LIST OF PUBLICATIONS

1. “Corrosion Inhibitor for carbon steel in ground water”.

2. “Influence of Sodium Sulphite on corrosion inhibition by Sodium Gluconate - Zn$^{2+}$ System”

3. “The role of phosphonates as transporters of Zn$^{2+}$ ions in the inhibition of carbon steel in neutral solutins containing chlorides”

4. “Corrosion inhibition by 2-Chloroethylphosphonic acid - Zn$^{2+}$ for carbon steel”
LIST OF PAPERS PRESENTED IN SYMPOSIUM

1. "Influence of biocide on the inhibition efficiency of 2-chloroethyl phosphonic acid-Zn$^{2+}$ system"

2. "Corrosion Inhibition by Polyvinyl Pyrrolidone"

3. "Influence of a dihydroxy dicarboxylic acid on the inhibition efficiency of phosphonate - Zn$^{2+}$ system"

4. "Corrosion Inhibition by a Surfactant"
The inhibition efficiency (IE) of a cationic surfactant in controlling corrosion of carbon steel immersed in ground water in the absence and presence of Zn²⁺ has been evaluated by weight loss experiment. The surfactant shows very good inhibition efficiency. The formulation consisting of 25 ppm surfactant is able to offer 87% inhibition efficiency. The influence of Zn²⁺ does not change the IE of the surfactant to a great extent. The nature of the protective film has been analysed by FTIR and fluorescence spectra. When the surfactant alone is used as inhibitor, the protective film is found to be UV fluorescent. The film consists of iron surfactant complex. When the surfactant is used along with Zn²⁺, the protective film is found to be UV fluorescent. The protective film consists of iron surfactant complex and Zn(OH)₂. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss experiment, UV visible absorption. FTIR and fluorescence spectra.

Keywords: Corrosion inhibition, ground water, steel and surfactant.

INTRODUCTION

Surfactants can be used alone as corrosion inhibitors [1] or in combination with other compounds, such as trans-cinnamaldehyde [2] or I-phenyl-2-propyne-1-01 [3], to improve their performance as inhibitors. A comparative study of the effectiveness of different organic surfactants in inhibiting carbon steel corrosion in a natural geothermal environment has been reported [4]. Non-ionic surfactants are found to have a marked inhibiting efficiency on iron in acidic media by absorption on to its surface [5]. The inhibition effect of non-ionic surfactants Tween 20, Tween 40, Tween 60, Tween 80 and 01 (EO)₄₆ on steel in acidic chloride solution has been investigated by studying their adsorption behaviour and the use of the gravimetric method in order to determine the inhibition efficiency [6]. Non-ionic surfactants prepared by direct esterification of fatty acids (stearic, oleic, recinoleic and linoleic) with polyethylene glycol have been used to prevent acid corrosion of admiralty [7]. Effect of metallic cations on corrosion inhibition of sodium dodecyl sulphonate, an anionic surfactant, for mild steel in hydrochloric acid has been reported [8]. The influence of a cationic surfactant, namely, N-cetyl-N, N, N-trimethyl ammonium bromide (CTAB) on the inhibition efficiency of the 1-hydroethane-1, 1-diphosphonic acid (HEDP)-Zn²⁺ system in controlling corrosion of mild steel in a neutral aqueous environment has been investigated [9-10]. It was observed that the formulation consisting of 50 ppm HEDP and 50 ppm Zn²⁺ had 98% inhibition efficiency (IE). Addition of CTAB, up to a concentration of 100 ppm did not lower the IE of the HEDP-Zn²⁺ system. However, a decrease in IE was noticed when the concentration of CTAB was > 150 ppm. The present work is undertaken

a to evaluate the inhibition efficiency of a cationic surfactant CTAB in controlling corrosion of carbon steel immersed in ground water whose physicochemical parameters are presented in Table I.

a to study the influence of Zn²⁺ on the inhibition efficiency of CTAB.

a to analyse the inhibitive film by FTIR and fluorescence spectra and
JOHN al al. — Corrosion inhibitor for carbon steel in ground water

...to propose a suitable mechanism of corrosion inhibition based on the results obtained from weight loss experiment, FTIR, UV visible absorbance and fluorescence spectra.

EXPERIMENTAL

Preparation of the specimens
Mild steel specimens (iron containing 0.02 to 0.03% S, 0.03 to 0.08% P, 0.4 to 0.5% Mn and 0.1 to 0.2% C) of the dimensions 1 x 4 x 0.2 cm were polished to mirror finish and degreased with trichloroethylene and used for the weight loss method and surface examination studies.

Weight loss method
Mild steel specimens, in triplicate, were immersed in 100 ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn²⁺, for a known period. 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 [11].

Surface examination study
The mild steel specimens were immersed in various test solutions for a period of three days. After three days, the specimens were taken out and dried. The nature of the film formed on the metal specimens was analysed by various surface analytical techniques.

<table>
<thead>
<tr>
<th>TABLE I: Physicochemical parameters of ground water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>Hardness</td>
</tr>
<tr>
<td>Chloride</td>
</tr>
<tr>
<td>Alkalinity</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
</tr>
<tr>
<td>Sulphate</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Total dissolved solid</td>
</tr>
<tr>
<td>Total solid</td>
</tr>
<tr>
<td>Total suspended solid</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>Chemical oxygen demand</td>
</tr>
</tbody>
</table>

FTIR spectra
These spectra were recorded in a Perkin Elmer - 1600 spectrophotometer.

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

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

RESULTS AND DISCUSSION

Weight loss study
The inhibition efficiencies (IE) of N-cetyl-N,N,N-trimethylammonium bromide (CTAB), in controlling corrosion of carbon steel immersed in ground water, in the absence and presence of Zn²⁺ are presented in Table II. It is found that CTAB shows good inhibition efficiency even at a low concentration of 25 ppm. Addition of 50 ppm Zn²⁺ to 25 ppm CTAB improves the inhibition efficiency from 87% to 92%. However, when the concentration of CTAB further increases (50, 75, 100, 125, 150 ppm), 50 ppm Zn²⁺ does not produce any remarkable change in the IE of CTAB.

TABLE II: Inhibition efficiencies (%) offered by inhibitor t carbon steel immersed in ground water

<table>
<thead>
<tr>
<th>CTAB ppm</th>
<th>Zn²⁺ ppm</th>
<th>SO</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>87</td>
<td>92</td>
</tr>
<tr>
<td>50</td>
<td>90</td>
<td>92</td>
</tr>
<tr>
<td>75</td>
<td>92</td>
<td>93</td>
</tr>
<tr>
<td>100</td>
<td>92</td>
<td>93</td>
</tr>
<tr>
<td>125</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>150</td>
<td>95</td>
<td>95</td>
</tr>
</tbody>
</table>
JOHN et al. — Corrosion inhibitor for carbon steel in ground water

band at 1142.2 cm\(^{-1}\) corresponds to C-N stretching. Thus CTAB is characterised by FTIR spectrum.

When carbon steel is immersed in ground water containing 50 ppm CTAB, the system has 90% IE. The FTIR spectrum of the protective film (KBr) is shown in Fig. 1b. The absorption bands at 2893.3, 2931.8 and 1086.4 cm\(^{-1}\) suggest the presence of CTAB on the metal surface as Fe\(^{2+}\)-CTAB complex formed on the anodic sites of the metal. The band at 1384.2 cm\(^{-1}\) is due to Zn(0H).j formed on the cathodic sites of the metal surface.

UV visible absorption spectra

The LTV visible absorption spectra of solutions are shown in Fig. 2. The UV visible absorption spectrum of a solution containing 50 ppm CTAB is given in Fig. 2a. The UV visible absorptions spectrum of a solution containing 50 ppm CTAB and 100 ppm Fe\(^{2+}\) is given in Fig. 2b. There is an increase in the absorbance. This suggests the formation of Fe\(^{2+}\)-CTAB complex in solution. A shoulder appears at 320 nm.

The fluorescence spectra

In the UV visible absorption spectrum, Fe\(^{2+}\)-CTAB complex shows a shoulder at 320 nm. So the emission spectrum was recorded of \(\lambda = 320 \text{ nm}\). The emission spectrum (\(\lambda = 320 \text{ nm}\)) of the film formed on the surface of carbon steel specimen, immersed in the solution containing 50 ppm CTAB is shown in Fig. 3a. Peaks appear at 527(28.2), 485(29.2) and 464(34.9) nm. The intensities of the peaks are given in the parenthesis. This spectrum is due to Fe\(^{2+}\)-CTAB complex present on the metal surface. The emission spectrum (\(\lambda = 320 \text{ nm}\)) of the film formed on the surface of the metal immersed in the solution containing 50 ppm CTAB and 50 ppm Zn\(^{2+}\) is shown in Fig. 3b. Peaks appear at 527(141.9), 485(175.8) and 467(217.7) nm.

Comparison of Figs. 3a and 3b reveals that the intensities of the peaks are higher when the carbon steel specimen is immersed in the solution containing 50 ppm CTAB and 50 ppm Zn\(^{2+}\), then when it is immersed in the solution containing 50 ppm CTAB. This suggests that more Fe\(^{2+}\)-CTAB complex is formed on the metal surface, when Zn\(^{2+}\) is added to the environment. This is in agreement with the result of the weight loss experiment according to which the inhibition efficiency of the CTAB (50 ppm) system is \(90\%\) and that of the CTAB (50 ppm)-Zn\(^{2+}\) (50 ppm) system is \(92\%\).

CONCLUSIONS

a The formulation consisting of CTAB offers good inhibition efficiency to carbon steel immersed in ground water,

b Addition of Zn\(^{2+}\) to this solution does not alter the inhibition efficiency very much.
JOHN et al. — Corrosion inhibitor for carbon steel in ground water

In the presence of CTAB, the protective film consists of Fe$^{2+}$-CTAB complex.

In the presence of CTAB-Zn$^{2+}$ system, the protective film consists of Fe$^{2+}$-CTAB complex and Zn(OH)$_2$.

Fig. 2: UV fluorescence spectra of film formed on surface of carbon steel immersed in various solutions
(a) film formed on carbon steel immersed in the solution containing 50 ppm CTAB
(b) film formed on carbon steel immersed in the solution containing 50 ppm CTAB and 50 ppm Zn

Acknowledgment: The authors are thankful to Dr N Palaniswamy, CSE Division, CECRI, Karaikudi, Dr G Karthikeyan, Gandhigram Rural Institute and Dr R Ramaraj, School of Chemistry, Madurai University for their help and encouragement.

REFERENCES
Influence of sodium sulphite on corrosion inhibition by the sodium gluconate -Zn$^{2+}$ system

A. John Amalraj
M. Sundaravadivelu
A. Peter Pascal Regis and
S. Rajendran

The authors

A. John Amalraj and M. Sundaravadivelu are b’rth based in the Department of Chemistry, Gandhigram Rural Institute (Deemed University), Tamil Nadu, India.
A. Peter Pascal Regis is based in the Department of Chemistry, St Joseph’s College, Trichy, Tamil Nadu, India,
S. Rajendran is based in the Department of Chemistry, G.T.N. Arts College, Dindigul, Tamil Nadu, India.

Corrosion prevention, Steel

Abstract

The inhibition efficiency of sodium gluconate (SG) in controlling corrosion of carbon steel immersed in the environment containing 60 ppm Cl$^{-}$ has been evaluated in the presence and absence of Zn$^{2+}$ by weight loss method. SG and Zn$^{2+}$ show a synergistic effect. The protective film has been analysed by FTIR and fluorescence spectra. The protective film consists of Fe$^{3+}$ -gluconate complex and Zn(OH)$_2$. The film is found to be UV-fluorescent. The IF. of the SG-Zn$^{2+}$ system increases in the presence of Na$_2$SO$_4$; but decreases in the presence of Na$_2$SO$_3$ and also in the presence of N-cetyl-N,N,N-trimethyl ammonium bromide. This study reveals that the transporting phenomenon plays a larger role than the scavenging of dissolved oxygen.

Electronic access

The current issue and full text archive of this journal is available at http://www.emerald-library.com/

Introduction

Gluconates and gluconic acids are known to be effective non-toxic inhibitors for iron and mild steel in cooling water (Kadek and Lepin, 1970; Mor and Bonino, 1979; Mor and Wrubl, 1976; Pandey et al., 1987; Vanlooyen and Zucher, 1990; Wrubl et al., 1985). They show synergistic effect with borate (Lahodny-Sarc, 1980; Lahodny-Sarc and Popov, 1988; Kadek et al., 1985; Singh et al., 1994). The influence of N-cetyl-N,N,N-trimethyl ammonium bromide on the inhibition efficiency of the calcium gluconate - Zn$^{2+}$ system has been studied (Rajendran et al., 2000a). The present work:

- investigates the influence of Zn$^{2+}$ on the inhibition efficiency of sodium gluconate (SG) in controlling corrosion of carbon steel immersed in the aqueous solution containing 60ppm CP,
- investigates the influence of Na$_2$SO$_4$, Na$_2$SO$_3$, and CTAB on the IE of the SG-Zn$^{2+}$ system; and
- proposes a suitable mechanism of corrosion inhibition based on the results of weight loss method, FTIR and fluorescence spectra.

Experimental

Preparation of the specimens

Mild steel specimens [iron containing 0.02 to 0.03 per cent S, 0.03 to 0.08 per cent P, 0.4 to 0.5 per cent Mn and 0.1 to 0.2 per cent C] of dimensions $1.0 \times 4.0 < 0.2 cm$ were polished to a mirror finish and degreased with trichlormethylene and used for the weight-loss method and surface examination studies.

Weight-loss method

Mild steel specimens, in triplicate, were immersed in 100ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn$^{2+}$.

The authors are thankful to Professor G. Trabanelli, Professor E. Kalman, Professor O. Lahodny-Sarc, Dr A. Al-Hashem, Kuwait Institute for Scientific Research and Jay Bryson Goodyear Tire & Rubber Company, USA, Professor G. Karthikeyan, Chemistry Department of GRI, Professor Ramaraj, Chemistry Department, Madurai Kamraj University and Sir Joseph’s Research and Development Trust, Dindigul, lor their help and encouragement.

Additional text:

- Electronic access
- The current issue and full text archive of this journal is available at http://www.emerald-library.com/
- Andereco with full color availability
- Vol 46 # Number 1 • CODI • pp. 53-57
- r MDJ University Press • ISSN 0026-1198
for three days. The weights of specimens before and after immersion were determined using a Mettler balance, AE-240. The corrosion inhibition efficiency (IE) was then calculated using the equation:

\[ IE = 100 \left[ 1 - \frac{W_2}{W_1} \right] \%
\]

where:

- \( W_1 \) = corrosion rate in the absence of inhibitor
- \( W_2 \) = corrosion rate in the presence of inhibitor

**Surface examination study**

The mild steel specimens were immersed in various test solutions for a period of three days. After three days, the specimens were taken out, washed with distilled water and dried. The nature of the film formed on the surface of the metal specimens was analyzed by various surface analysis techniques.

**FTIR spectra**

The surface film was scratched carefully and the powder obtained was thoroughly mixed so as to make it uniform throughout. The FTIR spectra of the powder (KBr pellet) were recorded in Perkin Elmer – 1600 spectrophotometer.

**Fluorescence spectra**

Fluorescence spectra were recorded in a Hitachi F – 4,500 fluorescence spectrophotometer. The scan speed was 240 nm/min, with slit (Ex/Em): 5.0 nm/5.0 nm. The PMT voltage was 700V and the response was auto shutter control.

**Results and discussion**

**Weight-loss method**

The inhibition efficiencies (IE) offered by various inhibitor system to carbon steel immersed in aqueous solution containing 60 ppm Cl\(^-\) for a period of three days are given in Table I. It is found that sodium gluconate offers some inhibition efficiency to carbon steel.

**Influence of Zn\(^{2+}\) on the inhibition efficiency of sodium gluconate**

It is seen from Table II that SG offers better inhibition efficiency (IE) in the presence of Zn\(^{2+}\). For example 150 ppm SG has only

---

**Table I** Corrosion inhibition efficiency (IE) of sodium gluconate (SG) offered to mild steel

<table>
<thead>
<tr>
<th>Cl(^-) ppm</th>
<th>SG ppm</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>25</td>
<td>3</td>
</tr>
<tr>
<td>60</td>
<td>50</td>
<td>4</td>
</tr>
<tr>
<td>60</td>
<td>75</td>
<td>6</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>8</td>
</tr>
<tr>
<td>60</td>
<td>125</td>
<td>10</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>15</td>
</tr>
</tbody>
</table>

15 per cent IE. But when 50 ppm Zn\(^{2+}\) is added, the IE increases to 78 per cent. This suggests that a synergistic effect exists between SG and Zn\(^{2+}\).

**Synergism parameters (S\(_t\))**

The synergism parameters (S\(_t\)) were calculated using the relation (Rajendran et al., 2000e)

\[ S_t = 1 - \frac{I_{1+2}}{I_{1}I_{2}} \%
\]

where:

- \( I_{1+2} = (I_1 + I_2) - (I_1 I_2) \)
- \( I_{1}I_{2} = \) combined inhibition efficiency of substance 1 and substance 2

The synergism parameters are given in Table II. The values of S\(_t\) (greater than 1) confirm the synergistic effect between sodium gluconate and Zn\(^{2+}\).

**FTIR spectra**

The FTIR spectra of pure SG is shown in Figure 1(a). The FTIR spectrum (KBr) of the film formed on the surface of the metal immersed in the solution containing 60 ppm Cl\(^-\) and 150 ppm SG is shown in Figure 1(b). The C = O stretching of sodium gluconate decreases from 1622cm\(^{-1}\) to 1617.3cm\(^{-1}\). This suggests the formation of iron gluconate.
complex on the anodic sites of the metal surface. The FTIR spectrum (KBr) of the film formed on the surface of the metal after immersion in the solution containing 60 ppm Cl⁻, 150 ppm SG, 50 ppm Zn²⁺ is shown in Figure 1(c). The C = O stretching frequency of SG decreases from 1622 cm⁻¹ to 1616.6 cm⁻¹. This suggests that sodium gluconate has coordinated with Fe³⁺ through O atom resulting in the formation of iron gluconate complex formed at the anodic sites of the metal surface. The peak at 1383.3 cm⁻¹ is due to Zn(OH)₂ formed at the cathodic sites (Sekine and Hiratawa, 1986; Rajendran et al., 2000b; John Anakraj et al., 2001).

Fluorescence spectra

The fluorescence spectra of the films formed on the surface of the metal immersed in various test solutions are given in Figure 2. The fluorescence spectrum (λex = 320 nm) of the film formed on the surface of the metal immersed in the solution containing 60 ppm Cl⁻ and 150 ppm SG, is shown in Figure 2a. Peaks appear at 373(21.54), 393(18.84), 412(16.92), 468(17.16), 482(13.89), 494(12.39), 527(12.14) (the peak intensity is given in the parentheses). The prominent peak at 469 nm is due to Fe-O bond (Rajendran et al., 2000b). This spectrum is due to Fe²⁺-SG complex formed on the metal surface.

The fluorescence spectrum (λex = 320 nm) of the film formed on the surface of the metal immersed in the solution containing 60 ppm Cl⁻, 150 ppm SG, 50 ppm Zn²⁺ is shown in Figure 2(b). Peaks appear at 370(29.23), 396(25.42), 410(22.24), 467(21.71), 483(16.97), 492(15.55), 527(13.27). The peak at 469 nm is due to Fe-O bond (Rajendran et al., 2000b). This spectrum is due to iron gluconate complex entailed in Zn(OH)₂. It is observed from Figure 2 that the peak intensities are higher in the presence of Zn²⁺ (Figure 2a). This suggests that the formation of Fe²⁺-SG complex on the metal surface is enhanced in the presence of Zn²⁺, which is in agreement with the weight loss experiments which reveal a synergistic effect between SG and Zn²⁺.

Influence of Na₂SO₃ on the inhibition efficiency of the SG-Zn²⁺ system

Influence of Na₂SO₃ on the inhibition efficiency of the SG-Zn²⁺ system is given in Table III. Usually, in the neutral aqueous environment, sodium sulphite will react with dissolved oxygen and thus improve the inhibition efficiency of the system. But, quite interestingly, in the present study, Na₂SO₃ lowers the inhibition efficiency of the SG-Zn²⁺ system. This suggests that the corrosion rate of carbon steel in the chloride environment containing SG and Zn²⁺ is influenced by some other factor also apart from dissolved oxygen. Further study will throw more light on these factors.

Influence of Na₂SO₄ on the inhibition efficiency of the sodium gluconate-Zn²⁺ system

It is seen from Table IV that addition of Na₂SO₄ to the SG-Zn²⁺ system improves the IE of the system. However the IE slowly decreases as the concentration of Na₂SO₄ increases.

Influence of CTAB on the inhibition efficiency of the SG-Zn²⁺ system

The influence of a cationic surfactant, namely, N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB), on the IE of the SG-Zn²⁺ system is given in Table V. It is found that, in general, it lowers the IE of the SG-Zn²⁺ system.

It is observed from the present study (cf. Tables III, IV and V) that the transport of
Table III Influence of Na$_2$SO$_3$ on the inhibition efficiency of the sodium gluconate-Zn$^{2+}$ system

<table>
<thead>
<tr>
<th>Cl$^-$ ppm</th>
<th>SG ppm</th>
<th>Zn$^{2+}$ ppm</th>
<th>Na$_2$SO$_3$ ppm</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>0</td>
<td>78</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>50</td>
<td>72</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>150</td>
<td>83</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>200</td>
<td>81</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>250</td>
<td>80</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>300</td>
<td>80</td>
</tr>
</tbody>
</table>

Table IV Influence of Na$_2$SO$_4$ on the inhibition efficiency of the sodium gluconate-Zn$^{2+}$ system

<table>
<thead>
<tr>
<th>Cl$^-$ ppm</th>
<th>SG ppm</th>
<th>Zn$^{2+}$ ppm</th>
<th>Na$_2$SO$_4$ ppm</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>0</td>
<td>78</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>50</td>
<td>89</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>150</td>
<td>83</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>200</td>
<td>81</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>250</td>
<td>80</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>300</td>
<td>80</td>
</tr>
</tbody>
</table>

Mechanism of corrosion inhibition by the sodium gluconate-Zn$^{2+}$ system

1. When the environment containing Cl$^-$ and Zn$^{2+}$ is prepared, there is formation of Zn$^{2+}$-gluconate complex in solution.
2. When carbon steel is immersed in this solution, the Zn$^{2+}$-gluconate complex diffuses from the bulk of the solution towards the metal surface.
3. On the metal surface, Zn$^{2+}$-gluconate complex is converted into Fe$^{2+}$-gluconate complex on the anionic sites. Zn$^{2+}$ is released.

$$\text{Zn}^{2+}\text{-gluconate} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+}\text{-gluconate} + \text{Zn}^{2+}$$

4. In released Zn$^{2+}$ combines with OH$^-$ to form Zn(OH)$_2$ on the cathodic sites.

$$\text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2\text{↓}$$

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

6. This protective film is found to be UV-fluorescent.

Table V Influence of CTAB on the inhibition efficiency of the SG-Zn$^{2+}$ system

<table>
<thead>
<tr>
<th>Cl$^-$ ppm</th>
<th>SG ppm</th>
<th>Zn$^{2+}$ ppm</th>
<th>CTAB ppm</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>0</td>
<td>78</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>10</td>
<td>65</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>50</td>
<td>71</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>100</td>
<td>62</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>150</td>
<td>56</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>200</td>
<td>55</td>
</tr>
</tbody>
</table>

Conclusions

1. Sodium gluconate (SG) offers some inhibition efficiency to carbon steel in the chloride environment (60 ppm).
2. In the presence of Zn$^{2+}$, it shows a synergistic effect.
3. The protective film consists of Fe$^{2+}$-gluconate complex and Zn(OH)$_2$.
4. The protective film is found to be UV-fluorescent.
(5) The transport of $\text{Zn}^{2+}$-gluconate complex from the bulk of the solution towards the metal surface is facilitated in the presence of $\text{Na}_2\text{SO}_4$ it is restricted in the presence of $\text{Na}_2\text{SO}_3$ and CTAB.

(6) The transport phenomenon plays a larger role than scavenging the dissolved oxygen.

References


The role of phosphonates as transporters of Zn\(^{2+}\) ions in the inhibition of carbon steel in neutral solutions containing chlorides

S. Rajendran, B.V. Apparao, N. Palaniswamy, A.J. Amalraj and M. Sundaravadvivelu

The authors

S. Rajendran is in the Department of Chemistry, S.T.N. Arts College (Autonomous), Dindigul, Tamilnadu, India. B.V. Apparao is in the Department of Chemistry, Regional Engineering College, Warangal, Andhra Pradesh, India. N. Palaniswamy is in the Corrosion and Engineering Division, Central Electrochemical Research Institute, Karakhudi, Tamilnadu, India. A.J. Amalraj and M. Sundaravadvivelu are in the Department of Chemistry, Gandhiagram University, Tamilnadu, India.

Keywords

Corrosion inhibitors, Acids, Steel

Abstract

Phosphonates have shown synergistic effects in combination with Zn\(^{2+}\) ions in controlling the corrosion of carbon steel immersed in neutral aqueous environments containing 50-ppm Cl\(^{-}\). The role of phosphonates in the presence of Zn\(^{2+}\) ions has been investigated by polarisation tests and weight loss results. It was observed that the phosphonates functioned as transporters of Zn\(^{2+}\) ions from the bulk of the solution towards the metal surface. The phosphonate-Zn\(^{2+}\) bond is sufficiently strong to carry Zn\(^{2+}\) ions from the bulk solution towards the metal surface, but is weak enough for them to break to form a phosphonate-Fe\(^{2+}\) bond at anodic sites on the metal surface. Inhibition efficiency increases when the phosphonate-Zn\(^{2+}\) complex remains in solution in soluble form. Inhibition efficiency decreased when the phosphonate-Zn\(^{2+}\) complex was precipitated in the bulk of the solution.

Electronic access

The current issue and full text archive of this journal is available at http://www.emeraldinsight.com/0003-5599.htm

Introduction

Prior to the 1960s, inorganic corrosion inhibitors such as chromate, polyphosphate and nitrite, were used for the protection of carbon steel in aqueous media. Though they provided a reliable measure of corrosion protection, the discharge of toxic materials was considered unacceptable due to environmental safety guidelines.

Between 1960 and 1980, in addition to polyphosphates, phosphonates, phosphonocarboxylic acids and polymers were used as inhibitors in neutral aqueous media.

Phosphonic acids have been extensively used as corrosion inhibitors, due to their hydrolytic stability, ability to form complexes with metal ions, and scale-inhibiting properties (Chiesa et al., 1985; Dupart et al., 1985; Fang et al., 1993; Felhos et al., 1999; Gonzalez et al., 1996; Kunteko, 1990; Rajendran et al., 2000; Rodin et al., 1987; Seline and Hirakawa, 1986; Zanzucchi and Thomas, 1988; Zhu and Zhou, 1989). They show synergistic effects in combination with Zn\(^{2+}\) ions.

The mutual influence of a phosphonate and Zn\(^{2+}\) in a phosphonate-Zn\(^{2+}\) system is an interesting area, which merits investigation in detail. Better inhibition efficiency is noticed when the phosphonate-Zn\(^{2+}\) complex remains in soluble form, i.e. in solution. On the other hand, when the phosphonate-Zn\(^{2+}\) complex is precipitated in the bulk of the solution, the inhibition efficiency decreases (Chiesa et al., 1985). The phosphonate-Zn\(^{2+}\) bond must be strong enough to carry Zn\(^{2+}\) ions from the bulk of the solution towards the metal surface, yet weak enough to break on the metal surface to form the phosphonate-Fe\(^{2+}\) complex on the anodic sites of the metal surface.

The role of phosphonates as transporters of Zn\(^{2+}\) ions from the bulk of the solution towards the metal surface is considered in this paper, using polarisation and weight-loss studies. The influence of the size of the Fe\(^{2+}\) phosphonate complex and the "Zn\(^{2+}\) transporting ability" of phosphonates on corrosion inhibition has also been investigated.

S. Rajendran expresses thanks to the University Grants Commission, New Delhi, India, for financial assistance and to Dr Jay Bryson of The Goodyear Tyre & Rubber Company, USA, for his help and encouragement.
Experimental

Preparation of the specimens
Carbon steel specimens (0.02 to 0.03% S, 0.03 to 0.08% P, 0.4 to 0.5% Mn, 0.1 to 0.2% C and the balance iron) of the dimensions 40 × 10 × 2mm were polished to a mirror finish, degreased with trichloroethylene, and used for weight-loss tests and surface examination studies. For potentiostatic polarisation studies, carbon steel rod encapsulated in Teflon, with an exposed cross-section of 5mm diameter, was used as the working electrode. The working surface was polished to a mirror finish and was degreased with trichloroethylene.

Weight-loss tests
Three carbon steel specimens were immersed in 10ml of the neutral aqueous test solutions (with a chloride content of 60ppm) containing various concentrations of the inhibitors [aminotrimethylene phosphonic acid (ATMP), and 1-hydroxyethane-1,1-diphosphonic acid (HEDP)] in the absence and presence of Zn²⁺ ions (as ZnSO₄·7H₂O), for a period of seven days. After exposure, corrosion products were removed with Clarke's solution (Wranglen, 1985), and the weights of the specimens before and after immersion were determined using a Mettler balance, type AE-240.

The inhibition efficiency (IE) was calculated using the relation:

\[ IE = 100\% - \left( \frac{W_2}{W_1} \right) \]

where: \( W_1 \) = Corrosion rate in the absence of inhibitor and: \( W_2 \) = Corrosion rate in the presence of inhibitor.

Potentiostatic polarisation studies

The polarisation studies were carried out in a three-electrode cell assembly, using carbon steel as the working electrode, platinum as the counter-electrode and saturated calomel electrode as the reference electrode. The cell was connected to a BioAnalytical Systems (BAS – 102A) electrochemical analyser with an IR compensation facility.

Results and discussion

Phosphonates, if used by themselves, are not good corrosion inhibitors. Nevertheless, they exhibit better inhibition efficiency on carbon steel (exposed in a neutral aqueous environment with 60ppm chloride ions) when used in combination with Zn²⁺, due to the synergistic effect of the zinc ions. The mechanism of corrosion inhibition is as follows:

1. When carbon steel is immersed in the neutral aqueous environment containing 60ppm Cl⁻, the anodic reaction is:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]

and the cathodic reaction is:

\[ 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^- \]

2. When an environment consisting of phosphonic acid and Zn²⁺ ions is prepared, a Zn²⁺-phosphonic acid (PA) complex is formed in the solution.

3. When the steel is immersed in this environment, the Zn²⁺-PA complex diffuses from the bulk of the solution to the metal surface.

4. On the surface of the metal, the Zn²⁺-PA complex is converted into an Fe³⁺-PA complex at the local anodic regions, because the iron complex is more stable than the zinc complex (Kuznetsov, 1990):

\[ \text{Zn}^{2+} + \text{PA} + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} - \text{PA} + \text{Zn}^{2+} \]

5. The released Zn²⁺ can then form a Zn(OH)₂ precipitate at local cathodic regions:

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \downarrow \]

6. Thus the protective film consists of the Fe³⁺-PA complex and Zn(OH)₂. This is the case with phosphonic acids such as HEDP, ATMP and 2-carboxyethyl phosphonic acid. In the case of phosphonic acids such as ethyl-2-chloroethyl and phenyl-phosphonic acids, the protective film also contains oxides of iron, in addition to Fe³⁺-PA complex and Zn(OH)₂.

It is assumed in the above mechanism that the phosphonate functions as a transporter of Zn²⁺ from the bulk of the solution to the metal surface. In order to confirm this, the potentiostatic polarisation tests were carried out.

Potentiostatic polarisation studies

(i) The role of HEDP in the HEDP-Zn²⁺ system

The potentiostatic polarisation curves for carbon steel immersed in various environments are presented in Figure 1. When carbon steel was immersed in an aqueous environment containing 60ppm Cl⁻, the corrosion potential was 389mV vs. SCE. When 100ppm Zn²⁺ was added to the above environment, the potential
shifted to a more negative potential (i.e. more cathodic) of -536mV vs SCE. This suggests
that the predominant action of the Zn²⁺ ions is on the cathodic reaction. Steel immersed
in solution containing 100ppm Zn²⁺ and 10 ppm HEDP had corrosion potential of -405mV vs
SCE. When various concentrations of HEDP (50, 100, 200, 300ppm) were added to the
environment, the corrosion potential shifted progressively to a more negative potential (i.e.
more cathodic): -531, -563, -575 and -609mV vs SCE respectively.

This behaviour suggests that, as the concentration of phosphonic acid was
increased, the amount of Zn²⁺ transported from the bulk of the solution to the metal
surface also increased; the amount of Zn(OH)₂ deposited at cathodic sites also
increased; and the cathodic reaction was more effectively prevented.

Thus, the polarisation tests revealed that phosphonates function as transporters of
Zn²⁺ from the bulk of the solution on to the metal surface. The anodic reaction is
controlled by the formation of Fe²⁺-PA complex on the anodic sites, and the cathodic
reaction is controlled by the formation of Zn(OH)₂ at cathodic sites.

Similar behaviour was observed for the systems containing 50ppm Zn²⁺ and various
concentrations of HEDP, namely, 10, 50, 100, 200 and 300ppm. The corrosion
potentials of steel immersed in these environments were -449, -528, -584, -597
and -632mV vs SCE respectively.
The role of phosphonates as transporters of \( \text{Zn}^{2+} \) ions

S. Rajendran et al.

immersed for a period of seven days in aqueous solution containing 60ppm CI, are given in Table I.

It can be observed that, for a given concentration of \( \text{Zn}^{2+} \), HEDP exhibited a higher inhibition efficiency than ATMP. For example, when the concentration of \( \text{Zn}^{2+} \) was 50ppm, HEDP showed 98 per cent inhibition even at a low concentration of 50ppm. However, ATMP at a 50ppm concentration had an inhibition efficiency of only 45 per cent. In order to achieve 98 per cent inhibitor efficiency, a relatively high concentration of ATMP (200ppm) was required. When the concentration of \( \text{Zn}^{2+} \) was increased, say from 50ppm to 100ppm, a still higher concentration of ATMP was required, but even 300ppm ATMP offered only 90 per cent inhibition efficiency.

The influence of phosphonic acid concentration on inhibition efficiency at a given \( \text{Zn}^{2+} \) ion concentration

It can be observed from Table I that, for a given concentration of \( \text{Zn}^{2+} \) ions, the inhibition efficiency increased, as the concentration of the phosphonic acid was increased. This is in agreement with the results of the polarisation studies, which indicated that, as the concentration of the phosphonic acid was increased, the transport of \( \text{Zn}^{2+} \) ions from the bulk of the solution on to the metal surface also increased, the extent to which controlling the cathodic reaction by deposition of \( \text{Zn(OH)}_2 \) precipitated at cathodic sites increased and, in consequence, the inhibition efficiency of the system increased. The concept was applicable to both the HEDP system and the ATMP system.

The influence of \( \text{Zn}^{2+} \) on the inhibition efficiency of phosphonic acid

It can be observed from Table I that, at higher phosphonic acid concentrations (100, 200, 300ppm), \( \text{Zn}^{2+} \) ions had no influence on the inhibition efficiency of the HEDP system. However, in the case of the ATMP system, the inhibition efficiency decreased, as the concentration of \( \text{Zn}^{2+} \) ions was increased (from 50ppm to 100ppm).

This observation can be explained by the fact, that at higher concentrations of \( \text{Zn}^{2+} \) ions, the \( \text{Zn}^{2+} \)-ATMP complex formed in the solution was stable (and insoluble), and was precipitated within the bulk of the solution itself. However, in the case of the HEDP system, even at higher concentrations of \( \text{Zn}^{2+} \) ions, the \( \text{Zn}^{2+} \)-HEDP complex remained soluble and in solution. Hence, the rate of transportation of \( \text{Zn}^{2+} \) ions to the metal surface was not retarded.

Comparison of the inhibition efficiencies of the HEDP-Zn\(^{2+}\) system and the ATMP-Zn\(^{2+}\) system

Analysis of results of weight loss tests, presented in Table I, reveals that, in the presence of \( \text{Zn}^{2+} \) ions, better inhibition efficiency was shown by HEDP than by ATMP. For example, the formulation consisting of 50ppm \( \text{Zn}^{2+} \) ions and 50ppm HEDP had an inhibition efficiency of 98 per cent, whereas the corresponding inhibition efficiency for the ATMP system was only 45 per cent. Similarly, with 100ppm \( \text{Zn}^{2+} \) ions in the test solution, a 98 per cent inhibition efficiency was exhibited in solution containing 50ppm HEDP, whereas the efficiency was only 50 per cent in the case of ATMP system. This was because, at a given concentration of \( \text{Zn}^{2+} \) ions, HEDP is a better transporter of \( \text{Zn}^{2+} \) than ATMP.

The conclusion was further supported by comparison of the corrosion potentials of carbon steel immersed in the 60ppm CI environment in the presence of HEDP-Zn\(^{2+}\), and the results from similar samples immersed in an environment inhibited by ATMP-Zn\(^{2+}\). It is evident from Table II that, at a given concentration of \( \text{Zn}^{2+} \) ions, the shift in the corrosion potential of steel to a more cathodic value was greater in the case of HEDP than in that of ATMP. For example, in the presence of 50ppm \( \text{Zn}^{2+} \), the addition of 300ppm HEDP shifted the corrosion potential to ~632mV vs SCE, whereas the addition of 300ppm ATMP shifted the corrosion potential only to ~585mV vs SCE.

As per the details given in Table I, the corrosion inhibition efficiencies for carbon steel of the HEDP were consistently greater.
Table II Corrosion potentials (mV vs. SCE) of carbon steel immersed in the test solution containing various concentrations of inhibitor

<table>
<thead>
<tr>
<th>Phosphonic acid (ppm)</th>
<th>Zn$^{2+}$ (50ppm)</th>
<th>Zn$^{2+}$ (100ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HEDP</td>
<td>ATMP</td>
</tr>
<tr>
<td>10</td>
<td>-449</td>
<td>-373</td>
</tr>
<tr>
<td>50</td>
<td>-528</td>
<td>-383</td>
</tr>
<tr>
<td>100</td>
<td>-584</td>
<td>-420</td>
</tr>
<tr>
<td>200</td>
<td>-597</td>
<td>-487</td>
</tr>
<tr>
<td>300</td>
<td>-632</td>
<td>-583</td>
</tr>
</tbody>
</table>

than for ATMP in the test solution. This may be explained as follows:

\[
\begin{align*}
\text{HEDP} & \quad \text{ATMP} \\
\quad & \\
\text{CH}_3 & \quad \text{CH}_3\text{P(O)(OH)}_2 \\
\left(\text{HO}_2\right)_C & - \quad \text{C}_2\text{P(O)(OH)}_2 \\
\text{OH} & \quad \text{CH}_3\text{P(O)(OH)}_2 \\
\end{align*}
\]

ATMP is a triphosphonic acid, while HEDP is a diphosphonic acid. Additionally, the electron-releasing capability of ATMP is greater than that of HEDP. In consequence, the ATMP-Zn$^{2+}$ complex is more stable in solution than the HEDP-Zn$^{2+}$ complex. Therefore, when the HEDP-Zn$^{2+}$ complex diffuses from solution to the metal surface, it splits easily into Zn$^{2+}$ ions and HEDP. Zn$^{2+}$ forms Zn(OH)$_2$ at the cathodic sites and HEDP forms the HEDP-Fc$^{2+}$ complex at the anodic sites. Since the ATMP-Zn$^{2+}$ complex is relatively more stable than the HEDP-Zn$^{2+}$ complex (Chiesa et al., 1985), it is not as easily split into Zn$^{2+}$ and ATMP, and hence the formation of Zn(OH)$_2$ and the ATMP-Fc$^{2+}$ complex on the cathodic and anodic sites is not so easily facilitated.

It is the formation of both Zn(OH)$_2$ and the Fe$^{2+}$-phosphonate complex on the metal surface which is responsible for corrosion inhibition. Additionally, it is probable, though this was not confirmed, that the molecular size of the Fe$^{2+}$-HEDP complex is larger than the molecular size of the Fe$^{2+}$-ATMP complex, because of the difference in their structures (ATMP is relatively more packed). This factor could also help to explain the greater corrosion inhibition efficiency of HEDP than that of ATMP in the presence of Zn$^{2+}$.

Two factors influence the order of inhibition efficiency: (i) molecular size of the iron phosphonate complex, and (ii) the ease with which the phosphonate transports Zn$^{2+}$ from the solution to the metal surface. If the size of the Fe$^{2+}$-ATMP complex is larger than the Fe$^{2+}$-HEDP complex, then the following explanation may be offered.

Conclusions

This study leads to the following conclusions:

- Phosphonates function as transporters of Zn$^{2+}$ from the bulk of the solution towards the metal surface.
- The molecular size of the Fe$^{2+}$-phosphonate complex and Zn$^{2+}$ transporting ability of the phosphonates influence the overall efficiency of corrosion inhibition.
- The "Zn$^{2+}$-transporting ability" of the phosphonates plays a more dominant role than the size of the Fe$^{2+}$-phosphonate complex.

References


