

INHIBITING EFFECT OF N,N-METHYLENE BIS ACRYLAMIDE ON ALUMINIUM CORROSION IN 0.3M HYDROCHLORIC ACID SOLUTION

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ABSTRACT

Aluminium (Al) and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their light weight, high thermal and electrical conductivity as well as high resistance to corrosion in a wide variety of corrosive environments and low cost. Generally, the corrosion resistance of metals, such as Al in corrosive environments, may be attributed to the formation of a protective tightly adhered invisible oxide film on the metal surface. The film reduces the corrosion of such metals. This film is generally stable in the solutions of p^H range about 4.5 to 8.5. However, due to the solubility of the film in strong acidic solution, the metal shows high rate of corrosion and dissolution in these conditions. For this reason, several methods have been devised for corrosion control. The commonly used method is the addition of organic corrosion inhibitors. The action of such organic inhibitors is due to adsorption of their molecules onto the metal surface, where the adsorbed film acts like a protective barrier between the metal surface and the corroding medium. The organic compounds that have been found very effective in inhibiting metal corrosion usually contain nitrogen, oxygen, sulphur and phosphorous in a conjugated system.

In the present study corrosion inhibition of aluminium metal in 0.3M HCl solution by N,N-MBA has been investigated using weight loss technique. It has been found that the N,N-MBA is an effective corrosion inhibitor for aluminium in HCl. The inhibition action is contributed to the formation of an adsorbed layer of inhibition on the metal surface which protects the metal against corrosion. The inhibition process of N,N-MBA obeys Langmuir adsorption isotherm. The corrosion inhibition is also proved by electrochemical impedance spectroscopy, Tafel polarization, FT-IR and SEM analysis.

Keywords: N,N-Methylene bisacrylamide, Aluminium, Tafel plot, Impedance spectroscopy

1. INTRODUCTION

Aluminium (Al) and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their light weight, high thermal and electrical conductivity as well as high resistance to corrosion in a wide variety of corrosive environments and low cost. Generally, the corrosion resistance of metals, such as Al in corrosive environments, may be attributed to the formation of a protective tightly adhered invisible oxide film on the metal surface. The film reduces the corrosion of such metals. This film is generally stable in the solutions of p^H

range about 4.5 to 8.5[1,2]. However, due to the solubility of the film in strong acidic solution, the metal shows high rate of corrosion and dissolution in these conditions. [3]. For this reason, several methods have been devised for corrosion control. The commonly used method is the addition of organic corrosion inhibitors.. The action of such organic inhibitors is due to adsorption of their molecules onto the metal surface, where the adsorbed film acts like a protective barrier between the metal surface and the corroding medium. The organic compounds that have been found very effective in inhibiting metal corrosion usually contain nitrogen, oxygen, sulphur and phosphorous in a conjugated system [4–11].In the present work N,N-MBA is used as a corrosion inhibitor for Aluminium in 0.3M HCl solution .

2. EXPERIMENTAL METHODS

2.1 .Materials and Methods

Aluminium samples having an elemental composition of Al- 99.3, Si-0.240%, Fe-0.241%, Cu-0.035%, Mn-0.102%, Ti-0.019%, Pb-0.014%, Zn- 0.043% are used. The samples are cut to dimensions of 4 cm×1 cm×0.15 cm, and It is used in the present study.

2.2 Preparation of Stock Solution

1 gm of N,N-MBA is dissolved in 0.3M HCl, and then made upto 100 ml in a standard measuring flask and from this stock solution is used for the analysis.

2.3 Determination of Surface Area of the specimen

The length, breadth and the thickness of aluminium specimens and the radius of the holes are determined with the help of Vernier calipers of high precision and the surface areas of the specimens are calculated.

2.4 Weight loss method

The weighed specimen, are suspended by means of glass hooks in 100 ml beakers containing 100 ml of aqueous solution of 0.3M HCl containing various concentrations of the inhibitor. After 1 hour immersion, the specimens are taken out, washed in running water, dried and weighed. From the change in weights of the specimen, corrosion rates are calculated using the following relationship.

$$\text{Corrosion rate} = \frac{\text{[loss in weight (mg)]}}{\text{[Surface area of the specimen (dm}^2\text{) } \times \text{ period of immersion (hours)]} \times \rho} \quad \text{----(1)}$$

ρ-density of the metal in g/cm²

The percentage of inhibition efficiency is calculated using the following equation

$$\text{IE\%} = \frac{\text{CR}_0 - \text{CR}_t}{\text{CR}_0} \times 100 \quad \text{----- (2)}$$

CR₀ = corrosion rate in the absence of inhibitor and

CR_t = corrosion rate in the presence of inhibitor .

2.5 Adsorption isotherm

The adsorption isotherm can be determined by assuming that inhibition effect is mainly due to the adsorption at metal /solution interface. Basic information on the adsorption of inhibitor on the metal surface can be provided by adsorption isotherm. In order to obtain the isotherm the fractional surface coverage values (θ) as a function of inhibitor concentration must be obtained. The values of θ are easily determined from the weight loss measurements by the ratio. % I.E /100, where % I.E inhibition efficiency is obtained by weight loss method. So it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitor on the aluminium surface.

2.6 Polarization measurements

The working electrode is immersed in test solution during 30 minutes until a steady state open circuit potential is obtained. Both anodic and cathodic polarization curves are recorded potentiodynamically platinum and Hg/ Hg₂Cl₂ / KCl are used as auxiliary electrode and reference electrode respectively. This is controlled by a personal computer.

2.7 EIS measurements

The electrochemical impedance spectroscopy is carried out using a transfer function analyzer, with a small amplitude ac. The double layer capacitance (C_{dl}) and the charge transfer resistance are obtained using AC impedance instrument Princeton Applied Research (Model – 7310).

2.8. FTI-R spectroscopy

FT-IR spectrum of inhibitor and their film on the surface of the metal are recorded using Spectrum RXI model ,PERKIN ELMER made in USA.

3. RESULTS AND DISCUSSION

Molecular structure of N,N-Methylene bis acrylamide used in the present study is given in Fig. 1

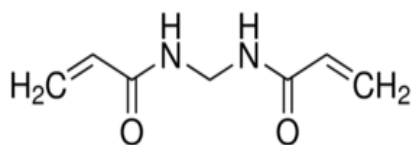


Fig. 1 structure of N,N-Methylene bis acrylamide.

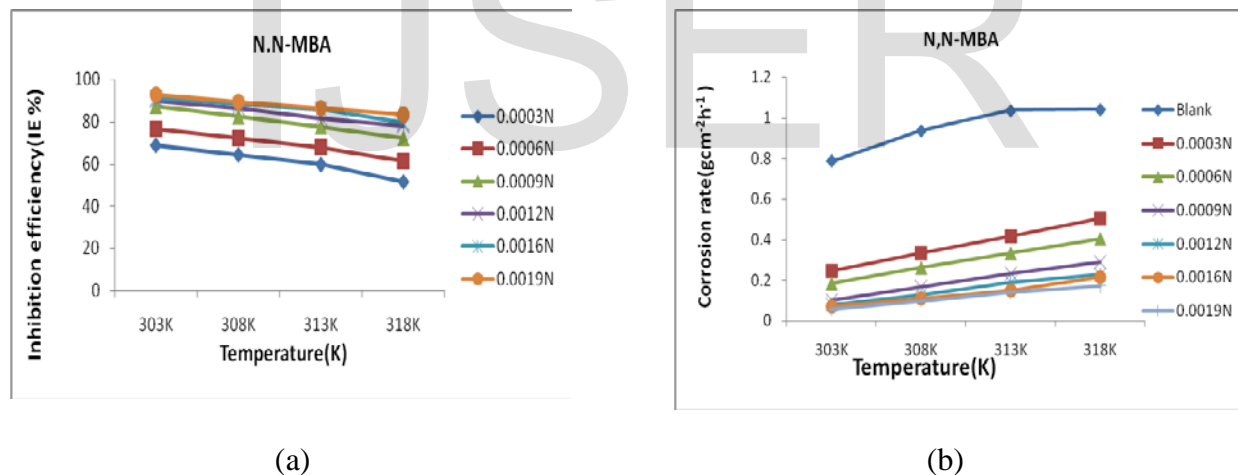
3.1 Weight loss measurements

Table. 1 The percentage inhibition efficiency and corrosion rate of aluminium in 0.3M HCl by N,N-MBA at 303K, 308K, 313K and 318K by weight loss method for 1 hour.

N,N-MBA (N)	Corrosion rate $\times 10^{-2}$ $g^{-2}h^{-1}$				θ				Inhibition Efficiency (%)			
	303 K	308 K	313 K	318 K	303K	308K	313K	318K	303K	308K	313K	318K
Blank	0.7861	0.9359	1.0364	1.0417	-	-	-	-	-	-	-	-
0.0003	0.246	0.334	0.418	0.504	0.686	0.6422	0.596	0.515	68.62	64.22	59.64	51.54
0.0006	0.184	0.231	0.334	0.405	0.764	0.720	0.677	0.611	76.49	72.01	67.76	61.12
0.0009	0.100	0.165	0.231	0.289	0.872	0.8233	0.776	0.722	87.24	82.33	77.68	72.21
0.0012	0.078	0.126	0.188	0.227	0.900	0.865	0.818	0.781	90.00	86.51	81.83	78.17
0.0016	0.070	0.109	0.148	0.215	0.910	0.8825	0.857	0.7936	91.04	88.25	85.71	79.36
0.0019	0.057	0.099	0.139	0.173	0.927	0.8937	0.865	0.8336	92.73	89.37	86.51	83.36

Fig. 2 Variation of inhibition efficiency on Aluminium corrosion with different concentration of N,N-MBA in 0.3M HCl at 303K, 308K, 313K and 318K for 1 hour.(a)

Fig.3. Variation of corrosion rate on Aluminium corrosion as a function of temperature for N,N MBA in 0.3M HCl at 303K, 308K, 313K and 318K for 1 hour.(b)



The corrosion rate (CR) obtained from weight loss method at different concentrations of N,N-MBA in 0.3M HCl at various temperatures are summarized in Table 1. The inhibition efficiency and the surface coverage θ values are calculated and given in Table1. The variation of inhibition efficiency with increase in inhibitor concentrations at various temperatures are shown in Fig 2. The variation of corrosion rate with increase in concentration of N,N-MBA at various temperatures are shown in Fig 3

The corrosion inhibition increases with increase in the inhibitor concentration and hence the corrosion rate decreases. This trend may result from the fact that adsorption and surface coverage increases with increase in the concentration of the inhibitor.

It is evident from fig 3 that CR increases with increase in the temperature . This indicates that the augmentation of temperature leads to the reduction of the inhibitor adsorption and acceleration of the dissolution process.

3.2 Adsorption isotherm

The surface coverage values (θ) calculated from weight loss measurements are fitted into the Langmuir adsorption isotherm. The Langmuir adsorption isotherm model has the form

$C/\theta = 1/K_{ads} + C$. Where C is the concentration, K_{ads} is the equilibrium constant of adsorption process. A plot of C/θ Vs C is linear and is shown in Fig 4. The regression coefficient and the slope of the lines are noted and tabulated in Table 2.

Fig. 4. Langmuir adsorption isotherm plot for corrosion of aluminium in 0.3 M HCl containing different concentration of N,N-MBA at 303K,308K,313K and 318K for 1 hour.

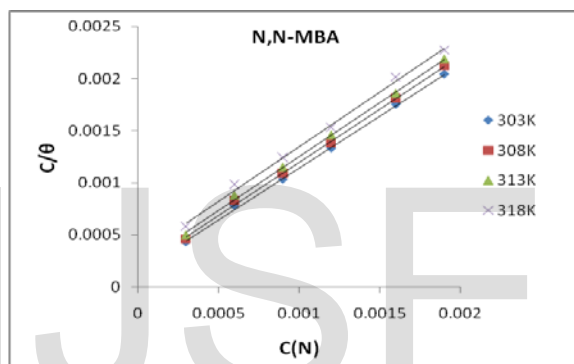


Table 2. Adsorption parameters calculated from Langmuir adsorption isotherm for N,N-MBA at 303K,308K,313K and 318K for 1 hour.

inhibitor	R^2	Slope	Intercept	$K_{ads} M^{-1}$	ΔG°_{ads} KJ mol ⁻¹	
N,N-MBA	303	0.998	0.996	0.00015	6667.66	-32.30
	308	0.998	1.020	0.00017	5882.35	-32.51
	313	0.998	1.034	0.00021	4761.98	-32.49
	318	0.997	1.047	0.00030	3334.3	-32.06

From the table. 2. it is found that the R^2 values for N,N-MBA are closer to unity. Also the slope values are closer to unity. The values show that it obeys Langmuir adsorption isotherm at all temperatures. This leads to the conclusion that every site holds only one inhibitor and there is no interaction between the molecules.

K_{ads} values are calculated from the equation

$$K_{ads} = \frac{1}{intercept} \dots\dots\dots(3)$$

The K_{ads} is related to the standard free energy of adsorption ΔG°_{ads} by the formula

$$K_{ads} = \frac{1}{55.55} \exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \text{-----(4)}$$

ΔG°_{ads} values are calculated using the above equation and tabulated in table 3.

The values of ΔG°_{ads} are negative and range from - 32.06 to -32.51 KJ mol⁻¹ for both N,N-MBA. The negative values indicate that the adsorption of the inhibitors on the aluminium surface is spontaneous. ΔG° values less than -40KJ/mol is indicative of physical adsorption and greater than -40kJ/mol is indicative of chemical adsorption. Here for N,N-MBA the ΔG° values lie between -20 KJ/mol to -40KJ/mol which shows that the mode of adsorption is mixed type. Hence it is suggested that chloride/iodide molecules are first adsorbed on the sites first making the surface negative and the protonated inhibitor are held on the surface by electrostatic interaction.

3.3. Electrochemical measurements

3.3.1. Tafel method

Figure 5 shows typical current-potential diagram of Al in 0.3M HCl in the absence and presence of N,N-MBA. Electrochemical parameters such as current density (i_{corr}), corrosion potential (E_{corr}), Tafel slopes and corrosion inhibition efficiency as function of inhibitor concentrations in 0.3M HCl are given in Table 3.

It is observed from the Tafel curve that there is a large reduction in the I_{corr} value which is a measure of the corrosion rate on the addition of inhibitor system. This confirms the results obtained by weight loss method. The E_{corr} value has shifted towards more negative value on the addition of inhibitor system and there is a large shift in the cathodic slope. This shows that the inhibitor is a cathodic inhibitor.

Fig. 5 Polarisation spectra of Aluminium immersed in 0.3M HCl (a) and in the presence of inhibitor N,N-MBA(b).

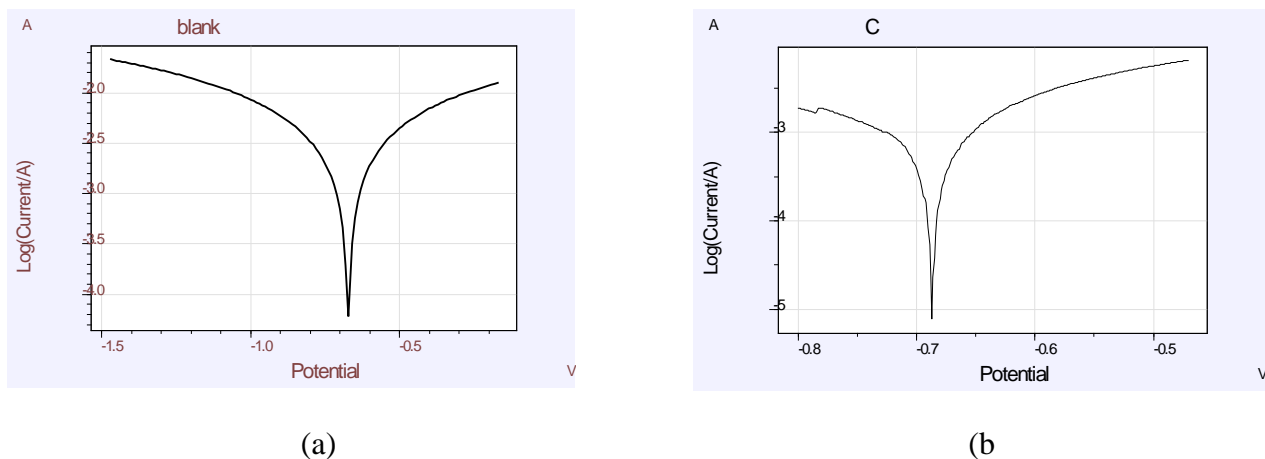


Table 3. Corrosion parameters of aluminium immersed in 0.3M HCl in the presence of inhibitor N,N-MBA.

system	Corrosion parameters						
	$E_{corr}(V)$	I_{corr} (A/cm ²)	R_p (ohm)	β_a (V/dec)	β_c (V/dec)	CR (mm/y)	IE %
Blank	- 0.6731	0.003218	36.52	0.604	0.950	35.1	-
Inhibitor N,N-MBA	-0.6868	0.0009135	39.77	0.256	0.191	9.926	71.61

3.3.2 Electrochemical Impedance spectroscopy

The impedance spectrum of aluminium in 0.3M HCl in the presence and absence of inhibitor system is shown in Fig 6. The results of impedance parameters (R_t and C_{dl}) for inhibitor are given in Table 4.

Fig. 6 Nyquist plot of Aluminium immersed in 0.3M HCl (a) and in the presence of inhibitor N,N-MBA(b)

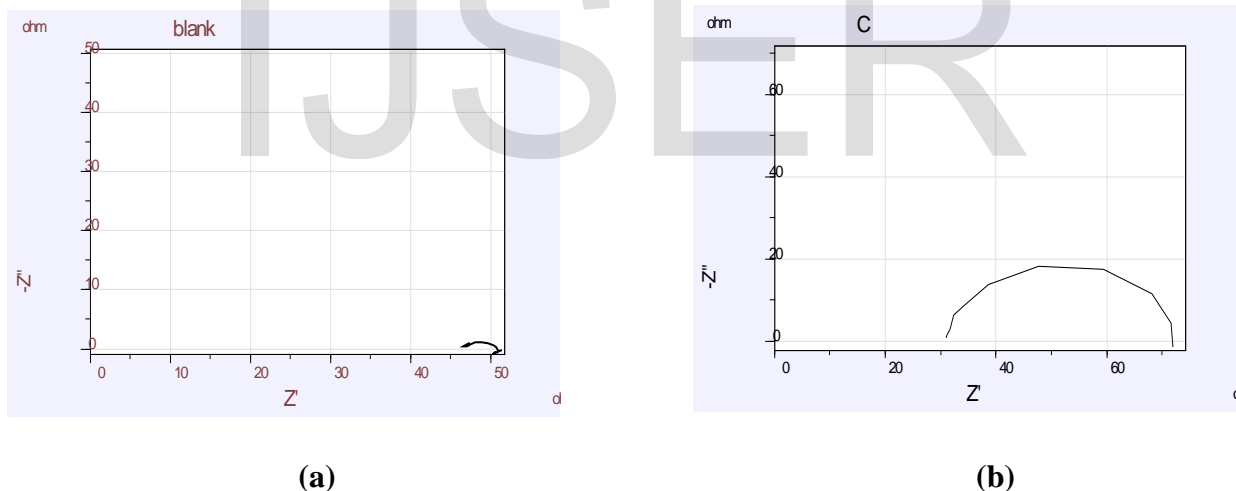


Table 4. The impedance parameters of Aluminium immersed in 0.30M HCl in the presence of inhibitor N,N-MBA.

system	Impedance parameters			
	$R_s(ohm)$	$R_{ct}(ohm)$	C_{dl} (F)	IE %
Blank	47.02	3.557	1.686	-
Inhibitor N,N-MBA	31.71	39-55	0.000039	91.0063

It is clear from the Fig (6) that the charge transfer resistance (R_t) value increase on the addition of inhibitor N,N-MBA but the value of double layer capacitance (C_{dl}) decreases due to decrease in local dielectric constant and increase in thickness of the electrical double layer, suggesting that the inhibitor molecules function by adsorption at the metal solution interface. Hence the inhibition efficiency has increased.

3.4 FT-IR analysis

FT-IR studies are performed to prove the adsorption of inhibitors on aluminium surface. Figure 7. show that FT-IR spectrum of pure sample of N,N-methylene bis acrylamide. The peaks observed at 3306, 1665, 2958, 1307, 1620 cm^{-1} is characteristic peaks corresponding to the stretching vibrations of the N-H, -C=O, C-H, C-N, C=C bonds of pure N,N-methylene bisacrylamide. Figure 8. show the spectrum of scrapped material of N,N-methylene bisacrylamide from the metal surface. The modified band at 3437, 1637 cm^{-1} is characteristic peaks corresponding to the stretching vibrations of N-H, -C=O. The presence of these bands indicates that the inhibitor is adsorbed on the surface of the metal. [12].

Fig 7. FT-IR spectrum of pure N,N-MBA\

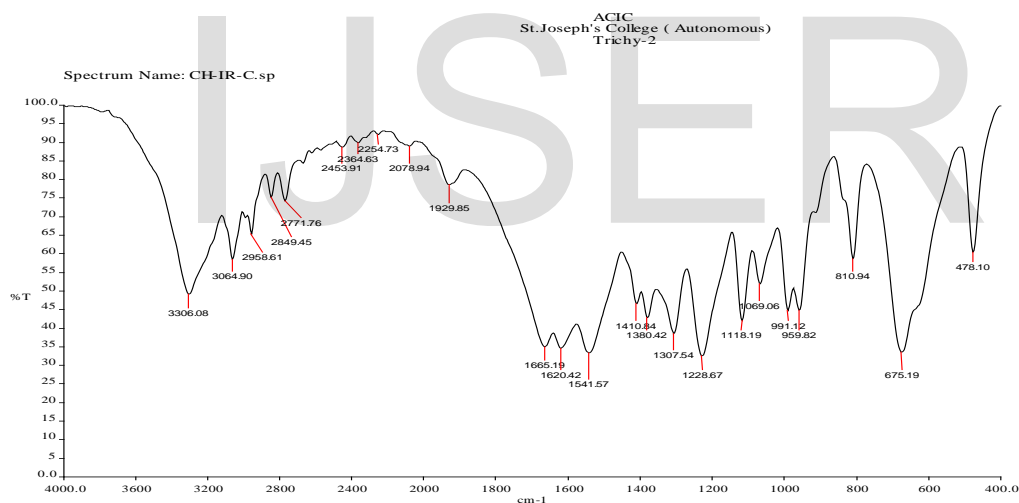
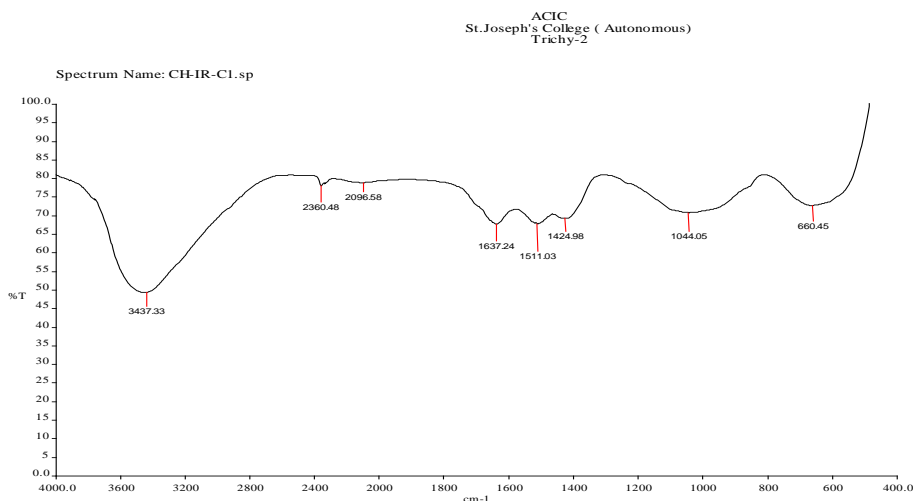


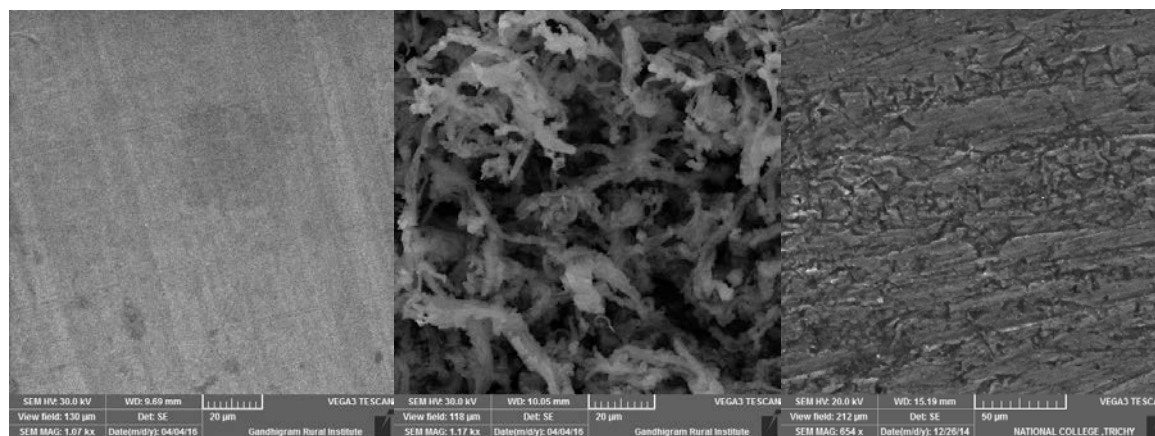
Fig. 8. FT-IR spectrum of film formed on Aluminium surface due to the presence of N,N-MBA



3.5 surface analysis

The metal pieces are immersed in 0.3M HCl with and without the inhibitor for one hour and SEM images of the polished surface without immersion and after immersion in 0.3M HCl with and without inhibitors are taken and shown in Fig 9(a-c).

Fig. 9. SEM images of aluminium (a) Polished aluminium (b) immersed in 0.3M HCl (c) immersed in 0.3M HCl + N,N-MBA.



a

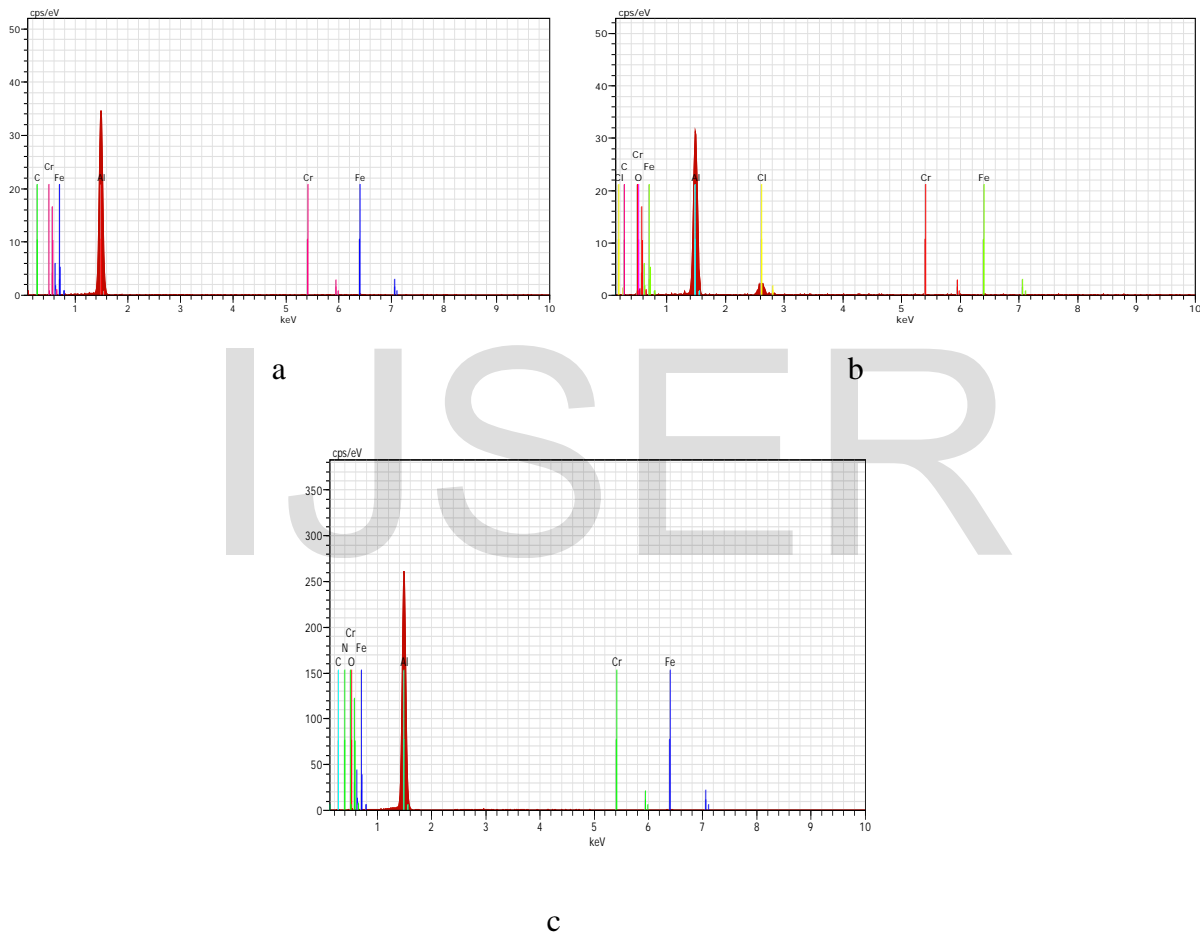
b

c

SEM micrographs and the corresponding EDX spectra of the surfaces of the samples are recorded in order to see the changes that occurred during the corrosion of aluminium in the presence and absence of the inhibitor system. Figure 9b shows that the aluminium immersed in 0.3 M HCl is highly

damaged; it can be concluded that the aluminium surface is highly corroded in aggressive acid media. This type of corrosion is typical in aggressive acid solutions. Figure 9c shows a smooth surface with deposited inhibitor on the surface of aluminium after the addition of inhibitor N,N-MBA to the 0.3M HCl solution. It is clearly seen from the SEM images that the irregularities in the surface due to corrosion are absent on the aluminium surface and the surface is almost free from corrosion in the presence of inhibitor.

Fig. 10. EDX images of aluminium (a) Polished aluminium (b) immersed in 0.3M HCl (c) immersed in 0.3M HCl +N,N-MBA.



The EDX data indicate the absence of chloride ion on the metal surface on the inhibited surface (Figure 10c). The presence of chloride ion in the blank and the absence of chloride ion in the presence of inhibitor, the presence of nitrogen carbon and oxygen on the surface when inhibitor is added clearly proves that inhibition is due to adsorption of N,N-MBA. From these results, it can be clearly concluded that N,N-MBA forms a uniform adsorbed layer on the surface and retards the corrosion.

4. CONCLUSION

From the overall experimental results the following conclusions can be deduced. Corrosion inhibition in the presence of N,N-Methylene bisacralamide in 0.3M HCl is studied using the weight loss method at 303, 308, 313 and 318K. The results obtained reveal that the inhibition efficiency increases with increase in the inhibitor concentration, at the same time inhibition efficiency decreases with increase in the temperature. The FT-IR Analysis confirms that the N,N-Methylene bisacralamide forms a layer on the Aluminium surface and prevents corrosion. The Langmuir adsorption isotherm is obeyed. The corrosion inhibition and the formation of adsorbed layer are confirmed by Tafel polarization, Impedance spectroscopy, SEM and EDX analysis.

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