International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.5, pp 2115-2121, July-Sept 2013

Corrosion Inhibition By Turn Bull's Blue

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Abstract : The inhibition efficiency (IE) of $K_4[Fe(CN)_6]$ in controlling corrosion of carbon steel in aqueous solution containing 60ppm Cl^- in the presence and absence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 100ppm $K_4[Fe(CN)_6]$ and 50 ppm Zn^{2+} offers 98% inhibition efficiency to carbon steel immersed in aqueous solution containing 60ppm Cl^-. A synergistic effect exists between $K_4[Fe(CN)_6]$ and Zn^{2+}. As immersion period increases, the inhibition efficiency of $K_4[Fe(CN)_6]$– Zn^{2+} system decreases.AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Turnbull's blue and $Zn(OH)_2$.
Key words: inhibition efficiency, corrosion, synergistic effect, carbon steel, protective film.

Introduction

Caron steel is used in the manufacturing of installations for the petroleum and oil refineries industries. The corrosion process of carbon steel is induced by the presence of moiturised environment gases like carbondioxide, oxygen and acids[1-2].

Several organic and inorganic inhibitors have been used to prevent corrosion of carbon steel in aqueous solution, because these compounds adsorb on the carbon steel surface forming a compact barrier film[3]. Inhibitors such as Chromate[4-5] Molybdate[6-7] Pertechnitate[8] Nitrate[9-10] Phosphate[11-12] Silicates[13] Cations[14] Organic inhibitors [15-17] Carboxylates[18-20] and Tannins[21-22] have been used as corrosion inhibitors. Much work has not been done using $K_4[Fe(CN)_6]$ as corrosion inhibitor.

Experimental

Preparation of Specimens

Carbon steel specimens [0.0267 %S, 0.06 % P, 0.4% Mn, 0.1%C and the rest iron] of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and decreased with trichloroethylene.

Weight – loss method

Carbon steel specimens in triplicate were immersed in 100 ml of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day.The weight of the specimens before and after were determined using shimadzu balance, model AY62. The corrosion products were cleansed with clarke's solution.The inhibition efficiency (I.E) was then calculated using the equation

$$IE = 100\ [1- (W_2 / W_1)\ ]\ \%$$

Where W_1 = Corrosion rate in the absence of the inhibitor and

W_2 = Corrosion rate in the presence of the inhibitor.

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed for surface analysis technique by FTIR spectra and fluorescence spectra.

FTIR Spectra

The film formed on the metal surface was carefully removed and mixed thoroughly with KBr. The FTIR spectra were recorded in a Jasco 460+ spectrophotometer.

AC impedance measurements

The instrument used for polarization study was used for AC impedance measurements also. The cell set up was the same as that used for polarization measurements. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

Result And Discussions

Analysis of results of the weight loss method

The corrosion rates of carbon steel immersed in 60 ppm Cl^- in the presence and absence of inhibitor systems are given in Table 1. The inhibition efficiencies (IE) are also given in this Table.

It is seen from Table 1 that the $K_4[Fe(CN)_6]$ is not a good inhibitor to carbon steel in aqueous solution containing 60 ppm Cl^-. Initially IE decreases and then increases of IE starting from 200 ppm $K_4[Fe(CN)_6]$. It may be due to the fact that $Fe^{3+} - K_4[Fe(CN)_6]$ complex goes into solution[23-24]. In the presence of higher concentration of Zn^{2+} (25ppm) the IE increases. For example, 200 ppm of $K_4[Fe(CN)_6]$ has 41 % IE in the presence of 25 ppm of Zn^{2+}.

When the concentration of Zn^{2+} is 50 ppm excellent IE is obtained at all concentrations of inhibitor . Here, $Zn^{2+} - K_4[Fe(CN)_6]$ complex is in solubilized form; more $K_4[Fe(CN)_6]$ is transported towards the metal surface. So IE is maximum ie 98% at these concentrations. A synergistic effect is noticed between Zn^{2+}-$K_4[Fe(CN)_6]$ complex[25]. For example 50ppm of Zn^{2+} has 10% IE; 100 ppm of $K_4[Fe(CN)_6]$ has 20% IE; but their combination has very excellent IE of 98%.

Table 1. $K_4[Fe(CN)_6]$ - Zn^{2+} system as corrosion inhibitor for carbon steel immersed in aqueous solution containing 60ppm Cl^- the inhibition efficiencies (IE) & Corrosion rates (CR) obtained by weight loss method. Inhibitor system : $K_4[Fe(CN)_6]$ Immersion period : 1 day

Cl^- ppm	$K_4[Fe(CN)_6]$ ppm	Zn^{2+} ppm					
		0		25		50	
		I.E %	CR mdd	I.E %	CR mdd	I.E %	CR mdd
60	0	-	23.64	10	10.64	15	10.50
60	50	42	13.71	25	18	98	0.47
60	100	27	17.25	28	17	98	0.47
60	150	22	18.56	28	17	98	0.47
60	200	31	16.43	41	14	98	0.47
60	250	16	20	23	18	98	0.47

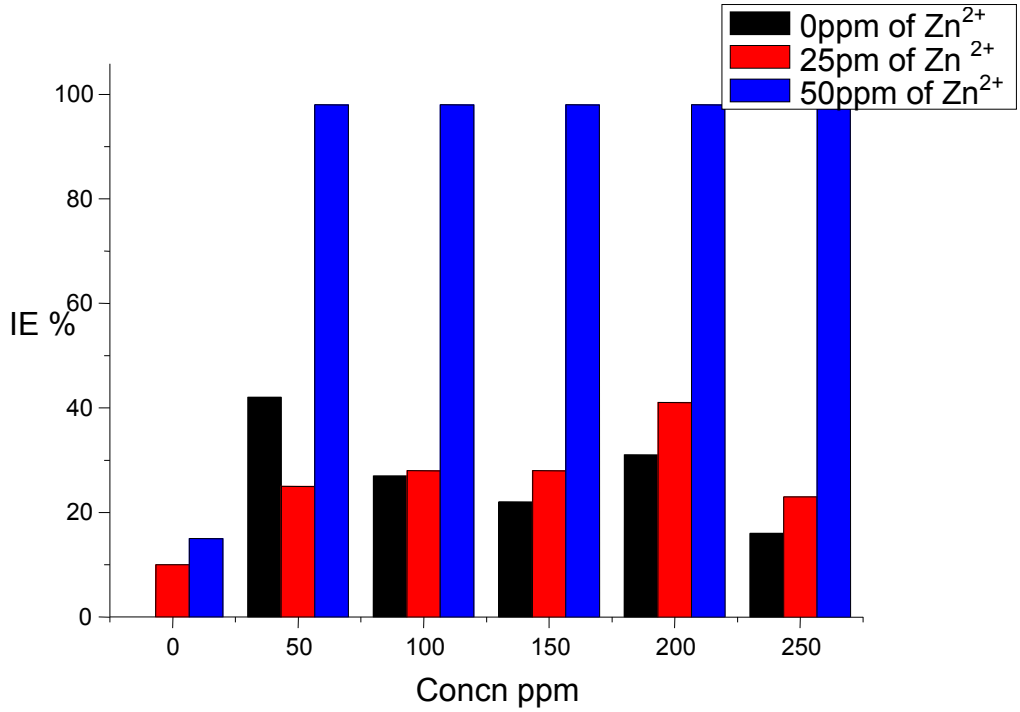

Figure 1. Graph Inhibition efficiency (IE) of $K_4[Fe(CN)_6]$- Zn^{2+} system of carbon steel immersed in aqueous solution containing 60ppm Cl^- (Immersion period- one day)

Influence of pH on the IE of $K_4[Fe(CN)_6]$ — Zn^{2+} System

At pH =7 the system shows 98 % IE. But when the pH is lowered

(5,3) by the addition of dil H_2SO_4 the IE decreases. This is due to the fact that when acid is added, the protective film is broken by the aggressive H^+ ion[26].

When the pH values are increased by the addition of dil NaOH solution the IE decreases. This is due to the fact that the protective film goes in to the solution at higher pH values.

Table 2. Influence of pH on the inhibition efficiencies of $K_4[Fe(CN)_6]$(100 ppm) — Zn^{2+} (50 ppm) system

pH	3	5	7	9	11
IE %	12	25	98	- 42	-50

Analysis of AC Impedance Spectra

The AC impedance spectra of carbon steel immersed in aqueous solution containing 60 ppm Cl^- in the presence and absence of inhibitors are shown in Fig.2. The impedance parameters namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 6. It is found that when carbon steel immersed in 60ppm Cl^-, the R_t value is 442.4 ohm cm^2 and C_{dl} value is 1.1518 x 10^{-8} $\mu F/cm^2$. When 100 ppm of $K_4[Fe(CN)_6]$ and 50 ppm of Zn^{2+} are added, the R_t value tremendously increases to 616.69 ohm cm^2 and the C_{dl} value decreases to 0.8263 x 10^{-8} $\mu F/cm^2$ [27].This indicates that a protective film is formed on the metal surface in the presence of inhibitors.

Table 3. AC impedance parameters of carbon steel immersed in aqueous solution containing 60ppm Cl^- in the absence and presence of inhibitors.
Inhibitors system : $K_4[Fe(CN)_6]$ — Zn^{2+}

Cl^- ppm	$K_4[Fe(CN)_6]$ ppm	Zn^{2+} ppm	R_t ohm cm^2	C_{dl} $\mu F/cm^2$
60	0	0	442.40	1.1518x 10^{-8}
60	100	50	616.69	0.8263 x 10^{-8}

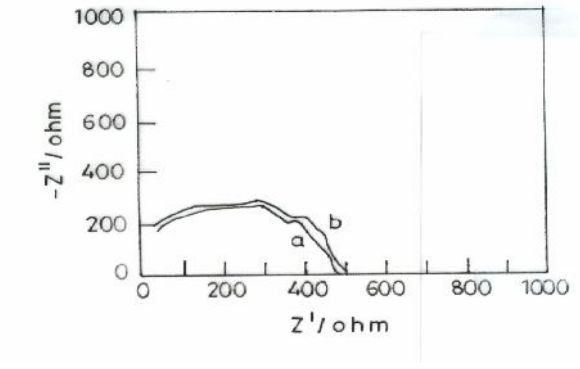

Figure 2. AC impedance spectra of carbon steel immersed in various test solution
(a) Cl^- 60ppm
(b) Cl^- 60ppm + $K_4[Fe(CN_6)]$ 100 ppm + Zn^{2+} 50ppm

Analysis of FTIR Spectra

The FTIR spectrum (KBr) of pure $K_4[Fe(CN)_6]$ is shown as spectrum in Fig. 3a.The $[Fe(CN)_6]^{3-}$ stretching frequency appears at 2092 cm^{-1}. The Fe^{3+}—$K_4[Fe(CN)_6]$ complex was prepared by mixing Fe^{2+} as (Ferrous sulphate $Feso_4.7H_2O$) and $K_4[Fe(CN)_6]$ solution. The FTIR spectrum of the complex is shown as spectrum 3b. The $[Fe(CN)_6]^{3-}$ stretching frequency shifted from 2092 cm^{-1} to 2072 cm^{-1}.The FTIR spectrum (KBr) the film formed on the surface of metal after immersion in the solution containing 60 ppm Cl^- ,10ppm Zn^{2+} and 100ppm $K_4[Fe(CN)_6]$ is shown as spectrum 3c. The $[Fe(CN)_6]^{3-}$stretching frequency shifted from 2072 to 2087cm^{-1}.

Resulting in the formation of Fe^{3+}-$K_4[Fe(CN)_6]$ on the anodic sites of the metal surface. The band at 1363 cm^{-1} is due to formation of $Zn(OH)_2$ on the cathodic sites. Thus the FTIR spectral study suggest that in the presence of Cl^-, $K_4[Fe(CN)_6]$ and Zn^{2+} the protective film formed[28-30] on the metal surface is Turnbull's blue $Fe_4[Fe(CN)_6]_3$ and $Zn(OH)_2$.

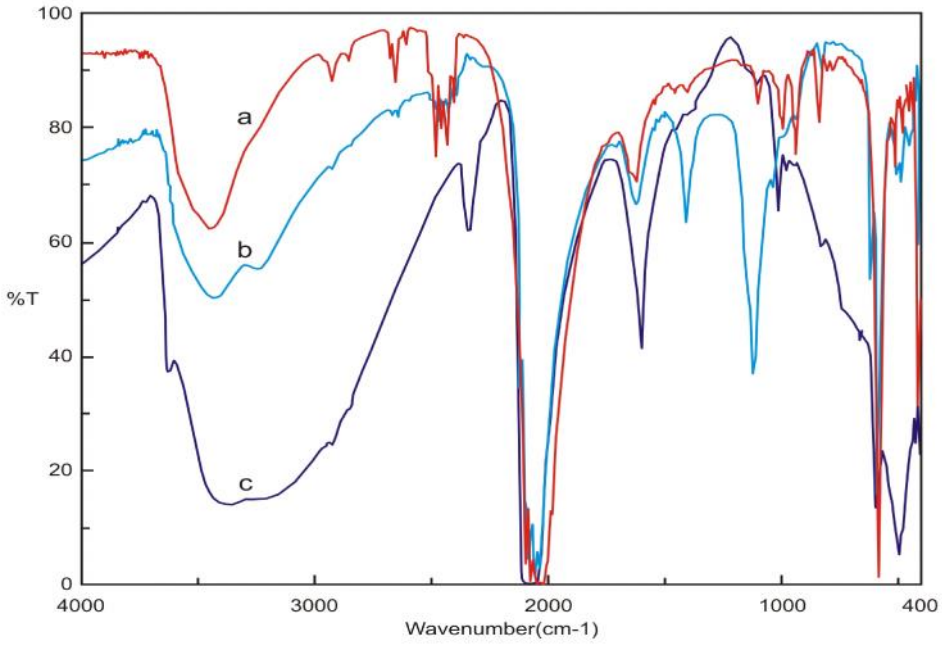

Figure 3. FTIR Spectra
(a) Solid $K_4[Fe(CN)_6]$
(b) Fe^{3+} — $K_4[Fe(CN)_6]$ complex prepared
(c) Film (KBr) formed on metal surface after immersion in solution containing Cl^- 60ppm + $K_4[Fe(CN_6)]$ 100 ppm and Zn^{2+} 10ppm

Analysis of Fluorescence Spectra

A few drops of the turnbull's blue complex prepared in a glass plate and dried.The emission spectrum of Turnbull's blue (λ_{ex} = 310 nm) was recorded.A peak appeared at 330 nm.The film formed on carbon steel surface after immersion in the solution containing 60 pm of cl^- ,200ppm of potassium ferrocyanide and 50ppm of Zn^{2+} was excited at λem 310 nm.A peak appeared at 335 nm.this matched with the peak obtained by excitation of turnbull's blue.This confirmed that the protective film consist of turnbull's blue.The slight variation in the peak position is due to the fact that in the film formed on metal surface[31], Turnbull's blue is entrailed in $Zn(OH)_2$.

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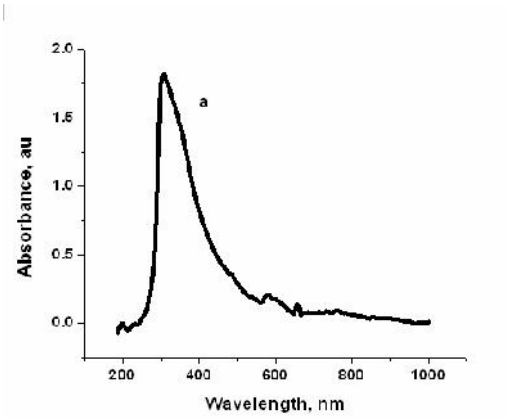

Figure 4. uv - visible absorbtion spectra

Mixing aqueous solution of $K_4[Fe(CN)_6]$ + $Fecl_3$

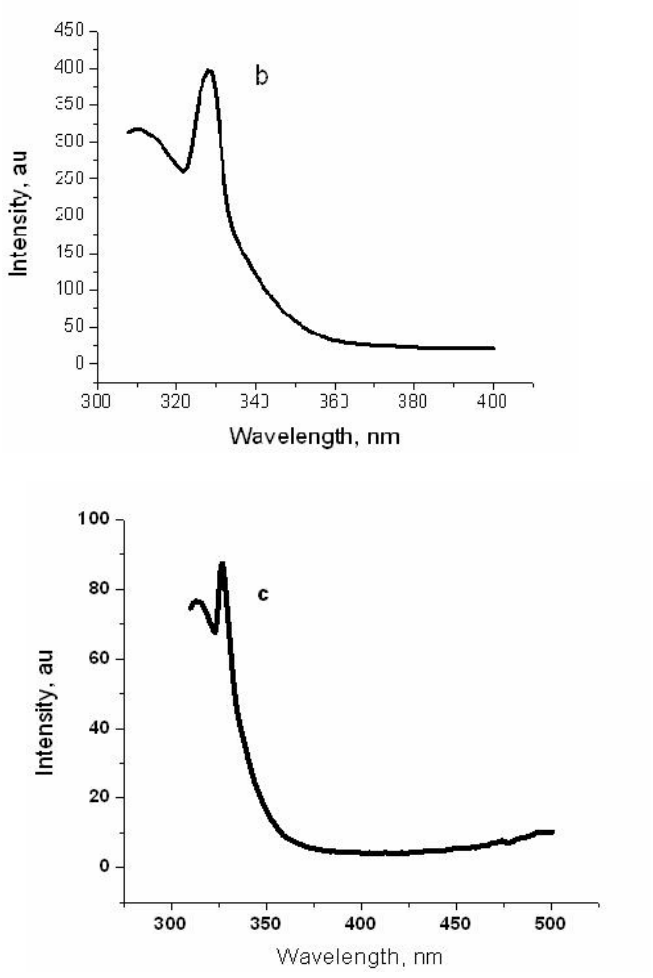

Figure 5. Fluorescence spectra b) Fe^{3+} – $K_4[Fe(CN)_6]$ complex prepared c)Film formed on metal surface after immersion in the solution containing Cl^- 60ppm + $K_4[Fe(CN_6)]$ 200 ppm + Zn^{2+} 50ppm - Turnbull's blue.

Conclusions

The present study leads to the following conclusions

- The formulation consisting of 60ppm Cl^- 50ppm Zn^{2+} and 100ppm $K_4[Fe(CN)_6]$ offers 98%. inhibition efficiency to carbon steel immersed in 60ppm Cl^-.
- A synergistic effect exists between $K_4[Fe(CN)_6]$ and Zn^{2+}
- As the immersion period increases, the inhibition efficiency decreases.
- AC impedance spectra reveal that a protective film formed on the metal surface.
- FTIR spectra reveal that a protective film is formed on the metal surface.

Acknowledgement

The authors are thankful to their management and university grants commission India for their help and encouragement.

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