

Sodium lignosulfonate as a friendly-environment corrosion inhibitor for zinc metal in acidic media

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Abstract

The corrosion inhibition property of sodium lignosulfonate is investigated by three different independent monitoring techniques. These methods include weight loss measurements, electrical conductance and potentiodynamic polarization. Solutions with and without sodium lignosulfonate in 0.01 M HCl and 0.1 M HCl were prepared at 20 °C to study the influence of sodium lignosulfonate on the corrosion of zinc sheets. The results obtained from the three different methods indicate the protection role of sodium lignosulfonate, which is considered as a friendly-environment corrosion inhibitor, in the corrosion of zinc sheets. The reduction of the zinc corrosion in solutions with HCl and different concentrations of sodium lignosulfonate using potentiodynamic polarization followed the order: 30 mM > 10 mM > 5 mM > 1 mM. The obtained results from weight loss, potentiodynamic polarization and electrical conductance experiments were in good agreement with each other.

Keywords:

Sodium lignosulfonate, Inhibitor, Potentiodynamic polarization, Electrical conductance.

1. Introduction

Corrosion is usually an undesirable reaction between a metal and a substance possessing a higher reduction potential. Industrial equipment undergoes serious problems that lead the industrial productivity to be limited due to such corrosion. The process of corrosion occurs slowly and occurs at surfaces of metals, but the losses incurred due to corrosion are enormous destruction of machines, equipment and different type of metallic products [1- 4].

Green chemistry aims at designing chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green-corrosion inhibitors are designed to function effectively and reduce the impact of such substances on the environment by breaking down them into innocuous degradation products after use [3] [5]. One promising substance is sodium lignosulfonate that could be used as corrosion inhibitor to develop new cleaning chemicals for green environments.

As shown in Fig. 1, sodium lignosulfonate contains both hydrophilic groups like sulfonic, hydroxyl groups and hydrophobic groups (carbon chains). Lignosulfonate can be

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regarded as poly-electrolyte that establishes electrostatic stabilization for colloidal systems [6]-[8]. Their properties make them suitable for many industrial applications like concrete and cement production, pesticides and dyes dispersion [9]. Few recent publications [9-11] have discussed the inhibition properties of lignosulfonate in corrosion process.

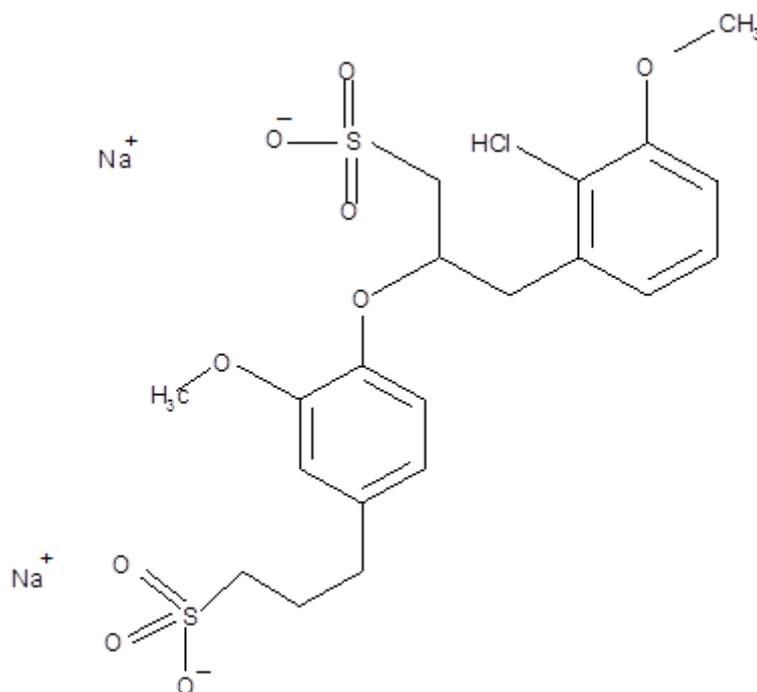


Fig. 1: The typical chemical structure of sodium lignosulfonate [7].

This research work is a part of a project that aims to protect the environment by utilizing the waste of biomass materials in different industrial applications. The inhibition behavior of alkali lignin in the corrosion was studied before by the same research group [12]. The current study suggests using sodium lignosulfonate as a friendly-environment substance in inhibiting corrosion of zinc. Sodium lignosulfonate is classified as a polymeric surfactant that can be obtained in the form of byproduct resulting from the production of wood pulp by sulfite process [6]. Weight loss measurements, electrical conductance and potentiodynamic polarization methods were employed to study the zinc corrosion in the absence and presence of sodium lignosulfonate [1, 13-14]. To the best of our knowledge, there are no studies have reported the use of electrical conductance in the corrosion process which is an advantageous feature of this study.

2. Experimental

2.1 Material used

Highly pure zinc sheets (99.0%) were purchased from Sigma-Aldrich (UK). Sodium lignosulfonate was purchased from Gainland Chemical (Deeside, UK). Besides, solutions of 0.01 mol L^{-1} HCl (for weight loss) and 0.1 mol L^{-1} HCl (for potentiodynamic polarization and electrical conductance measurements) were prepared by the dilution of concentrated HCl 37% (w/v) from Merck (UK) using deionized water. All chemicals and solvents used were of analytical reagent (AR) grade, and all solutions were prepared using deionized water.

2.2 Weight loss procedure

Zinc sheets (2.0 cm × 2.0 cm × 0.025cm) were polished down by emery papers of 100–800 grit and degreased with ethanol. The sheets were rinsed with distilled water, dried using filter paper and left in the oven at 50 °C for 3 hours [13]. The zinc sheets were weighted using a four digits analytical balance (FA2204, Shanghai Kingdak Company, China) and then immersed in the corrosive media (0.01 mol L⁻¹ HCl) in the presence and absence of 5, 10 and 30 mmol L⁻¹ of sodium lignosulfonate. The zinc sheets were taken out of the corrosive solution at various time intervals then washed by distilled water, dried using filter paper, then weighted accurately.

2.3 Electrical conductance measurements

Polished zinc sheets (2.0 cm × 2.0 cm × 0.025cm) were immersed inside a 0.1 mol L⁻¹ HCl solution in the presence and absence of 1, 10 and 30 mmol L⁻¹ of sodium lignosulfonate at 20 °C. The electrical conductance of the investigated solutions was measured using an electrical conductance meter (Portable, HI98188 Hanna instruments, USA). All experiments were made under stirring condition of 450 rounds per minute (rpm) and the values of electrical conductance were followed with time.

2.4 Potentiodynamic polarization measurements

Potentiodynamic polarization experiments were carried out using a VoltaLab PGZ100 potentiostat (Radiometer analytical SAS, Lyon, France) in a double-wall, three-electrode glass cell. Prior to measurements, the surface of the working electrode (Zn) was carefully polished by emery papers, rinsed several times with distilled water, and then sonicated for about 1 minute. Potentiodynamic polarization curves of zinc in 0.1 mol L⁻¹ HCl solution without and with 1mmol L⁻¹, 5 mmol L⁻¹, 10 mmol L⁻¹ and 30 mmol L⁻¹ of the inhibitor sodium lignosulfonate were recorded.

All potential values were reported versus the saturated calomel electrode (SCE) as a reference electrode and all measurements were carried out at room temperature. A platinum wire was used as an auxiliary electrode. All glassware used for electrochemical experiments were carefully cleaned by immersion in a solution of concentrated sulfuric acid overnight and followed by copious rinsing with distilled water.

3. Results and discussion

The corrosion inhibition of sodium lignosulfonate is firstly investigated by weight loss method and then by electrical conductance measurements. In the third part of this work, the potentiodynamic polarization experiments, as a monitoring method for the corrosion inhibition process, are presented and discussed.

3.1 Weight loss method

The inhibition efficiencies (I) and the corrosion rates of zinc (r) are calculated using the equations 1 and 2 respectively [13, 14]:

$$I \% = \left(1 - \frac{r}{r^o}\right) \times 100\% \quad (1)$$

$$r = \frac{m_1 - m_2}{St} \quad (2)$$

where r and r^o (g/m² day) are the corrosion rate in the presence and absence of sodium lignosulfonate, respectively. The m₁ and m₂ (g), respectively, are the weight of zinc sheet

before and after the immersion in the corrosive solution. S (in m^2) and t (in days) are the surface of the zinc sheet and exposure time, respectively.

The weight loss of zinc sheets versus time is graphically presented in Fig. 2 for solutions with 0, 5, 10 and 30 mmol L^{-1} sodium lignosulfonate in 0.01 M HCl. It is obvious from Fig. 2 that the weight loss of zinc sheets was less pronounced in the presence of sodium lignosulfonate which indicates the protection role of this substance. The reduction in zinc corrosion rate in the presence of different concentration of sodium lignosulfonate followed the order: 5 mmol L^{-1} > 10 mmol L^{-1} > 30 mmol L^{-1} . At 30 mmol L^{-1} , adhesion of lignosulfonate on the surface of zinc sheet was observed causing a positive reading in the weight of zinc sheet. The surface deposit is one of the main limitations of weight loss method [4, 13].

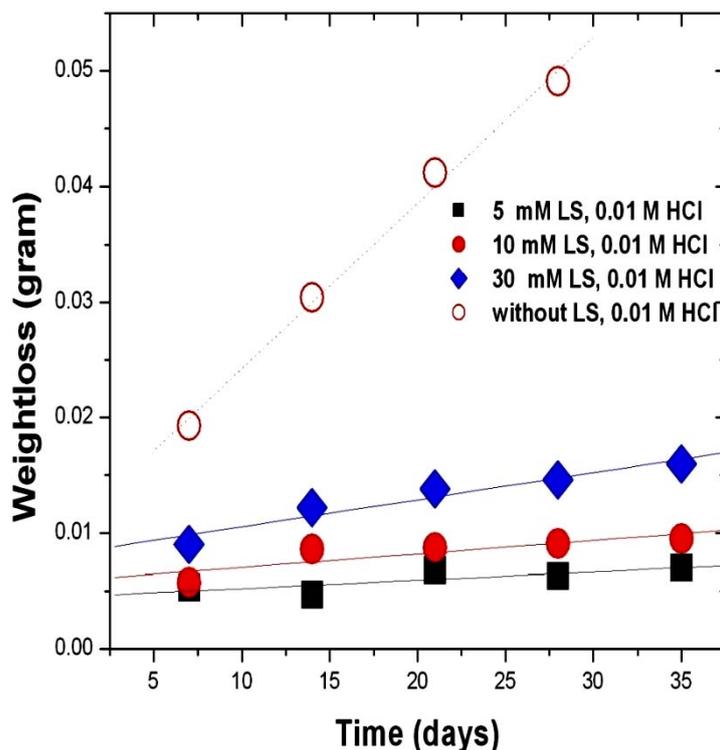


Fig. 2: The weight loss data of zinc sheets in the absence and presence of 5, 10 and 30 mmol L^{-1} sodium lignosulfonate (LS) in 0.01 mol L^{-1} HCl.

Fig. 3 shows the corrosion rates calculated from weight loss data. As indicated in Fig. 3, there was a significant reduction in the zinc corrosion rates in the presence of sodium lignosulfonate solutions compared to single 0.01 mol L^{-1} HCl.

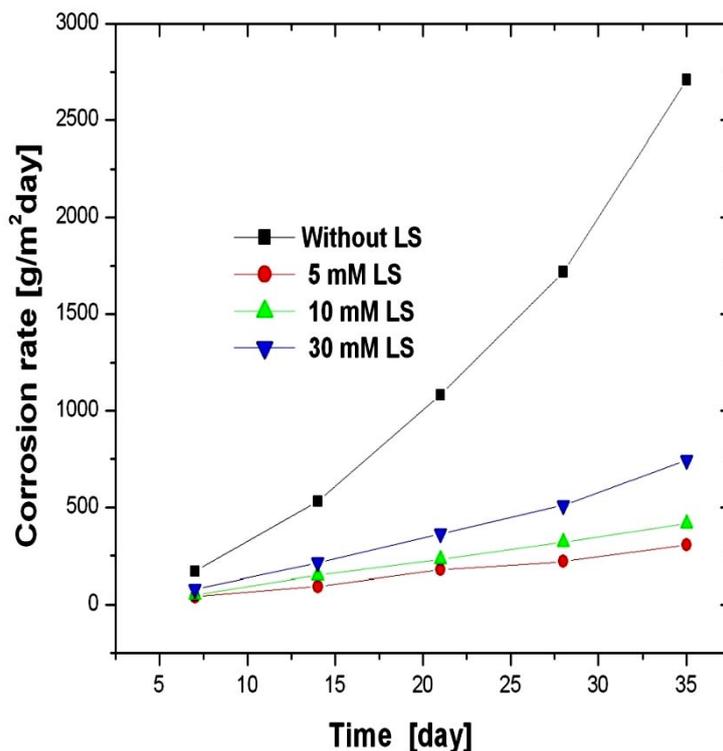


Fig. 3: The corrosion rates of zinc sheets with and without sodium lignosulfonate (LS) in 0.01 mol L^{-1} HCl.

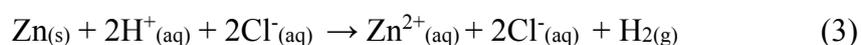
The variation of corrosion rates with and without lignosulfonate and the values of corrosion inhibition efficiencies in the presence of 5, 10 and 30 mmol L^{-1} of sodium lignosulfonate calculated from weight loss measurements are shown in Table 1.

Table 1: The values of corrosion rates and corrosion inhibition efficiencies in the presence of 0, 5, 10 and 30 mmol L^{-1} of sodium lignosulfonate in 0.01 mol L^{-1} HCl.

Time (day)	Corrosion rate without LS ($\text{g/m}^2 \text{ day}$)	5 mmol L^{-1} LS		10 mmol L^{-1} LS		30 mmol L^{-1} LS	
		Corrosion rate ($\text{g/m}^2 \text{ day}$)	Inhibition efficiency (%)	Corrosion rate ($\text{g/m}^2 \text{ day}$)	Inhibition efficiency (%)	Corrosion rate ($\text{g/m}^2 \text{ day}$)	Inhibition efficiency (%)
7	168.875	41.125	75.65	49.875	70.47	78.75	53.37
14	532	92.75	82.26	150.5	71.71	213.5	59.87
21	1081.5	178.5	83.53	231	78.63	362.25	66.51
28	1718.5	220.5	87.20	318.5	81.49	511	70.26
35	2708.125	306.25	88.70	415.625	84.65	743.75	72.54

3.2 Electrical conductance measurements

When a zinc sheet is placed in 0.1 mol L^{-1} HCl solution, it reacts with HCl, Zn starts to corrode and lead to producing of Zn^{2+} ions according to the chemical reaction (3):



The change of electrical conductance by time for solutions with 0.1 M HCl in the presence and absence of 1, 10, 30 mmol L⁻¹ of sodium lignosulfonate at 20 °C is shown in Fig. 4.

As the time increases the electrical conductance somehow decreases. We thought that electrical conductance has to increase by time as the corrosion process lead to an increase in zinc ions concentration. However, the electrical conductance was found to be decreased by time. Electrical conductance generally depends on ionic charge, concentration and mobility. According to equation 3, it is clear that H⁺ ions are replaced by Zn²⁺ ions. As the ionic mobility of H⁺ (ionic mobility $\lambda_{H^+}^+ = 349.65 \text{ S cm}^2 \text{ mol}^{-1}$) is almost six times higher than that of Zn²⁺ ions (ionic mobility $\lambda_{1/2Zn^{2+}}^+ = 52.5 \text{ S cm}^2 \text{ mol}^{-1}$) [15], a decrease in electrical conductance by time was observed.

It is also shown from Fig. 4 that the decrease in the electrical conductance by time is more pronounced in solutions with 0.1 mol L⁻¹ HCl compared to solutions with 0.1 mol L⁻¹ HCl plus sodium lignosulfonate, indicating the corrosion inhibition characteristic of sodium lignosulfonate. As the time increases the electrical conductance remains almost constant in the investigated short time interval, which demonstrates a significant inhibition property in the corrosion process.

The metal corrosion rate is thus reflected by the magnitude of conductance-time slopes. Fig. 4 shows the electrical conductance changes with and without sodium lignosulfonate. It is found that the changes in electrical conductance when sodium lignosulfonate does not exist in the corrosive solution is much more than the case when the sodium lignosulfonate is present. The obtained results by these experiments prove again the inhibition behavior of sodium lignosulfonate and indicate that electrical conductance is a simple but powerful method for corrosion investigations.

Sodium lignosulfonate contains sulfur and oxygen atoms as well as multiple bonds in its chemical structure (Fig. 1). Such atoms and bonds can be adsorbed onto metal surface and block its active sites and consequently reduce the corrosion rate. The organic compounds containing S, N and O are known to be effective inhibitors. The effectiveness of the functional atom in the adsorption processes varies according to the following sequence: S > N > O [3] [16]-[19]. The effectiveness of corrosion inhibitor thus depends on the electron density of these atoms as well as the electron density of SO₃ functional group.

3.3 Potentiodynamic measurements

Potentiodynamic polarization method has been used to investigate the corrosion behavior of zinc sheets in 0.1 mol L⁻¹ HCl solution as a function of sodium lignosulfonate surface adsorption. Increasing the HCl concentration does not change the trend of inhibition process.

Potentiodynamic polarization curves of zinc in 0.1 mol L⁻¹ HCl solution without and with different concentrations of the inhibitor sodium lignosulfonate were recorded at ambient air to simulate normal corrosion environment. It was observed that both the cathodic and anodic processes are hindered upon the addition of sodium lignosulfonate. The polarization curves were recorded for inhibitor concentrations of 1, 5, 10 and 30 mmol L⁻¹ at around 25 °C. The electrochemical parameters, such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel constants, b_a and b_c, and % inhibition efficiency, were calculated from Tafel plots [20]. In table 2 we report the corrosion rate, corrosion current and inhibition efficiency values of potentiodynamic experiments in the absence and presence of different concentrations of sodium lignosulfonate.

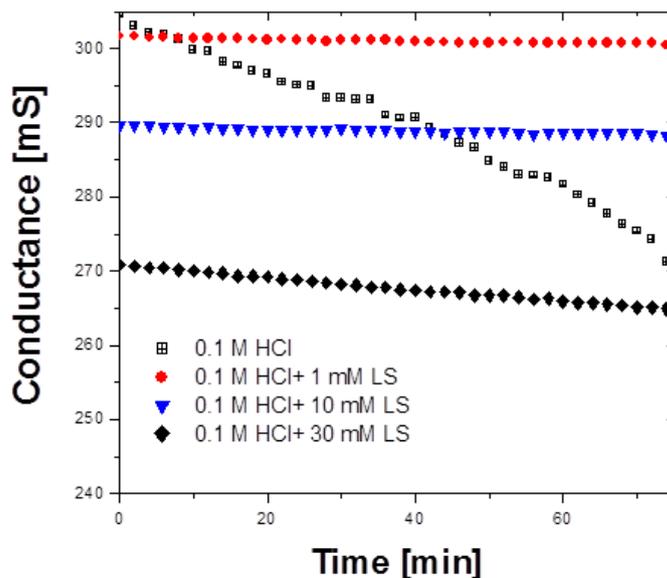


Fig. 4: The changes in electrical conductance by time for Zn sheets immersed in 0.1 mol L⁻¹ HCl solutions in the presence and absence of 1, 10 and 30 mM of sodium lignosulfonate (LS) at 20 °C.

It is observed that the presence of the inhibitor lowers the corrosion current density and reaches a minimum value at the highest inhibitor concentration (30 mmol L⁻¹). We also observed that E_{corr} values and the Tafel constants b_a and b_c have no significant change as a function of the inhibitor concentration, which indicates that sodium lignosulfonate behaves as a mixed type inhibitor. The values of inhibition efficiency indicate a pronounced protection behavior of sodium lignosulfonate in the corrosion process of zinc sheets. The inhibition efficiencies are 83.14, 69.46, 63.85 and 40.7% for solutions with 30, 10, 5 and 1 mmol L⁻¹ sodium lignosulfonate, respectively.

Table 2: Corrosion rate, corrosion current and inhibition efficiency values of potentiodynamic experiments in the absence and presence of sodium lignosulfonate (1, 5, 10 and 30 mmol L⁻¹) in 0.1 mol L⁻¹ HCl.

Sample description	Corrosion rate (mm/y)	Corrosion current I_{corr} (mA/cm ²)	Inhibition efficiency %
Without lignosulfonate	31.37 ± 0.93	2.088 ± 0.04	-
With 1 mM lignosulfonate	18.60 ± 1.15	1.238 ± 0.07	40.7
With 5 mM lignosulfonate	10.70 ± 0.60	0.671 ± 0.06	63.85
With 10 mM lignosulfonate	9.58 ± 0.52	0.637 ± 0.04	69.46
With 30 mM lignosulfonate	5.29 ± 0.45	0.352 ± 0.03	83.14

4. Conclusion

The result of this study include them in the following points:

- i. The Three independent techniques for monitoring the corrosion process indicate clear evidence of the inhibition behavior of sodium lignosulfonate against corrosion of zinc sheets in the dilute HCl solutions. These methods include potentiodynamic

polarization experiments, weight loss measurements as well as electrical conductance measurements.

- ii. The inhibition efficiencies obtained from potentiodynamic experiments range between 40.70 and 83.14%.
- iii. As expected, the inhibition efficiency increases as the concentration of lignosulfonate increases.

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