UNIVERSITI TEKNOLOGI MARA

STUDIES ON THE ADSORPTION AND CORROSION INHIBITION OF SUBSTITUTED BENZYLIDENE SCHIFF BASES ON MILD STEEL IN 1 M HCl

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

The objective of this thesis is to investigate the performance of newly synthesized substituted benzylidene Schiff bases as corrosion inhibitors of mild steel in 1 M HCl at 25°C. To accomplish this intention, a series of (E)-*N'*-benzylidene-N^4-phenylbenzene-1,4-diamine Schiff bases that contain different substituent groups at *para* position of benzylidene were synthesized and characterized *via* physical and spectroscopic analysis. The azomethine double bond (C=N) infrared spectra found for the Schiff bases are at around 1590-1604 cm^{-1}. From ^1H Nuclear Magnetic Spectroscopy (NMR) spectra, the azomethine proton (singlet) shifted in the range of δ 8.634-8.531 ppm, while the peaks at around δ 157.32-155.82 ppm found in ^{13}C NMR spectra are assigned for azomethine carbon. The corrosion inhibition performance of *N*-phenyl-1,4-phenylenediamine (NPPD), (*E*)-N^1-benzylidene-N^4-phenylbenzene-1,4-diamine (K1), *N*-[(*E*)-4-chlorobenzylidene]-*N'*-phenylbenzene-1,4-diamine (K2) and *N*-[(*E*)-4-methoxybenzylidene]-*N'*-phenylbenzene-1,4-diamine (K3) was measured in 1 M HCl using electrochemical methods which are polarization, Linear Polarization (LPR) and Electrochemical Impedance Spectroscopy (EIS). The analysis of substrate's surface *via* Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS) was employed to determine the Schiff base adsorption behaviour on the surface of mild steel in the acidic solution. The electrochemical results revealed that the corrosion inhibition efficiencies of the Schiff bases are higher and achieved up to 96.0% as found for K2, thus more effective than the other Schiff base in the series, and the parent amine of NPPD. The adsorption of inhibitors at the metal-solution interface are well described based on Langmuir adsorption isotherm because R^2 and slope values are almost to the value of 1. In further work, the temperature effect of Schiff bases in 1 M HCl also has been evaluated using polarization method. The inhibition efficiencies found for K2 inhibitor retains its great inhibitive effect and increase slightly until become almost constant at the highest temperature of 55°C. XPS measurements showed that studied Schiff bases mainly adsorbed *via* chemisorption interaction which involves coordination bond mainly electron donation from π electrons in the benzene ring and azomethine double to the empty orbital of metal. This is supported by ΔG_{ads} values which suggests the adsorption of Schiff base inhibitors on mild steel surface are due to the both combination of chemisorption and physisorption. The multilayers adsorption of inhibitors is due to subsequent layer physisorbed on the inner most (chemisorbed) layer *via* weak intermolecular hydrogen bonding of C-H-π between Schiff base molecules. The relationship between the corrosion inhibition efficiency with physicochemical and electronic properties of *N*-phenyl-1,4-phenylenediamine and Schiff bases was examined *via* density functional theory method. Theoretical results clearly shown that the corrosion inhibition efficiency of inhibitors are essentially depends on the frontier orbitals parameters as example by the increase of inhibition effciency always directly related to the decrease of band gap energy between HOMO and LUMO. It is proven there is an electron transfer interaction among the Schiff base molecules with the active sites at the metal surface.

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CHAPTER ONE
INTRODUCTION

1.1 RESEARCH BACKGROUND

The petroleum processing, agrotechnology, military, aerospace and transport industry are some of the many important industries in the 21st century. The materials used in these and many other industries needs to be well taken care of to prevent corrosion. Corrosion is one of the primary threats to any industry. The gradual destruction of materials by chemical reactions with its environment need to be well controlled. Nowadays, efficient corrosion control is one area that is taken seriously by the industries. Hence, the study of corrosion becomes more significant.

The main aspects that are taken into consideration in the study of corrosion are the safety of human lives, the economic impact of corrosion and conservation of materials. Lack of early detections of corrosion of highways, bridges, pipes, buildings or parking structures may be detrimental to health and become threat to human safety. If the deterioration of materials caused by its reaction with the surrounding environments is not dealt with, it can also cause massive economical loss. In major industries plant such as chemical processing, nuclear power, electrical power plants as as water treatment systems, major repairs and possible shutdowns are just a few the many consequences of poor corrosion management. Several years ago, the National Institute of Standards and Technology (formerly the National Bureau of Standards) estimated that the annual cost of corrosion in the United States was in the range of $9 billion to $90 billion. These figures confirmed by various technical organizations, including the National Association of Corrosion Engineers (Schweitzer, 2009).

In the effort of maintaining good corrosion protection systems, an increasing number of research in the development of new corrosion protection methods are done worldwide with metal corrosion rate and corrosion mechanism as its central theme. Established electrochemical methods are employed to give insight to both the thermodynamic and kinetic aspects of corrosion. These established methods have boundless practicality in forecasting materials operation and developing corrosion mitigation strategies, recognizing the changes effects in procedure and circumstances