Transport of Inhibitors and Corrosion Inhibition Efficiency

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ABSTRACT

The inhibition efficiency (IE) of various concentrations of a caffeine-Zn^{2+} system in controlling corrosion of mild steel immersed in an aqueous solution containing 60 ppm of Cl^- was evaluated by a weight-loss study. The formulation consisting of 50 ppm of caffeine and 50 ppm of Zn^{2+} showed 91% IE. A synergistic effect was noticed between caffeine and Zn^{2+}. The influence of sodium sulfite (Na_2SO_3), sodium dodecyl sulfate (SDS)—an anionic surfactant—pH, and a period of immersion on the IE of the caffeine-Zn^{2+} system has been evaluated. The transport of inhibitors toward the metal surface plays a major role in controlling corrosion of mild steel. Formation of micelles by surfactants changes the IE. The caffeine-Zn^{2+} system has better IE in the acidic medium than in basic medium. The IE decreased as the period of immersion increased. The protective film was analyzed by Fourier transform infrared spectroscopy. The film consisted of Fe^{2+}-caffeine complex and zinc hydroxide ($Zn[OH]_2$). The film was found to be UV-fluorescent.

KEYWORDS: caffeine, corrosion inhibition, inhibitor transport, mild steel, synergistic effect

INTRODUCTION

Environmentally friendly inhibitors have attracted several researchers. Natural products are nontoxic and they have been used widely as inhibitors. Natural products such as tannins[1-3] have been used as inhibitors. Extracts of plants such as *Cerum Petroselinum*, lupine, doum, and orange shells have been used as corrosion and scale inhibitors.[4] Pomegranate,[5] *Swertia angustifolia*,[6] and *Azadiracta indica*[7] have good inhibitive properties. The scale inhibition efficiencies of the aqueous extracts of plant materials, namely *Cordia latifolia*, Eucalyptus, and *Jasminum auriculatum* have been evaluated.[8] The goals of the present work were the following:

—to investigate the inhibition efficiency of caffeine, in controlling corrosion of mild steel immersed in an aqueous environment containing 60 ppm Cl^-, in the absence and presence of Zn^{2+}, using a weight-loss study

—to examine the influence of sodium sulfite (Na_2SO_3), an oxygen scavenger; sodium dodecylsulfate (SDS), an anionic surfactant; pH; and a period of immersion on the inhibition efficiency of the caffeine-Zn^{2+} system

—to analyze the protective film by Fourier transform infrared (FTIR) spectroscopy and fluorescence spectroscopy

—to propose a suitable mechanism of corrosion inhibition
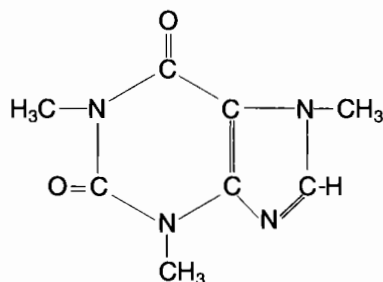
Scheme 1

EXPERIMENTAL PROCEDURES

Weight-Loss Measurements

Experiments were carried out using mild steel (MS) in an aqueous environment containing 60 ppm Cl^-. The MS sample was 1.0 cm by 4.0 cm by 0.2 cm (0.394 in. by 1.576 in. by 0.079 in.) with the following composition (wt%): 0.03 S, 0.04 P, 0.4 Mn, 0.15 C, and bal. Fe. The MS samples were polished to a mirror finish with 1/0, 2/0, 3/0, and 4/0 emery papers and degreased with trichloroethylene. Three MS samples were immersed in solutions containing various concentrations of the inhibitors for a period of 3 days. The corrosion products were cleaned with Clarke's solution.[9] The weights of the specimens before and after immersion were determined using a Mettler balance, AE-40[†]. The inhibition efficiency (IE) was calculated using the relation:

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

where W_1 is the corrosion rate in the absence of inhibitor and W_2 is the corrosion rate in the presence inhibitor.

Analysis of the Protective Film

The MS samples were immersed in various test solutions for a period of 3 days. After 3 days, the samples were taken out and dried. The film formed on the metal surface was carefully removed, mixed thoroughly with potassium bromide (KBr), and made as pellets. The FTIR spectra (KBr pellet) of the film formed on the MS samples were recorded in a Perkin Elmer 1600[†] spectrophotometer.

The fluorescence spectrum of the film formed on the MS samples was recorded in a Hitachi F-4500[†] fluorescence spectrophotometer.

RESULTS AND DISCUSSION

Weight-Loss Studies

Table 1 shows the values of IE from weight-loss measurements for different concentrations of caffeine and Zn^{2+}. It was found that caffeine as well as Zn^{2+} have good IE. However, their combination showed better IE. For example, 50 ppm caffeine had 8% IE and 50 ppm Zn^{2+} showed 41% IE. But, their combination had 91% IE. This suggested a synergistic effect existing between caffeine and Zn^{2+}.

When MS is immersed in a neutral aqueous environment, the anodic reaction is:

[†] Trade name.

TABLE 1
Weight Loss (mg) and IE (%) of the Caffeine-Zn^{2+} System
Offered to MS Immersed in the 60-ppm Cl^- Environment for 3 Days

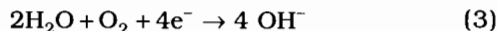| Caffeine (ppm)	Zn^{2+} (ppm)						
	0	25	50	75	100	125	150
0	(4.2)[(A)] —	(3.44) 18	(2.48) 41	(2.18) 48	(1.81) 57	(1.68) 60	(1.60) 62
25	(4.41) −5	(2.10) 50	(1.85) 56	(1.81) 57	(1.60) 62	(1.13) 73	(1.05) 75
50	(3.86) 8	(0.29) 93	(0.38) 91	(0.55) 87	(2.14) 49	(2.86) 32	(2.90) 31
75	(3.65) 13	(1.72) 59	(1.43) 66	(1.39) 67	(1.34) 68	(1.30) 69	(1.22) 71
100	(2.23) 47	(0.50) 88	(0.76) 82	(1.09) 74	(1.05) 75	(1.13) 73	(1.18) 72
125	(3.44) 18	(0.84) 80	(0.76) 82	(0.71) 83	(0.42) 89	(0.42) 90	(0.21) 95
150	(2.94) 30	(0.55) 87	(0.76) 82	(0.92) 78	(1.09) 75	(1.09) 74	(1.89) 55

[(A)] Weight loss is given in parenthesis.
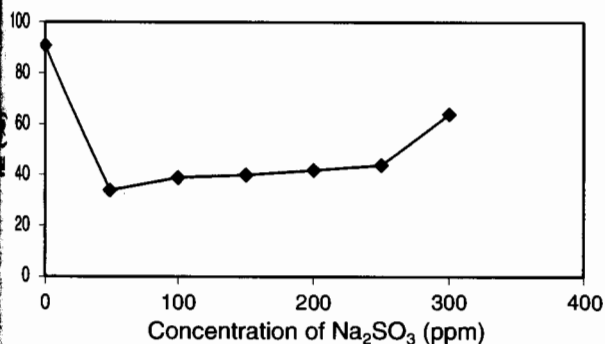
FIGURE 1. *Influence of Na₂SO₃ on the IE of the caffeine (50 ppm)-Zn²⁺ (50 ppm) system, offered to MS immersed in the chloride environment for 3 days.*

FIGURE 2. *Influence of SDS on the IE of the caffeine (50 ppm)-Zn²⁺ (50 ppm) system. Immersion period: 3 days.*

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (2)$$

The cathodic reaction is:

$$2H_2O + O_2 + 4e^- \rightarrow 4\ OH^- \qquad (3)$$

In the presence of caffeine, the anodic reaction was controlled by the formation of the Fe^{2+}-caffeine complex on the anodic sites of the metal surface. In the presence of caffeine and Zn^{2+}, the anodic reaction was controlled by the formation of the Fe^{2+}-caffeine complex and the cathodic reaction was controlled by the formation of zinc hydroxide ($Zn[OH]_2$) on the cathodic sites. Thus, the Fe^{2+}-caffeine system functioned as a mixed inhibitor, controlling anodic and cathodic reactions. This accounted for the synergistic effect existing between caffeine and Zn^{2+}.

Influence of Na₂SO₃ on the IE of the Caffeine-Zn²⁺ System

Addition of 50 ppm Na_2SO_3 to the formulation consisting of 50 ppm caffeine and 50 ppm Zn^{2+} decreased the IE from 91% to 34% (Figure 1). This suggested that in the presence of Na_2SO_3, the transport of caffeine and Zn^{2+} from the bulk of the solution toward the metal surface is prevented to some extent. Further addition of Na_2SO_3 increased the IE from 34% to 64%. This is due to the fact that in the presence of Na_2SO_3, the amount of dissolved oxygen in the solution is reduced by Na_2SO_3 getting oxidized to sodium sulfate (Na_2SO_4). This resulted in the increased IE of the system. However, in the presence of Na_2SO_3, the IE of the caffeine-Zn^{2+} system is decreased. This suggested that the transport of the inhibitor toward the metal surface from the bulk of the solution plays a major role than reducing the amount of dissolved oxygen in the solution, in controlling corrosion of MS in a chloride environment. Similar observations have been reported when Na_2SO_3 was added to the sodium gluconate ($C_6H_{11}NaO_7$)-Zn^{2+}
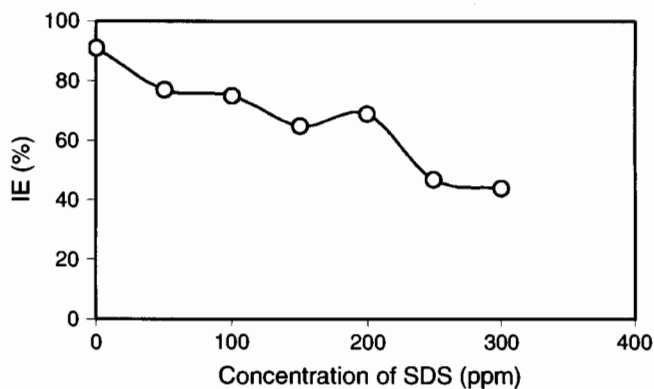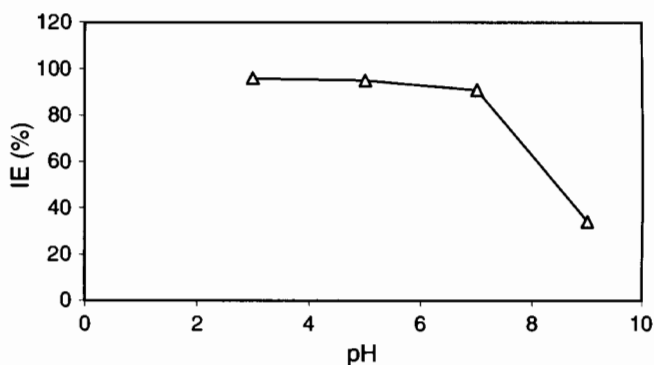

FIGURE 3. *Influence of pH on the IE of the caffeine (50 ppm)-Zn²⁺ (50 ppm) system. Immersion period: 3 days.*

system,[10] and when Na_2SO_3 was added to the SDS-Zn^{2+} system.[11]

Influence of SDS on the IE of the Caffeine-Zn²⁺ System

Figure 2 shows the influence of SDS on the IE of the caffeine-Zn^{2+} system. In the presence of SDS, the IE of the caffeine-Zn^{2+} system decreased. This decrease increased as the concentration of SDS increased. This suggests that SDS, an anionic surfactant, would have formed micelles at these concentrations, resulting in the restricted transport of the inhibitor system toward the metal surface from the bulk of the solution.

Influence of pH on the IE of the Caffeine-Zn²⁺ System

Figure 3 shows the influence of pH (addition of sulfuric acid [H_2SO_4]) on the IE of the caffeine system. At pH 3 very good IE of 96% was noticed. However, at pH 9 (addition of sodium hydroxide [NaOH]), IE decreased to 34%. This is due to the fact that in the presence of NaOH, Zn^{2+} is precipitated as $Zn(OH)_2$; the transport of Zn^{2+} toward the metal surface is restricted and hence a decrease in the IE.
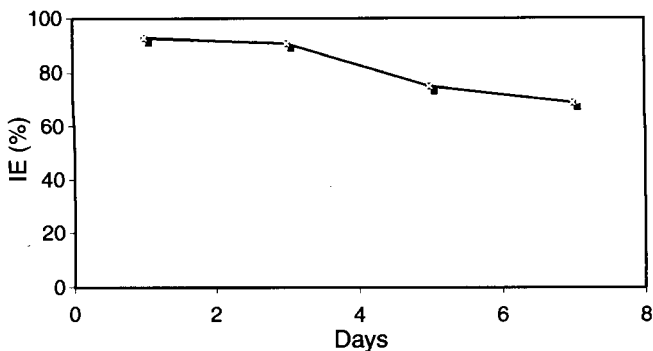
FIGURE 4. *Corrosion IE of the caffeine (50 ppm)-Zn^{2+} (50 ppm) system, as a function of immersion period.*

Influence of Immersion Period on the IE of the Caffeine-Zn^{2+} System

Figure 4 represents the corrosion IE of the caffeine-Zn^{2+} system as a function of time. It was found that IE decreased as the period of immersion increased. This is due to the fact that as the period of immersion increased the protective film formed on the metal surface slowly raptured, as a result of the constant attack of Cl^-, which was present in the solution. There is competition between two processes, namely formation of iron-caffeine complex and iron chloride. It appears that the formation of iron chloride is more favorable than the formation of the iron-caffeine complex. Moreover, the iron-caffeine complex film formed on the metal surface is converted into iron chloride, which goes into solution, and hence, the IE decreases as the immersion period increases.[11]

Analysis of the Protective Film

The FTIR spectrum (KBr pellet) of pure caffeine is shown as Spectrum A in Figure 5. The C=O stretching frequency appears at 1,658 cm⁻¹. The band resulting from the C⸺N ring stretching absorbs at 1,484.5 cm⁻¹. The CH₃ group absorption $\delta_s\,CH_3$ in CH₃—N appears at 1,403 cm⁻¹ and 1,429.8 cm⁻¹.[12]

Fe^{2+}-caffeine complex was prepared by mixing Fe^{2+} (as ferrous sulfate [$FeSO_4\cdot7H_2O$]) and caffeine solution. The FTIR spectrum of the complex is shown as Spectrum D in Figure 5. The C=O stretching shifted from 1,658 cm⁻¹ to 1,623 cm⁻¹. This was caused by the shift of the electron cloud of C=O toward Fe^{2+}, resulting in the formation of Fe^{2+}-caffeine complex. The C⸺N ring stretching shifted from 1,484.5 cm⁻¹ to 1,456 cm⁻¹. This suggests that the electron cloud of C⸺N bond coordinated with Fe^{2+} through N.

The FTIR spectrum (KBr) of the film formed on the surface of MS after immersion in the solution consisting of 60 ppm Cl^- and 50 ppm caffeine is shown as Spectrum B in Figure 5. The C=O stretching frequency shifted from 1,658 cm⁻¹ to 1,630 cm⁻¹.
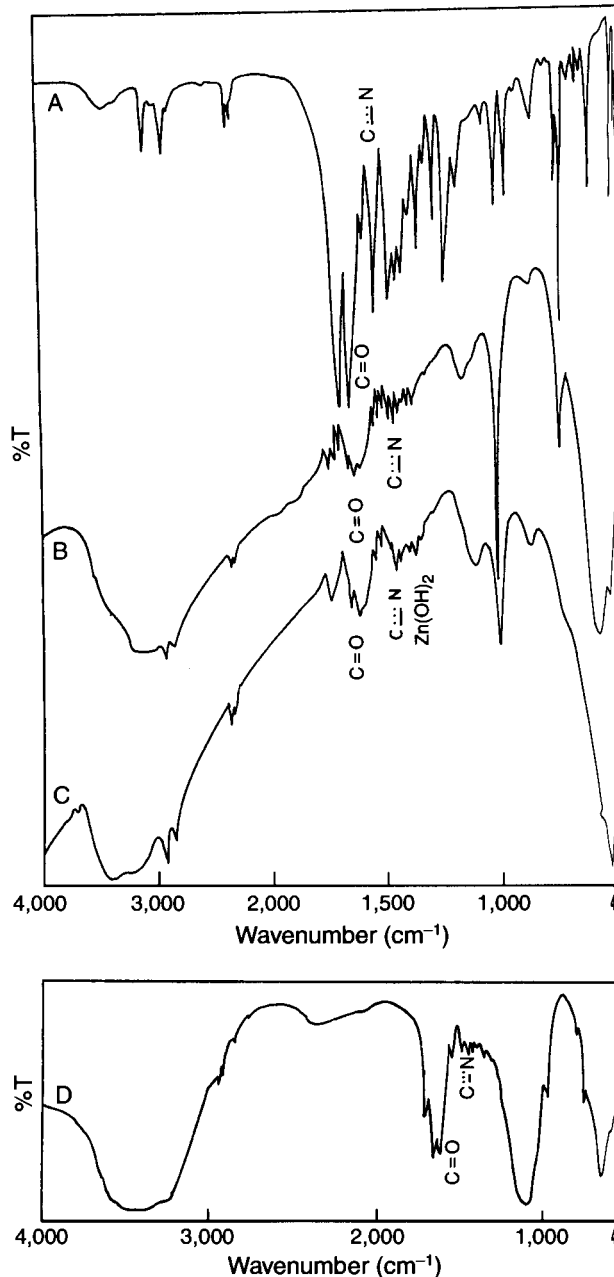

FIGURE 5. *FTIR spectrum of pure caffeine and that of film formed on MS samples after immersion in various test solutions: (A) pure caffeine, (B) 60 ppm Cl^- + 50 ppm caffeine, (C) 60 ppm Cl^- + caffeine ppm 50 + 50 ppm Zn^{2+}, and (D) Fe^{2+}-caffeine complex prepared.*

This was caused by the shift of the electron cloud of C=O bond toward Fe^{2+}, resulting in the formation of Fe^{2+}-caffeine complex on the anodic sites of the metal surface. The C⸺N ring stretching decreased from 1,484.5 cm⁻¹ to 1,467 cm⁻¹. This suggested that the electron cloud of the C⸺N bond coordinated with Fe^{2+} through N. Thus, FTIR spectral study suggests that in the presence of Cl^- and caffeine, the anodic reaction of metallic dissolution is controlled by the formation of the Fe^{2+}-caffeine complex.

The FTIR spectrum (KBr) of the film formed on the surface of MS after immersion in the solution containing 60 ppm Cl^-, 50 ppm caffeine, and 50 ppm Zn^{2+} is shown as Spectrum C in Figure 5. The $C=O$ stretching frequency decreased from 1,658 cm^{-1} to 1,628 cm^{-1}. This was caused by the shift of the electron cloud of the $C=O$ bond toward Fe^{2+}, resulting in the formation of Fe^{2+}-caffeine complex on the anodic sites of the metal surface. The $C\cdots N$ ring stretching decreased from 1,484.5 cm^{-1} to 1,464 cm^{-1}. This suggests that the electron cloud of $C\cdots N$ bond coordinated with Fe^{2+} through N. The band at 1,380 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites.[13-14] Thus, the FTIR spectral study suggests that in the presence of Cl^-, caffeine, and Zn^{2+}, the protective film consists of Fe^{2+}-caffeine complex and $Zn(OH)_2$.

Fluorescence Spectrum

The fluorescence spectrum (λ_{ex} = 300 nm) of the Fe^{2+}-caffeine complex prepared by mixing Fe^{2+} ion (as $FeSO_4 \cdot 7H_2O$) and caffeine solution is shown as Spectrum A in Figure 6. Peaks appeared at 468.2 nm and 533 nm. Zn^{2+}-caffeine complex was prepared by mixing Zn^{2+} ion (as zinc sulfate [$ZnSO_4 \cdot 7H_2O$]) and caffeine solution. It was excited at λ_{ex} = 300 nm. The emission spectrum is shown as Spectrum B in Figure 6. It did not show any prominent peak.

The fluorescence spectrum of the film formed on the surface of MS sample after immersion in the solution containing 60 ppm Cl^-, 50 ppm caffeine, and 50 ppm Zn^{2+} was recorded by exciting the film at λ_{ex} = 300 nm (Figure 6[c]). Peaks appeared at 418(12.17), 439(11.90), 469(16.30), 482(13.77), 491(12.5), and 534(16.01) nm. (The peak intensities are given in the parentheses). This fluorescence spectrum is the result of the Fe^{2+}-caffeine complex entrailed in $Zn(OH)_2$.

Mechanism of Corrosion Inhibition by the Caffeine-Zn^{2+} System

The weight-loss study revealed that the formulation consisting of 60 ppm Cl^-, 50 ppm caffeine, and 50 ppm Zn^{2+} has 91% IE. FTIR spectral study revealed that the protective film consisted of Fe^{2+}-caffeine complex and $Zn(OH)_2$. To explain the results, the following mechanism of corrosion inhibition is proposed:

—When the environment consisting of 60 ppm Cl^-, 50 ppm caffeine, and 50 ppm Zn^{2+} is prepared, there is formation of Zn^{2+}-caffeine complex in solution.

—When MS is introduced into this solution, there is diffusion of Zn^{2+}-caffeine complex toward the metal surface.

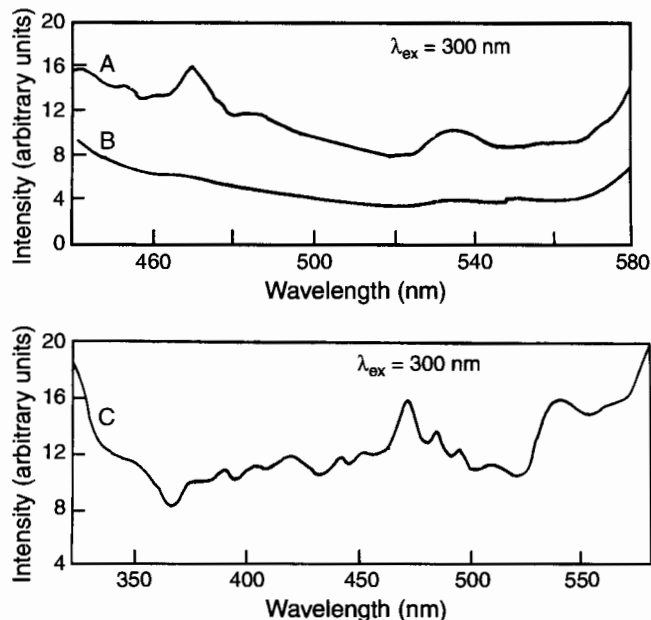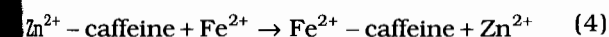—On the metal surface, zinc complex is converted into Fe^{2+}-caffeine complex on the anodic sites:

$$Zn^{2+} - caffeine + Fe^{2+} \rightarrow Fe^{2+} - caffeine + Zn^{2+} \qquad (4)$$

FIGURE 6. *Fluorescence spectra: (A) Fe^{2+}-caffeine complex prepared, (B) Zn^{2+}-caffeine complex prepared, (C) emission spectrum of the film formed on MS sample after immersion in the solution containing 60 ppm Cl^-, 50 ppm caffeine, and 50 ppm Zn^{2+}.*

—The released Zn^{2+} combines with OH^- to form $Zn(OH)_2$ on the cathodic sites:

$$Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2 \downarrow \qquad (5)$$

—Thus, the protective film consists of Fe^{2+}-caffeine complex and $Zn(OH)_2$.

CONCLUSIONS

❖ The caffeine-Zn^{2+} system shows a synergistic effect in controlling corrosion of MS immersed in 60 ppm Cl^-.
❖ The transport of the inhibitor toward the metal surface from the bulk of the solution plays a major role in reducing the amount of dissolved oxygen in the solution, in controlling corrosion of MS in chloride environment.
❖ Formation of micelles change the inhibitive effects of the inhibitor systems.
❖ The caffeine-Zn^{2+} has better IE in the acidic medium than in the basic medium.
❖ The IE of the caffeine-Zn^{2+} system decreases as the period of immersion increases.
❖ The protective film consists of Fe^{2+}-caffeine complex and $Zn(OH)_2$.
❖ The protective film is found to be UV-fluorescent.

ACKNOWLEDGMENTS

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