

Inhibitive behaviour of derivative of organic compound in RO product water storage system

C. Thangavelu^{*1}, T. Asokan², T. Kasilingam³ and M. Sekar³

¹Department of Chemistry, Govt. Arts College for Women, Nillakkottai, Dindugul, TN, India

²Department of Chemistry, Govt. Arts College, Tiruchirappalli, TN, India

³Department of Chemistry, Periyar E.V. R. College (Autonomous), Tiruchirappalli, TN, India

ABSTRACT

The RO product water is more corrosive than the water produced by thermal distillation, Multistage Flash (MSF) evaporation and Multi Effect Desalination (MED) methods due to high TDS level, particularly chlorides. A study has been conducted to investigate the corrosion behaviour of aluminium in RO product water. Studies have been carried out in static conditions in the absence and presence of inhibitors system (phosphonate and zinc). Inhibition efficiency (I.E) has been calculated by total – immersion test. The possibility of formation of protective complex has been confirmed by UV – visible adsorption spectral study. Electrochemical methods like A.C. impedance and D.C. polarization have been used to confirm the protective film formation and the type of inhibition respectively.

Keywords: Total – immersion test, Electrochemical and Spectral studies

INTRODUCTION

Aluminium is a relatively soft, lightweight, ductile, durable and malleable metal with appearance ranging from silvery to dull gray, depending on the surface roughness. It is nonmagnetic and does not easily ignite. Corrosion of aluminium and its alloys has been a subject of frequent studies due to their high technological value and wide range of industrial and house hold applications. Aluminium and its alloys are good corrosion resistant materials in neutral aqueous solution, due to the formation of passive film. Many industries use aluminium as storage system for RO product water. Because of the acidic nature of RO product water, storage system undergoes corrosion.

Some of the methods employed to reduce corrosion of aluminium is application of sulphur, oxygen or nitrogen containing organic compounds as corrosion inhibitors to hinder corrosion reaction and thus reduce corrosion rate [1-4].

These organic compounds function by forming a protective adsorption layer on aluminium surface which isolates the corroding metal from action of corrodent. One of such methods is the use of the organic inhibitors [5–10]. Most organic inhibitors are substances with at least one functional group, which considered as the reaction centre in the adsorption process. The adsorption of inhibitors is related to the presence of heteroatom as nitrogen [11-17] phosphorus and sulfur [19-21]. Surfactants have also been used as inhibitors [22-25]. This paper reports the corrosion behaviour of commercial aluminium metal in RO product water and the inhibition of corrosion of aluminium by Amino Trimethylene Phosphonic Acid (ATMB) and Zn²⁺. Total – immersion test and electrochemical techniques were used.

MATERIALS AND METHODS

2.1 Total – immersion test (Classical Weight – loss method)

The weighed Al coupons in triplicate were suspended by means of glass hooks in 150 mL beakers containing 100 mL of various test solution in RO product water and the weight losses were measured after fifteen days at a temperature of 30^oC, in air atmosphere the masses of specimens before and after the immersion period were determined using a digital balance (model AUY 220 SHIMADZU). The molecular structure of ATMP show in Fig 1.

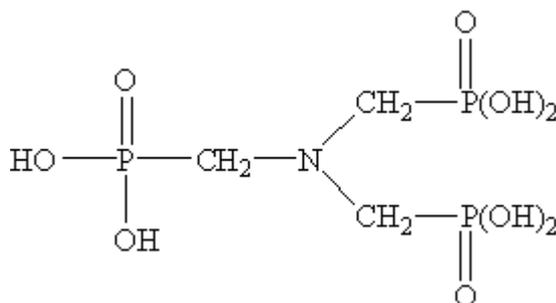


Fig 1. Molecular structure of ATMP

2.2 UV-visible absorbance spectra

The instrument model lambda 35 was used for recording UV-visible absorbance spectra.

2.3 Electrochemical studies

Both the potentiodynamic polarization studies and electrochemical impedance spectroscopic (EIS) studies were carried out using the electrochemical workstation model CHI- 760d and the experimental data were analysed by using the electrochemical software (Version: 12.22.0.0).

The measurements were conducted in a conventional three electrode cylindrical glass cell with platinum electrode as auxiliary electrode and saturated calomel electrode as reference electrode.

The working electrode was aluminium embedded in epoxy resin of polytetrafluoroethylene so that the flat surface of 1cm² was the only surface exposed to the electrolyte. The three electrodes set up was immersed in control solution of volume 100ml both in the absence and presence of the inhibitors formulations and allowed to attain a stable open circuit potential (OCP). The pH values of the solution were adjusted to 7.0 and the solutions were unstirred during the experiments.

Polarization curves were recorded in the potential range of -750 to -150 mV with a resolution of 2mV. The curves were recorded in the dynamic scan mode with a scan rate of 2mV s⁻¹ in the current range of -20mA to +20mA. The Ohmic drop compensation has been made during the studies. The corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) were obtained by extrapolation of anodic and cathodic regions of the Tafel plots.

Electrochemical impedance spectra in the form of Nyquist plots were recorded at OCP in the frequency range from 60 KHz to 10MHz with 4 to 10 steps per decade. A sine wave, with 10mV amplitude, was used to perturb the system. The impedance parameters viz., charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) were obtained from the Nyquist plots.

RESULTS AND DISCUSSION

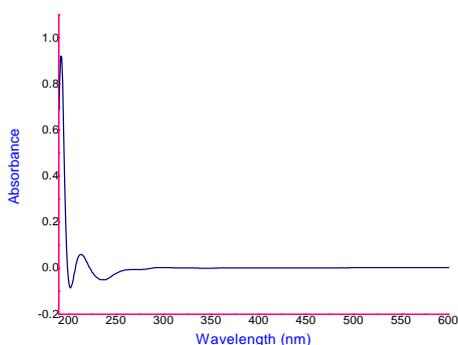
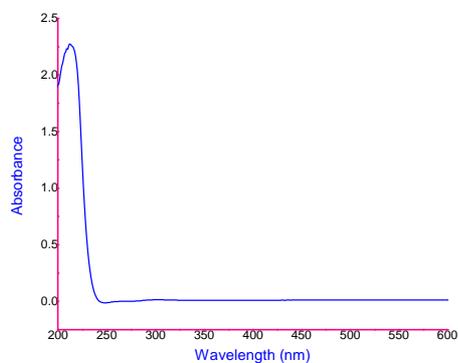
3. 1 Total – immersion test (Classical Weight – loss method)

Table1. Shows the data of total – immersion test, increase in concentration of inhibitor, decreases in inhibition efficiency of aluminium samples. The reduction in weight loss of Al samples as inhibitor in lower concentration may be attributed to adsorption of inhibitor on surface of Al and thereafter impede corrosion either by merely blocking reaction sites (anodic and cathodic) or by altering mechanism of anodic and cathodic processes. Suggests that inhibitor molecule were adsorbed at aluminium sample /solution interface where adsorbed species mechanically screen the coated part of aluminium surface from action of corrosive medium.

Table 1. Corrosion inhibition efficiencies of aluminium in RO product water in the presence and absence of inhibitor obtained by the total immersion test method. [Duration – 15 days]

S. No	Conc. of Zn ²⁺ (ppm)	Conc. of ATMP (ppm)	Inhibition efficiency (%)	Surface coverage (θ)
1	5	-	15	0.15
2	-	10	35	0.35
3	-	25	29	0.29
4	-	50	22	0.22
5	-	75	18	0.18
6	-	100	14	0.14
7	-	125	10	0.10
8	-	150	08	0.08
9	5	10	85	0.85
10	5	25	70	0.70
11	5	50	66	0.66
12	5	75	54	0.54
13	5	100	46	0.46
14	5	125	34	0.34
15	5	150	29	0.29

3.2 Analyses of UV-visible spectra

**Fig. 2a. UV-visible spectrum of 100ppm Al³⁺****Fig. 2b. UV-visible spectrum of 5ppm Zn²⁺+10ppmATMP + 100ppm Al³⁺**

A remarkable increase in absorbance is noticed in Fig. 2b compared to the Fig. 2a. These observations indicate that the possibility and formation of Zn²⁺ - ATMP complex and Al³⁺ - ATMP complex in bulk of the solution [26].

3.3 Potentiodynamic Polarization study

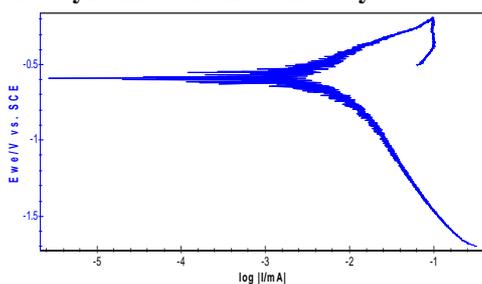
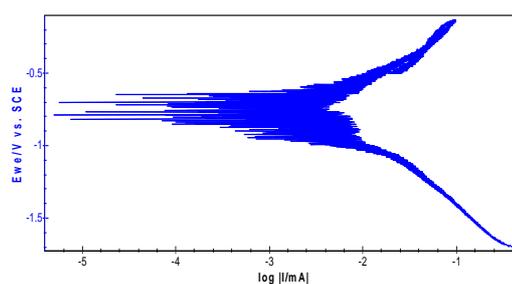
**Fig. 3a. Tafel curve of blank****Fig. 3b. Tafel curve of 5ppm Zn²⁺+10ppm ATMP**

Fig 3. (a & b) show polarization curves of Aluminium in RO product water in the absence and in the presence of inhibitor. It was found that the values of corrosion current density (I_{corr}) of aluminium in the presence of inhibitor were smaller than without addition of inhibitor (Fig. 2a). Furthermore, as presented in Fig.2b the addition of 5ppm Zn²⁺ + 10ppm ATMP shifts the corrosion potential (E_{corr}) value (from -535.960mV to -816.574mV) in studied inhibitor system. According to Ferreira and W.H. Li, if the displacement in corrosion potential is more than 85mV with respect to the corrosion potential of the blank, the inhibitor can be seen as cathodic or anodic type [27-28]. The maximum displacement was >85mV which indicated that the studied inhibitor system can be classified as cathodic inhibitor.

Table 2. The corrosion parameters of Tafel curves

S.No	Conc. of Zn ²⁺ (ppm)	Conc. of ATMP (ppm)	E _{corr} mV/SCE	I _{corr} μA/cm ²	β _a mV/SCE	β _c mV/SCE
1	Blank	-	-535.960	0.918	114.0	202.0
2	5	10	-816.574	0.0001	38.6	24.5

3.4 AC Impedance Spectral study

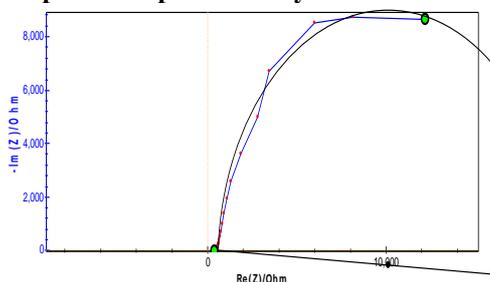


Fig. 4a. Nyquist plot of blank ATMP in RO product water

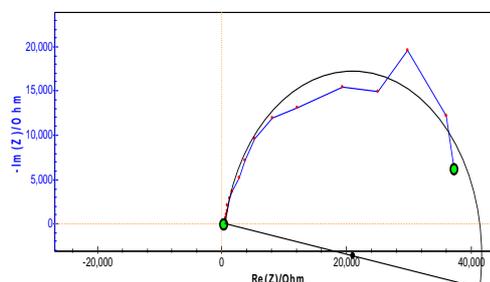
Fig. 4b. Nyquist plot of 5ppm Zn²⁺ + 10ppm ATMP

Fig 4 (a-b) shows in it is clear that the impedance curves are significantly changed with the presence of inhibitor. It is also found that from the Nyquist plot, even with the addition (or) absence of inhibitor does not alter the style of impedance curves, thus proposing a similar mechanism of inhibition is involved. It can be seen from the figure that the obtained Nyquist curves is due to the charge transfer process, mostly control the corrosion of aluminium. The low frequency inductive loop is owing to the growth and dissolution of the surface layer [29-30]. The impedance parameters derived from these plots are given in Table 3. As noted from Table3, the charge transfer resistance values (R_{ct}) substantially increased, and double layer capacitance (C_{dl}) decreased when 5ppm Zn²⁺ and 10ppm ATMP added as inhibitors.

Table 3. Corrosion parameters of Nyquist plots

S.No	Conc. of Zn ²⁺ (ppm)	Conc. of ATMP (ppm)	R _{ct} ohm cm ²	C _{dl} F.cm ² ×10 ⁻⁶
1	Blank	-	8046	17.67
2	5	10	19056	5.70

CONCLUSION

The following summarized main conclusions are drawn from the present study

- A formulation consisting of 5ppm Zn²⁺ and 10ppm ATMP can be used as a potent inhibitor to prevent corrosion of aluminium in RO product water storage system.
- The binary system ATMP (10ppm) - Zn²⁺(5ppm) is effective and has 85% IE.
- Significant synergism was attained by the combined application of Zn²⁺ -ATMP system
- The possibility of formation of complexes on Al metal surface is confirmed by UV- Visible Spectra
- Analyses of potentiodynamic polarization curve studies reveal that the formulation acts as a cathodic inhibitor.
- Analyses of impedance curve studies confirm the formation of protective film onto the aluminium metal surface.
- This new formulation is free from environmental hazards.

Acknowledgement

The author sincerely thanks University Grant Commission, New Delhi for its financial support to do this research project.

REFERENCES

- [1] M.N. Moussa, A.S. Fouda, A.T. Taha, A. Elnenaa. *Bulletin of the Korean Chemical Society*, **1998**, 9, 92–195.
- [2] L.M. Madkour, R.M. Issa, I.M. El-Ghrabawy. *J. chemical Research*, **1999**, 8, 408 - 409.
- [3] E.E. Ebenso, P.C. Okafor, O.E. Offiong, B.I. Ita, U.J. Ibok, U.J. Ekpe. *Bull. of Electrochemistry*, **2001**, 17(10), 459–464.
- [4] A. Aytac, U. Ozmen, M. Kabasakaloglu. *Mater. Chem. Phys.*, **2005**, 89(1), 176-181.
- [5] M. Hosseini, S.F.L. Mertens, M. Ghorbani, A.R. Arshadi, , *Mater Chem. Phys.***2003**, 78 , 800.
- [6] C. Küstü, C.K. Emregül, O. Atakol., *Sci.***2007**, 49 ,2800.
- [7] M.A. Quraishi, F.A. Ansari, D. Jamal, , *Mater. Chem. Phys.***2002**, 77 , 687.
- [8] R. Solmaz, G. Kardas, B. Yazici, M. Erbil, *Protec. Met.* **2005**,41 , 581.

- [9] F. Bentiss, M. Lebrini, H. Vezin, M. Lagrenee, , *Mater. Chem. Phys.* **2004**, 87, 18.
- [10] Shengtao Zhang, Zihua Tao, Weihua Li, Baorong Hou, *Appl. Surf. Sci.* **2009**, 255, 6757.
- [11] S.A. Ali, M.T. Saeed, S.U. Rahman, , *Corros. Sci.* **2003**, 45, 253.
- [12] S.M.A. Hosseini, A. Azimi, , *Corros. Sci.* **2009**, 51, 728–732
- [13] Z. Tao, S. Zhang, W. Li, B. Hou, , *Corros. Sci.* **2009**, 51, 2588.
- [14] Q.B. Zhang, Y.X. Hua, , *Electrochim. Acta* **2009**, 54, 1881.
- [15] M. Behpour, S.M. Ghoreishi, N. Soltani, M.S. Niasari, , *Corros. Sci.* **2009**, 51, 1073.
- [16] X. Li, S. Ding, H. Fu, , *Corros. Sci.* **2009**, 51, 1344.
- [17] S. Zhang, Z. Teo, W. Li, B. Hou, , *Appl. Surf. Sci.* **2009**, 255, 6757.
- [18] Y. Abboud, A. Abourriche, T. Saffajm M. Berrada, M. Charrouf, A. Bennamara, H. Hannache, , *Desalination* **2009**, 237, 175.
- [19] M.A. Qurashi, S.K. Shukla, *Phys. Mater. Chem.* **2009**, 113, 685.
- [20] G.E. Badr, , *Corros. Sci.* **2009**, 51, 2529.
- [21] C. Thangavelu, P. Patric Raymond, S. Rajendran, M. Sundaravadivelu. *Asian j. Research Chem.* **2011**, 4(3), 402-405.
- [22] A. A. El Maghraby, T. Y. Soror, *Advances in Applied Science Research*, **2010**, 1 (2): 156.
- [23] A. A. El Maghraby, T. Y. Soror, *Advances in Applied Science Research*, **2010**, 1 (2): 143.
- [24] M. Hany, L I. Abd El-Lateef, I. V. M. Aliyeva, T. I. Abbasov1, Ismayilov, *Advances in Applied Science Research*, **2012**, 3 (2):1185.
- [26] A. I. Babatunde, O. Ogundele, O. T. Oyelola and O. K. Abiola, *Advances in Applied Science Research*, **2012**, 3(6):3944-3949
- [27] E.S.Ferreira, C.Giacomellic, F.C.Giacomellic, and A.Spinelli, *Mater. Chem. Phys.* **2004**, 83(1), 129-134
- [28] W.H.Li, Q.He, C.L. Pei and B.R. Hou, *J. Appl. Electrochem*, **2008**, 38 (3), 289 – 295.
- [29] M.G.A.Khedr, M.S.Lashien, *Corros. Sci.* **1992**, 33, 137.
- [30] A.Sirajunisa, M.I.Fazal Mohamed and A.Subramania, *Der Chemica Sinica*, **2014**, 5(1), 148-156.