Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 108, No. 4, August 1996, pp. 399–405.
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Enhanced synergistic inhibition by calcium gluconate in low chloride media. Part I. Kinetics of corrosion

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MS received 4 December 1995; revised 21 June 1996

Abstract. 2-Carboxy ethyl phosphonic acid (2-CEPA) in the presence of Zn^{2+} ions synergistically inhibits mild steel corrosion in 60 ppm chloride solutions. Calcium gluconate (CG) enhances inhibition. Electrochemical and weight change methods are used to study synergistic inhibition, and the mechanism of inhibition is discussed.

Keywords. Calcium gluconate; 2-carboxyethyl phosphonic acid; synergistic inhibition.

1. Introduction

Interphase inhibitors are effective for the protection of steel against corrosion in neutral chloride medium. They form weakly soluble compounds with the metal ions in solution, which precipitate on to the surface to form a three-dimensional protective layer. Such inhibitors in the cooling water treatment are composed of phosphonic acids. Corrosion inhibitors with phosphonates and Zn^{2+} ions offer synergistic inhibition for copper-based alloys. Presence of calcium ions offers synergistic inhibition in presence of hydroxy ethylenidene-1, 1-diphosphonic acids (HEDP) (Kalman *et al* 1994). The presence of Ca^{2+} and Zn^{2+} ions enhances the efficiency of inhibition by synergism. Zn^{2+} ions in the presence of 2-CEPA are found to offer synergistic inhibition (Gunasekaran *et al* 1995) to mild steel corrosion in low chloride media. This work is an extension of the previous investigation and aims at understanding the enhancement of inhibition offered by calcium gluconate in the presence of Zn^{2+} ions and 2-CEPA. Electrochemical and weight change measurements were carried out to understand (i) whether metal cations enhance dissolution favouring the formation of the iron complex, and (ii) the role of calcium gluconate in enhancing the inhibition of corrosion.

2. Experimental

2.1 *Preparation of the specimens*

Mild steel (0·02–0·3% S, 0·3–0·8% P, 0·4–0·5% Mn and 0·1–0·2% C) was used. Specimens of dimensions 1 × 4 × 0·2 cm were used for weight change measurements.

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Table 1. Influence of calcium gluconate ion concentration on the corrosion of mild steel in 50 ppm Zn^{2+} ions + 60 ppm chloride solutions at 30°C.

Concentration of gluconate (ppm)	Acceleration inhibition	% inhibition
0	Acceleration	−20
20	Acceleration	−42
50	Acceleration	−28
80	Acceleration	−12
100	Inhibition	+ 6
120	Inhibition	+13
150	Inhibition	+22

Electrochemical measurements were carried out on 0·5 cm dia circular electrodes. Surfaces were polished successively with 1/0 to 4/0 emery paper and degreased with trichloroethylene.

2.2 *Weight change measurements*

Three mild steel specimens were immersed in the test solution for a period of 7 days. Changes in weight were followed to an accuracy of ± 5%. The percentage inhibition efficiency (% I) was calculated by

$$\% I = \left(\frac{W1 - W2}{W1} \right) \times 100$$

where $W1$, $W2$ are weight losses of steel in uninhibited and inhibited chloride solutions.

2.3 *Electrochemical measurements*

A three-electrode cell assembly was used. The mild steel specimen was used as the working electrode, a large platinum foil as the counter electrode and a saturated calomel electrode as the reference electrode. Polarisation studies were carried out using a B10 analytical system (BAS-100A) electrochemical analyser.

3. Results

Table 1 shows the influence of calcium gluconate (CG) on the corrosion of mild steel in 60 ppm Cl^- solutions containing 50 ppm Zn^{2+} ions. Inhibition was observed only when 100 ppm of CG was added to the solution. Fifty ppm of 2-CEPA when added to 60 ppm Cl^- solution containing 50 ppm Zn^{2+} ions offered slightly higher inhibition. Increase of *p*H (3 to 7) did not influence the percentage inhibition markedly (table 2). Addition of CG to the above solution enhanced the inhibition efficiency. In general, increase of *p*H and [CG] enhance inhibition.

More than 90% inhibition was observed in the *p*H range 5 to 7 when CG concentration was 50 ppm. This suggests the participation of hydroxyl ions and calcium gluconate in the inhibition process. An increase of *p*H to a value $\geqslant 8$ decreased the inhibition efficiency (table 3), which in turn suggests that a critical hydroxyl ion/calcium gluconate concentration determines the stability of the film.

Table 2. Inhibition (± 5%) of mild steel corrosion in 50 ppm Zn^{2+} ions + 50 ppm 2-CEPA + 60 ppm chloride solutions in the *p*H range 3–7. Effect of calcium gluconate ion concentration at 30°C.

	Gluconate ion concentration (ppm)						
*p*H	0	20	50	80	100	120	150
3	52	65	68	72	72	69	68
4	56	75	82	85	90	86	85
5	55	83	86	97	97	97	96
6	54	88	93	94	96	95	95
7	50	81	96	96	96	96	96

Table 3. Inhibition (± 5%) of mild steel corrosion in 50 ppm Zn^{2+} ions + 50 ppm 2-CEPA + 60 ppm chloride solutions in the *p*H range 8–9. Effect of calcium gluconate ion concentration at 30°C.

	Gluconate ion concentration (ppm)						
*p*H	0	20	50	80	100	120	150
8	26	58	75	84	84	79	78
9	5	13	50	78	74	74	73
10	2	8	40	62	70	68	65

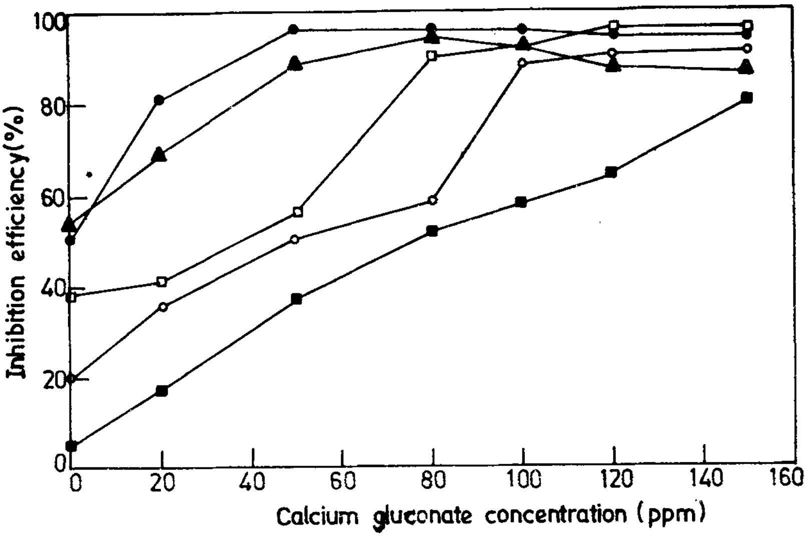

Figure 1. Variation of % inhibition efficiency with calcium gluconate concentration at different temperatures. ● 30°C, ▲ 50°C, □ 60°C, ○ 70°C, ■ 80°C.

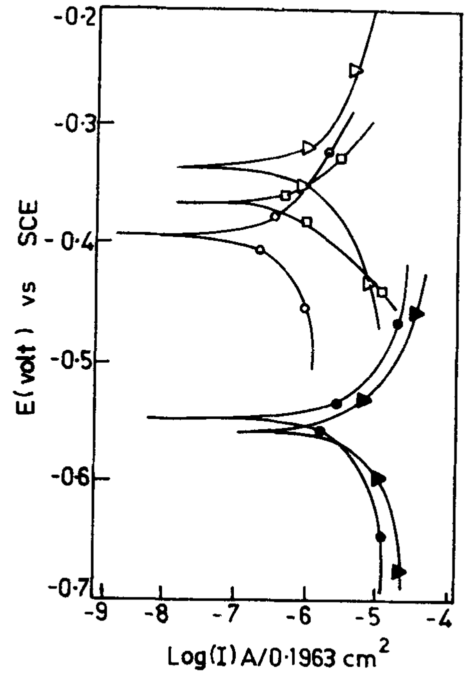

Figure 2. E–log I polarisation curves for the corrosion of mild steel in 60 ppm chloride solutions (pH 7) at 30°C. □ blank; ● 50 ppm CG + 50 ppm 2 CEPA, Δ 50 ppm CG; ○ 50 ppm CG + 50 ppm 2CEPA + 50 ppm Zn_{2+} ions; ▲ 50 ppm CG + 50 ppm Zn^{2+} ions.

Table 4. Parameters derived from polarisation curves at pH = 7 and temperature 30°C.

		Tafel slope (± 10 mV/decade)		Corrosion current density (μA/cm^2)	
Solution	E_{corr}(mV) vs. SCE	Anodic	Cathodic	Anodic	Cathodic
60 ppm chloride	−386	80	102	6	6
60 ppm chloride + 50 ppm CG	−546	88	110	8	8
60 ppm Cl^- + 50 ppm CG + 50 ppm 2-CEPA	−330	72	95	9·7	9·7
60 ppm Cl^- + 50 ppm CG + 50 ppm Zn^{2+} ions	−553	72	107	6·5	6·5

The temperature dependence of inhibition is interesting. Temperature rise decreases the inhibition suggesting that the metal complex formed on the surface dissolves to form soluble iron complexes in solution (figure 1). Figure 2 shows the typical polarisation curves for mild steel in 60 ppm Cl^- solutions (pH 7) at 30°C in the presence of Zn^{2+}

Table 5. Parameters derived from electrochemical measurements in 60 ppm chloride solutions at 30°C. Effect of *p*H and calcium gluconate ion concentration.

	E_{corr}(mV) vs. SCE ±5 mV		Tafel slope (mV/decade (±10 mV)				Corrosion current density (±1 μA/cm^2)	
			Anodic		Cathodic			
*p*H	A	B	A	B	A	B	A	B
3	−564	−602	77	85	109	104	11·7	10
4	−580	−589	77	86	109	104	11·7	10
5	−561	−550	76	76	128	104	4·0	3·3
6	−528	−515	74	69	132	105	1·7	1·6
7	−388	−394	84	72	100	110	0·2	0·2

A–100 ppm Zn^{2+} ions + 100 ppm 2-CEPA;
B–50 ppm Zn^{2+} ion + 50 ppm 2-CEPA + 50 ppm gluconate ion

ions, 2-CEPA and calcium gluconate. Acceleration of corrosion current density is seen in all solutions (table 4). Increase of *p*H shifts the corrosion potential to nobler values both in the presence and absence of gluconate, suggesting the participation of OH^- ions in the anodic passivating process.

Calcium gluconate addition did not influence the anodic Tafel slopes in the *p*H range 3–7 (table 5). This suggests that the dissolution of iron is not influenced by gluconate. Gluconate addition decreases the corrosion current densities at all *p*H values.

4. Discussion

The composition and the structure of the films formed on iron remain subjects of continued interest (Jayalakshmi and Muralidharan 1994). X-ray diffraction studies on the oxides of iron revealed the presence of $-Fe_2O_3$ in solutions at all *p*H levels irrespective of the nature of the iron substrate (Foley *et al* 1967). In chloride solutions, substitution of OH^- ions on the oxide by Cl^- ions takes place. Refait *et al* (1995) observed that various oxyhydroxy chloro complexes with the general formula $Fe_3(OH)_5Cl$ or $Fe_6(OH)_{11}Cl$ are formed on iron. Prolonged exposure results in the insertion of chloride ions and water molecules into the structure of $Fe(OH)_2$ leading to $3\,Fe(OH)_2 . Fe(OH)Cl . nH_2O$ (green rust, containing chloride).

Gluconate anion, GH_4^-, contains four hydrogen atoms of secondary alcohols (Sawyer 1964). The addition of gluconate to Zn^{2+} ions in solution results in the formation of a $Zn(GH_4)^+$ complex (Vasantha and Muralidharan 1994).

The dissolution of iron in aqueous media (Veerashanmugamani and Muralidharan 1985) may occur as in the following steps:

$$Fe + OH^- \leftrightarrow FeOH_{ads} + e.$$

$$FeOH_{ads} \rightarrow FeOH^+ + e,$$

$$FeOH^+ + OH^- \leftrightarrow Fe(OH)_2,$$

and at low *p*H (3–5) levels

$$FeOH^+ \leftrightarrow Fe^{2+} + OH^-$$

may also occur. In chloride solutions, the formation of the chloro complex may be assumed to be in equilibrium as (Donhaue and Nobe 1967)

$$\mathrm{Fe}^{2+} + m\mathrm{H_2O} + n\mathrm{Cl}^- \leftrightarrow \mathrm{Fe(OH)}_m(\mathrm{Cl}_n)^{2-n-m} + m\mathrm{H}^+,$$

where $m = 1{\cdot}7$ to $1{\cdot}8$; $n = 0{\cdot}3$ to $0{\cdot}2$.

In the presence of $\mathrm{Zn(GH_4)^+}$, the dissolution may be enhanced as

$$\mathrm{FeOH^+ + Zn(GH_4)^+ \leftrightarrow Zn(OH)^+ + Fe(GH_4)}.$$

The stability of $\mathrm{Zn(OH)^+}$ depends on the critical concentration of $(\mathrm{GH_4^-})$ ions and their ratio to $\mathrm{OH^-}$ ions. At $p\mathrm{H} > 7$, $\mathrm{Zn(OH)^+}$ may get converted to $[\mathrm{Zn(GH_4)}]^{2-}$, a solution soluble species. Owing to enhancement of $\mathrm{OH^-}$ ions in solution (at higher pH levels), the conversion of $\mathrm{Zn(OH)^+}$ to Zn $\mathrm{(OH)_2}$ may take place.

The 2-CEPA anions favour the dissolution of steel in the presence of $\mathrm{Zn^{2+}}$ ions and thus they offer synergistic inhibition as

$$\mathrm{Fe + H_2O \leftrightarrow FeOH_{ads} + H^+} + e$$

$$\mathrm{FeOH_{ads} \leftrightarrow FeOH^+_{ads}} + e$$

$$\mathrm{FeOH_{ads} \leftrightarrow ZnOH^+ + Fe^{2+}}$$

$$\mathrm{Fe^{2+} + H_2O + X^- \leftrightarrow [Fe(OH)(X)] + H^+}.$$

and

$$\mathrm{ZnOH^+ + H_2O \rightarrow Zn(OH)_2 + H^+}.$$

where X is the 2-CEPA anion.

Inhibition is caused by the stabilization of the surface film formed on steel. The activation energy for dissolution in chloride solutions is $-4{\cdot}84$ kcal/mol while in chloride solutions containing $\mathrm{Zn^{2+}}$, 2-CEPA and CG, it is 17·1 kcal/mole. This hindrance to dissolution is due to the formation of the $\mathrm{Zn(OH)_2}$, Fe(III), 2-CEPA–CG complex film,

$$\mathrm{Fe} + m\mathrm{H_2O} + n\mathrm{GH_4^-} + p\mathrm{X^-} \rightarrow \{\mathrm{Fe\ complex}\} + m\mathrm{H^+} + 2e.$$

Diffusion of the {Fe complex} and $\mathrm{H^+}$ ions away from the electrode influences the anodic Tafel Slope. At steady state

$$i_a = 2F\, D_{\mathrm{Fe\ complex}}[\mathrm{d}a_{\mathrm{Fe\ complex}}/\mathrm{d}x]_{x=0}.$$

$$= 2F[D\mathrm{H^+}/m\delta][a\mathrm{H^+}]_{x=0},$$

where x is the film/solution interface. At $x = 0$, $(\mathrm{H^+})_{x=0} = 0$,

$$i_a = 2F(D_{\mathrm{Fe\ complex}}/\delta)(a_{\mathrm{Fe\ complex}})_{x=0} = 2F(D_{\mathrm{H+}}/m\delta)(a_{\mathrm{H+}})_{x=0}$$

$$i_a = [2F\mathbf{k}_a(D_{\mathrm{H+}}/m\delta)]^{1/2}\exp[(1+\beta)F\Delta\phi/2RT).$$

This is confirmed by the observed anodic Tafel slope of 70 ± 10 mV/decade.

5. Conclusions

The dissolution of iron is accelerated by $\mathrm{Zn^{2+}}$ ions and the synergistic inhibition by $\mathrm{2CEPA + Zn^{2+}}$ ions is due to the formation of an Fe–2-CEPA complex. Calcium gluconate provides enhanced synergism by the formation of an iron phosphonogluconate complex.

Acknowledgement

One of the authors (CG) thanks the Council of Scientific and Industrial Research, New Delhi for a fellowship.

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