

Synergistic Effect of Calcium Gluconate and Zn^{2+} on the Inhibition of Corrosion of Mild Steel in Neutral Aqueous Environment

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As an alternative to the chromate containing corrosion inhibitors for mild steel in cooling water systems, the synergistic effect of calcium gluconate (CG) and Zn^{2+} on the inhibition of corrosion of mild steel in neutral aqueous environment containing 60 ppm Cl^- ion, a situation commonly encountered in cooling water systems, has been evaluated by the weight-loss method. The formulation consisting of 50 ppm Zn^{2+} and 200 ppm CG has 92% inhibition efficiency. A suitable mechanism of corrosion inhibition is proposed, based on the results obtained from the uv-visible absorption spectra and FTIR spectra. The protective film is found to be fluorescent and to consist of Fe^{2+} - gluconate complex, $Zn(OH)_2$ and $Ca(OH)_2$.

Key words: Corrosion inhibition, calcium gluconate, fluorescence, surface analysis, synergism parameter.

Introduction

Gluconates and gluconic acid are known to be effective non-toxic inhibitors for iron and mild steel in cooling water [1-6]. They show synergistic effect with borate [7-10]. It has been reported that the formation of soluble metal complexes with iron is one of the major problems with gluconate containing compounds and hence their effectiveness decreases within a few hours after immersion [10-11]. In the present work, the synergistic effect of calcium gluconate (CG) and Zn^{2+} has been evaluated by the weight-loss method. The nature of the protective film has been analysed using FTIR and fluorescent spectra. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from UV-visible absorption spectra, FTIR and fluorescence spectra.

Experimental

Preparation of the specimens

For weight-loss method and surface examination study, mild steel specimens (0.02–0.03 % S, 0.03–0.08 % P, 0.4–0.5 % Mn, 0.1–0.2 % C and rest Fe) of the dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish and degreased with trichloroethylene.

Weight-loss method

Mild steel specimens in triplicate were immersed in 100 ml of the test solutions for a period of seven days. The weights of the specimens before and after immersion were determined using a Mettler balance, AE-240. The corrosion products were cleaned with Clarke's solution [12]. The inhibition efficiency (I.E.) was calculated using the relation

$$I.E. = 100 [(W_1 - W_2)/W_1] \%$$

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

The UV-visible absorption spectroscopic study

The UV-visible absorption spectra of aqueous solutions were recorded using a Hitachi U-3400 Spectrophotometer.

FTIR spectroscopic study

Polished mild steel specimens were immersed in various test solutions for a period of seven days. After seven days, the metal specimens were taken out and dried. The surface film was scratched carefully and the

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powder obtained was thoroughly mixed so as to make it uniform throughout. FTIR spectrum of the powder (KBr pellet) was recorded using a Perkin-Elmer 1600 FTIR Spectrophotometer.

Fluorescence spectra

The fluorescence spectra were recorded by using a Hitachi F-4500 Fluorescence Spectrophotometer.

Results and discussion

Analysis of results of the weight-loss method

The corrosion rates of mild steel in neutral aqueous environment containing 60 ppm chloride in the absence and presence of inhibitor at various concentrations obtained by the weight-loss method are given in Table 1. The corrosion inhibition efficiencies of the calcium gluconate (CG) – Zn²⁺ system are also given in this Table. It reveals that while 200 ppm CG had 60% inhibition efficiency, 50 ppm Zn²⁺ was found to be corrosive. Interestingly, their combination showed 92% inhibition efficiency. This suggests a synergistic effect of the CG – Zn²⁺ system.

Table 1. Corrosion rates of mild steel in neutral aqueous environment (Cl⁻ = 60 ppm) in the presence and absence of inhibitor and the inhibition efficiencies obtained by weight-loss method

Inhibitor system: Calcium gluconate + Zn²⁺

Zn ²⁺ (ppm)	Ca-gluconate (ppm)	Corr. rate (mdd)	Inhib. Eff. (%)	Synergism parameter
0	0	15.54	—	—
50	0	19.11	23	
50	25	16.60	-4	-43.2
50	50	10.20	34	8.0
50	100	5.75	63	4.7
50	150	2.18	86	14.6
50	200	1.24	92	15.6
50	250	1.25	92	17.1
0	25	13.99	10	
0	50	13.68	12	
0	100	13.52	13	
0	150	6.84	56	
0	200	6.22	60	
0	250	5.28	66	

Synergism parameters

Synergism parameters were calculated using the relationship [13,14].

$$S_1 = \frac{(1 - I_{1+2})}{(1 - I'_{1+2})}$$

where, I₁₊₂ = (I₁ + I₂) - (I₁I₂), I₁ = inhibition efficiency of substance 1, I₂ = inhibition efficiency of substance 2 and I'₁₊₂ = inhibition efficiency of the system consisting of substance 1 and substance 2.

The values of the synergism parameters (S₁) are given in Table 1. The value of S₁ is found to be negative for the system consisting of 50 ppm Zn²⁺ and 25 ppm CG. This indicates the antagonistic effect existing between Zn²⁺ and CG at the above concentrations. The values of S₁ for other systems are found to be greater than 1. This suggests that synergistic effect exist between Zn²⁺ and CG. It is also learnt that for a given concentration of Zn²⁺, the value of synergism parameter depends on the concentration of CG.

Inhibition efficiency as a function of immersion period

The weight-loss of mild steel immersed in various environments as a function of immersion period is shown in Fig. 1. The inhibition efficiencies are also given in Fig. 1. It is observed that when mild steel is immersed in the environment containing 60 ppm Cl⁻, the weight-loss increased with immersion period (curve a).

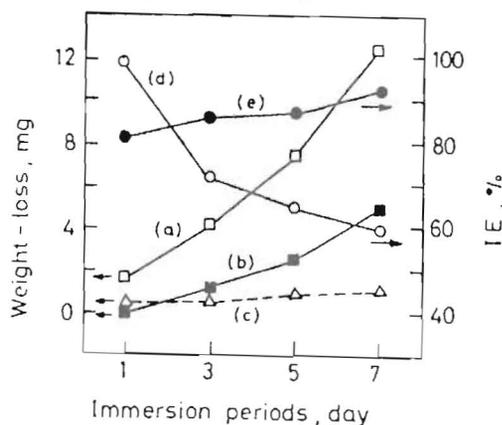


Fig.1. Weight-loss and inhibition efficiency as a function of immersion period, when mild steel is immersed in various environments.

(a): Cl⁻ 60 ppm; (b) & (d): Cl⁻ 60 ppm + CG 200 ppm
(c) & (e): Cl⁻ 60 ppm + CG 200 ppm + Zn²⁺ 50 ppm

When mild steel is immersed in the environment containing 60 ppm Cl^- and 200 CG, the weight-loss increases with time (curve b). However, the weight losses noticed are lower than that of the specimens immersed in the blank. It is also observed that the inhibition efficiency decreased with time (curve d). At the end of first day, the inhibition efficiency is 99 %. It decreases with time and comes down to 59 % at the end of the seventh day. This may be due to the fact that the protective film formed on the metal surface slowly dissolves.

When mild steel is immersed in the environment consisting of 60 ppm Cl^- , 200 ppm CG and 50 ppm Zn^{2+} , the weight-losses are lower than that of the specimens immersed in the blank (curve c). It is observed that the weight loss almost remains constant during 5-7th day. It is also observed that the inhibition efficiency increases with time (curve e). That is, in the presence of Zn^{2+} , the protective film formed on the metal surface is quite stable and the dissolution of the protective film is reduced to a considerable extent.

Analysis of the UV-visible absorption spectra

The uv-visible absorption spectra of various test solutions are shown in Fig. 2. The spectra suggest that Zn^{2+} and CG remain as an ion pair in the solution. There is a formation of Fe^{2+} - gluconate complex in the solution. In the presence of both Zn^{2+} and Fe^{2+} , gluconate forms complex with Fe^{2+} rather than with Zn^{2+} .

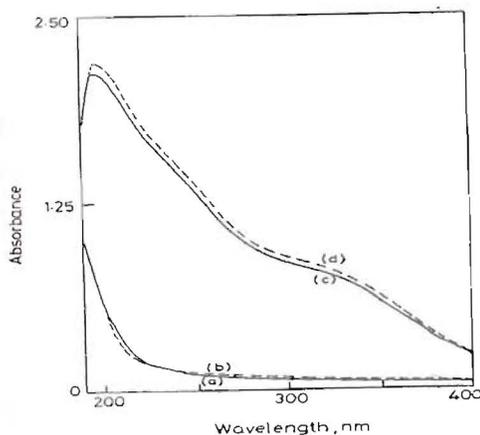


Fig. 2. UV-visible absorption spectra of various test solutions

- (a): CG 200 ppm; (b): CG 200 ppm + Zn^{2+} 50 ppm;
(c): CG 200 ppm + Fe^{2+} 100 ppm;
(d): CG 200 ppm + Fe^{2+} 100 ppm + Zn^{2+} 50 ppm

Analysis of the FTIR spectra

The FTIR spectrum of pure CG is shown in Fig.3 (curve a). The FTIR spectrum of the film formed on the surface of the metal immersed in the environment containing 60 ppm Cl^- , 200 ppm CG and 50 ppm Zn^{2+} is shown as curve b. It is observed that the C=O stretching frequency of the carboxylate anion of the gluconate has decreased from 1606 cm^{-1} to 1540 cm^{-1} . This suggests that the carboxyl group has been coordinated to Fe^{2+} resulting in the formation of Fe^{2+} -gluconate complex on the metal surface. The peak at 1483 cm^{-1} corresponds to $Ca(OH)_2$. The peak at 1360 cm^{-1} is due to $Zn(OH)_2$.

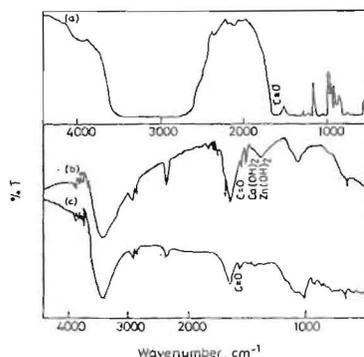


Fig. 3. FTIR spectra of pure CG (a) and of films formed on the surface of the metal immersed in various environments (a): pure CG; (b): Film formed on the surface of the metal immersed in the environment Cl^- 60 ppm + CG 200 ppm + Zn^{2+} 50 ppm; (c): Fe^{2+} - gluconate complex prepared by mixing Fe^{2+} solution and CG solution.

It is interesting to note that the pattern of the FTIR spectrum of the Fe^{2+} -gluconate complex formed on the metal surface matches with that of the Fe^{2+} -gluconate complex prepared by mixing Fe^{2+} and CG solutions (curve-c).

Analysis of the fluorescence spectra

The fluorescence spectra of the film formed on the surface of the metal immersed in various environments are shown in Fig. 4. The emission spectrum ($\lambda_{ex} = 330\text{ nm}$) of the surface of the metal immersed in the environment consisting of 60 ppm Cl^- and 200 ppm CG is shown as curve a. Peaks appeared at 465, 525 and 556 nm. A remarkable increase in intensity of the above peaks appeared when 50 ppm Zn^{2+} was added to the above environment. This suggests that the formation of Fe^{2+} -gluconate complex on the metal surface was enhanced by the presence of Zn^{2+} in the environment (curve b).

The corresponding excitation spectra ($\lambda_{em} = 465 \text{ nm}$) are also shown (curves c and d). Peaks appeared at 320, 350, 362 and 378 nm. The spectra also suggest that the formation of Fe^{2+} -gluconate complex on the metal surface was enhanced by the presence of Zn^{2+} in the environment.

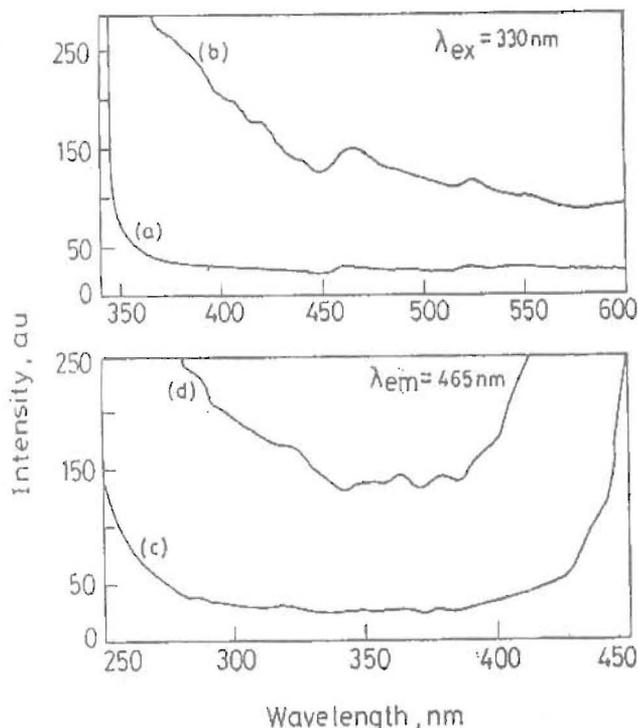


Fig. 4. Fluorescence spectra of the films formed on the surface of the metal immersed in various environments.

(a) and (c): Cl^- 60 ppm + CG 200 ppm
 (b) and (d): Cl^- 60 ppm + CG 200 ppm + Zn^{2+} 50 ppm

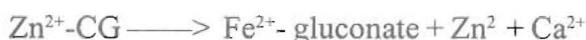
Mechanism of corrosion inhibition

Analysis of the results of the weight-loss method reveals that the formulation consisting of 50 ppm Zn^{2+} and 200 ppm CG had 92 % inhibition efficiency. The UV-visible absorption spectra suggest the formation of Zn^{2+} -CG ion pair and also Fe^{2+} -gluconate complex in solution. FTIR spectra suggest that Fe^{2+} -gluconate complex, $\text{Zn}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ were present in the film formed on the inhibited metal surface. The protective film was found to be fluorescent. In order to explain all these observations in the holistic way, the following mechanism of corrosion inhibition is proposed.

When the environment containing 60 ppm Cl^- , 50 ppm Zn^{2+} and 200 ppm CG is prepared, there is formation of Zn^{2+} -CG ion pair in the solution.

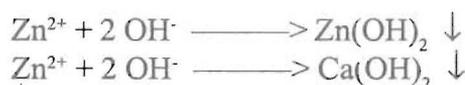
When the metal is immersed in this environment, the Zn^{2+} -CG ion pair diffuses from the bulk of the solution to the surface of the metal.

On the surface the metal, Zn^{2+} -CG ion pair is converted into Fe^{2+} -gluconate complex at the local anodic sites as the latter is more stable.



(The formation of Fe^{3+} -gluconate complex also to some extent cannot be ruled out)

The released Zn^{2+} ions and Ca^{2+} ions on the surface, form $\text{Zn}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ in the local cathodic regions.



Thus the protective film consists of Fe^{2+} -gluconate complex, $\text{Zn}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$.

Conclusion

The following conclusions are arrived at from the above results. The formulation consisting of 50 ppm Zn^{2+} and 200 ppm CG had 92% inhibition efficiency. The protective film consisted of Fe^{2+} -gluconate complex, $\text{Zn}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$. The protective film was found to be fluorescent. This formulation may be used in cooling water systems.

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