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The role of 1-hydroxyethane –1, 1-diphosphonic acid on corrosion inhibition performance of calcium gluconate in mild steel

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ABSTRACT

The corrosion rate of mild steel in low corrosive tap water in the absence and presence of 1-hydroxy ethane-1, 1-diphosphonic acid (HEDP) and calcium gluconate have been evaluated by weight loss, electrochemical polarization and AC impedance measurements. Presence of calcium gluconate considerably enhanced the corrosion inhibition efficiency of the widely used water treatment agent HEDP. At higher concentrations (>50ppm), HEDP was found to be aggressive towards mild steel. But a formulation consisting of 25ppm HEDP and 200ppm calcium gluconate was found to protect mild steel effectively.

Key words: Corrosion inhibitor, mild steel, HEDP, calcium gluconate,

INTRODUCTION

Incorporation of organic phosphonates in treatment of cooling water provides a reliable measure for corrosion prevention. The low toxicity, high stability to hydrolysis, high scale prevention and corrosion inhibition properties, make them suitable in water treatment industry.1-hydroxy ethane-1, 1-diphosphonic acid (HEDP) is the most widely used scale-controlling agent having medium efficiency in controlling mild steel corrosion[1-3]. The inhibition of corrosion by HEDP on iron and mild steel has been extensively studied. At low concentrations phosphonic acids form the insoluble iron complex capable of repairing the iron oxide layer, while at higher concentrations, HEDP showed an aggressive nature owing to the dissolution of the oxide layer, due to the formation of soluble iron complexes[4,5]. Bivalent metal cations play a significant role in the inhibitive action of HEDP [2]. Thus the influence of calcium ions and zinc ions on the corrosion inhibition performance of HEDP has been investigated in detail[4,6]. The influence of calcium ions on the adsorption of phosphonic acid on iron surfaces in neutral aerated media has been extensively studied by surface analytical and electrochemical methods. Calcium ion is believed to be incorporated into the oxide film that developed on mild steel surface to form a mixed oxide hydroxide complex[6].

Gluconates are known for their efficiency as corrosion inhibitors for mild steel and highly accepted for their environmental compatibility[7]. The inhibitive effect of gluconates on anodic metal dissolution and cathodic oxygen reduction reaction depends on the inhibitor concentration and nature of cations in solution as a gluconate salt in water[8,9]. Thus the of the beneficial effects of both gluconates and calcium ions on the corrosion inhibition properties of HEDP is investigated

EXPERIMENTAL

Samples and preparation

The electrodes were prepared from commercial grade mild steel of composition - iron, 0.02 % sulphur, 0.03 % phosphorous, 0.5% manganese and 0.2% carbon. The specimen used for weight loss tests were of size 40×20×3mm. In electrochemical tests surface area of mild steel coupons was 1cm^2. The electrodes were polished to metallographic grade 000, using different grades of emery papers, degreased with trichloroethylene, washed with distilled water and finally dried in a stream of air. All experiments were carried out in air-saturated solution at 28±1°C. The solutions were prepared in low corrosive tap water. The composition of which is shown in Table 1. All chemicals were reagent grade except HEDP, which was commercial grade.

Table 1: Composition of tap water

	Maximum	Minimum
PH	7.5	7.2
Conductivity (mmhos)	58	42
Dissolved oxygen (mg./L)	7.47	7.38
Total hardness (mg./L)	20.0	18.2
Calcium (mg./L)	6.41	5.82
Magnesium (mg./L)	0.972	0.846
Sulphate (mg./L)	Nil	Nil
Silicate (m.moles/L)	0.028	0.024
Total iron (mg./L)	0.515	0.293
Total dissolved solids (mg./L)	36.94	34.27
Fluoride (mg./L)	0.08	0.06
Chloride (mg./L)	55.2	48.7

Weight loss test

Weight loss tests were carried out with varying concentrations of calcium gluconate and HEDP and without inhibitors. All experiments were conducted in triplicate. The volumes of the solutions were kept at 200ml and the corrosion cells were tightly closed and kept quiescent.

Electrochemical tests

The experimental arrangement consisted of a potentiostat solartron S1 1280B electrochemical measurement unit and an IBM computer for data acquisition. The quasi steady state polarization curves were taken mostly from the corrosion potential to cathodic and anodic potentials at a scan rate of 2mV S^{-1}. Impedance measurements were carried out in frequency range 1Hz to 1KHz at 10mV rms amplitude.

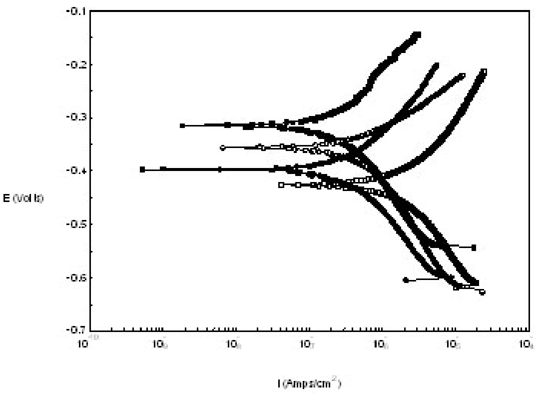
RESULTS AND DISCUSSION

The test results of weight loss experiments are illustrated in Table 2. It reveals that at high HEDP concentrations, the inhibition efficiency is lowered when used alone or together with calcium gluconate. However a synergistic effect is observed, which increases at lower concentrations of HEDP.

Table2: Corrosion inhibition efficiencies of mild steel in different inhibitor solutions

CG (ppm)	HEDP (ppm)	IE%
100	0	36
200	0	79
300	0	89
400	0	96
0	10	15
0	25	61
0	50	73
0	100	66
200	10	65
200	25	95
200	50	95
200	100	68

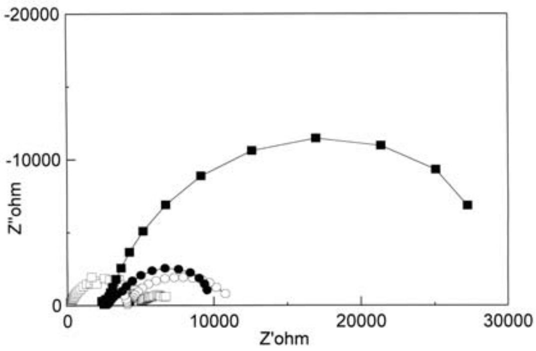
The current density-potential characteristics of mild steel in different solutions is illustrated in Fig. 1. The corrosion potential of the metal in the presence of calcium gluconate shifts towards anodic direction. The deviation of the anodic branch of polarization curve from the theoretical Tafel behaviour may be due to the spontaneous formation of a porous oxide layer on the electrode surface. The behaviour of corrosion current is in accordance with the results furnished by mass loss tests. The calculated values of corrosion potential,



´ 25ppm HEDP
■ 25ppm HEDP + 200 ppm calcium gluconate

○ 200 ppm calcium gluconate
□ Tap water

Fig. 1: Potentiodynamic polarization curves of mild steel immersed in different inhibitor solutions



¤ Tap water
■ 25ppm HEDP + 200 ppm calciumgluconate
´ 25ppm HEDP

Fig. 2: Nyquist plots for mild steel immersed in different inhibitor solutions

Table 3: Polarization parameters of mild steel in different solutions

	HEDP 25ppm	CG200ppm	200ppmCG+ 25ppmHEDP	Blank
-Ecorr.(V.SCE)	.397	.356	.314	.425
Ba(mV)	0.201187	0.16645	0.143515	0.26281
Bc(mV)	0.220347	0.18266	0.151965	0.27628
I corr.(Am/cm2)	4.816x10-6	2.05002x10-6	1.34419x10-6	8.6365x10-6
IE%	44	76	84.6	-

Table 4: Impedance parameters of mild steel immersed in different inhibitor solutions

	Cdl(Farad)	Rct(Ωcm2)	IE%
Blank	1.6003×10^{-4}	4983.25	-
25ppmHEDP	9.63×10^{-5}	7441.4	33
200ppmCG	7.088×10^{-5}	11245	54.8
25ppmHEDP +200ppmCG	5.558×10^{-5}	29294	82.9

corrosion current density and Tafel constants obtained from the polarization experiments are shown in Table III. The effectiveness of the inhibitor combination is clear from the lowest current density.

Fig. 2 shows the Nyquist complex plane impedance plots of mild steel immersed in different inhibitor solutions. The depressed semicircles shown in Nyquist plot in Fig 2 are usually interpreted as the result of formation of 3-D inhomogenous porous oxide layer at the corroding surface[10]. Juttner *et al*[11] explained such depressed semi circle as a result of simultaneous occurrence of charge transfer and transport process occurring in aerated neutral solutions.

The high Rp values shown in Table IV characterize the enhanced ability of HEDP to protect mild steel in the presence of calcium gluconate. More over HEDP gets incorporated into the calcium carbonate crystals at the surface, modifying its structure and diminishing the formation of scales [12]. The decrease in double layer capacitance also suggested the formation of a protective layer due to the adsorption of inhibitor molecules at the interface.

CONCLUSION

1. The enhanced inhibition efficiency of HEDP in protecting mild steel in presence of calcium gluconate is evident from the electrochemical tests and weight loss experiments
2. The corrosion inhibition performance of HEDP on mild steel can be considerably improved in presence of calcium gluconate
3. The anodic effect of HEDP and gluconate and the cathodic effect of calcium ions beneficially contribute for the protection of mild steel in neutral aqueous environments

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