Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **3(9),** 39-44, September **(2013)** *Res. J. Chem. Sci.*

Influnce of Polyvinyl Pyrolidone on Corrosion Resistance of Mild Steel Simulated Concrete Pore Solution Prepared in Well Water

Shanthi T.[1] and Rajendran S.[2]
[1]PG Department of Chemistry, Srinivasan College of Arts and Science, Perambalur-621212, INDIA
[2]Department of Chemistry, RVS School of Engineering and Technology, Dindigul, INDIA

Available online at: www.isca.in
Received 3rd August 2013, revised 4th September 2013, accepted 16th September 2013

Abstract

The inhibition efficiency (IE) of Polyvinyl pyrolidone (PVP) in controlling corrosion of carbon steel immersed in SCPS prepared in well water in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 50 ppm PVP and 50 ppm Zn^{2+} has 96 % IE. It is found that the inhibition efficiency (IE) of PVP increases by the addition of Zn^{2+} ion. A synergistic effect exists between PVP and Zn^{2+} .The mechanistic aspects of corrosion inhibition have been studied using polarization study and AC impedance spectra. The scanning electron microscopy (SEM) study confirms the protection of carbon steel surface by strong adsorption of PVP.

Keywords: Concrete corrosion, simulated concrete pore solution, mild steel, polyvinyl pyrolidone, well water.

Introduction

Corrosion is the destruction of metals and alloys by chemical and electrochemical reactions with its environment. It is a natural phenomenon which cannot be avoided, but it can be controlled and prevented using appropriate preventive techniques like metallic coating, anodic protection, cathodic protection and using inhibitors, etc. Inhibitors imparts very good role in the process of corrosion inhibition. The organic inhibitors containing hetero atoms like oxygen, nitrogen, sulphur and phosphorus, etc shows better corrosion inhibition by forming protective film on the metal surface. The order of corrosion inhibition efficiency of the compounds containing heteroatoms follows, O < N < S < P[1-4.] Application of polymers as corrosion inhibitors have been attracted several researchers[5-7.] Corrosion inhibition by conducting polymer has been studied[8]. The studies on corrosion inhibition of Polyacrylamide grafted with fenugreek mucilage[9] and polyvinylpyrrolidone have been reported[10]. The chelating properties of PVP make it useful in a multitude of applications in aqueous or polar organic solutions. The wide variety of usable solvents is due to the presence of imide, methylene and carbonyl groups in PVP[11]. There are numerous studies that investigated the corrosion inhibition of iron and iron alloys in acidic media[11-13,] neutral media[14], and basic media[15,16]. The corrosion inhibition studies of mild steel[17], aluminium[18] and zinc[19], etc in various aqueous environment have been studied.

The present work is undertaken: i. To evaluate the inhibition efficiency (IE) of PVP-Zn^{2+} incontrolling corrosion of carbon steel in well water (table 1), ii. To understand the mechanistic aspects of corrosion inhibition and formation of protective film on the metal surface by polarization and AC impedance spectra. iii. To analyze the protective film formed on the metals surface by scanning electron microscopy (SEM).

Material and Methods

Preparation of the specimens: Mild steel specimen (0.026% S, 0.06% P, 0.4% Mn and 0.1% C and rest Fe) of the dimensions 1.0 X 4.0 X 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies. The environment chosen is well water and the physico-chemical parameter of well water is given in table 1.

Table -1
Physico-chemical parameters of well water

Parameter	Value
pH	8.38
Conductivity	3110 1/cmΩ
TDS	2013 ppm
Chloride	665 ppm
Sulphate	14 ppm
Total hardness	1100 ppm

Simulated concrete pore solution (SCPS): A saturated calcium hydroxide solution is used in the present study, as SCP solution. The electrodes made of mild steel wire were immersed in the SCP solution and AC impedance, polarization study was carried out.

Weight Loss Method: Mild steel specimens in triplicate were immersed in 100 mL of SCPS prepared in well water containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one days. The corrosion product cleaned with[20]. The parameter of the marine media is given in table 1. The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY 210 model. Then the inhibition efficiency was calculated using the equation (1)

$I.E = 100\ [1-(W2/W1)]\ \%$ (1)

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively. The corrosion rate (CR) was calculated using the formula(2).

CR= [(Weight loss in mg) / (Area of the specimens in dm^2x immersion period in days) mdd (2)

Potentiodynamic Polarization: Polarization stud was carried out in Electrochemical impedence Analyser model CHI 660 A using a three electrode cell assembly was used. The working electrode was used as a rectangular specimen of carbon steel with the one face of the electrode of constant $1cm^2$ area exposed. A saturated calomel electrode(SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}) correction current (I_{corr}) and tafel slopes (anodic= ba and cathodic=bc) were calculated.

AC impedance measurement: AC Impedance study was carried out in Electrochemical Impedance Analyzer model CHI 660A using a three electrode cell assembly. The working electrode was used as a rectangular specimen of carbon steel with one face of the electrode of constant 1 cm^2 area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrode. AC impedance spectra were recorded after doing iR compensation. The real part (*Z*') and imaginary part (*Z*'') of the cell impedance were measured in ohms for various frequencies. The corrosion parameters such as charge transfer resistance (*R*t) and double layer capacitance (*C*dl) values were calculated.

Surface Characterization by Scanning Electron Microscopy (SEM): The mild steel immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of the carbon steel were examined using HITACHI S-3000 H computer controlled scanning electron microscope.

Results and Discussion

Analysis of results of weight loss study: The calculated inhibition efficiencies (IE) and corrosion rates (CR) of PVP in controlling corrosion of carbon steel immersed in simulated concrete pore solution in the absence and presence of Zn^{2+} ion are given in table 2. It is found that the inhibition efficiency (IE) of PVP increases by the addition of Zn^{2+} ion. The CR value decreases. The calculated value indicates the ability of PVP to be a good corrosion inhibitor.

Table- 2
Inhibition efficiencies (IE%) and corrosion rates (CR) obtained from PVP-Zn $^{2+}$ system, when mild steel immersed in saturated concrete pore solution prepared in well water

System	*IE %*	*CR* mdd
50 ppm PVP	78	8.58
100 ppm PVP	85	5.85
50 ppm PVP+Zn^{2+} 50 ppm	96	1.56
100 ppm PVP +Zn^{2+}50 ppm	96	1.56

Analysis of Polarization curves: The potentiodynamic polarization curves of carbon steel immersed in ground water in the absence and presence of inhibitors are shown in figure 1. The corrosion parameters such as corrosion potential (ECorr), Tafel slopes (anodic slope ba and cathodic slope bc), linear polarization resistance and corrosion current (ICorr) values were calculated and are given in table 3. When carbon steel was immersed in SCPS prepared in well water , the corrosion potential was -591 mV vs SCE (Saturated calomel electrode). When PVP (50 ppm) and Zn^{2+} (50 ppm) were added to the above system the corrosion potential shifted to the cathodic side -639 mV vs SCE. This indicates that the PVP-Zn^{2+} system control the cathodic reaction predominantly. Further, the LPR value increases from 7965 ohm cm^2 to 18605 ohm cm^2; the corrosion current decreases from 4.187 x 10^{-6} A/cm^2 to 1.926 x 10^{-6} A/cm^2. Thus, polarization study confirms the formation of a protective film on the metal surface. However the shift is not very much. Therefore it is concluded, that the system functions as a mixed type inhibitor. The anodic reaction is controlled by the formation of Fe^{2+} - PVP confirms on the anodic sites. The cathodic reaction (generation of OH^-) is controlled by formation of $Zn(OH)_2$ on the cathodic sites on the metal surface. Thus anodic reaction and cathodic reaction are controlled.

Table- 3
Corrosion parameters of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study

System	Ecorr mV vs. SCE	b_c mV/decade	b_a mV/decade	LPR ohmcm^2	Icorr Acm^{-2}
SCPS (blank)	-591	107	269	7965	4.187 x10^{-6}
SCPS + 50 ppm PVP + Zn $^{2+}$ 50 ppm	-639	114	297	18605	1.926 x10^{-6}

Analysis of AC impedance spectra: AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (*R*t) increases; double layer capacitance value (*C*dl) decreases and the impedance log (Z/ohm) value increases. The AC impedance spectra of carbon steel immersed in ground water the absence and presence of inhibitors (PVP-Zn^{2+}) are shown in figure 2 to figure 4. The AC impedance parameters namely charge transfer resistance (*R*t) and double layer capacitance (*C*dl) derived from Ny quist plots are given in table 4 The impedance value log (*Z*/ohm) derived from Bode plots are also given in table 4.

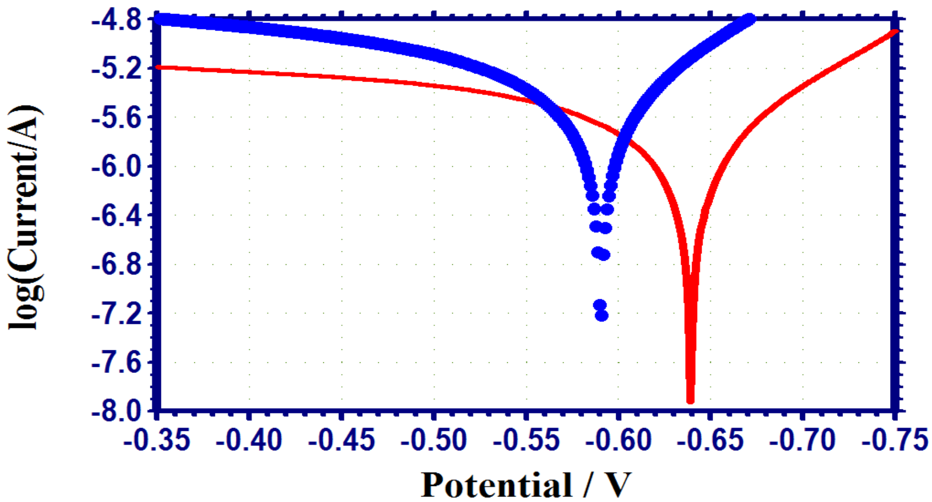


Figure-1
Polaraization curves ofmild steel immersed in various test solution
(a) SCPS (blank) (b) SCPS + 50 ppm PVP + Zn^{2+} 50 ppm

Table- 4
Impadance parameters of metals immersed in simulated concrete pore solution prepared in well water, obtained by AC impedance spectra

System	Nquist plot		Bode plot log (z/ ohm)
	R_t ohm. cm^2	C_{dl} Fcm^{-2}	
SCPS (blank)	3045	6.305×10^{-9}	3.4
SCPS + 50 ppm PVP + Zn^{2+} 50 ppm	10778	1.7814×10^{-9}	3.9

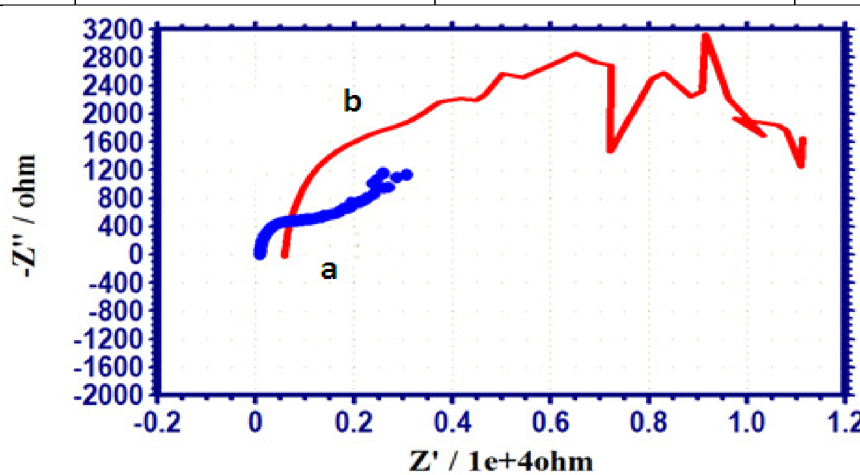


Figure-2
AC impedance spectrum of Mild steel immersed in various test solution
(a) SCPS(blank) (b) SCPS + 50 ppm PVP + Zn^{2+} 50 ppm (Nquist plot)

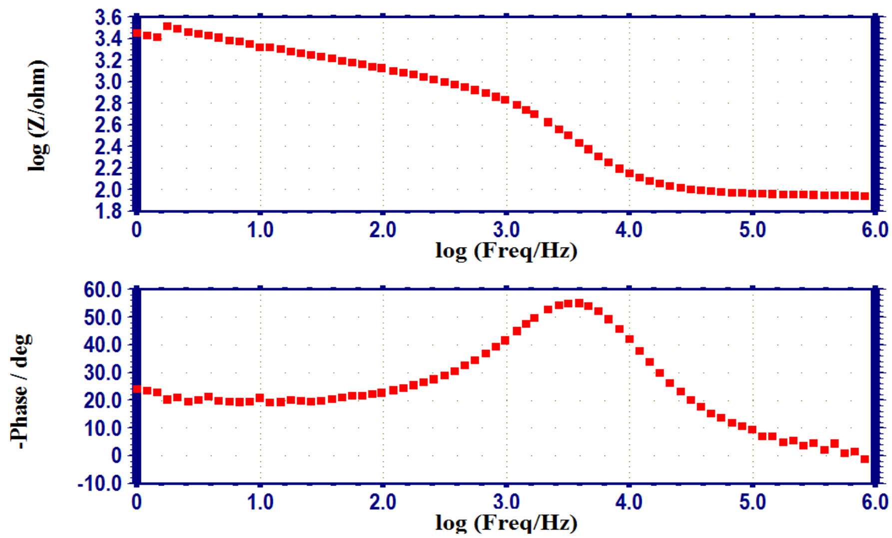


Figure-3
AC impedance spectrum of mild steel immersed in SCPS (Bode plot)

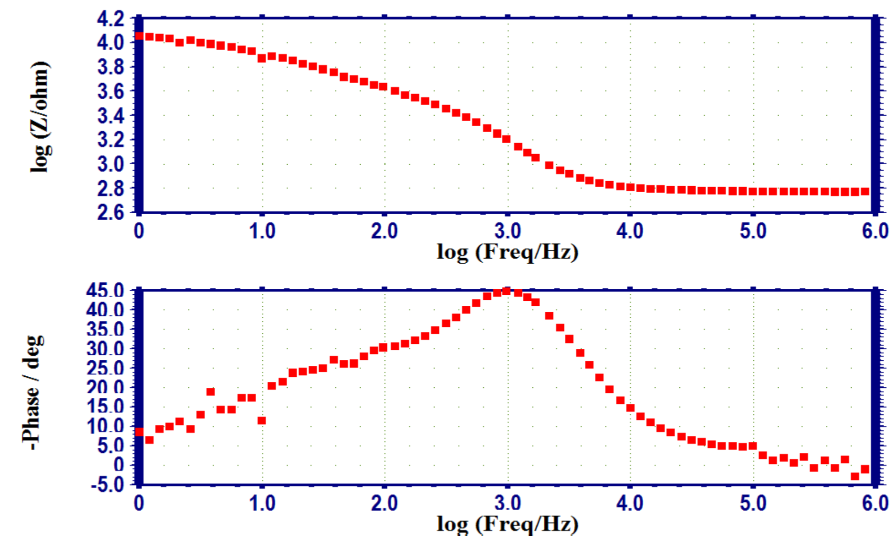
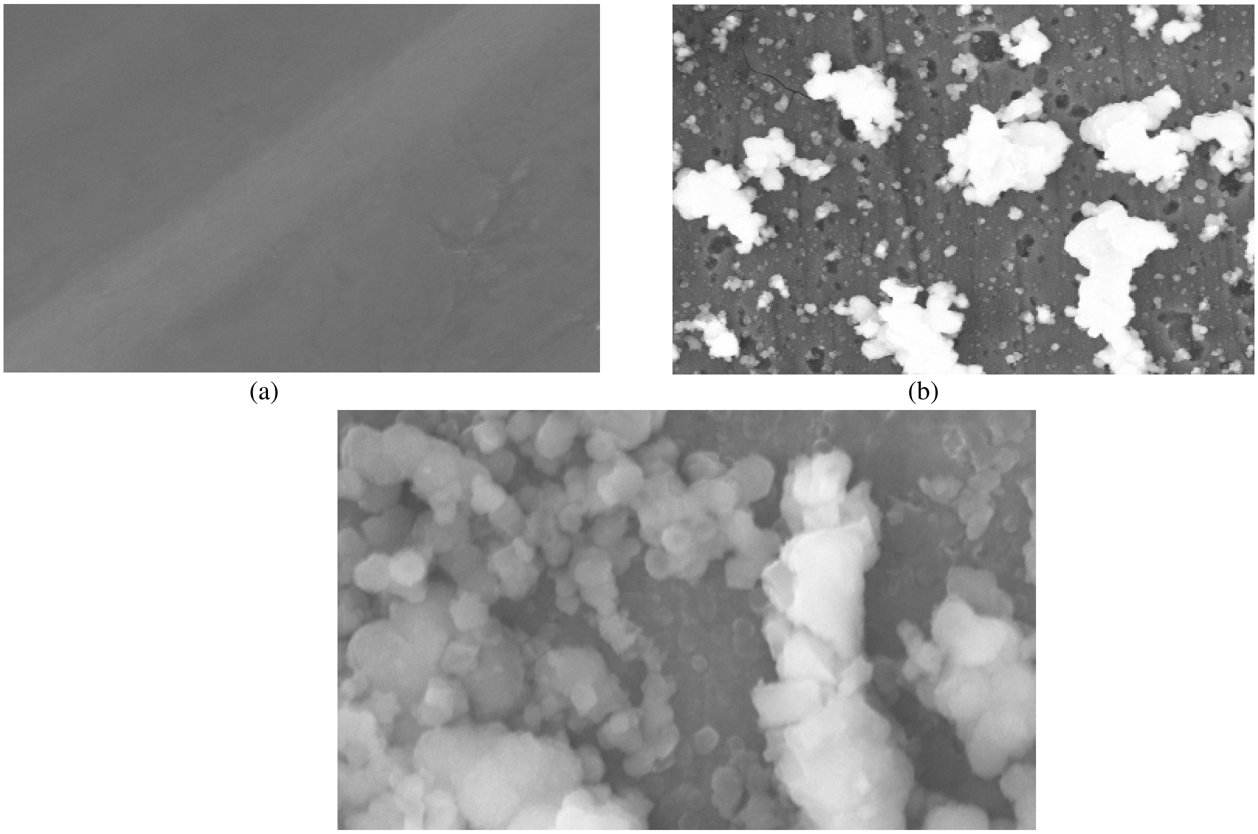


Figure-4
AC impedance spectrum of mild steel immersed in SCPS + 50 ppm PVP + Zn $^{2+}$ 50 ppm (Bode plot)

It is observed that when the inhibitors [PVP (50 ppm) + Zn^{2+} (50 ppm)] are added, the charge transfer resistance (*R*t) increase from 3045 ohm cm^2 to 10778 $ohmcm^2$. The *C*dl value decreases from 6.305 $x10^{-9}$ Fcm^{-2} to 1.7814 x 10^{-9} Fcm^{-2}. The impedance value [log(*Z*/ohm)] increases from 3.4 to 3.9. These results lead to the conclusion that a protective film is formed on the metal surface.

Scanning Electron Microscopy (SEM): SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined. The SEM micrograph (X 1000) of a polished carbon steel surface (control) in figure 5(a) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. The SEM micrograph (X 1000) of carbon steel specimen immersed in the ground water for one day is shown in figure 5(b) and figure 5(c) respectively.

The SEM micrograph of carbon steel immersed in simulated concrete pore solution prepared in well water is shown in figure 5(b). This shows the roughness of the metal surface which indicates the corrosion of carbon steel SCPS prepared in well water. The figure 5(c) indicates that in the presence of 50 ppm PVP and 50 ppm Zn^{2+} mixture in SCPS, the surface coverage increases which in turn results in the formation of insoluble complex on the metal surface. In the presence of PVP and Zn^{2+}, the surface is covered by a thin layer of inhibitors which effectively control the dissolution of carbon steel[21-27].



(a) (b)

(c)

Figure-5

SEM analysis of a) Polished Mild steel (control) b) Carbon steel immersed in SCPS (Blank) c) Carbon steel immersed in SCPS +50 ppm PVP + Zn^{2+} 50 ppm

Conclusion

The inhibition efficiency (IE) of Polyvinyl pyrolidone (PVP) in controlling corrosion of carbon steel immersed in simulated concrete pore solution prepared in well water in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 50 ppm PVP and 50 ppm Zn^{2+} has 96 % corrosion inhibition efficiency. Polarization study reveals that PVP – Zn^{2+} system controls the cathodic reaction predominantly. AC impedance spectra reveal that the formation of protective film on the metal surface. The SEM micrographs confirm the formation of protective layer on the metal surface.

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