EVALUATION OF TETRA-n-BUTYLAMMONIUM BROMIDE AS CORROSION INHIBITOR FOR MILD STEEL IN 1N HCl MEDIUM: EXPERIMENTAL AND THEORETICAL INVESTIGATIONS

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ABSTRACT

The corrosion inhibition behavior of Tetra-n-butylammonium bromide (TBAB) on mild steel (MS) in 1N HCl was investigated through experimental and theoretical studies. Inhibition efficiency is found to have increased by a rise in the concentration of TBAB. Experimental (weight loss study, potentiodynamic polarization, electrochemical impedance spectroscopy) results suggested that TBAB exhibits better inhibition efficiency. Thermodynamic studies were discussed. TBAB on the mild steel surface obey Langmuir adsorption isotherm. SEM and AFM studies confirm the adsorption and protective ability of TBAB on mild steel in 1N HCl medium. Formation of a protective layer on mild steel was characterized by FT-IR, UV-Visible and XRD studies. Furthermore, quantum chemical parameters were calculated. The results demonstrate the adsorption capability of TBAB on mild steel in 1N HCl medium. Quantum chemical calculations are in good agreement with results obtained from experimental methods.

Keywords: Corrosion Inhibition, Weight Loss Method, Polarization Study, XRD, AFM

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INTRODUCTION

Excessive corrosion on metals or alloys occurs in aggressive environments during descaling, cleaning, and acid pickling industrial processes.^{1,2} Corrosion of mild steel has drawn attention for its substantial application in industries as construction materials and it also attributes a good mechanical strength, low cost, and easy fabrication.³ To prevent corrosion, the metal surface is significantly masked with an inhibitive species to isolate from the corrosive environment.⁴⁻⁶ The utilization of organic molecules as a corrosion inhibitor is a practical method to protect the metal from dissolution in acid media.^{7,8} Heterocyclic based quaternary ammonium compounds (surfactants) are reported as effective inhibitors to reduce the surface tension of one or more components in an acidic environment.⁹⁻¹¹ Heterocyclic compounds having a π -conjugated double or triple bonds with heteroatoms (S, P, N, etc.) show remarkable corrosion inhibition. Interaction occurring among the heterocyclic compounds and surface of the metal through the adsorption centers leads to the formation of a protective layer on mild steel surfaces.¹²⁻¹⁴ They get formed either by physisorption or chemisorption. Adsorption depends on physicochemical properties such as a) structure of molecules, b) π -orbital character, and c) electronic density of the donor atoms.¹⁵⁻¹⁷ To reveal the nature of the interaction between the organic molecules and the metal surface, computational chemical methods are used as an important tool. The structure and electronic parameters of the inhibitor molecule can be obtained by means of theoretical calculations from the computational methodology. The increase in inhibition efficiency by 2, 5-dichloroaniline is revealed by quantum chemical calculation and is found to be due to the increase of HOMO Level which easily provides the free electrons to the metal surface.¹⁸ Similarly, pyridazine ring interaction with metallic atoms by electron density distributions of the FMOs is justified by computational quantum chemical methods.²⁹ Very few studies are carried out using the computational methodology for TBAB as a corrosion inhibitor and as well in HCl medium.

In the present work, we have attempted to study the consequence of tetra-n-butylammonium bromide in an environment of 1NHCl on mild steel. The corrosion prohibition capability of the TBAB on the substrate was examined through experimental and theoretical methods. Inhibition property was checked by the mass loss method, electrochemical studies, SEM, EDAX analysis, XRD, UV-Vis, FT-IR, AFM, and computational study. Weight loss studies carried out at dissimilar temperatures were familiar to draw Langmuir adsorption isotherm. Thermodynamic parameters attained from isotherms illustrate the interactive mode of tetra-n-butylammonium bromide over the metal specimen.

EXPERIMENTAL

Material

The elemental composition of the mild steel specimen (in % by weight) chosen in the present study: C-0.067, Mn-1.65, Si-0.145, S-0.006, P-0.02, Ni-0.04, Cr-0.198 and Fe balance. Mild steel specimens were polished with emery sheets (from grade 400-1200), degreased with acetone, washed with distilled water and finally dried in hot air. An aggressive medium of 1NHCl was prepared by using the analytical grade of 36% HCl and distilled water. 1% stock solution of inhibitor, tetra-n-butylammonium bromide of analytical grade was prepared. Concentrations ranging from 100 – 500 ppm of TBAB were used for the study.

Weight Loss Studies

Weight loss experiments have been carried out by immersing triplicate specimens in 1NHCl containing numerous TBAB concentrations at diverse temperatures ranging from 298 K to 328 K for about 1 h. After 1h, immersed metal samples were washed, dried, and re-weighed. The corrosion rate (CR) and inhibition efficiency (IE %) were calculated by the following expressions:¹⁹

$$IE(\%) = \frac{W_B - W_I}{W_B} \times 100 \quad (1)$$

$$CR (mmpy) = \frac{87.6 \times W}{ADT} \quad (2)$$

$$\theta = \frac{IE(\%)}{100} \quad (3)$$

Where, W_I and W_B are the weight loss of inhibited and uninhibited mild steel specimens. W , A , D , T , and θ are the weight loss (mg), area (cm^2), density (g cm^{-3}), immersion time (h), and surface coverage of metal specimen.

Electrochemical Studies

Electrochemical studies were performed using Biologic SP300 through a conventional three-electrode cell system consisting of mild steel as a working electrode, platinum wire as counter electrode and Ag/AgCl as a reference electrode²⁰. The working electrode was immersed in 1N HCl at different concentrations of TBAB. Tafel curves were performed with a potential range of -0.025 to + 0.025 mV at a scanning rate of 1 mVs^{-1} . Electrochemical impedance experiments were performed with a frequency range of 100000 to 0.010 Hz and an amplitude of 10 mV. The results have been fitted using EC-Laboratory software.

Surface Analysis

FT-IR and UV-Vis spectrum were recorded by Agilent Resolution Pro FT-IR spectrophotometer and Labman Scientific Instrument Pvt. Ltd double beam UV-Visible spectrophotometer respectively. XRD was carried out with XRD-PAN analytical X'pert powder Diffract meter using Cu-K α radiation ($\lambda = 0.15405 \text{ \AA}$). The surface morphological studies were performed using Field Emission Scanning Electron Microscope (FESEM) FEI quanta FEG 200 with an energy dispersive X-ray analyzer. AFM studies were performed by Scanning Probe Microscope 5100 Pico LE (Agilent Technologies).

Computational Studies

Frontier Molecular Orbital has been studied after the geometric optimization of TBAB and all theoretical calculations were carried out using the Gaussian 16 software²¹ to explore the characteristics of inhibitor.

The molecular structure of the inhibitor, TBAB, was optimized by the density functional theory (DFT) with B3LYP correlation functional²²⁻²³ and the 6-31G (d, p) basis set. Computations were carried out using the dipole moment (μ), ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η), and number of transferred electrons (ΔN) were calculated by following equations;

$$I = -E_{\text{HOMO}} \quad (4)$$

$$A = -E_{\text{LUMO}} \quad (5)$$

$$\chi = \frac{(I+A)}{2} \quad (6)$$

$$\eta = \frac{(I-A)}{2} \quad (7)$$

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} - \eta_{\text{inh}})} \quad (8)$$

RESULTS AND DISCUSSION

Weight Loss Studies

The corrosion rate and the inhibition efficiencies were plotted against different concentrations of TBAB for mild steel immersed in 1N HCl for about 1 hour at room temperature (298 K) are shown in Fig.-1. The results reveal (in Fig.-1) inhibition efficiency increases and the rate of corrosion decrease with an increase in the concentration of TBAB. Inhibitor performance at various concentrations is shown in Table-1. The highest inhibition efficiency of 93% was observed for 500 ppm of TBAB. It is attributed due to the adsorbed inhibitor molecules to the active sites of the mild steel surface, replacing the water molecule and chloride ions.

Table-1: Inhibitor Performance of Mild Steel in 1N HCl Solution with and without TBAB at 298K

Conc.(ppm)	CR (mm/y)	Θ	IE (%)
0	168.17	-	-
100	89.38	0.46	46
200	77.34	0.53	53
300	52.93	0.68	68
400	24.85	0.85	85
500	11.14	0.93	93

Fig.-1: The Corrosion Rate and the Inhibition Efficiencies at Different Concentrations of TBAB for Mild Steel immersed in 1N HCl for about 1 hour at 298K

Consequences of Temperature And Thermodynamic Parameters

Table-2 lists inhibition efficiency of TBAB and corrosion rate of mild steel in 1N HCl with the increase in temperature from 298 K to 328 K. The table shows that the effectiveness of inhibition reduces from 93% to 41% for TBAB at 500ppm with the rise in temperature.²⁴ The decrease in inhibition efficiency revealed the physical adsorption occurring between TBAB and the mild steel, while the corrosion rate increases

due to the desorption of inhibitor molecules from the mild steel surface (Fig.-2). The activation energy of the corrosion studied according to the Arrhenius equation is given by:

$$CR = A \exp \frac{-E_a}{RT} \quad (9)$$

Where, E_a is the corrosion activation energy, A is a frequency factor, T is a temperature in Kelvin, and R is the gas constant. The Arrhenius plots, $\log CR$ Vs $1000/T$ of mild steel in 1N HCl at the range of temperature, 298 K -328 K is presented in Fig.-3. The values of E_a were determined from the slope of the linear line and are presented in Table-3. From the table that the E_a value increased from 27.50 kJ mol⁻¹ to 39.15 kJ mol⁻¹ with increasing inhibitor concentrations. Increasing E_a value shows the prevention of charge/mass transfer reaction between the mild steel and corrosion medium.²⁵ However, the increase in E_a values shows the physical adsorption of the inhibitor molecules on the metal surface and which decreases appreciably with an increase in temperature.²⁶ The entropy and the enthalpy of activation of the corrosion process were calculated using the following relation,

$$CR = \frac{RT}{Nh} \exp \left(\frac{\Delta S}{R} \right) \exp \left(\frac{-\Delta H}{RT} \right) \quad (10)$$

Where, N is the Avogadro number, and h is the Planck's constant. Figure-4 shows the graph of $CR/T(K^{-1})$ Vs. $1000/T(K^{-1})$. The obtained linear line with a slope of ΔS and intercept of ΔH are shown in Table-3. Positive values of ΔH direct the endothermic behavior for mild steel corrosion in the 1N HCl medium. The negative values of entropy or decrease in entropy values confirm that the activated complex is of lower order containing inhibitor.²⁷ That is the protective film formed above the metal specimen becomes well-ordered²⁸.

Fig.-2: Inhibition Efficiency (IE%) for Mild Steel in 1NHCl with Altered Concentrations of TBAB at 298K – 328K

Table-2: The Results of Weight Loss Measurement in the Absence and Presence of TBAB at 298 K -328 K

Conc. (ppm)	298 K		308 K		318 K		328 K	
	CR (mm/y)	IE (%)	CR (mm/y)	IE (%)	CR (mm/y)	IE (%)	CR (mm/y)	IE (%)
Blank	166.17	-	46.14	-	36.33	-	28.08	-
100	89.38	46	26.30	43	31.65	13	24.96	11
200	77.34	53	22.62	51	24.29	33	21.95	22
300	52.98	68	20.50	56	21.73	40	19.61	30
400	24.85	85	15.82	66	14.82	59	17.94	36
500	11.14	93	7.35	84	11.36	69	16.49	41

Table-3: Activation Energy and Thermodynamic Parameters of TBAB on the Specimen Surface immersed in 1NHCl at 298K -328K

Conc (ppm)	E _a (kJ mol ⁻¹)	ΔH* (kJ mol ⁻¹)	-ΔS* (J mol ⁻¹ K ⁻¹)
0	27.50	61.50	86.52
100	31.79	60.93	87.39
200	34.05	62.18	82.48
300	34.86	62.59	79.93
400	38.76	63.13	77.01
500	39.15	68.11	75.22

Fig.-3: Arrhenius Plots of Mild Steel Corrosion in 1N HCl in Diverse Concentrations of TBAB at 298 K -328 K

Fig.-4: Transition State Plots for Mild Steel in 1N HCl with and without TBAB at 298 – 328 K

Adsorption Isotherm

The adsorption isotherm is used for learning the inhibitory action through the interaction among the inhibitor molecules and the metal surface during the inhibition process. The adsorption mode depends on the inhibitor structure, temperature and corrosion potential of the metal/medium interface.²⁹⁻³⁰ Surface coverage values used to study the adsorption isotherm. By Langmuir adsorption isotherm, the surface coverage (θ) obtained from weight loss data is related to the adsorption constant (K_{ads}) and the inhibitor concentration (C_{inh}) as in the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (11)$$

Fig.-5: Langmuir Adsorption Isotherm for TBAB on Mild Steel Surface immersed in 1N HCl at 298K-328K

Table-4: K_{ads} and ΔG_{ads} of TBAB on Mild Steel immersed in 1NHCl at 298K-328K

Temperature (K)	R^2	K_{ads} ($L\ g^{-1}$)	ΔG_{ads} ($kJ\ mol^{-1}$)
298	0.9592	3.13	-12.78
308	0.9802	2.15	-12.25
318	0.9559	0.97	-10.55
328	0.9428	0.65	-9.80

Langmuir plot (C/θ against C) displays a linear line as exposed in Figure 5 with R^2 data close to 0.9802 for TBAB at 298 K – 328K. The best fit of R^2 indicates that the TBAB adsorption on the metal surface obeys the Langmuir adsorption isotherm. The values of K_{ads} and ΔG_{ads} are assumed in Table 4. The data in the table clearly show that K_{ads} decrease with rising temperature. This indicates adsorbed inhibitor molecules on the mild steel that can desorb by increasing temperature. The K_{ads} can be correlated to calculate adsorption free energy by following relation:³¹

$$\Delta G_{ads} = -RT \ln 55.5 K_{ads} \quad (12)$$

Where, R is the gas constant, and T is the temperature.

The negative values of free energy adsorption suggest that the adsorption of TBAB is spontaneous. Usually, ΔG_{ads} values are less than $-40\ kJ\ mol^{-1}$ is related to physical adsorption, while ΔG_{ads} values around $-40\ kJ\ mol^{-1}$ or higher are consistent with chemical adsorption as a result of the transfer or sharing of electrons from the inhibitor molecule to the metal surface³². For the studied inhibitor TBAB, the ΔG_{ads} values are less than $-20\ kJ\ mol^{-1}$ designates TBAB adsorption is the physisorption type.

Electrochemical Studies

Potentiodynamic Polarization Studies

Figure. 6 displays a polarization graph for mild steel in the test solution without and with TBAB. Polarization parameters comprise Tafel anodic slopes and Tafel cathodic slopes, corrosion potential (E_{corr}), corrosion current density (I_{corr}), corrosion rate, and inhibition efficiency are shown in Table-5. It is observed that the increase of concentration of inhibitor, decreases the I_{corr} values. The E_{corr} values suggest that the inhibitor acts as anodic as well as cathodic on account of unnoticeable difference in the E_{corr} values between the inhibited and uninhibited system.

Corrosion rate (CR) and inhibition efficiency (IE%) are calculated by following equations:³³

$$CR(\text{mm/y}) = \frac{0.00327 \times I_{\text{corr}} \times \text{Eq.wt}}{D} \quad (13)$$

$$IE(\%) = \frac{I_{\text{corr}}^0 - I_{\text{corr}}}{I_{\text{corr}}^0} \times 100 \quad (14)$$

In the equation, I_{corr}^0 and I_{corr} are the corrosion current densities of mild steel without and with TBAB in 1N HCl, respectively. The best efficiency of TBAB is about 89.66% at 500 ppm.

Table-5: Tafel Parameters for Mild Steel in 1NHCl Solutions without and with TBAB

Conc. (ppm)	$-E_{\text{corr}}$ (mV)	I_{corr} ($\mu\text{A cm}^{-2}$)	β_a (mV/dec)	β_c (mV/dec)	CR (mm/y)	IE (%)
Blank	481.951	1 291.444	31.7	34.6	1.513 91	-
100	479.421	1 121.774	38.9	38.8	1.315 01	13.13
200	480.496	1 061.505	29.5	29.2	1.244 36	17.80
300	470.016	418.723	35.8	33.4	0.490 852	67.57
400	465.133	340.087	22.9	25.7	0.398 67	73.66
500	462.801	133.504	22.7	17.2	0.156 501	89.66

Fig.-6: Electrochemical Polarization Curves for Mild Steel Corrosion in 1N HCl in the Presence and Absence of TBAB

Electrochemical Impedance Studies

Mild steel corrosion in 1N HCl solution was studied at altered concentrations of TBAB using impedance spectra. The obtained results are reported in Fig.-7. From the figure clearly seen the size of the semicircle, concentrations of inhibitor revealed, in the size of the semicircle is bigger than that of uninhibited and the size of the semicircle rises with increasing concentrations of TBAB. Thus a rise in the values of charge transfer resistance is observed. All Nyquist spectra fitted with an equivalent circuit in Fig.-9. The equivalent circuit comprises Solution resistance (R_s) and Double-layer capacitance (C_{dl}) which is parallel to charge transfer resistance (R_{ct}).

The double-layer capacitance of a circuit includes R_{ct} , which was calculated by the following equation:³⁴

$$C_{dl} = \frac{1}{2\pi f_{\text{max}} R_{ct}} \quad (15)$$

Where, f_{max} represents the maximum frequency of imaginary components of the impedance.

The inhibition efficiency of mild steel is calculated by the following equation,

$$IE(\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}^0} \times 100 \quad (16)$$

Where, R_{ct}^0 and R_{ct} are the charge transfer values with and without TBAB respectively.

Table-6 depicts Nyquist parameters, R_{ct} value increases while C_{dl} value decreases with an increasing inhibitor concentration. C_{dl} value decreases, which is a result of TBAB that get adsorbed on the MS. The values of C_{dl} are always smaller in inhibited metal than uninhibited. From Table-6, C_{dl} value decreases from $20.40 \times 10^{-3} \text{ cm}^2$ to $2.34 \times 10^{-3} \text{ cm}^2$. This indicates the rate of corrosion is low. R_{ct} values increased from $3.30 \Omega \cdot \text{cm}^2$ to $10.19 \Omega \cdot \text{cm}^2$. This suggests that the inhibitor molecule is present at the MS/solution boundary. The inhibition efficiency increase is perceived to rise in TBAB. The maximum inhibition efficiency values were obtained at 67.57%. Corresponding bode plots obtained from MS in 1N HCl with and without TBAB are presented in Figure 8. It was found that the phase plots contribute only one time constant at around 100 Hz and also peak broad wing is maximum with increasing TBAB concentration due to TBAB molecules adsorbed the surface of the specimen. Their adsorption is proportional to the inhibitor concentrations³⁵⁻³⁶ which ensures that the tested inhibitor exhibits good inhibiting performance for mild steel in 1NHCl solution. The results from impedance and polarization studies are in respectable covenant with weight loss method.

Fig.-7: Nyquist Plots for Mild Steel in 1NHCl containing Various Concentrations of TBAB

Fig.-8: Bode Impedance for Mild Steel in 1NHCl containing Different Concentrations of TBAB at 298 K
Table-6: Impedance Parameters of Mild Steel in 1N HCl containing Various Concentrations of TBAB

Conc (ppm)	R_{ct} ($\Omega \cdot \text{cm}^2$)	C_{dl} (F/cm^2)	IE (%)
Blank	3.30	20.40×10^{-3}	-
100	3.66	18.86×10^{-3}	9.84
200	4.50	11.72×10^{-3}	26.62

300	9.05	2.74×10^{-3}	63.50
400	10.13	2.42×10^{-3}	67.39
500	10.19	2.34×10^{-3}	67.57

Fig.-9: Equivalent Circuit for Inhibited Mild Steel Sample

FT-IR Analysis

Fourier Transform Infra-Red analysis has been used to study the contact among TBAB and sample surface in the 1N HCl solution. Figure-10 show the spectra of mild steel immersed in 1N HCl with 500ppm of TBAB as well as the TBAB itself. As shown in Figure 10 (a) the bands at 3297, 1621 and 656 cm^{-1} are attributed to NH, C-H and C-C bonds of TBAB. The spectrum of inhibited metal in corrosive medium. Figure-10(b) shows the same peaks are shifted to 3413, 1642 and 698 cm^{-1} respectively. This indicates that TBAB adsorbed on the mild steel surface through the heteroatom of inhibitor. Hence it can stay assumed that the functional group of inhibitor takes synchronized by the surface of the mild steel ensuing in the development of a $[\text{Fe}^{2+}\text{-TBAB}]$ complex over the metal, which encourages the reserve of mild steel³⁷

Fig.-10: FTIR Spectra for (a) TBAB and (b) Inhibited Mild Steel

UV-Visible Spectroscopy

Figure-11 shows the UV-visible absorption spectra for TBAB solution and the inhibited solution after immersion of mild steel in 1N HCl containing TBAB for about 1 hour. A hyperchromic shift was observed in the absorption band. This was due to the formation of the complex between the TBAB and Fe^{2+} in 1N HCl solution.³⁸⁻³⁹ Furthermore, there are no important deviations in the shape of the spectrum between the two solutions.

XRD Analysis

XRD was used to confirm the film made on the mild steel with or without TBAB, respectively. Figure-12 b shows a peak at $2\Theta = 51.41^\circ$ can be suggested for iron oxides. The peaks owing to Fe appear at $2\Theta = 44.55^\circ, 64.78^\circ, \text{ and } 82.14^\circ$. It shows that the immersion of mild steel in 1N HCl without TBAB contains oxides of iron. Figure. 12 a demonstrate the inhibited mild steel with TBAB, an intense peak can be seen at $2\Theta = 44.42^\circ, 64.70^\circ, 82.04^\circ$ due to iron.⁴⁰⁻⁴¹ However, the absence of peak around 51.41° indicates the absence of iron oxides. These results also confirm the protective layer formed on the mild steel sample.

Fig.-11: UV-Visible Spectra for the Solution of (a) Pure TBAB and (b) Mild Steel in Inhibiting System

Fig.-12: XRD for Mild Steel After Immersion in 1N HCl (a) in the Presence and (b) the Absence of TBAB

SEM and EDAX Studies

SEM and EDAX were used to check the formation of a defensive layer of TBAB taking place in the specimen. SEM image of mild steel in 1N HCl with and without TBAB for 1 hour period is shown in Fig.-13 and 14. Figure-13 shows that the metal was harshly rusted attributable to acid corrosion. The mild steel specimen surface was highly damaged and is full of roughness in the absence of an inhibitor. The corresponding EDAX spectrum shows the elements such as Fe, C, and O. The Fe and C peak is due to the constituent of the mild steel specimen, O peak shows the presence of corrosion products such as oxides of iron. The inhibited specimen surface was better than uninhibited specimen surface, because of the development of a protective film of TBAB that had adsorbed on a metal surface. The EDAX spectra (Fig.-14) shows only Fe and C peaks aimed at the specimen in 500 ppm of TBAB in 1N HCl. The absence of oxygen peak indicates that the corrosion products are restricted as a result of TBAB adsorbed taking place at a mild steel surface.

AFM Analysis

The 2D and 3D images of mild steel immersed in 1N HCl solution without and with 500 ppm of TBAB for 1 hour at 298K are shown in Fig.-15. Figure-15a displays highly damaged surface of mild steel in 1N HCl, due to acid attack. However, with the addition of 250ppm of TBAB (Fig.-15 b), the mild steel surface is found with a smooth surface indicating the formation of a protective layer on the metal surface by the adsorption of TBAB. AFM parameters such as the root mean square roughness (R_q), average roughness (R_a), and maximum peak to valley height (R_{p-v}) for mild steel in the absence and presence of TBAB are given in Table-7. The values of R_q , R_a , and R_{p-v} in the presence of inhibitor were decreased to 228.1, 175.2, and 146.49 nm from the respective values (276.6, 232.4, and 159.17 nm) of uninhibited mild steel surface. This demonstrates TBAB as an effective corrosion inhibitor for mild steel in 1N HCl medium by the formation of a protective layer.

Fig.-13: SEM and EDAX of An Uninhibited Mild Steel Specimen

Fig.-14: SEM and EDAX for Inhibited Mild Steel Specimen

Table-7: AFM Roughness Parameters of Mild Steel

Sample	R_q /nm	R_a /nm	R_{p-v} /nm
1N HCl	276.6	232.4	159.17
1N HCl + TBAB	228.1	175.2	146.49

Fig.-15: 2D and 3D AFM Images of Mild Steel immersed in (a) 1N HCl and (b) presence of TBAB.

Quantum Mechanical Studies

Quantum mechanical studies were carried out to elucidate the microscopic molecular structure of TBAB. The optimized structure of TBAB is depicted in Fig.-16. The HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Occupied Molecular Orbital) are shown in Fig.-17. The calculated E_{HOMO} , E_{LUMO} , ΔE , μ , I , A , χ , η , and ΔN are presented in Table-8.

Fig.-16: Optimized Structure of TBAB

Fig.-17: (a) HOMO, (b) LUMO of TBAB

The molecular orbital energies E_{HOMO} and E_{LUMO} , describe the chemical reactivity of the corrosion inhibitor molecules. It is seen from Fig.-17 that the LUMO orbitals of TBAB spread over the entire molecule. On the other hand, the HOMO of TBAB is on the bromide ion. Hence, the interaction of TBAB with the positively charged mild steel surface is through Br^- ion. The E_{HOMO} and E_{LUMO} calculated from DFT analysis were determined to be -4.38 and 1.20 eV, respectively. Thus the charge transferred from HOMO to empty orbitals of Fe atom. Furthermore the lower energy gap, $\Delta E=5.58\text{eV}$ can be associated with the electron transfer and chemical reactivity of the TBAB molecule. Energy gap value in the range of 6.40 to 3.38eV showed higher inhibition efficiency⁴² and thus develops an electrostatic interaction between TBAB and mild steel. The value of $\Delta N= 0.9690 (<3.6)$ ⁴³ indicates the tendency of TBAB donates electrons to the metal surface. As per the reported literature, lower electronegativity (χ), lower global hardness (η) and higher dipole moment (μ) values of inhibitor molecule favor their inhibition performance due to stronger metal-inhibitor binding⁴⁴. The higher the dipole moment ($\mu = 11.7128\text{ D}$) than that of a water molecule ($\mu = 1.8546\text{ D}$)⁴⁵ has higher abilities to react with metal surface physically or chemically. Hence, this indicates that the TBAB gets strongly adsorbed on the mild steel surface by replacing the water molecules. Minimum χ value shows higher electron density and higher inhibition efficiency. TBAB has a minimum χ value of 1.59eV compared to the χ value of Fe 7eV.⁴⁶ Thereby, the electron transfer continues till the chemical potential becomes equal Hence minimum the χ value, higher will be the inhibition efficiency.

Table-8: Quantum Chemical Data of TABA

Parameters	Value
E_{HOMO} , eV	-4.38156
E_{LUMO} , eV	1.20123
ΔE , eV	5.58279
μ , D	11.7128
I , eV	4.38156
A , eV	-1.20123
χ , eV	1.59016
η , eV	2.79139
ΔN	0.96902

CONCLUSION

Tetra-n-butyl ammonium bromide has been studied as a corrosion inhibitor for mild steel in 1N HCl medium by experimental and theoretical methods. The experimental outcomes display that TBAB performance by way of a competent inhibitor for mild steel corrosion and attain an extreme inhibition efficiency of 93% at 500 ppm concentration. Adsorption of TBAB molecules of the mild steel follows the Langmuir isotherm. The values of ΔG_{ads} less than -20 kJ mol^{-1} reveal that the adsorption of TBAB on the MS is impulsive and predominantly occurs by physisorption. EIS results point out that corrosion inhibition of TBAB takes place due to the creation of a defensive coating. Tafel results show that the investigated TBAB is a mixed type inhibitor. UV-Visible spectra suggest metal- inhibitor interactions, while AFM and SEM images were confirmed that the TBAB protects the mild steel surface from metal corrosion. Quantum chemical studies that recommend that adsorption of TBAB happen through Br^- ion. Theoretical calculations are made in respectable covenant with the experimental outcomes.

ACKNOWLEDGMENT

We acknowledge the Nanotechnology Research Centre (NRC), SRMIST for providing AFM and SEM-EDAX facilities.

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