RESEARCH ARTICLE

Influence of Polyvinyl Alcohol on Corrosion Resistance of Mild Steel Simulated Concrete Pore Solution Prepared in Well Water

T. SHANTHI[1] and S. RAJENDRAN[2]

[1]P.G. Department of Chemistry,
Srinivasan College of Arts and Science, Perambalur-621212, India

[2]Department of Chemistry,
RVS School of Engineering and Technology, Dindigul, India

shanchem23@gmail.com

Abstract: Corrosion resistance of mild steel in simulated concrete pore solution (SCPS) prepared in well water in the absence and presence of polyvinyl alcohol (PVA) and Zn^{2+} has been evaluated by weight loss method. It was observed that when PVA is added the corrosion inhibition efficiency (IE) increases. As the concentration of PVA increases, inhibition efficiency also increases. Addition of Zn^{2+} improves of IE further. 50 ppm of PVA has 50% IE. 100 ppm of PVA shows 90% IE. When 50 ppm of Zn^{2+} was added to the above system, both system shows 94% IE. The mechanistic aspects of corrosion inhibition have been studied using AC impedance spectra. The scanning electron microscopy (SEM) study confirms the protection of mild steel surface by strong adsorption of PVA.

Introduction

Corrosion is the destruction of metals and alloys by chemical and electro chemical reaction with its environment. It is a natural phenomenon which cannot be avoided, but it can be controlled and prevented using appropriate techniques like metallic coating, anodic protection, cathodic protection and using inhibitors *etc*. Inhibitors have very good role in the presence of corrosion inhibition. The organic inhibitors contain hetero atom like oxygen, nitrogen, sulphide and phosphorous. It shows better corrosion efficiency of the compounds containing hetero atom follows O<N<S<P[1,2]. Application of polymers as corrosion inhibitors have been attracted several researchers[3,4]. Corrosion inhibition by conducting polymer has been studied[5]. The use of polymers as corrosion inhibitors has attracted considerable attention. Polymers such as poly (vinyl pyrolidone), poly ethylamine, polyaniline, polysiloxane and polyethylene glycol methyl ether, have been widely reported[6-13]. The application of

water soluble polymers as corrosion inhibitors of metal in different media has been cited. The inhibition efficiency of poly(vinyl alcohol) in controlling the corrosion of mild steel was investigated[14-16]. The inhibitors such as poly (vinyl alcohol) and polyethylene glycol were found to obey Temkin, Freundlich and Frumkin adsorption isotherm from the fit of the experimental data[17]. A saturated solution of calcium hydroxide is used as simulated concrete pore solution[18,19]. The aim of the present study is to investigate the corrosion resistance of mild steel in simulated concrete pore solution in presence of polyvinyl alcohol and Zn^{2+} combination to mild steel in well water. The physicochemical parameters of the well water taken in preset study are given Table 1. The corrosion inhibition efficiency was collected using weight loss, polarization and AC impedance studies. The protective film formed on the metal surface characterized using morphological studies such as scanning electron microscopy (SEM).

Table 1. Parameters of well water

Parameter	Value
pH	8.38
Conductivity	3110 μ mhos/cm
TDS	2013 ppm
Chloride	665 ppm
Sulphate	14 ppm
Total hardness	1100 ppm

Experimental

Mild steel specimen was used in the present study (Composition (wt%):0.026 S, 0.06% P, 0.4% Mn, 0.1% C and balance iron[20]) of the dimensions 1.0x4.0x0.2 cm were polished to a mirror finish and decreased with trichloroethylene and used for the weight loss method.

Simulated concrete pore solution (SCPS)

A saturated calcium hydroxide solution was used in the present study, as SCP solution. The electrodes made of mild steel wire were immersed in the SCP solution and AC impedance spectra was carried out.

Mass-loss method

Mild steel specimens in triplicate were immersed in 100 mL of simulated concrete pore solution (SCPS) containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day. The weight of the specimens before and after immersion was determined using Shimadzu balance, model AY 210. The corrosion products were cleansed with Clarke's solution[21]. Then the inhibition efficiency (I.E.) was then calculated using the equation (1)

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

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 (Eq. 2)

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

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was the same. The real part (Z^1) and imaginary part (Z^{11}) of the cell impedance

were measured in ohms at various frequencies. The values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

Surface examination study

The mild steel specimens were immersed in various test solutions for a period of one day. After one day the specimens were taken out and dried. The nature of film formed on the surface of metal specimens was analysed by surface analysis technique, SEM.

Scanning electron microscopy

The mild steel specimens immersed in various test solutions for one day were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the mild steel surface were carried out by scanning electron microscopy (SEM) using HITACHI –S-3000H SEM.

Results and Discussion

Analysis of weight loss study

The calculated inhibition efficiencies (IE) and corrosion rates (CR) PVA in controlling corrosion mild steel immersed in simulated concrete pore solution in the absence and presence of Zn^{2+} ion are given in Table 2. The calculated value indicates the ability of PVA to be a good corrosion inhibitor. PVA alone shows some IE, but the combination of PVA 50 ppm and Zn^{2+} 50 ppm shows 94 % IE. This suggests a synergitic effect exists between PVA and Zn^{2+} ion.

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

System	IE %	*CR* mdd
50 ppm PVA	50	19.5
100 ppm PVA	90	3.9
50 ppm PVA+Zn^{2+} 50 ppm	94	2.3
100 ppm PVA+Zn^{2+}50 ppm	94	2.3

*Analysis of AC impedance spectra*

AC impedance spectra of mild steel immersed in simulated concrete pore solution prepared in well water in the absence and presence of inhibitor and Zn^{2+} are shown in the Figures 1 to 2. The Nquist plots are shown in Figure 1. The Bode plots are shown in Figures 2a and 2b. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values are derived from Nquist plots. Impedance values, log (z/ohm) are derived from Bode plots. The results are summarized in Table 3.

Table 3. Impedance parameters of metals immersed in simulated concrete pore solution prepared in well water, obtained by AC impedance spectra
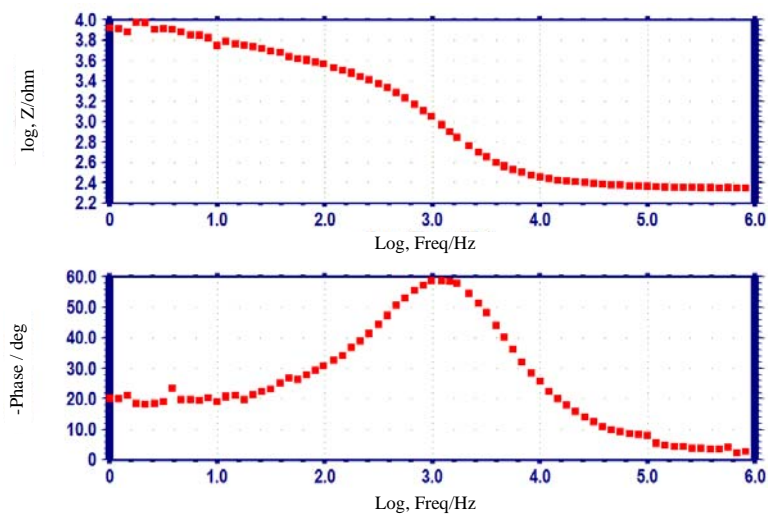
System	Nquist plot		Bode plot
	R_t ohm. cm^2	C_{dl} Fcm^{-2}	log z/ohm
SCPS (blank)	3045	6.305×10^{-9}	3.4
SCPS + 50 ppm PVA +50 ppm Zn^{2+}	8951	2.145×10^{-9}	4.0
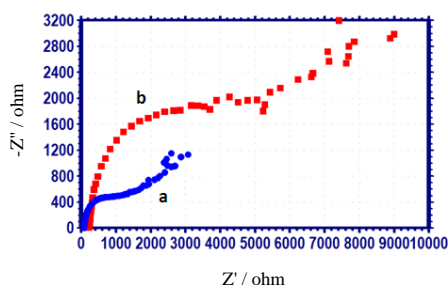
Figure 1. AC impedance spectrum of mild steel immersed in various test solution; (a) SCPS (blank) (b) SCPS + PVA 50 ppm + Zn^{2+} 50 ppm (Nquist plot)
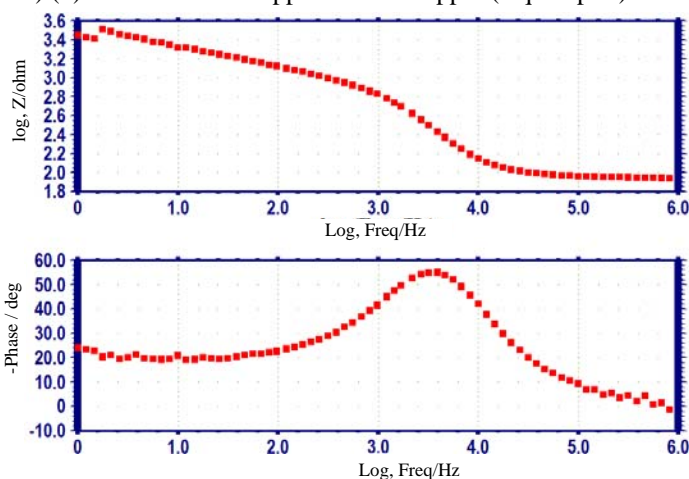
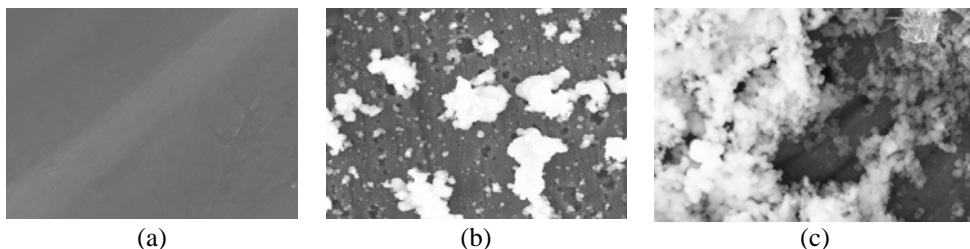**Figure 2a.** AC impedance spectrum of mild steel immersed in SCPS (Bode plot)

Figure 2b. AC impedance spectrum of mild steel immersed in SCPS + PVA 50 ppm Zn^{2+} 50 ppm (Bode plot)

When corrosion rate of a metal decreases due to formation of protective film, the charge transfer resistance value increases and double layer capacitance value decreases, the impedance value log (z/ohm) increases[18-26]. It is observed from Table 3, the R_t value 3045 ohm. cm^2, the C_{dl} Value is 6.305×10^{-9} F cm^{-2} and the impedance value is 3.4 log (z/ohm). When 100 ppm PAA and 50ppm Zn^{2+} are added to above the solution. The R_t value 8951 ohm. cm^2 increases, the C_{dl} Value is 2.145×10^{-9} F cm^{-2} decreases and the impedance value is 4.0 log (z/ohm) increases. The increases charge transfer resistance (R_t) value, the double layer capacitance (C_{dl}) value decreases and the impedance value (z) increases. This confirms the formation of protective film formed on the metal surface. This accounts for the better inhibition efficiency of the PVA –Zn^{2+}.

Scanning electron microscopy

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 mild steel, the SEM micrographs of the surface examined. The SEM micrograph (X 1000) of a polished mild steel surface (Control) in Figure 3(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 micrographs (X 1000) of mild steel specimen immersed in the SCPS for one day is shown in Figure 3(b) and Figure 3(c) respectively.

The SEM micrographs of mild steel surface immersed in the SCPS is shown in Figure 3(b). This shows the roughness of the metal surface which indicates the corrosion of mild steel in SCPS. The Figure 3(c) indicates that in the presence of 50 ppm PVA 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 PVA and Zn^{2+}, the surface is covered by a thin layer of inhibitors which effectively control the dissolution of mild steel[27].

(a)	(b)	(c)

Figure 3. SEM analysis of a) Polished mild steel (control); b) mild steel immersed in SCPS(Blank); c) mild steel immersed in SCPS + + PVA 50 ppm + Zn^{2+} 50 ppm

Conclusion

The inhibition efficiency (IE) of polyvinylalcohol (PVA) in controlling corrosion of mild steel immersed in simulated concrete pore solution prepared in well water in the absence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 50 ppm PVA and 50 ppm Zn^{2+} has 94% corrosion inhibition efficiency. AC impedance spectra reveals that a protective film is formed on the metal surface. The SEM micrographs confirm the formation of protective layer on the metal surface.

References

1.   Doneelly B D, Downie T C, Grzeskowaik R, Hamburg H R and Short D, *Corros Sci.,* 1997, **38,** 109.
2.   Subramaniam N C, Shesadri B S and Mayanna S M, *Corros Sci.,* 1993, **34(4)**, 563-571.
3.   Umoren S A, Ogbobe O, Igwe I O and Ebenso E E, *Corros Sci.,* 2008, **50(7**), 1998-2006.
4.   Umoren S A, Solomon M M, Udosoro I I and Udoh A P*, Corros Sci*., 2010, **52(4),** 1317-1325**.**
5.   Gelling V J, Wiest M M, Dennis E T, Bierwagen G P and Wallace G G, *Pro Org Coatings* , 2001, **43(1-3)**, 149-157; http://dx.doi.org/10.1016/S0300-9440(01)00186-2
6.   Wang H, Niu L, Hong Q,Su X Wu and Feng Hua Wei*, Chin Chem Let*t., 2004, **15,** 486-496.
7.   Herrasti P, Ocon P, Ibanez A and Fatas E*, J Appl Electrochem*., 2003, **33(6)**, 533-542.
8.   Le D P, Yoo Y H, Kim J G, Cho S M and Son Y K, *Corros Sci*., 2009, **51(2)**, 330-338; http://dx.doi.org/10.1016/j.corsci.2008.10.028
9.   Finsgar M, Fassbender S, Nicolini F and Milosev I*, Corros Sci* ., 2009, **51(3)**, 525-533; http://dx.doi.org/10.1016/j.corsci.2008.12.006
10.   Jianguo Y, Lin W, Otieno- Alego V and Schweinsberg D P, *Corros Sci*., 1995, **37(6)**, 975-985; http://dx.doi.org/10.1016/0010-938X(95)00008-8
11.   Schweinsberg D P, Hope G A, Trueman A and Otieno- Alego V, *Corros Sci*., 1996, **38(4)**, 587-599; http://dx.doi.org/10.1016/0010-938X(95)00148-D
12.   Azioune A, Marcozzi M , Revello V and Pireaux J-J*, Surf Interface Anal*., 2007, **39**, 615-623.
13.   Dubey A K and Sing G, *Port Electrochim Acta.,* 2007, **25**, 221-235.
14.   Rajendran S, Sridevi S P, Anthony N, John Amalraj A and Sundravadivelu M*, Anti Corros Meth Mater.*, 2005, **52**, 102-111; DOI:10.1108/00035590510584816
15.   Umoren S A, Ebenso E E, Okafor P C and Ogbobe O, *Pigment Resin Tech.*, 2006, **35,** 346-354; DOI:10.1108/03699420610711353
16.   Umoren S A, Ogbobe O, Ebenso E E and Ekpe U J, *Pigment Resin Tech*, 2006 **35,** 284-291; DOI:10.1108/03699420610692896
17.   Umoren S A, Ebenso E E, Okafor P C, Ogbobe O and Ekpe U J, *J Appl Polym Sci*, 2007,**103,** 2810-2819; DOI:10.1002/app.25446
18.   Allaharam S R and Khodayari M, *Anti-Corros Methods Mater.,* 2008, **55**, 250.
19.   Mennucci M M, Banczek E P, Rodrigues P R P and Coasta I, *Cement Concrete Compos.,* 2009, **418(28**), 31.
20.   Arocia Selvi J, Rajendran S, Garga Srin V, John Amalraj A and Narayanaswamy B, *Port Electrocheim Acta,* 2009, **27,** 1-11; DOI:10.4152/pea.200901001
21.   Wranglen G, Introduction to corrosion and protection of metals (Chapman and Hall, London)*,* 1985, 236.
22.   Leema Rose A, Noreen Antony, Felicia Rajarnmal Selva Rani A, Peter Pascal Regis and Rajendran S, *Zastit Mater.*, 2009**, 50***,* 167.
23.   Rajendran S, Kanagamani M, Sivakalaivani M, Jeyasundari J, Narayanasamy B and Rajam K, *Zastita Mater.*, 2008**, 49,** 19.
24.   Sathiyabama J, Rajendran S, Arocia Selvi J and Jeyasundari J, *Open Corros J.,* 2009**, 2,** 77-82; DOI:10.2174/1876503300902009077
25.   Agnesia Kanimozhi S and Rajendran S, *Int J Electrochem Sci.*, 2009, **4(3)**, 353-388.
26.   Kalaivani R, Narayanasamy B, Selvi J A, Amalraj A J, Jeyasundari J and Rajendran S, *Port Electrochim Acta*, 2009, **27(2),** 177-187; DOI:10.4152/pea.200902177
27.   Samide A, Ciuciu A and Negrila C, *Port Electrocheim Acta,* 2010**, 28(6),** 385-396.