Chapter 3

CHAPTER- 3

EXPERIMENTAL METHODS

Reagents and Chemicals

All chemicals used were of Analar grade and used as such. Melting points were determined in open capillaries and are uncorrected.

3.1 Materials: Commercial cold rolled mild steel, copper and aluminium of the following composition were used.

Mild steel Composition

S. No	Element	Composition%
1	Carbon	0.084
2	Manganese	0.369
3	Silicon	0.129
4	Phosphorous	0.025
5	Sulphur	0.027
6	Chromium	0.022
7	Molybdenum	0.011
8	Nickel	0.013
9	Iron	Rest %

Copper composition

S. No	Element	Composition %
1	Zinc	9.50
2	Tin	0.019
3	Lead	0.013
4	Iron	0.019
5	Nickel	0.013
6	Sulphur	0.043
7	Antimony	0.016
8	Copper	Rest %

Aluminium composition

S. No	Element	Composition%
1	Silicon	0.40
2	Iron	0.53
3	Copper	0.13
4	Titanium	0.036
5	Nickel	0.021
6	Lead	0.036
7	Tin	0.033
8	Aluminium	Rest %

For weight loss measurements, rectangular coupons of dimension 5 cm X 2 cm X 0.05 cm were used. For electrochemical methods rods of mild steel, copper and aluminium of same composition with an exposed area of 0.785 cm^2 and rest covered with Teflon were used.

Preparation of corrosive solution

1M H_2SO_4 was prepared using double distilled water. The acid solution was standardized using previously standardized sodium hydroxide solution A stock solution of the inhibitor (1000 ppm) was prepared in 1M H_2SO_4. Various concentrations were made from the stock by proper dilution using 1M H_2SO_4.

3.2 Synthesis of inhibitors

All the starting compounds were obtained from commercial sources. The progress of the reaction and the purity of the synthesized compounds were ensured by TLC using silica gel as stationary phase. Benzodiazepines have been prepared by condensation of *o*-phenylenediamine with chalkone or ketone[1]. A diverse range of acidic reagents have been used as catalysts. In the current study sulphated zirconia was used.

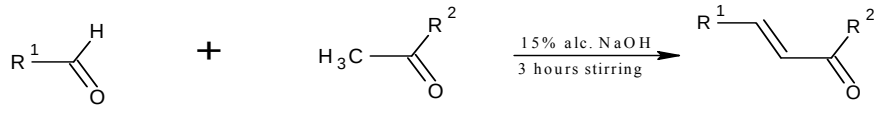
Preparation of catalyst

Zirconium hydroxide was prepared from an aqueous solution of zirconium oxy chloride by the addition of dilute ammonium hydroxide. To the aqueous solution of zirconium oxy chloride, an aqueous solution of ammonia was added drop wise with

vigorous stirring until the pH of the solution reaches 8. The precipitate obtained was washed with distilled water several times to free from chloride ions and then dried at 393K for 24h. The product thus obtained was ground to fine powder and immersed in 0.5 M H_2SO_4 solution for 30 min. Excess water was evaporated on a water bath and the resulting sample was oven dried at 393K for 12h and calcined at 873K for 4h.

Preparation of chalcones

Chalkones were prepared by base catalyzed Claisen-Schmidt condensation between aldehydes and ketones (Scheme-1).15% alcoholic solution of sodium hydroxide was added drop wise to a mixture containing 0.01M aromatic aldehydes and 0.01M acetone /acetophenone in alcohol. The mixture was stirred for 3h, while cooling in ice and left overnight. The solid separated was washed repeatedly with water and recrystallised from alcohol.

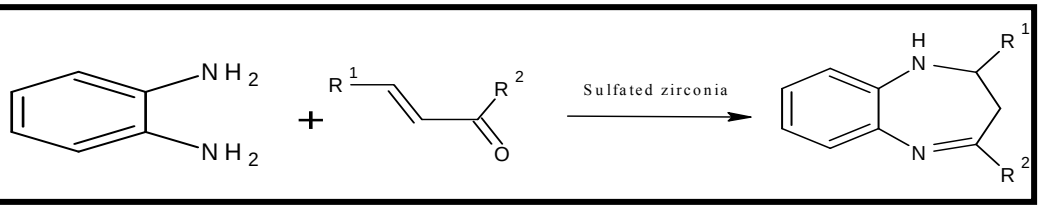


R^1 = Phenyl, 2-hydroxy phenyl, 3-Ethoxy- 4-hydroxy phenyl; R^2= methyl, phenyl

Scheme-1

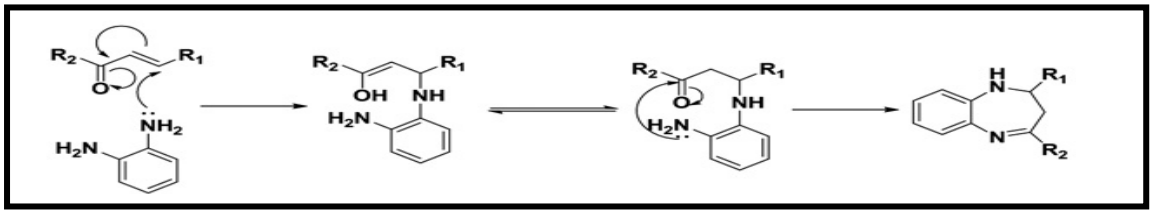
Synthesis of benzodiazepine derivatives

1, 5-benzodiazepines were synthesized by condensing *o*-phenylenediamine and chalkones with a catalytic amount of sulfated zirconia (Scheme-2). The reaction mixture was stirred in a round bottomed flask using a magnetic stirrer for 1h. 10 mL of dichloromethane was added to the reaction mixture and the catalyst was recovered by filtration. The 1, 5-benzodiazepines were purified by recrystallisation using ethanol.



Scheme-2

The proposed mechanism for the synthesis of benzodiazepines is reported in the literature[2] (Scheme-3).

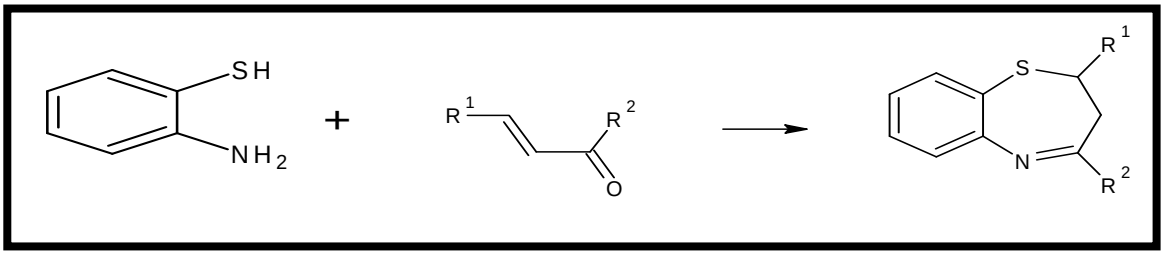


Scheme-3

Benzothiazepines and benzoxazepines were synthesized by reaction of chalkones with *o*-aminothiophenol and *o*-aminophenol using similar procedure.

Synthesis of Benzothiazepines[3]

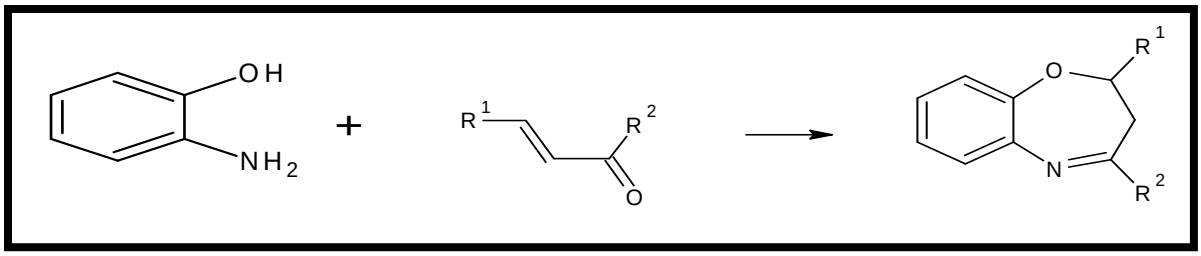
0.01M of chalkones and 0.01M of *o*-aminothiophenol were dissolved in 10 mL of boiling methanol. 2 drops of piperidine was added and the mixture was cooled. 10 mL of methanol was added and heated until the slurry was dissolved. Then 1mL of glacial acetic acid was added and the mixture was left at room temperature. The yellow crystals of benzothiazepines separated were filtered and recrystallised further with methanol.



Scheme-4

Synthesis of Benzoxazepines[4]

To 50 m L of methanolic solution of the chalkone (0.01M), 2-aminophenol (0.01 M) was added followed by few drops of glacial acetic acid. The mixture was refluxed for about 3-5 h. The solvent was distilled off under reduced pressure and the solid thus obtained was recrystallized from ethanol.



Scheme-5

The synthesized compounds were characterized by FTIR spectra. NMR Spectroscopy was recorded for a representative compound.

3.3 Evaluation of corrosion inhibition efficiency

3.3.1 Weight loss method

Specimen preparation[5]

Mild steel, copper and aluminium specimens were pickled with 1:1 HCl. The specimens were washed, dried and polished successively using emery sheets of 100, 120 and 180 grades degreased with acetone and dried. The plates were kept in a desicator to avoid the absorption of moisture.

Experimental procedure

Weight loss measurements

The polished mild steel specimens were weighed using Denver analytical balance (Precision ± 0.1 mg) and immersed in 100 mL of 1M H_2SO_4 containing various concentrations of the inhibitors using glass hooks. Care was taken to ensure the complete immersion of the specimen. After 3h of immersion the specimens were removed, washed with water, dried and weighed. From the initial and final weights of the specimen, the weight loss was calculated. The measurements were carried out with triplicate specimens and the average weight loss was recorded. The degree of surface coverage, inhibition efficiency and corrosion rate were calculated from the weight loss[6],

$$\text{Surface coverage } (\theta) = \frac{\text{Weight loss without inhibitor} - \text{Weight loss with inhiitor}}{\text{Weight loss without inhibitor}}$$

$$\text{IE } (\%) = \frac{(\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor}}{\text{Weight loss without inhibitor}} \text{ X } 100$$

$$\text{Corrosion rate (mpy)} = \frac{534 \text{ X Weight loss in mgms}}{\text{Density X Area in sq.inch X Time in hours}}$$

The effect of temperature on corrosion and inhibition was studied at different temperatures in the range (303-333K). A digital thermostat (0.5°C accuracy) was used for maintaining the temperature. All experiments were carried out under static condition.

3.3.2 Potentiodynamic polarization studies

Electrochemical studies were performed on IVIUM compact stat/potentiostat with a three electrode cell assembly. Platinum foil was used as counter electrode and saturated calomel electrode as the reference electrode. Mild steel / copper / aluminium rod was used as working electrode. Prior to the measurements the electrodes were immersed in 1M sulphuric acid with various concentrations of the inhibitors at the open circuit potential for 30 minutes to reach a stable state. The potential range was –200 mV to +200 mV with respect to the open circuit potential at a constant scan rate of 1mV/s. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), cathodic and anodic Tafel slopes (b_a and b_c) were calculated from the plot of potential vs. log current using IVIUM SOFT software installed in the instrument.

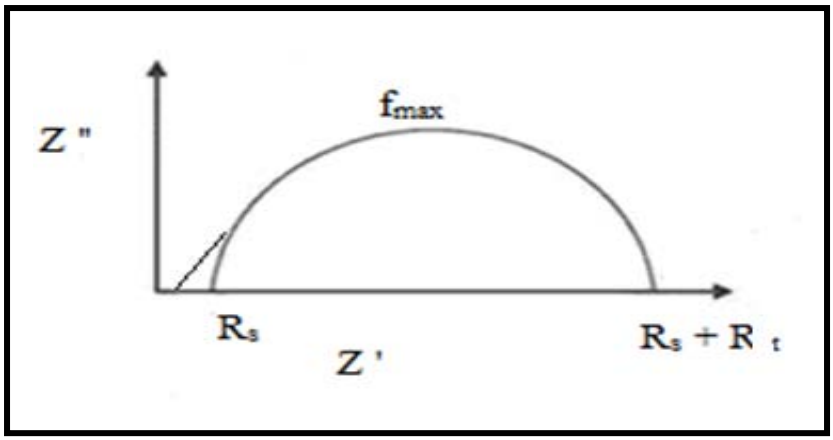
The inhibition efficiency was calculated from I_{corr} by using the formula[7],

$$\text{IE (\%)} = \left(1 - \frac{I_{corr}}{I^{o}_{corr}}\right) \text{X } 100$$

Where, I_{corr} and I^{o}_{corr} are the corrosion current densities in the absence and presence of benzodiazepine derivatives.

3.3.3 Electrochemical AC impedance spectroscopy (EIS)

The same cell setup employed for polarization study was used for EIS study also. The electrochemical impedance measurements were carried out using AC signal in the frequency range of 10 kHz to 0.01 Hz at the open circuit potential with a peak to peak amplitude of 10 mV. The real (Z') and the imaginary (Z'') component of the cell impedance were measured in ohm cm^2 at various frequencies and plotted in the form of Nyquist plots. The impedance parameters such as charge transfer resistance R_t, double layer capacitance C_{dl}, were obtained by fitting the experimental results to a most appropriate equivalent circuit which was used to model the metal solution interface.



R_t values were calculated from the difference in impedance at lower and higher frequencies.

C_{dl} is obtained using the equation[8],

$$C_{dl} = \frac{1}{2\pi f_{max} R_t}$$

f_{max} is the frequency at which Z" value is maximum. The percentage inhibition efficiency was calculated from R_t using the equation[9],

$$IE\ (\%) = \frac{R_{t(inh)} - R_{t(blank)}}{R_{t(inh)}} X\ 100$$

Where $R_{t\ (inh)}$ and $R_{t\ (blank)}$ are the charge transfer resistances for mild steel immersed in 1M H_2SO_4 with inhibitor and without inhibitors respectively.

3.3.4 Synergism study

The effect of addition of surfactants on corrosion inhibition performance of some selected benzodiazepines was studied by weight loss methods for mild steel in 1M sulphuric acid. The inhibitors were used at a lower concentration range (10-100 ppm) with a fixed concentration (20 ppm) of two surfactants-one cationic cetyl trimethyl ammonium bromide (CTAB) and one anionic sodium dodecyl sulphate (SDS). The surfactants were purchased from Merck chemicals, India. To determine the existence of the synergism phenomenon between the synthesized compounds and surfactants, synergism parameter was evaluated.

$$S_{\circ} = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$

Where $\theta_{1+2} = (\theta_1+\theta_2) - \theta_1\,\theta_2$ where θ_1= surface coverage by surfactant; θ_2= surface coverage by inhibitor, θ'_{1+2} = surface coverage of mixture of surfactant and organic inhibitor.

3.3.5 Surface morphology analysis

The surface of the mild steel after immersion in 1M H_2SO_4 in the absence and presence of inhibitors was examined by surface analysis techniques.

(i) SEM with EDX

The morphology of the mild steel surface was studied by scanning electron microscope CARL ZEISS UK. The polished metal (Mild steel, copper, Aluminium) coupons immersed in 1M H_2SO_4 and 1M H_2SO_4 containing 200 ppm of the benzoheteroazepines were examined. EDX spectra were used to determine the elements present on the surface.

(ii) Atomic force microscopy (AFM)

Atomic force microscopy is the high resolution scanning probe microscopy used to display the surface microstructures of the specimen in three dimensional model. The metal specimens were immersed in 1M H_2SO_4 with and without the inhibitors for 3 h, rinsed with double distilled water, dried and subjected to investigation. The surface morphology of the mild steel surface was examined using VEECO CP II Atomic force microscope. The scan size of the recorded AFM image is 15µm X 15µm.

3.3.7 FTIR Spectra

The interaction of the inhibitor molecules with the surface of the metal specimens was studied using FTIR spectra. The metal specimens were immersed in 1M H_2SO_4 containing higher concentration of the inhibitor for 3h. The specimens were removed, rinsed with distilled water, dried. FTIR spectra were recorded for the coupons using ATR-FTIR spectrometer (Shimadzu, Japan).

3.3.8 NMR Spectra

One of the synthesized benzodiazepine 2, 4-diphenyl-2, 3-dihydro-1*H*-1, 5-benzodiazepine (DPBD) was characterized by NMR spectra (both ^{1}H and ^{13}C) recorded on Bruker Avance III model instrument using DMSO as solvent.

3.3.9 Quantum chemical studies

Geometry optimizations were carried out with Becke's three parameter exchange functional along with Lee-Yang-Parr non- local correlation functional (B3LYP) with 6-31G + G (d, p) basis set for neutral and protonated molecules using Gaussian 09 program provided with Gauss-View software. Fukui functions were evaluated through Mulliken population analysis using the same software.

References

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