



Inhibition of Mild Steel Corrosion in 1 M HCl Solution by 1-Propanaminium *N,N,N*-tributyl bromide

B.S. PRATHIBHA^{1,*}, P. KOTTEESWARAN² and V. BHEEMA RAJU³

¹Department of Chemistry, B.N.M. Institute of Technology, Post Box No.7087, 27th Cross, 12th Main, Banashankari II Stage, Bengaluru-560 070, India

²Department of Chemistry, Kalasalingam University, Krishnankoil-626 126-626 190, India

³Department of Chemistry, Dr. Ambedkar Institute of Technology, Bengaluru-560 056, India

*Corresponding author: Fax: +91 80 26710881; E-mail: pratbnmit@gmail.com

(Received: 23 May 2011;

Accepted: 20 December 2011)

AJC-10861

The effect of 1-propanaminium *N,N,N*-tributyl bromide (TPAB) on the corrosion of mild steel in 1 M HCl solution has been investigated in relation to the concentration of the inhibitor as well as temperature by corrosion monitoring techniques such as polarization measurements and electrochemical impedance spectroscopy. Results obtained revealed that TPAB is a mixed type inhibitor. The adsorption of inhibitor on mild steel surface obeys the Langmuir adsorption isotherm equation. Both thermodynamic and kinetic parameters have been obtained by adsorption theory and kinetic equations. The results obtained by polarization and EIS are in good agreement.

Key Words: Mild steel, Polarization curves, EIS, Corrosion inhibitors, 1-Propanaminium *N,N,N*-tributyl bromide.

INTRODUCTION

Mild steel has found extensive application in various industries. It undergoes corrosion, but to a greater extent in acidic environment. Acidic solutions are used extensively in chemical and several industrial processes such as acid pickling, acid cleaning, acid descaling *etc.* Corrosion inhibition of mild steel is a matter of theoretical as well as practical importance. It is well documented that the development of new corrosion inhibitors of non-toxic type, which do not contain heavy metals and organic phosphates is very important¹. Among alternatives corrosion inhibitors, organic products containing one or more polar functions [with N, O and S atoms] have shown to be quite efficient to prevent corrosion². A large number of organic compounds are known as corrosion inhibitors for mild steel. However, only a few non-toxic and ecofriendly compounds have been investigated as corrosion inhibitors. The influence of various aliphatic and aromatic quaternary ammonium salts on the corrosion of mild steel in acid solutions has been extensively studied³. The inhibitory effect of *N*-decyl pyridinium derivatives on the dissolution of iron in HCl & H₂SO₄ solutions has been studied by some workers^{4,5}. In the present work, we have investigated the inhibitive action of 1-propanaminium *N,N,N*-tributyl bromide (TPAB) on the corrosion of mild steel in 1 M HCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy. 1-Propanaminium

N,N,N-tributyl bromide is used in the manufacture of antibiotics, phase transfer catalyst, antimicrobials, emulsifying agent, antiseptic agent, surface active agents *etc.* The structure of the inhibitor TPAB is as shown in the Fig. 1.

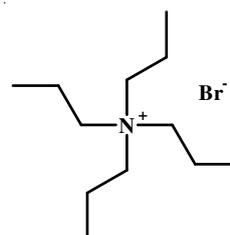


Fig. 1. Structure of 1-propanaminium *N,N,N*-tributyl bromide (TPAB)

EXPERIMENTAL

1-Propanaminium *N,N,N*-tributyl bromide (TPAB) is dissolved in 1 M HCl solution at various concentrations (10^{-2} , 6×10^{-3} , 4×10^{-3} , 2×10^{-3} and 10^{-3} M) and the solution in the absence of TPAB was taken as blank for comparison. Aggressive solution (1 M HCl), was prepared by dilution of reagent grade 34 % HCl with double distilled water. Composition of the mild steel was Fe, 98.7; C, 0.223; Mn, 0.505; Si, 0.164; S, 0.05. The cylindrical rod specimen was welded with copper wire for electrical connection and embedded in Teflon holder using epoxy resin with an exposed area 1 cm². Before each

experiment, the electrode was first mechanically polished with various grades of emery paper (0/0, 2/0, 3/0 and 4/0) and then cleaned with methanol and acetone followed by cleaning with double distilled water.

Electrochemical experiment: Electrochemical experiments were performed in a conventional three electrode cell, mild steel welded with copper wire and embedded in Teflon holder using epoxy resin with an exposed area 1 cm² as working electrode, a platinum foil of 1 cm² was used as counter electrode and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary. All potentials are measured with respect to the saturated calomel electrode. Measurements were performed using electrochemical work station CHI 660C model.

Potentiodynamic polarization curves were obtained by scanning the potential range from -200 mV + E_{corr} to +200 mV + E_{corr} at a scan rate of 10 mV/s after 1 h immersion time in 1 M HCl and 1 M HCl + inhibitor solutions. Electrochemical impedance measurements were carried out at open-circuit potential over a frequency range of 0.01 Hz-100 KHz. The sinusoidal potential perturbation was 10 mV in amplitude. Electrochemical data were obtained after 1 h of immersion with the working electrode at the rest potential and all tests have been performed in non-deaerated solutions under stirred conditions. Potentiodynamic polarization curves were also obtained at different temperatures to calculate the activation energy of the inhibitor adsorption to mild steel surface.

RESULTS AND DISCUSSION

Potentiodynamic polarization: Fig. 2 shows potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of TPAB. It is clear from the Fig. 2 that both anodic and cathodic reactions of mild steel corrosion were suppressed in the presence of TPAB in 1 M HCl and the suppression effect increases with the increase in the concentration of TPAB. Electrochemical kinetics parameters *i.e.*, corrosion potential (E_{corr}), cathodic and anodic Tafel slope (b_a and b_c) and corrosion current density (i_{corr}), obtained by extrapolation of the Tafel lines, are presented in Table-1. The inhibition efficiencies are also given in Table-1. The inhibition efficiency (IE) is calculated by

$$IE, \% = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100$$

where, i_{corr} and i_{corr}^0 is the corrosion current density with and without inhibitor.

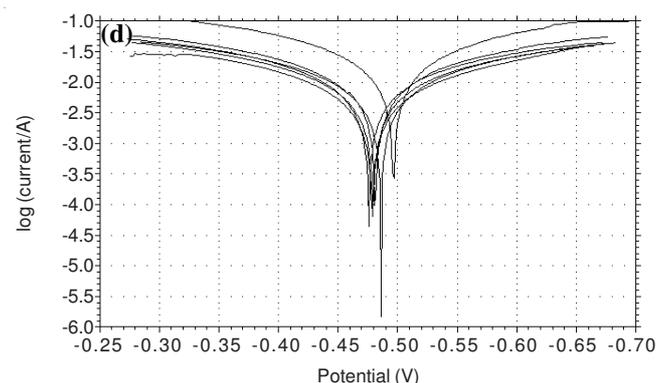
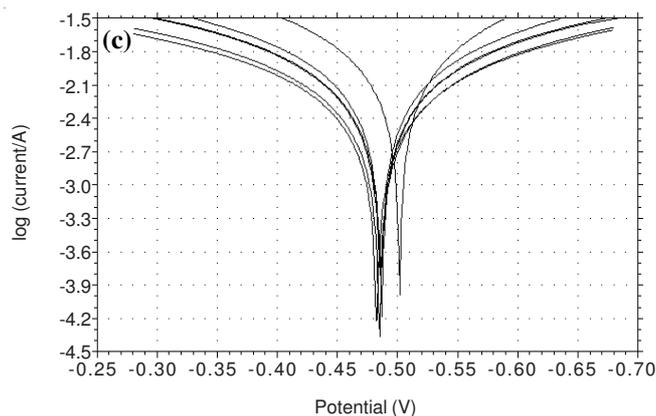
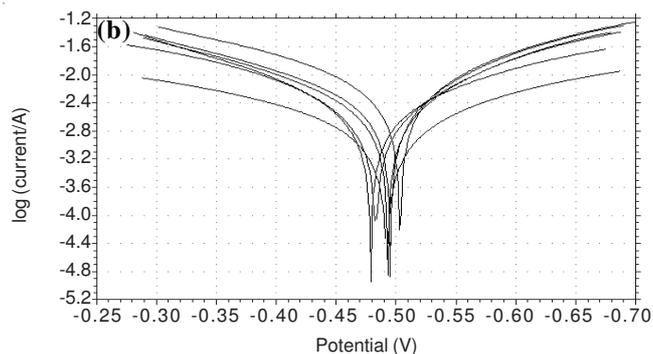
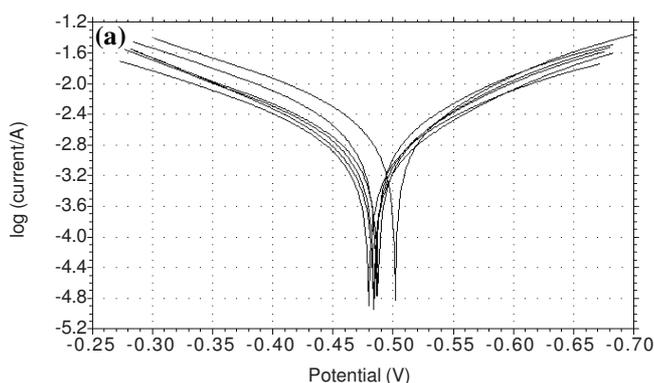


Fig. 2. Typical Tafel plots of mild steel in 1 M HCl in presence and absence of different concentration of TPAB at a) 25 °C; b) 35 °C; c) 45 °C; d) 55 °C

E_{corr} values of inhibited and uninhibited system do not vary significantly which shows that the addition of studied TPAB affected both anodic and cathodic reactions suggesting that TPAB is a mixed type inhibitor⁶.

Electrochemical impedance spectroscopy: It is clear from the Fig. 3 that the impedance response changes with the addition of the inhibitor molecules. The aim of EIS is to obtain more information concerning the dynamics and influence of working electrode in the presence of TPAB. All experimental plots approximately have a semicircular shape in the complex plane, with the centre under the real axis, which is a typical behaviour for solid electrodes that suggest the frequency dispersion of the impedance data⁷. The general equivalent circuit model used to analyze the electrical behaviour in the presence of inhibitors (Fig. 3). The associated parameters are solution resistance (R_s), charge transfer resistance (R_{ct}) and constant phase element (CPE). Taking in to account the non-ideal

TABLE-1
ELECTROCHEMICAL POLARIZATION PARAMETER
FOR MILD STEEL IN 1 M HCl CONTAINING
DIFFERENT CONCENTRATION OF TPAB
AND AT DIFFERENT TEMPERATURE

Concentration (M)	E_{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	b_a (1/V)	b_c (1/V)	IE_1 (%)
298 K					
HCl	-502.1	2640	6.590	7.683	
1×10^{-3}	-483.7	1152	6.630	7.419	31.8
2×10^{-3}	-482.3	1344	6.563	7.951	38.2
4×10^{-3}	-476.8	1523	6.565	7.836	42.3
6×10^{-3}	-473.4	1606	6.697	7.180	49.1
1×10^{-2}	-483.8	1800	7.397	8.112	56.4
308 K					
HCl	-501.8	6354	5.593	6.302	
1×10^{-3}	-491.1	4148	5.823	6.953	34.7
2×10^{-3}	-488.9	3388	6.176	6.956	46.7
4×10^{-3}	-488.2	2618	4.951	5.565	58.8
6×10^{-3}	-475.9	3346	5.844	5.843	47.3
1×10^{-2}	-481.2	2615	6.736	7.578	58.8
318 K					
HCl	-500.5	14130	4.978	5.278	
1×10^{-3}	-484.0	7490	4.982	5.018	47.0
2×10^{-3}	-483.6	9060	4.767	5.033	35.6
4×10^{-3}	-482.4	7388	5.010	4.922	47.7
6×10^{-3}	-479.6	5370	4.907	4.938	62.0
1×10^{-2}	-481.3	5549	5.010	4.858	60.7
328 K					
HCl	-494.8	26620	4.957	4.848	
1×10^{-3}	-477.9	13630	4.625	4.817	48.8
2×10^{-3}	-472.9	11370	4.678	5.145	57.3
4×10^{-3}	-483.9	10540	4.796	4.796	60.4
6×10^{-3}	-476.5	7649	5.145	4.678	71.3
1×10^{-2}	-476.6	9882	4.187	4.625	62.9

frequency response of the display data, a constant phase element was used instead of an ideal capacitance. Constant phase element can represent all frequency dependent electrochemical phenomena, such as double layer capacitance, diffusion process and local frequency dispersion due to the microscopic roughness of the metal surface^{8,9}.

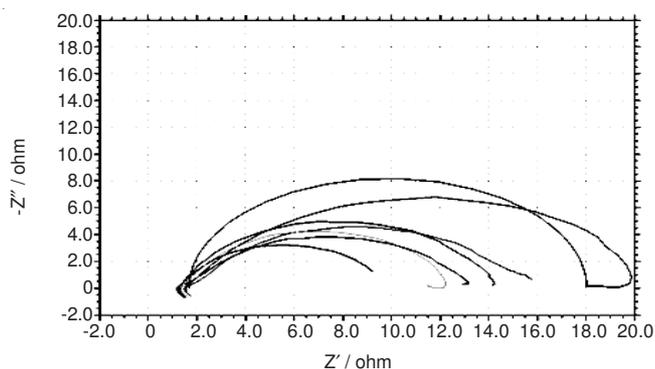


Fig. 3. Nyquist plots of mild steel in 1 M HCl in the presence and absence of different concentration of TPAB at 25 °C

The impedance of a constant phase element is described by the equation:

$$Z_{\text{CPE}} = Y^{-1}(i\omega)^{-n}$$

where, Y is a proportional factor, i is $\sqrt{-1}$, ω is $2\pi f$ and n has the meaning of a phase shift, n is a factor satisfying the condition

$0 \leq n \leq 1$. The fitted data follows almost the same pattern as the experimental results with R(QR) equivalent circuit using the software of ZsimpWin. The characteristic parameters associated to EIS are given in Table-2. The values of Y_{dl} has decreased trend for the adsorption of the inhibitor on the metal surface, suggesting the inhibitor molecules displace the water molecules and other ions originally adsorbed on the metal surface. The values of n_{dl} related to $(\text{CPE})_{\text{dl}}$ are found in the 0.74-0.85 interval indicating the electrode surface is partially heterogeneous¹⁰.

TABLE-2
IMPEDANCE PARAMETERS OF MILD STEEL IN 1 M HCl
IN ABSENCE AND PRESENCE OF DIFFERENT
CONCENTRATION OF TPAB AT 25 °C

Concentration (M)	Y_{dl} ($\Omega^{-1} \text{cm}^{-2} \text{S}^{\text{ndl}} 10^{-4}$)	n_{dl}	R_{ct} (Ω)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	IE_2 (%)
1 M HCl	18.2	0.8561	9.979	927.8	
1×10^{-3}	34.05	0.7819	13.51	1440.0	26
2×10^{-3}	30.77	0.7578	18.56	1232.0	46
4×10^{-3}	28.82	0.7601	20.35	1177.0	50
6×10^{-3}	29.62	0.7483	22.25	1186.6	55
1×10^{-2}	14.64	0.7807	25.80	583.3	61

Inhibition efficiency is also calculated from the Nyquist plots as follows:

$$IE_2 (\%) = \frac{R_{\text{ct}} - R_{\text{ct}}^0}{R_{\text{ct}}} \times 100$$

where, R_{ct} and R_{ct}^0 are the charge transfer resistance of mild steel with and without inhibitor molecules.

The double layer capacitance C_{dl} was calculated by the following equation:

$$C_{\text{dl}} = \frac{(Y_{\text{dl}} \times R_{\text{ct}})^{\frac{1}{n}}}{R_{\text{ct}}}$$

Inhibition efficiencies and other calculated impedance parameters are given in Table-2. When the inhibitor concentration increases, C_{dl} values tend to decrease. It can be attributed to the decrease in local dielectric constant or increase in thickness of surface film layer by the adsorption of the inhibitor molecules on the metal solution interface. According to the expression of the layer capacitance presented in the Helmholtz model.

$$C_{\text{dl}} = \frac{\epsilon \epsilon^0 s}{d}$$

where, d is the thickness of the surface film, S the surface of the electrode, ϵ^0 the permittivity of the air and ϵ is the local dielectric constant. All the Nyquist plots obtained were semicircle in nature and the diameter of the semicircles were changed with change in inhibitor concentration. It is clear from these plots that the impedance response of mild steel in uninhibited HCl has significantly changed after the addition of TPAB into the corrosive solutions. The semicircles observed to be depressed into the Z' (real axis) of Nyquist plot, which is often referred to as frequency dispersion as a result of the non-homogeneity or roughness of the metal surface¹¹. The obtained semicircle cuts the real axis at higher and lower frequencies. At higher end, the intercept corresponds to R_s , solution

resistance and at lower frequency end corresponds to $R_s + R_{ct}$. The difference between these two values gives R_{ct} , the charge transfer resistance. The value of R_{ct} is a measure of the electron transfer across the surface and is inversely proportional to corrosion rate. The semicircle shaped Nyquist plots indicate the formation of a barrier on the surface and a charge transfer process mainly controlling the corrosion of mild steel¹¹.

Adsorption isotherm studies: It is generally accepted that organic molecules inhibit corrosion by adsorption at the metal/solution interface and that the adsorption depends on the molecules chemical composition, the temperature and the electrochemical potential at the metal/solution interface. In fact, the solvent H_2O molecules could also adsorb at metal/solution interface¹². So the adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasisubstitution process between the organic compound in the aqueous phase and water molecule at the electrode surface¹³. Among the three isotherms assessed Langmuir isotherm is found to provide best description of the adsorption behaviour of the investigated TPAB as evident from straight line plot

obtained $\frac{c}{\theta}$ when $\frac{c}{\theta}$ is plotted against C as shown in Fig. 4.

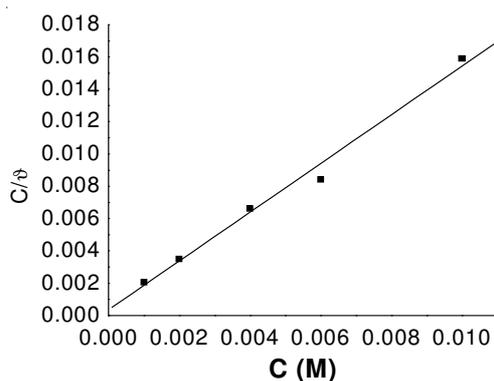


Fig. 4. Langmuir adsorption isotherm

Langmuir adsorption isotherm equation $\frac{c}{\theta} = \frac{1}{K} + C$

The equilibrium constant of the adsorption process was found from the straight line obtained in the $\frac{c}{\theta}$ vs. concentration graph and is related to the free energy of adsorption.

$$\Delta G^0 = -RT \ln(55.5K_{ads})$$

The negative values of ΔG^0_{ads} obtained indicates spontaneous adsorption of the inhibitor molecules on the metal surface¹⁴. Generally, values of ΔG^0_{ads} up to -20 KJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than -40 KJ/mol involves sharing or transfer of electron from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorptions)¹⁵. Table-3 shows that the value of ΔG^0_{ads} is between -20 KJ/mol and -40 KJ/mol, probably mean that both physical adsorption and chemical adsorption would take place.

Effect of temperature: Corrosion of mild steel in 1 M HCl was studied in the temperature range 25-55 °C in the absence and presence of inhibitor. The dependence of logarithm

TABLE-3
ADSORPTION PARAMETERS AT DIFFERENT
TEMPERATURES STUDIED FOR TPAB

Temperature (K)	R	Slope	K	$-\Delta G^0_{ads}$ (KJ mol ⁻¹)
298	0.99398	1.1641	473.93	-25.22
308	0.9858	1.6386	840.34	-27.53
318	0.9849	1.4681	588.29	-27.48
328	0.9945	1.5081	2795.65	-32.59

of corrosion current on the reciprocal of absolute temperature ($1/T$) for 1 M HCl is presented in the Fig. 5. Linear plots were obtained, which indicates that it follows Arrhenius equation given by:

$$\ln i_{corr} = \frac{-E_a}{RT} + \ln A$$

where, A = Arrhenius factor, R = Gas constant, T = Absolute temperature.

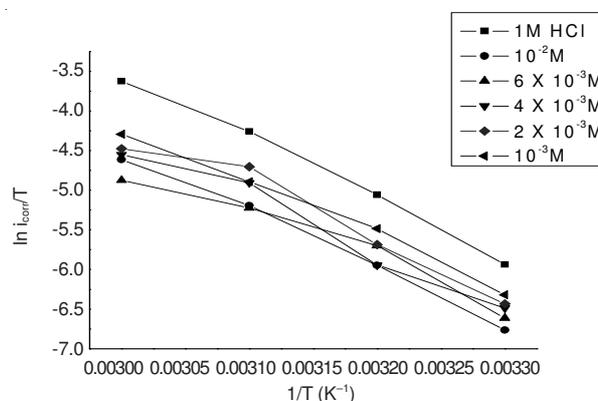


Fig. 5. Arrhenius plots for mild steel in 1 M HCl without and with various concentrations of TPAB

The E_a values obtained from the slope of the linear plot are presented in Table-4. From the table it is seen that E_a decreases in the presence of TPAB compared to an appreciable increase in adsorption process of the inhibitor on the metal surface with rise in temperature (chemisorption). Enthalpy of adsorption ΔH^0_{ads} and entropy of adsorption ΔS^0_{ads} for the corrosion of mild steel in 1 M HCl in the presence of TPAB was obtained by applying transition state equation given by:

$$\log(i_{corr}/T) = [\log(R/Nh) + \Delta S^0_{ads}/2.303 RT] - \Delta H^0_{ads}/2.303 RT$$

where, N = avogadro number, h = Planck's constant. R = Gas constant, T = absolute temperature. Fig. 6 shows the plot of $\log(i_{corr}/T)$ vs $1/T$ for blank and with inhibitor. Linear plots were obtained and from the slope ($-\Delta H^0_{ads}/2.303RT$) and intercept of the linear plots, enthalpy of adsorption and entropy of adsorption were obtained. The calculated values are given in Table-5. The result shown in the table indicates that the enthalpy of adsorption decreases in the presence of the inhibitor compared to the blank solution, which further supports the chemisorption mechanism. In all cases, negative values of entropy of adsorption were obtained. The negative values are indicative of increase in the system order¹⁶. The entropy of activation, ΔS^0_{ads} , was negative both in the absence and presence of inhibitor, implying that the activated complex represented the rate determining step with respect to the association rather than dissociation step.

TABLE-4
VALUES OF ACTIVATION ENERGY (E_a) FOR THE CORROSION OF MILD STEEL IN 1 M HCl WITHOUT AND WITH TPAB

Concentration (M)	E_a (KJ mol ⁻¹)
1M HCl	64.28
1×10^{-2}	59.88
6×10^{-3}	47.30
4×10^{-3}	56.87
2×10^{-3}	56.99
1×10^{-3}	55.40

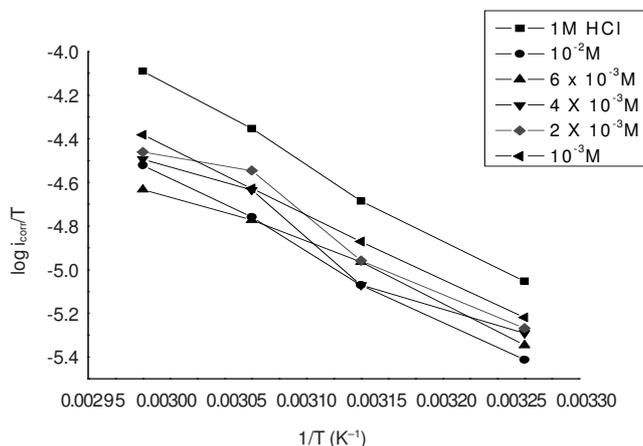
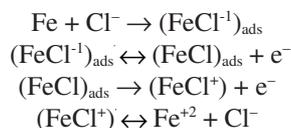


Fig. 6. Transition state plots for MS in 1 M HCl without and with various concentrations of TPAB

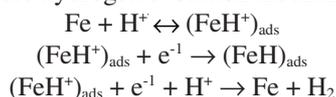
TABLE-5
THERMODYNAMIC PARAMETERS FOR MS IN 1M HCl WITHOUT AND WITH DIFFERENT CONCENTRATION OF TPAB

Inhibitor concentration (M)	ΔH_{ads}^0 (KJ mol)	ΔS_{ads}^0 (J mol)
1 M HCl	53.35	-115.89
1×10^{-2}	49.54	-135.52
6×10^{-3}	30.09	-167.47
4×10^{-3}	46.55	-143.66
2×10^{-3}	47.22	-140.28
1×10^{-3}	45.80	-144.15

Mechanism of adsorption: In hydrochloric acid solution the following mechanism is proposed for the corrosion of mild steel¹⁷. The anodic dissociation of mild steel is:



The cathodic hydrogen evolution mechanism is:



Generally corrosion inhibition mechanism in acidic medium is due to the adsorption of the inhibitor onto the metal surface. Four types of adsorption may take place by organic molecules at metal/solution interface namely; (1) Electrostatic attraction between the charged molecules and charged metal; (2) Interaction of unshared electron pairs in the molecule with the metal; (3) Interaction of π electron with the metal; (4) Combination of 1 and 3¹⁸.

The process of adsorption is influenced by the nature and charge of the metal, chemical structure of the inhibitor and

the type of aggressive electrolyte. The charge of the metal surface can be determined from the potential of zero charge (PZC) on the correlative scale (ϕ_c)¹⁹ by the equation:

$$\phi_c = E_{\text{corr}} - E_{q=0}$$

where, $E_{q=0}$ is the potential of the zero charge. However, value obtained in HCl is -502.1 mv vs. saturated calomel electrode.

Banerjee and Mallhotra²⁰ reported the PZC of mild steel in HCl solution is -530 mv vs. saturated calomel electrode. Therefore the value of ϕ_c is +27.9 mv vs. saturated calomel electrode, so the metal surface acquires slight positive charge. TPAB may chemisorb at steel/solution interface via chemical bond between positively charged nitrogen atoms and negatively charged mild steel surface as follows: Steel surface is positively charged in presence of HCl medium. While bromide ion is negatively charged, as a result the specific adsorption of bromide ion occurs onto mild steel surface, causing negatively charged surface of steel. By means of electrostatic attraction, quaternary ammonium cation easily reaches mild steel surface, so bromide ion acts as an adsorption mediator for bonding metal surface and TPAB. This gives rise to the formation of an adsorption composite film in which Br^- ion are sandwiched between metal and positively charged part of inhibitor. This film acts as a barrier facing corrosion process.

Conclusion

Potentiodynamic polarization curves reveal that TPAB acts as a mixed type inhibitor. The inhibition efficiency increases with increase in concentration and increase in temperature which leads to the decrease in activation energy of corrosion process. The adsorption of TPAB obey's Langmuir adsorption isotherm. The adsorption process is spontaneous and exothermic.

REFERENCES

1. I. Sekine, Y. Nakahata and H. Tanabe, *Corros. Sci.*, **28**, 987 (1988).
2. S.W. Dean Jr, R. Derby and G.T. Vondembussche, *Mater. Perform.*, **20**, 47 (1981).
3. R. Driver and R.J. Meakins, *Br. Corros. J.*, **12**, 46 (1977).
4. A. Frignani, F. Zucchi and M. Monticelli, *Br. Corros. J.*, **18**, 1 (1983).
5. L. Mezaros, B. Lengyel, T. Garai and G. Trabaneli, *Acta Chim. Hung.*, **127**, 113 (1990).
6. H.A. Sorkhabi and D. Seifzadeh, *Appl. Surf. Sci.*, **239**, 154 (2005).
7. K. Bilkova, N. Hackerman and M. Baross, *NACE Corrosion*, **2**, 2284 (2002).
8. F. Deflorain, V.B. Miskovic Stankovic, P.L. Bonara and L. Fedrizzi, *Corros.*, **50**, 446 (1994).
9. K. Juttner, *Electrochim. Acta*, **35**, 1501 (1990).
10. G. Gao, C.H. Liang and H. Wang, *Corros. Sci.*, **49**, 1840 (2007).
11. B.S. Prathibha, P. Kotteeswaran and V. Bheemaraju, *J. Electrochem. Soc. India*, **59**, 127 (2010).
12. J.Y. Zou and B.H. Yang, *Mater. Prot.*, **21**, 4 (1998).
13. M. Sahin, S. Bilgic and H. Yilmaz, *Appl. Surf. Sci.*, **195**, 1 (2002).
14. M. Lebrini, F. Bentiss, H. Venzin and M. Lagrenee, *Corros. Sci.*, **48**, 1279 (2006).
15. W.H. Liq, He, S.T. Zhang, C.L. Pei and B.R. Hou, *J. Appl. Electrochem.*, **38**, 289 (2008).
16. A.Y. El-Etre, *Corros. Sci.*, **45**, 2485 (2003).
17. A. Yurta, B. Balaban, S.U. Kandemir, G. Bereket and B. Erk, *Mater. Chem. Phys.*, **85**, 420 (2004).
18. H. Sharky, M. Yuasa, I. Sekine, R.M. Issa, H.Y. El-Baradie and G.K. Gomma, *Corros. Sci.*, **40**, 2173 (1998).
19. A.A. Herman, M.S. Morad and M.H. Wahdan, *J. Appl. Electrochem.*, **34**, 95 (2004).
20. G. Banerjee and S.N. Malhotra, *Corrosion (NACE)*, **48**, 10 (1992).