Corrosion Inhibition by Prussian Blue

R. Kalaivani,[1] B. Narayanaswamy,[2] J. A. Selvi,[3]
A. J. Amalraj,[4] J. Jeyasundari,[3] S. Rajendran[3,*]

[1] *Department o f Chemistry, Kalasalingam University, Anandnagar,*
Krishnankoil 626 190. Srivilliputhur, India
[2] *Department of Chemistry, Thiagarajar College of Engineering, Madurai-625006. India*
[3*] *Corrosion Research Centre, Post Graduate and Research Department of Chemistry,*
GTN Arts College, Dindigul-624005, India
[4] *Department of Chemistry, Loyola College, Chennai, India*

Abstract

The inhibition efficiency (IE) of $K_3[Fe(CN)_6]$ in controlling corrosion of carbon steel in aqueous solution containing 60 ppm of Cl^- in the presence and absence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 100 ppm $K_3[Fe(CN)_6]$ and 50 ppm Zn^{2+} offers 98% inhibition efficiency to carbon steel immersed in aqueous solution containing 60 ppm Cl^-. A synergistic effect exists between $K_3[Fe(CN)_6]$ and Zn^{2+}. As immersion period increases, the inhibition efficiency of $K_3[Fe(CN)_6]— Zn^{2+}$ system decreases. Polarization study reveals that this formulation controls the cathodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Prussian blue and $Zn(OH)_2$. The film is found to be UV fluorescent.

Keywords: corrosion inhibition, carbon steel, Prussian blue, synergistic effect.

Introduction

Several inhibitors have been used to prevent corrosion of carbon steel in aqueous solution. Inhibitors such as chromate [1,2], molybdate [3,4] pertechnitate [5], nitrate [6,7], phosphate [8,9], silicates [10], cations [11], organic inhibitors [12,13], carboxylates [14,15,16] and tannins [17,18], have been used as corrosion inhibitors. Much work has not been done using $K_3[Fe(CN)_6]$ as corrosion inhibitor.
The present work is undertaken

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* Corresponding author. E-mail address: srmjoany@sify.com

(i)   to evaluate the inhibition efficiency (IE) of $K_3[Fe(CN)_6]$ in controlling the corrosion of carbon steel in aqueous solution containing 60 ppm of Cl⁻, in the absence and presence of Zn^{2+};

(ii)   to analyse the protective film formed on the carbon steel by FTIR spectra and fluorescence spectra;

(iii)   to understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization studies and AC impedance analysis;

(iv)   to propose a suitable mechanism for corrosion inhibition.

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 immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution [19]. The inhibition efficiency (IE) 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.

Fluorescence spectra
These spectra were recorded in a Hitachi F─4500 fluorescence spectrophotometer.

Polarization study
Polarization studies were carried out in an H & CH electro chemical work station impedance analyser model CHI 660A.

A three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

AC impedance measurements

The instrument used for polarization study was used for AC impedance measurements too. The cell set up was the same as that used for polarization measurements. The real part (Z') and the 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.

$$R_t = (R_s + R_t) - R_s$$

where R_{ss} = solution resistance, and

$$C_{dl} = 1 / 2 \pi R_t f_{max}$$

where f_{max} = maximum frequency

Results 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 Tables 1-4. The inhibition efficiencies (IE) are also given in these Tables.

It is seen from Table 1 that $K_3[Fe(CN)_6]$ is not a good inhibitor to carbon steel in aqueous solution containing 60 ppm Cl^-. Initially IE increases and then decreases, starting from 200 ppm $K_3[Fe(CN)_6]$. It may be due to the fact that $Fe^{2+} - K_3[Fe(CN)_6]$ complex goes into solution.

Table 1. Corrosion rates (CR) of carbon steel immersed in aqueous solution containing 60 ppm Cl^- and the inhibition efficiencies (IE) obtained by weight loss method. Inhibitor system: $K_3[Fe(CN)_6]$; immersion period: 1 day.

Cl^- (ppm)	$K_3[Fe(CN)_6]$ (ppm)	Zn^{2+} (ppm)	CR (mdd)	IE (%)
60	0	0	23.64	-
60	50	0	19.5	18
60	100	0	18.9	20
60	150	0	16.31	31
60	200	0	-	24
60	250	0	29	-23

Influence of Zn^{2+} on the inhibition efficiency of $K_3[Fe(CN)_6]$

In the presence of 10 ppm of Zn^{2+}, there is a decrease in the IE of the $K_3[Fe(CN)_6]$ system [Table 2]. This may be due to the fact that $K_3[Fe(CN)_6]$ is

not transported towards the metal surface; ie., Zn^{2+}—$K_3[Fe(CN)_6]$ complex is precipitated in the bulk of the solution.

In the presence of higher concentration of Zn^{2+} (25ppm) the IE increases [Table 3]. For example, 100 ppm of $K_3[Fe(CN)_6]$ has 42 % IE in the presence of 25 ppm of Zn^{2+} .

Table 2. Corrosion rates (CR) of carbon steel in an aqueous solution containing 60 ppm Cl^-, in presence of Zn^{2+} and the inhibition efficiency (IE) obtained by weight loss method. Inhibitor: $K_3[Fe(CN)_6]$ + Zn^{2+}; immersion period: 1 day.

Cl^- (ppm)	$K_3[Fe(CN)_6]$ (ppm)	Zn^{2+} (ppm)	CR (mdd)	IE (%)
60	0	0	23.64	-
0	0	10	22.22	6
60	50	10	19	19
60	100	10	20	15
60	150	10	21	12
60	200	10	27	-15
60	250	10	30	-27

Table 3. Corrosion rates (CR) of carbon steel in an aqueous solution containing 60 ppm Cl^-, in presence of Zn^{2+} and the inhibition efficiency (IE) obtained by weight loss method. Inhibitor: $K_3[Fe(CN)_6]$ + Zn^{2+}; immersion period: 1 day.

Cl^- (ppm)	$K_3[Fe(CN)_6]$ (ppm)	Zn^{2+} (ppm)	CR (mdd)	IE (%)
60	0	0	23.64	-
0	0	25	10.64	10
60	50	25	16.4	31
60	100	25	13.7	42
60	150	25	15.4	35
60	200	25	20	14
60	250	25	15	-38

Table 4. Corrosion rates (CR) of carbon steel in an aqueous solution containing 60 ppm Cl^-, in presence of Zn^{2+} and the inhibition efficiency (IE) obtained by weight loss method. Inhibitor: $K_3[Fe(CN)_6]$ + Zn^{2+}; immersion period: 1 day.

Cl^- (ppm)	$K_3[Fe(CN)_6]$ (ppm)	Zn^{2+} (ppm)	CR (mdd)	IE (%)
60	0	0	23.64	-
0	0	50	10.50	15
60	50	50	0.47	98
60	100	50	0.47	98
60	150	50	0.47	98
60	200	50	0.47	98
60	250	50	0.47	98

When the concentration of Zn^{2+} is 50 ppm, excellent IE is obtained at all concentrations of the inhibitor [Table 4]. Here, Zn^{2+}-$K_3[Fe(CN)_6]$ complex is in

solubilized form: more $K_3[Fe(CN)_6]$ is transported towards the metal surface. So IE is maximum, ie., 98% at these concentrations. A synergistic effect is noticed between Zn^{2+}-$K_3[Fe(CN)_6]$ complex. For example 50 ppm of Zn^{2+} have 10% IE; 100 ppm of $K_3[Fe(CN)_6]$ have 20% IE; but their combination has very excellent IE of 98%.

Influence of duration of immersion on the influence of $K_3[Fe(CN)_6]$ (100 ppm) – Zn^{2+} (50ppm) system

As the duration of immersion increases the IE decreases [Table 5]. This may be due to the fact that, as the period of immersion increases the protective film formed on the metal surface, namely, Fe^{2+}—$K_3[Fe(CN)_6]$ complex, is broken by the aggressive chloride ions present in the solution. Here there is a competition between the formation of $FeCl_2$ (and also $FeCl_3$) and the formation of Fe^{2+}—$K_3[Fe(CN)_6]$ complex. As the immersion period increases, the formation of $FeCl_2$ is more favoured than the formation of Fe^{2+}—$K_3[Fe(CN)_6]$ complex at the anodic sites of the metal. Hence, a decrease in the IE is noticed as the period of immersion increases.

A similar observation has been made in the corrosion prevention of carbon steel by polyvinyl pyrrolidone [20].

Table 5. Influence of the immersion period on the inhibition efficiency of $K_3[Fe(CN)_6]$ (100 ppm)-Zn^{2+} (50 ppm) system.

Days	1	3	5	7
Inhibition efficiency (%)	98	61	1.8	-31

Influence of pH on the IE of $K_3[Fe(CN)_6]$ — Zn^{2+} system

At pH =7 the system shows 31% IE [Table 6]. 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.

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 into the solution at higher pH values. Usually, Prussian blue is soluble in sodium hydroxide.

Table 6. Influence of pH on the inhibition efficiency of $K_3[Fe(CN)_6]$ (50 ppm) - Zn^{2+} (25 ppm) system.

1	pH	3	5	7	9	11
2	IE %	12	27	31	-5.3	-46

Analysis of polarisation curves

The potentiodynamic polarization curves of carbon steel immersed in aqueous solution containing 60 ppm Cl^- are shown in Fig. 1. The corrosion parameters are given in Table 7. When carbon steel is immersed in aqueous solution containing 60 ppm Cl^-, the corrosion potential is -487 mV vs. SCE. The anodic slope (b_a) is

153 mV and the cathodic slope (b_c) is 220 mV. The corrosion current (I_{corr}) is 1.5849×10^{-5} A/cm^2. When 100 ppm of $K_3[Fe(CN)_6]$ and 50 ppm of Zn^{2+} are added to the above system, the corrosion potential shifts to the cathodic side (-527 mV vs. SCE). This suggests that this formation controls the cathodic reaction predominantly. In the presence of this inhibitor system, the corrosion current decreases from 1.5849×10^{-5} A/cm^2 to 0.6309×10^{-5} A/cm^2. This suggests the inhibitive nature of this inhibitor system. The anodic slope and the cathodic slope are 106 and 73 mV vs. SCE, respectively. This suggests that the anodic reaction is controlled by the formation of $Fe^{2+}-K_3[Fe(CN)_6]$ complex on the anodic sites of the metal surface, and the cathodic reaction is controlled by the formation of $Zn(OH)_2$ on the cathodic sites.
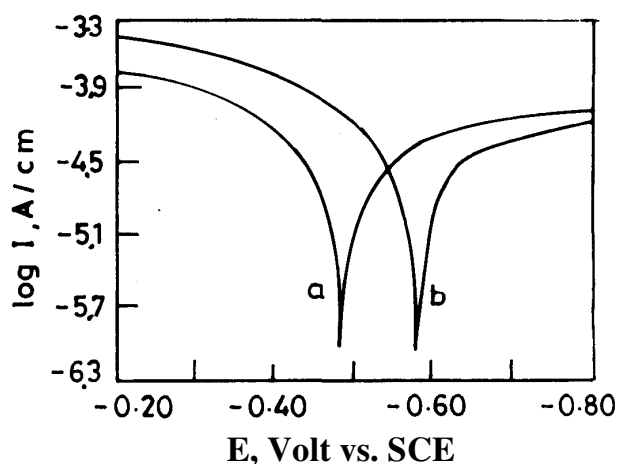
Figure 1. Polarization curves of carbon steel in various test solutions: (a) Cl$^-$ 60 ppm; (b) Cl$^-$ 60 ppm + $K_3[Fe(CN_6)]$ 100 ppm + Zn^{2+} 50 ppm.

Table 7. Corrosion parameters of carbon steel immersed in aqueous solution containing 60 ppm Cl$^-$, in the presence and absence of the inhibitor, obtained by polarization method.

system	E_{corr} (mV vs. SCE)	b_a (mV)	b_c (mV)	I_{corr} (A/cm^2)
NaCl	-487	153	220	1.5849×10^{-5}
$K_3[Fe(CN)_6]$	-566	153	53	0.6309×10^{-5}

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 8. It is found that, when carbon steel is immersed in 60 ppm Cl$^-$, the R_t value is 442.4 ohm cm^2 and C_{dl} value is 1.1518×10^{-8} μF/cm^2. When 100 ppm of $K_3[Fe(CN)_6]$ and 50 ppm of Zn^{2+} are added, the R_t value tremendously increases to 523.84 ohm cm^2, and the C_{dl} value decreases to 0.9727×10^{-8} μF/cm^2. This indicates that a protective film is formed on the metal surface in the presence of the inhibitors.

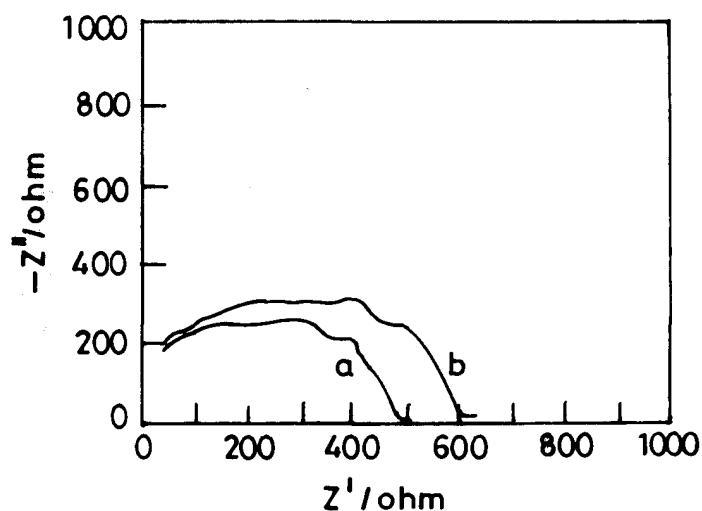**Figure 2.** AC impedance spectra of carbon steel immersed in various test solutions: (a) Cl^- 60 ppm; (b) Cl^- 60 ppm + $K_3[Fe(CN_6)]$ 100 ppm + Zn^{2+} 50 ppm.

Table 8. AC impedance parameters of carbon steel immersed in aqueous solution containing 60 ppm Cl^-, in the absence and presence of the inhibitors. Inhibitor system: $K_3[Fe(CN)_6] - Zn^{2+}$.

S.No	Cl^- (ppm)	$K_3[Fe(CN)_6]$ (ppm)	Zn^{2+} (ppm)	R_t (ohm cm^2)	$C_{dl}(\mu F/cm^2)$
1	60	0	0	442.40	1.1518×10^{-8}
2	60	100	50	523.84	0.9727×10^{-8}

Analysis of FTIR spectra

The FTIR spectrum (KBr) of pure $K_3[Fe(CN)_6]$ is shown as spectrum (a) in Fig. 3. The $[Fe(CN)_6]^{3-}$ stretching frequency appears at 2117.46 cm^{-1}. The Fe^{2+}-$K_3[Fe(CN)_6]$ complex was prepared by mixing Fe^{2+} as (Ferrous sulphate $FeSO_4.7H_2O$) and $K_3[Fe(CN)_6]$ solution. The FTIR spectrum of the complex is shown as spectrum (b) in Fig. 3. The $[Fe(CN)_6]^{3-}$ stretching frequency shifted from 2117.46 cm^{-1} to 2080.82 cm^{-1} [21].

The FTIR spectrum (KBr) of the film formed on the surface of metal after immersion in the solution containing 60 ppm Cl^-, 10 ppm Zn^{2+} and 100 ppm $K_3[Fe(CN)_6]$ is shown as spectrum (c) in Fig. 3. The $[Fe(CN)_6]^{3-}$ stretching frequency shifted from 2080.82 cm^{-1} to 2106.85 cm^{-1}.

This indicates the formation of Fe^{2+}-$K_3[Fe(CN)_6]$ on the anodic sites of the metal surface. The band at 1372 cm^{-1} is due to formation of $Zn(OH)_2$ on the cathodic sites. Thus, the FTIR spectral study suggests that in the presence of Cl^-, $K_3[Fe(CN)_6]$ and Zn^{2+}, the protective film formed on the metal surface is Prussian blue $Fe_4[Fe(CN)_6]_3$ and $Zn(OH)_2$ [21].
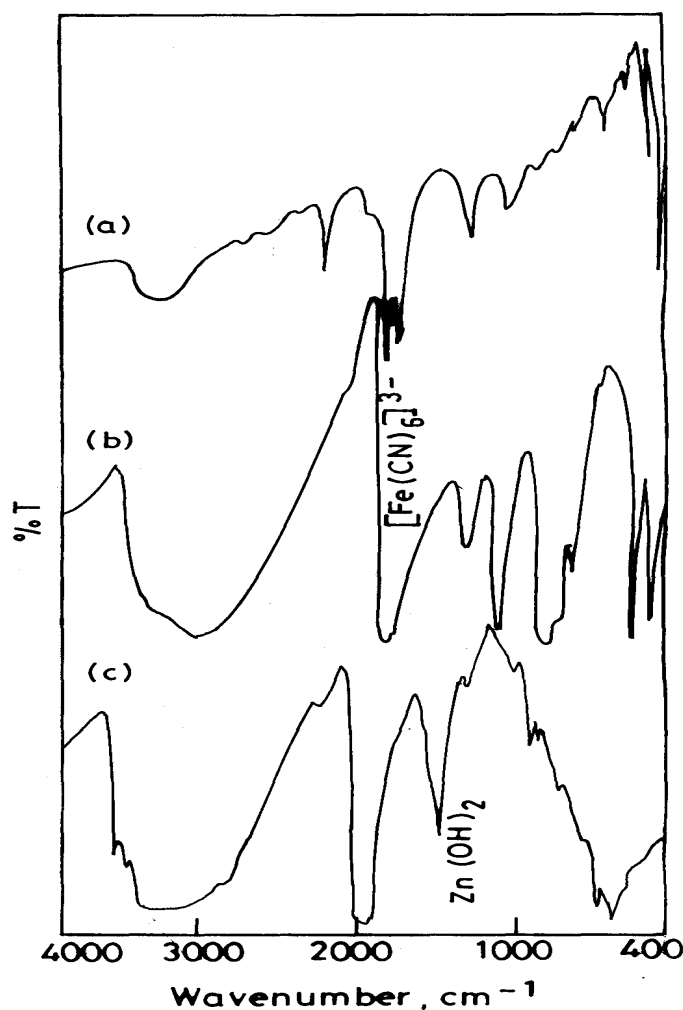
Figure 3. FTIR spectra: (a) solid $K_3[Fe(CN)_6]$;(b) Fe^{2+} - $K_3[Fe(CN)_6]$ prepared complex; (c) film (KBr) formed on metal surface after immersion in solution containing Cl^- 60 ppm + $K_3[Fe(CN_6)]$ 100 ppm and Zn^{2+} 10 ppm.

Analysis of fluorescence spectra

The emission spectrum (λ_{ex} = 385 nm) of the solid potassium ferricyanide is shown in Fig 4a. Peaks appeared at 429 nm, 500 nm and 527 nm. The corresponding excitation spectrum (λ_{em} = 527 nm) is shown in Fig 4b. Peaks appeared at 228 nm, 258 nm, 275 nm, 375 nm and 388 nm.

An iron complex of $K_3[Fe(CN)_6]$ was prepared by mixing a few drops of $K_3[Fe(CN)_6]$ solution and freshly prepared ferrous sulphate solution, being obtained a blue precipitate (Prussian blue). It was evaporated to dryness. Its emission spectrum (λ_{ex} = 360 nm) is shown in Fig. 4c. A peak appeared at 429 nm. The corresponding excitation spectrum (λ_{em} = 429 nm) is shown in Fig 4d. A peak appeared at 218 nm.

The emission spectrum (λ_{ex} = 360 nm) of the blue film formed on the surface of the metal after immersion in the solution containing 60 ppm Cl^-, 100 ppm $K_3[Fe(CN)_6]$ and 10 ppm Zn^{2+} is shown in Fig. 4e. The corresponding excitation

spectrum (λ_{em} = 429 nm) is shown in Fig. 4f. The peaks appeared in these spectra matched with those of the prepared Prussian blue. This confirmed that the protective film formed on the surface of the metal is Prussian blue.
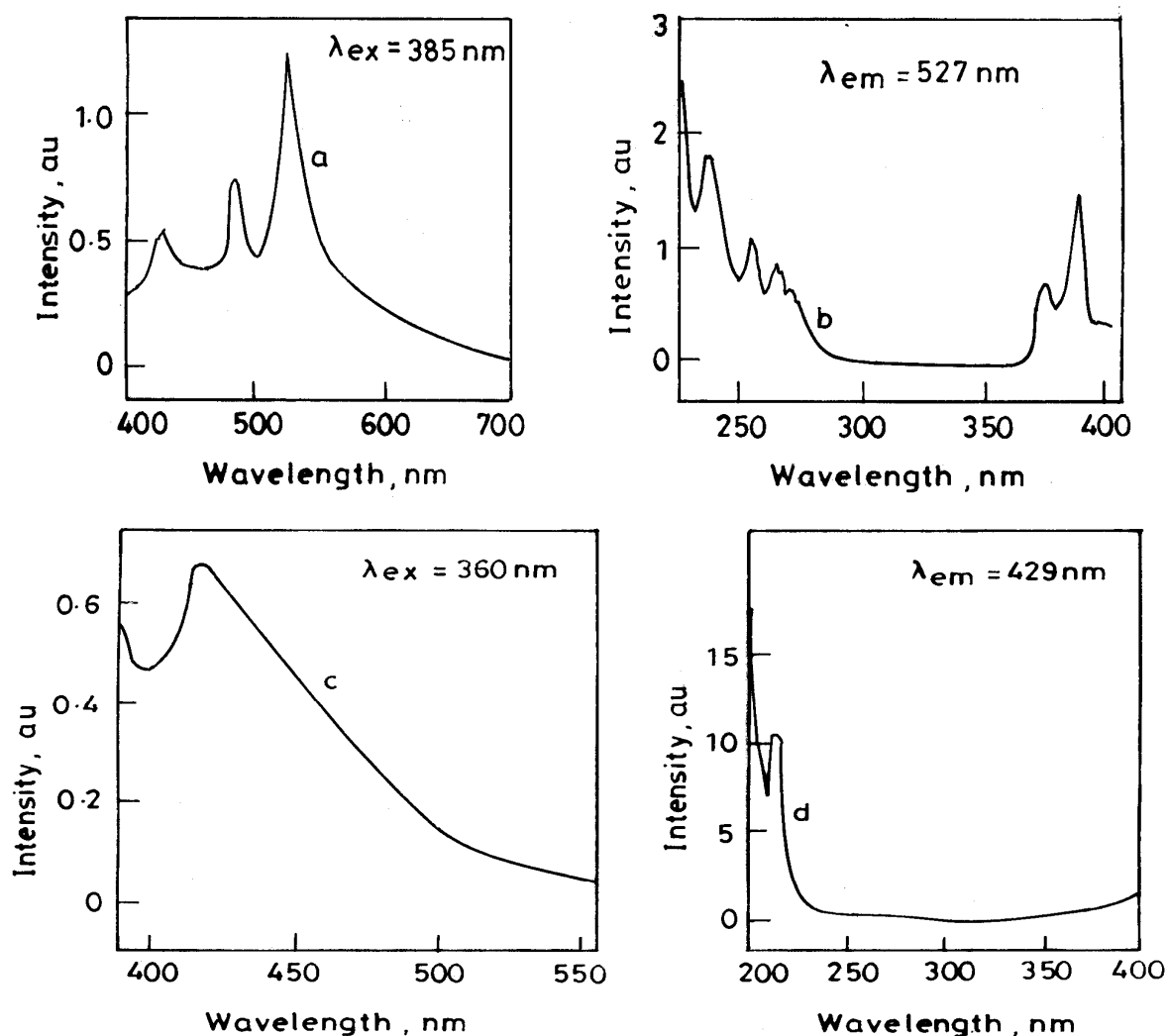

Figure 4. Fluorescence spectra. (a) and (b): emission and excitation spectra of solid $K_3[Fe(CN)_6]$; (c) and (d): emission and excitation spectra of Prussian blue.

Mechanism of corrosion inhibition

Weight loss study reveals that the formulation consisting of 60 ppm Cl^- and 100 ppm $K_3[Fe(CN)_6]$ and 50ppm of Zn^{2+} offers 98% IE to carbon steel immersed in aqueous solution containing 60 ppm Cl^-. A synergistic effect exists between $K_3[Fe(CN)_6]$ and Zn^{2+}. Polarization study reveals that this formulation controls the cathodic reaction predominantly. AC impedance spectra reveal that the protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Prussian blue and $Zn(OH)_2$.
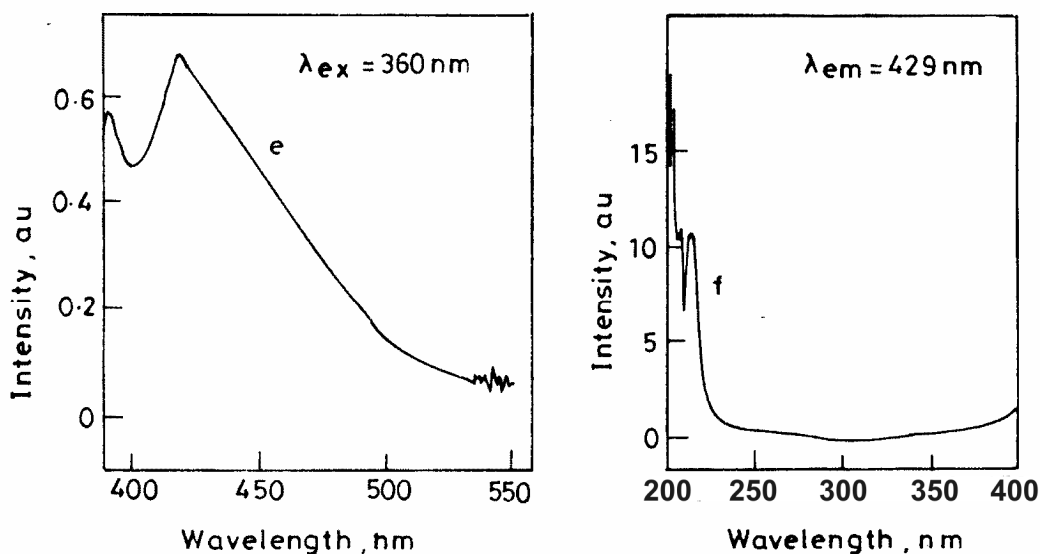
Figure 4 (cont.). Fluorescence spectra. (e) and (f): emission and excitation spectra of the film formed on metal surface after immersion in the solution containing 60 ppm Cl⁻, 100 ppm K₃[Fe(CN)₆], 100 ppm and 10 ppm Zn²⁺.

In order to explain the above facts in a holistic way the following mechanism of corrosion inhibition is proposed:

- when the formulation consisting of 60 ppm Cl⁻ 100 ppm $K_3[Fe(CN)_6]$ and 50 ppm Zn^{2+} is prepared, there is formation of $Zn^{2+} - K_3[Fe(CN)_6]$ complex in solution;
- when carbon steel is immersed in the solution, the $Zn^{2+}-K_3[Fe(CN)_6]$ diffuses from the bulk of the solution towards the metal surface;
- on the metal surface, $Zn^{2+}-K_3[Fe(CN)_6]$ complex is converted into $Fe^{2+} - K_3[Fe(CN)_6]$ complex; Zn^{2+} is released;
- the released Zn^{2+} combines with OH⁻ to form $Zn(OH)_2$ on the cathodic sites

$$Zn^{2+} + 2\,OH^- \rightarrow Zn(OH)_2 \;\downarrow$$

- thus the protective film consists of Prussian blue and $Zn(OH)_2$. This accounts for the synergistic effect.

Conclusions

The present study leads to the following conclusions:

- the formulation consisting of 60 ppm Cl⁻ 50 ppm Zn^{2+} and 100 ppm $K_3[Fe(CN)_6]$ offers 98% inhibition efficiency to carbon steel immersed in 60 ppm Cl⁻;
- a synergistic effect exists between $K_3[Fe(CN)_6]$ and Zn^{2+};
- as the immersion period increases, the inhibition efficiency decreases;
- polarization study reveals that this formulation controls the cathodic reaction predominantly;

- AC impedance spectra reveal that a protective film is formed on the metal surface;
- FTIR spectra reveal that a protective film is formed on the metal surface;
- the film is also found to be UV fluorescent.

References
1. G.B. Hatch, *Corrosion Inhibitors*, Ed. C.C. Nathan, NACE, Houston, Texas, U.S.A (1973) 126.
2. J. Golden, J.E.O. Mayne, *Br.Corrosion J.* 13 (1978) 45.
3. J.P.G. Farr, M. Saremi, *Surface Technology* 19 (1983)137.
4. W.D. Robertson, *J. Electrochem. Soc.* 98 (1951) 94.
5. C.B. Wooten , *Japan kokai* 75, 68, 645 (Appl 30.11.76)
6. M. Cohen, *Corrosion* 32 (1976) 461.
7. S. Sanyal, *Bull. Electrochem.* 6 (1990) 392
8. G.B. Hatch, *Ind. Eng. Chem.* 44 (1952) 1775.
9. J.L. Mansa, Szybalski, *Corrosion* 8 (1952) 381.
10. K.S. Rajagopalan, K. Venu, *Indian J. Techn.* 6 (1968) 239.
11. J.W. Wood, J.S. Beecher, P.S. Laurence, *Corrosion* 13 (1957) 41.
12. M. Iovchev, 8th International Congress on Metallic Corrosion, *Publ. Dechema Frankfurt* 2 (1981) 1488.
13. E.D. Mor, C. Wrubl, *Br. Corrosion J.* 11 (1976) 199.
14. D. Vanloyen, G. Zucher, *Werkst. Korros.* 11 (1990) 613.
15. E.V. Bogatyreva, S.A. Balezin, *Zh. Priklad. Khim.* 35 (1962) 550.
16. E.V. Bogatyreva, V.V. Nagaev, *Zh. Priklad. Khim.* 35 (1962) 550.
17. Yu.I. Kuzentsov, S.V. Oleynik, N.N. Andreev, S.S. Vesely, *6th Europ. Symp. Corrosion Inhibitors*, Ferrara, Italy, 1 (1985) 567.
18. P.J. Deslauriers, *Mater. Perform. NACE* 11 (1985) 35.
19. G. Wranglen, *Introduction to Corrosion and Protection of Metals*, Chapman & Hall, London, (1985) 236.
20. S.K. Selvaraj, A. John Kennedy, A.J. Amalraj, S. Rajendran, N. Palaniswamy, *Corrosion Rev.* 22 (2004) 219.
21. Richard A. Nyquist, Ronald O. Kagel, *Infra Red Spectra of Inorganic Compounds,* Academic Press, New York and London - 1971 (971) 64,65 & 68.