The Inhibiting Effects of Alkyl Benzene Sulphonate and the Magnetic Field on Aluminum Corrosion in Acidic Solution

A. K. Maaytah, N. A. F. Al-Rawashdeh*a,b*

*a Chemistry Department, Jordan University of Science & Technology, P.O. Box 3030, Irbid-22110, Jordan.

*b Department of Chemistry, College of Science, United Arab Emirates University, P.O. Box 17551, Al Ain, Abu Dhabi, UAE. Tel:+971-3-7134184; Fax: +971-3-7671291; E-mail: nathir@uaeu.ac.ae

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Abstract

Corrosion inhibition of aluminum (Al) in hydrochloric acid (HCl) by linear alkyl benzene sulphonate (LABS) in the presences and absences of external magnetic field has been studied using weight-loss and hydrogen evolution methods. Magnetic field of 0.1 T was applied. The inhibition action depends on the chemical structure and the concentration of the inhibitor, the concentration of the corrosive medium, the temperature, and the presence of an external magnetic field. The percentage inhibition efficiency (%IE) of aluminum corrosion with LABS is slightly increased in the presences of an external magnetic field. Results of weight loss method are highly consistent with those obtained by hydrogen evolution method and both indicate that the %IE increases with increasing inhibitor concentration, and the presence of external magnetic field. The %IE decreases as the concentration of HCl increases. For the tested additives, an increase in the temperature was found to decrease the %IE.

Keywords: Aluminum; Weight loss; Hydrogen evolution; Acidic corrosion; Magnetic field.

Introduction

From a purely thermo-dynamical point of view aluminum is an active metal. However, in oxygen containing environment (air, water), aluminum is rapidly covered with a dense inert oxide layer [1]. The thickness of the oxide layer may vary as a function of temperature and environment. Oxide films formed in air at room temperature are 2-3 nm thick on pure aluminum. Heating to 425 °C may give films up to 20 nm [2]. If the oxide film is damaged, e.g. by a scratch, new oxide will immediately form on the bare metal [3]. This way aluminum is given excellent corrosion protection. Aluminum has a natural corrosion protection from its oxide layer, but if exposed to aggressive environments it may corrode. The following factors may affect the stability of the aluminum oxide and thereby cause corrosion: (i) the oxide is not stable in acidic (pH < 4) or alkaline (pH > 9) environments [1], (ii) aggressive ions (chlorides, fluorides) may attack the oxide locally, and (iii) presence of certain elements (Ga, Tl, In, Sn, Pb) may become incorporated in the oxide and destabilize it [4]. Furthermore, corrosion may occur to an aluminum surface coated with an organic material which is considered as a localized corrosion and called filiform corrosion. This type of corrosion takes the form of randomly distributed thread-like filaments, and is sometimes called vermiform or warm track corrosion. Aluminum is susceptible to this type filiform corrosion in a

* Corresponding author: Tel. +971-3-7134184, Fax: +971-3-7671291, E-mail: nathir@uaeu.ac.ae
relative humidity range of 75 to 90% with a temperature between 20 to 40 °C. Typical filament growth rates average is about 0.1 mm/day. Filament width varies with increasing humidity from 0.3 to 3 mm.

The depth of penetration in aluminum can be as deep as 15 µm. Numerous coating systems used on aluminum are susceptible to filiform corrosion, including nitrocellulose, epoxy, polyurethane, alkyd, epoxy and vinyls. Condensates containing chloride, bromide, sulphate, carbonate and nitrate ions stimulate filiform corrosion [5].

Several groups of organic compounds have been reported to exert inhibitive effects on the corrosion of aluminum. However, the protective activity afforded generally has been poor. The extent of adsorption of an inhibitor depends on many factors [6]: (a) the nature and the surface charge of the metal; (b) the mode of adsorption of the inhibitor; (c) the inhibitor’s chemical structure; and (d) the type of the aggressive solution. The presence of heteroatoms (such as: oxygen, nitrogen, sulfur, phosphorus), triple bonds, and aromatic rings in the inhibitor’s chemical structure enhance the adsorption process. It has been reported that the inhibition efficiency (I%) of heterocyclic organic compounds follows the sequence: oxygen < nitrogen < sulfur < phosphorus [7-9].

Corrosion of aluminum and its alloys has been the subject of numerous studies due to their importance in the recent civilization. Accordingly, numerous studies on the inhibition of aluminum corrosion using organic substances have been conducted [10-14]. Recent studies have shed light on the effects of sulfur-containing compounds such as thiourea and its derivatives on the inhibition of aluminum corrosion [15, 16].

Magnetic field usually affects the magnetic species each according to its nature (ferromagnetic, paramagnetic or diamagnetic); one expects that chemical reactions involving such species will be affected if a magnetic field is applied. Moreover, elementary physics shows that charged particles in motion, such as ions, will be subjected to Lorenz force caused by the application of a magnetic field. Lorenz force is proportional to the charge of the ion (\( q \)), to its velocity (\( \nu \)) and to the magnetic field (\( B \)), taking directions into consideration, through the following equation \( F = q \nu \times B \), and meaning that positive ions and negative ions moving in the same direction will be affected by forces in opposite directions depending on the sign of (\( q \)). Moreover the force should be perpendicular to both \( \nu \) and \( B \).

Charged chemical species in a solution will have Brownian motion caused by thermal energy. When these particles are subjected to an external magnetic field, their motion will be affected and will be organized accordingly. Little work has been done on the effect of magnetic field on chemical reactions [17-21].

In the present work, the weight loss method and the hydrogen evolution method both were applied to investigate the inhibition of aluminum corrosion by linear alkyl benzene sulphonate (LABS) and by applying externally applied magnetic fields.
Experimental

Pure aluminum (99.95%) was supplied in the form of sheets (Aldrich). The organic inhibitor linear alkyl benzene sulphonate (LABS) (purity 97%) was supplied by sulphochemical company-Jordan and was used as received. All solutions were made up from Analar hydrochloric acid in triply distilled water. Before measuring, all tested aluminum samples were mechanically polished using emery paper 800, degreased with acetone, washed with distilled water, dried in alcohol and ether, and then weighed using Electronic Semimicro Balance Sartorius 2024 MP6 with precision of ±0.01 mg.

The weight loss experiments were carried out using metallic aluminum sheets having the dimensions (30 x 10 x 0.5 mm, exposed total area = 6.4 cm²), weighed and immersed for 1 hr in 10 ml of Analar HCl solutions (2.0-3.5 M) containing different concentrations of LABS (200-1000 ppm). After testing all samples were rinsed thoroughly with triply distilled water, dried, and weighed again. The measurements were carried out at different temperatures (303-333 K) using a water thermostat controlled to ±0.5 K. To study the effect of magnetic field on corrosion using weight loss method, same experimental procedure was repeated in the presence of an externally applied magnetic field (0.1 T). The magnetic field was measured by Holl-Probe, Leybol-Heraeus. Prior to experiments; all the solutions were deaerated by passing nitrogen gas for 15 min. Scheme 1 shows the experimental setup of the corrosion in the flux of magnetic field.

The amount of hydrogen evolved from the corrosion reaction of aluminum was measured using a homemade experimental setup (Scheme 2).
Results and Discussion

Variation of aluminum weight loss in various concentrations of HCl at 333 K, in absence and presence of external magnetic field (0.1 T) are shown in Figure1. Figure 1 shows that the weight loss values (mg) of aluminum increased as the concentration of HCl increased. Remarkably, in the presence of externally applied magnetic field (0.1 T) the weight loss value is lower, especially at higher concentrations of HCl. The magnetic fields decelerate the rate of corrosion of aluminum sheets in acidic medium at a 333 K, which is in contract to what have been observed at 298 K. In a previous study it has been observed that the magnetic fields accelerate the rate of corrosion of aluminum sheets in acidic medium at 298 K \[21\].
Figure 1: The weight loss curves of aluminum in various concentrations of HCl at 333 K, in absence and presence of external magnetic field (0.1 T).

The weight loss curves of the aluminum sheets with addition of the inhibitor in 3.5 M HCl at various temperatures without and with externally applied magnetic fields (0.1 T) are shown in Figures 2 and 3, respectively.

Figure 2: Effect of LABS concentration on weight loss (mg) in absence of external magnetic field, at various temperatures. Immersion time 1 h, [HCl] = 3.5 M.
Figure 3: Effect of LABS concentration on weight loss (mg) in the presence of external magnetic field (0.1 T), at various temperatures. Immersion time 1 h, [HCl] = 3.5 M.

The curves in Figure 2, without externally applied magnetic fields, show that the weight loss values (mg) of aluminum in 3.5 M HCl solution containing LABS are decreased as the concentration of the inhibitor increased, i.e. the corrosion inhibition strengthened with the increase of the surfactant concentration. The trend of LABS in externally applied magnetic fields (Figure 3) is similar to that observed without externally applied magnetic fields but with slight reduction in weight loss at all temperatures. In addition, the curves in Figures 2 and 3 show that when the concentration of the tested surfactant is greater than 600 ppm, the weight loss of aluminum does not change remarkably, this trend was observed at all temperatures. The critical micelle concentration (CMC) of LABS is 650 ppm [22]. In another word, when the concentration of surfactant reaches its CMC value, the adsorbed amount of inhibitor and its coverage to the aluminum’s surface reached maximum value. The results obtained reveal that the weight loss of aluminum in the presence of a magnetic field was less than that in the absence of a magnetic field at the same concentration range of the inhibitor. Thus, an applied magnetic field appeared to assist the rate of passivation (formation of Al₂O₃) on the surface [19]. The results obtained were in agreement with previously published results of aluminum and iron [18,19]. One of the magnetic field effects was due to the Lorentz force [23]. The effects of temperature and concentration of the inhibitor on weight loss of aluminum in HCl in the absence and presences of magnetic field have been studied, and the results of these effects were summarized in Figures 4 and 5. It's remarkably from these figures that as temperature...
increases the weight loss increases due to the higher dissolution of aluminum at higher temperature. Furthermore, for the concentration of the tested surfactant above the CMC (650 ppm), the weight loss of aluminum does not change remarkably.

**Figure 4:** Variation of weight loss (mg) with temperature at various concentrations of LABS, in the absence of magnetic field. Immersion time 1 h, [HCl] = 3.5 M.

**Figure 5:** Variation of weight loss (mg) with temperature at various concentrations of LABS, in the presence of magnetic field (0.1 T). Immersion time 1 h, [HCl] = 3.5 M.
The loss in weight of the aluminum sheets in the presence of the tested inhibitor (LABS) at various concentrations (200 to 1000 ppm) was determined in different HCl concentrations and temperatures. At each concentration of the inhibitor, the percentage inhibition efficiency (% IE) is calculated using the relationship [24]:

\[
% \text{IE} = \frac{W_u - W_i}{W_u} \times 100\%
\] (1)

Where \(W_i\) and \(W_u\) are the weight loss with and without the inhibitor, respectively. Figures 6 and 7, shows the variation in %IE of LABS according to its concentration in 3.5 M HCl at various temperatures in the absences and presences of a magnetic field, respectively. The results show less inhibition efficiency of LABS in absences than presences of magnetic field. All tests show a slight decrease in the %IE with increasing temperature, but the inhibitive effect still persists even at higher temperature (333 K). This behavior indicates that the adsorbed molecules formed a barrier film on the aluminum surface [25].

Figure 6: Variation of inhibition efficiency (%IE) with LABS concentration in 3.5 M HCl in the absences of magnetic field at various temperatures.
The effect of external magnetic field, inhibitor, and temperature on the hydrogen evolutions of the corrosion of aluminum sheets in HCl are shown in Figures 8-12. The results of these figures emphasize the observations obtained by weight loss measurements, where it can be concluded that the presences of inhibitor and external magnetic field is needed to increase the inhibition of corrosion of aluminum in acidic medium.
**Figure 8:** The hydrogen evolution curves of aluminum in various concentrations of HCl at 333 K, in absence and presence of external magnetic field (0.1 T).

**Figure 9:** Effect of LABS concentration on hydrogen evolution curves in absence of external magnetic field, at various temperatures. Immersion time 1 h, [HCl] = 3.5 M.
Figure 10: Effect of LABS concentration on hydrogen evolution curves in the presence of external magnetic field (0.1 T), at various temperatures. Immersion time 1 h, [HCl] = 3.5 M.

Figure 11: Variation of hydrogen evolution curves with temperature at various concentrations of LABS, in the absence of magnetic field. Immersion time 1 h, [HCl] = 3.5 M.
Figure 12: Variation of hydrogen evolution curves with temperature at various concentrations of LABS, in the presence of magnetic field (0.1 T). Immersion time 1 h, [HCl] = 3.5 M.

Using the results of hydrogen evolution method obtained in absence and presence of magnetic field (0.1T), the corrosion rate of aluminum is determined by using the relation:

\[
W_{\text{corr}} = \frac{\Delta m}{S \times t}
\]  

Where \(\Delta m\) is the mass loss, \(S\) is the surface area aluminum sheet and \(t\) is the immersion period.

Table 1 shows the corrosion rate and the percentage inhibition efficiency of the inhibitor (LABS) at various concentrations (200-1000 ppm) in 2.5 M HCl in an immersion period 1 hr, at 333 K. Closer inspection of Table 1 reveals that the inhibition efficiency (%IE) increases with increasing inhibitor concentration, and in presence of external magnetic field reaching a maximum inhibition efficiency of 37.89% at its highest values.
Table 1: Corrosion rate (mg/cm².h) and percentage inhibition efficiency of inhibitors at various concentrations in 2.5 M of HCl at 333 K.

<table>
<thead>
<tr>
<th>Inhibitor Conc. (ppm)</th>
<th>0.1 Tesla</th>
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<tr>
<td></td>
<td>Wcorr (%)</td>
<td>%IE</td>
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<td>1000</td>
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Inspection of the data in Table 1 reveals that LABS appeared to act as inhibitor over the studied concentration range. The corrosion rate values indicate that the external magnetic field has a reasonable effect on the inhibition of aluminum in LABS. The reduction in the dissolution of aluminum in the presence of LABS inhibitor may be attributed to the sulphonate ion present in the functional group. It is obvious that the inhibition effect of LABS increases with increasing its concentration and reaches a value where the weight loss of aluminum does not change remarkably.

Reaching a limiting value in the weight loss is related to the formation of a monolayer film on the adsorbate over the surface of the metal [26]. This phenomenon is more likely to take place when the concentration of the surfactant is near its CMC. In this study for the tested inhibitor, it has been observed that the weight loss did not reached a limiting value (plateau) but only a remarkable decrease in the changes in weight loss has been observed. This result indicates that the tested inhibitor (LABS) does not form a complete monolayer film at the experimental conditions of this study.

When discussing inhibition action of surface-active agents various factors must be taken into consideration [27]. These include the number of functional groups taking part in the adsorption of the inhibitor molecule and their electron charge density, molecular size and geometry, mode of interaction, heats of hydrogenation and of additives. Most likely, the adsorption of LABS occurs through the adsorption of the sulphonate ion at the surface of the aluminum. Thus, due to steric effect of alkyl chain the adopted spatial orientation of LABS on the metal surface doesn't allow the formation of complete monolayer film.

It is known that passive metals corrode according to the so-called pitting mechanism, which includes four main steps: breakdown of passivity, early stages of pit growth, late stages of pit growth, and repassivation phenomena [28]. The breakdown of passivity may be caused by the mechanism of chloride penetration through the oxide film; the passive layer breaking mechanism as well as the mechanism of chloride adsorbed at the oxide surface and accelerated transfer of metal cations to the electrolyte. The formation of micelle structure, which develops in a pit domain during its
growth, plays an essential part in these mechanisms. According to our results, we suggest that the magnetic field could affect the structure of the repassivating deposits of LABS. We came to the conclusion that under the influence of magnetic field the initial LABS particles reorient themselves in such a way that the interaction energy between the LABS micelles and magnetic field would become minimal. In addition, the observed corrosion magneto inhibition effect could be explained in terms of field assisted formation of the oxides with higher degree of dispersion. This effect was evident from the decrease in mass loss.

Conclusions

The anionic surfactant tested (LABS) shows a reasonable inhibition for aluminum corrosion in acidic medium in the presences and absences of external magnetic field. Its ability as an inhibitor differs in the presences and absences of external magnetic field. This is quite probably due to differences of mode of adsorption, and the field-assisted formation of the deposited micelle with a superior capacity to pit repassivation. The %IE increases with increasing inhibitor concentration and decreasing the corrosive media concentration. In addition, there are quite increase in the %IE in the presences of magnetic field. Thus, the presences of a magnetic field suppress corrosion reactions of aluminum sheets with addition of the inhibitor in HCl at various temperatures. The %IE decreases with increasing temperature as a result of the higher dissolution rate of aluminum at higher temperatures.

References