RESEARCH PAPER | Chemistry | Volume : 3 | Issue : 10 | Oct 2013 | ISSN - 2249-555X

Corrosion Inhibition of Aluminium by Diethylene Triamine Pentamethylene Phosphonic Acid

KEYWORDS: Corrosion inhibition, aluminium, DTPMP, FTIR

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ABSTRACT *The inhibition efficiency (IE) of DTPMP in controlling corrosion of aluminium in an aqueous solution at pH3 in the presence and absence of Zn^{2+} has been evaluated by mass loss method. The formulation consisting of 200 ppm DTPMP and 10 ppm Zn^{2+} offers 98% inhibition efficiency to aluminium in an aqueous solution at pH3. A synergistic effect exists between DTPMP and Zn^{2+}. Polarization study reveals that this formulation controls the anodic reaction predominantly. FTIR spectra reveal that the protective film consists a complex formed between the DTPMP- $A1^{3+}$.*

Introduction
Aluminium has a great economic and industrial importance owing to its low cost, light weight and high thermal and electrical conductivity. An important feature of aluminium is its corrosion resistance due to the formation of a protective film on its surface upon exposure to the atmosphere or aqueous solutions(eg.,Brett,1992). Hydrochloric acid and sulphuric acid solutions are used for pickling of aluminium or for its chemical or electrochemical etching. It is very important to add a corrosion inhibitor to decrease the rate of aluminium dissolution in such solutions. Organic inhibitors are often used to protect metallic materials against corrosion in acidic as well as in alkaline media. It is generally agreed that chemisorption of organic molecules can lead to corrosion inhibition either by physically blocking the surface active sites or by retarding the electrochemical reactions.

The addition of organic and inorganic compounds increase the corrosion inhibition efficiency. Water soluble carboxylic acids have been used as corrosion inhibitor. Choi, Kim & You (2002), used a new all organic multi-component inhibitor blend composed of citric acid /phosphonates (hydroxy ethylidene diphosphnic acid, HEDP)/acrylate copolymer/ isothiozolone.

Experimental methods
Preparation of the aluminium specimens

Commercial aluminium specimens of dimensions 1.0x4.0x0.2 cm^3 containing 95% pure aluminium were polished to mirror finish, degreased with trichloroethylene, and used for the mass-loss method and for surface examination studies.

Mass-loss Method
Three aluminium specimens were immersed in 100ml of the solution containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} for a period of one day at pH3.
The weight of the specimen before and after immersion was determined using Shimadzu balance AY62. Inhibition efficiency (IE) was calculated from the relationship.

$$IE = 100\ [1-(W2/W1)]\%$$

WhereW1 and W2 are the corrosion rates in the absence and presence of the inhibitor, respectively.

Potentiodynamic polarization study

Polarization study was carried out in an H and CH electrochemical work station impedance analyser model CHI 660A. A three electrode cell assembly was used. Aluminium was used as working electrode, platinum as counter electrode and saturated calomel electrode(SCE) as reference electrode. The corrosion parameters such as linear polarization resistance(LPR), corrosion potential, Ecorr , corrosion current, Icorr and tafel slopes (ba and bc) were measured.

FTIR Spectra

The film formed on the metal surface was carefully removed and mixed thoroughly with KBr. The FTIR spectra were recorded in a Perkin Elmer 1600 spectrophotometer.

Analysis of the results of mass loss method

The values of IE for different concentration of DTPMP in the absence and presence of Zn^{2+} in an aqueous solution at pH3 for a period of one day obtained from the mass loss method are given in Table 1.
It is found that DTPMP alone has some IE. It increases as the concentration of DTPMP increases. As the concentration of Zn^{2+} increases, a synergistic effect exists between DTPMP and Zn^{2+}. For example, 200ppm of DTPMP has 67% IE. 10ppm of Zn^{2+} has 10% IE .However, interestingly the formulation consisting of 200ppm of DTPMP and 10ppm of Zn^{2+} has 98% IE (ie) mixture of inhibitors shows better inhibition efficiency than the individual inhibitors (eg. Guo, Hu, Huang & Song, 2011).In presence of Zn^{2+} more amount of DTPMP is transported towards the metal surface. On the metal surface Al^{3+} - DTPMP complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is controlled.

The result of cathodic reaction is the generation of OH^- , which is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus the anodic and cathodic reactions are controlled effectively. This accounts for the synergistic effect existing between Zn^{2+} and DTPMP.

Table 1.Inhibition efficiency (IE%) obtained from DTPMP-Zn^{2+} system, when aluminium is immersed in an aqueous solution at pH3
Inhibitor system : DTPMP-Zn^{2+}
Immersion period:1 day

DTPMP	Zn^{2+}(ppm)				
	0	5	10	25	50
	IE(%)	IE(%)	IE(%)	IE(%)	IE(%)
0	-	5	10	13	15
50	59	82	83	91	95
100	62	86	88	95	97

150	64	91	94	96	98
200	67	94	98	98	98
250	69	96	98	98	98

Analysis of potentiodynamic polarization study

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process. If a protective film is formed on the metal surface, the linear polarization resistance value (LPR) increases and the corrosion current value (Icorr) decreases.

The potentiodynamic polarization curves of aluminium immersed in an aqueous solution at pH3 in the absence and presence of inhibition are shown in Fig.1. When aluminium is immersed in an aqueous solution at pH3 the corrosion potential is 806 mV vs SCE. The formulation consisting of 200 ppm of DTPMP and 10 ppm of Zn^{2+} shifts the corrosion potential to -710 mV vs SCE ie the corrosion potential shifts to the anodic (noble) direction (from -806 mv to -710 mV). This suggests that anodic reaction is controlled predominantly, indicating that the dissolution of the metal is reduced , since more DTPMP is transported to the anodic sites in the presence of Zn^{2+}.Now, the shifts in the anodic and cathodic slopes can be compared (Fig.1) .Addition of 200 ppm of DTPMP and 10 ppm of Zn^{2+} to an aqueous solution at pH3 shifts the anodic slope value to a large extent ie from 219 to 171mV/dec. Thus the formulation of 200 ppm of DTPMP and 10ppm Zn^{2+} controls the anodic reaction predominantly and to some extent controls the cathodic reaction by the formation $Zn(OH)_2$ on the cathodic sites of the metal. The corrosion current for an aqueous solution at pH3 is 7.411x 10-7 A/cm^2.The corrosion current for formulation of DTPMP 200ppm)-Zn^{2+}(10 ppm) has decreased to 3.422 x 10-7 A/cm^2. The current of aluminium dissolution decreased significantly, indicating that the metal surface was passivated by the formed inhibitor layer. The passivity of aluminium is probably due to the formation of the DTPMP-Al^{3+} surface layer.It was discussed in the literature that the anodic action of phosphonic acids is mainly based on the formation of insoluble complexes at the anodic sites of the metal surface. This indicates that a protective film is formed on the metal surface. Further the LPR value increases from 6.332 x 104 ohmcm^2 to 1.158 x 105 ohmcm^2. While studying the corrosion behaviour of metals in artificial sweat and also by Kalanithi, Mary Anbarasi, Rajendran & Yesu Thangam, 2009 while studying inhibition of corrosion of carbon steel in dam water by sodiummolybdate -Zn^{2+} .

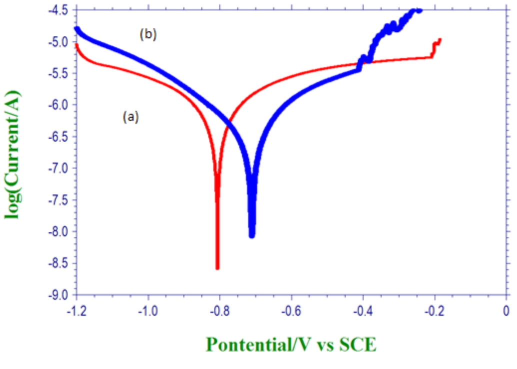

Fig.1. Polarization curves of aluminium immersed in various test solutions at pH3
a) Aqueous solution (blank)
b) Aqueous solution cointaining 200 ppm of DTPMP and 10 ppm of Zn^{2+}

Analysis of FTIR Spectra

FTIR spectrometer is a powerful instrument that is used to determine the type of bonding for organic inhibitors absorbed on the metal surface Lalitha, Rajeswari & Ramesh, 2005 & Soliman, 2011.

FTIR spectra have been used to analyze the protective film formed on a metal surface. FTIR spectrum (KBR) of pure DTPMP is given in Fig.2a. The CN stretching frequency occurs at 1111.95 cm^{-1} and that P-O stretching frequency appears at 1058.56 cm^{-1}. The FTIR spectrum of the film scratched from the surface of the metal immersed in an aqueous solution for one day containing 200 ppm of DTPMP and 10 ppm of Zn^{2+} at pH3 is shown in Fig.2b. It is seen from the spectrum that the C-N stretching frequency of DTPMP in the free state has shifted from 1111.95 cm^{-1} to 1226.42cm^{-1} and P-O stretching frequency of DTPMP in the free state has shifted from 1058.56 cm^{-1} to 1103.31 cm^{-1}. These shifts indicate that the N and O atoms are coordinate to form Al^{3+}-DTPMP complex on the anodic sites of the metal surface (Cross, 1990).The peak at 1370.24cm^{-1} is due to Zn-O stretching. The peak at 3428.73 cm^{-1} is due to OH stretching. Similar observations have been made by Manivannan & Rajendran (2011), while studying the IE of Succinic acid Zn^{2+} system. Thus the FTIR spectral studies lead to the conclusion that the protective film consists of Al^{3+} - DTPMP complex and Zn $(OH)_2$.

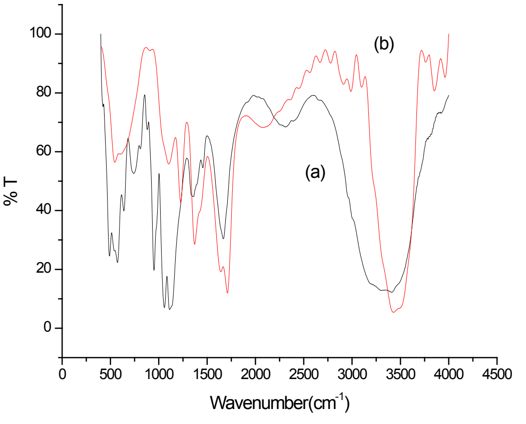

Fig.2. FTIR spectra Pure a) Pure DTPMP
b) Film formed on metal surface after immersion in an aqueous solution containing 200 ppm of DTPMP- 10 ppm of Zn^{2+}

Conclusion

The present study leads to the following conclusions

- The formulation consisting of 200ppm of DTPMP and 10ppm of Zn^{2+} offers 98% IE to aluminium immersed in an aqueous solution at pH3;
- Polarization study reveals that the composition of TSC (200ppm) - Zn^{2+} (10ppm) function as the anodic inhibitor;
- FTIR spectral reveals that a protective film formed on the metal surface.

Volume : 3 | Issue : 10 | Oct 2013 | ISSN - 2249-555X

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