รายงานการวิจัย

เรื่อง

อิทธิพลของโซเดียมโดเดคซิลซัลเฟตต่อพฤติกรรมการกัดกร่อนของเหล็กกล้าไร้สนิมชนิด 304 ในสารละลายกรดกำมะถัน

Influence of Sodium Dodecyl Sulfate on Corrosion Behavior of 304 Stainless Steel in Sulfuric Acid

โดย

นายสุธา สุทธิเรืองวงศ์

ภาควิชาเคมี คณะวิทยาศาสตร์

สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

งานวิจัยนี้ได้รับทุนวิจัยจากทุนวิจัยคณะวิทยาศาสตร์

ประจำปีงบประมาณ 2549

Influence of Sodium Dodecyl Sulfate on Corrosion Behavior of 304 Stainless Steel in Sulfuric Acid

Abstract

Influence of sodium dodecyl sulfate (SDS) on corrosion behavior of AISI 304 stainless steel in 1 N sulfuric acid has been investigated by using the potentiodynamic polarization technique at 25°C. The saturated calomel electrode was used as a reference electrode and platinum mesh was applied as a counter electrode. The solution was saturated with air during polarization. According to surface tension measurements, the critical micelle concentration (CMC) of SDS in 1 N sulfuric acid was found to be 8×10^{-4} mol/dm^3. The concentration of SDS was set in a range below and above the CMC for corrosion measurements. Potentiodynamic polarization curves showed that when the concentration of SDS increased the corrosion current density was increased and the polarization resistance was decreased. The true passive region was not observed from the solution containing SDS. This can be explained in term of the difficulty of passive film formation due to the interference of SDS during anodic polarization.

บทคัดย่อ

อิทธิพลของโซเดียมโดเดคซิลซัลเฟตต่อพฤติกรรมการกัดกร่อนของเหล็กกล้าไร้สนิมชนิด 304 ในสารละลายกรดกำมะถันได้ถูกศึกษาด้วยเทคนิคโพเทนชิโอไดนามิกโพราไรเซชัน ที่ 25 °C โดยการใช้ขั้วไฟฟ้าคาโลเมลเป็นขั้วอ้างอิง และโลหะแพลทินัมเป็นขั้วตรงข้าม สารละลายอิ่มตัวด้วยอากาศระหว่างการทดลอง จากผลของการวัดแรงตึงผิว พบว่าค่าความเข้มข้นไมเซลวิกฤตของโซเดียมโดเดคซิลซัลเฟตในสารละลายกรดซัลฟูริก 1 N เท่ากับ 8×10^{-4} mol/dm^3 ค่าความเข้มข้นของโซเดียมโดเดคซิลซัลเฟตในชุดการทดลองถูกปรับให้มีค่าทั้งต่ำและสูงกว่าค่าความเข้มข้นไมเซลวิกฤต ผลจากโพเทนชิโอไดนามิกโพราไรเซชันแสดงให้เห็นว่าเมื่อความเข้มข้นของโซเดียมโดเดคซิลซัลเฟตเพิ่มมากขึ้น ค่ากระแสเนื่องจากการกัดกร่อนมีค่าสูงขึ้น และค่าความต้านทานต่อการถูกโพราไรซ์มีค่าลดลง นอกจากนั้นยังไม่พบชั้นป้องกันการกัดกร่อนในสารละลายที่มีโซเดียมโดเดคซิลซัลเฟตอยู่ด้วย ซึ่งอาจจะเป็นเพราะโซเดียมโดเดคซิลซัลเฟตมีการรบกวนการสร้างชั้นดังกล่าวระหว่างการโพราไรซ์ไปทางด้านอาโนด

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

1. Introduction

Type 304-stainless steel has wide scope of applications in different industries because of its good workability and corrosion resistance. However the use of stainless steels in high corrosive condition can lead to the deterioration of the properties of stainless steel in form of pitting, crevice corrosion, and stress corrosion cracking [1-3]. In order to overcome the corrosion problem 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 inhibitors and inhibiting materials. Inhibitor 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. According to the literature, sodium dodecyl sulfate (SDS) was an effective corrosion inhibitor on copper corrosion in acidic solution [4,5]. The investigation was done by polarization technique. From weight loss measurements, SDS also found to be effective inhibitor for nickel and aluminum in acidic solution [6,7].

In this study, a typical anionic surfactant, SDS, was chosen in order to investigate the corrosion behavior of 304 stainless steel in 1 N sulfuric acid. The concentration of SDS was set in a range above and below critical micelle concentration (CMC).

2. Experimental

2.1. Critical micelle concentration measurement

The critical micelle concentration of SDS surfactant in 1 N H_2SO_4 was evaluated using Du Nouy ring tensiometer. The surface tension measurements were carried out at 25 °C. The various concentrations of SDS in 1 N sulfuric acid solution used in surface tension measurements were listed in Table 1. The measurement was repeated two times for each concentration and the average surface tension has been reported.

2.2. Preparation of the samples

The AISI 304 stainless steel was cut to have the dimension of 2.0×2.5 cm^2. The samples were polished with emery paper grade 600, 1000, and 1200 respectively. After that they were cleaned with ethanol in ultrasonic bath and dried with hot air prior the electrochemical measurement.

Table 1: The various test concentration of SDS in 1 N H_2SO_4 solution

[SDS] in 1 N H_2SO_4 (mol/dm^3)	5×10^{-5}	1×10^{-4}	6×10^{-4}	1×10^{-3}	5×10^{-3}

Table 2: The concentration of SDS in 1 N H_2SO_4

Solution	[SDS] in 1 N H_2SO_4	
	mol/dm^3	×CMC
1	2.0×10^{-4}	0.25
2	4.0×10^{-4}	0.50
3	8.0×10^{-4}	1
4	1.6×10^{-3}	2
5	3.2×10^{-3}	4

2.3. Electrochemical measurement

A three-electrode system has been applied to potentiodynamic polarization measurement at 25°C. The working electrode was a 304 stainless steel sample immersed in 600 ml of 1 N H_2SO_4 in the absence and presence of sodium dodecyl sulfate solution depending on the test condition. The concentrations of SDS in 1 N sulfuric acid used in this study are listed in Table 2. The exposure area of the sample was approximately 7.5 cm^2. A saturated calomel electrode (SCE, SHE = SCE + 241 mV) was used as a reference electrode by connecting to the sample via Luggin probe. The tip of Lugging probe was placed almost touching the surface of sample during measurement. Platinum mesh was used as a counter electrode. The 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.

After immersion, the sample was cathodically polarized to -500 mV for 10 minutes before polarization. Then the potential was increased from -500 to 1,500 mV. The potentiodynamic scan rate during polarization was fixed at 600 mV/h. At the end of scanning, the potentiodynamic polarization curve was obtained. Afterward, this curve was arranged in a form of Tafel plot, log current density (log i) versus potential (E). The Tafel method was applied to determine Tafel slope and corrosion current density (i_{corr}) as well as corrosion potential (E_{corr}).

3. Results and discussion

3.1. Critical micelle concentration (CMC)

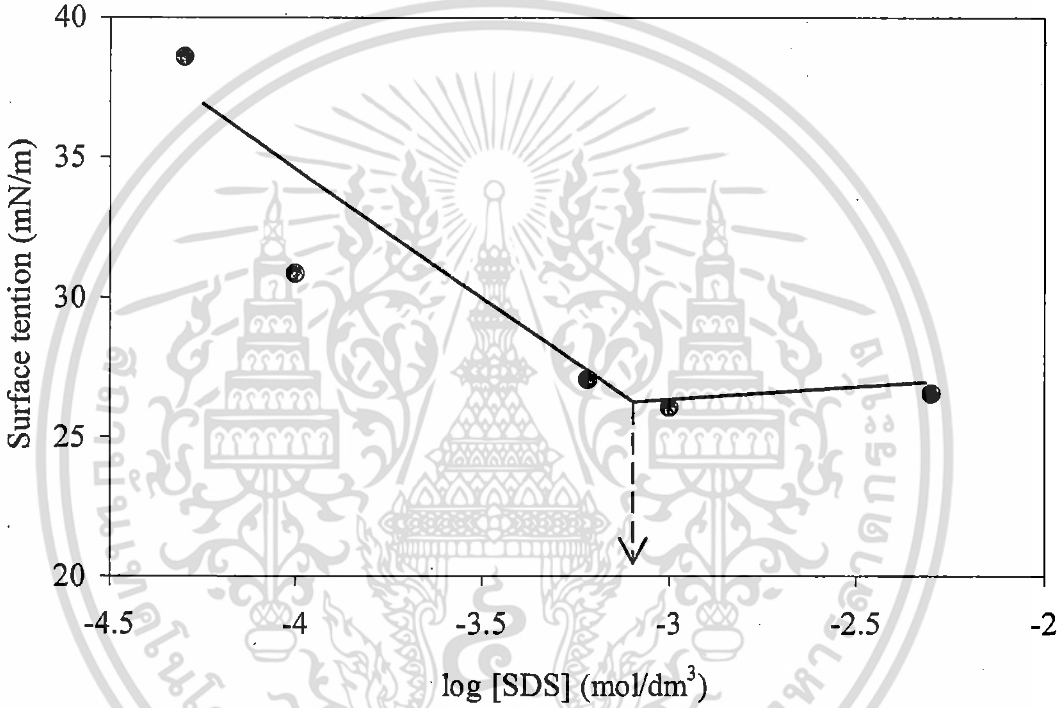

Fig. 1. Surface tension of SDS in 1 N H_2SO_4 at 25°C

The critical micelle concentration of SDS surfactant in 1 N H_2SO_4 was determined by surface tension measurement using Du Nouy ring tensiometer. Surface tension data were shown in Table 3. Fig. 1 shows the plot between surface tension and log [SDS] in order to determine the critical micelle concentration. The CMC of SDS in 1 N sulfuric acid is therefore approximately 8×10^{-4} mol/dm^3.

In general, when the concentration of surfactant in the solution increases the percentage of the surface area covered by the monolayer surfactant is increased. The monolayer normally inhibits the corrosion by blocking the corrosive media from attacking the metal surface. After the concentration of surfactant in the solution reaches CMC, micelle starts to form and disperses in the solution. An extra addition of surfactant into the solution above CMC does not significantly increase the percentage of the surface coverage.

Table 3: Surface tension of 1 N H_2SO_4 with SDS

[SDS] in 1 N H_2SO_4 (mol/dm^3)		Average surface tension
[SDS]	log [SDS]	(mN/m)
5×10^{-5}	-4.30	38.57
1×10^{-4}	-4.00	30.86
6×10^{-4}	-3.22	27.06
1×10^{-3}	-3.00	26.06
5×10^{-3}	-2.30	26.55

3.2. Inhibition test

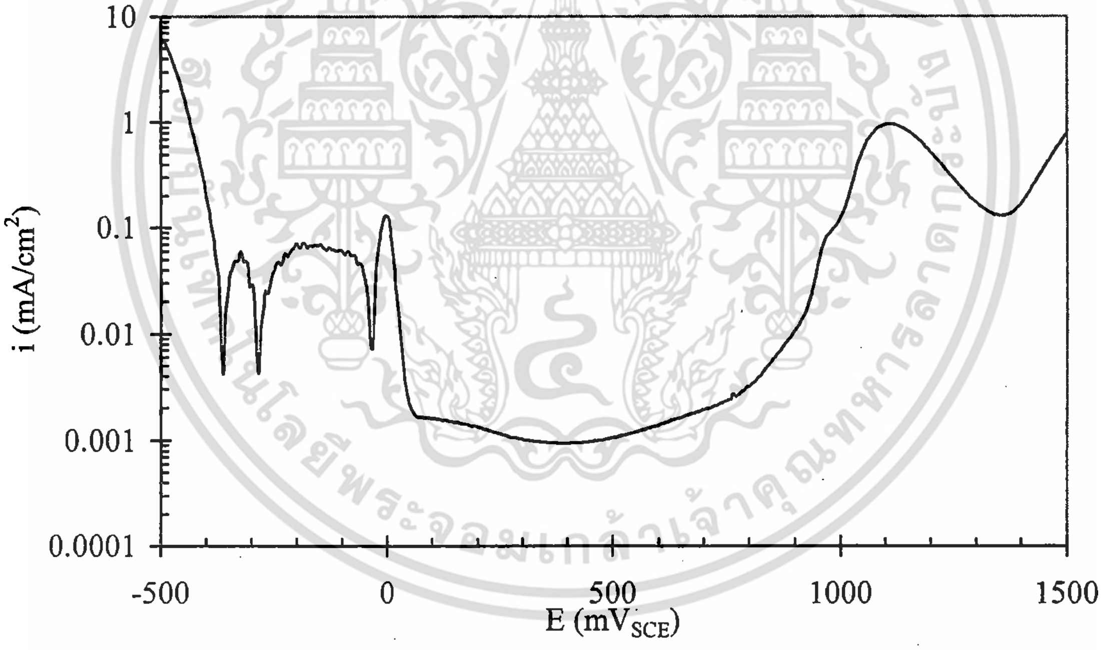

Fig. 2. Polarization curve of 304 stainless steel in 1 N H_2SO_4

In order to study the influence of surfactant on corrosion behavior of stainless steel in acidic solution, corrosion tests were carried out by applying potentiodynamic polarization technique. Fig. 2 shows a polarization curve obtained from 304 stainless steel sample in 1 N sulfuric acid solution. The polarization curve consists of three regions; active, passive, and transpassive region. This is due to the fact that stainless steel can form an oxide film or protective barrier in oxidizing environment and this film is later destroyed in high anodic overvoltage.

In case of high concentration of SDS (2 times and 4 times higher than CMC), the passive region can not be observed in these polarization curves as shown in Fig. 3. It is clear that there was no true passivation of 304 stainless steel in the acidic solution with high amount of SDS.

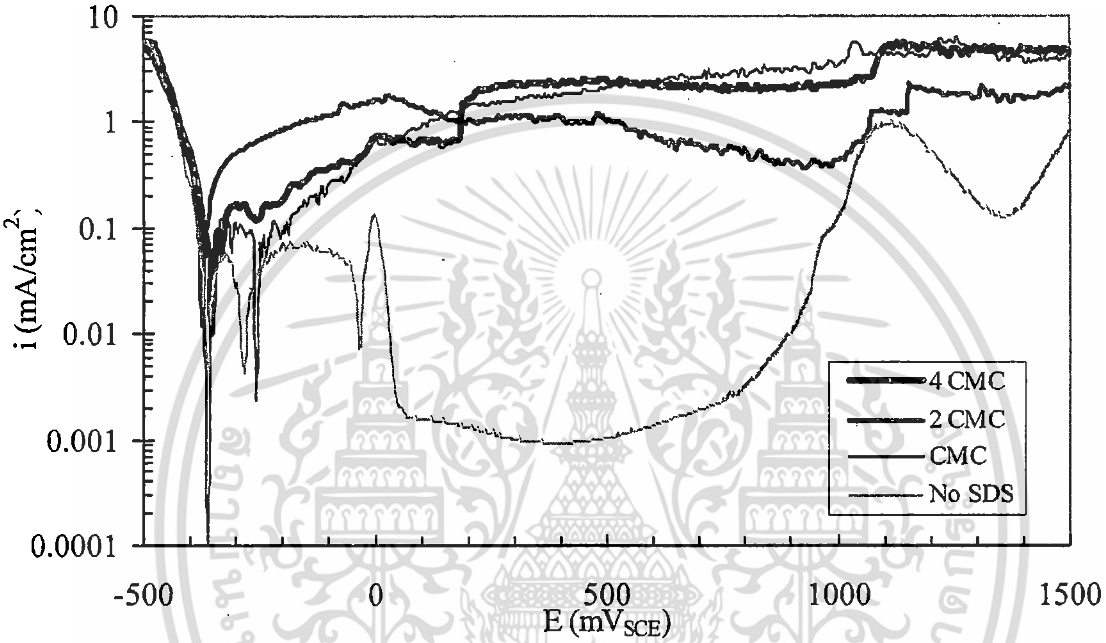

Fig. 3. Polarization curves of 304 stainless steel in 1 N H_2SO_4 with various concentrations of SDS above CMC

At low concentration of SDS (e.g., 0.5 CMC), it can be observed from the polarization curves that there were decrements in current density during polarization at approximately 0 and 850 mV$_{SCE}$. However the current density did not further decrease with increasing anodic polarization. The current density started to increase again shortly after polarization was increased. This implies that stainless steel itself tries to form passive film but it was not a success. The observation was also found in 0.25 CMC polarization curves shown in Fig. 4. According to the mentioned results, the stainless steel has a difficulty to form passive film in acidic solution containing SDS.

The electrochemical parameters; cathodic and anodic Tafel slope (b_c and b_a), corrosion potential (E_{corr}), corrosion current density (i_{corr}), and polarization resistance (R_p), were evaluated and given in Table 4. The corrosion current density was found to increase with increasing concentration of SDS in the acidic solution. Polarization resistance (R_p) decreased when the concentration of SDS was increased. These suggest an ineffectiveness of SDS as a corrosion inhibitor for stainless steel.

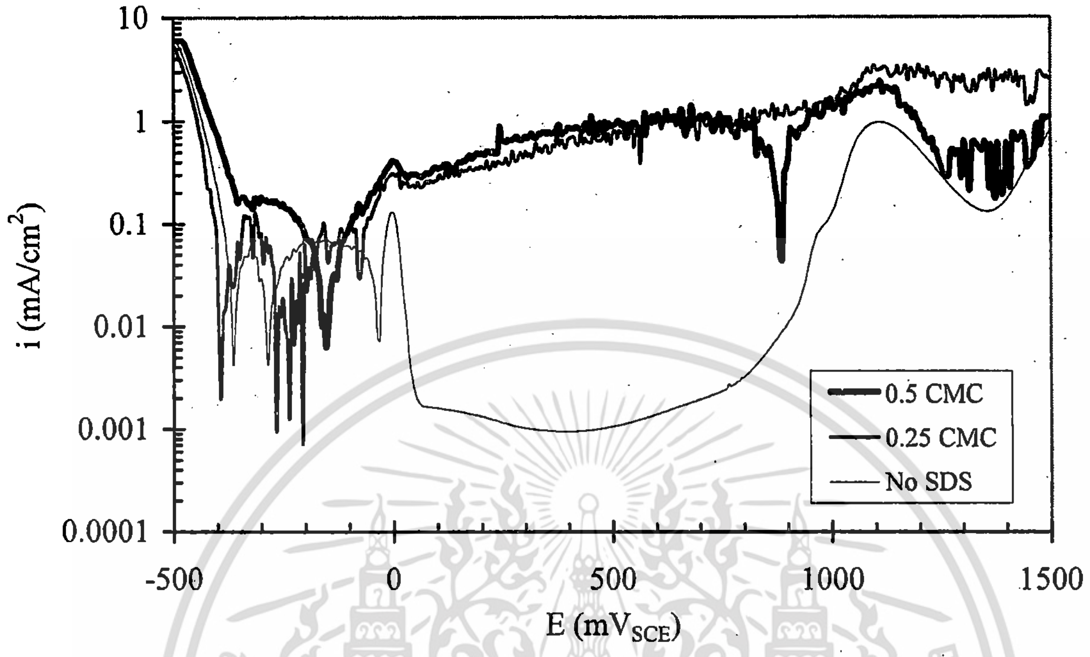

Fig. 4. Polarization curves of 304 stainless steel in 1 N H_2SO_4 with various concentrations of SDS below CMC

Table 4: Electrochemical parameters

[SDS] in 1 N H_2SO_4 (×CMC)	E_{corr} (mV_{SCE})	b_c (mV/decade)	b_a (mV/decade)	i_{corr} (mA/cm^2)	R_p ($\Omega\cdot cm^2$)
-	-360	32	20	0.010	537
0.25	-387	29	21	0.013	407
0.5	-140	67	17	0.017	346
1	-355	47	13	0.019	233
2	-372	42	28	0.033	221
4	-351	50	30	0.047	173

Stainless steel can normally form passive film in acidic solution to prevent further oxidation or corrosion. In this study, the surface of stainless steel was positively charged during anodic polarization; therefore SDS surfactants were able to adsorb their negatively charged head group on stainless steel surface. The adsorption of surfactant could in general inhibit the corrosion as described before. However, in case of stainless steel, the adsorption of surfactant interfere the process of passive film formation. The negatively charged head group of SDS could also exclude O^{2-} in the solution which is necessary for passive film formation. These lead to an incomplete passive film on the surface of stainless steel even the solution was saturated with the oxygen.

4. Conclusion

The true passive region was not observed form the polarization curves of stainless steels in 1 N sulfuric acid containing sodium dodecyl sulfate. This can be explained in term of the difficulty of passive film formation due to the interference of SDS during anodic polarization. Therefore sodium dodecyl sulfate is ineffective to inhibit the corrosion of 304 stainless steel especially in high anodic overvoltage condition.

5. Acknowledgements

The authors acknowledge the financial support of the research project from the Faculty of Science, KMITL. The authors would like to thank Asst. Prof. Dr. Pachernchai Chaiyasith and Asst. Prof. Dr. Chonlada Ritvirulh for kindly supplying the corrosion cell and SDS.

References

[1] E. Hür, G. Bereket, Y. Şahin, Mater. Chem. Phy., Article in press

[2] R. Nishimura, Y. Maeda, Corr. Sci. **2004**, 46, 343

[3] Z. Wei, P. Duby, P. Somasundaran, J. Coll. Interf. Sci. **2003**, 259, 97

[4] R. Fuchs-Godec, V. doleček, Coll. Surf. A: Physicochem. Eng. Aspects **2004**, 244, 73

[5] R. Villamil, P. Corio, J. Rubim, S. Agostinho, J. Electroanaly. Chem. **1999**, 472, 112

[6] R. Guo, T. Liu, X. Wei, Coll. and Surf. A: Physicochem. Eng. Aspects **2002**, 209, 37

[7] T. Zhao, G. Mu, Corr. Sci. **1999**, 41, 1937