INHIBITION OF CORROSION OF ALUMINIUM IN ALKALINE MEDIUM BY POLY(VINYL ALCOHOL) (PVA)

R. Kalaivani[a]*, P. Thillai Arasu [b] and S. Rajendran[c]

Keywords: polyvinylalcohol; aluminium; weight-loss method; synergistic effect; protective film

The inhibition efficiency of polyvinylalcohol (PVA) in controlling corrosion of aluminium in well water in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 250 ppm of PVA and 25 ppm of Zn^{2+} offers 85 % inhibition efficiency. It is found that the inhibition efficiency of PVA increases by addition of Zn^{2+} ion. A synergistic effect exists between PVA and Zn^{2+}. The mechanistic aspects of corrosion inhibition have been studied using polarization study. Also FTIR spectra reveal that the protective film consists of PVA - Zn^{2+} complex and $Zn(OH)_2$. The scanning electron microscopy confirms the protection of aluminium surface by strong adsorption of PVA. A suitable mechanism for corrosion inhibition is proposed based on the results from the above studies.

* Corresponding Authors
  *E-Mail: vaniraj21@yahoo.com
[a] Department of Chemistry, Research Scholar, Manonmanium SundaranarUniversity,Thirunelveli 627132,Tamilnadu, India.
[b] Deparment of Chemistry,Kalasalingam, University,Srivilliputhur 626126, Tamilnadu, India.
[c] RVS School of Engineering & Technology, Dindigul - 624 005,Tamilnadu, India.

Introduction

Water is the most commonly used cooling fluid to remove unwanted heat from heat transfer surfaces. In recent years, the need to conserve water in order to meet the demand of industry. Presently, due to environmental Concerns, non-polluting inhibitors are used. Among various inhibitors polyvinyl alcohol is chosen as corrosion inhibitors because polyvinyl alcohol has excellent film forming,[1-3] emulsifying, and adhesive properties. It is also resistant to oil, grease and solvent. It is odorless and non toxic. It have functional groups such as –OH linkage, this group interact with metal surface through active centers of polymer.[4-6] It acts as protective film and prevents corrosion. The study of corrosion inhibition of aluminium in H_2SO_4 in presence of polyvinylalcohol (PVA) and polyethylene glycol(PEG) as inhibitors at 30-60 °C by using gravimetric, gasometric and thermometric techniques,[7] found that corrosion inhibition efficiency increases with increase in concentration of PVA and PEG. Rajendran et al[8] investigated the corrosion behaviour of carbon steel using polyvinyl alcohol(PVA) in neutral aqueous solution containing 60 ppm of Cl^- in the absence and presence of ions using weight loss method. It offered 81% inhibition efficiency, the corrosion and inhibition behaviour of aluminium[9] in HCl in the presence of polyvinyl pyrrolidone (PVP) and polyacrylamide (PAL) their blends in the temperature range of using weight loss and hydrogen evolution techniques has been reported that polyvinylalcohol, used in eye drops and hard contact lens solution as a lubricant, PVA fiber, as reinforcement in concrete, as a surfactant for the formation of polymer encapsulated nanobeads. Much work has not been done on aluminium metal by polyvinyl alcohol.

Molecular structure of polyvinylalcohol is shown in scheme 1. Space filling model of is shown in scheme 2.
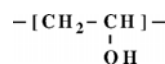
Scheme 1. Polyvinylalcohol (ethene-1-ol)
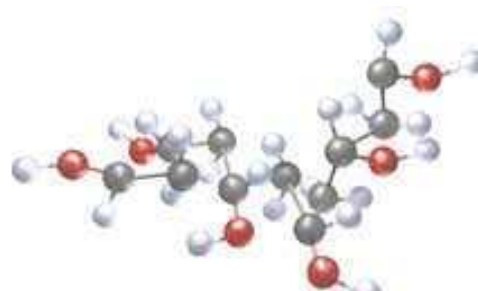
Scheme 2. Space filling model of polyvinyl alcohol

The present work deals

i) To evaluate the inhibition efficiency of polyvinylalcohol(PVA) in controlling corrosion of aluminium at *pH* 11 in the absence and presence of Zn^{2+}

ii) To study the synergistic effect exist between PVA - Zn^{2+} system.

iii) To analyse the protective film by FT-IR spectra and SEM techniques.

iv) To study the AC impedance spectra to know the mechanistic aspects of corrosion inhibition.

v) To propose a suitable mechanism of corrosion inhibition based on the results from the above studies.

Materials and methods

Preparation of the specimens

The commercial aluminium specimens (95 % of purity) of the dimentions 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 were made.

Weight – loss method

Aluminium specimens were immersed in various concentrations of the inhibitor solution in the presence and absence of Zn^{2+} for a period of 24 h. The weight of the specimens before and after were determined using Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution. The inhibition efficiency (%) was then calculated using the equation

$$E = 100 \left[1 - \frac{W_2}{W_1} \right] \qquad (1)$$

where

W_1 = corrosion rate in the absence of the inhibitor and
W_2 = corrosion rate in the presence of the inhibitor.

AC impedance measurements

The AC impedance spectra were recorded in the same instrument which was used for polarization study. The cell set up was the same as that used for polarization measurements. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance R_t, and the double layer capacitance C_{dl} were calculated.

$$R_t = (R_s + R_t) - R_s \qquad (2)$$

where

R_s = solution resistance

$$C_{dl} = 1 / 2 \text{л} R_t f_{max} \qquad (3)$$

where

f_{max} = maximum frequency

Surface examination study

The aluminium specimens were immersed in various test solutions for a period of 24 hours and then taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed for surface analysis technique by FTIR spectra and fluorescence spectra.

FT-IR Spectra

The film formed on the metal surface was carefully removed and mixed thoroughly with KBr. The FTIR spectra were recorded in a Jasco 460+ spectrophotometer.

RESULTS AND DISCUSSION

Analysis of the results of weight loss method

The *IE* values of PVA at different concentrations in the absence and presence of Zn^{2+} in well water for a period of one day obtained from the weight loss method are given in Table 1.

The inhibition efficiency of PVA increases as its concentration increases. From the table it is clear that Zn^{2+} in the absence of inhibitor also has some *IE*. As the concentration of Zn^{2+} increases, inhibition efficiency also increases. A synergistic effect exist between PVA and Zn^{2+}. It is observed from the Table 1, 250 ppm of PVA only has 50 % *IE* and 25 ppm of Zn^{2+} alone has 22 % *IE*. However, their combination consisting of 250 ppm of PVA and 25 ppm of Zn^{2+} has 85% inhibition efficiency. The observed improvement in the protection efficiency is attributed to the synergistic effect,[10-13] which results from the combination of two inhibitors PVA and Zn^{2+} which results in the formation of complex between Zn^{2+}-PVA, hence the inhibitor molecules are readily transported from the bulk to the metal surface. A thin film was observed on the surface of the inhibited metal during the weight-loss measurements.

The corrosion rates of aluminium with various concentrations of PVA and Zn^{2+} systems immersed in well water for the same period are given in Table 1. From the Table 1, it is clear that in the presence of Zn^{2+} corrosion rate (*CR*) decreases as the concentration of PVA increases. This behaviour is due to the increase in the adsorption amount of the inhibitor on aluminium metal surface.[14-15]

Table 1. *IE* and *CR* of aluminium in solution containing various concentration of PVA in presence and absence of Zn^{2+} at *p*H 11

PVA ppm	Zn^{2+}, ppm					
	0		**25**		**50**	
	IE, %	*CR, mdd*	*IE, %*	*CR, mdd*	*IE, %*	*CR, mdd*
0	----	----	22	14.2	11	16.1
50	50	9.1	68	5.8	65	6.4
100	56	8.0	75	4.5	70	5.4
150	60	7.3	80	3.6	72	5.1
200	63	6.7	85	2.7	75	4.5
250	65	6.4	85	2.7	80	3.6

Synergism parameter (S_I)

The synergism parameter (S_I) is calculated using the relation

$$S_I = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$

where

$\theta_{1+2} = (\theta_1 + \theta_2) - ((\theta_1 . \theta_2))$
θ_1 = surface coverage of inhibitor (PVA)

θ_2 = surface coverage of co-inhibitor (Zn^{2+})

θ'_{1+2} =combined surface coverage of inhibitors (PVA) and (Zn^{2+})

Surface coverage = IE/100

S_I approaches 1 when no interaction between the inhibitors. $S_I > 1$, synergistic effect exist between the two inhibitors. In the case of . $S_I < 1$, negative interaction takes place between system are shown in Figs. 1-3. It is clear from the plots that the impedance response of aluminium was significantly changed after addition of the two inhibitors, (i.e *CR* increases). The calculated synergism parameter values for PVA and Zn^{2+} system are given in Table 2a and in 2b respectively. In the case of PVA - Zn^{2+} system , the S_I value is found to be greater than one for 25 ppm of Zn^{2+} with various concentrations of PVA, indicating the synergistic effect exist between Zn^{2+} of concentrations of 25 ppm with various concentrations of PVA. S_I value is found to be less than unity for 50 ppm Zn^{2+} with various concentrations of PVA which indicates a lack of synergism between 50 ppm of Zn^{2+} with various concentrations of PVA.[16-18]

Table 2a. Synergism parameters for PVA - Zn^{2+} (25 ppm) system when aluminium immersed in well water

PVA, ppm	θ_1	θ_2	θ'_{1+2}	S_I
50	0.50	0.37	0.66	0.96
100	0.56	0.37	0.72	0.93
150	0.60	0.37	0.75	0.90
200	0.63	0.37	0.77	0.92
250	0.65	0.37	0.78	1.1

Table 2b. Synergism parameters for PVA-Zn^{2+} (50 ppm) system when aluminium immersed in well water

PVA, ppm	θ_1	θ_2	θ'_{1+2}	S_I
50	0.50	0.15	0.58	1.33
100	0.56	0.15	0.63	1.45
150	0.60	0.15	0.66	1.7
200	0.63	0.15	0.68	2.1
250	0.65	0.15	0.75	1.99

Analysis of the results of AC impedance spectra

AC impedance spectra have been used to detect the formation of film on the metal surface. Nyquist plot and Bode plot representations of aluminium in well water in the absence and presence of the inhibitors. The impedance diagrams obtained almost have a semicircular appearance. This indicates that the corrosion of aluminium in alkaline solution is mainly controlled by a charge transfer process. The impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 4.

When aluminium is immersed in solution containing 250 ppm of PVA and 25 ppm of Zn^{2+} at *p*H 11 in the presence and absence of inhibitors are shown in Fig 1.
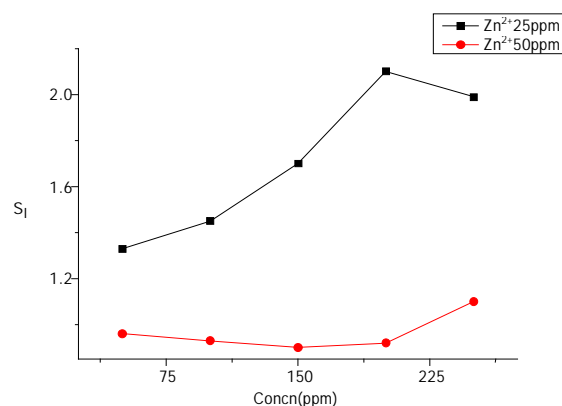

Figure 1. Graph of synergism effect exist in PVA- Zn^{2+} system in the corrosion of aluminium immersed in well water (Immersion period-one day)

It is found that when aluminium in well water at pH11, the R_t value is 396.4 Ω cm^2 and C_{dl} value is 1.2865×10^{-8} μF cm^{-2}. When 250 ppm of PVA and 25 ppm Zn^{2+} are added the R_t value tremendously increased to 2086 ohm cm^2 and the C_{dl} value is decreased to 2.44×10^{-9} μF cm^{-2}.[19-24] This indicates the protective film is formed on the metal surface in the presence PVA .The bode plots are shown in Fig 4. It is observed that in the absence of the inhibitors the real impedance value [(log(Z ohm^{-1})] is 2.69. In the presence of inhibitors this value increases to 3.38.

Table 3. The impedance parameters of aluminium immersed in well water at *p*H 11 in presence and absence of inhibitor obtained by AC impedance method

System	R_t Ohm cm^2	C_{dl} F cm^{-2}	Impedance (log Z ohm^{-1})
Well water	396.4	1.2865×10^{-8}	2.69
Test solution PMMA=250 ppm+Zn^{2+}=25ppm	2086	2.44×10^{-9}	3.38

Analysis of the FT-IR spectra

FTIR spectra have been used to analyze the protective film formed on metal surface. FTIR spectrum (KBr) of pure PVA is given in Fig.4a. The aliphatic C-H stretching frequency peaks appears at 2928.5 cm^{-1}. The secondary alcoholic C-O stretching absorption peak takes place at 1062 cm^{-1}. The bands at 1383 cm^{-1} and 765.88 cm^{-1} are due to bending C-H of methyl groups. The FT-IR spectrum of the film formed on the aluminium surface after immersion in the well water for one day containing 250 ppm of PVA and 25 ppm of Zn^{2+} is shown in Fig 4b. The OH stretching frequency decreased from 3459 cm^{-1} to 3417 cm^{-1}. The C-O stretching frequency decreased from 1062 cm^{-1}to 1116 cm^{-1}. This suggest that the oxygen atom of PVA was coordinated with Al^{3+} on the anodic sites of the aluminium metal surface, resulting in the formation of Al^{3+} - PVA complex. The peak at 620 cm^{-1} which may be due to Zn-O bending mode of vibration. The band at 3459 cm^{-1} is due to OH stretching frequency of Zn(OH)$_2$ the formed at cathodic sites metal surface.[25]
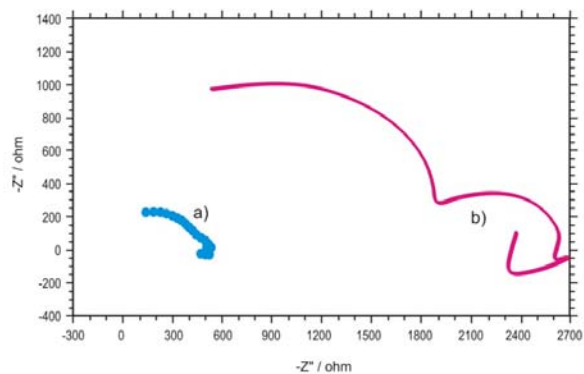
Figure 2. AC impedance spectra of aluminium immersed in various test solutions a) well water b) well water containing 250 ppm of PVA and 25 ppm of Zn^{2+}
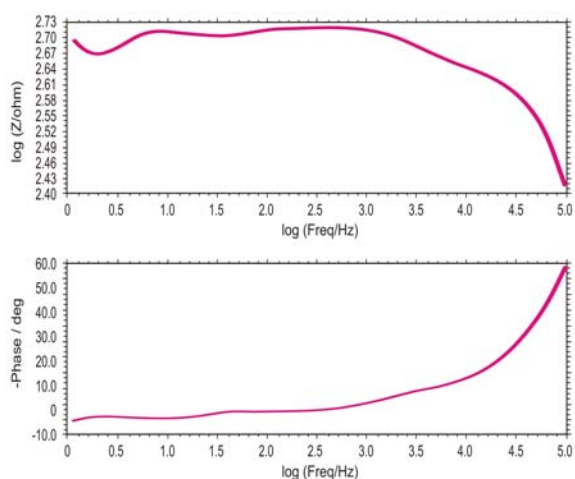

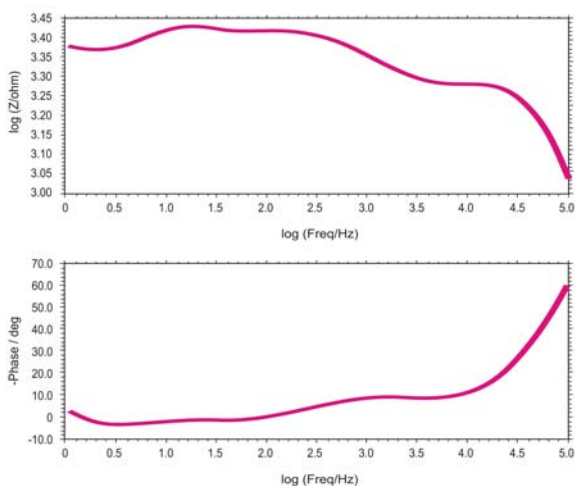**Figure 3a**. Bode plots of aluminium immersed in well water

Figure 3b. Aluminium immersed in well water + 250 ppm of PVA and 25 ppm of Zn^{2+}

Analysis of surface metal by SEM

SEM technique provides a pictorial representation of the surface. To understand the nature of the surface film in the presence and absence of inhibitors and the extent of corrosion products of aluminium, the SEM micrographs of the surface are examined.[26-28]
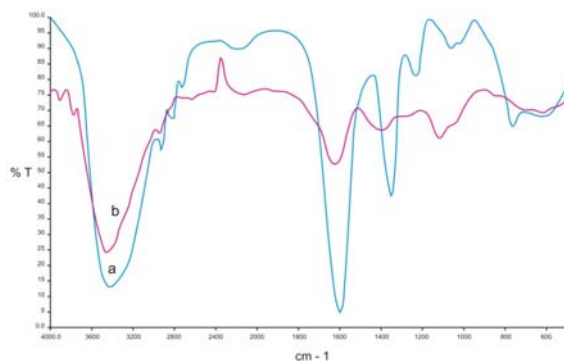

Figure 4. FTIR Spectra a) pure PVA b) film formed on metal surface after immersion in well water containing 250 ppm of PVA and 25 ppm of Zn^{2+}

The SEM images of different magnifications (X1000) of aluminium specimen and aluminium immersed in well water for one day in the presence and absence of inhibitors system are shown in Figure 5 as images (a, b and c) respectively.

The SEM micrographs of the surface of the polished aluminium metal (control) in Fig 5 images (a) illustrate the very smooth surface of the metal. These show the absence of any corrosion products formed on the metal surface.

The images (b) denote the SEM micrographs of aluminium surface immersed in well water. They show the type of rough surface of the uniform corrosion of the aluminium surface in well water, indicating in an inhibitor free solution, the surface is highly corroded.

Images (c) confirm that in the presence of 250 ppm of PVA and 25 ppm of Zn^{2+} at pH 11in well water, the rate of corrosion is suppressed , as it seen from the decrease in corroded areas. This is a result of the formation of insoluble complex on metal surface (PVA - Al^{3+}) and the surface is covered by a thin layer of inhibitors which effectively controls the dissolution of aluminium metal from corrosion process. The above results are line with the interpretation made by.[29,30]

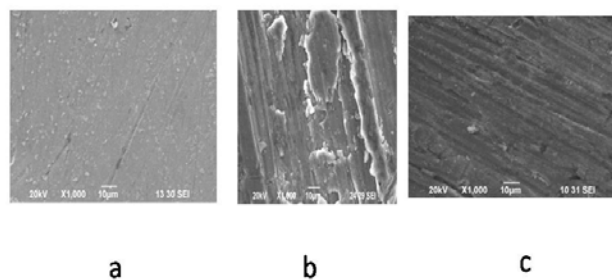a   b   c

Figure 5. SEM micrographs of (magnification the surface of the polished aluminium (x1000) of a) polished aluminium metal b) aluminium immersed in well water c) aluminium immersed in well water + 250 ppm of PVA and 25 ppm of Zn^{2+}

Mechanism of corrosion inhibition

The weight – loss reveals that the formation of aluminium immersed in solution containing 250 ppm of PVA and 25 ppm of Zn^{2+} offers 95 % IE at pH 11. A synergistic effect exist between PVA and Zn^{2+}. AC impedance spectra reveal

that a protective film formed on the metal surface also it confirmed by FTIR spectra. SEM showed the surface morphology of metal surface.

The mechanism of corrosion inhibition was proposed by the following ways:

When the formulation consisting of 250 ppm of PVA and 25 ppm of Zn^{2+} at pH 11 was prepared, there is formation of PVA - Zn^{2+} complex in solution.

When aluminium is immersed in the solution, the PVA - Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface.

On the surface of metal PVA - Zn^{2+} complex is converted to PVA - Al^{3+} complex and Zn^{2+} is released.

$$[PVA - Zn^{2+}] + Al^{3+} \rightarrow [PVA - Al^{3+}] + Zn^{2+}$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$$
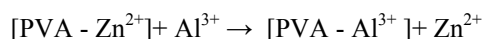
Conclusion

The formulation consisting of 250 ppm of PVA and 25 ppm of Zn^{2+} offers 85 % inhibition efficiency to aluminium immersed in solution at pH 11 by the weight-loss method. A synergistic effect exists between PVA and Zn^{2+}. AC impedence study showed that a protective film formed on metal surface. FTIR spectra analysed the film formed on the metal surface.

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