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 perencat-perencat 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" (E_r) 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.

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HCl - hydrochloric acid
H_2SO_4 - sulphuric acid
P - phosphorus
Se - selenium
S - sulphur
N - nitrogen
O - oxygen
π - pi
CMC - critical micelle concentration
M - 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
A - surface area
CR - corrosion rate
I - inhibition efficiency
E_{corr} - corrosion potential

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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 [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 (RSO_3^-), or sulfate ($ROSO_3^-$). 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 [5]. Whereas, the synthesized anionic surfactant with phosphate group by Tawfik [15] 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:

1) 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.

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