

The Inhibition Mechanism of Surfactant Composite for Mild Steel Corrosion in NaCl Solution

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The corrosion inhibition of sodium deodecylbenzenesulfonate (SDBS) surfactant and ZnSO₄ on mild steel in 0.05 M NaCl solution was conducted through the impedance spectroscopy and linear polarisation measurement. The inhibitors performance was measured separately and as a mixed composite of both at a ratio of 200:200 ppm. Results obtained from both these measurements indicate high corrosion inhibition of the mild steel substrates was achieved. Porosity calculation of the formed inhibition layer was done through the obtained linear polarisation data, and its dielectric properties were deduced from the impedance measurements. Two possible structures of the formed inhibitive layers are proposed. The first structure involved the formation of a stable but porous zinc oxide/hydroxide layer with the surfactant filling up the pores, thus forming a continuous inhibitive barrier film layer while the second, involved a formation of a continuous inhibitive barrier layer due to the chelation of the surfactant and ZnSO₄ compounds. The results obtained also indicated that corrosion resistance induced by the inhibitive barrier layers is much more dependent on its charge transfer resistance properties rather than its dielectric properties and that the corrosion inhibition provided is not directly related to the double-layer capacitance values of the barrier layer.

Keywords: mild steel; corrosion; surfactant; ZnSO₄; protective layer

I. INTRODUCTION

Various surface chemical pre-treatments approaches were employed to protect metals from corroding when exposed to aggressive environments. Among them are, acid pickling followed by alkaline pre-treatment, surface passivation through electro-chemically synthesized conversion coatings and the use of chemical inhibitors and/or sol-gel based surface pre-treatment (Sababi *et al.*, 2017; Rodrigues *et al.*, 2013). In most cases, however, chemical inhibitors are more commonly used for mild steel structures exposed in aggressive environments (Alinejad *et al.*, 2017; Liu *et al.*, 2016; Mobin & Khan, 2014; Umoren & Solomon, 2017; Wang *et al.*, 2015; Zhou *et al.*, 2015). There are various types of chemical inhibitors available, ranging from

inorganic to organic inhibitors. Inorganic inhibitors tend to promote metal oxidation to form a passive oxide coating layer that is resistant towards corrosion attack, while organic inhibitors are usually adsorbed on the metal surfaces through heteroatoms and/or chemical bonds forming thin barrier layers (Umoren & Solomon, 2017). The latest research trend is towards promoting the use of non-toxic, economical, and more environmentally friendly green materials as corrosion inhibitors (Mobin *et al.*, 2017; Mobin & Khan, 2014). One approach is the use of surfactants which is known to comply with these requirements. Surfactant can contain electronegative atoms such as nitrogen, oxygen and sulfur that interact with the metal surface and thus delay corrosion reactions (Deyab, 2007). A wide number of

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surfactants are available on the market, such as anionic, cationic, non-ionic and zwitterionic surfactants (Umoren & Solomon, 2017). An anionic surfactant, sodium dodecylbenzene sulfonate (SDBS) has been reported to be successfully used as corrosion inhibitors for metal (Sha *et al.*, 2019; Qiang *et al.*, 2017). The compound contains a long nonpolar hydrocarbon chain which makes it hydrophobic. Adsorption of this hydrophobic compound on metal can prevent water from reaching the metal surface, thereby reduces the corrosion of metal. Significant inhibition performance was obtained when SDBS was used in conjunction with zinc sulphate (Ismail & Harun, 2019), Al_2O_3 (Sha *et al.*, 2019), cerium nitrate (Liu *et al.*, 2016) and lanthanum chloride (Zhou *et al.*, 2015).

In this work, sodium dodecylbenzene sulfonates (SDBS) incorporated with ZnSO_4 was investigated to enhance the corrosion resistance of mild steel in NaCl solution. Evaluation of the protective layer barrier properties was performed using linear polarization resistance (LPR) measurements and electrochemical impedance spectroscopy (EIS) test. Based on the data obtained, the inhibition mechanism of the SDBS: ZnSO_4 mixtures on mild steel were evaluated through its charge transfer resistance properties as well as its dielectric properties.

II. MATERIALS AND METHOD

The mild steel substrates used has a chemical composition of (wt%) 0.60% Mn, 0.15% C, 0.030% P, 0.035% S and 99.185% Fe. Its surface abraded with emery papers (500, 800, 1200, 2400 grit sizes) before used. The sample was cleaned twice with deionized water and acetone before leaving it to dry. Analytical grades of sodium dodecylbenzenesulfonates (SDBS) was obtained from Aldrich, while zinc sulfate (ZnSO_4) was supplied by HmBG chemicals, and used as received. The inhibitor solutions were prepared by dissolving each of the SDBS and ZnSO_4 in 0.05 M NaCl solution and stirred for 15 minutes. The concentrations of SDBS used for the study is 200 ppm, and 200 ppm for ZnSO_4 . Then, a mix solution of 200 ppm:200 ppm of both SDBS and ZnSO_4 was prepared. This was done by first dissolving SDBS in sodium chloride solution, followed by ZnSO_4 and was stirred for 15 minutes. Deionized water was used to prepare all the solutions.

A. Electrochemical measurement

A conventional three-electrode cell of Ag/AgCl reference electrode coupled to a Luggin capillary, a platinum counter electrode, and a mild steel sample as a working electrode were used. The working electrode was prepared by embedding a 1 cm^2 mild steel sample into epoxy resin, leaving an exposed area of 0.054 cm^2 . The test solution used was 0.05 M NaCl consisting of ZnSO_4 , SDBS and a mixture of both compounds. All measurements were taken at 25°C after one hour of immersion in the test solution. The electrochemical impedance spectroscopy (EIS) was carried out at the open circuit potential (OCP) within the frequency range of 10 kHz-20 mHz with AC signals of amplitude 10 mV peak to peak. Meanwhile, the polarization measurement was conducted in a range from -100 mV to +100 mV vs. OCP with a scan rate of 1 mV/s. All electrochemical experiments were conducted using the Autolab potentiostat/galvanostat model PGstat302N. The data were analyzed using the Nova software version 1.11.

III. RESULT AND DISCUSSION

Figure 1 illustrates the Nyquist and Bode diagrams obtained from the impedance measurements. The Nyquist plot obtained, could measure the charge transfer resistance and double-layer capacitance exhibits a single depressed semicircle when moving from high to low frequencies (Qian *et al.*, 2013; Tian *et al.*, 2018). The spectra clearly show a larger diameter of the semicircle for samples immersed in a sodium chloride solution containing each of the two inhibitors when compared to the blank solution. However, when these two inhibitors were mixed, the diameter of the semicircle was significantly increased. There was a significant increase in the total impedance value of the charge transfer processes and thus a more effective corrosion inhibition. The high impedance effect of the inhibitors is seen through the high total impedance values obtained at the low frequency of the Bode plot. The subsequent increase in the phase angle value that shifted towards a higher frequency, further confirms an increase in the total corrosion resistant of the mild steel.

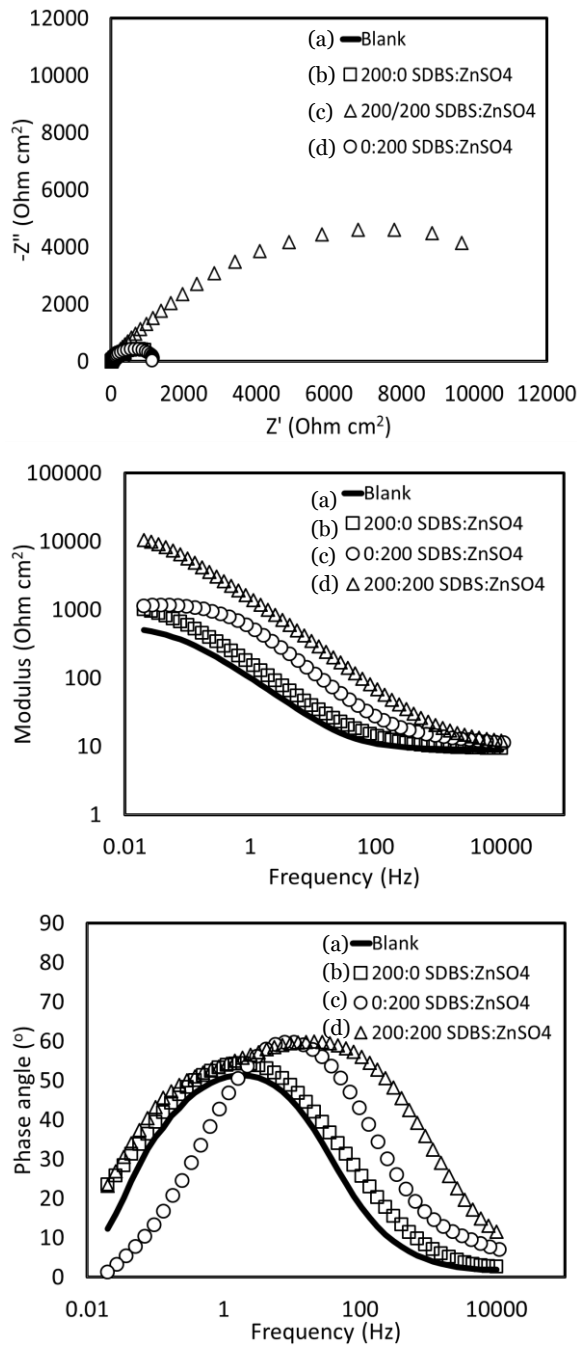


Figure 1. Typical impedance spectra of bare mild steel after immersion for 1 h in 0.05 M NaCl (a) without inhibitor (Blank), (b) with 200:0 ppm SDBS:ZnSO₄ (c) with 0:200 ppm SDBS:ZnSO₄ (d) with 200:200 ppm SDBS:ZnSO₄

An equivalent electrical circuit (EEC) is used to fit the experimental data obtained. This is shown in Figure 2. The circuit comprises of R_s , solution resistance, R_{ct} , charge transfer resistance, and C_{dl} , double-layer capacitance. Due to the non-ideal capacitive behaviour, a constant phase element (CPE) was introduced instead of using a pure capacitor (Qian, 2013; Ismail *et al.*, 2015). The result was

shown in Table 1. Data fit the EEC revealed higher R_{ct} values obtained for mild steel immersed in NaCl solution containing either SDBS or ZnSO₄ when compared to blank. This confirms that both compounds are able to resist corrosion of mild steel. Although the compounds can each act to resist corrosion individually, however, their combination was found to be more effective. The inhibition efficiency of 96% was obtained at a ratio of 200:200 ppm SDBS:ZnSO₄. According to Alinejad, this phenomenon is associated with the formation of a good protective coating layer of complex molecules that prevents the electrolyte from diffusing towards the mild steel surface (Alinejad *et al.*, 2017). A significant decrease in C_{dl} values was also obtained from 175 μ F for the blank to 15 μ F when both SDBS and ZnSO₄ were added. It was speculated that this is due to both the displacement of the water molecules on the mild steel surface by both the zinc cations and SDBS mixture and the presence of Zn²⁺ and SO₄²⁻ ions within the protective layer which contributed to the lower total dielectric values (Rao *et al.*, 2011).

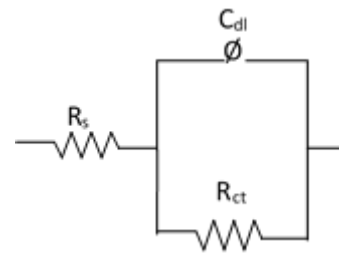


Figure 2. An equivalent electrical circuit used to fit the experimental data

Table 1. EIS measurement of the effects of SDBS and ZnSO₄ on steel surfaces after immersion for 1h in 0.05M NaCl

Concentration (ppm)		R_{ct} (Ohm cm ²)	C_{dl} (μ F)	η_{EIS} (%)
SDBS	ZnSO ₄			
0	0	603	175	-
200	0	1414	140	57
0	200	1246	14	52
200	200	14688	15	96

Polarisation measurements of the pre-treated samples were also obtained. As evidenced by the data obtained, the mixture of 200:200 ppm ZnSO₄ : SDBS gives the smallest

i_{corr} value, indicating a high corrosion resistance provided by the formed protective layer (Ismail *et al.*, 2019). The slight shift to a less negative value of the E_{corr} when compared to the blank shows the mixture inhibitors provided an anodic inhibition effect on the corrosion reaction. In addition to these values, the percentage porosity of the protective layer was also determined through the use of equation 1 (Creuz *et al.*, 2000; Chaudhari & Patil, 2010)

$$P = \frac{R_{po}}{R_{pi}} \times 10^{-(|\Delta E_{\text{corr}}|/\beta_a)} \quad (1)$$

Where P is the total porosity, ΔE_{corr} is the difference between corrosion potentials, R_{po} and R_{pi} are the polarization resistances for the blank and with inhibitors respectively. β_a is the anodic Tafel slope for the blank sample.

Table 2 shows the percentage porosity of the protective layer, which was at its smallest value when a ratio of 200:200 SDBS :ZnSO₄ which contributed further to the total high resistance towards corrosion of the mild steel. Figure 3 and Table 3 show a less negative potential difference value (ϕ) of the surface of the mild steel in the presence of ZnSO₄ when compared to the blank solution. This phenomenon is related to the zero charge potential of the surface after the adsorption of ZnSO₄ on the mild steel surface. It was speculated less negative potential effect of the ZnSO₄ on the mild steel surface tends to promote the adsorption of SDBS compound. The electrostatic adsorption between SDBS and Al₂O₃ also was described by Sha *et al.* in which promotes the formation of a more compact protective layer on the brass surface (Sha *et al.*, 2019).

Table 2. Influence of the SDBS and ZnSO₄ on the polarization measurements of mild steel after immersion for 1 h in 0.05 M NaCl

Concentration (ppm)		β_a (mV/dec)	β_c (mV/dec)	E_{corr} (V)	i_c ($\mu\text{A}/\text{cm}^2$)	P (%)
SDB	ZnSO ₄					
S						
0	0	110	219	-0.532	21.42	-
200	0	90	118	-0.458	10.76	72
0	200	58	178	-0.619	10.20	80
200	200	72	89	-0.476	1.07	9

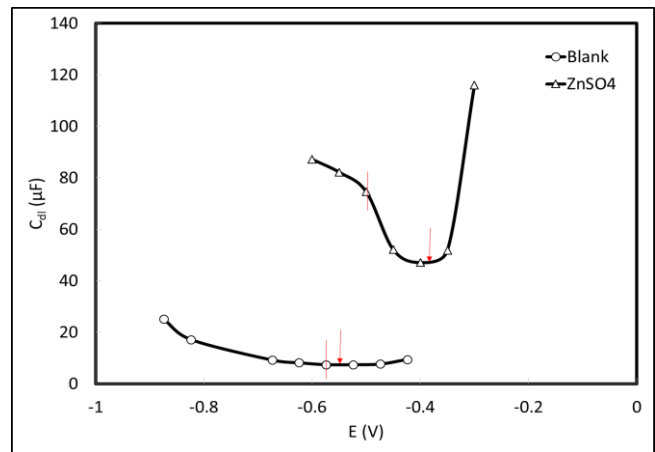


Figure 3. Variation of capacitance, C_{dl} of mild steel with potential measured in 0.05 M NaCl

Table 3. Values of E_{cor} , E_{pzc} and ϕ for mild steel in 0.05 M NaCl

Solution	E_{cor} (V)	E_{pzc} (V)	ϕ (V)
0.05 M NaCl	-0.500	-0.38	-0.12
0.05 M NaCl + 200 ppm ZnSO ₄	-0.574	-0.499	-0.075

There are two possible structures of the ZnSO₄:SDBS mixture protective layer proposed, on the mild steel that accounts the porosity and capacitance values obtained from the experiments. The first structure is in the form of the formation of a stable but porous zinc oxide/hydroxide layer with the SDBS filling up the pores that block the porosity as illustrated in Figure 4(a). In this case, zinc oxide/hydroxide layer blocks the oxidation reaction of mild steel, while SDBS clogged the coating pores, resulting in the higher R_{ct} value and higher corrosion resistance. At the same time, the value of C_{dl} is decreased caused by the low dielectric values of zinc oxide/hydroxide that then increases the ionic properties of the layer. Therefore it allows the transfer of charges during the measurement, consequently reduces the C_{dl} values.

The second possible structure proposed involves the chelation of SDBS and ZnSO₄ compounds. In this case, zinc oxide/hydroxide are suspended in the SDBS layer, which blocks the oxidation of iron on the surface, consequently, reduces the cathodic reaction, Figure 4(b). Both these structural models proposed, would result in an increase of the R_{ct} value and a decreased C_{dl} values of the protective layer as obtained in EIS measurement results.

This result is consistent with the finding by Sha *et al.* who reported that SDBS can be adsorbed faster onto the brass surface when both SDBS and Al_2O_3 nanoparticles co-exist in which forming a better protective layer (Sha *et al.*, 2019). This is attributed to the electrostatic adsorption between Al_2O_3 nanoparticles and SDBS and the increase in the CMC of SDBS caused by Al_2O_3 . Both of these factors promote the formation of a more compact protective layer on the brass surface.

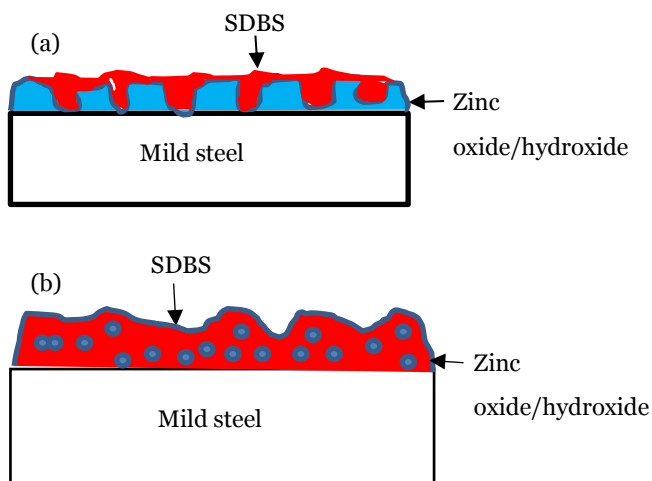


Figure 4. Formation of corrosion protection layers on mild steel surface in NaCl solution containing 200:200 ppm ZnSO_4 :SDBS mixtures

It has often been regarded that good pre-treatment barrier protection is associated with a barrier layer that could provide high-charge transfer resistant. This property is critical for corrosion barrier protection layer as it means that it could impede the charge flow through it and thus forms an effective insulative layer to prevent metal from corroding. However, the charge flow will occur if water can diffuse through the barrier layer, thus providing pathways to facilitate charge transfer processes (Alinejad *et al.*, 2017). A barrier layer that absorbs water through diffusion would eventually exhibit a higher double-layer capacitance value at high frequency, due to the higher dielectric constant of water. This experiment was observed that pre-treating the mild steel individually with SDBS or ZnSO_4 contributes to an almost equal charge transfer resistance values, thus giving almost the same inhibition efficiency. Consequently, SDBS exhibits a higher C_{dl} value compared to ZnSO_4 which

may indicate the higher concentration of water in the layer as compared to ZnSO_4 layer (Table 1). It was seen here that pre-treatment with SDBS alone gives a higher C_{dl} value than that of ZnSO_4 , while the R_{ct} for both systems were about the same, hence proving an almost equal corrosion inhibition efficiency by both pre-treatment. This is further supported by the results on corrosion current i_{corr} , obtained through the polarisation resistance measurements, which indicated an almost equal values (Table 2) for both systems. On the other hand, when a mixture of equal proportion of SDBS and ZnSO_4 was made as to the pre-treatment layer, a much higher R_{ct} value was obtained and consequently a high inhibition efficiency, with an almost equal value of C_{dl} when compared to ZnSO_4 pre-treatment alone. Combining both as a mixture as pre-treatment provided a much higher charge transfer resistance value and corrosion resistance. It was also observed, that the mixture of both compounds at the ratio of 200:200 ppm was able to produce a barrier layer of low double-layer capacitance value at high frequency, indicating no water absorption through diffusion happened throughout the experiment. Thus, the experiment shows that different barrier protection layers that possess different dielectric properties may result in the same corrosion protection ability. In this case, corrosion inhibition of the barrier layers is much more dependent on its R_{ct} properties than its dielectric properties. Corrosion inhibition is not directly reliant on C_{dl} values of the barrier layer.

IV. CONCLUSION

In this paper, the corrosion behaviour of mild steel in NaCl solution was investigated by electrochemical measurements. The charge transfer resistance R_{ct} of the mild steel increased, and the capacitance values C_{dl} decreased correspondingly to the formation of insoluble zinc hydroxide/oxide protective layer together with the SDBS compound on the mild steel surface. The mild steel exhibited high corrosion resistance due to the maximum impedance and minimum corrosion current density of the mild steel in NaCl solution. In this case, the barrier layer's corrosion inhibition is not directly reliant on its C_{dl} values but rather on its charge transfer resistance properties of the barrier layer.

Two inhibition mechanisms were proposed. The first mechanism is the mild steel surface was mainly covered by a porous zinc hydroxide/oxide layer. SDBS clogged the pores and blocks the porosity of the layer resulting in high impedance value. The second mechanism is due to the chelation between SDBS and ZnSO_4 , that contributes to higher barrier properties.

V. ACKNOWLEDGEMENT

The authors would like to thank the Faculty of Applied Sciences, Universiti Teknologi MARA, for permitting to

publish this paper and the Malaysian Rubber Board for their technical support of the tasks. Lastly, immense gratitude to the Fundamental Research Grant Scheme, Malaysian Ministry of Education with Grant Number 600-IRMI/FRGS 5/3 (037/2019) for funding this research work.

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