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RESEARCH ARTICLE

The Inhibition Effect of Corrosion of Carbon Steel in Seawater by Diethylene Triamine Pentamethylene Phosphonic Acid and Al^{3+} System

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Abstract: The inhibition of the corrosion of carbon steel in seawater by diethylene triamine pentamethylene phosphonic acid (DTPMP) and Al^{3+} has been investigated using weight loss and electrochemical measurements. The results show that 65% inhibition efficiency is achieved with binary system consisting of 250 ppm of DTPMP and 50 ppm of Al^{3+}. Polarization curves indicate that the system is a mixed inhibitor. The surface morphology of the metal surface is examined using the scanning electron microscope.

Keywords: Corrosion inhibition, Carbon steel, Seawater, SEM

Introduction

Corrosion is the gradual destruction of material, usually metal, by chemical reaction with its environment. Seawater is a complex natural electrolyte. Because corrosive natural electrolytes exist abundantly in seawater, carbon steel under seawater is eroded gradually by means of chemical reactions[1-3]. The corrosion is severe due to the presence of chloride ions and dissolved oxygen. Carbon steel is widely used in infrastructure in marine environments[4]. It is also used in industry where the metal is exposed to acid corrosion. So, it is imperative to study the corrosion aspect and find out suitable corrosion inhibitors to be used in seawater. Several phosphonic acids have been used as corrosion inhibitor[5-7]. Phosphonic acids are organic compounds containing $R\text{-}PO(OH)_2$ or $R\text{-}PO(OR)_2$ groups. They are effective chelating agents that are used in cooling water and desalination systems to inhibit scale formation and corrosion. Phosphonic acids are extensively used now-a-days due to their complex-forming abilities, high stability under harsh conditions and low toxicity**.** The inhibition efficiency of phosphonates depends on the number of phosphono groups in a molecule and also on different substituents.

The present work have been focused to explore the following aspects; a) to find out the corrosion inhibition effects of diethylene triamine pentamethylene phosphonic acid (DTPMP) and Al^{3+} system on carbon steel in seawater medium using weight-loss method; b) electrochemical techniques provide information on the corrosion rate, as well as on processes at interfaces affected by additives; c) to study the surface morphological changes during iron corrosion by Scanning Electron Microscopy (SEM); d) to propose a suitable mechanism of corrosion inhibition based on the results from the above studies.

Experimental

Carbon steel specimen (0.0267% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to mirror finish and degreased with trichloroethylene.

Weight loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Al^{3+} for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleaned with Clarke's solution[8]. The inhibition efficiency (IE) was then calculated using the equation:

$$IE = 100\,[1- (W_2/W_1)]\ \%$$

Where W_1 is the weight loss value in the absence of inhibitor and W_2 is the weight loss value in the presence of inhibitor.

Polarization study

Polarization studies were carried out with a CHI-electrochemical workstation with impedance model 660A. A three-electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

Scanning electron microscopic studies (SEM)

The carbon steel samples immersed in blank solution and in the inhibitor solution for a period of one day were removed, rinsed with double distilled water, dried and observed under a scanning electron microscope to examine the surface morphology. The surface morphology measurements of carbon steel were examined using JEOL-MODEL 6390 computer-controlled scanning electron microscope.

Results and Discussion

Weight loss method

Table 1 gives values of the corrosion inhibition efficiencies and the corresponding corrosion rates of diethylene triamine pentamethylene phosphonic acid (DTPMP) - Al^{3+} in controlling corrosion of carbon steel in seawater for a period of 24 hours. The DTPMP alone has high rate of corrosion. The inhibition efficiency of DTPMP is improved by adding various concentrations of Al^{3+}. Similar observations have been made by Umamathi *et al.*[9] where they have improved the inhibition efficiency of Na_3PO_4 on EDTA by addition of Zn^{2+} ion. Mary Anbarasi *et al.*[10] have improved the inhibition efficiency of heptane sulphonic acid by addition of Zn^{2+} ion. However, with increasing the concentration of DTPMP as well as Al^{3+}, the maximum inhibition is achieved and the corrosion rate is decreased. It is found that 250 ppm of DTPMP and 50 ppm of Al^{3+} has 65% inhibition efficiency. The inhibition efficiency increases with the increase of concentration of inhibitors.

Table 1. The inhibition efficiency (IE%) and the corrosion rate (mm/y) of DTPMP – Al^{3+} system are determined by weight loss method

DTPMP ppm	Al^{3+}, ppm					
	0		25		50	
	IE, %	CR, mm/y	IE, %	CR, mm/y	IE, %	CR, mm/y
0	-	0.1858	6	0.1747	12	0.1635
50	20	0.1486	38	0.1152	51	0.0910
100	28	0.1338	44	0.1040	54	0.0855
150	39	0.1133	48	0.0966	59	0.0762
200	46	0.1003	50	0.0929	62	0.0706
250	50	0.0929	53	0.0873	65	0.0650

Potentiodynamic polarization study

Polarization study has been used to detect the formation of protective film on the metal surface[11,12]. The polarization curves of carbon steel immersed in various test solutions are shown in Figure 1. It shows that there is a clear reduction of both anodic and cathodic currents in the presence of DTPMP and Al^{3+} compared with those for the blank solution. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (b_c and b_a) and linear polarization resistance (LPR) are given in Table 2.

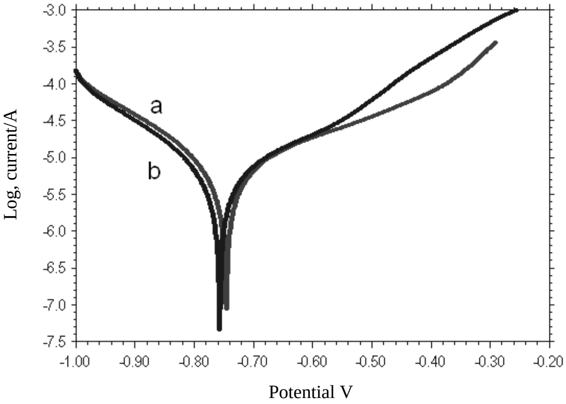


Figure 1. Polarization curves of carbon steel immersed in; a) seawater; b) seawater + DTPMP 250 ppm + Al^{3+} 50 ppm

Table 2. Corrosion parameters of carbon steel immersed in seawater in the presence and absence of inhibitor obtained by polarization method

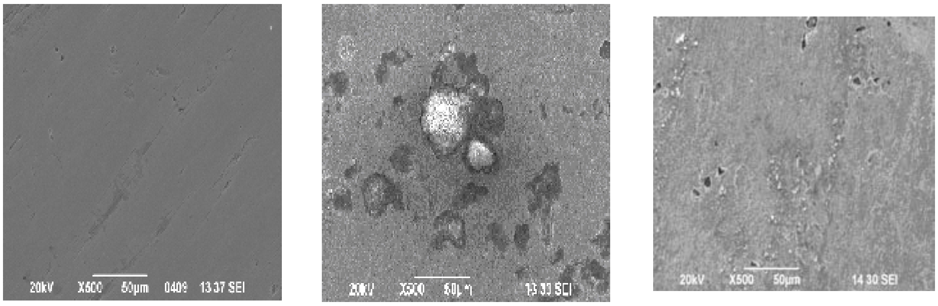
Systems	E_{corr} mV Vs SCE	I_{corr} A/cm^2	b_a mV/dec	b_c mV/dec	LPR ohm cm^2
Seawater	-746	6.351×10^{-6}	228	157	6.356×10^3
Seawater + DTPMP (250 ppm) + Al^{3+}(50 ppm)	-757	5.668×10^{-6}	215	155	6.916×10^3

When carbon steel is immersed in seawater, the corrosion potential is -746 mV *vs.* SCE. The formulation consisting of 250 ppm DTPMP + 50 ppm Al^{3+} shifts the corrosion potential to -757 mV *vs.* SCE. The corrosion potential shift is very small. This suggests that the DTPMP – Al^{3+} formulation functions as a mixed inhibitor controlling the anodic reaction and cathodic reaction to the same extent. This is further confirmed from the shifts in the anodic slope (228 to 215 mV/ dec^{1}) and in the cathodic slope (157 to 155 mV dec); they are nearly equal indicating that this system acts as a mixed inhibitor.

The corrosion current value and LPR value for seawater are 6.351x10^{-6} A/cm^{-2} and 6.356x10^{3} ohm cm^{2}. For the formulation of 250 ppm of DTPMP and 50 ppm of Al^{3+}, the corrosion current value has decreased to 5.668x10^{-6} A/cm^{-2} and the LPR value has increased to 6.916x10^{3} ohm cm^{2}. The fact that the LPR value increases with decrease in corrosion current indicates adsorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate with the formation of a protective film on the metal surface.

SEM investigation

The scanning electron micrographs of carbon steel are shown in Figure 2. The SEM micrograph of polished carbon steel surface (control) is shown in Figure 2a. This shows the smoothness of the metal surface. This implies the absence of any corrosion product formed on the metal surface. The SEM micrograph of carbon steel immersed in seawater is shown in Figure 2b. This shows the roughness of the metal surface by the corrosive environment and the porous layer of corrosion product is present. Pits are observed on the metal surface. Figure 2c shows that the presence of 250 ppm of DTPMP and 50 ppm of Al^{3+} in seawater gives the formation of thick films on the carbon steel surface. This may be interpreted as due to the adsorption of the inhibitor on the metal surface incorporating into the passive film in order to block the active site present on the carbon steel surface[13,14].



a b c

Figure 2. SEM micrographs (magnification-x500) of; a) polished carbon steel (control); b) carbon steel immersed in seawater; c) carbon steel immersed in seawater containing 250 ppm of DTPMP and 50 ppm of Al^{3+}

Mechanism of corrosion inhibition

In order to explain the above results, the following mechanism of corrosion inhibition is proposed: When carbon steel is immersed in an aqueous solution, the anodic reaction is,

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

The corresponding cathodic reaction is reduction of oxygen to hydroxyl ions,

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

When the formulation consists of 250 ppm of DTPMP and 50 ppm Al^{3+} in seawater, there is formation of DTPMP – Al^{3+} complex in solution.

When carbon steel is immersed in this environment, the DTPMP – Al^{3+} complex diffuses from the bulk of the solution to the metal surface. The DTPMP – Al^{3+} complex is converted into DTPMP – Fe^{2+} complex on the anodic sites of the metal surface, the stability of Fe^{2+} – DTPMP complex is higher than the corresponding Al complex.

$$Al^{3+} - \text{DTPMP} + Fe^{2+} \rightarrow Fe^{2+} - \text{DTPMP} + Al^{3+}$$

The released Al^{3+} combines with OH^- to form $Al(OH)_3$ on the cathodic sites of the metal surface.

$$Al^{3+} + OH^- \rightarrow Al(OH)_3$$

Thus, the protective film consists of Fe^{2+} – DTPMP complex and $Al(OH)_3$.

Conclusion

The conclusions drawn from the results may be given as the formulation consists of 250 ppm of DTPMP and 50 ppm of Al^{3+} has 65% IE. Polarization study suggests that the system is a mixed inhibitor. SEM micrographs confirm the formation of protective layer on the metal surface.

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