ROLE OF Zn^{2+} IN ENHANCING THE INHIBITION EFFICIENCY OF TRISODIUM CITRATE

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The inhibition efficiency (IE) of trisodium citrate (TSC)-Zn^{2+} system in controlling corrosion of mild steel in well water has been evaluated by weight loss method. A synergistic effect exists between TSC and Zn^{2+}. The formulation consisting of 50 ppm of TSC and 25 ppm of Zn^{2+} provides 87% of IE. FTIR spectra reveal that the protective film consists of Fe^{2+}-TSC complex and Zn(OH)$_2$. Polarization of study confirms the formation of a protective film on the metal surface .The inhibitor system controls the cathodic reaction predominantly.

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Introduction

Metals are extracted from their ores by reduction process. When metals come in contact with the environment, especially oxygen and moisture, they deteriorate .This process, we call, corrosion. Corrosion is the desire of pure metals to go back to its original state of ores. Corrosion is a natural, spontaneous and thermodynamically stable process. The process of corrosion can be controlled but it cannot be prevented. There are many methods by which corrosion can be controlled one such method is the use of inhibitors. These inhibitors when added is small quantity, decrease the rate of corrosion. Corrosion inhibitors usually contain polar groups with atoms such as nitrogen, sulphur and oxygen. Correspondingly inhibitors include a wide list of organic and inorganic compounds[1] containing the functional groups such as aldehydes,[2] amines,[3,4] amino acids, [5,6] nitrocompounds,[7,8] amides, [9,10] ester,[11,12] thio compounds,[13,14] phosphates, [15,16] phosphonates, [17,18] ketones,[19,20] and carboxylic acids [21-23] Trisodium citrate has carboxyl groups and hydroxyl groups. Such compounds are expected to have good inhibition efficiency.

The present work in undertaken (i) to evaluate the inhibition efficiency of trisodium citrate (TSC)- Zn^{2+}system in controlling corrosion of mild steel in well water, (ii) to analyse the protective film by FTIR spectroscopy and (iii) to study the mechanistic aspects of corrosion inhibition by polarization study.

MATERIALS AND METHODS

Metal specimens

Mild steel specimen was used in the present study. (Composition (wt %): 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron. The dimension of the specimen was 1 x 4 x 0.2 cm. The molecular structure of trisodium citrate is shown in scheme 1.
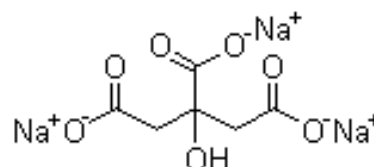
Scheme 1. Structure of trisodium citrate

The inhibition efficiency of TSC-Zn^{2+} system in controlling corrosion of mild steel in well water (Table 1) has been evaluated.

Table 1. Parameters of well water

Parameters	Value
pH	8.38
Conductivity	3110 $\mu\Omega^{-1}$ cm^{-1}
Chloride	665 ppm
Sulphate	14 ppm
TDS	2013 ppm
Total hardness	1100 ppm

Weight –Loss Method

Mild steel specimens in triplicate were immersed in 100 ml of well water containing various concentration of TSC in the presence and absence of Zn^{2+} for three days. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62.The corrosion products were cleansed with Clarke's solution [24].

The inhibition efficiency (IE, %) was then calculated using the equation:

$$IE = 100 * \left[1 - \frac{W_2}{W_1} \right] \qquad (1)$$

where

W_1 - corrosion rate in the absence of the inhibitor,

W_2 - corrosion rate in the presence of the inhibitor.

Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The three-electrode assembly is shown in Scheme 2. The working electrode was mild steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic = b_a and cathodic = b_c) and Linear polarization resistance (*LPR*) were calculated.
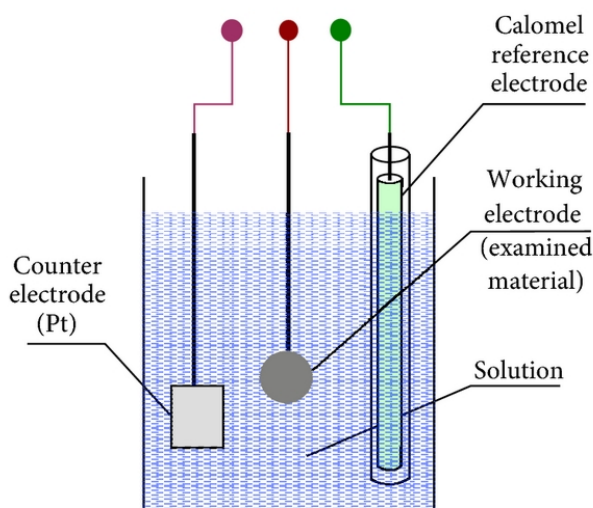
Scheme 2. Circuit diagram of three-electrode cell assembly.

FTIR Spectra

FTIR spectra were recorded in a Perkin – Elmer1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made into pellets and FTIR spectra were recorded.

Result and Discussion

Analysis of Results of Weight-loss method

Corrosion rates of mild steel immersed in well water in the absence and presence of tri sodium citrate (TSC) and Zn^{2+} are given in Table 2. It is observed that TSC alone has some inhibition efficiency. As the concentration of TSC increases inhibition efficiency also increases. 50 ppm of TSC has 13% inhibition efficiency and 250 ppm of TSC has 30%.

Table 2. Corrosion rates (CR) of mild steel immersed in well water and the inhibition efficiency obtained by weight loss method.

TSC ppm	Zn^{2+}					
	0 ppm		25 ppm		50 ppm	
	CR	IE%	CR	IE%	CR	IE%
0	1a24.67	-	22.20	10	20.97	15
50	2a21.46	2b13	3.20	87	9.87	60
100	3a19.74	3b20	4.93	80	11.84	52
150	4a18.50	4b25	9.87	60	14.30	42
200	5a18.25	5b26	11.10	55	16.03	35
250	6a17.27	6b30	12.33	50	17.26	30

Immersion period: 3 Days; CR =Corrosion Rate; IE =Inhibition Efficiency

Influence of Zn^{2+} on the inhibition efficiency of TSC

When Zn^{2+} is added to TSC the corrosion inhibition efficiency TSC to a great extent .This suggests that a synergistic effect exists between Zn^{2+} and the inhibitor namely TSC. Similar synergistic effect existing between Zn^{2+} and inhibitors has been reported by several researchers.[25-29] The synergistic effect between Zn^{2+} and TSC can be explained as follows .When TSC and Zn^{2+} are mixed,Zn^{2+}-TSC complex is formed . It is transported towards the metal surface. On the metal surface, Zn^{2+}-TSC complex is broken. The released TSC combines with Fe^{2+} (formed on the metal surface due to corrosion process) resulting in the formation of Fe^{2+}-TSC complex. Fe^{2+}-TSC is more stable than Zn^{2+}-TSC.

The released Zn^{2+} combines with OH^- formed by cathodic reaction and $Zn(OH)_2$ is precipitated on the cathodic site of the metal surface. The Zn^{2+}-TSC bond is strong enough to carry the complex towards the metals surface and it is weak enough to break in presence of Fe^{2+}.This accounts for the breaking of Zn^{2+}-TSC complex and formation of Fe^{2+}-TSC complex .[30-33]

Analysis of polarization curve

Polarization study has been used to know it a protective film is found on the metal surface. If a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and corrosion current decreases .[34-38]
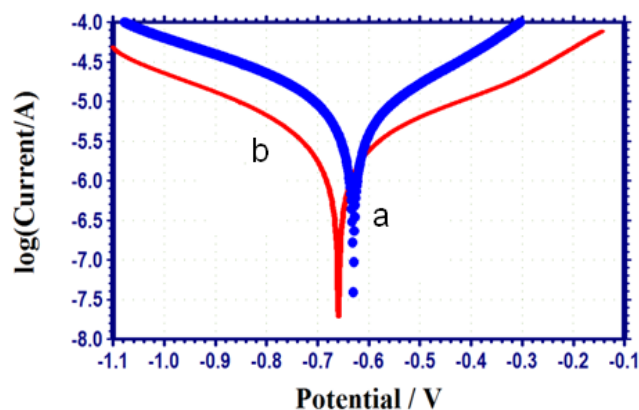

Figure 1. Polarization curve of mild steel immersed in various test solutions: a) well water b) well water + TSC 50 ppm+ Zn^{2+} 25 ppm

Table 3. Corrosion parameters of mild steel is immersed in well water in the absence and presence of inhibitor obtained by polarization method.

System	E_{corr}, mV*	b_a, mV**	b_c, mV**	*LPR*, ohm cm^2	I_{corr}, A cm^{-2}
well water	-630	202	194	7799.9	5.537x10^{-6}
well water+A	-659	186	208	23589.8	1.810x10^{-6}

A = TSC 50ppm + Zn^{2+}25 ppm,*mV vs SCE; **mV in one decade

The potentiodynamic polarization curves of mild steel immersed in various test solutions are shown in fig 1.The corrosion parameters ,namely, corrosion potential (E_{corr}), Tafel slopes(b_c= cathodic b_a =anodic), linear polarization resistance (*LPR*) and corrosion current (I_{corr}) are given in Table 3.

When mild steel is immersed in well water the corrosion potential is -630 mV vs SCE. The *LPR* value is 7799.9 ohmcm^2. The corrosion current is 5.537x10^{-6} Acm^{-2}. When inhibitors (TSC 50 ppm +Zn^{2+} 50 ppm) are introduced into the system, the *LPR* value increases tremendously from 7799.9 to 23589.8 ohm cm^2. Increases in LPR value is an indication of formation protective film formed on the metal surface.[39-43] This is also supported that by the fact that there is a sharp decrease in the corrosion current value; the corrosion current decreases from 5.537x10^{-6} to 1.810x10^{-6} A cm^{-2}. It is observed that the corrosion potential has shifted to the cathodic side (-630 to -659 mV vs SCE), in presence of inhibitors. This suggests that the cathodic reaction is controlled predominantly in presence of inhibitor system. When 2.5 ml of Zn is added to TSC solution 87% IE is obtained for 50 ppm of TSC. However as the concentration of TSC increases the inhibition efficiency decreases.

This is due to the fact that, as the concentration of TSC , the Zn^{2+}-TSC complex becomes more stable and bond is not broken in presence of Fe^{2+}.This accounts for the decreases in the IE in presence of higher concentration of TSC. Similar reason can be given for the decrease in IE of 50 ppm Zn^{2+}-TSC system . It is observed that 50 ppm Zn^{2+}-50 ppm TSC system has 60 %IE. However the IE decreases as the concentration of TSC increases.

Analysis of FTIR spectra

FTIR spectroscopy has been used to analyse the protective film formed on the metal surface.[44] The FTIR spectrum of pure TSC is shown in Fig 2(a).The >C=O stretching frequency of the carboxyl group appears that 1647cm^{-1}.The -OH stretching frequency appears that 3432 cm^{-1}. The FTIR spectrum of the film formed on mild steel surface after immersion in the solution containing 50 ppm of TSC and 25 ppm of Zinc is shown in Fig 2(b). It is observed that the >C=O stretching frequency has shifted from 1647cm^{-1} to 1608 cm^{-1}. The - OH stretching frequency shifted from 3432 cm-1 to 3417 cm^{-1}.This indicates that the oxygen atoms of the carboxyl group and -OH have coordinate with Fe^{2+} resulting in the formation of Fe^{2+}-TSC complex formed on the anodic sites of the metal surface. The peaks at 1274.92 cm^{-1} and 612.17cm^{-1} are due to Zn-O bon . The –OH stretching frequency appears at 3417cm^{-1}.These observation suggest that Zn(OH)$_2$ is formed on the cathodic sites of the metal surface .[45-48]
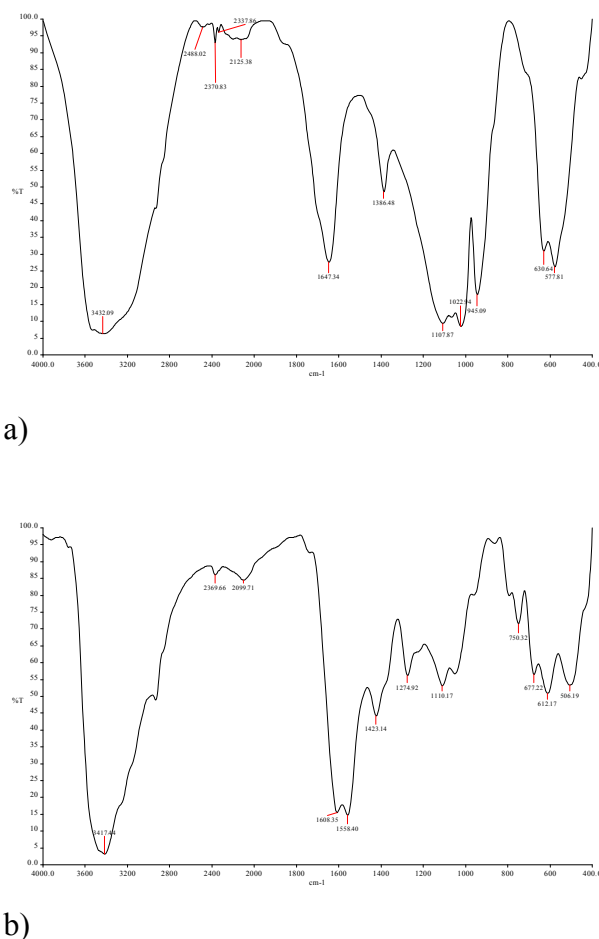

a)

b)

Figure 2. IR spectra of pure TSC (a) and film formed on TSC after immersion in containing 50 ppm of TSC and 15 ppm of Zn^{2+} (b)

Conclusion

The inhibition efficiency (IE) of trisodium citrate(TSC)-Zn^{2+} system is controlling corrosion of mild steel in well water has been evaluated by weight loss method.

A synergistic effect exists between TSC and Zn^{2+} . The formulation consisting of 50 ppm of TSC and 50 ppm of Zn^{2+} provides 87% IE.FTIR spectra reveal that the protective film consists of Fe^{2+}-TSC complex and Zn(OH)$_2$. Polarization study confirms the formation of protective film on the metal surface .The inhibitor system controls the cathodic reaction predominantly

Acknowledgement

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