CHAPTER IV

MATERIALS AND METHODS FOR CORROSION INHIBITION STUDIES

4.1 MATERIALS

The metals used for the corrosion studies are copper and mild steel. Rectangular specimens ($4.8 \times 1.9 \times 0.12$ cm^3 size) were used for weight loss studies and circular coupons were used for electrochemical studies. The metal pieces are initially cleaned in acid solutions and then polished successively with 1-4/0 finer grades of emery paper. It is further polished on a slow rotating wheel using plain kerosene on the cloth to mirror bright finish. All specimens were finally cleaned according to the procedure of ASTM standard G-1-72 [1-6].

4.2 METHODS FOR STUDYING CORROSION

4.2.1 Weight Loss Studies

The weight loss experiments were carried out under total immersion conditions in test solution maintained at room temperature. The experiments were carried out in a beaker containing 250ml solutions. After exposure, the specimens were removed, washed initially under running tap water, to remove the loosely adhering corrosion product and finally cleaned as per the recommendation of ASTM. Then the weight loss was determined by a sensitive analytical balance (0.1mg). Similar experiments were conducted with different inhibitor concentrations to find out the effect of inhibitor concentration on corrosion rate and inhibition efficiency. In each case duplicate experiments were conducted and showed that the second results were within $\pm$ 1% of the first. Whenever the variations were very large, the data were confirmed by a third test. The percentage inhibition efficiency, % IE was calculated using the relation:

$$\% \text{ IE} = \frac{W_0 - W}{W_0} \times 100 \qquad (1)$$

where W_0 and W are the weight losses in the uninhibited and inhibited solutions respectively.

4.2.2 Electrochemical Studies

Electrochemical tests were carried out in a conventional three-electrode polymethylmethacrylate, PMMA (room temperature)/Borosilicate glass cell (high temperature) with platinum ($1cm^2$ surface area) as auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode. The working electrode first immersed in the test solution for establishing a steady state open circuit potential (OCP), and then electrochemical measurements were carried out with a computer programmed Gill AC electrochemical workstation (ACM, U.K, model no: 1475). Experimental set up for room temperature and high temperature studies are given in Fig.4.1(i-iii). Electrochemical impedance spectroscopy (EIS) measurements were carried out in different suitable frequency ranges for different metals. In the case of impedance studies, %IE is calculated with the equation:

$$\%IE = 1 - \frac{R_{ct}^{o}}{R_{ct}} \qquad (2)$$

Where R_{ct}^{o} and R_{ct} are the values of the charge transfer resistance observed in the absence and presence of the inhibitor molecule.

The potentiodynamic polarization curves obtained in the potential range from -250 mV to +250 mV with a sweep rate of 1 mV/ sec. The corrosion inhibition efficiency was calculated using the relation:

$$\% IE = 1 - \frac{i_{corr}}{i_{corr}^{o}} \; x \; 100 \qquad (3)$$

where i_{corr}^{0} and i_{corr} are uninhibited and inhibited corrosion current density respectively.

4.2.3 Adsorption Studies

The first step in the inhibition of metallic corrosion is the adsorption of organic molecule at the metal/solution interface. It depends on the molecule's chemical composition, temperature and the electrochemical potential at the metal/solution interface. In fact, the solvent H_2O molecules could also adsorb

at the metal/solution interface. Thus the adsorption of inhibitor molecule from the aqueous solution can be considered as a quasi-substitution process between the organic compounds in the aqueous phase [$Org_{(sol)}$] and water molecules at the electrode surface[$H_2O_{(ads)}$] [7].

$$Org_{(sol)} + x\ H_2O_{(ads)} \leftrightarrow Org_{(ads)} + x\ H_2O_{(sol)} \tag{4}$$
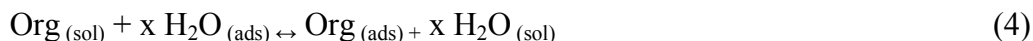
where x is the size ratio (number of water molecules replaced by one molecule of organic inhibitor).

Basic information on the interaction between the inhibitor molecule and the metal surface can be obtained from the adsorption isotherm. In order to obtain the isotherm, linear relation between surface coverage (θ) values (θ = % IE /100; from impedance or polarization studies) and inhibitor concentration (C_{inh}) must be found. For Langmuir isotherm

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{5}$$

where K_{ads} is the equilibrium constant of the adsorption process.

4.2.4 Computational Studies

Quantum chemical calculations and geometry optimizations were performed using ab initio calculations and the density functional theory (DFT). Ab initio calculations were carried out using the Hatree-Fock (HF) method. The Becke's three- parameter hybrid functional combined with the Lee, Yang and Parr correlation function (B3LYP) was employed in the DFT calculations using 6-31G (d) basis set. All the quantum chemical calculations were carried with complete geometry optimization using Gaussian-03W programme package [8-10].

The chemical reactivity of different sites of the molecule was evaluated by Fukui indices, defined by:

For nucleophilic attack

$$\smallint_k{}^+ = q_{N+1} - q_N \tag{6}$$

For electrophilic attack

$$\int_k^- = q_N - q_{N-1} \tag{7}$$

where q_N, q_{N-1} and q_{N+1} are the electronic population of the atom k in neutral, cationic and anionic systems respectively [11-12]. The condensed Fukui function is to the local reactivity descriptor and thus can be used only for comparing reactive atomic centers within the same molecule where as condensed softness indices allowing the comparison of the reactivity between similar atoms of different molecules, condensed softness indices which can be calculated easily starting from the relation between the Fukui function $\int(r)$ and the local softness $S(r)$.

$$S(r) = ((\partial \rho(r)/\partial N)_{v(r)} (\partial N/\partial \mu)_{v(r)} = \int(r) S \tag{8}$$

As shown by De Profit et al. [13-14], the B3LYP functional appears to be reliable for calculating $\int(r)$ and $\int_k$ indices. The molecular dynamics simulations were performed to understand the adsorption behavior of the molecule on metal (110) surface using Material Studio 4.3 programme package. The metal substrate with (110) plane was first optimized to minimum energy, and then the addition of the molecule on the metal (110) surface was simulated using the compass force field [15-16].

4.2.5 Scanning Electron Microscopy

The surface morphologies of the samples in the absence and presence of inhibitor molecule was carried out using a digital Scanning Electron Microscope model SU6600 (Serial No: HI-2102-0003) with an accelerating voltage of 20.0 kV, at a scan speed~Slow5 and calibration scan speed of 25. Samples were attached on the top of an aluminium stopper by means of carbon conductive adhesive tape. All micrographs of the specimen were taken at the magnification of 500 xs. These samples underwent the same pre-treatment as used in electrochemical experiments before recording the SEM image.

4.3 REFERENCES

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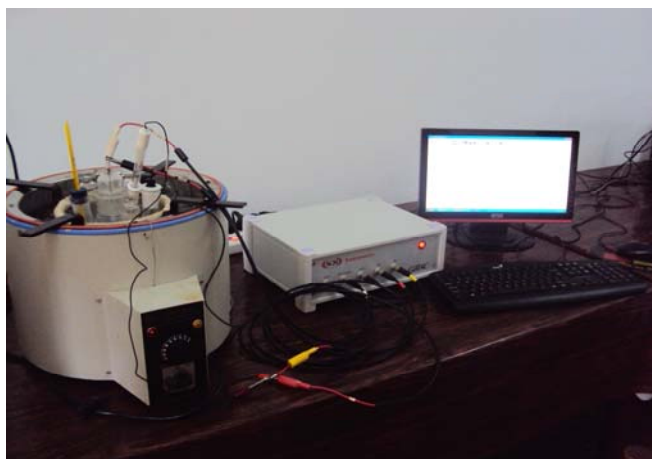
Fig. 4.1.i

Fig. 4.1.ii

Fig. 4.1.iii
FIg.4.1 Experimental setup for (i-ii) room temperature & (iii) for high
temperature Studies.