



## Corrosion inhibition efficiency of newly synthesized quaternary ammonium salt in 1M HCl

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The newly synthesized quaternary ammonium salt, 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide has been characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR. It has been examined for its corrosion efficiency by the weight loss method by immersing in a 1M HCl solution. The surface morphology is characterized using Scanning Electron Microscopy and it exhibited the variation between corroded surface and inhibited surface of carbon steel. Energy-Dispersive X-ray spectroscopy also shown the differences in composition of the corroded and surface coated with inhibitor. The efficiency of the inhibitor is investigated by varying the concentration of the inhibitor from 100 to 500 ppm and over a temperature range from 25 to 45°C. Inhibitor efficiency is maximum in the concentration range of 500 ppm and found to be 77.75% at 45°C. The plot of concentration against surface coverage revealed that, the present system follows Langmuir's adsorption isotherm. Compared to acidic medium, inhibitor excelled its maximum efficiency in the neutral medium.

**Keywords:** 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide, Adsorption isotherm, Corrosion inhibitor, Corrosion rate, Inhibitor efficiency, Quaternary ammonium salt.

The corrosion damage of structural components is a significant threat, especially for industries because almost all the metals are susceptible to corrosion. The extent of damage depends upon the type of material, nature of the surface, and type of environment it is exposed<sup>1</sup>. Different techniques and methods are adopted in the fortification of corrosion. Among the various techniques, corrosion inhibitors play a significant role in controlling corrosion. These inhibitors form a barrier on the metallic surface and prevent the metal from further corrosion<sup>2</sup>. The chemical and physical adsorption of pyridine quaternary ammonium salt on N80 in 5M HCl<sup>3</sup>, the advantages of halide free ionic liquids derived from ammonium as harmless corrosion inhibitors on API 5L X60 in the presence of 1M H<sub>2</sub>SO<sub>4</sub><sup>4</sup>, the corrosion inhibition performance of indolizine derivatives on N80 steel in 15 wt.% HCl, 20 wt.% HCl and 12% HCl + 3% HF<sup>5</sup>, active expired organic drug as an inhibitor on mild steel specimen in NaCl medium<sup>6</sup>, corrosion inhibition by aminotris (methylene phosphonic) acid (ATMP) for C38 carbon steel in 1M HCl<sup>7</sup> and its adsorption, and quaternary ammonium-based cationic

surfactants on carbon steel in 15% HCl<sup>8</sup> were reported recently. Another class of eco-friendly corrosion inhibitors like extracts of orange peel exhibited 99.19% efficiency in the presence of 0.25% waste extract at room temperature<sup>9</sup> on mild carbon steel in 1M HCl, leaf extract on mild steel in hydrochloric acid environment<sup>10,11</sup> were also explored in the literature. This paper discloses the corrosion inhibitor efficacy of newly synthesized quaternary ammonium salt, 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide (DDEDDB) evaluated by weight loss method. The surface of the carbon steel was analysed by SEM as well as EDX to investigate the ability of the inhibitor. The corrosion rate change was also determined by changing the parameters like temperature and pH of the medium.

### Experimental Section

#### Materials

N, N, N', N' tetramethylethylenediamine (Lancaster, Chennai, India), 1-Bromo decane (Aldrich, Chennai, India), HCl, ethanol, and acetone (Merck, Mumbai, India) were used as received. Doubly distilled water

was used as a solvent. Carbon steel coupons of composition C = 0.7%, P = 0.03%, Mn = 0.3-0.6%, S = 0.035%, Si = 0.5-0.75% and remainder as iron, of size (0.62 in<sup>2</sup>) was used for weight loss determination.

### Methods

#### *Synthesis of inhibitor: 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide*

By adding one and two moles of N, N, N', N' tetramethylethylenediamine, and 1-Bromo decane, quaternary ammonium salt was synthesized using a 250 mL flask. The reaction mixture was refluxed in an oil bath with vigorous stirring for 6 h and at 60°C. The corrosion inhibitor formed during refluxing was filtered and recrystallized with ethanol to get pure 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide (DDEDB) (Scheme 1).

#### Preparation of electrolyte and coupons

The electrolyte of 1M HCl was prepared by diluting analytical grade 37% HCl and used for the studies.

Carbon steel coupons were mechanically polished before immersion with emery sheets and degreased with acetone and dried in oven.

#### Corrosion tests

##### *Weight loss method*

The test coupons of 0.62 in<sup>2</sup> were weighed initially and immersed in 80 mL of 1M HCl for 24hrs with and without exposure to a corrosion inhibitor. After immersion, the weight of the coupons was recorded. The experiment was repeated in triplicates to avoid errors during analysis. Corrosion rate (CR) and inhibitor efficiency<sup>12</sup> were calculated using equations 1 and 2, respectively.

Corrosion Rate = 0.1 mm/y (4 mpy)

$$\text{mils per year} = 534 * W / D * A * t \quad \dots (1)$$

where 1 mil = 10<sup>-3</sup> in

W = Weight loss in mg

D = Density of the coupon (g/cm<sup>3</sup>)

A = Area of the coupon (in<sup>2</sup>)

T = Time exposed (hr)

*Inhibitor efficiency*(%) =

$$100(CR_{\text{uninhibited}} - CR_{\text{inhibited}}) / CR_{\text{uninhibited}} \quad \dots (2)$$

#### Surface analysis

The surface changes were analyzed by subjecting the coupons to Scanning Electron Microscope (SEM). The analysis was done by immersing the coupons in 1M HCl solution, with and without the inhibitors. The specimen's surface and the inhibitor's chemical composition were also analyzed by Energy-Dispersive X-ray spectroscopy (EDX).

## Results and Discussion

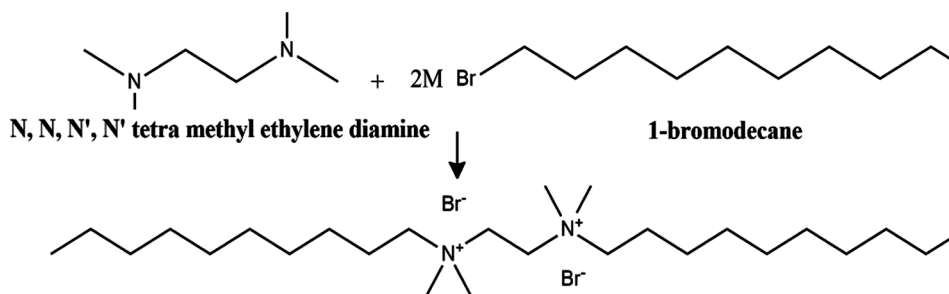
#### Characterization

##### *FT-IR of 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide*

Figure 1 shows FT-IR spectra of the synthesized quaternary ammonium salt. The peak at 948 cm<sup>-1</sup> is due to the rocking of the CH<sub>2</sub> group, C-N stretching vibration at 1227 cm<sup>-1</sup>, peak at 1488 cm<sup>-1</sup> is due to in plane bending of methylene protons and peak at 1397 cm<sup>-1</sup> is due to the presence of methylene out of plane bending. Peaks at 2788 and 2926 cm<sup>-1</sup> are symmetric and asymmetric stretching of CH<sub>2</sub> group. The broad peak at 3448 cm<sup>-1</sup> is due to the presence of moisture in the quaternized ammonium compounds; it confirms the hygroscopic nature of the salt.

##### *<sup>1</sup>H NMR of 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide*

Figure 2a shows the respective signals in the <sup>1</sup>H NMR of DDEDB. The methylene protons at 3.5 ppm (attached between the nitrogen groups), the methylene proton at 3.2 ppm (attached to the nitrogen group), the methylene group from the 1- Bromo decane signals at 1.69, 1.35, and 1.24 ppm, respectively. The methyl groups attached to the nitrogen atom produce the



Scheme1 — Synthesis of 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide

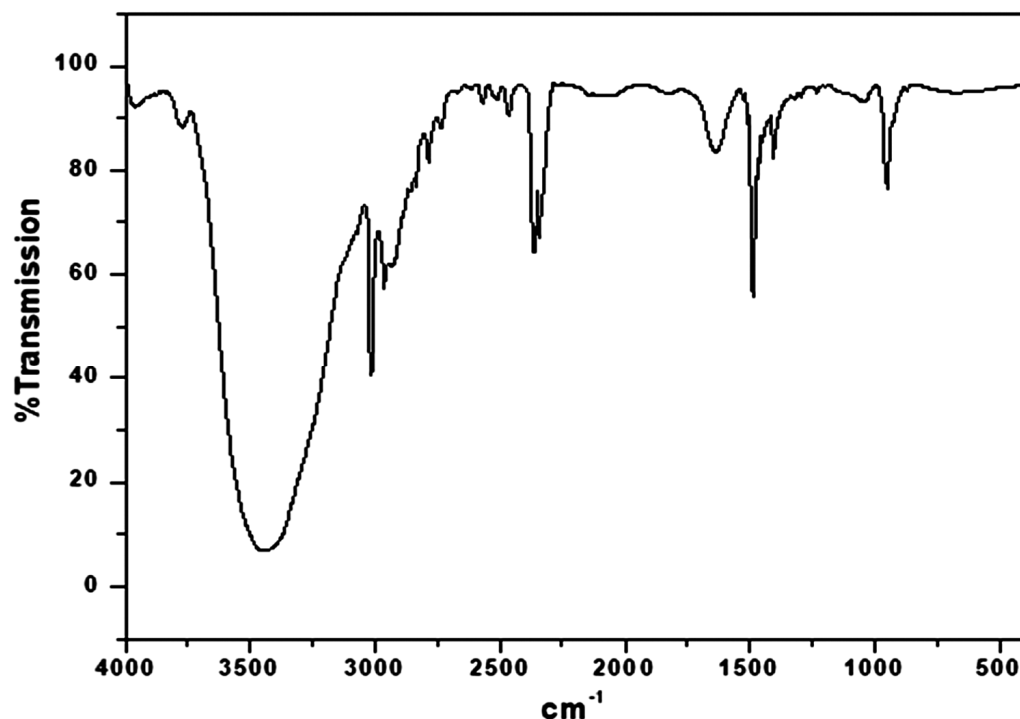


Fig. 1 — FT-IR 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide

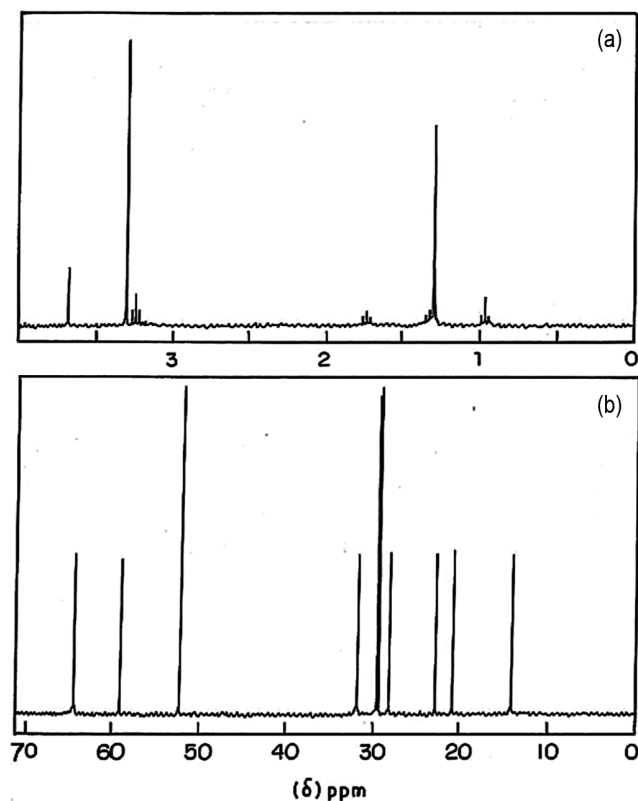


Fig. 2(a-b) — (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR of 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide

signal at 3.35 ppm and the terminal methyl group at 0.94.

*$^{13}\text{C}$  NMR of 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide*

The  $^{13}\text{C}$  NMR of DDEDB is given in Fig. 2b. The signal at 58 ppm is due to methylene protons between the nitrogen atoms; the N- $\text{CH}_2$  protons produce a signal at 65.2 ppm. The rest of the methylene group present in the alkyl chain produces signals at 21.5, 22.4, 28.9, 29.8 and 32.5 ppm. The signal identifies the methyl groups attached to the nitrogen atom producing signals at 53.5 ppm and the terminal methyl groups with 15.2 ppm.

**Elemental analysis of 1, 4-Bis (dimethyl decyl) ethylene diammonium bromide**

The synthesized DDEDB was subjected to elemental analysis and found to be carbon as 50.23 (Calculated-55.91), nitrogen 4.58 (Calculated-5.02), hydrogen 8.83 (Calculated -10.47), and for bromine 25.91 (Calculated 28.61).

**Effect of concentration of DDEDB on corrosion rate**

The concentration of DDEDB was varied in the range of 0 ppm to 500 ppm, and coupons were immersed in 1M HCl solution. Weight of the

coupons were taken before and after the immersion of coupons. This procedure was repeated for three different temperatures viz. 25, 35, and 45°C. Based on the weight loss, the corrosion rate (Fig. 3a) and inhibitor efficiency (Fig. 3b) were found using equations 1 and 2, respectively. The decrease in corrosion rate was observed with an increase in the concentration<sup>13</sup> of DDEDDB, and inhibiting the efficiency of the DDEDDB increased and exhibited maximum at 500 ppm. The investigated quaternary ammonium salts' inhibitive properties are ascribed to electrostatic cation adsorption in the outer part of the Helmholtz layer, assuming the blocking and energetic effects would have played an essential role in the inhibition mechanism.

#### Effect of temperature on corrosion rate at 500 ppm

The corrosion rate was determined in the range of 25 to 45°C and by varying the concentration of DDEDDB from 0-500 ppm to ascertain the inhibiting

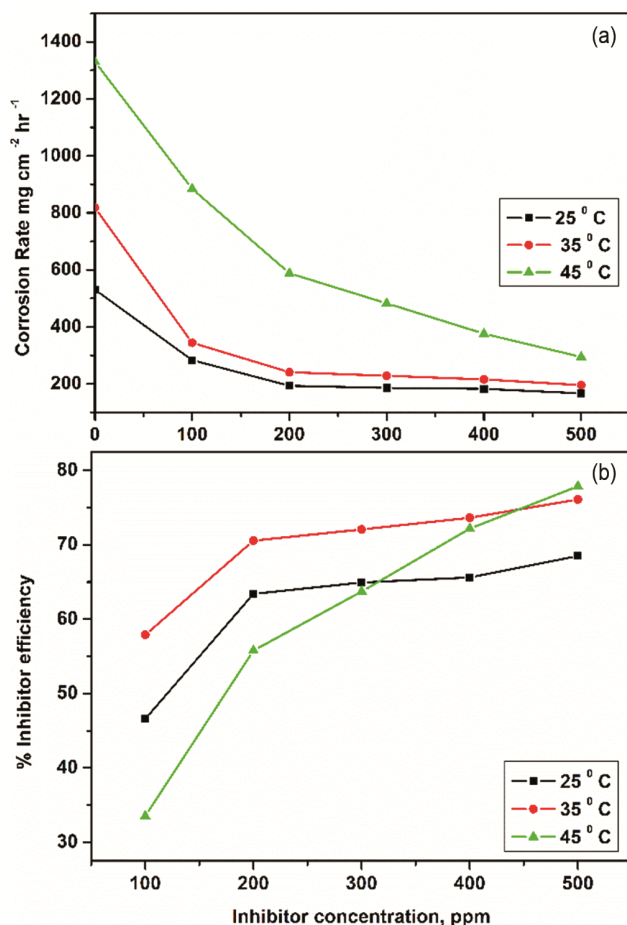


Fig. 3(a-b) — (a) Corrosion rate Vs. Concentration and (b) Inhibitor efficiency Vs. Concentration

efficiency of DDEDDB. For every 10°C rise in temperature, and every 100 ppm rise in concentration, corrosion rates were calculated as per equation 1. Corrosion efficiency was calculated as per equation 2 and shown in Fig. 4. Corrosion efficiency increased with temperature<sup>14</sup> and observed that efficiency was high at 35°C in all the concentrations, but it decreased when the temperature increased further. But inhibitor efficiency was slightly increased at 45°C, only at 500 ppm of DDEDDB, showed the efficiency as 77.85% at 500 ppm. The inhibitor forms a thin film on the surface of the mild steel, which prevents further corrosion caused by the acid attack. A plot of 1/T versus log CR (Fig. 5a) was drawn to investigate the mechanism of inhibition. Based on the plot, the activation energy of the system at different concentrations was determined and listed in the Table 1.

The activation energy ( $E_a$ ) of the DDEDDB was found to be 13.89 kJ mol<sup>-1</sup> at 500 ppm and for the blank, 23.49 kJ mol<sup>-1</sup>. That is, an increase in concentration from 100ppm to 500 ppm, resulted in a decrease of activation energy. The decrease in  $E_a$  may be attributed to chemisorption<sup>15</sup>, But in some cases, an increase in concentration showed as an increase in  $E_a$ ; this is attributed to physisorption<sup>16</sup>.

#### Effect of pH

As the inhibitor's corrosion efficiency was maximum with 500 ppm, its impact by varying the pH in 2-8 was found out. The corrosion rate increased with a decrease in pH. As the pH approached the neutral, there was a sudden decrease in the corrosion rate. The efficiency of

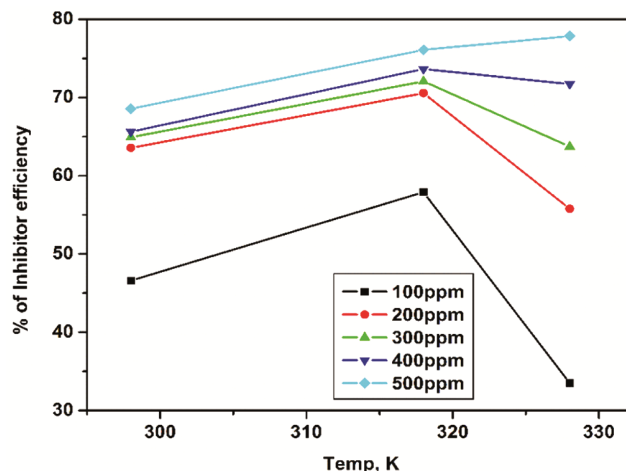


Fig. 4 — Inhibitor efficiency Vs. Temperature

DDEDB with the change in  $pH$  at 500 ppm is shown in Fig. 5b

#### Adsorption Isotherm

The adsorption isotherm is another parameter to find the efficiency of the adsorption of corrosion inhibitor on the metallic surface. Adsorption isotherms are vital in determining the mechanism of organic electrochemical reactions. To evaluate the best fit adsorption isotherm, the degree of surface coverage,  $\theta$  was fitted graphically with the concentration of the inhibitor  $C$ . Based on the plots, straight lines were obtained between  $C$  and

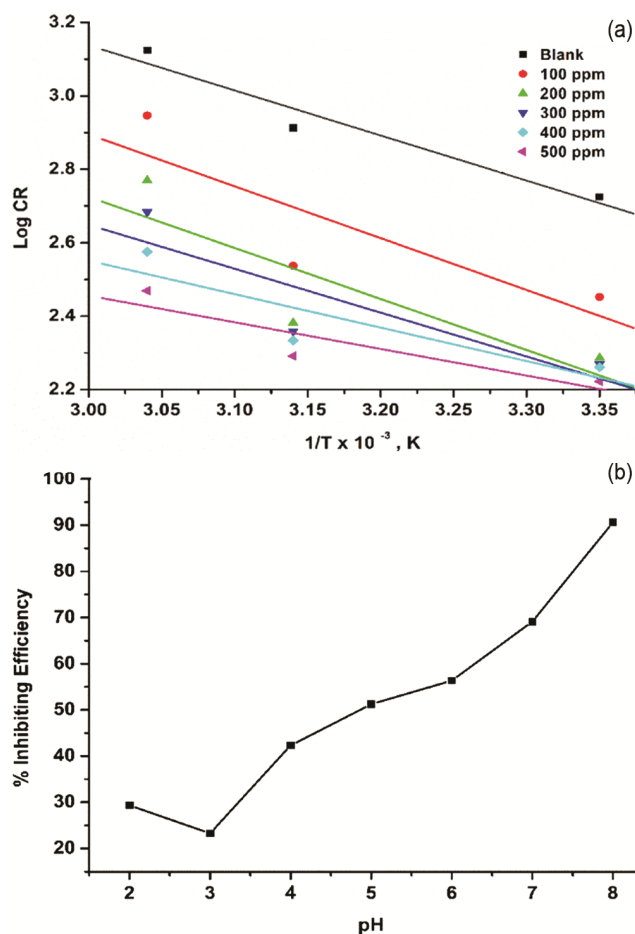


Fig. 5(a-b) — (a) Effect of temperature and (b) Effect of  $pH$  of the DDEDB on the inhibiting efficiency

Table 1 — Activation energy of corrosion of mild steel in 1M HCl in presence and absence of DDEDB

Concentration of DDEDB, ppm	Blank	100	200	300	400	500
Activation Energy, $\text{kJ mol}^{-1}$	23.49	27.02	26.59	22.88	17.44	13.89

Table 2 — Adsorption Parameters

Inhibitor	$C/\theta \sim C$ , Slope			$C/\theta \sim C$ , the linear correlation coefficient		
	25°C	35°C	45°C	25°C	35°C	45°C
DDEDB	1.42325	1.2944	1.16896	0.9918	0.9961	0.92

$C/\theta$  with coefficient nearly equal to  $1^{17}$  as given in Table 2. Thus, it proves that it is fitting the Langmuir adsorption model. Figure 6 depicts the graph of the Langmuir adsorption isotherm at three different temperatures for DDEDB as adsorption is of Langmuir character, adsorption may be monolayer.

#### FT-IR of the adsorbed inhibitors

The Fourier transform infrared spectra of the adsorbed inhibitor were recorded (Fig. 7). The specimen was collected after dipping the coupons into the inhibitor solution leaving it for several minutes.

The coupon was dried in an air oven. The adsorbed inhibitor was visible on the mild steel coupon, so it has been gently scratched<sup>18</sup> with a spatula and checked for adsorption characteristics. Signals around 2925 and 2844  $\text{cm}^{-1}$  indicate the asymmetric and symmetric stretching of the inhibitor. The bending vibration has been observed around 1380  $\text{cm}^{-1}$ . The presence of C-N stretching on 1117  $\text{cm}^{-1}$  confirms the absorption of the inhibitor (quaternary ammonium salt).

#### SEM analysis

The pure non-coated mild steel has been recorded with a scanning electron microscope and is given in

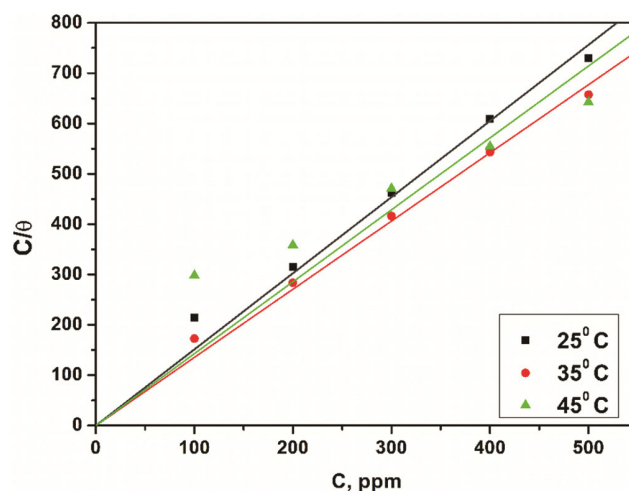


Fig. 6 — Adsorption isotherm of DDEDB

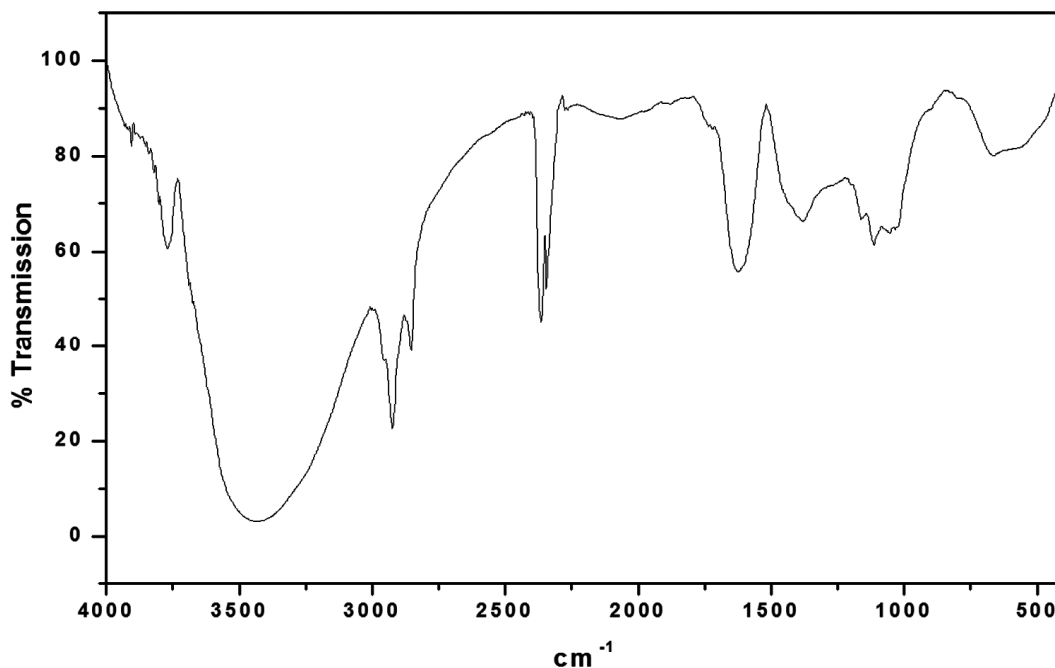


Fig. 7 — FT-IR of the adsorbed inhibitor on the mild steel

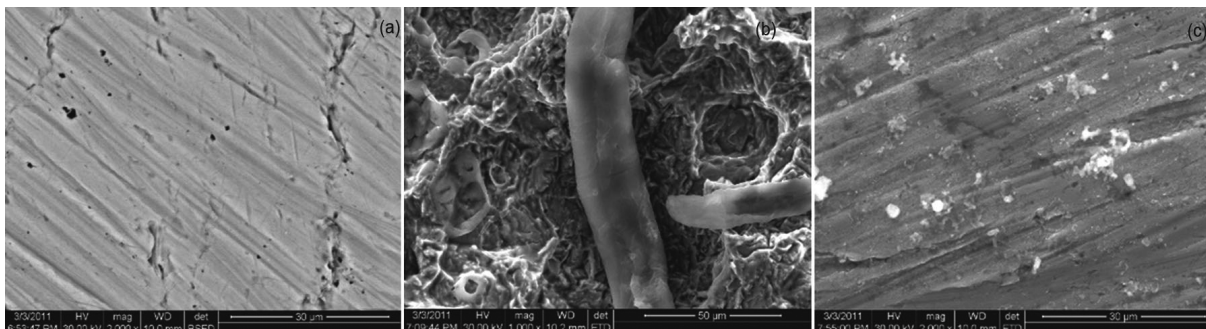


Fig. 8 — SEM – (a) pure mild steel (b) corroded mild steel and (c) inhibited mild steel

Fig. 8a. The SEM pictures show a clear view of the non-coated and rust-free mild steel. The scratch marks present in the mild steel due to the removal of rust from the coated surface by an emery paper. The coupons have well degraded before the sample run. So it doesn't have any kind of adhesion over the surface of the mild steel. The acid-dipped coupons (Fig. 8b) establish the corroded surface of mild steel. The acid has solvated the iron present in the metal surface, which has been confirmed by the damaged body. Moreover, the eroded holes have been seen everywhere in the sample, confirming the mild steel's acid attack. Fig. 8(c) shows the adsorbed layer by the synthesized inhibitor. Formation of a protective surface by the inhibitor on the metal surface enables inhibiting

mechanism. Thus the inhibitor is actively inhibiting the mild steel surface from acid corrosion.

#### EDX analysis

EDX spectra were recorded for mild steel before, after immersing, and in the presence of inhibitor in 1M HCl solution. Figure 9 (a) shows the absence of oxygen, which signifies no oxygen layer formed on the surface. Figure 9 (b) shows additional lines due to the presence of O, Cl. It indicates that mild steel had undergone corrosion when it was in contact with the acid medium. Figure 9 (c) shows extra lines for N due to the presence of the inhibitor. Thus the inhibitor has bonded with mild steel on the surface, and the same has been signified through the IR spectra.

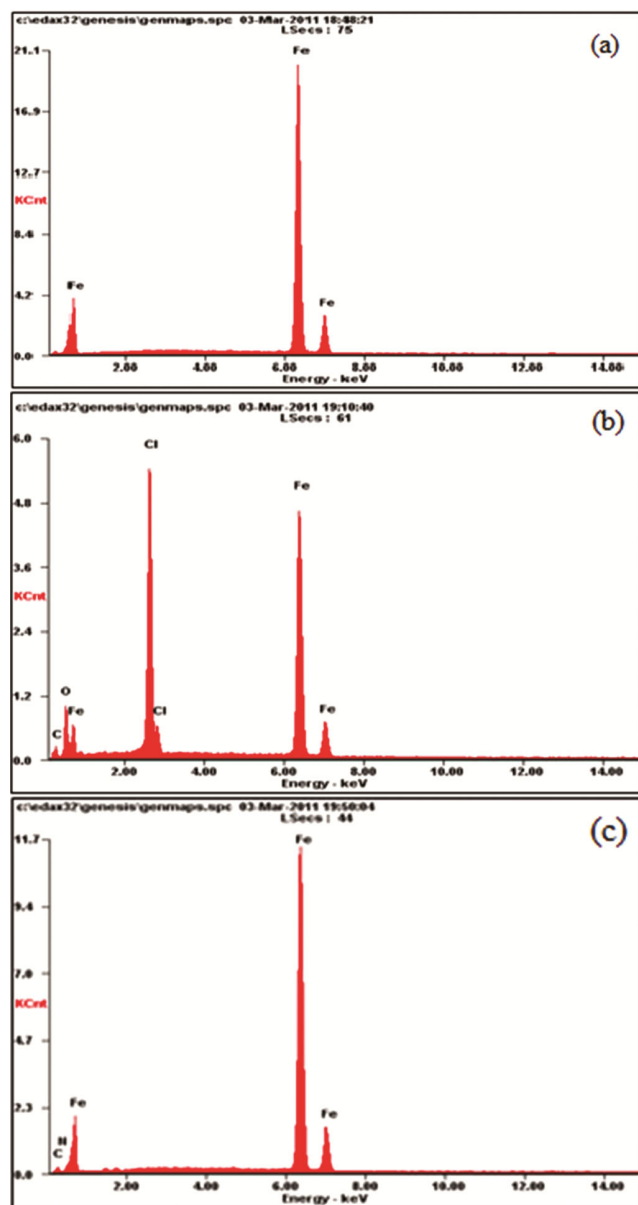


Fig. 9 — EDX – (a) pure mild steel (b) corroded mild steel and (c) inhibited mild steel

## Conclusion

Quaternary ammonium salts have been used extensively as inhibitors against the acid corrosion of iron and steel. The synthesized quaternary ammonium salt show good corrosion inhibition on the mild steel, in the presence of 1M HCl solution because of the binding of organic molecules on the metal surface. It formed a bond between the polar head groups and the

metal surface, reduced the corrosion attack. Weight loss studies, SEM and EDX analysis established the same. Maximum efficiency of 77.85% was observed when the concentration was 500ppm at 45°C. Energy of activation of the system reduced with increase in concentration. Thus, adsorption mechanism followed the Langmuir model of chemisorption. Efficient adsorption may be due to the presence of both the Br<sup>-</sup> ion and the quaternary ammonium ion present in the inhibitor.

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