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RESEARCH ARTICLE

Inhibitive Nature of Carboxymethylcellulose with Zn^{2+} Ion

R. KALAIVANI[a*], P. THILLAI ARASU[b] and S. RAJENDRAN[c]

[a]Department of Chemistry, Manonmanium Sundaranar University, Thirunelveli-627132, India

[b]Department of Chemistry, Kalasalingam University, Srivilliputhur-626 126, India

[c]Department of Chemistry, RVS School of Engineering and Technology, Dindigul-624 005, India

vaniraj21@yahoo.com

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Abstract: Inhibition efficiency (IE) of carboxymethylcellulose in controlling corrosion of aluminium in well water at pH11 has been evaluated by weight loss method in the presence and absence of Zn^{2+} ion. The formulation consisting of 250 ppm of carboxymethylcellulose (CMC) and 25 ppm of Zn^{2+} has 95% inhibition efficiency. Polarisation study revealed that this formulation controls the cathodic reaction predominantly. AC impedance spectra revealed that a protective film is formed on the metal surface and the protective film was analysed by the technique of scanning electron microscope (SEM) and atomic force microscopy (AFM).

Keywords: Aluminium, Inhibition efficiency, Protective film, Metal surface, Polarisation study

Introduction

Corrosion is the deterioration of metals or alloys consequent loss of solid metallic material through chemical or electrochemical attack by environment at its surface[1]. Aluminium is the passivity metal. It oxidizes very quickly, the oxide layer is chemically bound to the surface of metal and it seals the core aluminium from any further reaction. The aluminium dipped in well water[2] at pH11, the film set dissolute in order to protect the aluminium from corrosion by using carboxymethylcellulose(CMC) as an inhibitor. carboxymehylcellulose is a polymer which possess adsorption site[3-10] and the anion part of the polymer tendency to form a bridge between the metal and cation related to its polarisability. Several inhibitors have been used to control corrosion of aluminium. Abdallah *et al.*[11] investigated the effect of polyamide compounds on the corrosion behaviour of aluminium in oxalic acid solutions using potentiostatic and potentiodynamic polarization techniques, Shukla *et al.*[12] reported that the mechanism of corrosion of aluminium by polyethylene glycol as corrosion inhibitor in acidic medium using weight loss method, potentiodymamic and galvanostatic polarization measurements. In aqueous alkaline media aluminium pigments react by the evolution of hydrogen, this corrosion reaction inhibited by addition of different kinds of water soluble polymers with carboxyl groups like polyacrylic acid,styrene-maleic acid or styrene-acrylate copolymers[13], Meena *et al.*.[14] have examined the synergistic effect between CMC and Zn^{2+} on the corrosion inhibition of carbon steel in NaCl solutions. Sedahmed *et al.*[15] have studied the use of formulation containing polyethylene oxide, polyacrylamide and CMC as corrosion inhibitors for iron in neutral and acidic media using electrochemical methods, Paulomi *et al.*[16] have discussed the antifoulants such as sodium acrylate, Carboxy-methylcellulose (CMC) for clay and $CaCO_3$ dispersion. Rajendran *et al.*[17] have reported the corrosion inhibition of carbon steel by CMC in a chloride environment. Two polymers such as polyvinyl benzyl trimethyl-ammonium chloride (PVBA) and polydiallyldimethylammonium chloride(PDDA) were used to inhibit aluminium in primary cells with aluminium anodes and alkaline electrolyte[18]. Umoren[19] investigated the corrosion behaviour of aluminium exposed to H_2SO_4 and its inhibition using Gum Arabic(GA) at the range of 30-60 ^{0}C using weight loss and thermometric methods. The corrosion and inhibition behaviour of aluminium in HCl in the presence of polyvinyl-pyrrolidone (PVP), polyacrylamide (PAL) and their blends in the temperature of 30-60 ^{0}C using weight loss, hydrogen evolution and thermometric techniques have been reported[20].

Carboxymethylcellulose (CMC) is used to make water soluble adhesives and binders used in wall paper paste as thickners and stabilisers in processed foods and powdered cellulose are used as inactive fillers in tablets. Much work has not been done on aluminium metal by carboxymethylcellulose.

In this work we have proposed to investigate; i) the inhibition efficiency of carboxymethylcellulose (CMC) in controlling corrosion of aluminium at pH11 in the absence and presence of Zn^{2+}, ii) to study the influence of immersion period on the inhibition efficiency of the CMC-Al^{3+} system, iii) to analyse the protective film by SEM techniques and iv) to study the AC impedance spectra to know the mechanistic aspects of corrosion inhibition. On the basis of the experimental results we have proposed a suitable mechanism of corrosion inhibition.

Experimental

The commercial aluminium specimens (95% of purity) of the dimensions 1.0x4.0x0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

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 hours. The weight of the specimens before and after were determined using Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution[21]. The inhibition efficiency (IE) was then calculated using the equation

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

Where W1 = Corrosion rate in the absence of the inhibitor and W2 = 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.

$$R_t = (R_s + R_t) - R_s$$

Where R_s = Solution resistance

$$C_{dl} = 1 / 2 \pi R_t f_{max}$$

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 by SEM.

Scanning electron microscope

The aluminium metal specimen was immersed in blank and inhibitor solution for a period of one day. It was removed from the solution and rinsed with double distilled water. Then it was dried. The surface morphology was examined using Scanning Electron Microscope.

Results and Discussion

Weight loss method

The corrosion rate (CR) and inhibition efficiency of carboxymethylcellulose in controlling corrosion of aluminium in well water at pH11 is given in Table 1. The inhibition efficiency at various concentrations of CMC has been calculated. The inhibition efficiency increases with increasing the concentration of the carboxymethylcellulose. A synergistic effect exist at 250 ppm of CMC[22-23] and 25ppm of Zn^{2+}. At this concentration inhibition efficiency was 95%.

Table 1. CR of aluminium in solution containing various concentration of CMC in presence and absence of Zn^{2+} at pH11

CMC ppm	Zn^{2+} ppm					
	0		25		50	
	I.E %	CR mm/y	I.E %	CR mm/y	I.E %	CR mm/y
0	-	-	48	5.4	50	3.6
50	48	9.4	75	4.5	65	6.4
100	50	9.1	80	3.6	69	5.6
150	55	8.2	82	3.3	72	5.1
200	60	7.3	85	2.7	75	4.5
250	62	6.9	95	0.9	78	4.0

Influence of immersion period on the inhibition efficiency

The influence of immersion period on the inhibition efficiency of the given of 250 ppm of CMC and 25ppm of Zn^{2+} system is given in Table 2 . As the immersion period increases, the inhibition efficiency decreases. This is due to the fact that protective film is ruptured by the continuous attack of ions present[24-25] in well water like OH^-,Cl^-. There is competition between formation of Al^{3+}-CMC complex and $AlCl_3$ or $Al(OH)_3$. It appears that the formation of $AlCl_3$ is more favoured than formation of complex (Al^{3+}- CMC).

Table 2. Influence of duration of immersion on the inhibition efficiency (%) of 250 ppm of CMC and 25 ppm of Zn^{2+} system

System	Immersion period, days			
	1	3	5	7
Aluminium in well water at pH11	58	52	48	42
Solution containing 250 ppm of CMC and 25 ppm of Zn^{2+} at pH11	95	72	60	50

AC impedance spectra

The AC impedance spectra of aluminium immersed in well water and solution containing 250 ppm of CMC and 25 ppm of Zn^{2+} at pH11 are shown in Figure 1. The impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 3. When aluminium immersed in well water at pH11, R_t value is 396.4 Ohmcm^2 and C_{dl} value is 1.2865x10^{-8} F/cm^2. When 250 ppm of CMC and 25 ppm Zn^{2+} are added, the R_t value tremendously increased to 2372 ohmcm^2 and the C_{dl} value is decreased to 2.150x10^{-9}µF/cm^2. This indicates the protective film is formed on the metal surface in the presence CMC [26-27]. When there is corrosion protection, the R_t value increases and C_{dl} value decreases[28].

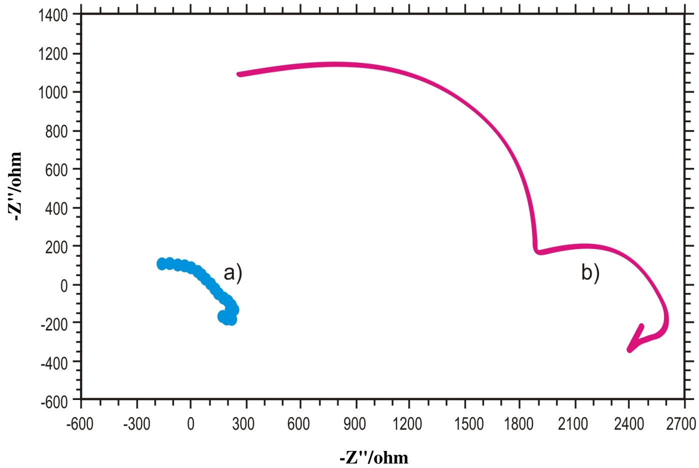
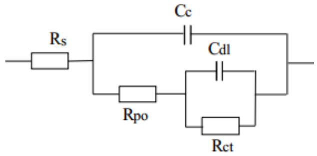


Figure 1. AC impedance spectra of aluminium immersed in various test solutions a) well water b) well water containing 250 ppm of CMC and 25 ppm of Zn^{2+}

Table 3. The impedance parameters of aluminium immersed in well water at pH11 in presence and absence of inhibitor obtained by AC impedance method

System	R_t ohmcm^2	C_{dl} µF/cm^2
Well water at pH11	396.4	1.2865x10^{-8}
Solution containing 250 ppm of CMC +25 ppm of Zn^{2+}	2372	2.150x10^{-9}

The two semicircle pattern is indicative of impaired protective coatings. The protective coating consists of Al^{3+} - inhibitor complex and also Al_2O_3. However this film is broken by the aggressive ion present in the well water. The equivalent circuit diagram is shown in Scheme 1.



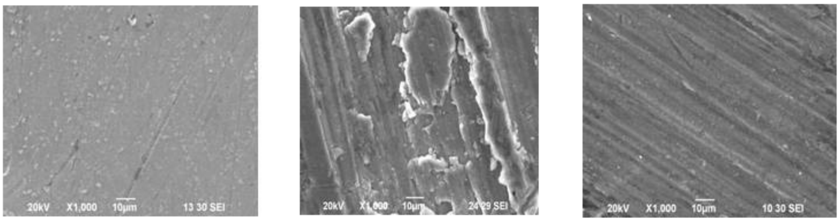
Scheme 1. Equivalent circuit for a failed coating

C_c - The capacitance of the intact coating, R_{po} - pore resistance, R_{ct} - charge transfer resistance, R_s – solution resistance, C_{dl} – double layer capacitance

Surface analysis of metal by SEM

SEM technique analysed the surface of aluminium metal in presence and absence of inhibitor. The images of aluminium immersed in well water period of one day system taken at magnifications (X1000) are shown in Figure 2 as images were labelled as a, b & c.

The surface of the polished metal was very smooth, but in absence of inhibitor, the surface is very rough due to corrosion; in presence of inhibitor the surface is smooth because of formation of the complex Al^{3+}-CMC which inhibits the corrosion[29-30].



a b c

Figure 2. SEM micrographs (magnificationx1000) of (a) Aluminium metal (control) (b) Aluminium immersed in well water (c) Aluminium well water containing 250 ppm of CMC and 25 ppm of Zn^{2+}

Mechanism

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

- When the formulation consisting of 250 ppm of CMC and 25 ppm of Zn^{2+} at pH11 is prepared, there is formation of CMC- Zn^{+2} complex in solution.
- When aluminium is immersed in this solution, CMC- Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface.
- On the surface of metal CMC- Zn^{2+} complex is converted to CMC- Al^{3+} complex with the release of Zn^{2+}

$$\text{CMC-}Zn^{2+} + Al^{3+} \rightarrow \text{CMC-}Al^{3+} + Zn^{2+},\ \ Zn^{2+} + OH^- \rightarrow Zn(OH)_2$$

Conclusion

The formulation consisting of 250 ppm of CMC and 25 ppm of Zn^{2+} offers 95% inhibition efficiency to aluminium immersed in solution at pH11 by the weight-loss method. AC impedence study showed that a protective film formed on metal surface. SEM images confirm the formation of protective layer on the metal surface.

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