Influence of Sodium Dodecyl Sulfate on Corrosion Behavior of 304 Stainless Steel

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Abstract

Influence of sodium dodecyl sulfate (SDS) on corrosion behavior of AISI 304 stainless steel in 0.01 N HCl solutions has been investigated by using the potentiodynamic polarization technique at 25°C. The saturated calomel electrode was used as a reference electrode and platinum plate was applied as a counter electrode. The solution was saturated with air during polarization. The critical micelle concentration (CMC) has been evaluated by conductivity measurements. The concentration of SDS was set in a range below and above the CMC for corrosion measurements. Corrosion current density of 304 stainless steel does not depend on the concentration of sodium dodecyl sulfate in HCl solution. Sodium dodecyl sulfate increases pitting resistance of 304 stainless steel in HCl solution.

Keywords: Corrosion, Passivation, Pitting, Stainless steel, Sodium dodecyl sulfate

1. Introduction

AISI 304 stainless steel has a wide scope of applications in many industries because of the good corrosion resistance. However the use of stainless steels in high corrosive conditions can lead to the deterioration of the properties of stainless steel such as pitting, crevice corrosion, and stress corrosion cracking [1,2]. In order to overcome the corrosion problems of metal in general, several techniques have been applied, such as anodic and cathodic protection, coating layer on stainless steel, oxidizing treatment, and the application of inhibiting materials. Inhibitors can be separated into 4 kinds: organic inhibitors, inorganic inhibitors, surfactant inhibitors, and mixed material inhibitors. The surfactant inhibitors seem to have many advantages due to their low price, low toxicity and high inhibition capacity [3].

According to the literature, an anionic surfactant called sodium dodecyl sulfate (SDS) was an effective corrosion inhibitor for copper in acidic solution. The investigation performed by polarization technique revealed that SDS was a good anodic inhibitor at low anodic overvoltage and the adsorption of the inhibitor followed the Langmuir isotherm [3,4]. From weight loss measurement, SDS was also found to be an effective inhibitor for nickel in acidic solution. The inhibition efficiency of surfacetant for nickel increased with the increase of SDS concentration [5]. The adsorption of the anion surfactants such as SDS on an aluminum surface was found to be the main reason to cause the corrosion inhibition [6]. Inhibition efficiency of SDS on carbon steel has also been studied. The

protective film consisted of Fe^{2+}-SDS complex was found on the metal surface [7].

Surfactants are amphiphilic and contain a hydrophilic head and a hydrophobic tail in the molecule. During dissolution, the surfactant molecules adsorb on the surface, resulting in the blocking of the surface from aggressive media. They can also assemble in the bulk solution into aggregates that are known as micelles. The concentration at which surfactants begin to form micelles is called critical micelle concentration or CMC [8-10].

In this study, the anionic surfactant SDS was added into HCl solution with concentration of 0.01 N. The concentration of SDS was set in a range above and below critical micelle concentration. The Potentiodynamic polarization technique, which is widely used as a tool for corrosion study, was applied to investigate the corrosion behavior of 304 stainless steel in acidic environment with various concentrations of SDS [11-13].

2. Materials and Methods

2.1 Preparation of samples

The AISI 304 stainless steel plate was cut to obtain a circular shape with a diameter of 1.6 cm. The samples were wet polished with emery paper grade 600, 1000, and 1200 respectively. After that they were cleaned with ethanol in ultrasonic bath at 44 kHz and dried with hot air prior electrochemical measurement.

2.2 Critical micelle concentration measurement

The critical micelle concentration (CMC) of SDS in 0.01 N HCl was determined by measuring the conductivity of solution at $25^{o}C$. This CMC of SDS in HCl was evaluated and reported in results and discussion section. The CMC value was used to adjust the concentration of SDS in

HCl solution in order to obtain acidic solutions with different concentrations of SDS below and above CMC for further electrochemical measurements, as can be seen in Table 1.

2.3 Electrochemical measurements

A three-electrode cell system has been applied to potentiodynamic polarization measurement at $25^{o}C$. The working electrode was an AISI 304 stainless steel sample immersed in 600 ml of acidic solution in the absence and presence of SDS depending on the test conditions. The concentrations of SDS in HCl solutions used in this study are listed in Table 1. The sample was placed in the sample holder with crevice-free sealing. The exposure area of the sample was approximately 1 cm^2. A saturated calomel electrode (SCE, SHE or standard hydrogen electrode = SCE+0.241 V) was used as a reference electrode by connecting to the sample via Luggin probe. The tip of Luggin probe was placed almost touching the surface of sample during measurement. A platinum plate was used as a counter electrode. An air pump was installed to provide circulation in the solution. The solution was therefore saturated with oxygen. All three electrodes were then connected to an Autolab potentiostat/galvanostat controlled by computer. The potential resolution is better than 0.001 V. After immersion, the sample was cathodically polarized to -0.500 V for 5 minutes. Then the potential was increased from -0.750 to 1.500 V. The potentiodynamic scan rate during polarization was fixed at 1.000 V h^{-1}. At the end of scanning, the potentiodynamic polarization curve was obtained. Afterward, this curve was arranged in a form of a Tafel plot, log current density (log i) versus potential (E). The Tafel extrapolation was applied to determine corrosion current density (i_{corr}) as well as corrosion potential (E_{corr}).

Table 1 The various concentrations of SDS in 0.01 N HCl.

[SDS] related to CMC	[SDS] in 0.01 N HCl (10^{-3} mol dm^{-3})
0	0
0.25×CMC	1.7
0.5×CMC	3.5
CMC	6.9
2×CMC	13.8

Chronoamperometry at 0.600 V for 1 h was also applied in order to examine the pitting corrosion of stainless steel in 0.01 N HCl with and without SDS addition. Scanning electron microscope has been used to investigate the surface of stainless steel.

3. Results and Discussion

3.1 Critical micelle concentration

In general, when the concentration of surfactant in the solution increases, the percentage of the surface area covered by the layer of surfactant from adsorption is increased. The layer normally inhibits the corrosion by blocking the corrosive media from attacking the metal surface. After the concentration of surfactant in the solution reaches CMC, micelles start to form and disperse in the solution. An extra addition of surfactant into the solution above CMC does not significantly increase the percentage of the surface coverage [14].
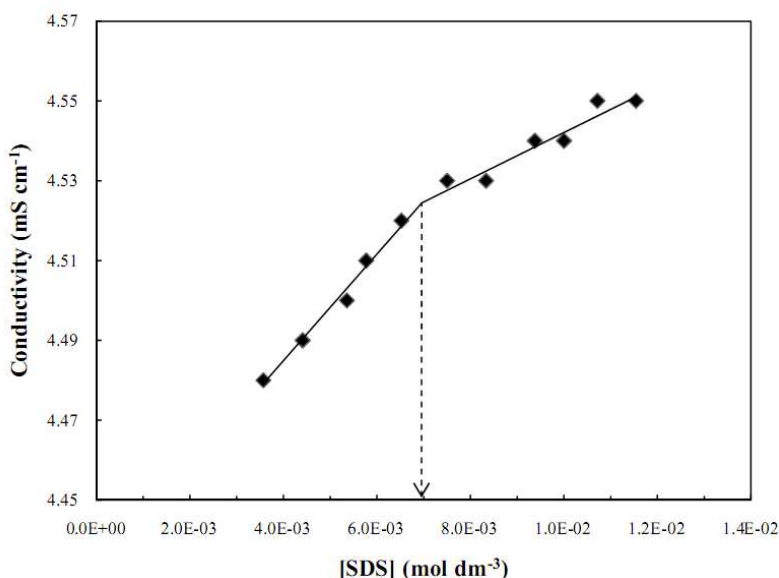

Fig. 1 Conductivity of 0.01 N HCl solution with the presence of SDS at various concentrations

As can be seen in Fig. 1, after addition of SDS into 0.01 N HCl, the conductivity of the solution is increased. This is due to the higher concentration of

sodium and docecyl sulfate ions. Once the concentration has reached the critical micelle concentration, micelles started to form. The size of micelle from the aggregation is much larger when compared to single molecule of surfactant. Moreover, the mobility of such a large micelle is lower than single surfactant molecule. Therefore, the rate of increase of the conductivity is lower. This is observed by a change in slope of concentration and conductivity graph. The obtained CMC of SDS in 0.01 N HCl is equal to 6.9×10^{-3} mol dm^{-3}.

It is well known that the CMC of SDS in distilled water is about 8.0×10^{-3} mol dm^{-3}. The observed depression of the CMC of SDS in acidic solution is primarily due to a reduction in the electrostatic repulsion between anionic hydrophilic head group and, consequently, a smaller contribution of repulsion opposing micellization. Therefore, in acidic environment, anionic surfactant starts forming micelles easier and causes CMC of SDS in 0.01 N HCl to be lower than that reported in distilled water. Rahman and Brown also reported a reduction of CMC of SDS with decreasing pH of the solution [15].

3.2 Corrosion behavior

Potentiodynamic polarization curves of 304 stainless steel in 0.01 N HCl are shown in Fig. 2. The active, passive, and transpassive behavior can be observed. The acidic solution was saturated with oxygen. Therefore the stainless steel can be readily passivated. According to Tafel extrapolation, the corrosion current densities (i_{corr})

of all samples are approximately 1.1×10^{-3} mA cm^{-2} as can be seen in Table 2. The corrosion current density is a direct representative of uniform corrosion rate. As we can observe, there is no significant difference in uniform corrosion rate of stainless steel whether in SDS containing 0.01 N HCl or in 0.01 N HCl alone. Stainless steel has its own natural passive oxide layer. There was no anodic overvoltage applied to the sample at corrosion potential where corrosion current density has been evaluated. The oxidation of the sample was not then accelerated. The protective layer can effectively separate the aggressive media out of the stainless steel with or without the presence of SDS layer on the surface. Therefore the addition of SDS in low or high concentration did not lead to any significant improvement in uniform corrosion resistance of stainless steel in 0.01 N HCl.

Corrosion potential (E_{corr}) was slightly shifted to a more active value with increasing concentration of SDS in acidic solution. The values of corrosion potential are summarized in Table 2. The corrosion potential of sample in 0.01 N HCl without addition of SDS is -0.173 V whereas a potential of -0.290 V is obtained from 2×CMC solution. The shift of corrosion potential to a more active value suggests lower oxidizing power of the solution due to SDS addition. However this effect seems to be not significant on corrosion rate because it leads to almost constant corrosion current density, as mentioned earlier.

Table 2: Electrochemical parameters of 304 stainless steel in 0.01 N HCl in absence and presence of SDS.

[SDS] in 0.01 N HCl (×CMC)	i_{corr} (mA cm^{-2})	E_{corr} (V_{SCE})	E_{pit} (V_{SCE})	E_{trans} (V_{SCE})
0	1.1×10^{-3}	-0.173	0.200	-
0.25	1.2×10^{-3}	-0.242	0.377	-
0.5	1.2×10^{-3}	-0.251	0.800	-
1	1.1×10^{-3}	-0.266	-	1.300
2	1.1×10^{-3}	-0.290	-	1.300

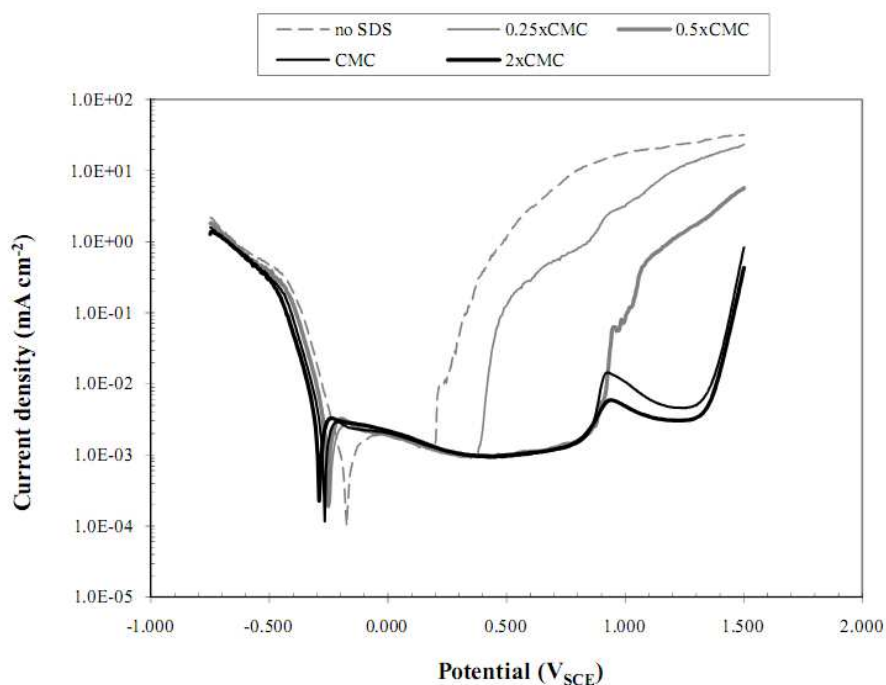**Fig. 2** Potentiodynamic polarization curves of 304 stainless steel in 0.01 N HCl with various concentrations of SDS.

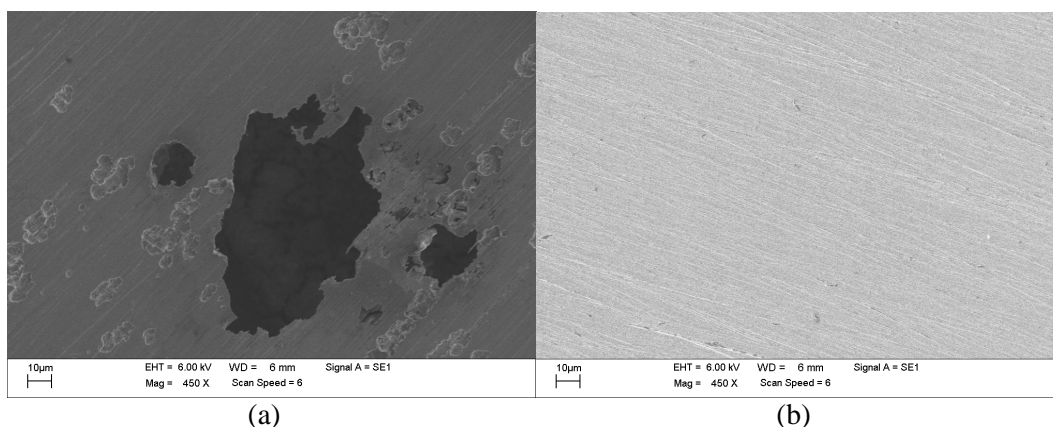(a)   (b)

Fig. 3 Scanning electron micrographs of stainless steel after chronoamperometry at 0.600 V for 1 h in 0.01 N HCl; (a) without SDS addition; (b) with SDS at CMC.

The electrochemical parameter that has been clearly altered after SDS addition was the pitting potential (E_{pit}). The pitting potential of 304 stainless steel in 0.01 N HCl without SDS addition was observed to be the lowest at 0.200 V. With addition of SDS, extra adsorbed layer of surfactant can form on the natural protective oxide layer of stainless steel. The percentage of SDS layer coverage on the surface increases with increasing concentration of SDS before reaching CMC. Therefore it is more difficult for aggressive media to initiate pitting on the surface of stainless steel by destroying such natural oxide with additional surfactant protective layer. The pitting potential was then shifted to a more noble value and the passive range was longer.

With the presence of SDS in solution, pitting requires higher oxidizing potential to occur. Once the concentration of SDS reaches CMC, the surface of stainless steel was fully covered by surfactant layer and the transpassive potential (E_{trans}) of about 1.300 V was obtained after secondary passivation. No pits were observed. The pitting corrosion of stainless steel samples from solution containing SDS at CMC and beyond was totally inhibited because the pitting potential was in the oxygen evolution region. Therefore the reported potential of 1.300 V should be stated as a transpassive potential rather than pitting potential. Wei et al. also reported similar total pitting inhibition by surfactants when pitting potential was raised to the oxygen evolution potential in 0.1 M NaCl [16]. The anodic parts of polarization curves obtained from the solution containing SDS at CMC and beyond are almost identical, especially at high anodic overvoltage. On the other hand, an increase of SDS concentration above CMC did not significantly change the passive behavior of stainless steel. This confirms that CMC is an optimum concentration of anionic surfactant in order to inhibit pitting corrosion of 304 stainless steel in dilute 0.01 N HCl.

Fig. 3 shows the surface of stainless steel after chronoamperometry at 0.600 V for 1 h in 0.01 N HCl in absence of SDS (Fig.3 (a)) and presence of SDS at CMC (Fig.3 (b)). According to Fig. 2, the potential of 0.600 V for the polarization curve obtained from the solution without SDS is clearly higher than the pitting potential. And for the solution with SDS at CMC, a potential of 0.600 V is still in the passive region. Pitting can be observed all over the surface of stainless steel without SDS addition after measurement. For the same potential, with the same oxidizing power, the stainless steel with addition of SDS at CMC shows no sign of pitting corrosion.

4. Conclusions

The following conclusions can be summarized from the present work:

1. Corrosion current density of 304 stainless steel does not depend on the concentration of sodium dodecyl sulfate in HCl solution.

2. Sodium dodecyl sulfate increases pitting resistance of 304 stainless steel in 0.01 N HCl solution.

5. Acknowledgements

6. References

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