Conductivity Method as a New Monitoring Technique for Corrosion and Corrosion Inhibition Processes of Zinc Metal

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Abstract

Conductivity method was successfully examined to monitor the corrosion and corrosion inhibition processes. Measurements of electrical conductivity of three different corrosive solutions (HCl, NaOH, and NaCl) with two different concentrations containing zinc sheets in absence and presence of four different concentrations of sodium lignosulfonate (1.0, 5.0, 10.0, and 20.0 mM) were performed at 20 ºC. The analysis of curves that illustrate the changes of conductivity of these solutions provides qualitative information about the strength of corrosion as well as the extent of corrosion inhibition behavior. The effect of sodium lignosulfonate as a corrosion inhibitor was very obvious in acidic medium (For both 0.10 and 1.0 M HCl) and less visible in other two media.

Keywords: conductivity, sodium lignosulfonate, corrosion, inhibition, corrosion monitoring.

1.Introduction

Corrosion monitoring is a practice that was conducted by many researchers in the last decades to determine the amount of corrosion and the rate of metal loss in the environment [1]. Corrosion monitoring techniques play a significant role in resisting

corrosion and in reducing its effects. These techniques basically fall into six categories: Electrical resistance monitoring, electrochemical methods, hydrogen monitoring, weight loss coupons, non-destructive testing techniques and analytical techniques [2]. Some of analytical techniques include the drawing off fluid samples for analysis in laboratories where the areas of interest under this item are metal ion counts, oxygen counts, conductivity, and pH measurements [3].

The electrochemical methods in this field are complicated and require special expertise where isolation from oxygen gas by using nitrogen gas is necessary [1]. Unlike the electrochemical techniques, the conductivity method used in this study is available and simple method and not affected by pressure of oxygen as well as its results are easy to interpret [4].

This study focuses on measuring the variations of electrical conductivity of three different corrosive media containing zinc sheets in the absence and presence of four different concentrations of sodium lignosulfonate to study corrosion and corrosion inhibition processes. The three selected corrosive media were HCl (1.0 M and 0.10 M), NaOH (1.0 M and 0.10 M) and NaCl solution (5.0% and 0.50% w/w). Using the electrical conductivity method to monitor corrosion and corrosion inhibition processes was used in this study for the first time.

2.Materials and methods

2.1 Materials used

Pure zinc sheets (99.0%) were purchased from Sigma-Aldrich (UK). Grinded sodium lignosulfonate was provided from Gainland Chemical (Deeside, UK). Solutions of 0.10 M HCl and 1.0 M HCl were prepared from concentrated HCl 37% (w/w) that was purchased from Merck (UK). Solutions of 0.10 M and 1.0 M NaOH and solutions of 0.50% and 5.0% (w/w) NaCl were prepared from extra pure NaOH and NaCl, which are provided from S.C. chemical company (New Berlin, USA). All solutions were prepared using deionized water.

2.2 Electrical conductivity measurements

Polished zinc sheets (2.0 cm × 2.0 cm × 0.025 cm) were immersed inside the three different corrosive solutions (HCl, NaOH, and NaCl) in the presence and absence of 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonate at 20 °C. The electrical conductivity of the investigated solutions was measured using CC-501 conductometer (Elmetron, Witosa, Poland). The repeatability of the readings is equipped with custom LCD display taking series of measurements with set time

interval. The conductivity meter contains temperature compensation mode and internal data logger for 200 measurements with time date and temperature. The conductometer co-operates with Pt-1000 temperature probe with Chinch connector.

The newest generation electronic elements used in the conductometer made its memory independent to power supply. All experiments were made under stirring condition of 450 rounds per minute (rpm) and the values of electrical conductivity were followed with time.

3.Results and discussion

In order to investigate zinc corrosion process and its inhibition by sodium lignosulfonate, two different concentrations with three different corrosive media were selected. The results of these experiments are summarized in the following sections.

3.1   Electrical conductance measurements in HCl solutions:

When zinc sheet is immersed in HCl solution, it corrodes according to the following chemical reaction [5]:

$$Zn_{(s)} + 2H^+_{(aq)} + 2Cl^-_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Cl^-_{(aq)} + H_{2(g)} \qquad (1)$$
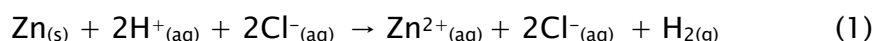
As shown in Figure 1, the value of electrical conductivity per mS/cm of 1.0 M HCl solution containing zinc sheet decreases with time. Generally, the electrical conductivity depends on many factors like ionic charge and ionic mobility, in addition to the ionic concentration when dealing with molar conductivity. According to equation 1, it is clear that H^+ ions are replaced by Zn^{2+} ions and a comparison between the ionic molar conductance of H^+ ($\lambda^+_{H+} = 349.65$ S cm^2 mol^{-1}) and the ionic molar conductance of Zn^{2+} (($\lambda^+ 1/2 Zn^{2+} = 52.5$ S cm^2 mol^{-1}) [6] gives us an explanation of why this decrease in values of electrical conductivity with time of 1.0 M HCl solution that containing the zinc sheet.

As shown in Figure 1, the decrease in electrical conductivity with time is more pronounced in the solution of 1.0 M HCl compared to the solutions of 1.0 M HCl containing different concentrations of sodium lignosulfonate which demonstrates a significant inhibition property of lignosulfonate in the corrosion process.
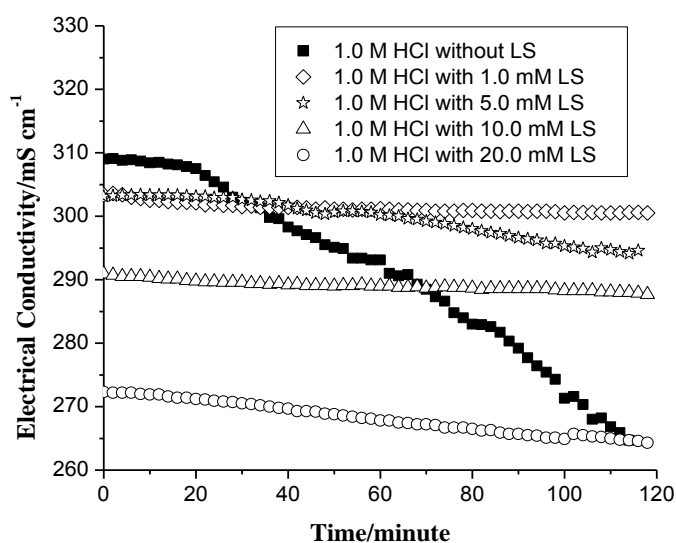
Figure 1: The changes in electrical conductivity with time for Zn sheets immersed in 1.0 M HCl solutions in the presence and absence of 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonate (LS) at 20 ºC.

The slope values of the changes of electrical conductivity of 1.0 M HCl solutions with and without sodium lignosulfonate (LS) are listed in Table 1. The slope value was taken from the linear portion of the plot. The significant difference between the slope value of 1.0 M HCl solution without LS (slope= -0.39919) and solutions containing 1.0, 5.0, 10.0 and 20.0 mM LS indicates the inhibition behavior of LS against the corrosion of zinc sheets in the presence of 1.0 M HCl solution.

Table 1: The slope values of changes of electrical conductivity in different solutions of 1.0 M and 0.10 M HCl containing zinc sheets and 0, 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonates (LS).

Solution description	Slope value in 1.0 M HCl	Slope value 0.1 M HCl
Without LS	- 0.39919	- 0.01081
With 1.0 mM LS	- 0.02105	- 0.0083
With 5.0 mM LS	- 0.02113	- 0.00168
With 10.0 mM LS	- 0.02069	- 0.00318
With 20.0 mM LS	- 0.02101	- 0.00488

Figure 2 shows the variation of electrical conductivity of 0.10 M HCl solutions in the presence and absence of sodium lignosulfonate. An obvious difference between the decrease of electrical conductivity of 0.10 M HCl solutions containing zinc sheets in the presence and absence of 1.0, 5.0, 10.0 and 20.0 mM of LS that is shown in Figure 2.
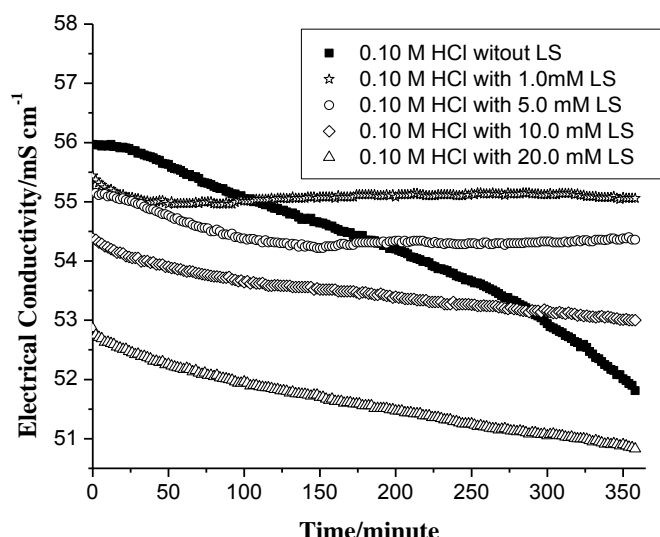

Figure 2: The changes in electrical conductivity with time for Zn sheets immersed in 0.10 M HCl solutions in the presence and absence of 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonate (LS) at 20 ºC.

The slope values of the variation of electrical conductivity of 0.10 M HCl solutions with and without LS are listed in Table 1. As in the previous case, the obvious difference of the conductivity–time slope value of the solution without LS (slope= –0.01081) and, for instance, the solution contains 5.0 mM LS (slope= –0.00168) indicates the inhibition property of LS against the corrosion process in acidic medium.

Other information can be deduced from the above measurements is that the corrosion of zinc metal in 0.10 M HCl was weaker than that in 1.0 M HCl, which will be in a good agreement with the slope values of variation of electrical conductivity with time of the solutions of 1.0 M HCl and 0.10 M HCl (Table 1). It means that the conductivity measurements provide qualitative information about the strength of corrosion as well as the extent of the inhibition behavior.

The corrosion behavior of zinc in acidic medium is efficiently inhibited by compounds containing nitrogen, oxygen and sulfur atoms [7–9]. Generally, such compounds increase the hydrogen overvoltage on zinc metal. Hydrogen overvoltage can be described as the difference between the hydrogen's equilibrium reactions in a

solution and the hydrogen itself present in the solution when it begins to form a corrosive reaction with metal [10].

Most corrosion inhibitors are organic compounds, which mainly contain nitrogen, sulfur or oxygen atoms and multiple bonds or aromatic rings in their structures and they reduce the corrosion rate by block the active sites on the metal surfaces [11–16].

3.2 Electrical conductance measurements in NaOH solutions:

When zinc sheet is immersed in NaOH solution, it corrodes according to the following chemical reaction [17]:

$$Zn_{(s)} + 2Na^+_{(aq)} + 2OH^-_{(aq)} \rightarrow Na_2ZnO_{2\,(s)} + H_{2(g)} \tag{2}$$
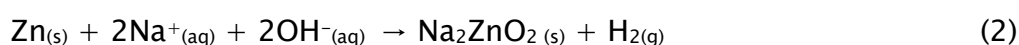
As shown in Figure 3, the value of electrical conductivity of NaOH solution containing zinc sheet decreases with time. According to chemical reaction 2, it is clearly that the total ionic mobilities in the products side are less than that in the reactants side. The difference of electrical conductivity between a solution of 1.0 M NaOH in the absence of LS and solutions of 1.0 M NaOH in the presence of 1.0, 5.0, 10.0 and 20.0 mM of LS was unnoticeable as in Figure 3.
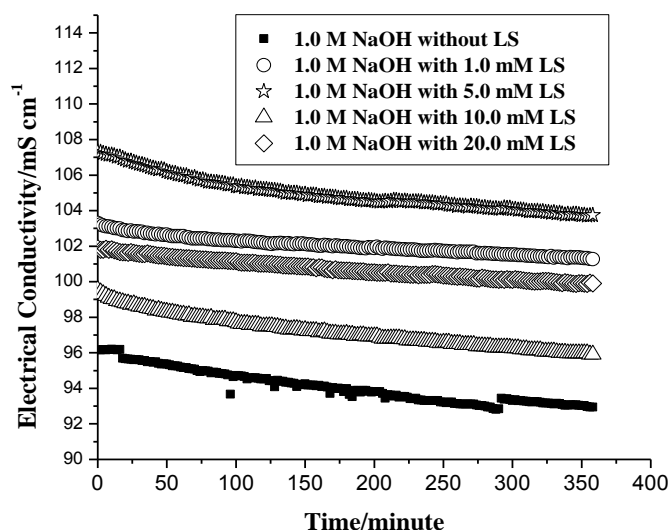

Figure 3: The changes in electrical conductivity with time for Zn sheets immersed in 1.0 M NaOH solutions in the presence and absence of 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonate (LS) at 20 ºC.

As indicated in Table 2, most of the slope values of the conductivity changes with time of the solutions of 1.0 M NaOH with 1.0, 5.0, 10.0 and 20.0 mM LS are less than in the case of 1.0 M NaOH without LS.

Table 2: the slope values of changes of electrical conductivity in different solutions of 1.0 M and 0.10 M NaOH containing zinc sheets and 0, 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonates (LS).

Solution description	Slope value 1.0 M NaOH	Slope value 0.10 M NaOH
Without LS	- 0.00871	- 0.00635
With 1.0 mM LS	- 0.00458	- 0.00492
With 5.0 mM LS	- 0.00802	- 0.00452
With 10.0 mM LS	- 0.00850	- 0.00484
With 20.0 mM LS	- 0.00536	- 0.00384

Figure 4 shows the changes of electrical conductivity readings of 0.10 M NaOH solutions containing zinc sheets with and without LS. It is found that the corrosion process in this solution is slow as indicated by the slope values of the curves that shows the variation of electrical conductivity of these solutions with time (see Table 2). In this case, the corrosion inhibition behavior of LS is less obvious than in basic medium at 1.0 M NaOH due to the weakness of corrosion of zinc metal in 0.10 M NaOH solution.

As indicated in Table 2, the difference in the slope values of the 0.10 M NaOH solution without LS (slope= –0.00635) and the same solution containing 1.0 mM LS (slope= –0.00492) indicate again the corrosion inhibition behavior of LS.

The variation of conductivity readings of corrosive media containing zinc sheets with and without inhibitor indicates the strength of corrosion process and the inhibition behavior. The inhibition behavior of LS will be clear if the corrosion is strong, so that in the case of testing 0.10 M NaOH as corrosive medium, the inhibition behavior of LS was less visible than in acidic medium.
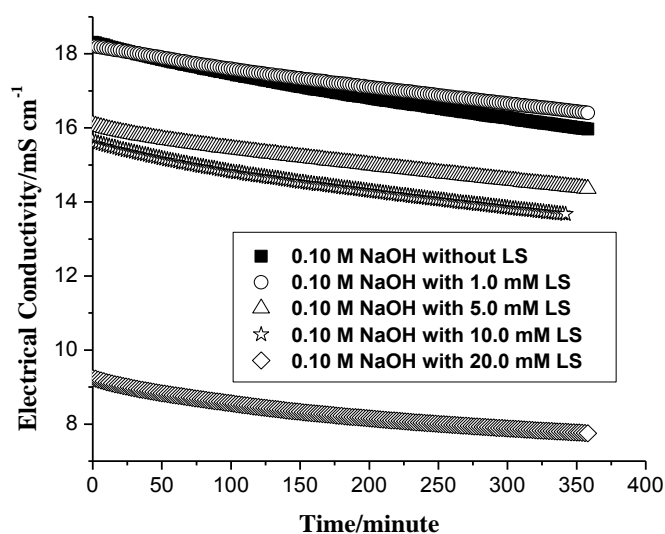
Figure 4: The changes in electrical conductivity with time for Zn sheets immersed in 0.10 M NaOH solutions in the presence and absence of 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonate (LS) at 20 ºC.

3.3 Electrical conductance measurements in NaCl solutions:

Figure 5 shows the variation of electrical conductivity of 5.0% (w/w) NaCl solutions in the presence and absence of LS. As shown in Figure 5, the conductivity of the solution without LS decreases with time, while the same solution with different concentration of LS, the conductivity increases slightly with time. These changes show again the role of LS in the inhibition of corrosion process.

The slope values of the variation of electrical conductivity of NaCl solutions in the presence and absence of 1.0, 5.0, 10.0 and 20.0 mM of LS with time that are listed in Table 3 indicate again the inhibition behavior of LS.
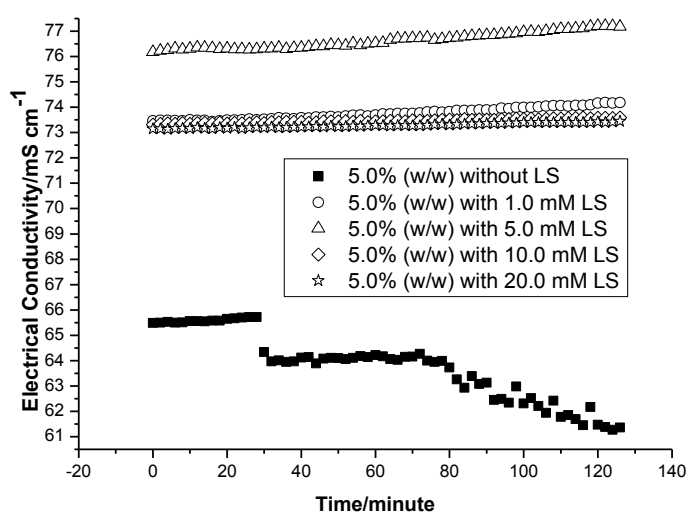
Figure 5: The changes in electrical conductivity with time for Zn sheets immersed in 5.0% (w/w) NaCl solutions in the presence and absence of 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonate (LS) at 20 °C.

Table 3: the slope values of changes of electrical conductivity in different solutions of 5.0% and 0.50% (w/w) NaCl containing zinc sheets and 0, 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonates (LS).

Solution description	Slope value 5.0% (w/w) NaCl	Slope value 0.50% (w/w) NaCl
Without LS	⊶ 0.03440	4.52241×10^{-4}
With 1.0 mM LS	0.00270	2.05963×10^{-4}
With 5.0 mM LS	0.00308	3.13257×10^{-4}
With 10.0 mM LS	0.00275	3.11204×10^{-4}
With 20.0 mM LS	0.00243	3.12502×10^{-4}

Figure 6 shows the variation of electrical conductivity of 0.50% (w/w) NaCl solutions with and without LS. As shown in Figure 6, the values of electrical conductivity of NaCl solution containing zinc sheet were increasing with time. This increasing of electrical conductivity was due to the conversion of Zn to Zn^{+2}. In case of NaCl solutions, there is no replacing of Zn^{+2} ions with H^{+} as occurs in the acidic medium or with OH^{-} as occurs in the basic medium.
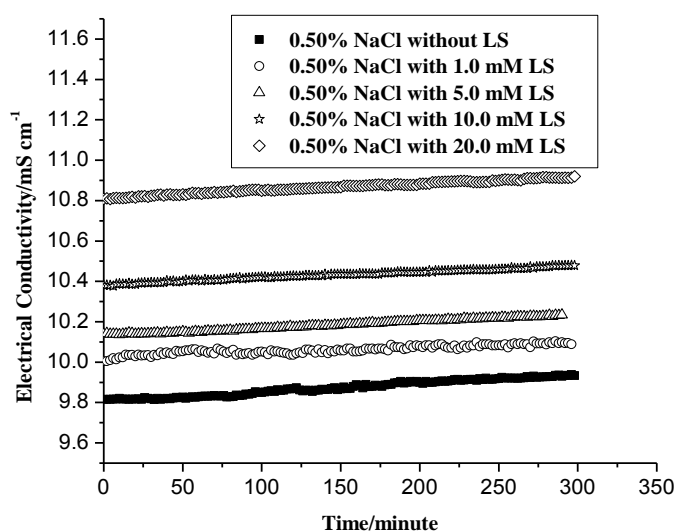
Figure 6: The changes in electrical conductivity with time for Zn sheets immersed in 0.50% (w/w) NaCl solutions in the presence and absence of 1.0, 5.0, 10.0 and 20.0 mM of sodium lignosulfonate (LS) at 20 ℃.

The slope values of the change of electrical conductivity of 0.50 (w/w) NaCl solutions with and without LS are listed in Table 3. Again, the difference of the slope values of the solution without LS (slope= 4.52241×10^{-4}) and, for example, the solution contains 1.0 mM LS (slope= 2.05963×10^{-4}) indicates the inhibition property of LS against the corrosion process in the neutral medium.

The inhibition behavior of lignosulfonate is already affirmed [8, 18, 19], but the new in this study that HCl (1.0 M and 0.10 M), NaOH (1.0 M and 0.10 M) and NaCl solution (5.0% and 0.50% w/w) were tested as corrosive media. A result from this study is testing the conductivity method to be a new and simple monitoring tool of corrosion and corrosion inhibition processes.

4. Conclusion

This study succeeds in using the conductivity method as a new monitoring tool to provide qualitative information about the strength of corrosion as well as the extent of the inhibition behavior. The variation of conductivity readings of three different corrosive media containing zinc sheets in the absence and presence of four different concentrations of sodium lignosulfonate indicates the inhibition behavior of sodium lignosulfonate in the three selected corrosive media. The inhibition behavior of sodium lignosulfonate was very pronounced in acidic medium and less visible in a basic medium (0.10 M NaOH) and neutral medium (0.50%NaCl).

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