Inhibition effect of Arabic gum and cellulose acetate coatings on aluminium in acid/base media

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Abstract. Nowadays aluminium is broadly used for battery purpose due to its conductivity, non toxic and economic reasons. Arabic gum and cellulose acetate are used as potential inhibitors to hinder corrosion effect on aluminium plate immersed in a solution of hydrochloric acid or sodium hydroxide. This investigation has studied the corrosion rate in terms of different concentrations of acid or base media. The average inhibition efficiency in the interested concentration range of both HCl and NaOH (0.1 M – 3.0 M) for 1 x 1 cm^2 aluminium (Al) plate coated by 20% Arabic gum (AG) and 5% cellulose acetate (CA) with each thickness of 0.5 mm is found to be higher than 90%. The electrochemical behavior of corrosion effect is examined by cyclic voltammetric performance with respect to HCl or NaOH media. This investigation is useful especially for the study of Arabic gum and cellulose acetate utilized as polymer inhibitor in strong corrosive media.

1.Introduction

Increased aluminium utilization in many fields due to its conductivity, non toxic and low cost reasons has attracted strong interest to study the corrosion effect of aluminium in strong corrosive media such as acid or base media. Large utilities of aluminium batteries with its limitation in relative short life-time have generated ideas in seeking for materials that might overcome aluminium batteries obstacle. Carbon polymers conjugated with heteroatomic organic constituents (N, O, and S) assumed to possess characters related to strong inhibition effect [1]. In addition, the hydroxyl group of polysaccharides may increase polarity character of a polymer causing the polymer more dissolved in aqueous media.

Arabic gum classified as conjugated polysaccharides with glucoprotein originally came from East Africa assumed to possess good inhibition character related to its heteroatomic (N, O, and S) properties [1]. Besides, Arabic gum has other benefit properties in relation to its safety, high solubility in aqueous media and large molecular size. Several investigations were made to examine the role of Arabic gum in association with aluminium and mild steel corrosion in strong acid media, and even Arabic gum showed better inhibition character to aluminium rather than to mild steel [1].

Cellulose acetate as a synthetic material is an ester of acetic acid and cellulose, which has been largely used in photographic film, glues, and synthetic fibres. Cellulose acetate as its polysaccharide type with its hydroxyl group may enhance its polarity behaviour on reason of increasing aqueous solubility. Cellulose acetate membrane has been largely used in many industries on account of its availability, high flux, and hydrophilic character [2]. Recently, a derivate of cellulose acetate was produced to increase its resistance toward chlorine and biocompability [3].

On account of this matter, this investigation is interested in the study of inhibition effect of Arabic gum (AG) and cellulose acetate (CA) on aluminium corrosion in hydrochloric acid and sodium hydroxide solutions. The commercial aluminium 1100 plate (1 x 1 cm^2) is coated by AG as the first layer followed by CA as the second layer immersed in different concentrations of respective both HCl and NaOH solutions in the range of 0.1 M – 3.0 M. The electrochemical behaviour of corrosion – inhibition event has been investigated through cyclic voltammetric performance. Up to date, the Al corrosion using AG inhibitor has already been investigated, however, the utilization of double layer inhibitors with respect to AG and CA is assumed to be a new finding. Moreover, this study is intended to give benefit related to the knowledge of corrosion – inhibition process particularly involved with double layer inhibitor.

2. Material and Experimental

2.1 Materials

Materials used in this paper include commercial aluminium 1100 plate (1 x 1cm^2). Arabic gum and cellulose acetate purchased from Elnasr Ltd., and both electrolytes NaOH and NaCl purchased from Merck. Alcohol 70% was used for cleaning Al plate with a composition of 96.4% Al, 1.1% Mg, 0.7% Mn, 0.5% Fe, 0.2% Si, 0.2% Cu, and other undetected impurities.

2.2 Coating process of Al plate with polymer

The coating process is as follows:
  1. To prepare an aqueous solution of AG (20%).
  2. To paste the AG solution on Al plate (1x1 cm^2) and allowed to dry on air for 24h.
  3. To prepare an aqueous solution of CA (5%).
  4. To paste the CA solution as the second layer and dried on air for 24h.
  5. To connect the bottom part of Al plate to a copper wire (15cm) and used as working
     electrode.
Each membrane polymer has thickness of 0.5 mm. A digital calliper was used to measure the thickness.

2.3 Determination of corrosion rate and inhibition efficiency

The determination of corrosion rate (CR) is derived from the Faraday's law expressed in equation (1),

$$CR = \frac{m}{tA} = \frac{iM}{zF} \qquad (1)$$

For aluminium, "m" is the mass of Al in mg, "t" is the time in sec, "A" is the surface area of Al in cm^2, "i" is the current density in μA/cm^2 if "CR" expressed in mg/dm^2/day. 1 F = 96 500 coulomb/mole and 1 coulomb = 1 ampere. sec., "z" = 3 for Al since it involved with 3 electrons transfer, "M" is the molecular weight of Al, i.e. 27 g/mole. Hence, "CR" in mm/y is defined by the current density "i" in

$\mu A/cm^2$ obtained from instrumental measurement multiply by a constant of 0.00327 and a factor of "M/zD" as described in equation (2) [4].

$$CR = 0.00327 \, \frac{iM}{zD} \qquad (2)$$

"D" is the density of material, for Al = 2.7 g/cm^3.

The inhibition efficiency in this case is described as follows:

$$\text{Inhibition efficiency} = \frac{CRo - CR}{CRo} \times 100\%$$

CRo = corrosion rate without inhibitor

CR = corrosion rate with inhibitor

2.4 Cyclic voltammetry

The cyclic voltammetric performances are executed by a potentiostat of Corr Test Electrochemical Workstation using Corr Show application. A standard calomel electrode (SCE), platinum electrode, and aluminum connected to copper wire were used as reference electrode, auxiliary electrode, and working electrode, respectively. The current density, "i", was obtained from the polarization curve of current density vs. time and then determined the average current density during 60 sec. running. Then this average current density was used to determine the CR as stated in equation (2) above. Each measurement of CR was done for three replications. The measurements of current density were done for both Al plate immersed in HCl and NaOH. The cyclic voltammetry is an electrochemical curve of current vs. potential represented the oxidation reduction process in the electrochemical reaction of Al plate in the presence or absence of AG and CA for both aqueous solutions of HCl and NaOH, respectively.

3. **Results and Discussion**

3.1 Corrosion rate

All data of CRs related to a state using polymer inhibitor or free immersed both in HCl and NaOH aqueous solution in triplicate measurements, respectively, are not presented here due to space reason, however, the data results are shown in graphical presentations that are clearly to be understood. Generally, all the CR increased when concentrations of both HCl and NaOH increased (figure 1 and figure 2).
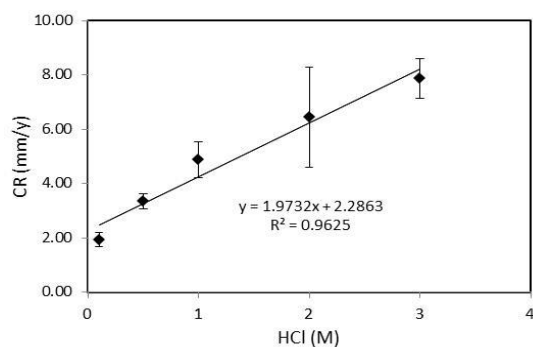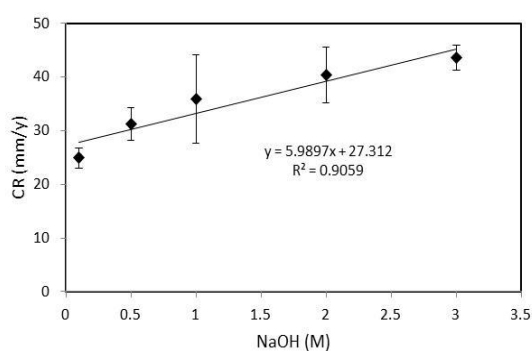
Figure 1. Corrosion rate of Al plate (1x1 cm^2) coated by 20% AG and 5% CA immersed in HCl.
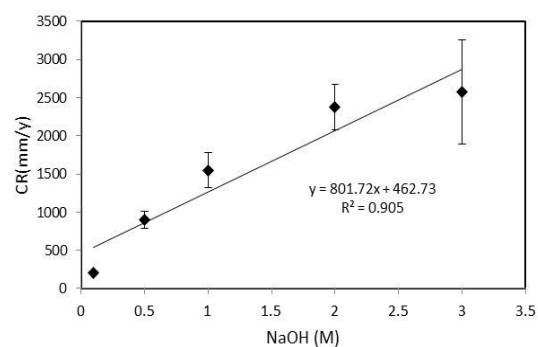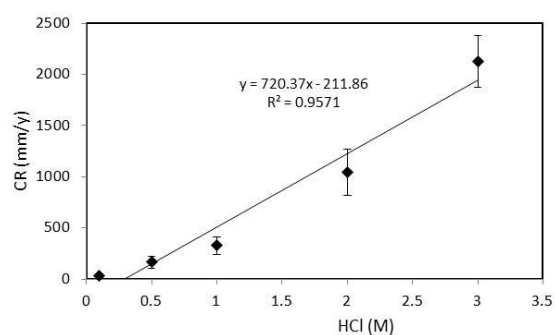

Figure 2. Corrosion rate of Al plate (1x1 cm^2) free of AG and CA immersed in HCl.

Regarding the values of CR in figure 1, the values of CR for Al plate in HCl are much lower in the presence of AG and CA (figure 1) compared to that in the absence of AG and CA (figure 2). Similar patterns are also shown in figure 3 and figure 4 when the Al plate immersed in NaOH. This is reasonable since AG and CA are polymers protected the Al plate from corrosive media (HCl and NaOH). The double layers of protecting polymers look strengthened the inhibition effect on Al plate corrosion. This phenomenon is justified by the high values of inhibition efficiency (Table 1) as the average values of inhibition efficiency for HCl and NaOH are found to be 97.13% and 95.79%, respectively.

Figure 3. Corrosion rate of Al plate (1x1cm^2) coated by 20% AG and 5% CA immersed in NaOH.

Figure 4. Corrosion rate of Al plate (1x1 cm^2) free of AG and CA immersed in NaOH.

3.2 Inhibition efficiency

Table 1. Inhibition efficiency of Al plate (1x1 cm^2) in the presence or absence of AG and CA immersed in HCl and NaOH, respectively. Triplicate measurement.

| HCl aq.	Absence of Ag-CA	Presence of Ag-CA	Inhibition efficiency	NaOH aq.	Absence of Ag-CA	Presence of Ag-CA	Inhibition efficiency
0.1M	19.624	1.928	90.17 %	0.1M	210.083	24.914	88.14 %
0.5M	164.134	3.346	97.96 %	0.5M	898.720	31.259	96.52 %
1M	328.455	4.869	98.51 %	1M	1549.549	35.883	97.68 %
2M	1042.308	6.443	99.38 %	2M	2373.334	40.432	98.30 %
3M	2125.198	7.869	99.63 %	3M	2573.318	43.600	98.31 %
Average inhibition efficiency in HCl			97.13 %	Average inhibition efficiency in NaOH			95.79 %

3.3 Cyclic voltammetry

The electrochemical behaviour of Al plate corrosion in both HCl and NaOH are shown by their cyclic voltammetric performances (figures 5 – 8). Al corrosion by HCl in the absence of protective layers AG and CA occurred very rapidly particularly at higher acid concentrations that it means the redox reaction occurred so fast and as a result, the oxidation and reduction peaks changed very fast [5] causing a fluctuated response (figure 5) except at the lowest concentration of HCl (0.1M). According to Xhanari and Finsgar [6], at higher acid concentration (pH 3 – 4) chloride ion may dissolve Al through the formation of AlCl$_3$, which is soluble in water.

On the other hand, in the presence of AG and CA layers redox reaction between Al and water are almost totally hindered by those polymers coating Al plate and as a result, redox reaction almost apparently not occurred, it means there is no any oxidation or reduction peak as reflected by smooth lines of their CV performance (figure 6). In addition, in the presence of AG and CA the current yield is extremely low about in the order of 10^{-7} ampere/cm^2 (figure 6).

In the case of Al plate immersed in NaOH, the OH$^-$ ion from NaOH enable to form hydrogen bond in water that may retard the migration rate of ions especially at lower concentration of NaOH [7]. This condition reflects the CV performance in NaOH (figure 7) that smooth lines observed for lower concentrations of NaOH (0.1 – 2M). Previous investigation reported a gray colour formed at the surface of Al when Al immersed in higher concentration of KOH as an indicator of the formation of Al$_2$O$_3$ layer [5].

As in the case of figure 7, the oxidation peak of the CV of NaOH 3M is apparently shown, it means that at higher concentration of NaOH (3M) the migration of ions in water is getting slower. Moreover, this investigation found the oxidation peak of the CV of NaOH 3M observed at about 1.0V (figure 7), and this case is in agreement with the facts finding obtained by the former report [8] using Al silicon coated by methyl cellulose. In the context of Al coated by AG and CA layers in NaOH media, the OH$^-$ from NaOH may attack the acetyl group of CA resulted the acetyl group broke down from CA lowering the adherence of CA to AG [5]. Furthermore, the deacetylation process may reduce the protective function of CA that should be underlined in the case of using CA as protective layer for any metal in base media such as NaOH [5].
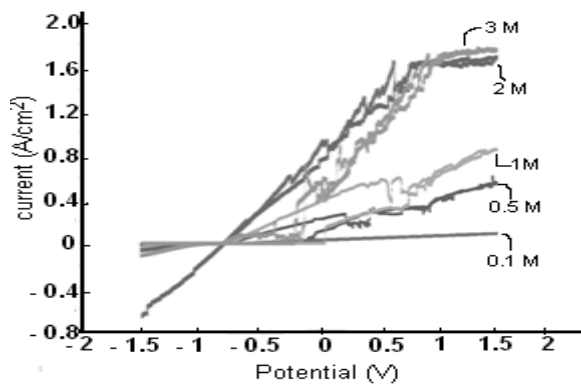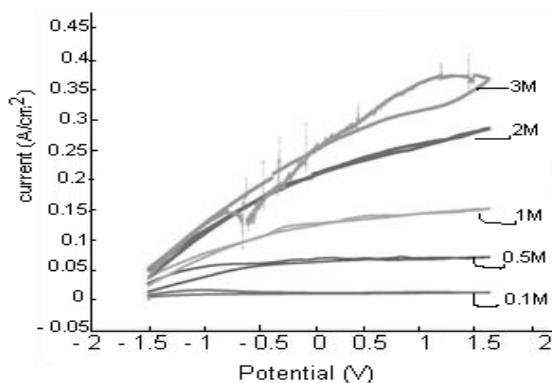
Figure 5. CV performance of Al plate free of AG and CA immersed in HCl (0.1M – 3.0 M).
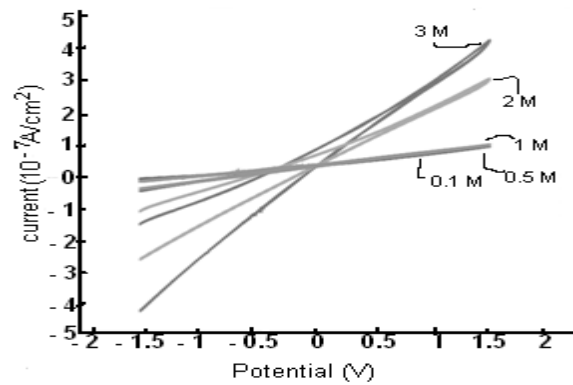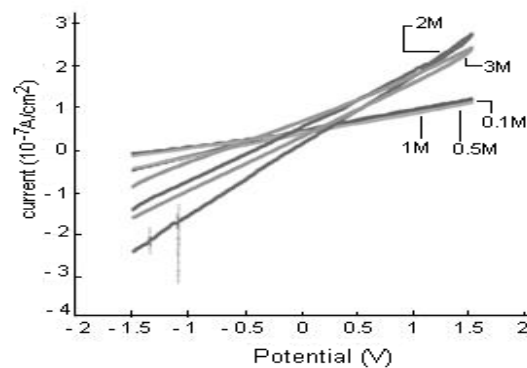

Figure 6. CV performance of Al plate coated by AG and CA immersed in HCl (0.1M – 3.0 M)

As in the case of Al corrosion in HCl media using AG and CA as protective layers, similar phenomenon with regard to the CV performance (figure 8) is also found with Al corrosion in NaOH using the same double layer polymer (AG and CA) as protective agent.

Figure 7. CV performance of Al plate free of AG and CA immersed in NaOH (0.1M – 3.0 M).

Figure 8. CV performance of Al plate coated by AG and CA immersed in NaOH (0.1M – 3.0 M).

The CV of figure 8 shows smooth lines performance for all concentrations of NaOH used (0.1-3M), which attributed no any redox reaction occurred during scanning process that it means the protective membrane layers (AG and CA) almost retarded the ions migration in aqueous solution. It should be noted that the current values in the CV of figure 8 is in the order of 10^{-7} ampere/cm^2 as the same order

found with that in HCl (figure 6). This phenomenon is strengthened by the justification of its average inhibition efficiency (higher than 90%) for both HCl and NaOH as reported in Table 1.

4. Conclusions

1. Arabic gum and cellulose acetate have function as thin layer organic coating to prevent chemical reaction between Al and other substituent in corrosive media such as high concentration of strong acid.

2. The hetero-aromatic part (N, O and S) in polymer plays important role in reducing by-product reaction on Al surface. In addition, the polysaccharides in both polymers (AG and CA) increase polarity properties yielding better water solubility.

3. Arabic gum and cellulose acetate are members of organic coating group.

Acknowledgement

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