl1}	C_{dl2}	
RW	4078.8	--	3.33×10^{-9}	--	3.653
RW + Cu^{2+} 25 ppm	4749.2	--	1.907×10^{-9}	--	3.694
RW + Cu^{2+} 50 ppm	3516.3	--	2.57×10^{-9}	--	3.513
RW + Cu^{2+} 25 ppm + TSC 100 ppm	2459.4	1467	3.65×10^{-9}	4.7×10^{-6}	3.633
RW + Cu^{2+} 25 ppm + TSC 300 ppm	1135.4	2130	7.9×10^{-9}	26×10^{-6}	3.542

When carbon steel was immersed in rain water the R_t value was as high as 4078.8 ohm cm^2 . When 25 ppm of Cu^{2+} was added, the R_t value increased to 4749.2 ohm cm^2 . It indicates the formation of a protective film on the metal surface. Perhaps it is due to the deposition of Cu on the metal surface, which prevented further corrosion.



This view of prevention of corrosion is further supported by the decrease in double layer capacitance value (From 3.33×10^{-9} to 1.907×10^{-9} $\mu F/0.5 cm^2$) and increase in impedance [log(z/ohm)] value (from 3.653 to 3.694).

It is interesting to note that, whereas polarization study revealed as increase in the corrosion current, AC impedance spectra revealed the formation of protective Cu deposition on the metal surface, in the presence of 25 ppm of Cu^{2+} . This may be due to the fact that where as polarization study rapidly measures the rate of electron transfer reactions, AC impedance spectra patiently records the formation of protective film on the metal surface.

Further research in this regard will lead to development of interesting new concepts.

When 50 ppm of Cu^{2+} was added to the environment, the R_t value decreased from 4078.8 to 3516.3 ohm cm^2 . This indicated the process of corrosion at 50 ppm of Cu^{2+} . It is interesting to note that where as 25 ppm of Cu^{2+} offered protection, 50 ppm of Cu^{2+} accelerated corrosion. From this evidence, it is inferred that at 50 ppm of Cu^{2+} , pitting corrosion commences [13].

The concept of acceleration of corrosion upon addition of 50 ppm of Cu^{2+} was further supported by a decrease in C_{dl} value (from 3.33×10^{-9} to 2.57×10^{-9} $\mu F/0.5 cm^2$) and also a decrease in impedance [log (z/ohm)] value (from 3.653 to 3.513).

Influence of trisodium citrate (TSC) on the corrosion behaviour of iron in the presence of Cu^{2+}

When 100 ppm of TSC was added to 25 ppm of Cu^{2+} two semi circles were observed. One was

due to the corrosion of iron ($Fe \rightarrow Fe^{2+} + 2e^-$) and corresponding two R_t values were obtained. The other was due to the prevention of corrosion process. The one in the high frequency region was due to film formed on the metal surface ($R_t = 2459.4$ ohm cm^2). The other charge transfer resistance value was 1567 ohm cm^2 . It was observed that the charge transfer resistance value was only 1567 ohm cm^2 , which is small, when compared with the blank value of 4078.8 ohm cm^2 , in the absence of any addition of inhibitors.

This indicates that the formation of protective film (deposition of Cu on the metal surface or formation of Fe^{2+} -TSC complex on the metal surface) on the metal surface was not effective.

This is attributed to the fact that in presence of TSC, Cu^{2+} is enclaved by the formation of Cu^{2+} - TSC complex in solution. The amount of Cu^{2+} and TSC transported towards the metal surface is reduced.

When 300 ppm of TSC was added to 25 ppm of Cu^{2+} , again, two semicircles were observed (Fig. 2A e). The first semicircle was due to the formation of protective film. The resistance of the film was 1135.4 ohm cm^2 . The second semicircle gave a charge transfer resistance of 130 ohm cm^2 .

The resistance (R_t) (113.4 ohm cm^2) of the film of the Cu^{2+} -300 ppm TSC system was less, when compared to R_t value for the film resistance of the Cu^{2+} - 100 ppm TSC system. That is electron transfer rate is high in the Cu^{2+} -300 ppm TSC system. The R_t value of second semicircle of the Cu^{2+} -300 ppm TSC system was higher than R_t value of the Cu^{2+} -100 ppm TSC system.

This indicated the formation of a compact protective film on the metal surface. The protective film may consist of deposited Cu and compact Fe^{2+} -TSC complex. In presence of higher concentration of TSC, more Cu^{2+} -TSC complex is transported towards the metal surface. This enhances the formation of protective film on the metal surface.

ce and hence higher protective efficiency, when compared with the Cu^{2+} 25 ppm – TSC 100 ppm system.

However, this R_t value of 2130 ohm cm^2 is low when compared with the blank value (4078.8 ohm cm^2). This observation reveals that more Cu^{2+} -TSC complex was precipitated in the bulk of the solution. The amount of Cu^{2+} -TSC complex transported towards the metal surface was relatively less; and hence an overall decrease in the protective nature of the Cu^{2+} -300 ppm TSC system. The decrease in protective efficiency of this system

when compared with the blank is further supported by the decrease of impedance value, $\log(z/\text{ohm})$, from 3.65 to 3.542. (Bode plots)

Analysis of cyclic voltammograms

The cyclic voltammograms of carbon steel immersed in various test solutions are shown in Fig.3. In general, the cyclic voltammograms do not show any characteristic peaks and redox couples. The bulging out nature of Figs.3d and e in the presence of citrate ions indicate the protective nature of Cu^{2+} - TSC systems.

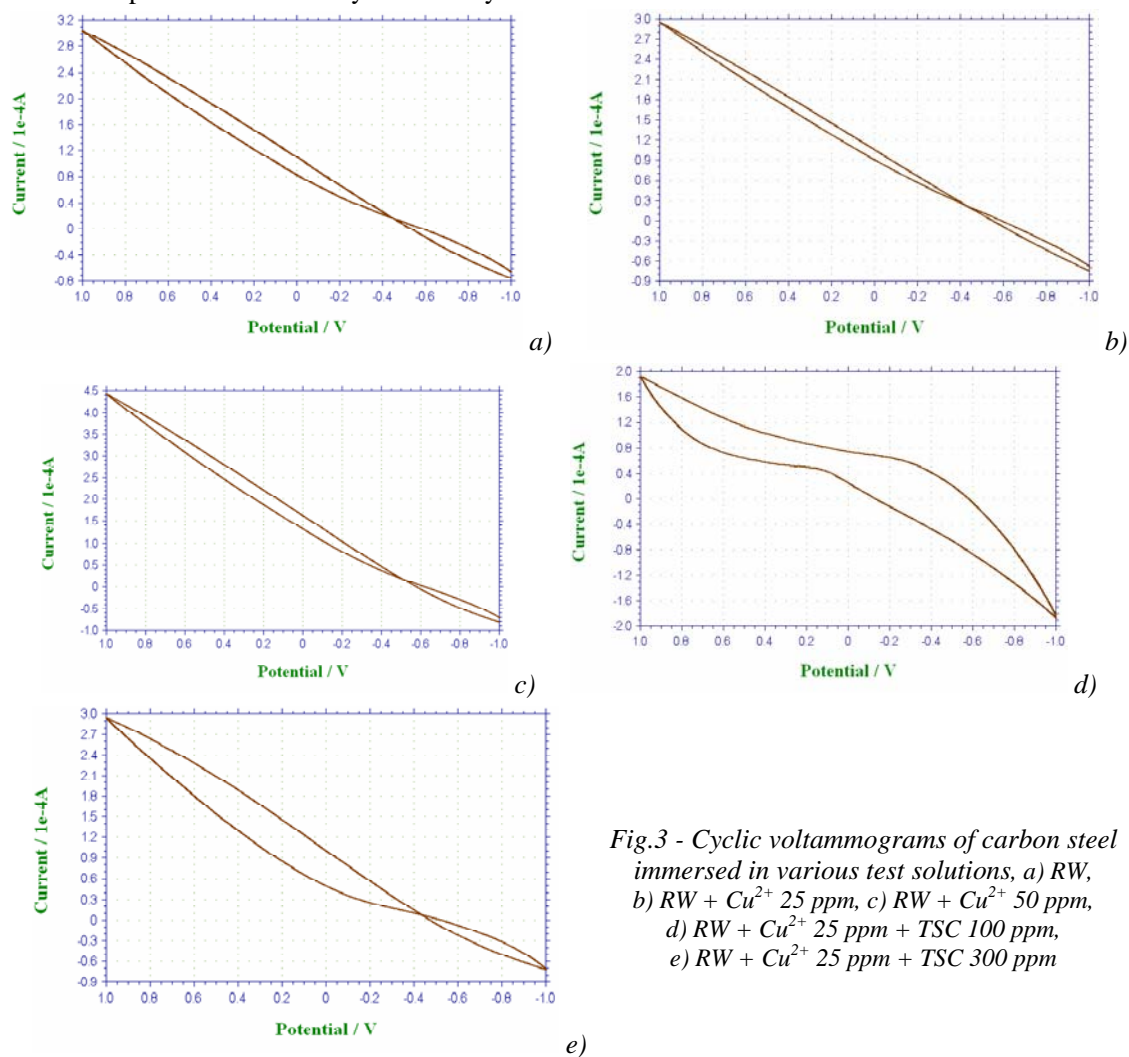


Fig.3 - Cyclic voltammograms of carbon steel immersed in various test solutions, a) RW, b) RW + Cu^{2+} 25 ppm, c) RW + Cu^{2+} 50 ppm, d) RW + Cu^{2+} 25 ppm + TSC 100 ppm, e) RW + Cu^{2+} 25 ppm + TSC 300 ppm

Analysis of FTIR spectra

The FTIR spectrum (KBr) of pure trisodium citrate (TSC) is shown in Fig. 4a. The C=O stretching frequency appear at 1598 cm^{-1} . The FTIR spectrum of the film formed on metal surface after immersion in the solution containing rain water, 25 ppm Cu^{2+} and 300 ppm TSC is shown in Fig.4b.

The C=O stretching frequency has shifted from 1598 cm^{-1} to 1606 cm^{-1} . This suggested that TSC has coordinated with Fe^{2+} , on the metal surface, through oxygen atom of TSC, resulting in the formation Fe^{2+} - TSC complex on the anodic sites of metal surface. Thus the protective film consists of Fe^{2+} -TSC complex formed on the metal surface.

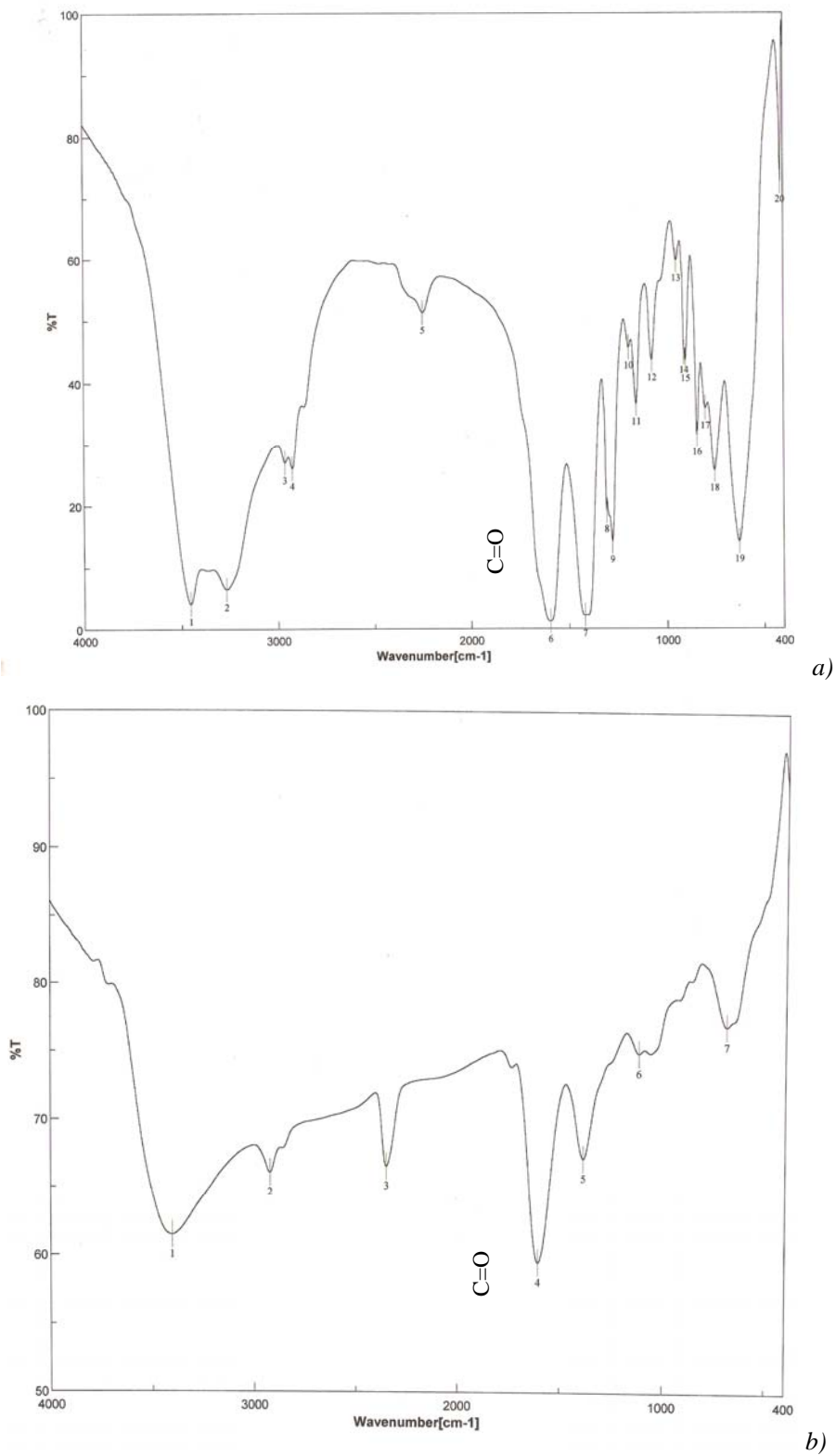


Fig.4 - FTIR spectra, a) Pure TSC, b) Film formed on metal surface after immersion in the aqueous solution containing rain water, 250 ppm Cu²⁺ and 300 ppm TSC

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