CORROSION INHIBITION STUDIES BY SURFACTANTS IN THE PRESENCE OF 2-METHYL THIOPHENE ON MILD STEEL

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ABSTRACT

In this research, three surfactants, namely cetyl trimethyl ammonium bromide (CTAB), sodium lauryl sulfate (SLS) and polysorbate-80 (Tween 80) have been examined as corrosion inhibitors for mild steel in absence and presence of a thiophene derivative (2-methyl thiophene) in 2 M hydrochloric acid (HCl). The inhibition action was investigated through weight loss, potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The morphology before and after placing mild steel in the corrosive media was studied by scanning electron microscopy (SEM). The inhibition efficiencies of these inhibitors were found to be depended on surfactant concentration, immersion time and temperature. Adsorption isotherm was tested with Langmuir, Freundlich and Temkin models. It was found that the adsorption of surfactants CTAB/SLS/Tween 80 in absence and presence of 2-methyl thiophene on mild steel surface fitted best to the Langmuir adsorption isotherm. From the polarization curve, the inhibition of surfactants in presence of 2-methyl thiophene was observed to be a mixed type. The interactive effects of inhibitor immersion time, temperature and concentration were optimized for maximum response of inhibition efficiency using Response Surface Methodology (RSM) based on Historical Data. The potential of zero charge (PZC) at the metal-solution interface was determined for surfactants in absence and presence of 2-methyl thiophene to provide the mechanism of inhibition. The positive value of Antropov's "rational" corrosion potential (E_r) for all the surfactants with respect to potential of zero charge (E_{PZC}) suggested that mild steel surface is positively charged at open circuit potential in the presence of these inhibitors. So, the most efficient surfactant in presence of 2-methyl thiophene as corrosion inhibitor follows this sequence: SLS > CTAB > Tween 80.

ABSTRAK

Dalam penyelidikan ini, tiga surfaktan iaitu sitil trimetil ammonium bromida (CTAB), natrium lauril sulfat (SLS) dan polisorbat-80 (Tween 80) telah dikaji sebagai perencat kakisan bagi keluli lembut dengan ketiadaan dan kehadiran terbitan tiofena (2-metil tiofena) di dalam asid hidroklorik (HCl) 2 M. Tindakan perencatan telah dikaji melalui teknik pengurangan berat, teknik pengutuban potensiodinamik dan spektroskopi impedans elektrokimia (EIS). Morfologi sebelum dan selepas meletakkan keluli lembut di dalam media mengakis telah dikaji dengan mikroskopi electron pengimbas (SEM). Kecekapan perencatan perencatperencat ini didapati bergantung kepada kepekatan surfaktan, masa rendaman dan suhu. Isoterma penjerapan telah diuji dengan model Langmuir, Freundlich dan Temkin. Didapati penjerapan surfaktan CTAB/SLS/Tween 80 dengan ketiadaan dan kehadiran 2-metil tiofena pada permukaan keluli lembut adalah paling sesuai dengan isoterma penjerapan Langmuir. Daripada lengkung pengutuban, didapati perencatan surfaktan dengan kehadiran 2-metil tiofena adalah jenis campuran. Kesan interaktif masa rendaman, suhu dan kepekatan perencat telah dioptimumkan untuk gerak balas maksimum kecekapan perencatan menggunakan kaedah permukaan gerak balas (RSM) berdasarkan data sejarah. Keupayaan cas sifar (PZC) pada antara muka logam-larutan telah ditentukan bagi surfaktan dengan ketiadaan dan kehadiran 2-metil tiofena untuk memberi mekanisma perencatan. Nilai positif keupayaan kakisan Antropov "rasional" (Er) bagi setiap surfaktan terhadap keupayaan cas sifar (E_{PZC}) mencadangkan bahawa permukaan keluli lembut adalah bercas positif pada keupayaan litar terbuka dengan kehadiran perencat-perencat ini. Jadi, surfaktan yang paling cekap dengan kehadiran 2-metil tiofena sebagai perencat kakisan adalah mengikut urutan berikut: SLS> CTAB> Tween 80.

TABLE OF CONTENTS

TITLE

	DECLARATION		
	DEDICATION		
	iv		
	ABST	ГКАСТ	v
	vi		
TABLE OF CONTENTS			vii
	LIST	OF TABLES	X
	LIST	OF FIGURES	xii
	LIST	OF SYMBOLS	xvii
	LIST	OF APPENDICES	xviii
CHAPTEI	R 1	INTRODUCTION	1
	1.1	Introduction	1
	1.2	Class of Surfactants	2
	1.3	Types of Surfactants	2
	1.4	Physical Adsorption	4
	1.5	Chemical Adsorption	4
	1.6	Background of Study	5
	1.7	Problem Statement	6
	1.8	Objectives of Study	7
	1.9	Scope of Study	7
	1.10	Significance of Study	8
CHAPTER 2		LITERATURE REVIEW	9
	2.1	Introduction	9
	2.2	Organic Inhibitors	9
	2.3	Thiophene Derivative	13
	2.4	Surfactant Inhibitors	14

	2.4.1	Cationic surfactant	15
	2.4.2	Anionic surfactant	19
	2.4.3	Nonionic Surfactant	20
2.5	Mixtu	re of inhibitor	22
2.6	Respo	nse Surface Methodology (RSM)	23
CHAPTER 3	RESE	ARCH METHODOLOGY	25
3.1	Introdu	uction	25
3.2	Chemi	cals and Materials	26
3.3	Metho	ds	27
	3.3.1	Weight Loss Method	27
	3.3.2	Adsorption Considerations	27
		3.3.2.1 The Langmuir Isotherm	28
		3.3.2.2 The Freundlich Isotherm	29
		3.3.2.3 The Temkin Isotherm	30
	3.3.3	Activation Parameters	31
	3.3.4	Electrochemical Method	33
	3.3.5	Measurement of Potential of Zero Charge	35
	3.3.6	Response Surface Methodology (RSM) Historical Data	using 35
	3.3.7	Scanning Electron Microscopy (SEM)	36
CHAPTER 4	RESU	LTS AND DISCUSSIONS	39
4.1	Weigh	t Loss Measurements	39
	4.1.1	Effect of Inhibitor Concentration	39
	4.1.2	Effect of Exposure Time	42
	4.1.3	Effect of Temperature	44
4.2	Adsor	ption Isotherm	48
4.3	Activa	tion Parameters	53
4.4	Potent	iodynamic Polarization Curves	57
4.5	Electro	ochemical Impedance Spectroscopy (EIS)	62
4.6	Potent	ial of Zero Charge (E _{PZC})	70

4.7	4.7 Adsorption Mechanism				
4.8	Response Surface Methodology (RSM) using Data	Historical 78			
	4.8.1 Fitting the Response Surface Models	78			
	4.8.2 Diagnostic Model	84			
	4.8.3 Modelling	91			
	4.8.4 Optimization	96			
4.9	Scanning Electron Microscopy (SEM)	102			
CHAPTER 5	CONCLUSION	107			
5.1	Conclusion	107			
REFERENCES		109			
APPENDIX		117			

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 3.1	Molecular and structure formulae of surfactants and	
	thiophene derivative	26
Table 3.2	Experiment design for simulation using historical data	35
Table 3.3	Model summary statistics	37
Table 4.1	Corrosion inhibition efficiencies and activation energies of	
	the inhibitors at 2 h of immersion time at 303 K	41
Table 4.2	Analysis of adsorption of CTAB on mild steel based on	
	Langmuir, Freundlich and Temkin equations	50
Table 4.3	Analysis of adsorption of SLS on mild steel based on	
	Langmuir, Freundlich and Temkin equations	51
Table 4.4	Analysis of adsorption of Tween 80 on mild steel based on	
	Langmuir, Freundlich and Temkin equations	52
Table 4.5	Adsorption parameters obtained from weight loss method	
	at 2 hours immersion time	56
Table 4.6	Electrochemical parameters obtained from polarization	
	curve	60
Table 4.7	EIS parameters for corrosion of carbon steel in 2 M HCl in	
	absence and presence of 2-methyl thiophene with different	
	concentrations of surfactants at 303 K	68
Table 4.8	Values of E_{corr} , E_{PZC} and E_{r} for mild steel in 2 M HCl	
	solution containing CTAB/SLS/Tween 80 in absence and	
	presence of 2-methyl thiophene at 303 K	70
Table 4.9	ANOVA table for inhibition efficiency of CTAB in	
	absence of methyl thiopene	79
Table 4.10	ANOVA table for inhibition efficiency of CTAB in	
	presence of methyl thiophene	79
Table 4.11	ANOVA table for inhibition efficiency of SLS in absence	
	of methyl thiophene	80

Table 4.12	ANOVA table for inhibition efficiency of SLS in presence	
	of methyl thiophene	81
Table 4.13	ANOVA table for inhibition efficiency of Tween 80 in	
	absence of methyl thiophene	81
Table 4.14	ANOVA table for inhibition efficiency Tween 80 in	
	presence of methyl thiophene	82
Table 4.15	Comparing the performances of the models from ANOVA	84
Table 4.16	Criteria for obtaining the optimum response of CTAB in	
	absence of thiophene derivative	96
Table 4.17	Criteria for obtaining the optimum response of CTAB in	
	presence of thiophene derivative	97
Table 4.18	Criteria for obtaining the optimum response of SLS in	
	absence of thiophene derivative	98
Table 4.19	Criteria for obtaining the optimum response of SLS in	
	presence of thiophene derivative	99
Table 4.20	Criteria for obtaining the optimum response of Tween 80	
	in absence of thiophene derivative Criteria for obtaining	100
Table 4.21	the optimum response of Tween 80 in presence of	
	thiophene derivative	101

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
Figure 3.1	Equivalent circuit for the mild steel surface/corrosive media	
	interface for CTAB in presence of 2-methyl thiophene at 1 \times	
	10 ⁻³ M	34
Figure 4.1	The effects of the inhibitor concentration on the inhibition	
	efficiency, in 2 M HCl, in the abnsence and presence of methyl	
	thiophene at 2 h of immersion time at 303 K	40
Figure 4.2	Effect of exposure time on the inhibition efficiency of CTAB	
	in 2 M HCl in absence and presence of 2×10^{-5} M methyl	
	thiophene at 303 K to 363 K	43
Figure 4.3	Effect of exposure time on the inhibition efficiency of SLS in	
	2 M HCl in absence and presence of 2×10^{-5} M of methyl	
	thiophene at 303 K	43
Figure 4.4	Effect of exposure time on the inhibition efficiency of Tween	
	80 in 2 M HCl in absence and presence of 2×10^{-5} M of methyl	
	thiophene at 303 K	44
Figure 4.5	Effect of temperature on the inhibition efficiency for mild steel	
	in 2 M HCl in absence of 2×10^{-5} M of thiophene derivative	
	and various concentrations of CTAB at 2 hours immersion	
	time.	45
Figure 4.6	Effect of temperature on the inhibition efficiency for mild steel	
	in 2 M HCl in presence of 2×10^{-5} M of thiophene derivative	
	and various concentrations of CTAB at 2 hours immersion	
	time.	46
Figure 4.7	Effect of temperature on the inhibition efficiency for carbon	
	steel in 2 M HCl in absence of 2 \times 10 $^{-5}$ M of thiophene	
	derivative and various concentrations of SLS at 2 hours of	
	immersion time	46

Figure 4.8	Effect of temperature on the inhibition efficiency for carbon	
	steel in 2 M HCl in presence of 2×10^{-5} M of thiophene	
	derivative and various concentrations of SLS at 2 hours of	
	immersion time	47
Figure 4.9	Effect of temperature on the inhibition efficiency for carbon	
	steel in 2 M HCl in absence of 2 \times 10 ⁻⁵ M of thiophene	
	derivative and various concentrations of Tween 80 at 2 hours	
	of immersion time	47
Figure 4.10	Effect of temperature on the inhibition efficiency for carbon	
	steel in 2 M HCl in presence of 2 \times 10 ⁻⁵ M of thiophene	
	derivative and various concentrations of Tween 80 at 2 hours	
	of immersion time	48
Figure 4.11	The relationship between log CR and $1/T$ for carbon steel	
	dissolution in different concentrations of CTAB in absence of	
	2×10^{-5} M methyl thiophene in 2 M HCl at 2 h immersion time	53
Figure 4.12	The relationship between log CR and $1/T$ for carbon steel	
	dissolution in different concentrations of CTAB in presence of	
	2×10^{-5} M methyl thiophene in 2 M HCl at 2 h immersion time	54
Figure 4.13	The relationship between log (CR/T) and $1/T$ for carbon steel	
	dissolution in different concentrations of CTAB in absence of	
	2×10^{-5} M methyl thiophene in 2 M HCl at 2 h immersion time	55
Figure 4.14	The relationship between log (CR/T) and $1/T$ for carbon steel	
	dissolution in different concentrations of CTAB in presence of	
	2×10^{-5} M methyl thiophene in 2 M HCl at 2 h immersion time	55
Figure 4.15	Polarization curves of CTAB for mild steel in 2 M HCl in the	
	absence of methyl thiophene	59
Figure 4.16	Langmuir isotherm adsorption model of CTAB in absence and	
	presence of methyl thiophene on steel surface by polarization	
	technique	64
Figure 4.17	Impedance response of the mild steel in 2 M HCl containing	
	CTAB in an absence and presence of 2-methyl thiophene at 1	
	\times 10 ⁻³ M: (a) Nyquist, (b) Bode modulus and (c) Phase bode	
	plots.	64

Figure 4.18	Impedance response of the mild steel in 2 M HCl containing	
	SLS in an absence and presence of 2-methyl thiophene at 5 \times	
	10 ⁻³ M: (a) Nyquist, (b) Bode modulus and (c) Phase bode	
	plots.	65
Figure 4.19	Impedance response of the mild steel in 2 M HCl containing	
	CTAB in an absence and presence of 2-methyl thiophene at 1	
	\times 10 ⁻³ M: (a) Nyquist, (b) Bode modulus and (c) Phase bode	
	plots.	66
Figure 4.20	Langmuir isotherm adsorption model of CTAB in absence and	
	presence of methyl thiophene on steel surface by impedance	
	technique spectroscopy	67
Figure 4.21	The plot of C_{dl} vs. applied potential for mild steel in 2 M HCl	
	containing CTAB/SLS/Tween 80 in absence and presence of	
	2-methyl thiophene at 303 K	71
Figure 4.22	The expected scheme of adsorption of surfactants alone on	
	carbon steel surface: (a) CTAB, (b) SLS and (c) Tween 80	76
Figure 4.23	The expected scheme of adsorption of surfactants in presence	
	of thiophene derivative on carbon steel surface: (a) CTAB, (b)	
	SLS and (c) Tween 80	77
Figure 4.24	Residual diagnostics for inhibition efficiency of CTAB alone:	
	(a) normality; (b) residuals vs. predicted and (c) predicted vs.	
	actual	85
Figure 4.25	Residual diagnostics for inhibition efficiency of CTAB in a	
	presence of methyl thiophene: (a) normality; (b) residuals vs.	
	predicted and (c) predicted vs. actual	86
Figure 4.26	Residual diagnostics for inhibition efficiency of SLS alone: (a)	
	normality; (b) residuals vs. predicted and (c) predicted vs.	
	actual	87
Figure 4.27	Residual diagnostics for inhibition efficiency of SLS in a	
	presence of methyl thiophene: (a) normality; (b) residuals vs.	
	predicted and (c) predicted vs. actual	88

predicted vs. actual89Figure 4.29Residual diagnostics for inhibition efficiency of Tween 80 in a presence of methyl thiophene: (a) normality; (b) residuals vs. predicted and (c) predicted vs. actual90Figure 4.30Contour plots for model in absence and presence of inhibition efficiency between time and temperature (AB): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene93Figure 4.31Contour plots for model in absence and presence of inhibition efficiency between time and concentration (AC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene94Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.32Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.33Ramp function graph for SLS in an absence of thiophene derivative98Figure 4.34Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative91Figure 4.38Ramp function graph for Tween 80 in an absence of thiophene derivative91Figure 4.33Ramp function graph for SLS in a presence of thiophene derivative91Figure 4.34Ramp function graph for Tween 80 in an absence of thiophene derivative91Figure 4.35Ramp function gr	Figure 4.28	Residual diagnostics for inhibition efficiency of Tween 80 alone: (a) normality; (b) residuals vs. predicted and (c)	
a presence of methyl thiophene: (a) normality; (b) residuals vs. predicted and (c) predicted vs. actual90Figure 4.30Contour plots for model in absence and presence of inhibition efficiency between time and temperature (AB): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + 		predicted vs. actual	89
predicted and (c) predicted vs. actual90Figure 4.30Contour plots for model in absence and presence of inhibition efficiency between time and temperature (AB): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene93Figure 4.31Contour plots for model in absence and presence of inhibition efficiency between time and concentration (AC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene94Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.32Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative98Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101	Figure 4.29	Residual diagnostics for inhibition efficiency of Tween 80 in	
Figure 4.30Contour plots for model in absence and presence of inhibition efficiency between time and temperature (AB): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene93Figure 4.31Contour plots for model in absence and presence of inhibition efficiency between time and concentration (AC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene94Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.32Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for SLS in an absence of thiophene derivative98Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative91Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101		a presence of methyl thiophene: (a) normality; (b) residuals vs.	
efficiency between time and temperature (AB): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene93Figure 4.31Contour plots for model in absence and presence of inhibition efficiency between time and concentration (AC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene94Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.33Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for SLS in an absence of thiophene derivative98Figure 4.35Ramp function graph for SLS in a presence of thiophene derivative91Figure 4.36Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.37Ramp function graph for Tween 80 in a presence of thiophene derivative101		predicted and (c) predicted vs. actual	90
alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene93Figure 4.31Contour plots for model in absence and presence of inhibition efficiency between time and concentration (AC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene94Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.33Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for SLS in an absence of thiophene derivative98Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative91Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101	Figure 4.30	Contour plots for model in absence and presence of inhibition	
thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene93Figure 4.31Contour plots for model in absence and presence of inhibition efficiency between time and concentration (AC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene94Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.33Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for SLS in an absence of thiophene derivative98Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative99Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101		efficiency between time and temperature (AB): (a) CTAB	
Figure 4.31Contour plots for model in absence and presence of inhibition efficiency between time and concentration (AC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene94Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.33Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for SLS in an absence of thiophene derivative98Figure 4.35Ramp function graph for SLS in a presence of thiophene derivative90Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101		alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS +	
efficiency between time and concentration (AC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene 94 Figure 4.32 Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene 95 Figure 4.33 Ramp function graph for CTAB in an absence of thiophene derivative 97 Figure 4.34 Ramp function graph for SLS in an absence of thiophene derivative 98 Figure 4.35 Ramp function graph for SLS in an absence of thiophene derivative 99 Figure 4.36 Ramp function graph for SLS in a presence of thiophene derivative 100 Figure 4.37 Ramp function graph for Tween 80 in an absence of thiophene derivative 101 Figure 4.38 Ramp function graph for Tween 80 in a presence of thiophene		thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene	93
alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene94Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.33Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for SLS in an absence of thiophene derivative98Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101	Figure 4.31	Contour plots for model in absence and presence of inhibition	
thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene94Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.33Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for CTAB in a presence of thiophene derivative98Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101		efficiency between time and concentration (AC): (a) CTAB	
Figure 4.32Contour plots for model in absence and presence of inhibition efficiency between temperature and concentration (BC): (a) CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene derivativeFigure 4.33Ramp function graph for CTAB in an absence of thiophene derivativeFigure 4.34Ramp function graph for CTAB in a presence of thiophene derivativeFigure 4.35Ramp function graph for SLS in an absence of thiophene derivativeFigure 4.36Ramp function graph for SLS in a presence of thiophene derivativeFigure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivativeFigure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative		alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS +	
Image: Second		thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene	94
CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS + thiophene, (e) Tween 80 alone and (f) Tween 80 + thiopheneFigure 4.33Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for CTAB in a presence of thiophene derivative98Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative90Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative100Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101	Figure 4.32	Contour plots for model in absence and presence of inhibition	
+ thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene95Figure 4.33Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for CTAB in a presence of thiophene derivative98Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative90Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative100Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101		efficiency between temperature and concentration (BC): (a)	
Figure 4.33Ramp function graph for CTAB in an absence of thiophene derivative97Figure 4.34Ramp function graph for CTAB in a presence of thiophene derivative98Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative99Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative100Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101		CTAB alone, (b) CTAB + thiophene, (c) SLS alone, (d) SLS	
derivative97Figure 4.34Ramp function graph for CTAB in a presence of thiophene derivative98Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene derivative101		+ thiophene, (e) Tween 80 alone and (f) Tween 80 + thiophene	95
Figure 4.34Ramp function graph for CTAB in a presence of thiophene derivative98Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene101	Figure 4.33	Ramp function graph for CTAB in an absence of thiophene	
derivative98Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene101		derivative	97
Figure 4.35Ramp function graph for SLS in an absence of thiophene derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene101	Figure 4.34	Ramp function graph for CTAB in a presence of thiophene	
derivative99Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene101		derivative	98
Figure 4.36Ramp function graph for SLS in a presence of thiophene derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene101	Figure 4.35	Ramp function graph for SLS in an absence of thiophene	
derivative100Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene101		derivative	99
Figure 4.37Ramp function graph for Tween 80 in an absence of thiophene derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene101	Figure 4.36	Ramp function graph for SLS in a presence of thiophene	
derivative101Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene		derivative	100
Figure 4.38Ramp function graph for Tween 80 in a presence of thiophene	Figure 4.37	Ramp function graph for Tween 80 in an absence of thiophene	
		derivative	101
derivative 102	Figure 4.38	Ramp function graph for Tween 80 in a presence of thiophene	
		derivative	102

Figure 4.39	Scanning electron micrographs of carbon steel samples after	
	immersed in: (a) 2-M HCl, (b) 2 M HCl + CTAB (1×10^{-3} M),	
	(c) 2 M HCl + CTAB (1 × 10 ⁻³ M) + methyl thiophene (2 × 10 ⁻	
	⁵ M)	103
Figure 4.40	Scanning electron micrographs of carbon steel samples after	
	immersed in: (a) 2-M HCl, (b) 2 M HCl + SLS (5×10^{-3} M),	
	(c) 2 M HCl + SLS (5 \times 10 ⁻³ M) + methyl thiophene (2 \times 10 ⁻⁵	
	M)	104
Figure 4.41	Scanning electron micrographs of carbon steel samples after	
	immersed in: (a) 2-M HCl, (b) 2 M HCl + Tween 80 (5 \times 10 ⁻³	
	M), (c) 2 M HCl + Tween 80 (5 \times 10 ⁻³ M) + methyl thiophene	
	$(2 \times 10^{-5} \text{ M})$	105

LIST OF SYMBOLS

HCl	-	hydrochloric acid
H_2SO_4	-	sulphuric acid
Р	-	phosphorus
Se	-	selenium
S	-	sulphur
Ν	-	nitrogen
0	-	oxygen
π	-	pi
CMC	-	critical micelle concentration
М	-	molarity
EIS	-	electrochemical impedance spectroscopy
SEM	-	scanning electron microscopy
CTAB	-	cetyl trimethylammonium bromide
SLS	-	sodium lauryl sulphate
Tween 80	-	polysorbate 80
PZC	-	potential of zero charge
XEN	-	xanthenes
XAN	-	xanthone
XION	-	xanthione
DMP	-	2-((dehydroabietylamine)methyl)-6-methoxyphenol
W	-	weight
А	-	surface area
CR	-	corrosion rate
Ι	-	inhibition efficiency
E _{corr}	-	corrosion potential

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
Appendix A	Polarization curves of CTAB for carbon steel in 2 M HCl in	
	the presence of methyl thiophene	116
Appendix B	Polarization curves of SLS for carbon steel in 2 M HCl in	
	the absence of 2-methyl thiophene	116
Appendix C	Polarization curves of SLS for carbon steel in 2 M HCl in	
	the presence of 2-methyl thiophene	117
Appendix D	Polarization curves of Tween 80 for carbon steel in	
	2 M HCl in the absence of 2-methyl thiophene	117
Appendix E	Polarization curves of Tween 80 for carbon steel in	
	2 M HCl in the presence of 2-methyl thiophene	118
Appendix F	Nyquist plot of CTAB for carbon steel in 2 M HCl in	
	absence of 2-methyl thiophene	118
Appendix G	Bode modulus plot of CTAB for carbon steel in 2 M HCl in	
	absence of 2-methyl thiophene	119
Appendix H	Phase bode plot of CTAB for carbon steel in 2 M HCl in	
	absence of 2-methyl thiophene	119
Appendix I	Nyquist plot of CTAB for carbon steel in 2 M HCl in	
	presence of 2-methyl thiophene	120
Appendix J	Bode modulus of CTAB for carbon steel in 2 M HCl in	
	presence of 2-methyl thiophene	120
Appendix K	Phase bode plot of CTAB for carbon steel in 2 M HCl in	
	presence of 2-methyl thiophene	121
Appendix L	Nyquist plot of SLS for carbon steel in 2 M HCl in absence	
	of 2-methyl thiophene	121
Appendix M	Bode modulus plot of SLS for carbon steel in 2 M HCl in	
	absence of 2-methyl thiophene	122
Appendix N	Phase bode plot of SLS for carbon steel in 2 M HCl in	
	absence of 2-methyl thiophene	122

Appendix O	Nyquist plot of SLS for carbon steel in 2 M HCl in presence	
	of 2-methyl thiophene	123
Appendix P	Bode modulus plot of SLS for carbon steel in 2 M HCl in	
	presence of 2-methyl thiophene	123
Appendix Q	Phase bode plot of SLS for carbon steel in 2 M HCl in	
	presence of 2-methyl thiophene	124
Appendix R	Nyquist plot of Tween 80 for carbon steel in 2 M HCl in	
	absence of 2-methyl thiophene	124
Appendix S	Bode modulus plot of Tween 80 for carbon steel in 2 M HCl	
	in absence of 2-methyl thiophene	125
Appendix T	Phase bode plot of Tween 80 for carbon steel in 2 M HCl in	
	absence of 2-methyl thiophene	125
Appendix U	Nyquist plot of Tween 80 for carbon steel in 2 M HCl in	
	presence of 2-methyl thiophene	126
Appendix V	Bode modulus plot of Tween 80 for carbon steel in 2 M HCl	
	in presence of 2-methyl thiophene	126
Appendix W	Phase bode plot of Tween 80 for carbon steel in 2 M HCl in	
	presence of 2-methyl thiophene	127
Appendix X	Langmuir isotherm adsorption model of CTAB in presence	
	of methyl thiophene on steel surface by impedance	
	technique spectroscopy	127
Appendix Y	Langmuir isotherm adsorption model of SLS in absence of	
	methyl thiophene on steel surface by impedance technique	
	spectroscopy	128
Appendix Z	Langmuir isotherm adsorption model of SLS in presence of	
	methyl thiophene on steel surface by impedance technique	
	spectroscopy	128
Appendix AA	Langmuir isotherm adsorption model of Tween 80 in	
	absence of methyl thiophene on steel surface by impedance	
	technique spectroscopy	129
Appendix AB	Langmuir isotherm adsorption model of Tween 80 in	
	presence of methyl thiophene on steel surface by impedance	
	technique spectroscopy	129

Appendix AC	Simulation results of corrosion inhibitor of CTAB alone	130
Appendix AD	Simulation results of corrosion inhibitor of CTAB in	
	presence of thiophene	132
Appendix AE	Simulation results of corrosion inhibitor of SLS alone	134
Appendix AF	Simulation results of corrosion inhibitor of SLS in presence	
	of thiophene	136
Appendix AG	Simulation results of corrosion inhibitor of Tween 80 alone	138
Appendix AH	Simulation results of corrosion inhibitor of Tween 80 in	
	presence of thiophene	140
Appendix AI	Calculation of potential of zero charge (PZC)	142

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, many industries used pipelines as a means of transportation. For instance, pipeline is widely used to transport petroleum. It has a lot of benefits since it can transport any stable chemical through it. Yet, metal pipeline are prone to corrosion especially in the presence of acid. Many studies have been done in order to prevent these phenomena from happening. One of the efficient ways to solve this problem is by using corrosion inhibitor.

Many kinds of corrosion inhibitors have been employed [1]. Corrosion inhibitors have many interests in research for centuries [2-4]. Inhibitor is one significant method to overcome corrosion in aggressive media. One of the main functions of the inhibitor is to remove water molecule or any existence corrosion-active species from the metal surface and have the ability to interact with anodic and cathodic reaction sites in order to retard the oxidation and reduction process.

Generally, corrosion occurred in the presence of oxygen and water and involving oxidation and reduction processes at anodic and cathodic site of reaction, respectively [5]. Inhibitors can be classified into four types, that are (i) inorganic inhibitor, (ii) organic inhibitor, (iii) surfactant inhibitor and (iv) mixed material inhibitors.

Organic compounds have been widely used as a corrosion inhibitor as it contains nitrogen, sulfur and oxygen atoms and an aromatic ring [6]. Heteroatom and aromatic rings act as a reaction center of the adsorption process [7]. The role of the inhibitor is to substitute water on the surface of metal as well as to prevent an oxidation

and reduction from occurring. It will react with anodic and cathodic reaction site at the surface. Furthermore, it prevents water and corrosion-active species to get onto the surface of metal $[\underline{8}]$.

It was found that surfactant plays an important role in the inhibition process by adsorbing itself onto the metal surface via their functional groups [8] Surfactant inhibitor can be divided into four types: Normally, surfactant has a hydrophilic (water loving) and a hydrophobic (water hating) part. It is capable of reducing surface tension at the metal surface without using a high concentration of surfactant. Many researchers have showed that surfactant is capable of inhibiting the corrosion [9-14].

1.2 Class of Surfactants

The surfactant can be divided into three classes, depends on used intention and preferences.

- (i) Used as emulsifiers, foaming agents, wetting agents, dispersants, etc.
- (ii) Based upon the specific chemical structure of its hydrophobic and hydrophilic part (eg, oxygen, nitrogen, amide and sulfonamide).
- (iii) Based on the charge carried by the surface-active part of the molecules; anionic, cationic, nonionic and amphoteric (and zwitterionic), which are commonly known in industry.

1.3 Types of Surfactants

Surfactants can be classified into four types, which are anionic, cationic, nonionic and amphoteric (zwitterionic) surfactants. It depended on their head group charge.

- (i) An anionic surfactant is the reaction product of an organic compound such as a high molecular weight or alcohol with an inorganic compound such as sodium hydroxide or sulfuric acid, yielding a product wherein the hydrophilic head group carries the negative charge such as carboxyl (RCOO⁻), sulfonate (RSO₃⁻), or sulfate (ROSO₃⁻). The anionic surfactants have the advantage of being high and stable foaming agents. Sodium lauryl sulfate (SLS) acts as an inhibitor on corrosion of mild steel in hydrochloric acid shows very good in efficiency [<u>5</u>]. Whereas, the synthesized anionic surfactant with phosphate group by Tawfik [<u>15</u>] showed increasing in inhibition efficiency with increasing the inhibitor concentration.
- (ii) Cationic surfactants are formed in reactions where alkyl halides react with primary, secondary, or tertiary fatty amines. The hydrophilic group has a positive charge. Cationic surface-active materials will be adsorbed on the positive charge surface by electrostatic force and neutralized the surface charge. Cationic surfactants are too expensive but have some special properties such as germicidal action, which make them useful for certain special applications.
- (iii) Amphoteric surface-active material can form anionic or cationic when add to water and depends on the pH system used. This surfactant has both the anionic and cationic ends and this type of surfactant normally has an amino and carboxylate group. Amphoteric surfactants are mostly used in the production of shampoo and personal care product because it is not too strong.
- (iv) Nonionic surface-active agents have a hydrophobic/hydrophilic balance. Examples include polyoxyethylenated alkylphenols, alcohol ethoxylates, alkylphenol ethoxylates and alkanolamides. These surfactants have the advantage that they are not affected by water hardness or pH change as the anionic and cationic surfactants are.

1.4 Physical Adsorption

Physical adsorption or physisorption is well known as a weak molecular forces knowing as van der Waals forces that occurred between the adsorbate and the adsorbent. In this study, adsorbate is referring to inhibitor ions or dipoles, while adsorbent is the electrically charged surface metal. During the adsorption process, the electrical double layer is occurred between the metal/solution interfaces giving the surface charge to the metal. There is no bond broken or formed during the adsorption process. In physisorption, multilayer of adsorption might occur.

One of the examples that can explain the concept above is the inhibition process occurred between cationic inhibitor and the metal surface in acidic media. As we know, in acidic solution, there is an existence of halide ions. At the beginning, these halide ions was oriented dipoles adsorb on the metal surface giving the negative charge of the surface metal. This phenomena will increase the adsorption of the cationic inhibitor to the metal surface due to electrostatic forces occurred.

1.5 Chemical Adsorption

The other type of bonding/forces occurred at the metal/inhibitor interface is chemical adsorption or chemisorption. This adsorption involved a strong covalent bond, which is there are bonds broken and formed during the process. Normally, the chemisorption process occurred at high temperature because its required high activation energy in order to allow bonds broken or bonds forming. The chemisorption process is more slowly compared to the adsorption process.

The of nature of the metal and inhibitor plays an important role in chemisorption process due to charge sharing or charge transfer that might occurred during the process. Inhibitors having an aromatic ring and heteroatom such as nitrogen, sulfur and oxygen atoms will increase the probability of the electron transfer occurred between these inhibitors and the metal surface that having vacant, low-energy electron orbitals. The electron transfer occurred due to the lone-pair electrons or π

electrons of the inhibitors that will react as a reaction center during the chemisorption process.

1.6 Background of Study

Corrosion is the commonly known as metal deteriorates. The corrosion process takes place when the metal is having a contact with oxygen or water molecule. The process involved at both anodic and cathodic sites of the surface metal, which is the oxidation and reduction process occurred. This process is known as electrochemical process, having the same features as a battery.

In many industries, corrosion of metallic materials in acidic media has cost a lot of money. In order to reduce the cost, the use of corrosion inhibitors have become interest and many kinds of inhibitor have been developed and well analyzed according to the types of metal and corrosive media. Organic inhibitor is well known in acid corrosion due to its aromatic ring and heteroatoms (nitrogen, sulfur and oxygen atom) involved. Aromatic ring and heteroatom are believed to have the ability to remove the water molecule or any corrosive-active species from the metal surface. The good inhibitor must have an interaction with anodic and cathodic sites of the metal in order to retard the oxidation and reduction process. Hence, it can prevent the corrosion from occurring [16].

Besides organic inhibitor, surfactant inhibitor has a lot of attention too because of the chemical structure of its head group. Surfactant inhibitor can inhibit the corrosion process by either physisorption (electrostatic) or chemisorption process. It depends on the charge of the metal surface and head groups of the surfactant [16]. The use of surfactant inhibitor has proven to reduce the corrosion rate of metals in acidic media and became the main reason why the adsorption studies of inhibition process of surfactant inhibitor has a lot attention and considerable importance [17, 18].

1.7 Problem Statement

Mild steel has been applied in many industries because of its good mechanical properties and reasonable cost. However, the corrosion process of mild steel in acidic media cannot be avoided. Hence, the use of corrosion inhibitor can reduce the corrosion rate or protect the steel surface from the acidic media. The most popular used corrosion inhibitors are organic inhibitors due to its aromatic ring and heteroatoms (nitrogen, sulfur and oxygen atom).

Thiophene derivatives have been widely used as organic inhibitors. Thiophene derivative, namely 2-methyl thiophene will be used and investigate in this study in order to inhibit the corrosion process of mild steel. This thiophene derivative was chosen because of its heterocyclic compound containing sulfur atoms that believe have the ability to retard the oxidation and reduction process involved at the steel surface. Heterocyclic compounds represent a potential class of corrosion inhibitors. Moreover, high molecular weight organic compounds, for instance surfactants, have become an attraction in corrosion field. Besides, surfactants also is expected to have a high efficiency as a corrosion inhibitor in acidic media due to its long hydrocarbon chain that can help the adsorption of surfactant inhibitor on the steel surface with high surface coverage. Hence its efficiency will improve. According to Rosen [19], mixed surfactants have been widely used in industrial applications. However, very few studies have been devoted to mixed inhibitors of surfactant and organic compound.

The aim of this work is to study the inhibition effect of three types of surfactant (Cetyl trimethylammonium bromide (CTAB), Sodium lauryl sulfate (SLS) and Polysorbate 80 (Tween 80)) in absence and presence of 2-methyl thiophene on mild steel in 2 M hydrochloric acid (HCl) in order to improve the protective action of the inhibitor, thus, enhance the inhibition efficiency as corrosion inhibitor. This study will be extended to study the mechanism involved at metal interface by determined its potential of zero charge (E_{pzc}) using electrochemical impedance spectroscopy (EIS) method.

1.8 Objectives of Study

The aim of this work is:

- To investigate the inhibition action of surfactants (CTAB, SLS and Tween 80) in absence and presence of 2-methyl thiophene against corrosion of mild steel in 2 M HCl using weight loss method, potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS),
- 2) To investigate the effect of various concentrations of surfactants (2×10^{-5} M 1×10^{-3} M of CTAB and 1×10^{-4} M 5×10^{-3} M of SLS and Tween 80), immersion time (2-6 hours) and temperature (303 K 363 K) in absence and presence of 2×10^{-5} M methyl thiophene on inhibition efficiency using historical data of Response Surface Methodology (RSM),
- 3) To postulate the mechanism of corrosion inhibition by the surfactants in absence and presence of 2-methyl thiophene by determined the potential of zero charge (E_{pzc}) of mild steel using electrochemical impedance spectroscopy (EIS) method.

1.9 Scope of Study

In this research, the surfactants (CTAB, SLS and Tween 80) in absence and presence of 2×10^{-5} M methyl thiophene will be used as inhibitors on mild steel under various concentrations of surfactants (2×10^{-5} M – 5×10^{-3} M), immersion time (2-6 hours) and temperature (303 K – 363 K). The inhibitors will be tested on mild steel in 2 M hydrochloric acid (HCL) solutions and its efficiency will be investigated under different experimental conditions using weight loss method, potentiodynamic polarization techniques and electrochemical impedance spectroscopy (EIS). In addition, the synergistic effects will be discussed when the thiophene derivative was added to the corrosive solutions containing various concentrations of CTAB, SLS and Tween 80. Thiophene derivative was chosen because of its sulphur atom in

heterocyclic compounds has proved very good for inhibition of metal corrosion in acidic solutions. The results obtained from weight loss method will be optimizing using Response Surface Methodology (RSM) in order to study the interactive effects of inhibitor concentration, time and temperature for maximum response of inhibition efficiency. The surface morphologies of mild steel will be observed by Scanning electron microscopy (SEM). Besides, the mechanism involved at the metal-solution interface will be elucidated by the potential of zero charge (PZC) data from EIS.

1.10 Significance of Study

This study is expected to elucidate the mechanism of inhibition by surfactants in absence and presence of thiophene derivative and explain the observed inhibition efficiency of inhibitors on mild steel in acid medium. In the current study the efficiency of surfactants (CTAB, SLS and Tween 80) in addition of 2-methyl thiophene on mild steel is expected to enhance corrosion inhibition with increasing concentration of the surfactants.

REFERENCES

- ORUBITE-OKOROSAYE, K.J., I R; OCHEI, M; AKARANTA, O, Synergistic Effect of Potassium Iodide on Corrosion Inhibition of Mild Steel in HCl. J. Appl. Sci. Environ. Manage, 2007. 11(2): p. 27-31.
- M.M. Caroline, P.C., C.S. Hannes, K. Boris, and A.A. Ilhan, "Inhibition and promotion of copper corrosion by CTAB in a micro reactor system. Langmuir, 2008. 24: p. 14269-14275.
- El-Maksoud, S.A.A., The effect of organic compounds on the electrochemical behaviour of steel in acidic media. A review. International Journal of Electrochemical Science, 2008. 3(5): p. 528-555.
- Antonijevic, M.M.a.P., M.B., *Copper Corrosion Inhibitors*. International Journal of Electrochemical Science, 2008. **3**: p. 1-28.
- KUMAR, A., Corrosion Inhibition of Mild Steel in Hydrochloric Acid by Sodium Lauryl Sulfate (SLS). E-Journal of Chemistry 2008. 5(5): p. 275-280.
- Hegazy, M.A., M. Abdallah, and H. Ahmed, Novel cationic gemini surfactants as corrosion inhibitors for carbon steel pipelines. Corrosion Science, 2010. 52(9):
 p. 2897-2904.
- Negm, N.A., et al., Effectiveness of some diquaternary ammonium surfactants as corrosion inhibitors for carbon steel in 0.5M HCl solution. Corrosion Science, 2010. 52(6): p. 2122-2132.
- Rozenfeld, I.L., Corrosion inhibitors. 1981, New York: McGraw-Hill.
- Youp Ryu, D. and M.L. Free, *Evaluation of mild steel corrosion using a new surfactant inhibition model.* Anti-Corrosion Methods and Materials, 2006. **53**(1): p. 12-18.
- Minhaj, A., Saini, P.A., Quraishi, M.A. and Farooqi, I.H., Corrosion Prevention and Control. A study of natural compounds as corrosion inhibitors for industrial cooling systems. Vol. 46. 1999.
- Shalaby, M.N., Osman, M.M. and El Feky, A.A., Anti-Corrosion Methods and Materials. Effect of some organic surfactants on corrosion inhibition of steel in sea water,. Vol. 46. 1999: MCB University Press.

- Elachouri, M., Hajji, M.S., Salem, M., Kertit, S., Aride, J., Coudert, R. and Essassi, E., *Corrosion (Houston)*. Some Nonionic Surfactants as Inhibitors of the Corrosion of Iron in Acid Chloride Solutions. Vol. 52. 1996: NACE International.
- Zhao, T.a.M., G., *The adsorption and corrosion inhibition of anion surfactants on aluminium surface in hydrochloric acid.* Corrosion Science, 1999. **41**(No. 10): p. 1937-1944.
- Elachouri, M., Hajji, M.S., Salem, M., Kertit, S., Aride, J., Coudert, R. and Essassi,
 E., Some nonionic surfactants as inhibitors of the corrosion of iron in acid chloride solutions. Corrosion (Houstan), 1996. 52(2): p. 103-108.
- Tawfik, S.M. and N.A. Negm, Synthesis, characterization and evaluation of some anionic surfactants with phosphate group as a biodegradable corrosion inhibitor for carbon steel in acidic solution. Journal of Molecular Liquids, 2016. 215: p. 185-196.
- Hegazy, M.A., M. Abdallah, and H. Ahmed, Novel cationic gemini surfactants as corrosion inhibitors for carbon steel pipelines. Corrosion Science. Vol. 52. 2010. 2897-2904.
- Bastidas, J.M., Pinilla, P., Cano, E., Polo, J.L. and Miguel, S., Copper corrosion inhibition by triphenylmethane derivatives in sulphuricd acid media. Corrosion Science, 2003. 45(2): p. 427-449.
- Bolzan, A.E., Wakenge, I.B., Piatti, R.C.V., Salvarezza, R.C. and Arvia, A.J., The behaviour of copper anodes in aqueous thiourea-containing sulphuric acid solutions. Journal of Electroanalytical Chemistry, 2001. 501(1-2): p. 241-252.
- Rosen, M.J.a.H., X. Y., Synergism in binary mixtures of surfactants. Journal of the American Oil Chemists' Society, 1982. 59(12): p. 582-585.
- El-Etre, A.Y., *Khillah extract as inhibitor for acid corrosion of SX 316 steel*. Applied Surface Science, 2006. 252(24): p. 8521-8525.
- Obi-Egbedi, N.O., I.B. Obot, and M.I. El-Khaiary, *Quantum chemical investigation* and statistical analysis of the relationship between corrosion inhibition efficiency and molecular structure of xanthene and its derivatives on mild steel in sulphuric acid. Journal of Molecular Structure, 2011. **1002**(1-3): p. 86-96.
- Kosari, A., et al., *Theoretical and electrochemical assessment of inhibitive behavior* of some thiophenol derivatives on mild steel in HCl. Corrosion Science, 2011.
 53(10): p. 3058-3067.

- Mallaiya, K., et al., Electrochemical characterization of the protective film formed by the unsymmetrical Schiff's base on the mild steel surface in acid media. Electrochimica Acta, 2011. 56(11): p. 3857-3863.
- Liu, B.-Y., et al., Corrosion inhibition and adsorption behavior of 2-((dehydroabietylamine)methyl)-6-methoxyphenol on mild steel surface in seawater. Thin Solid Films, 2011. **519**(22): p. 7836-7844.
- Hosseini, S.M.A., M.J. Bahrami, and P. Pilvar, Adsorption effect of 1-((2hydroxynaphtalen-1-yl) (phenyl)methyl)urea on the carbon steel corrosion in hydrochloric acid media. Materials and Corrosion, 2010. 61(10): p. 866-871.
- Bahrami, M.J., S.M.A. Hosseini, and P. Pilvar, Experimental and theoretical investigation of organic compounds as inhibitors for mild steel corrosion in sulfuric acid medium. Corrosion Science, 2010. 52(9): p. 2793-2803.
- Quraishi, M.A., et al., *Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of Murraya koenigii leaves.* Materials Chemistry and Physics, 2010. **122**(1): p. 114-122.
- Benabdellah, M., et al., *Corrosion inhibition of steel in molar HCl by triphenyltin2– thiophene carboxylate.* Arabian Journal of Chemistry, 2010. **4**(3): p. 243-247.
- Bentiss, F., et al., Corrosion control of mild steel using 3,5-bis(4-methoxyphenyl)-4amino-1,2,4-triazole in normal hydrochloric acid medium. Corrosion Science, 2009. 51(8): p. 1628-1635.
- Zhang, Q.B. and Y.X. Hua, Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. Electrochimica Acta, 2009. 54(6): p. 1881-1887.
- Papavinasam, S.a.A., M.F., Piperidones and Tetrahydrothiopyrones as Corrosion Inhibitors for Copper in Sulphuric Acid. Corrosion Science, 1991. 32: p. 193-203.
- K.F.Khaled, a.N.A.A.-M., A Predictive Model for Corrosion Inhibition of Mild Steel by Thiophene and Its Derivatives Using Artificial Neural Network. International Journal of ELECTROCHEMICAL SCIENCE, 2012. 7: p. 1045 - 1059.
- Fouda A. S., A., T.F., Ahmed, E.S. and Abou-elmagd, B.S., Performance of some thiophene derivatives as corrosion inhibitors for 304 stainless steel in aqueous solutions. 2013. 39: p. 2641–2661.

- Fouda, A.S., Ibrahim, A.A. and El-behairy, W.T., *Thiophene derivatives as corrosion inhibitors for carbon steel in hydrochloric acid solutions*. 2014. 6(5): p. 144-157.
- Fouda, A., M. Diabb, and D. Badawya, Adsorption and Corrosion Inhibition Characteristics of Some Thiophene-3-Carbohydrazide Derivatives on Low Carbon Steel in Hydrochloric Acid Solutions. International Research Journal of Pure and Applied Chemistry, 2015. 8(2): p. 81-95.
- Asefi, D., M. Arami, and N.M. Mahmoodi, *Electrochemical effect of cationic gemini* surfactant and halide salts on corrosion inhibition of low carbon steel in acid medium. Corrosion Science, 2010. 52(3): p. 794-800.
- Wang, X., H. Yang, and F. Wang, A cationic gemini-surfactant as effective inhibitor for mild steel in HCl solutions. Corrosion Science, 2010. 52(4): p. 1268-1276.
- Saleh, M.M. and A.A. Atia, Effects of structure of the ionic head of cationic surfactant on its inhibition of acid corrosion of mild steel. Journal of Applied Electrochemistry, 2006. 36(8): p. 899-905.
- Hegazy, M.A., A novel Schiff base-based cationic gemini surfactants: Synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid solution. Corrosion Science, 2009. 51(11): p. 2610-2618.
- Negm, N.A., et al., *Biocidal and anti-corrosive activities of benzoimidazol-3-ium cationic Schiff base surfactants.* Engineering in Life Sciences, 2011. **11**(5): p. 496-510.
- Badawi, A.M., et al., Novel quaternary ammonium hydroxide cationic surfactants as corrosion inhibitors for carbon steel and as biocides for sulfate reducing bacteria (SRB). Materials Chemistry and Physics, 2010. 124(1): p. 458-465.
- Al-Sabagh, A.M., et al., Corrosion Inhibition Efficiency in Relation to Micellar Interaction Parameters of Cationic/Nonionic Surfactant Mixtures for Carbon Steel Pipelines in 1 M HCl Solution. Journal of Dispersion Science and Technology, 2009. 30(10): p. 1411-1423.
- Migahed, M.A., *Electrochemical investigation of the corrosion behaviour of mild steel in 2M HCl solution in presence of 1-dodecyl-4-methoxy pyridinium bromide*. Materials Chemistry and Physics, 2005. **93**(1): p. 48-53.
- Palomar, M.E., et al., Imidazolium, Pyridinium and Dimethyl-Ethylbenzyl Ammonium Derived Compounds as Mixed Corrosion Inhibitors in Acidic Medium. Journal of Surfactants and Detergents, 2010. 14(2): p. 211-220.

- Amin, M.A., Understanding the inhibitory effect of sodium oleate on the corrosion of Al and Al-Cu alloys in 1.0 M H<inf>3</inf>PO<inf>4</inf>solution-Polarization studies. Journal of Applied Electrochemistry, 2009. **39**(5): p. 689-696.
- Migahed, M.A., E.M.S. Azzam, and A.M. Al-Sabagh, *Corrosion inhibition of mild steel in 1 M sulfuric acid solution using anionic surfactant*. Materials Chemistry and Physics, 2004. 85(2-3): p. 273-279.
- Hegazy, M.A. and M.F. Zaky, Inhibition effect of novel nonionic surfactants on the corrosion of carbon steel in acidic medium. Corrosion Science, 2010. 52(4): p. 1333-1341.
- Hegazy, M.A., et al., An investigation of three novel nonionic surfactants as corrosion inhibitor for carbon steel in 0.5M H2SO4. Corrosion Science, 2012. 54: p. 219-230.
- Al-Sabagh, A.M., et al., Corrosion inhibition behavior of new synthesized nonionic surfactants based on amino acid on carbon steel in acid media. Journal of Molecular Liquids, 2016. 219: p. 1078-1088.
- Bedair, M.A., et al., Synthesis, electrochemical and quantum chemical studies of some prepared surfactants based on azodye and Schiff base as corrosion inhibitors for steel in acid medium. Corrosion Science, 2017. 128: p. 54-72.
- Negm, N.A., et al., Amide type nonionic surfactants: Synthesis and corrosion inhibition evaluation against carbon steel corrosion in acidic medium. Journal of Molecular Liquids, 2018. 256: p. 574-580.
- Gopi, D., et al., A study on new benzotriazole derivatives as inhibitors on copper corrosion in ground water. Corrosion Science, 2009. **51**(10): p. 2259-2265.
- Tamilselvi, S. and S. Rajeswari, *The effect of triazoles and surfactants on the corrosion inhibition of carbon steel in acid solution*. Anti-Corrosion Methods and Materials, 2003. 50(3): p. 223-231.
- Gopi, D., Bhuvaneswaran, N., Rajeswarai, S. and Ramadas, K., Synergistic effect of thiourea derivatives and non-ionic surfactants on the inhibition of corrosion of carbon steel in acid environments. Anti-Corrosion Methods and Materials, 2000.
 47(6): p. 332-338.
- Chauhan, V.S., Bhardwaj, N.K. and Chakrabarti, S.K., *Application of response surface* methodology and central composite design for the optimization of talc filler and

retention aid in papermaking. Indian Journal of Chemical Technology, 2013. **20**: p. 121-127.

- Ajeigbe, S.O., Basar, N., Hassan, M.A. and Aziz, M., Optimization of corrosion inhibition of essential oils of Alpinia galanga on mild steel using Response Surface Methodology. ARPN Journal of Engineering and Applied Sciences, 2017. 12(9): p. 2763-2771.
- Faleiro, R.M.R., et al., *Statistical modeling of charcoal consumption of blast furnaces based on historical data*. Journal of Materials Research and Technology, 2013.
 2(4): p. 303-307.
- Shahavi, M.H., Hosseini, M., Jahanshahi, M., Darzi, G.N., Optimization of encapsulated clove oil particle size with biodegradable shell using design expert methodology. Pakistan Journal of Biotechnology, 2015. 12(2): p. 149-160.
- Jeirani, Z., Mohamed Jan, B., Si Ali, B., Noor, I.M, See, C.H. and Saphanuchart, W.P., Prediction of the optimum aqueous phase composition of a triglyceride microemulsion using response surface methodology. J. Ind. Eng. Chem., 2013a. 19(4): p. 1304-1309.
- Jeirani, Z., Mohamed Jan, B., Si Ali, B., Noor, I.M, See, C.H. and Saphanuchart, W.P., Prediction of water and oil percolation thresholds of a microemulsion by modeling of dynamic viscosity using response surface methodology. J. Ind. Eng. Chem., 2013b. 19(2): p. 554-560.
- Karami, H.R., M. Keyhani, and D. Mowla, *Experimental analysis of drag reduction in the pipelines with response surface methodology*. Journal of Petroleum Science and Engineering, 2016. **138**: p. 104-112.
- Chan, C.H., et al., Analysis of face milling performance on Inconel 718 using FEM and historical data of RSM. IOP Conference Series: Materials Science and Engineering, 2017. 270.
- Xiagang Yang, B.L., Haizeng Wang & Baorong Hou, Inhibition of CTAB on the corrosion of mild steel in hydrochloric acid. Journal of Dispersion Science and Technology, 2011. 32(5): p. 672-676.
- Goudarzi, N., Peikari, M., Zahiri, M.R., and Mousavi, H.R., Adsorption and corrosion inhibition behavior of stainless steel 316 by aliphatic amine compounds in acidic soultion. Arch. Metall. Mater., 2012. 57: p. 845-851.

- Abd-El-Nabey, B.A., Abdel-Gaber, A.M., Khamis, E., Morgaan, A.I.A., and Ali, N.M.
 , Inhibition of corrosion of brass in 0.1 M H₂SO₄ by thioxoprymidinone derivatives. Int. J. Electrochem. Sci., 2013a. 8: p. 11301-11326.
- Vermeulan, T.H., Vermeulan, K.R. Hall, L.C., *Fundamental*. Vol. 5. 1966: Ind. Eng. Chem.
- Langmuir, I., *The adsorption of gases on plane surfaces of glass, mica and platinum*.J. Am. Chem. Soc., 1918. **40**: p. 1362-1403.
- Webber, T.N.a.C., Pore and solid diffusion models for fixed bed adsorbers. J. Am. Inst. Chem. Eng., 1974. 20: p. 228-238.
- Hutson, N.D.a.Y., R.T., Adsorption. J. Colloid Inter Sci., 2000.
- Voudrias, E., Fytianos, F. and Bozani, E., Sorption description isotherms of Dyes from aqueous solutions and waste water with different sorbent materials. Global Nest, The Int. J., 2002. 4: p. 75-83.
- Mohan, S.a.K., J., Removal of lignin and tannin color from aqueous solution by adsorption on to activated carbon solution by adsorption on to activated charcoal. Environ. Pollut., 1997. **97**: p. 183-187.
- Guadalupe, R., Reynel-Avila, H.E., Bonilla-Petriciolet, A., Cano-Rodriguez, I., Velasco-Santos, C. and Martinez-Hernandez, A.L., *Recycling poultry feathers for Pb removal from wastewater: kinetic and equilibrium studies*. Proceedings of World Academy of Science, Engineering and Technology, 2008. 30.
- Goldberg, S., Equations and models describing adsorption processes in soils. Soil Science Society of America Vol. 677. 2005, s. Segoe Road, Madison, WI 53711, USA: Chemical Processesin Soils, SSSA Book Series.
- Temkin, M.I.a.P., V., Kinetics of ammonia synthesis on promoted iron catalyst. Acta Phys. Chim. USSR, 1940. 12: p. 327-356.
- Aharoni, C.a.U., M., *Kinetics of activated chemisorption. Part 2. Theoretical models.*J. Chem. Soc. Faraday Trans., 1977. **73**: p. 456-464.
- Abiola, O.K.a.O., N.C., Adsorption of (4-amino-2-methyl-5-pyrimidinyl methylthio) acetic acid on mild steel from hydrochloric acid solution (HCl)-Part 1. Mater. Chem. Phys., 2004. 83: p. 315-322.
- Behpour, M., Ghoreishi, S.M., Salavati-Niasari, M. and Ebrahimi, B., Evaluating two new synthesized S-N Schiff bases on the corrosion of copper in 15 % hydrochloric acid. Mater. Chem. Phys., 2008. 107: p. 153-157.

- Solmaz, R., Investigation of the inhibition effect of 5-((E)-4-phenylbuta-1,3dienylideneamino)-1,3,4-thiadiazole-2-thiol Schiff base on mild steel corrosion in hydrochloric acid Corrosion Science, 2010. 52: p. 3321-3330.
- Xu, B., Yang, W.Z., Liu, Y., Yin, X.S., Gong, W.N. and Chen, Y.Z., Experimental and theoretical evaluation of two pyridinecarboxaldehyde thiosemicarbazone compounds corrosion inhibitors for mild steel in hydrochloric acid solution. Corrosion Science, 2014. 78: p. 260-268.
- Haruyama, S., Tsuru, T. and Gijutsu, B., J. Jpn. Soc. Corros. Eng., 1978. 27.
- Rosenfeld, I.I., Corrosion inhibitors. 1981, New York: McGraw-Hill.
- El Mehdi, B., Mernari, B., Traisnel, M., Bentiss, F. and Lagrenee, M., Mater. Chem. Phys., 2002. **77**: p. 489-496.
- Fouda, A.S., et al., Performance of some thiophene derivatives as corrosion inhibitors for 304 stainless steel in aqueous solutions. Research on Chemical Intermediates, 2012. 39(6): p. 2641-2661.
- Asefi, D., N.M. Mahmoodi, and M. Arami, *Effect of nonionic co-surfactants on corrosion inhibition effect of cationic gemini surfactant*. Colloids and Surfaces
 A: Physicochemical and Engineering Aspects, 2010. 355(1-3): p. 183-186.
- Negm, N.A., et al., Gravimetric and electrochemical evaluation of environmentally friendly nonionic corrosion inhibitors for carbon steel in 1M HCl. Corrosion Science, 2012. 65: p. 94-103.