Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 108, No. 4, August 1996, pp. 407–413.

# Enhanced synergistic inhibition by calcium gluconate in low chloride media. Part II. Surface film characterisation

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MS received 4 December 1995; revised 21 June 1996

**Abstract.** 2-Carboxy ethyl phosphonic acid (2-CEPA) in presence of zinc ions synergistically inhibits mild steel corrosion in 60 ppm chloride solutions. Addition of calcium gluconate provides enhanced inhibition. Spectrochemical analyses of the solution and the surface inhibitor film reveal the presence of Zn $(OH)_2$ and iron phosphono gluconate complex.

**Keywords.** Synergistic inhibition; calcium gluconate; 2-carboxy ethyl phosphonic acid.

## 1. Introduction

Phosphonate based cooling water inhibitors offer protection by forming three-dimensional layers on the metal surfaces. Hydroxyethylidine-1, 1-diphosphonic acid (HEDP) inhibited corrosion of mild steel by a precipitative mechanism by forming insoluble iron complexes and repairing the porous oxide layer. (Kalman *et al* 1994). X-ray-induced photoelectron spectroscopy, Auger spectroscopy and radio isotope techniques were used to study the adsorption of the effect of $Ca^{2+}$ ions and the adsorption of HEDP on steel (Varallyai *et al* 1991; Veres *et al* 1992). Spectrochemical analysis of the surface film formed on iron in chloride solutions containing $Zn^{2+}$ ions, 2-carboxy ethyl phosphonic acid (2-CEPA) and calcium gluconate (CG) was carried out to understand the composition of the film.

## 2. Experimental

### 2.1 *Examination of surface films*

Mild steel specimens (1 × 4 × 0·2 cm) were polished and completely immersed in 60 ppm chloride solutions with and without inhibitors. After specified time intervals, these specimens were taken out and washed with distilled water and dried. The dried specimens and the immersing solutions were used for spectral analysis.

X-ray diffraction studies were carried on surface films formed under various test conditions using a computer-controlled X-ray powder diffractometer (Joel 8030) with

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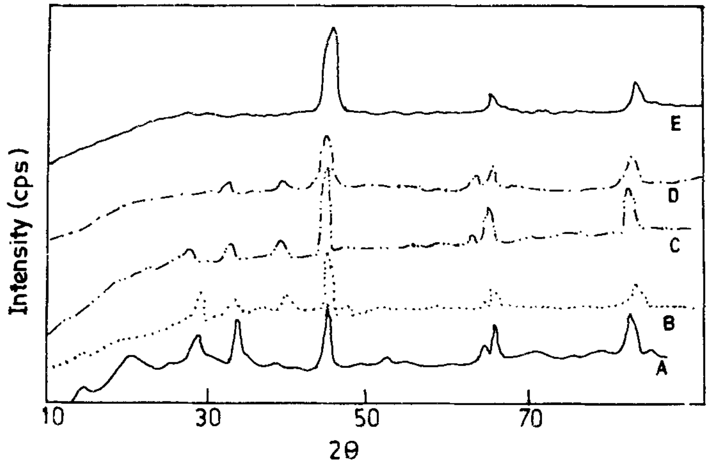

**Figure 1.** XRD patterns obtained on the surface film formed on mild steel immersed in different solutions at *p*H 7 at the end of 3 days. (A) 60 ppm $Cl^-$, (B) 60 ppm $Cl^-$ + 50 ppm CG, (C) 60 ppm $Cl^-$ + 50 ppm CG + 50 ppm 2-CEPA, (D) 60 ppm $Cl^-$ + 50 ppm CG + 50 ppm $Zn^{2+}$, (E) 60 ppm $Cl^-$ + 50 ppm CG + 50 ppm $Zn^{2+}$ + 50 ppm 2-CEPA.

$CuK_\alpha$ (Ni-filtered) radiation ($\lambda = 1{:}5418$ Å) at a rating of 40 kV, 20 mA. The scan rate was 0·05–20° per step and the measuring time was one second per step.

UV-visible diffused reflectance spectra of the films formed on the metal were recorded using a Hitachi-U 3400 spectrophotometer. UV-luminescence emission spectra of the film were recorded using a Hitachi-650 108 fluorescence spectrophotometer equipped with a 150 W xenon lamp and Hamamatsu K 929 photo multiplier tube. The emission spectra were corrected for the spectral response of the photomultiplier tube. X-ray photo electron spectroscopic (ESCA) analysis was carried out on the films formed on the metal. The surface film formed on mild steel was scratched carefully and the powder obtained was thoroughly mixed so as to make it uniform. FTIR spectrum of the powder (KBr pellet) was recorded using Perkin–Elmer 1600 FT–IR spectrophotometer.

### 2.2 *Preparation of the metal complexes*

AnalaR grade chemicals such as 2-carboxy ethyl phosphonic acid (2-CEPA) supplied by Aldrich, USA were used. The ferric–2-CEPA complex was precipitated when dilute neutral $FeCl_3$ solution was added to a 2-CEPA solution maintained at *p*H 7. The precipitate was washed and dried.

A ferric–2-CEPA–CG complex was precipitated when dilute neutral $FeCl_3$ solution was added to 2-CEPA and calcium gluconate solution maintained at *p*H 7. The precipitate was washed and dried.

## 3. Results

XRD patterns of the specimen surfaces (figure 1) showed $Fe_3O_4$ peaks at $2\theta = 35°$ and 42° and $\gamma$-FeOOH peaks at $2\theta = 30°$ and 65° The surface films obtained in 60 ppm $Cl^-$ solution and 60 ppm $Cl^-$ solutions containing 50 ppm $Zn^{2+}$ showed the presence of

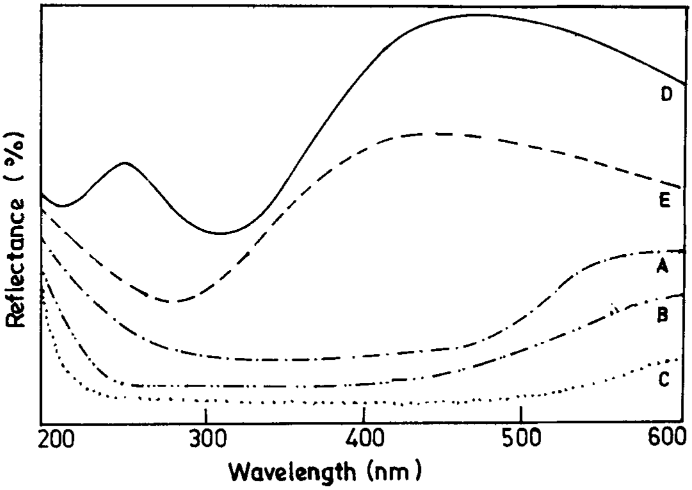

**Figure 2.** UV reflectance spectra of the surface film formed on mild steel immersed in different solutions at *p*H 7 at the end of two days. (A) 60 ppm $Cl^-$, (B) 60 ppm $Cl^-$ + 50 ppm $Zn^{2+}$ + 50 ppm CG, (C) 60 ppm $Cl^-$ + 50 ppm CG + 50 ppm 2-CEPA, (D) 60 ppm $Cl^-$ + 50 ppm CG + 50 ppm 2-CEPA + 50 ppm $Zn^{2+}$, (E) 60 ppm $Cl^-$ + 100 ppm $Zn^{2+}$ + 10 ppm 2-CEPA

$Fe_3O_4$ and *x*-FeOOH. The surface film obtained after immersing in 60 ppm chloride solution containing $Zn^{2+}$, 2-CEPA and CG (each 50 ppm) exhibited different behaviour. The pattern corresponds to iron oxide disappearance, as only Fe peaks at $2\theta = 44°$, 65° and 82° were seen.

UV-reflectance spectra (figure 2) of the surface dipped in 60 ppm $Cl^-$, and $Zn^{2+}$ with CG and CG + 2-CEPA solutions revealed a wavelength transition of 550 nm indicating the presence of iron oxide on the surface. The surface dipped in the solution containing CG, 2-CEPA and $Zn^{2+}$ ions indicated not only the absence of iron oxide but the appearance of a new peak at 305 nm. Surfaces dipped in a solution containing $Zn^{2+}$ + 2-CEPA showed a peak at 290 nm (curve E in figure 2). The appearance of this peak suggests the formation of an iron (II)–2-CEPA complex. However, the presence of Zn (II)–2-CEPA complex is not inferred. The appearance of a peak at 305 nm (curve D in figure 2) is due to the presence of the iron complex. The shift in wavelength from 290 to 350 nm suggests that gluconate addition modifies the iron–2-CEPA surface film already formed on iron in $Zn^{2+}$ + 2-CEPA solutions.

UV-visible absorption spectra of the solution was obtained to identify the nature of complex present in the solution (figure 3). Fresh calcium gluconate exhibited a peak at 295 nm. Introduction of $Zn^{2+}$ ions caused the appearance of an additional peak at 255 nm. After immersion of steel in $Zn^{2+}$ CG solution for 2 days, the surface exhibited an increase in peak intensity at 255 nm and a decrease at 295 nm. The specimen immersed in the $Zn^{2+}$ + 2-CEPA + CG solution at the end of 2 days exhibited interesting features. The intensity of the 255 nm peak increased compared to that of 295 nm peak. This suggests that the formation of $Zn^{2+}$–2-CEPA–CG complex in the solutions.

UV-luminescence emission spectra of mild steel surfaces dipped in $Zn^{2+}$ + 2-CEPA solution excited at 404 nm showed the presence of peaks at 445 and 465 nm (figure 4).

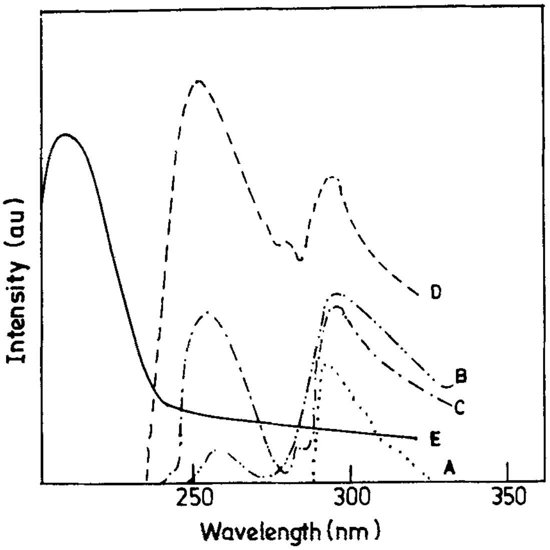

**Figure 3.** UV absorbance spectra of solution containing various cations and anions in 60 ppm chloride solutions - Effect of time of immersion of steel. (A) 50 ppm CG (10 minutes), (B) 50 ppm CG + 50 ppm $Zn^{2+}$ (10 minutes), (C) 50 ppm CG + 50 ppm $Zn^{2+}$ (2 days), (D) 50 ppm CG + 50 ppm $Zn^{2+}$ + 50 ppm 2-CEPA (2 days) (E) 100 ppm $Zn^{2+}$ + 100 ppm 2-CEPA (2 days).

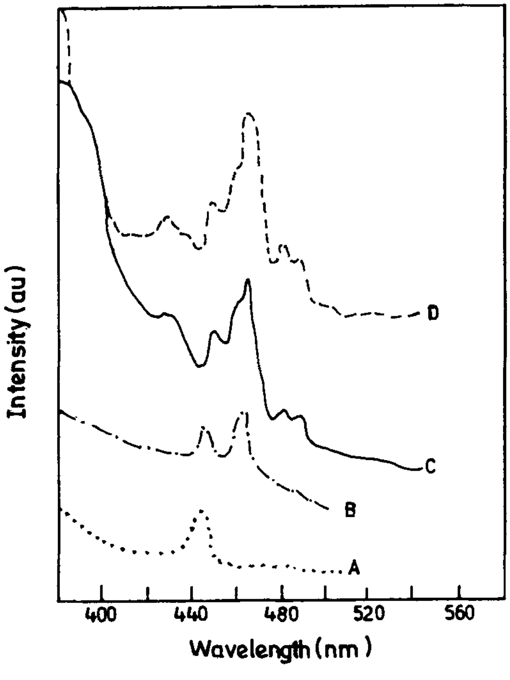

**Figure 4.** UV luminesence emission spectra of various solutions - Effect of time of immersion of steel. (A) 100 ppm $Fe^{3+}$ + 100 ppm 2-CEPA (10 minutes), $\lambda_{ex}$ = 404 nm, (B) 100 ppm $Zn^{2+}$ + 100 ppm 2-CEPA (7 days), $\lambda_{ex}$ = 404 nm, (C) 50 ppm $Zn^{2+}$ + 50 ppm CG + 50 ppm 2-CEPA (7 days), $\lambda_{ex}$ = 348 nm, (D) 50 ppm $Fe^{3+}$ + 50 ppm 2-CEPA + 50 ppm CG (10 minutes), $\lambda_{ex}$ = 348 nm.

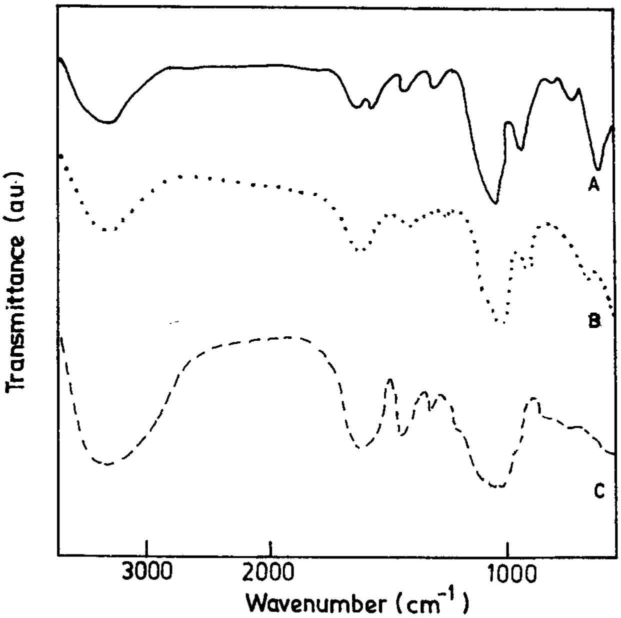

**Figure 5.** FT–IR spectra of the various solids and surface films formed on iron. (A) 100 ppm $Zn^{2+}$ + 100 ppm 2-CEPA (3 days), (B) 50 ppm $Zn^{2+}$ + 50 ppm CG + 50 ppm 2-CEPA (3 days), (C) Fe(III)–CG–2-CEPA solid complex.

But mild steel dipped in $Zn^{2+}$ + 2–2-CEPA + CG did not show any peak when excited at 404 mn. The above surface film when excited at 348 nm exhibited peaks at 430, 445, 465 and 485 nm. Fe(III)–2-CEPA and Fe(III)–2-CEPA–CG complexes were prepared and UV-luminescence spectra were taken. The Fe(III)–2-CEPA complex showed a peak at 445 nm when excited at 404 nm. This confirms that the peak at 445 nm is due to the Fe–2-CEPA complex (Kuzetsov and Rastohikov 1992; Yamashita *et al* 1994). The Fe(III)–2-CEPA–CG complex exhibited peaks at 430, 445, 465 and 485 nm when excited at 384 nm. This suggests that the surface film formed on metal immersed in $Zn^{2+}$ CG + 2-CEPA solution is the Fe–2- CEPA–CG complex.

In order to confirm the presence of an iron complex, FT–IR spectra of the surface film on steel dipped in various solutions were obtained (figure 5). The spectra for the film obtained from $Zn^{2+}$ + 2-CEPA exhibited a band for the carboxyl shift from 1715 to 1598 cm$^{-1}$ suggesting the participation of the carboxyl group in the complex formations. The stretching virbational frequency of the phosphonyl group ($-P=O$) gave a band at 1100 cm$^{-1}$. The asymmetric $PO_3$ and symmetric $PO_3$ were indicated by the bands at 1033 cm$^{-1}$ and 912 cm$^{-1}$ (Palta *et al* 1984). The presence of $Zn(OH)_2$ was also indicated by a band at 1320 cm$^{-1}$.

FT–IR spectra of the complex prepared by mixing $Fe^{3+}$, 2-CEPA and CG were obtained to understand the spectra of the surface film formed on mild steel dipped in a solution containing 50 ppm each of CG, $Zn^{2+}$ and 2-CEPA. The bands at 1033 and 912 cm$^{-1}$ are due to asymmetric and symmetric stretching frequencies of $PO_3$ respectively. The band at 1615 cm$^{-1}$ may be due to the COOH group from 2-CEPA as well as CG and the band at 3420 cm$^{-1}$ is due to hydroxyl group from both 2-CEPA and CG.

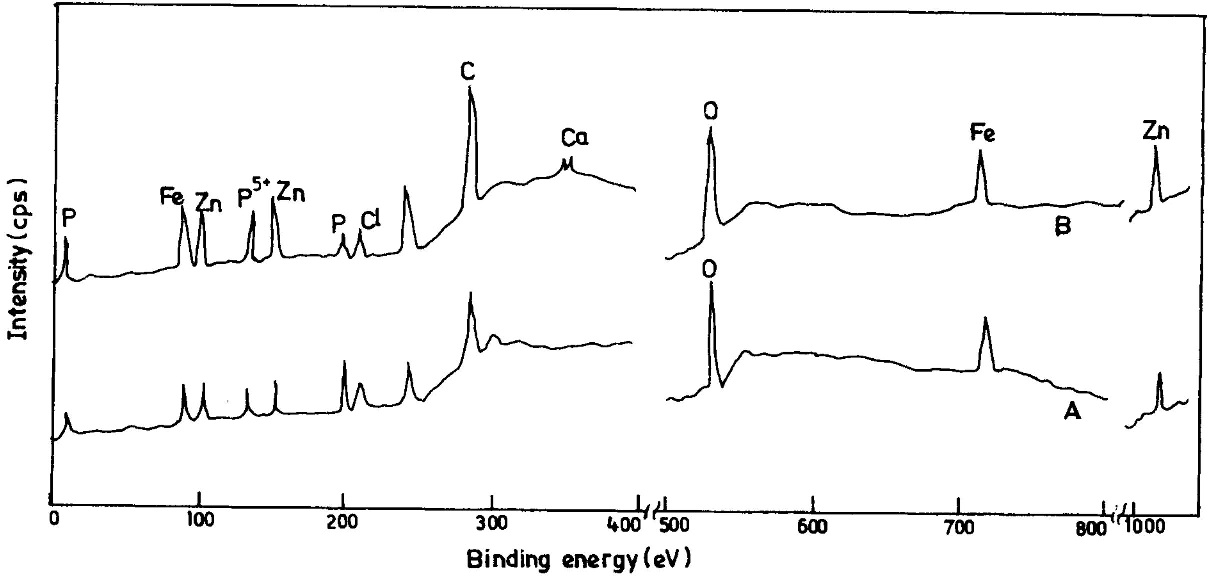

**Figure 6.** ESCA (counts vs. binding energy) of the surface film formed on mild steel immersed in different solutions. (A) 100 ppm $Zn^{2+}$ + 100 ppm 2-CEPA, (B) 50 ppm $Zn^{2+}$ + 50 ppm 2-CEPA + 50 ppm CG.

The ESCA pattern of the protective film formed on mild steel surface in $Zn^{2+}$ + 2-CEPA system is shown in figure 6. The peaks at 13 eV ($3S1/2$), 134 eV ($2P4_2$) and 191 eV ($2S1/2$) indicated the presence of a phosphorous atom. The peak at 134 eV was due to phosphorous in phosphoric acid ($-PO_3H_2$ or $P^{5+}$). Peaks of Zn were seen at 94 eV ($2S1/2$), 140 eV $3S1/2$) and 1022 eV ($2P3/2$). The peaks at 94 eV ($3P1/2$) and 721 eV ($2P4_2$) are mainly due to the $Fe^{2+}$ and $Fe^{3+}$ ions.

The peak at 294 eV is due to the carbon atom. A peak at 201 eV is due to the chloride ion. The observed peak at 534 eV is due to oxygen ($ISH/2$) in phosphoric acid attached to the iron atom. This suggests that the oxygen in phosphoric acid is bonded to an iron atom and the presence of $Zn^{2+}$ ions in the film is also envisaged.

In presence of GC, the ESCA pattern exhibited interesting features. A weak band around 352 eV suggests the presence of a small number of $Ca^{2+}$ ions in the film. The peak at 294 mm when expanded shows three peaks with varying intensities. The peaks at 290, 293 and 296 eV are due to the presence of C–C, C–O, –C=O groups. The intensity of the peak at 293 eV was more than 290 eV suggesting the participation of a larger number of C–O bands than of C–C bands. The incorporation of gluconate in the protective film is also envisaged.

## 4. Conclusions

Spectrochemical analysis of surface film formed on steel in the 60 ppm chloride solutions containing zinc ions. 2 CEPA and calcium gluconate revealed that the film contained zinc hydroxide along with iron oxide. On the surface of iron oxides, a 3-dimensional iron-phosphono gluconate complex may exist providing more stability to the surface film.

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