

Polyvinyl Alcohol – Sodium Nitrite Water Soluble Composite as a Corrosion Inhibitor for Mild Steel in Simulated Cooling Water

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Abstract

The inhibitive action of polyvinyl alcohol –sodium nitrite (PVASN) composite on the corrosion of mild steel in simulated cooling water (SCW) has been investigated by weight loss and potentiodynamic polarization. The effect of composite concentration (PVA/SN) , pH, and exposure time on corrosion rate of mild steel were verified using 2 levels factorial design and surface response analysis through weight loss approach, while the electrochemical measurements were used to study the behavior of mild steel in (SCW) with pH between 6 and 8 and in absence and presence of (PVA) in solution containing different concentration of NaNO_2 . It was verified that all three main variables studied were statistically significant while their interaction is less pronounced.

Key Words

Corrosion, Polyvinyl alcohol, Electrochemical Measurements, Weight loss method, Polarization Resistance, Factorial Design

Introduction

Valuable metals, such as mild steel, aluminum, copper and zinc are prone to corrosion when they are exposed to aggressive media (such as acids, bases ,and salt) [1]. Therefore, there is a need to protect these metals against corrosion. The best option available for the protection of metals against corrosion has been found to be using of inhibitors [2].

The control of corrosion in recirculating cooling system is achieved by maintaining relatively small quantities of corrosion inhibitors in the cooling water. Corrosion inhibitors retard the destruction of metals by chemical or electrochemical reactions with their environment. Most of the inhibitors used in cooling water,

are either alone or in combination with one or more other corrosion inhibitors [3]. The open recirculating system, with longer holding times at higher temperatures in the presence of higher dissolved solids concentrations, produces more sever corrosion, scaling, microbiological growth [4].

Many inhibitors have been used in cooling water systems to solve these problems [5]. Particularly, chromates and many other metals. However, the popularity of inhibitors containing heavy metals are diminishing, because of the concern over their toxic effects on aquatic and possibly animal life [6].

As a result, the current trend for inhibitor usage towards more environmentally friendly ‘green’ chemicals. The objective of this study

was to develop environmentally acceptable multi-component inhibitors that inhibit corrosion.

Experimental Method

1. Material

The working electrodes (1.99 x 0.99Cm) used were made from carbon steel of 2 mm thickness. Its composition was: (C= 0.06-0.18, Mn= 0.27-0.63, P= 0.035, S= 0.035, Si= 0.025).

2. Solution

The chemical composition of water solution used throughout the experiment was as given in table (1):

Table1, Component and Concentration ions of cooling water

Component	Concentration, ppm
Na ⁺	441
Cl ⁻	303
SO ₄ ⁻²	352
HCO ₃ ⁻	123
CO ₃ ⁻²	37

The test solution was prepared by dissolving 500 ppm NaCl, 520 ppm Na₂SO₄, 170 ppm anhydrous NaHCO₃, and 66 ppm Na₂CO₃ in one liter of distilled water. Inhibitor solution was prepared by dissolving appropriate amount of (PVASN) in the SCW. The pH of the solution was adjusted by using dilute solutions of NaOH or HCl.

3. Weight Loss Method

The coupons were smoothed by emery paper, rinsed, dried with benzene, acetone and weighed on a digital scale. Each of the coupon was designated and its initial weight was recorded. After each test, the specimen was washed with running tap water,

scrubbed with a brush to remove corrosion products, then washed with tap water followed by distilled water and dried on clean tissue, immersed in benzene, dried, immersed in acetone, dried and left in a desiccator over silica gel for one hour before weighting to the 4th decimal.

4. Polarization Technique

The electrochemical cell was composed of platinum counter electrode, prepared mild steel specimen as working electrode and saturated calomel electrode (SCE) as a reference electrode. The corrosion potential (E_{corr}) was measured against SCE. The corrosion cell parts were joined to each other, then connected to potentiostat, ammeter and voltmeter. Starting with cathodic polarization until reaching the corrosion potentials, then continuing with anodic polarization. The potential was changed (20-25mV) for each step after one minute period the current was recorded.

Results and Discussion

1. Weight Loss Method

Table (2) represents the low and high levels factor, the matrix of the factorial design and results are shown in tables (3 and 5) representing the three types of synthetic cooling water with increasing concentration factor respectively.

Table 2, Original variable

Main variable	Original variable	Low level -1	High level +1
pH	X1	6	8
PVASN, ppm	X2	1000/250	2000/500
Exposure time, hr	X3	24	48

Table 3, 2³ Factorial design experiments with 2 levels for first concentration factor cooling water (SCW1)

No.	pH	PVASN	Time	Corrosion rate(gmd)
1	-1	-1	-1	6.7253
2	-1	+1	-1	3.3657
3	+1	-1	-1	4.3555
4	+1	+1	-1	1.7429
5	-1	-1	+1	9.7533
6	-1	+1	+1	5.4087
7	+1	-1	+1	7.2655
8	+1	+1	+1	2.9987

Table 4, 2³ Factorial design Experiments with 2 levels for second concentration factor cooling water (SCW2)

No.	pH	PVASN	Time	Corrosion rate(gmd)
1	-1	-1	-1	6.2379
2	-1	+1	-1	2.9363
3	+1	-1	-1	4.096
4	+1	+1	-1	1.5081
5	-1	-1	+1	9.3688
6	-1	+1	+1	4.7723
7	+1	-1	+1	6.5961
8	+1	+1	+1	2.7599

gmd=gm/m².dayTable 5, 2³ Factorial design Experiments with 2 levels for third concentration factor cooling water (SCW3)

No.	pH	PVASN	Time	Corrosion rate(gmd)
1	-1	-1	-1	5.8354
2	-1	+1	-1	2.6618
3	+1	-1	-1	3.8912
4	+1	+1	-1	1.064
5	-1	-1	+1	8.7308
6	-1	+1	+1	4.5734
7	+1	-1	+1	6.1797
8	+1	+1	+1	2.3656

The results were analyzed using the analysis of variance (ANOVA) as appropriate to experimental design used. The regression equations obtained for the three types mentioned after analysis of variance gives the levels of corrosion rates of mild steel as function of different variables: pH, PVA/NaNO₂ ratio, and time of exposure.

All terms regardless of their significance are included in the

following equations for SCW1, SCW2, and SCW3 respectively:

$$Y_1 = 5.2 - 1.11X_1 - 1.82X_2 + 1.15X_3 + 0.1X_1X_2 - 0.115X_1X_3 - 0.33X_2X_3 \dots(1)$$

$$Y_2 = 4.78 - 1.045X_1 - 1.79X_2 + 1.09X_3 + 0.185X_1X_2 - 0.15X_1X_3 - 0.31X_2X_3 \dots(2)$$

$$Y_3 = 4.41 - 1.04X_1 - 1.97X_2 + 1.05X_3 + 0.087X_1X_2 - 0.153X_1X_3 - 0.245X_2X_3 \dots(3)$$

Where Y_i is the response, that is corrosion rate of mild steel, and X_1 , X_2 , and X_3 are the coded values of the test variables, pH, PVA/NaNO₂ ratio, and exposure time respectively.

According to equations 1, 2, and 3:

1. The main factors, pH, and the ratio of PVA/NaNO₂ have negative effects in all types of synthetic cooling water (i.e., decreases the corrosion rate) regardless of increasing the concentration factor from 1 to 3. Keeping in mind that the ratio of PVA/NaNO₂ to be more pronounced in decreasing the corrosion rate than the pH.

2. The main factor, exposure time, have positive effect in all types of synthetic cooling water (i.e., increasing the corrosion rate), and its effect is almost the same regardless increasing the concentration factor.

2. Polarization Technique

Electrochemical cell was composed of platinum counter electrode, prepared mild steel specimen as working electrode and saturated calomel (SCE) as a reference electrode.

2.1. Open Circuite Potential

Open circuit potential measurements were carried out for different types of synthetic cooling waters in absence and presence of NaNO₂ as corrosion

inhibitor. It is apparent from fig. 1 through 3 that the open circuit potential of pure (blank) cooling water in the absence of inhibitor (i.e., NaNO_2) decreases rapidly with time and finally reaches a steady state value. This variation of open circuit potential with time reveals the corrosivity of water on mild steel. However, in presence of NaNO_2 corrosion inhibitor, the steady state potential is shifted more towards the noble direction by increasing the concentration of inhibitor. The effect of mixtures of constant concentration of NaNO_2 and different concentration of PVA on the steady state potential was investigated as shown in figures 1 through 3. It is quite obvious that these mixtures exhibit a pronounce effect on the steady state towards the noble potential compared to pure NaNO_2 solution which shows a significant effect on the steady state potential shifted to more positive potential. This shifting explains the anodic nature of inhibitor and reveals the inhibiting of anodic reaction more than the cathodic one.

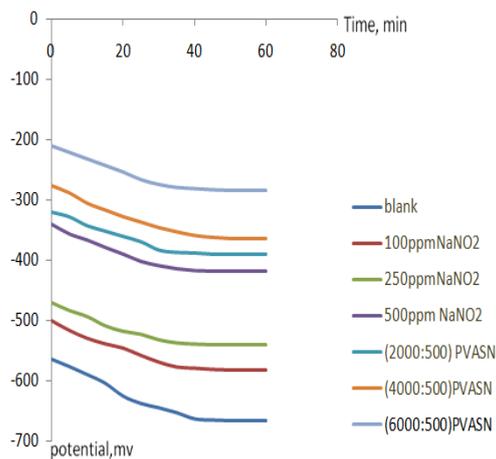


Fig.1, The relation between Potential and time for mild steel in SCW1 in the absence and presence of different concentrations of NaNO_2 and with polyvinyl alcohol

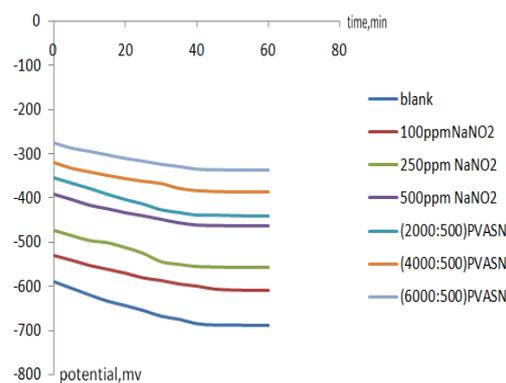


Fig.2, The relation between Potential and time For mild steel in SCW2 in the absence and presence of different concentrations of NaNO_2 and with polyvinyl alcohol

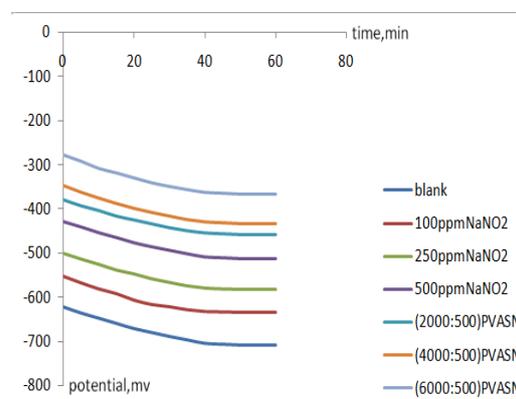


Fig.3, The relation between Potential and time for mild steel in SCW3 in the absence and presence of different concentrations of NaNO_2 and with polyvinyl alcohol

2.2. Electrochemical Polarization Studies

The corrosion of steel in water is an electrochemical process, and therefore does not obey ohm's law $V = I R$. However, Stern and Geary showed theoretically that ohm's law holds approximately if the polarization of the corrosion interface is constrained to be within $-30, +30$ mv of the rest potential. This investigation studies the extent to which the techniques "Linear Polarization Resistance", LPR, and "Tafel extrapolation method" can be applied in order to obtain representative values of the corrosion rate in synthetic cooling water environment.

The polarization behavior of mild steel in synthetic cooling water SCW1, SCW2, and SCW3 in presence and absence of inhibitor are shown in fig. 4 through 9 respectively.

The electrochemical behavior of mild steel in simulated cooling water using polarization technique through monitoring the corrosion rates by Linear Polarization Resistance technique and Tafel Extrapolation method are shown in fig. 10 and 11 respectively.

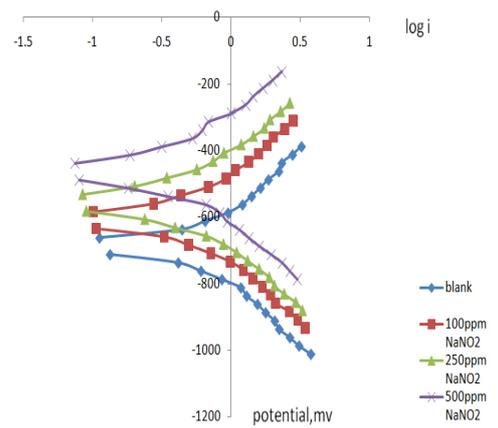


Fig.6, Polarization curves of low carbon steel in SCW2 in presence of NaNO₂ only

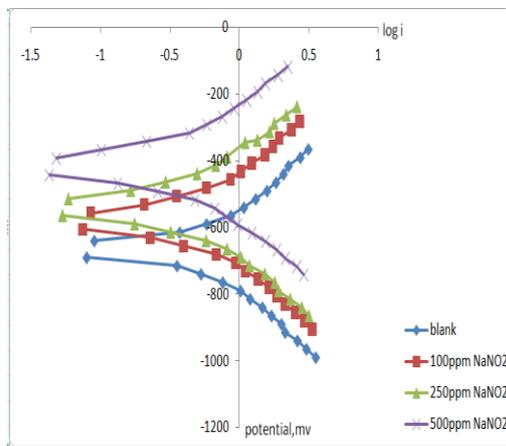


Fig.4, Polarization curves of low carbon steel in SCW1 in presence of NaNO₂ only

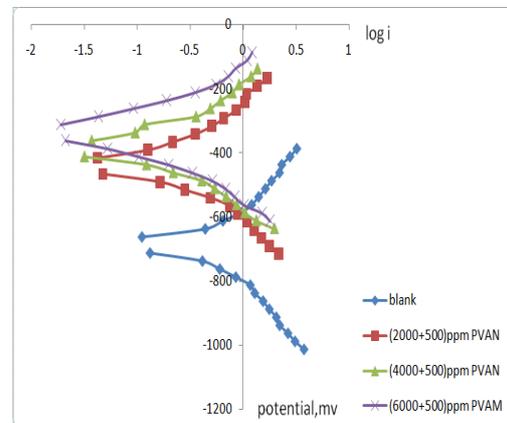


Fig.7, Polarization curves of low carbon steel in SCW2 in presence of composite

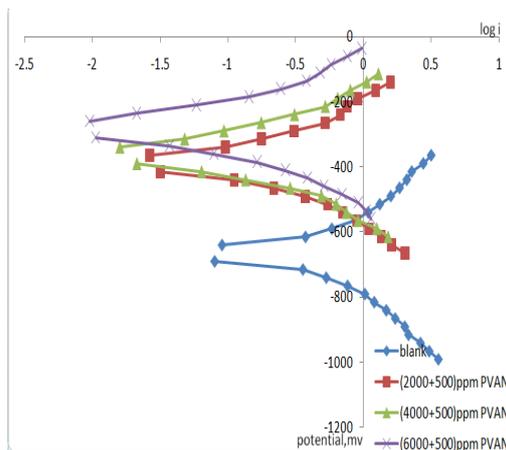


Fig.5, Polarization curves of low carbon steel in SCW1 in presence of Composite

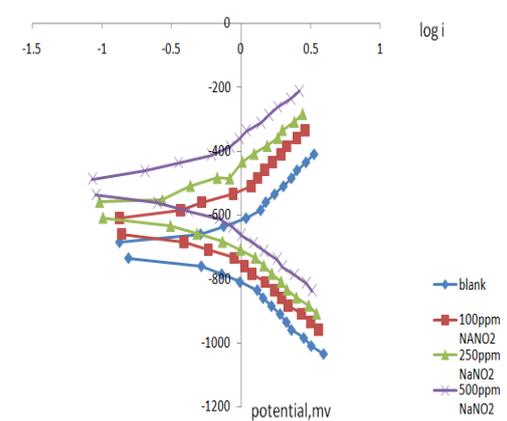


Fig.8, Polarization curves of low carbon steel in SCW3 in presence of NaNO₂ only

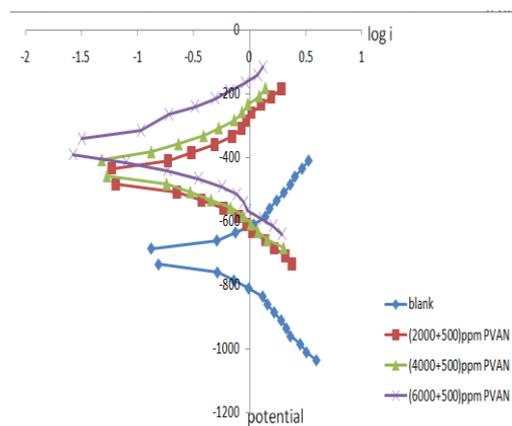


Fig.9, Polarization curves of low carbon steel in SCW2 in presence of composite

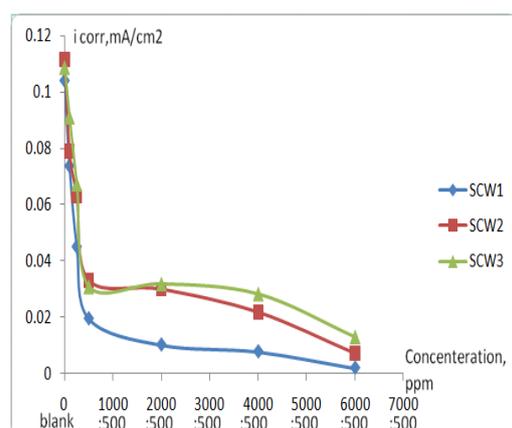


Fig.10, The relation between PVA/SN ratio and i_{corr} in different synthetic cooling water as calculated by resistance polarization approach

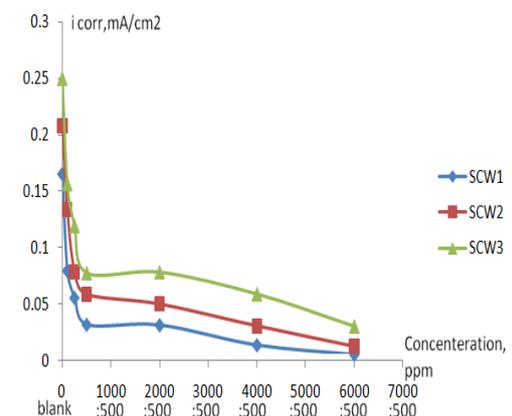


Fig.11, The relation between PVA/SN ratio and i_{corr} in different synthetic cooling water as calculated by Tafel approach

Also, it is evident from fig. 12 and 13 that the inhibition efficiency increases

with increase in inhibitor concentration in all SCW's under investigation.

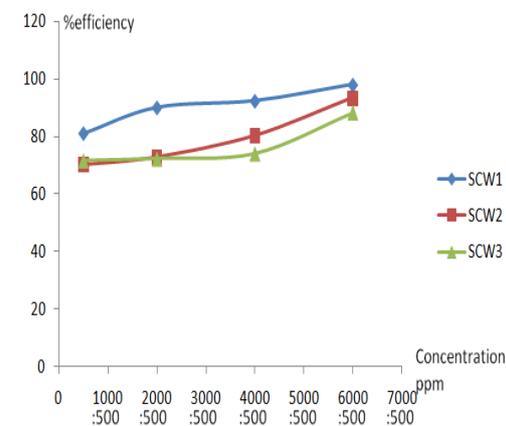


Fig.12, The relation between Inhibitor efficiency and PVA/SN ratio in different synthetic cooling water using resistance polarization method

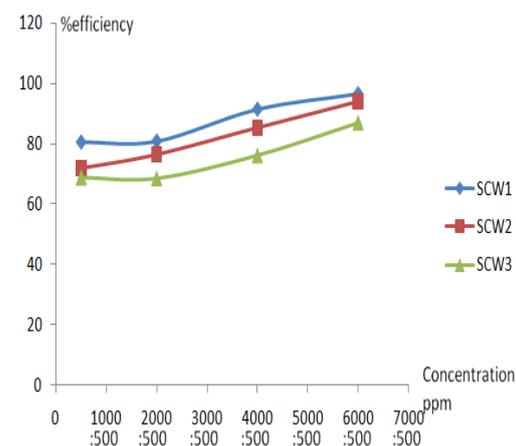


Fig.13, The relation between Inhibitor efficiency and PVA/SN ratio in different synthetic cooling water using Tafel method

2.3. Adsorption Studies

The fractional dependence of the surface covered, θ , at the concentration, c , of the inhibitor, was tested graphically by fitting it to Langmuir Isotherm, which assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. Fig. 14 and 15 show linear plots for c/θ versus c . with $R^2= 0.993$ for NaNO_2 alone and $R^2= 0.996$ for different concentration of PVA in

synthetic cooling waters under investigation.

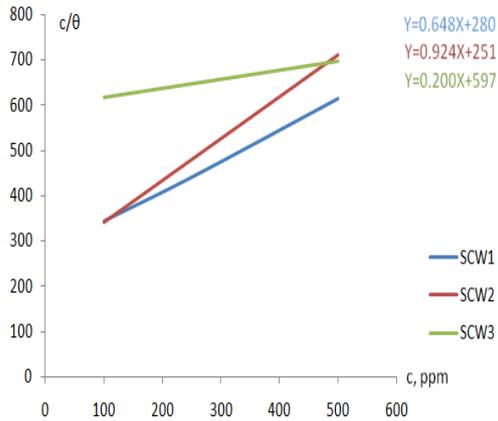


Fig.14, The relation between c/θ and c , inhibitor concentration of NaNO_2 in synthetic cooling waters

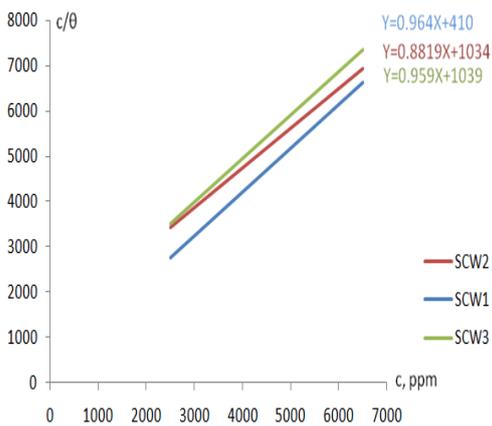


Fig.15, The relation between c/θ and c , blend of inhibitor PVASN ratio in synthetic cooling waters

Conclusions

1. The inhibition action of PVASN ratio increase with increase of inhibitor concentration and the pH.
2. Increasing the blend inhibitor concentration (PVASN) leads the open circuit potential to increase to more noble value, indicating the anodic nature of the blend used.
3. Statistically, the interaction effect of the variables in multi-variable regression was found to be insignificant.
4. On the basis of Gibbs free energy experimentally observed,

physiosorption mechanism has been proposed for the inhibition action of the inhibitor blend through Langmuir isotherm.

References

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