Corrosion Inhibition of Mild Steel By 1-Benzyl-3-Methylimidazolium Chloride in 2M H$_2$SO$_4$ And 3.5% Nacl Media

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Abstract -The acid and chloride corrosion inhibition process of mild steel in 2M H$_2$SO$_4$ and 3.5% NaCl media by 1-benzyl-3-methylimidazolium chloride (BMIC) has been investigated using weight loss method, potentiodynamic polarization and electrochemical impedance spectroscopy. The inhibition efficiency increased with increase in the concentration of the inhibitor in both media. The effect of temperature on the corrosion behavior in the presence of inhibitor was studied in the temperature range of 308-328K. The adsorption of the studied inhibitor on the mild steel obeyed Langmuir adsorption isotherm. Protective film formation against acid and chloride attack was confirmed by Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) techniques.

Keywords - Imidazolium chloride, Inhibition, Corrosion, Steel, Acid, Chloride

1. INTRODUCTION

Mild steel is widely used in many industrial applications. In most industrial processes, the acidic solutions are commonly used for the pickling, industrial acid cleaning, acid descaling oil well acidifying, etc.[1-4] and mild steel also comes in contact with chloride ions very frequently under numerous conditions and circumstances in industries. Chloride ions are known to be aggressive towards mild steel and cause severe corrosion problems. Many examples exist of their use in combination with other inhibitors to improve the protection of metals [5-7]. Corrosion prevention systems favor the use of environmental chemicals with low or zero environmental impacts. The decreasing of corrosion rate of metals provides saving of resources and economical benefits during the industrial applications as well as increasing the lifetime of equipment and also decreasing the dissolution of toxic metals from the components into the environment. Therefore, the prevention of metals used in industrial applications from corrosion is vital that must be dealt with. The use of organic molecules as corrosion inhibitors is one of the most practical methods for protecting metals against the corrosion and it is becoming increasingly popular.

Organic compounds bearing heteroatom's with high electron density such as phosphor, sulphur, nitrogen, oxygen or those containing multiple bonds which are considered as adsorption centers, are effective as corrosion inhibitor [8,9]. Ionic liquids (Imidazolium chloride) are organic salts that melt below 100°C. Unlike traditional solvents, ionic liquids are comprised entirely of ions. The interest in ionic liquids stems from their potential as "green solvents" because of chemical and thermal stability, nonflammability, very low or negligible vapour pressure, high ionic conductivity, and a wide electrochemical potential window, which makes them potentially attractive alternative for volatile organic solvents. Recently, a variety of applications [10-13] of ionic liquids have been widely investigated. In particular, the most extensively studied ionic liquids are based upon the imidazolium cation. Imidazolium compounds are reported to show corrosion resistant behavior on copper [14] mild steel and Aluminum. It was found that the action of such inhibitors depends on the specific interaction between functional groups and the metal surface, due to the presence of the CN group and electronegative nitrogen in the molecule.

B. About the study

The purpose of this paper is to evaluate 1-benzyl-3-methylimidazolium chloride (BMIC) as corrosion inhibitor for mild steel in different media. The adsorption and inhibition efficiency of this inhibitor was investigated and the thermodynamic adsorption parameter in absence and presence of inhibitor was calculated. The molecular formula of the BMIC is C$_{11}$H$_{13}$N$_2$$^+$ Cl$^-$ and its chemical structure is shown in Fig.1.
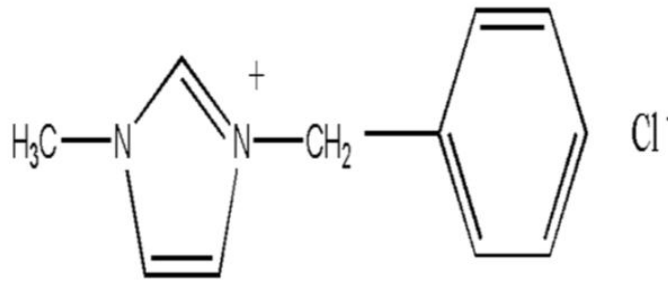
Fig 1. Chemical structure of BMIC

II. EXPERIMENTAL

A. Preparation of Electrode

The mild steel specimens were cut from a cylindrical rod to a length of 5cm and inserted to polyester resin leaving only 0.5 cm^2 of the surface area exposed to electrolyte. The electrical conductivity was provided by a copper wire. The chemical composition of working electrode (wt) was C (0.13%), Mn (0.39%), Si (0.18%), S (04%), P (0.40%) and Fe (remainder).

B. Test Solutions

The corrosion tests were performed in 2M H_2SO_4 solution and 3.5% NaCl solution in the absence and presence of BMIC. The inhibitor (BMIC) was purchased from Sigma Aldrich Company. The corrosive solution of 2M H_2SO_4 (AR grade) and 3.5% NaCl (AR grade) were prepared in distilled water and used for all studies. The concentrations of the inhibitor employed were varied from 0.002M to 0.01M in acid medium and 0.0002M to 0.001M in chloride medium. For each experiment, a freshly prepared solution was used.

C. Weight Loss Measurements

The mild steel specimens of 3cmx3cmx0.6cm dimensions were abraded with different grades of emery papers, washed with distilled water, degreased with acetone, dried with air. After weighing accurately the specimens were immersed in solutions containing 2M H_2SO_4 solution in acid medium and 3.5% NaCl solution in chloride medium with and without various concentrations of BMIC. The experimental studies were performed at different temperature (from 308K to 328K) maintained in a thermostated water bath. The temperature maintenance in all immersion was around 24 hrs. The solution volume was 100 ml. The coupons were withdrawn from the tested solution, washed thoroughly with distilled water followed by acetone and dried with air, then weighed again. Weight loss was used to calculate the corrosion rate (ρ) and inhibition efficiency (IE) as follows:

$$\rho = \frac{W_b - W_a}{st} \qquad (1)$$

where W_b and W_a are the specimen weight before and after immersion in the test solution respectively, S is the surface area of the specimen and t is the end time of each experiment. The IE (%) values were being calculated from WL data by using Eq. (2):

$$IE_{WL}\ (\%) = (\rho^0 - \rho)/\ \rho^0 \times 100 \qquad (2)$$

where ρ^0 is a corrosion rate without inhibitor and ρ is a corrosion rate with inhibitor.

D. Electrochemical Measurements

Polarization study was carried out using H & CH electrochemical workstation impedance Analyzer Model CHI 604D provided with iR compensation facility, using three-electrode cell assembly. A double wall one-compartment cell with a three-electrode configuration was used. Mild steel was used as a working electrode and platinum electrode as counter electrode and calomel as reference electrodes. The corrosion parameters such as linear polarization (LPR), Corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (b_c and b_a) were measured. During the polarization study, the scan rate (v/s) was 0.001; Hold time at Ef (s) was zero and quiet time (s) was 2. AC impedance spectra were recorded in the same instrument using three-electrode cell assembly. The real part and imaginary part of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were calculated using the relation:

$$R_{ct} = (R_s + R_{ct}) - R_s \qquad (3)$$
$$C_{dl} = \tfrac{1}{2}\pi R ct f_{max} \qquad (4)$$

Where f_{max} = maximum frequency and R_s = Solution resistance. AC impedance was recorded with initial E(v) = 0 High frequency (Hz) = 1×10^5, Low frequency (Hz) = 0.1, Amplitude (v) = 0.005 and Quiet time (s) = 2. The working surface area was 0.5cm^2, abraded with emery paper (grade 600-1200) on test face, rinsed with distilled water, degreased with acetone, and dried with a cold air steam. Before measurement the electrode was immersed in test

solution at open circuit potential (OCP) for 20 min to be sufficient to attain a stable state. All electrochemical measurements were carried out at 308K using 100ml of electrolyte (2M H_2SO_4 and 3.5% NaCl) in stationary condition. Each experiment was repeated at least three times to check the reproducibility.

E. Scanning Electron Microscopy (SEM)

The mild steel specimens were immersed in acid and chloride solutions in the presence and absence of inhibitor for a period of 24 h. After 24 h, the specimens were taken out and dried. The nature of the surface film formed on the surface of the mild steel specimen was analyzed by using JEOL (JSM 6390) Scanning electronic microscopy.

F. Fourier Transform- Infrared spectroscopy (FT-IR)

The BMIC (Coated on KBr disc) was characterized by FT-IR spectroscopy (8400S SHIMADZU spectrometer. After immersion in 2M H_2SO_4 and 3.5% NaCl with addition of BMIC for 24 h, the specimen was cleaned with distilled water, dried with a cold air. Then the thin adsorption layer formed on steel surface was rubbed and it was characterized by the same spectrophotometer.

III. RESULT AND DISCUSSION

A. Weight Loss Measurements

The corrosion rate of mild steel specimens after exposure to 2M H_2SO_4 solution and 3.5% NaCl solution at different temperatures ranging from 308-328K with and without the addition of various concentrations of BMIC was calculated and the data obtained are given in Table 1. It can be seen that, the addition of inhibitor to the aggressive solution reduces the corrosion rate of mild steel. The maximum inhibition efficiency was found to be 83.38% in acid medium at 0.01M and 80.79% in chloride medium at 0.001M at 308K, which indicated that BMIC was a good inhibitor in both media. Table 1 shows that the corrosion rate decreased and inhibition efficiency increased with increasing inhibitor concentration in both media suggests that the inhibitor molecule act by adsorption on the metal surface and the decrease of inhibition efficiency with increase of temperature in acid and chloride media (Fig.2&3), which could be attributed to the shift of the adsorption-desorption equilibrium toward desorption .
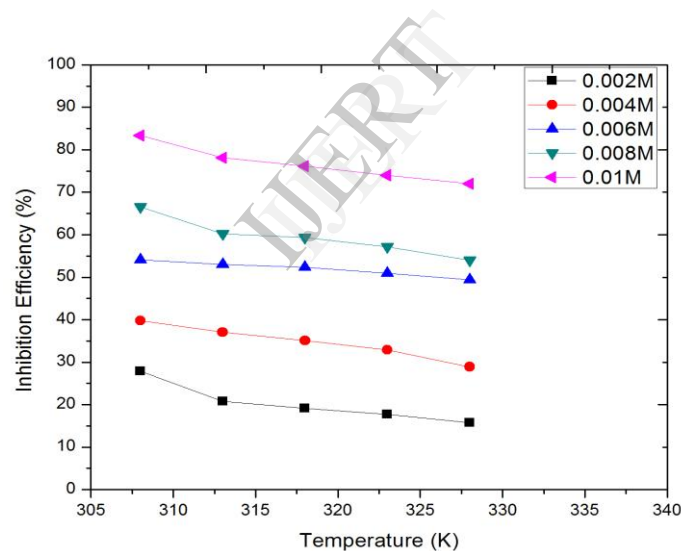

Fig 2. Dependence of mild steel corrosion rate on the concentration, Inhibition efficiency for different temperature and Inhibition efficiency for different concentrations of BMIC in acid medium at different temperatures.

Table 1 **C**orrosion rate, Inhibition efficiency and Surface area data obtained from weight loss method for mild steel in acid medium of BMIC & chloride medium of BMIC.

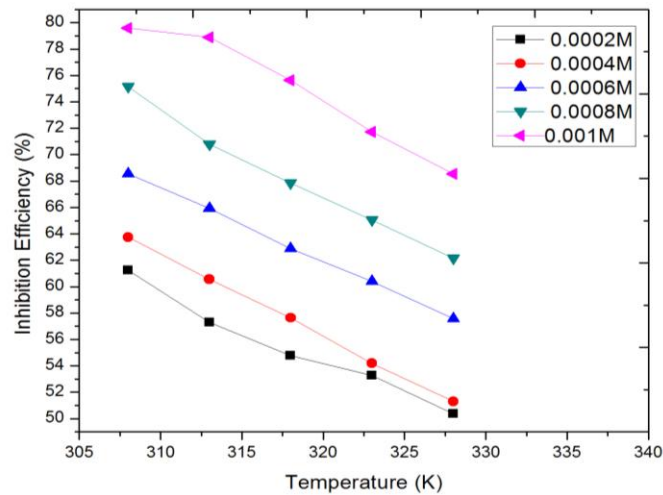| T (K)	Acid medium of BMIC				Chloride medium of BMIC			
	Conc. (M)	$\rho \times 10^{-5}$ (gcm^{-2}min^{-1})	IE (%)	θ	Conc. (M)	$\rho \times 10^{-6}$ (gcm^{-2}min^{-1})	IE (%)	θ
308	Blank	9.819	-	-	Blank	5.243	-	-
	0.002	7.079	27.90	0.2790	0.0002	2.031	61.26	0.6126
	0.004	5.911	39.80	0.3980	0.0004	1.901	63.74	0.6374
	0.006	4.512	54.05	0.5405	0.0006	1.649	68.54	0.6854
	0.008	3.289	66.50	0.6650	0.0008	1.302	75.17	0.7517
	0.01	1.631	83.38	0.8338	0.001	1.007	80.79	0.8079
313	Blank	9.940	-	-	Blank	5.347	-	-
	0.002	7.871	20.81	0.2081	0.0002	2.283	57.31	0.5731
	0.004	6.259	37.03	0.3703	0.0004	2.109	60.55	0.6055
	0.006	4.668	53.05	0.5305	0.0006	1.823	65.91	0.6591
	0.008	3.955	60.22	0.6022	0.0008	1.563	70.78	0.7078
	0.01	2.174	78.13	0.7813	0.001	1.128	78.90	0.7890
318	Blank	9.957	-	-	Blank	5.451	-	-
	0.002	8.056	19.10	0.1910	0.0002	2.465	54.78	0.5478
	0.004	6.462	35.10	0.3510	0.0004	2.309	57.64	0.5764
	0.006	4.744	52.35	0.5235	0.0006	2.023	62.90	0.6290
	0.008	4.049	59.34	0.5934	0.0008	1.753	67.83	0.6783
	0.01	2.372	76.17	0.7617	0.001	1.328	75.64	0.7564
323	Blank	9.964	-	-	Blank	5.59	-	-
	0.002	8.198	17.72	0.1772	0.0002	2.613	53.26	0.5326
	0.004	6.687	32.89	0.3289	0.0004	2.561	54.19	0.5419
	0.006	4.885	50.98	0.5098	0.0006	2.214	60.40	0.6040
	0.008	4.272	57.13	0.5713	0.0008	1.953	65.06	0.6506
	0.01	2.588	74.03	0.7403	0.001	1.58	71.74	0.7174
328	Blank	9.972	-	-	Blank	5.686	-	-
	0.002	8.398	15.79	0.1579	0.0002	2.821	50.38	0.5038
	0.004	7.09	28.90	0.2890	0.0004	2.769	51.30	0.5130
	0.006	5.045	49.41	0.4941	0.0006	2.413	57.56	0.5756
	0.008	4.584	54.03	0.5403	0.0008	2.153	62.14	0.6214
	0.01	2.793	71.99	0.7199	0.001	1.788	68.55	0.6855

Fig.3.Dependence of mild steel corrosion rate on the concentration, Inhibition efficiency for different concentrations of BMIC in chloride medium at different temperatures.

B. Potentiodynamic Polarization Measurements

The representative potentiodynamic polarization curves of mild steel in 2M H_2SO_4 and 3.5% NaCl solution in the absence and presence of various concentrations of BMIC are shown in Fig 4(a&b). The values of related electrochemical parameters i.e. corrosion potential (E_{corr}), corrosion current density (i_{corr}), corrosion rate and inhibition efficiency were calculated from the related polarization curves and are given in Table 2. The inhibition efficiency was calculated from polarization measurements according to the relation given below;

$$IE\% = (i^0_{corr} - i_{corr} / i^0_{corr}) \times 100 \qquad (5)$$

where i^0_{corr} and i_{corr} are the uninhibited and inhibited corrosion current densities, respectively.

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As it can be clearly seen from fig 4a, the presence of inhibitor causes a prominent decrease in the corrosion rate, i.e., shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials, and to lower values of current densities. Namely, both cathodic and anodic reactions of mild steel electrode corrosion are inhibited by BMIC in 2M H_2SO_4. This may be ascribed to adsorption of inhibitor over the corroded surface. This reveals that BMIC can be classified as mixed type inhibitor in 2M H_2SO_4 medium. It follows from fig 4b that the BMIC suppressed the cathodic reaction to great extent than anodic one. This behavior is typical of mixed type inhibitor with cathodic predominance in 3.5% NaCl medium
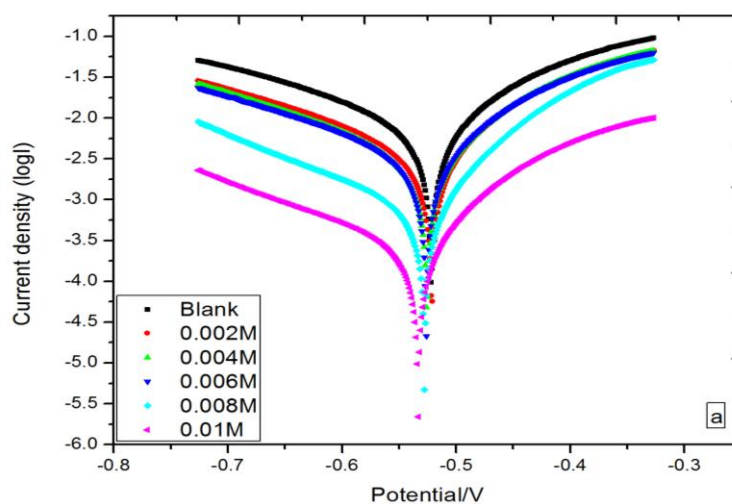

Fig 4a. Tafel plots for mild steel immersed in 2 M H_2SO_4 and 3.5% NaCl containing different concentration of BMIC at 308K.
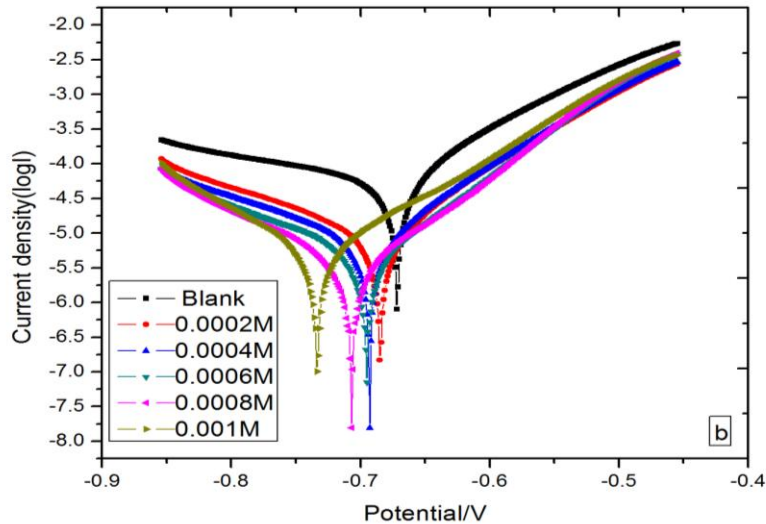
Fig.4b. Tafel plots for mild steel immersed in 2 M H_2SO_4 and 3.5%NaCl containing different concentration of BMIC at 308K

Table 2 Potentiodynamic polarization parameters for the corrosion of mild steel in 2M H_2SO_4 and 3.5%NaCl in the absence and the presence of BMIC.

Medium	C_{inh}(M)	E_{corr}(mV)	i_{corr}(Acm^{-2})	b_c (V/decade)	b_a (V/ decade)	R_p (Ω/cm^2)	%IE
2MH_2SO_4	Blank	-522	8.766×10^{-3}	5.129	6.860	4.10	-
	0.002	-516	4.175×10^{-3}	5.383	7.661	8.00	53.01
	0.004	-521	3.637×10^{-3}	5.353	7.888	9.00	58.50
	0.006	-521	3.788×10^{-3}	5.125	7.699	9.00	56.78
	0.008	-523	9.888×10^{-4}	5.286	7.538	27.8	58.50
	0.01	-528	3.646×10^{-4}	4.917	8.755	87.2	84.70
3.5%NaCl	Blank	-672	8.148×10^{-5}	4.266	9.908	412.10	-
	0.0002	-673	1.021×10^{-5}	5.022	11.704	2415.8	87.46
	0.0004	-681	8.495×10^{-6}	5.120	11.913	2846.3	89.57
	0.0006	-722	6.155×10^{-6}	5.352	9.633	3443.0	92.40
	0.0008	-683	4.991×10^{-6}	5.310	13.662	4260.9	93.87
	0.001	-695	3.419×10^{-6}	5.450	13.397	5880.6	95.80

Cathodic current potential curves give rise to parallel Tafel lines indicating that hydrogen evolution reaction by the BMIC investigated occur by simple adsorption mode and the mechanism is the same with and without inhibitor. In anodic domain, the addition of BMIC in both media leads to decrease in the current densities in large potential domain. In this case desorption rate of BMIC is raised more than its adsorption [15]. From Table 2 reveals that the corrosion current (i_{corr}) decreases and inhibition efficiency increases with the inhibitor concentration. No definite trend was observed in the shift of corrosion potential (E_{corr}) values, in the presence of various concentrations of BMIC in both media. This result suggests that the addition of BMIC reduces anodic dissolution and also retards hydrogen evolution reactions as

would be expected and therefore BMIC on mild steel is caused by geometric blocking effect [16].

C. Electrochemical Impedance Spectroscopy

Measurements

The effect of inhibitor concentration on the impedance mild steel in 2M H_2SO_4 and 3.5% NaCl media at 308K is presented in Fig 5(a&b). The curves show a similar type of Nyquist plot for mild steel in the presence of various concentrations of BMIC in acid medium. As seen in Fig 5a, the Nyquist plot contains depressed semi-circles indicating a charge transfer process mainly controlling the corrosion of mild steel. Such behavior is

characteristic for solid electrodes and often referred to frequency dispersion, has been attributed to roughness and other inhomogeneities of the solid surface [17]. From fig. 5b shows the Nyquist plots of mild steel in 3.5% NaCl without and with different concentrations of BMIC. From these plots, the impedance response of mild steel in uninhibited in acid and chloride solution has significantly changed after the addition of BMIC in the corrosive solutions. This indicated that the impedance of the inhibited substrate has increased with increasing concentration of inhibitor. The characteristic parameters associated to the impedance diagram (R_{ct}, C_{dl} and IE) are given in Table 3. In the case of impedance studies, IE% was calculated as:

$$IE\% = (R^{1}_{ct} - R_{ct} / R^{1}_{ct}) \times 100 \qquad (6)$$

Where R_{ct} and R^{1}_{ct} are uninhibited and inhibited charge transfer resistance respectively. It is clear from Table 3 that

charge transfer resistance increased after addition of inhibitor concentration. On the other hand, the values of C_{dl} decreased with increase in the inhibitor concentration. This situation was the result of an increase in the surface coverage by the inhibitor in both media, which led to an increase in the inhibition efficiency [18]. This decrease in C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of double layer, suggested that BMIC molecules function by adsorption at the metal/solution interface.[19].

The results obtained from polarization show a similar trend for the tested compound as those obtained from impedance and weight loss measurements but yield different value of inhibition efficiency due to different experimental conditions.
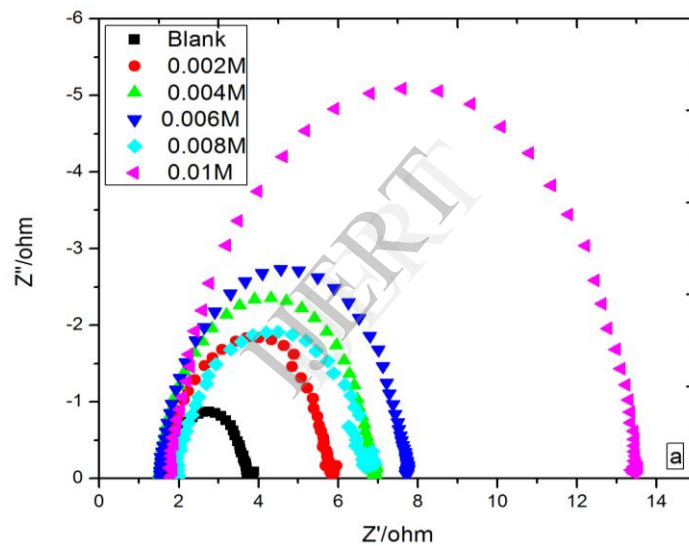

Fig 5a. Nyquist plots for mild steel immersed in 2 M H_2SO_4 and 3.5%NaCl containing different concentration of BMIC at 308K.
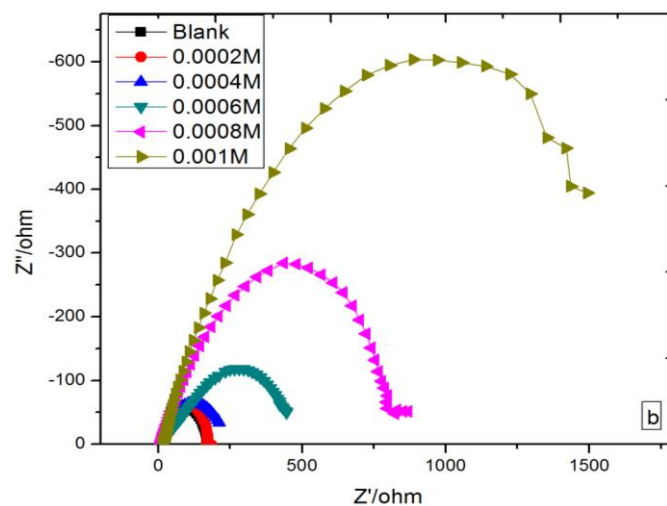

Fig.5b. Nyquist plots for mild steel immersed in 2 M H_2SO_4 and 3.5%NaCl containing different concentration of BMIC at 308K.

Table 3 Electrochemical impedance parameters for mild steel in 2M H_2SO_4 and 3.5%NaCl in the absence and the presence of BMIC.

Medium	C_{inh}(M)	R_s(Ωcm^2)	R_{ct}(Ωcm^2)	C_{dl}(F/cm^2)	%IE
2MH_2SO_4	Blank	1.636	2.080	8.647×10^{-2}	-
	0.002	1.693	4.137	2.097×10^{-2}	49.72
	0.004	1.502	5.436	1.232×10^{-2}	61.74
	0.006	1.536	6.206	9.367×10^{-3}	66.48
	0.008	1.837	10.703	3.372×10^{-3}	80.57
	0.01	1.839	11.671	2.680×10^{-3}	82.18
3.5%NaCl	Blank	11.81	156.59	1.790×10^{-5}	-
	0.0002	11.16	159.84	1.560×10^{-5}	2.030
	0.0004	10.99	200.01	1.225×10^{-5}	21.73
	0.0006	11.60	433.30	3.151×10^{-5}	63.86
	0.0008	11.52	788.18	7.089×10^{-7}	80.13
	0.001	9.070	1424.93	1.848×10^{-7}	89.01

D. Effect of Temperature

Temperature is an important parameter in studies on metal dissolution studies. To assess the effect of temperature on corrosion and corrosion inhibitive process, mass loss experiments were performed at 5K intervals in the temperature range 308–328K in uninhibited acid and inhibited solutions containing different concentrations of BMIC. The relationship between the corrosion rate (ρ) and temperature (T) are expressed by the Arrhenius equation.

$$\log \rho = \log A - E_a / 2.303RT \qquad (7)$$

Where A is the frequency factor, E_a is the activation energy, R is the gas constant (R=8.314 J $mol^{-1}K^{-1}$) and T is the absolute temperature. Linear plots were obtained by plotting $\log \rho$ against 1/T for the corrosion of mild steel in the absence and presence of different concentrations of inhibitor in acid and chloride media (Fig.6 (a&b)). The slope of the line was ($-E_a$/2.303R) and the intercept of the line extrapolated to (1/T=0) gave log A. The values of E_a were calculated from the slope of the straight lines and are listed in Table 4.

In general E_a values in the presence of inhibitor were greater than its absence clearly indicated that the corrosion reaction of mild steel was inhibited by BMIC. E_a values for the inhibited system increase with inhibitor concentration in both acid and chloride media. At concentration of 0.006M in acid medium for BMIC, there is slightly decrease in E_a value is observed (Fig.7) with further increase in inhibitor concentration. The decrease in the E_a value at a level of inhibitor efficiency was reported

in the literature [20,21]. The values of E_a values in the presence of inhibitor were greater than its absence clearly indicated that the corrosion reaction of mild steel was inhibited by BMIC. The increase in the activation energy in the presence of inhibitor signified physical adsorption. This conclusion was confirmed by the decrease in inhibition efficiency with increasing temperature. The change in enthalpy (ΔH^*) and entropy (ΔS^*) for the formation of activated complex in the transition state could be obtained from the transition state equation:

$$\log \rho /T = \{(\log R/ hN) + (\Delta S^*/2.303R)\} - (\Delta H^*/ 2.303RT) \qquad (8)$$

Where h is the Planck's constant, N is the Avogadro's number and R is the gas constant. A plot of $\log \rho$ /T vs 1/T gave straight line (Fig.8 (a&b)). The slope was ($-\Delta H^*$/2.303R) and the intercept was {(log R/hN + (ΔS^*/2.303R)}, from which the values of ΔH^* and ΔS^* were calculated and presented in Table 4. The positive values of enthalpies (ΔH^*), ranged from 80.3-158.9 kJ/mol in acid medium and 114.4-189kJ/mol in chloride medium, reflected the endothermic nature of the steel dissolution process. The negative values of entropies (ΔS^*) implied that the activated complex in the rate determining step represented an association rather than dissociation step meaning that a decrease in disorder took place on going from reactants to the activated complex [22]. Thus a greater degree of orderliness appeared during its transformation from reactant to activated complex. In addition, the negative values of ΔS^* in the presence of inhibitor than its

absence implied that the presence of inhibitor created a near-equilibrium corrosion system state [23].
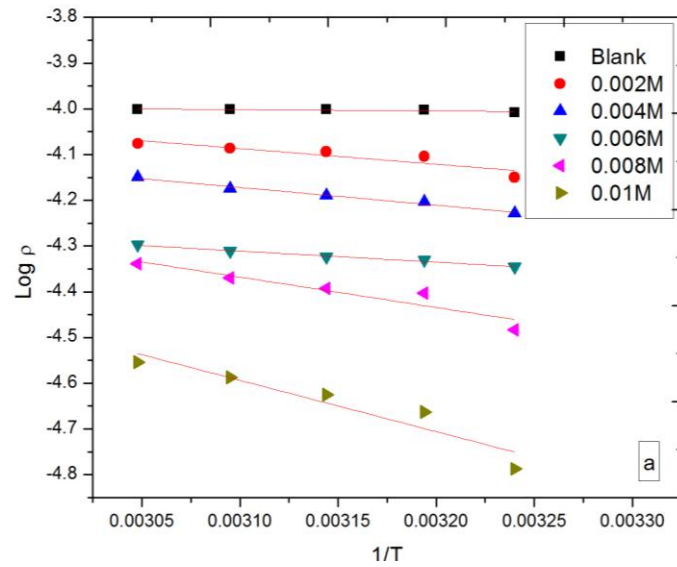

Fig 6a. Arrhenius plots for mild steel in the absence and presence different concentrations of BMIC in acid and chloride media.
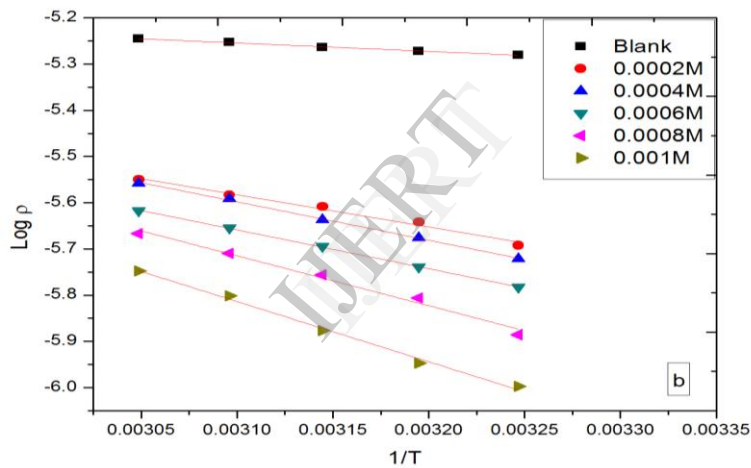

Fig 6b. Arrhenius plots for mild steel in the absence and presence different concentration of BMIC in acid and chloride media.
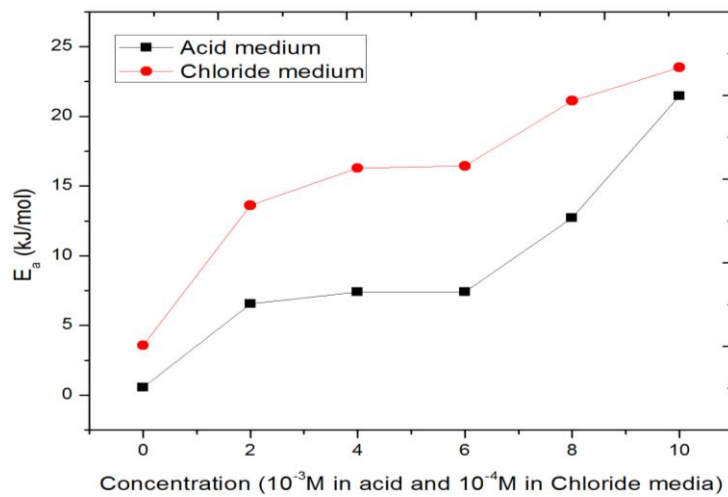

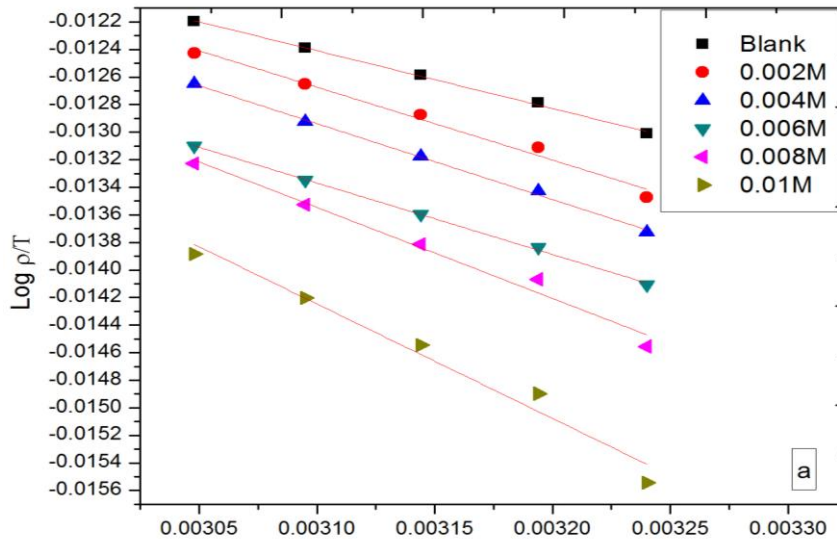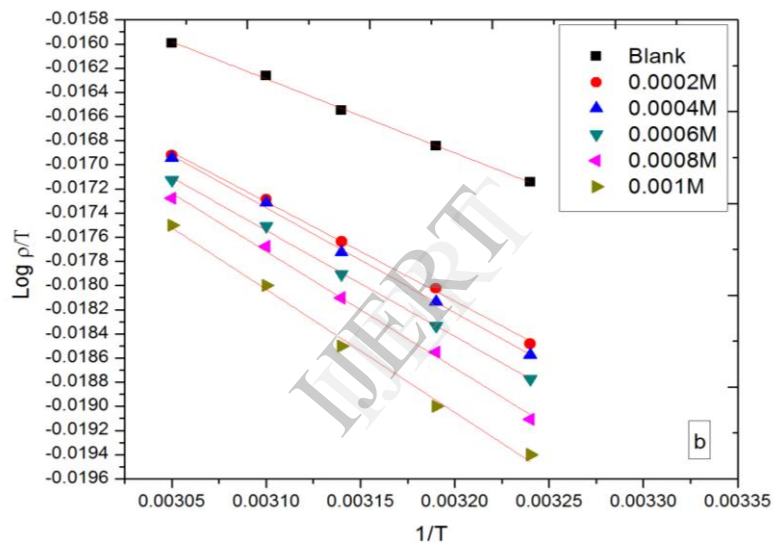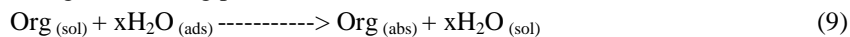Fig 7. Dependence of apparent activation energy on the concentration of 1-BMIC

Fig 8a. Transition state plots for mild steel in the absence and presence different concentrations of BMIC in acid and chloride media.

Fig.8b. Transition state plots for mild steel in the absence and presence different concentrations of BMIC in acid and chloride media.

E. Adsorption Isotherm and Thermodynamic Parameters

The adsorption of surfactants at metal/solution interfaces can markedly change the corrosion resisting properties of metals. The efficiency of organic molecules as good corrosion inhibitors mainly depends on their adsorption ability on the metal surface. So, the investigation of the relation between corrosion inhibition and adsorption is of great importance. The adsorption of organic inhibitors at the metal/solution interface takes place through the replacement of water molecules by organic inhibitor molecules according to following process [24].

$$Org_{(sol)} + xH_2O_{(ads)} \text{-----------} > Org_{(abs)} + xH_2O_{(sol)} \tag{9}$$

Where $Org_{(sol)}$ and $Org_{(ads)}$ are organic molecules in the solution and adsorbed on the metal surface, respectively. x is the number of water molecules replaced by the organic molecules.

Table 4 Corrosion kinetic parameters for mild steel in 2M H_2SO_4 and 3.5%NaCl in absence and presence of different concentration of BMIC.

C_{inh}(M)	E_a (kJ/mol)	ΔH^*(kJ/mol)	ΔS^*(J/mol/K)
Acid medium			
Blank	0.56	80.3	-490.79
0.002	6.55	101.2	-490.74
0.004	7.39	105.4	-490.72
0.006	7.41	99.2	-490.76
0.008	12.71	126.4	-490.68
0.01	21.46	158.9	-490.59
Chloride medium			
Blank	3.56	114.4	-490.76
0.0002	13.62	153.1	-490.66
0.0004	16.29	161.8	-490.64
0.0006	16.44	163.5	-490.64
0.0008	21.12	179.7	-490.59
0.001	23.51	189.0	-490.56

The adsorption on the corroding surfaces never reaches the real equilibrium and tends to reach an adsorption steady state. However, when the corrosion rate is sufficiently small, the adsorption steady state has a tendency to become a quasi-equilibrium state. In this case, it is reasonable to consider the quasi-equilibrium adsorption in thermodynamic way using the appropriate equilibrium isotherms. It is essential to know the mode of adsorption and the adsorption isotherm that can give valuable information on the interaction of inhibitor and metal surface. In order to clarify the nature and the strength of adsorption the experimental results have been fitted to a series of adsorption isotherms and the best fit was obtained with the use of Langmuir adsorption isotherm.

Langmuir adsorption isotherm can be expressed by the following equation.

$$C_{inh}/\theta = 1 / K_{ads} + C_{inh}$$
(10)

Where C_{inh} is inhibitor concentration. θ is the degree of the coverage on the metal surface and K_{ads} is the equilibrium constant for the adsorption-desorption process. A plot of log C/θ vs log C gave straight line (Fig.9 (a&b)). From intercept of the straight lines, the values of K_{ads} were calculated as given in Table 5. From the table the correlation coefficients are very good and K_{ads} values decreases with increasing temperature shows that the

BMIC was physically adsorbed on the mild steel surface. The equilibrium constant for the adsorption-desorption process is related to the standard free energy of adsorption (ΔG°_{ads}) according to relation:

$$\Delta G^\circ_{ads} = -RTln(55.5K_{ads})$$
(11)

Where R is the gas constant, T is the temperature and 55.5 is the molar concentration of water in solution. Generally the standard free energy of adsorption values of -20kJmol[-1] or less negative are associated with an electrostatic inter action between charged molecules and charged metal surface (physical adsorption): those of -40kJmol[-1] or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [25,26]. The values of ΔG_{ads} were calculated from equation (11) and are recorded in Table 5**.** The negative values of ΔG_{ads} clearly indicated that spontaneous adsorption of BMIC on mild steel surface took place through physical adsorption mechanism in both media. Usually, values of ΔG_{ads} up to -20 KJ/mol (as obtained in this study) signified physical adsorption, which was consistent with electrostatic interaction between charged molecules and a charged metal [23, 27]. Another form of Langmuir's adsorption isotherm was used to calculate the enthalpy of adsorption [60].

$$logK = (-logC_{H2O} + \Delta S^{\circ}_{ads}/2.303R) - \Delta H^{\circ}_{ads}/2.303RT \qquad (12)$$

where C_{H2O} is the molar concentration of water molecules, ΔH°_{ads} is the standard heat of adsorption and ΔS°_{ads} is the standard entropy of adsorption. The plots of log K versus 1/T are shown in Fig.10. The slope of the linear part of the curves is equal to $-\Delta H^{\circ}_{ads}/2.303R$ and the intercept is (-

$logC_{H2O} + \Delta S_{ads}/2.303R$), from which the values of ΔH°_{ads} and ΔS°_{ads} were calculated and their values are given in Table 5. The negative values of ΔH°_{ads} reflect the exothermic behavior of inhibitor on mild steel surface. ΔS°_{ads} values were negative (decrease in entropy) because adsorption of these inhibitors was exothermic and ΔH°_{ads} values were more negative than ΔG°_{ads} values.

Fig.9a: Plot of log C/θ versus log C for mild steel in 2M H_2SO_4 and 3.5% NaCl containing different concentrations of inhibitor.

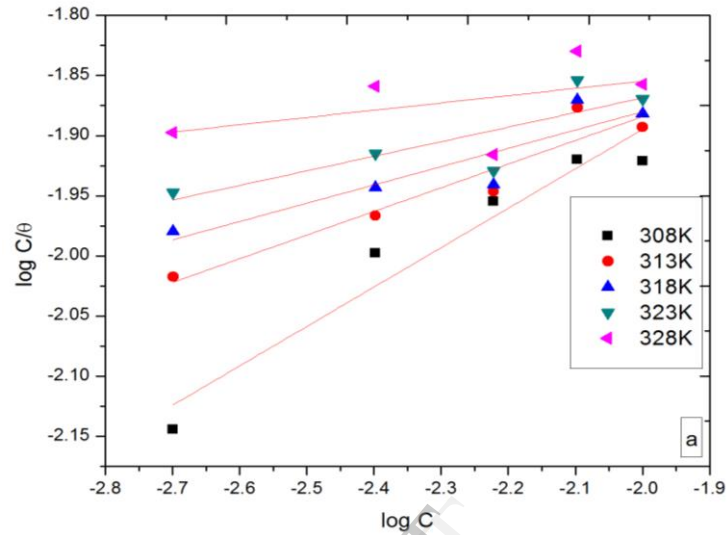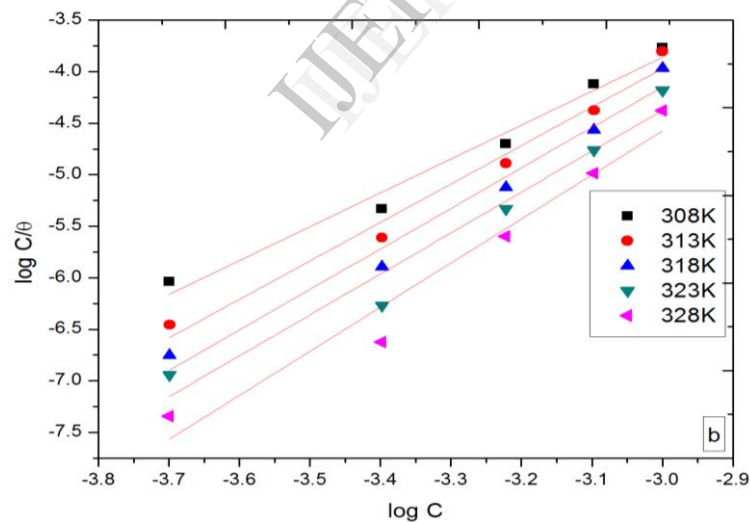Fig 9b: Plot of log C/θ versus log C for mild steel in 2M H_2SO_4 and 3.5% NaCl containing different concentrations of inhibitor.
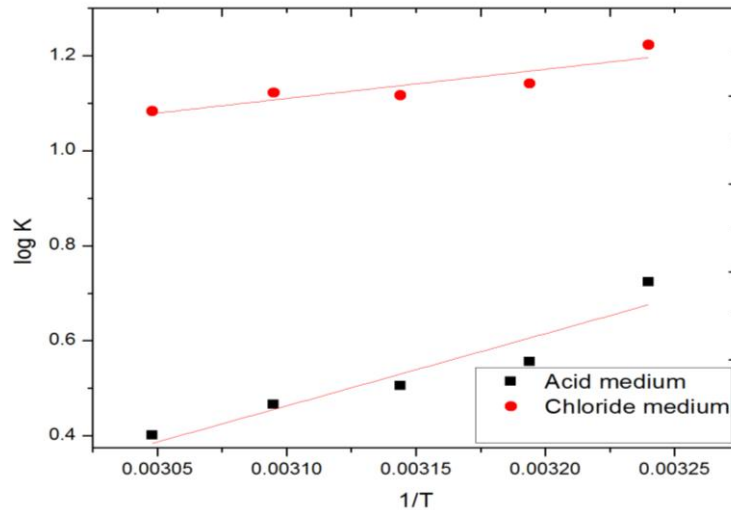
Fig.10. Plot of log k versus 1/T for mild steel in 2M H_2SO_4 and 3.5% NaCl containing different concentrations of inhibitor.

Table 5 Thermodynamic adsorption parameters for BMIC in mild steel of 2M H_2SO_4 and 3.5% NaCl media at different temperatures

Temp(K)	K_{ads} $(10^{-2}M^{-1})$	ΔG^0_{ads}(kJ/mol)	ΔH^0_{ads}(kJ/mol)	ΔS^0_{ads}(kJ/mol)
Acid medium				
308	5.297	-10.60		
313	3.594	-10.67		
318	3.206	-10.82	-28.59	-84.7
323	2.922	-10.97		
328	2.518	-10.95		
Chloride medium				
308	16.69	-10.29		
313	13.84	-10.49		
318	13.08	-10.62	-11.58	-19.54
323	13.25	-10.79		
328	12.11	-10.95		

F. Scanning Electron Microscopy Studies

The SEM images of mild steel in 2M H_2SO_4 and 3.5% NaCl solution in the absence and presence of BMIC after 24 h exposure are given in Fig .11(a&b) and 12(a&b). As it is shown in 11a and 12a, the mild steel surface was strongly damaged in the absence of inhibitors due to metal dissolution in corrosive solution. The surface was highly porous; the large and deep holes appeared. However, the appearances of mild steel surfaces were significantly different after the addition of inhibitors to the corrosive solution. It can be seen from Figs.11b and 12b that, the dissolution rate of mild steel reduced and the smooth surfaces appeared by formation of a protective film on the metal surface.
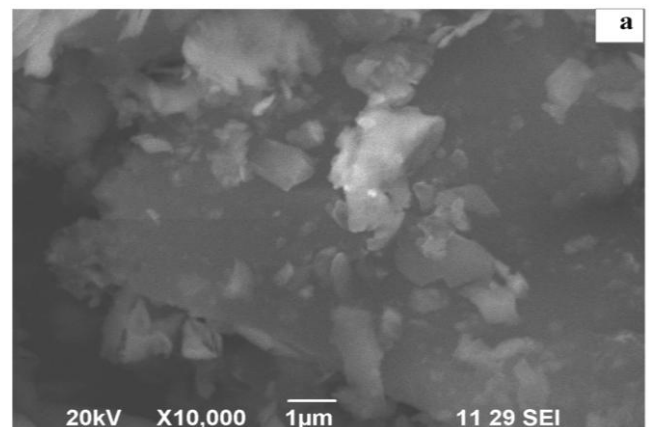

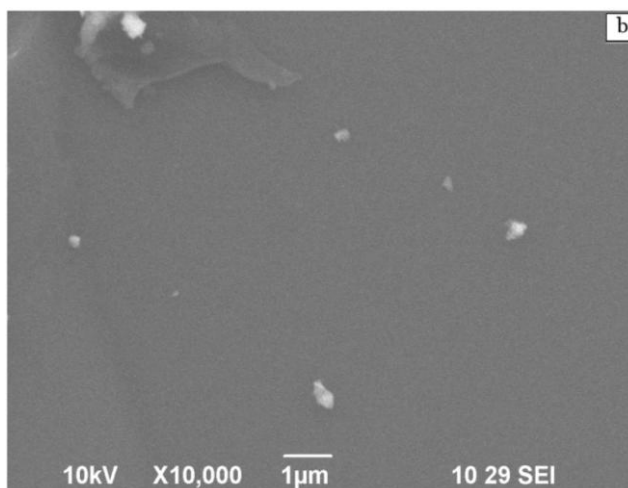Fig.11a. SEM images of mild steel in 2M H_2SO_4 a) without inhibitor.

Fig.11b. SEM images of mild steel in 2M H_2SO_4 b) with inhibitor.
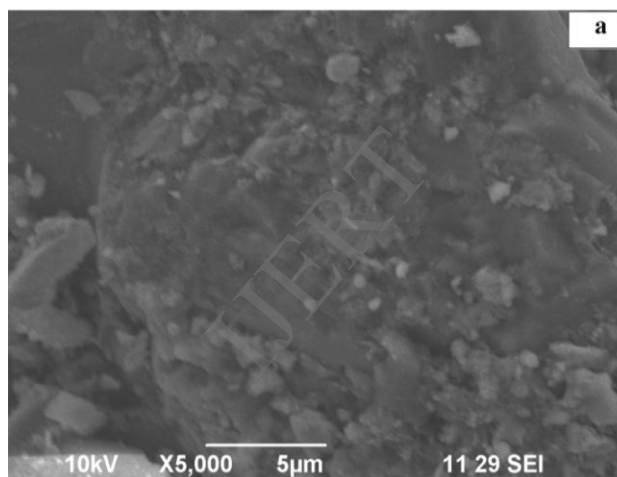

Fig.12a. SEM images of mild steel in 3.5%NaCl a) without inhibitor.
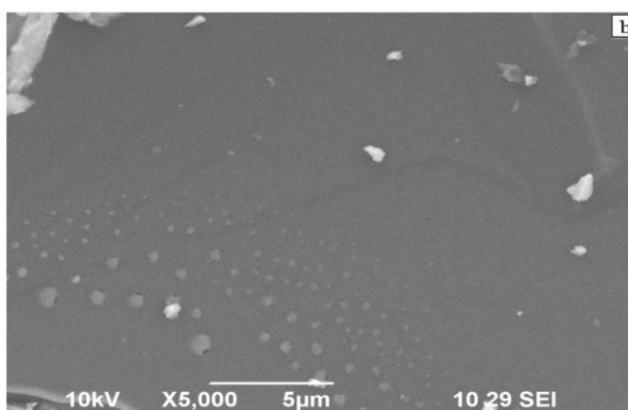

Fig.12b. SEM images of mild steel in 3.5%NaCl b) with inhibitor.

G. FT-IR Studies

Several researchers [28] have confirmed that FTIR spectrometer is a powerful instrument that can used to determine the type of bonding for organic inhibitors absorbed on the metal surface. In this paper, FTIR spectrometer was used to identify whether there was adsorption and to provide new bonding information on the steel surface after immersion inhibited H_2SO_4 and NaCl solution.

The Fourier transform infrared spectroscopy of pure BMIC is shown in Fig. 13a and the FTIR spectrum of adsorbed protective layer formed on the surface after immersion in 2M H_2SO_4 and 3.5%NaCl containing BMIC is shown in the Fig. 13(b&c). The frequencies and assignment of FTIR by BMIC, acid containing BMIC and chloride containing BMIC were shown in Table 6.

Table 6 Frequencies and assignment of adsorption of FTIR by BMIC, acid containing BMIC and chloride containing BMIC

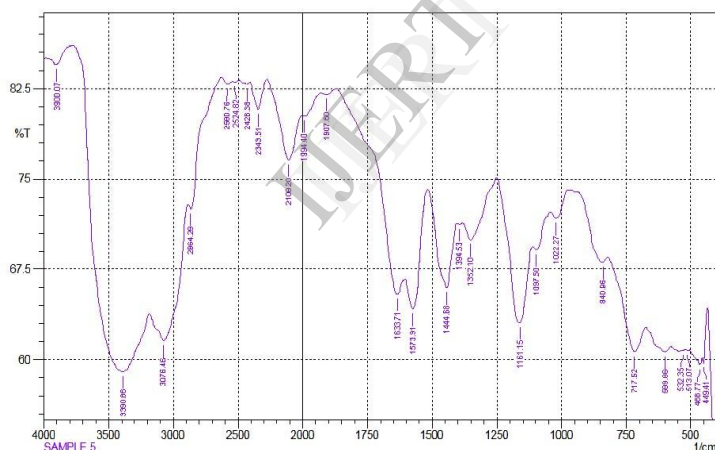| BMIC (frequency in cm^{-1})	H_2SO_4 containing BMIC (frequency in cm^{-1})	NaCl containing BMIC (frequency in cm^{-1})	Assignment
3390.86	3367.71	3367.71	N-H stretch
1633.71	1616.35	1616.35	C=N stretch
1444.68	1473.62	1471.69	C-H bend of –CH$_2$ group
1352.10	1384.89	1369.46	N-heteroaromatic imidazole ring
			C-N stretch
1161.15,1097.50 &1022.27	1271.09	1257.59	
			C-H bend in benzene
840.96& 717.52	829.39	837.11&725.23	

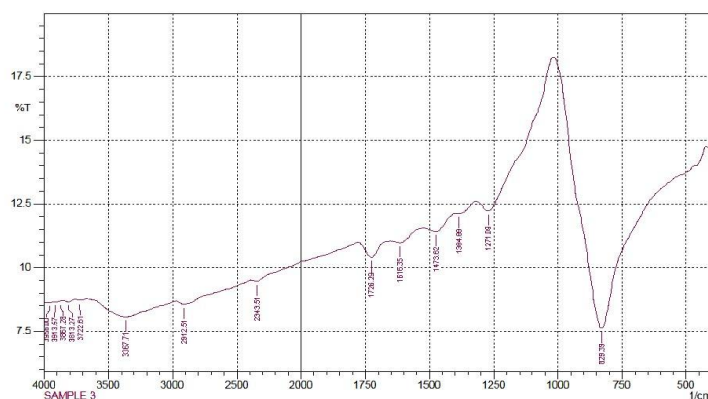Fig. 13a.: FT-IR spectra of BMIC.

Fig.13b. FT-IR spectra of adsorbed layer formed on the mild steel after immersion in 2M H_2SO_4 containing inhibitor.
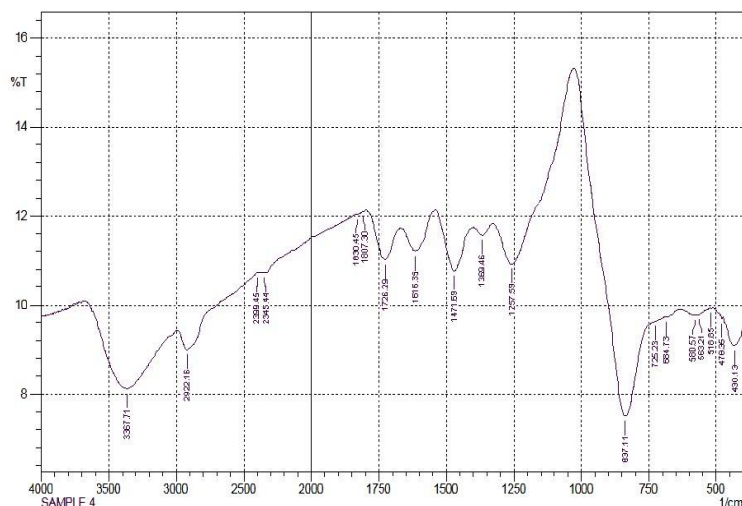
Fig.13c. FT-IR spectra of adsorbed layer formed on the mild steel after immersion in 3.5%NaCl containing inhibitor.

1V. CONCLUSION

Concluding the experimental part, it was clearly demonstrated that all the three techniques used, especially electrochemical techniques are able to characterize and to follow the inhibition of corrosion process promoted by 1-benzyl-3-methylimidazolium chloride (BMIC) and it was found to be a good inhibitor for the corrosion of mild steel in $2MH_2SO_4$ and 3.5%NaCl media. The polarization curves indicated mixed type indicator of both anodic and cathodic processes in acid medium and typical of mixed type inhibitor with cathodic predominance in chloride medium. The electrochemical impedance diagrams showed mainly capacitive loop, which can be attributed to the formation of adsorbed layer on the steel surface. Inhibition efficiency increases with increase in BMIC concentration, but decrease with increase in temperature in both media. The adsorption BMIC on mild steel surface obeyed Langmuir adsorption isotherm. The thermodynamic parameters reveal that the inhibition of corrosion by BMIC is due to the formation of a physisorbed film on the metal surface.

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