Chapter II

Experimental

II- EXPERMENTAL

II.1. Chemicals used: -

The chemicals used in this work purchased from different international companies and all were analytical grade as shown in Table 2.

Table 2: Chemicals used throughout the present investigation

Materials	Molecular structure	M. Wt	Source
1, 4 Diamino butane	$H_2N\text{-}(CH_2)_4\text{-}NH_2$	88.15	Merck
1, 8 Diamino octane	$H_2N\text{-}(CH_2)_8\text{-}NH_2$	144.26	Merck
1, 4 Phenylene diamine	$H_2N\text{-}C_6H_4\text{-}NH_2$	138.13	Merck
p- Hydroxy benzoic acid	$HO\text{-}C_6H_4\text{-}COOH$	138.13	Avacado
Dimethyl dichloro silane	$(CH_3)_2SiCl_2$	129	Fluka
Ethanol amine	$HO\text{-}(CH_2)_2\text{-}NH_2$	61.08	Merck
4-amino phenol	$HO\text{-}C_6H_4\text{-}NH_2$	109.13	Merck
Triethyl amine	$(C_2H_5)_3N$	149.19	Merck
Tetrahydrofurane	C_4H_8O	80.17	Honyl limited

II.2. Preparation of Compounds under Investigations:

II.2.1. Amidation:

II.2.1.1. Preparation of organoamide compounds (I, II & III)

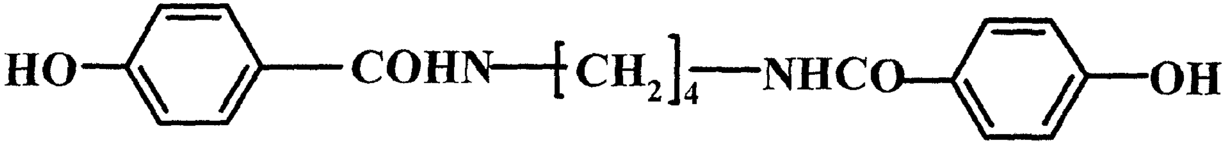
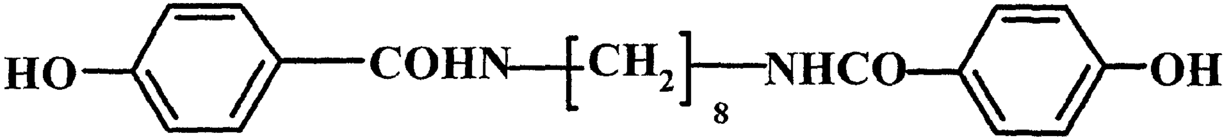
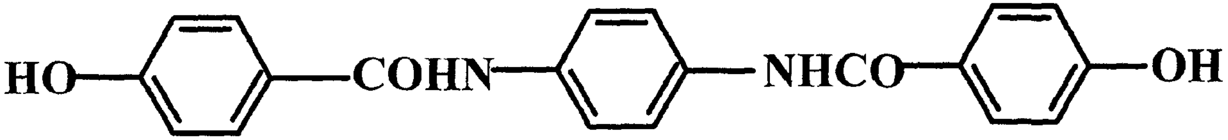
p-hydroxybenzoic acid (0.5) mol was added to (0.25) mol of either 1,4 diaminobutane, 1,8 diaminooctane or 1,4 phenelenediamine into a three necked round bottomed flask equipped with a mechanical stirrer, condenser and a thermometer. The reaction mixture was heated to 170 - 190°C until the theoretical amount of water has been collected using Dean Stark apparatus. The products I, II&III were purified and their structures were confirmed by (FTIR) and (^{1}HNMR) spectroscopy. Table **(3)** illustrates the name and the chemical structures of the prepared compounds.

II.2.2. Sililation

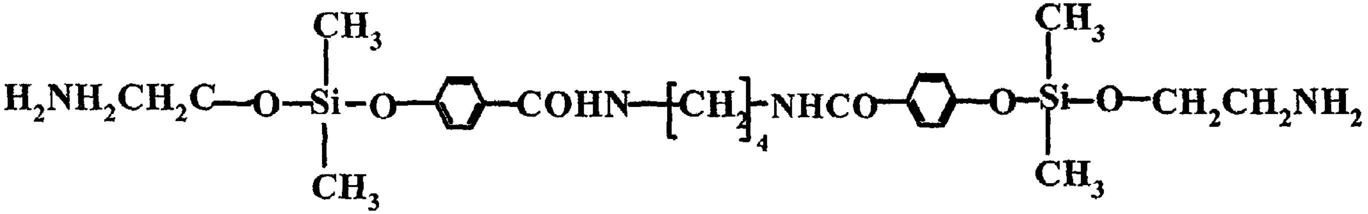
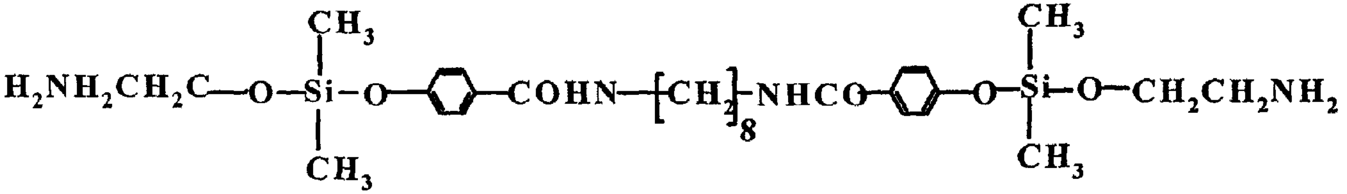
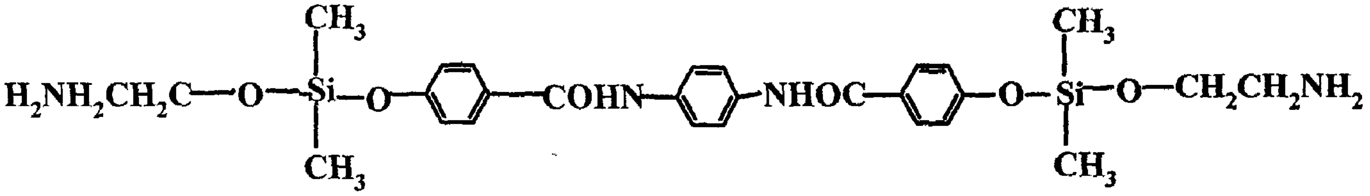
II.2.2.1. Preparation of organoamide siloxane compounds (IV, V& VI)

In a three necked flask equipped with mechanical stirrer, pressure dropping funnel, (0.05) mol of either compounds I, II or III were added to (0.1) mol of ethanolamine in presence of tetrahydrofurane (THF) as solvent and triethylamine as acid acceptor. Then (0.05) mol of dimethyldichlorosilane (DMDCS) dissolved in 20 ml of (THF) was added drop wise while stirring under inert atmosphere for 1 hr at 30°C .The temperature was raised gradually to 65°C and the mixture was refluxed for 3 hrs. The products IV, V& VI were obtained and purified by vacuum distillation and confirmed by (FTIR) and (^{1}HNMR) spectroscopy. Table **(3)** illustrates the name and the chemical structures of the prepared compounds.

Table 3: Chemical Structure of the Prepared Compounds

NO.	NAME	STRUCTURE
I	Bis-(P- hydroxyl phenyl amido) butane	
II	Bis-(P- hydroxyl phenyl amido) octane	
III	Bis-(P- hydroxyl phenyl amido) benzen	

Continued Table 3:

NO.	NAME	STRUCTURE
IV	p,p –bis (dimethyl siloxane ethylamine benzamide)butane	
V	p,p – bis(dimethyl siloxane ethylamine benzamide) octane	
VI	p,p –bis (dimethyl siloxane ethylamine benzamide)phenlene	

II.3. Characteristic properties of the prepared compounds:-

II.3.1. Infra-red **analysis (FTIR)**

The IR spectra of the prepared compounds were confirmed by using FT.IR spectrometer model type mattson – infinity series bench top 961. The wave number and intensities of the IR bands of the different types of the function groups were determined in a range of 4000- 500 cm^{-1}.

*II.3.2. Nuclear mag***netic resonance ^{1}HNMR**

The ^{1}HNMR of the prepared compounds were confirmed by 300 MHZ spectrometer W-P-300, Bruker. The solution for ^{1}HNMR analysis was prepared by dissolving the prepared compounds in dimethyl sulphoxide.

II.4. Chemical Composition of the Investigated Materials

The carbon steel alloy used in this investigation was provided from Suez oil company type B37 has the following chemical composition.

Element	**C**	**Mn**	**P**	**Sn**	**Si**	**Fe**
weight%	0.3	0.03	0.04	0.045	0.02	rest

II.5. Test Specimens and Treatment

II.5.1. For weight loss measurements

The test specimens were used in the form of sheets of dimensions 2×2×0.2 cm, and of ≈ 6g average weight, the specimens were first mechanically polished by grinding with emery paper from 240 to 1200 grit to obtain a smooth surface degreased with acetone, then washed with double distilled water, and finally dried between two filter papers and weighed.

The test specimens were suspended by suitable glass hooks at the edge of the basin, and under the surface of the test solution by about 1 cm. After specified time of immersion specimens were taken out of the test solution, then rinsed with distilled water, dried as before and weighed again. The average weight loss at a certain time for each set of three samples was taken in mg cm^{-2} and recorded.

II. 5.2. For Electrochemical Measurements

II. 5.2. 1. Preparation of working electrode

The working electrode of carbon steel alloy was made from the same materials as short segments having a total surface area of about 0.867 cm^2.These electrodes were fixed into Pyrex glass tubing using (araldite), and weld from one side to a copper wire for electric connection.

The exposed area was polished with different emery papers in the normal way starting from coarser to finer, followed by degreasing with acetone and finally washing with double distilled water, just before insertion in the electrolytic cell.

II.6. Preparation of Electrolyte Solutions

II.6.1. Hydrochloric *acid*

Approximately 5M hydrochloric acid solution was prepared by diluting the appropriate volume of concentrated chemically analytical grade 37% HCl with double distilled water. The concentration of the acid was checked by titration of an appropriately diluted portion with standard solution of sodium carbonate. From this stock concentrated solution, exactly 2M, 1M and 0.5 M hydrochloric acid solution were prepared by dilution with double distilled water.

II.6.2. Inhibitor *solutions*

100 ml stock solutions of compounds (I - IX) were prepared by dissolving the desired weight of each compound in 100ml of absolute ethanol, and then the six different concentrations 100,200,300,400,500 and 600ppm were prepared by dilution with known concentration of hydrochloric acid.

II.7. Procedures Used For Corrosion Measurements

II.7.1- Weight-loss measurements according to ASTM G31

The specimen of the given metal prepared as described before (total surface area ≈ 9.6 cm^2) was immersed in 100 ml of (0.5M, 1M and 2M HCl solution) in absence and presence of different concentrations of inhibitors, respectively at 23±2°C to determine the effect of concentration, also this method is repeated to determine the effect of temperature of 500 ppm of each compound at 35, 45, 55 and 65°C, respectively. This was carried out in covered beaker to prevent contact with air and allows the escape of evolved gases. After 12 hr of immersion period, the test specimens were removed, washed with bi-distilled water, dried by a jet of air and finally weighted. The change in weight was recorded to the nearest 0.0001g. Pre-calculation were always made to avoid scratching of the specimen during washing after exposure. Therefore, the weight loss was given by

$$\Delta W = W_1 - W_2 \qquad \textbf{(II.1)}$$

Where W_1 and W_2 are the weight of specimen before and after immersion, respectively. The inhibition efficiency % I was computed by the equation:

$$I\% = \frac{\Delta W - \Delta W_i}{\Delta W} x100 \qquad \textbf{(II.2)}$$

Where ΔW and ΔW_i are the weight losses per unit area in absence and presence of the inhibitors, respectively.
The corrosion rate was computed by the equation:

$$mpy = \frac{KW}{DAT} \qquad \textbf{(II.3)}$$

Where,

K $= 3.45 \times 10^6$

W = weight loss, g ; D = density of specimen in g cm^{-3}

A = area of specimen, cm^2

T = exposure time, in hours.

II.7.2. Electrochemical measurements

Electrochemical experiments were carried out by means of impedance equipment (Tacussel- Radiometer PGZ 301) and controlled with Tacussel corrosion analysis soft ware (Voltamaster 4), connected to a personal computer. Measurements were obtained using the electrochemical cell containing five openings: three of them were used for the electrodes and two for nitrogen bubbling during all the experiments .The counter electrode was a platinum electrode and the reference electrode was a saturated calomel electrode (SCE). All potentials in the text are quoted versus this electrode. The surface area of working electrode was 0.867cm^2 and mounted in a glass tube with araldite epoxy.

II.7.2.1- Open circuit potential:

The potential of carbon steel alloy electrode was measured against saturated calomel electrode (SCE) in 1 M HCl solution in absence and presence of different concentrations of each inhibitor.

II.7.2.2. Potentiodynamic polarization technique according to ASTM -G5-94

The polarization measurements were carried out and the anodic and cathodic polarization curves were recorded under a constant sweep rate of 20 mvs^{-1}, initial potential -1000 mV and final potential 0 mV. The inhibition efficiencies were determined from corrosion currents calculated automatically by voltamaster from Tafel extrapolation method.

II.7.2.3. Electrochemical impedance (EIS) according to ASTM - G106-89

The EIS measurements were performed at open circuit potential in the frequency range from 100 kHz to 10 mHz, with an alternating current amplitude of 10 mV. Each measurement was taken after 24 hr of immersion in corresponding solution .The data were analyzed using program Z SimpWin data analysis software to obtain the equivalent current circuit for each compound.

II.7.2.4. Scanning electron microscopy (SEM)

A JEOL (5300 Japan) scanning electron microscope were utilized to document the surface morphology of various specimens of carbon steel alloy in case of polished surface only and that immersed in 1M hydrochloric acid in absence and presence of inhibitors at 300 and 500 ppm for 24 hr .This instrument was operated in a secondary electron imaging mode with an accelerating voltage of either 10 or 20 KeV. Magnifications ranging from 50 to 10000 X could be obtained by this tool. In the present investigation two magnifications were selected, 750 and 2000X.

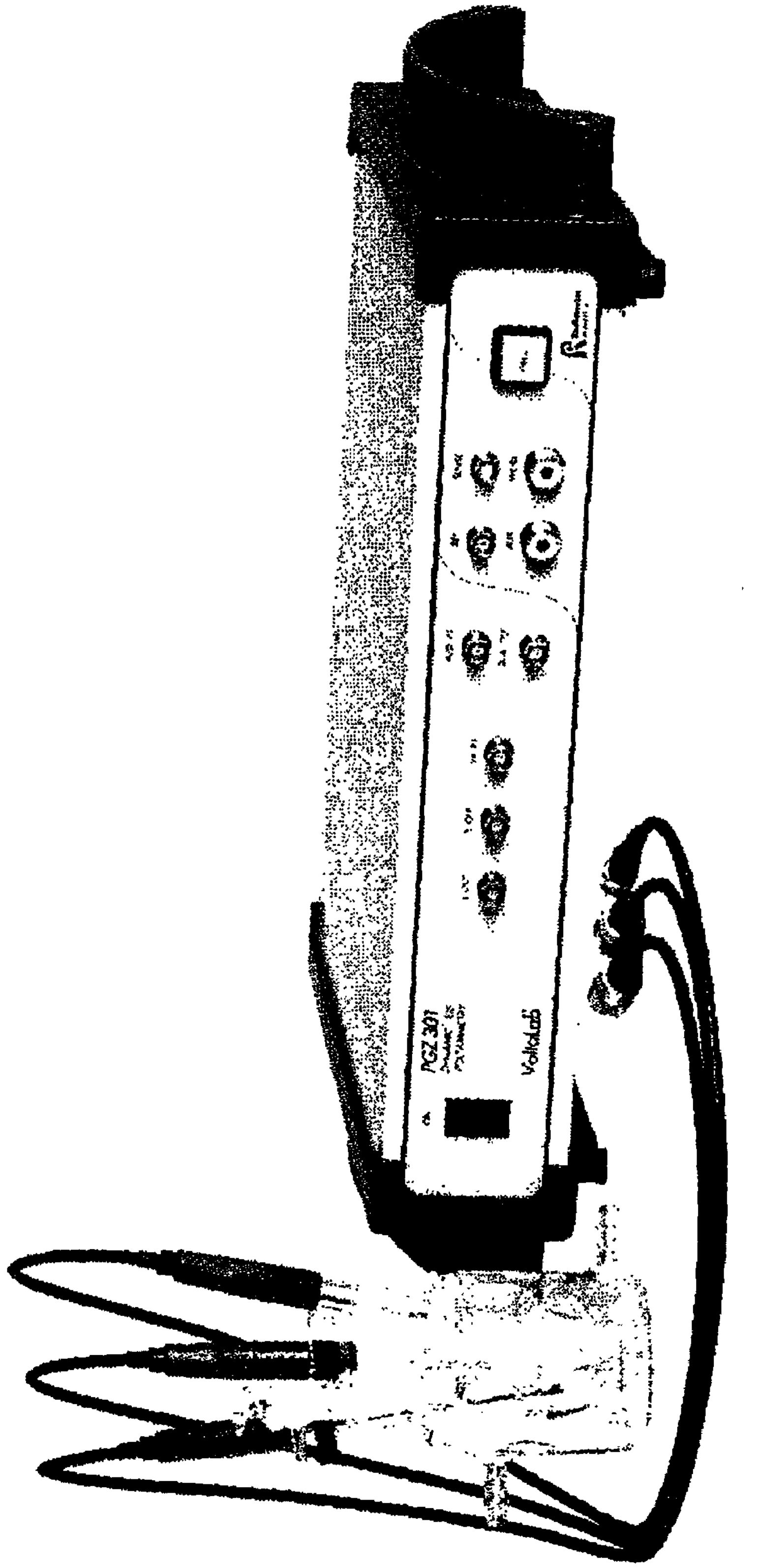


Fig. (1): Electrochemical Impedance Instrument

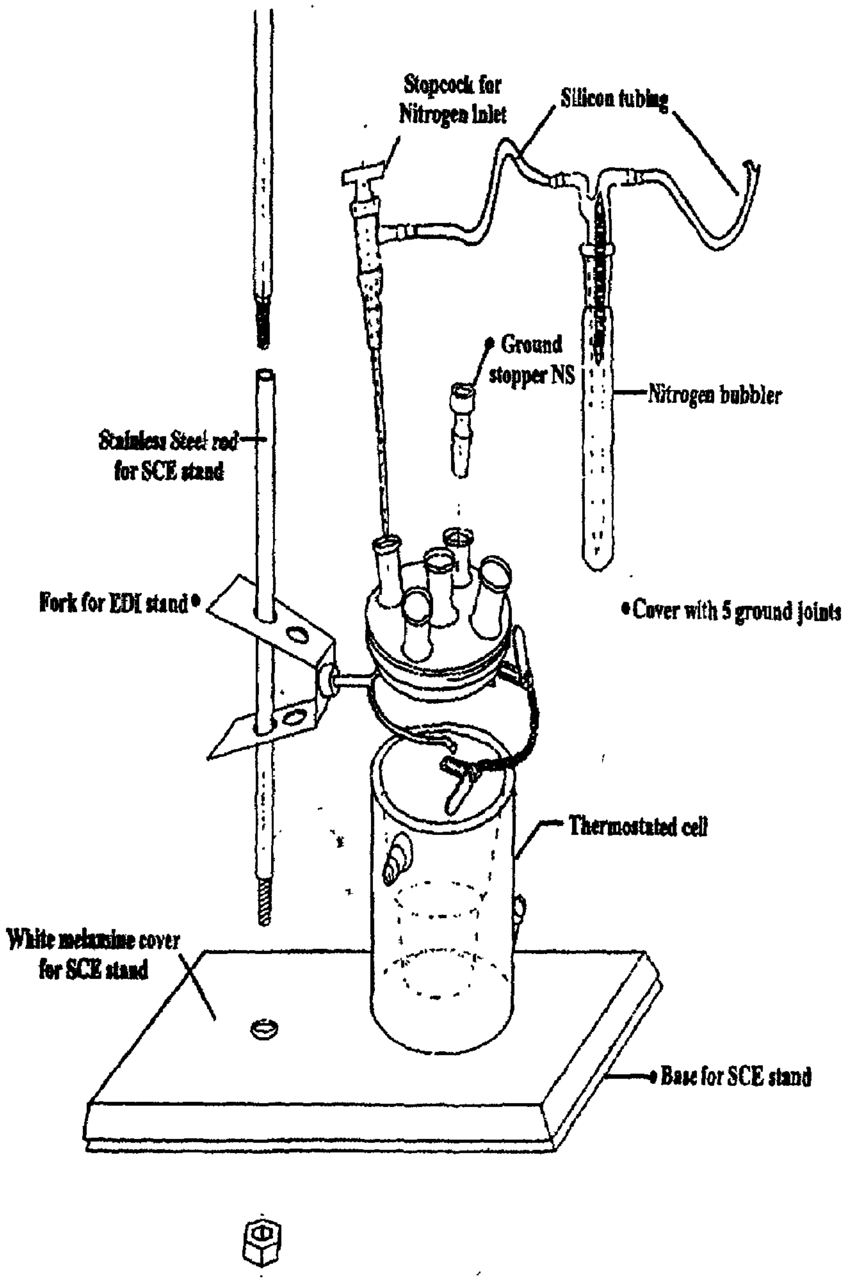


Fig.(2): Electrochemical cell