

Effect of Anions on the Corrosion Inhibition of Aluminum in HCl using Ethyl Trimethyl Ammonium Bromide as Cationic Inhibitor

G.Y. Elewady*, I.A. El-Said and A.S. Fouada

Chemistry Department, Faculty of Science, El-Mansoura University, El-Mansoura-35516, Egypt

*E-mail: ghadaelewady@yahoo.com

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The corrosion inhibition of aluminum in hydrochloric acid solution in the presence of ethyl trimethyl ammonium bromide (ETMAB) at temperature range of 30-50°C was studied using the weight loss and polarization techniques. The effect of addition of anions (I⁻, SCN⁻, Br⁻) is also reported. The inhibition efficiency (%IE) increased with increase in concentration of ETMAB. The addition of the anions increased the inhibition efficiency to a considerable extent. The inhibitive action of ETMAB was discussed on the bases of its adsorption on the metal surface, which follow Freundlich adsorption isotherm. The synergistic effect of ETMAB and anions was discussed. Galvanostatic polarization curves indicated that the inhibitor behaves as mixed-type inhibitor.

Keywords: Corrosion inhibition, anions, HCl, synergism, ethyl trimethyl ammonium bromide

1. INTRODUCTION

Aluminum is an important subject of research because it is very abundant and easy to handle. In addition, aluminum is justified by low price, high electrical capacity and high energy density (1). Aluminum is extensively used in various industrial operations and the study of its corrosion inhibition in pickling baths is of great important. The corrosion behavior of aluminum has been studied in acid media. On addition of halide salt to sulphuric acid solution containing organic inhibitor, co-operative effect results which inhibits iron corrosion (2,3). Halides have been reported to inhibit the corrosion of some metals in strong acids and this effect depends on the ionic size and charge, the electrostatic field set up by the negative charge of the anion on adsorption sites and the nature and concentration of halide ions (2,4-6). Several authors (7-9) have reported that organic inhibitors in acid electrolyte become protonated, changing into cations which have only a slight effect as corrosion inhibitors. In acid solutions, if iodide, bromide or chloride ions are added to the electrolyte along with organic

compounds, this might greatly enhance the inhibition action due to the synergistic effect (10-13). There are different theories concerning the nature of the anion organic inhibitor film (14).

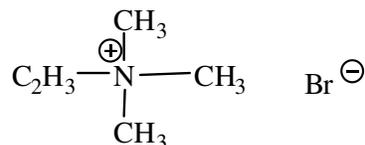
The objective of the present study is to investigate the corrosion inhibition of aluminum in 1M hydrochloric acid medium using the cationic inhibitor ethyl trimethyl ammonium bromide (ETMAB) in absence and in the presence of the anions I^- , SCN^- and Br^- and to propose a suitable mechanism for the inhibition.

2. EXPERIMENTAL PART

Aluminum test pieces of 99.53% purity were used. Al sheets with dimension 2.0 x 2.0 x 0.2 cm³ were used for weight loss measurements. For anodic and cathodic Tafel polarization measurements, a cylindrical rod embedded in araldite with exposed surface area of 1.0 cm² was employed. Prior to each experiment the surface of aluminum was mechanically polished with different grades of emery paper in order to obtain a smooth surface followed by ultrasonically degreasing with alkaline mixture (15), then rinsed with bidistilled water and finally dried. For weight loss measurements the cleaned Al sheets was weighed before and after immersion in 100 ml of the test solution for the required time. The temperature was adjusted to 30±0.1°C.

Polarization curves were carried out galvanostatically using Amel Galvanostate model-549. Three compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used, the third is the working electrode.

The measurements were performed in 1M HCl without and with the investigated inhibitor and the used anions. The name and the molecular structure of the cationic inhibitor is



Ethyl trimethyl ammonium bromide (ETMAB)

Inhibitive efficiencies (%IE) and the surface coverage (θ) were calculated from weight loss measurements using the following equations

$$\%IE = \left(\frac{W_{\text{free}} - W_{\text{inh}}}{W_{\text{free}}} \right) \times 100 \quad (1)$$

$$\theta = 1 - \frac{W_{\text{inh}}}{W_{\text{free}}} \quad (2)$$

where W_{free} and W_{inh} are the loss in weight of specimens in absence and in the presence of inhibitor.

For galvanostatic polarization %IE and θ were calculated employing the formulae.

$$\%IE = \left(\frac{i_{free} - i_{inh}}{i_{free}} \right) \times 100 \quad (3)$$

$$\theta = 1 - \frac{i_{inh}}{i_{free}} \quad (4)$$

where i_{free} and i_{inh} are the corrosion current densities in absence and in the presence of inhibitor, respectively.

All chemicals and reagents were of analytical grade.

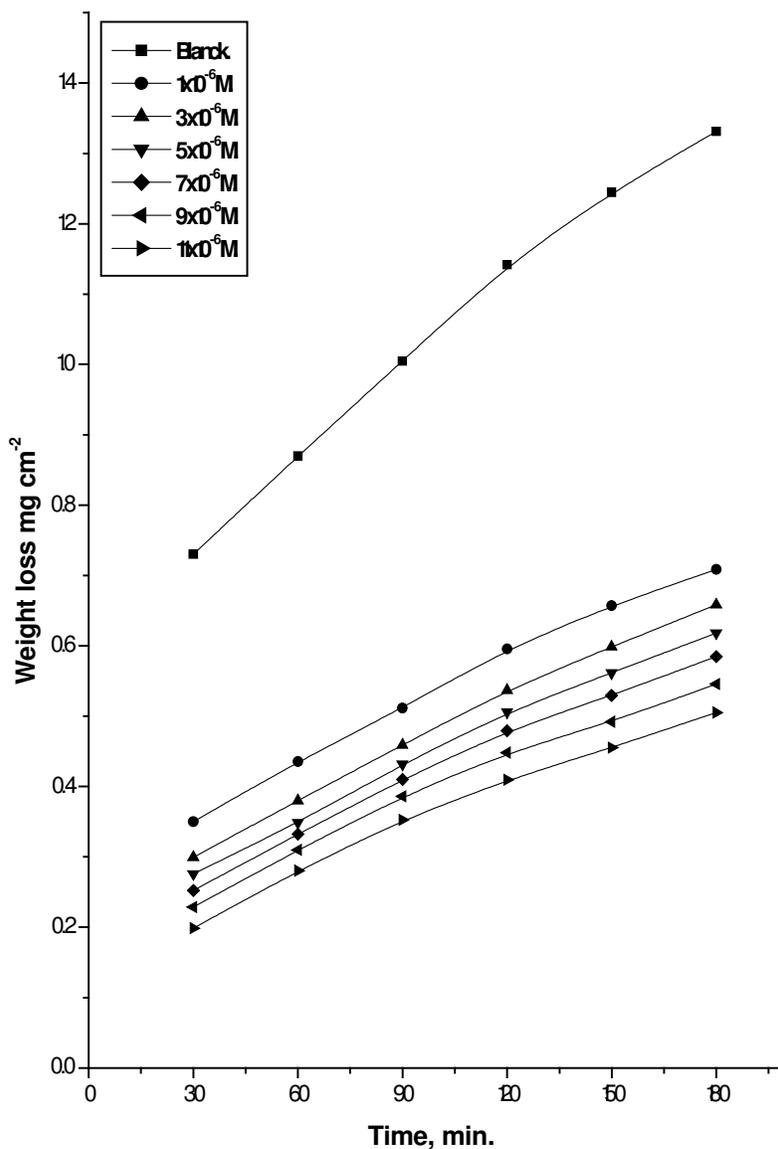


Figure 1. Weight loss-time curves for the corrosion of Al in 1M HCl in absence and in the presence of different concentrations of ETMAB at 30°C.

3. RESULTS AND DISCUSSION

3.1. Inhibition of Al corrosion

Figure (1) represents the data of weight loss time curves for Al corrosion in 1M HCl in absence and in the presence of different concentrations of the used inhibitor (ETMAB) at 30°C. As shown from this Figure, by increasing the concentration of this compound the weight loss of Al samples are decreased. This means that the presence of this organic compound retards the corrosion of Al in 1M HCl or in other words, this compound act as inhibitor. The linear variation of the weight loss with time in uninhibited and inhibited 1M HCl indicates the absence of insoluble surface films during corrosion. In absence of any surface films, the inhibitor is first adsorbed, onto the metal surface and thereafter impeded corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes. The %IE was calculated and represented in Table (1). In- spection of the data in Table (1) reveals that ETMAB acts as inhibitor for corrosion of Al in hydrochloric acid solution. A parameter (θ), which represents the part of the metal surface covered by the inhibitor molecules was calculated for different inhibitor concentrations and listed in Table (1). From the data of Table (1) reveals that θ increases as the inhibitor concentration (C) is increased.

Table 1. Effect of ETMAB concentration on the %IE and θ for Al corrosion in 1M HCl as obtained from weight loss measurements (immersion time, 2h) at 30°C.

Concentration M	%IE	θ
1.0×10^{-6}	52.50	0.53
3.0×10^{-6}	59.80	0.60
5.0×10^{-6}	61.50	0.62
7.0×10^{-6}	62.50	0.63
9×10^{-6}	63.90	0.64
1.1×10^{-5}	68.90	0.69

3.2. Effect of anions and synergistic consideration on the corrosion and corrosion inhibition

Figure (2) shows the weight loss-time curves for the dissolution of Al in 1M HCl in absence and in the presence of different concentrations of the used inhibitor in presence of 10^{-2} M Γ ions. The same behavior was exhibited by other anions SCN^- and Br^-

The values of the inhibition efficiency (%IE) for various concentrations of inhibitor in the presence of specific concentration of these anions are given in Table (2). It is observed that the %IE of the inhibitor increases on addition of these different anions. The strong chemisorptions of these anions on the metal surface are responsible for the synergistic effect (16).

The synergistic inhibition effect was evaluated using a parameters S_θ obtained from the surface coverage values (θ) of the anion, cation and both. Aramaki and Hackerman (17) calculated the synergism parameter S_θ using the following equation as

$$S_{\theta} = 1 - \theta_{1+2} / 1 - \theta_{1+2}^{-} \quad (5)$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$, θ_1 is the surface coverage by anion, θ_2 is the surface coverage by cation and θ_{1+2}^{-} is the measured surface coverage by both the anion and cation.

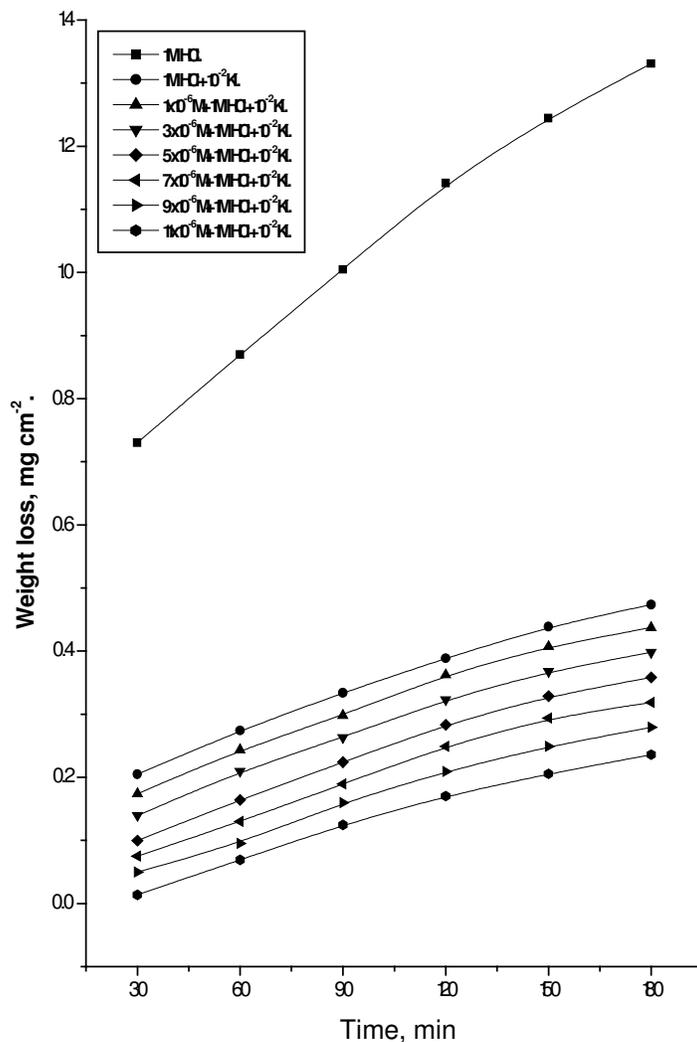


Figure 2. Weight loss - time curves for Al dissolution in 1M HCl in absence and in the presence of different concentration of ETMAB without and with addition of 1.0×10^{-2} M KI at 30°C.

The calculated values of S_{θ} are presented in Table (3). As can be seen from this Table, values of S_{θ} nearly equal to unity, which suggests that the enhanced inhibition efficiencies caused by the addition of the used anions to the cationic inhibitor (ETMA⁺) is only due to the synergistic effect. This can be explained on the basis that halides and SCN⁻ ions have a great tendency to be adsorbed on the surface and this may be responsible for the synergistic effect of anion +ETMAB. It may therefore also be concluded that anions are initially chemisorbed on the metal surface, ETMA⁺ cation is then

adsorbed by coulombic attraction on the metal surface, where the anions is already chemisorbed and thus suppresses the self corrosion rate by the increase in surface coverage.

Table 2. Effect of 1.0×10^{-2} M anion on %IE and θ for Al corrosion in 1M HCl and in presence of different concentrations of ETMAB as obtained from weight loss method (immersion time, 2h) at 30°C.

Concentration M	I ⁻		SCN ⁻		Br ⁻	
	%IE	θ	%IE	θ	%IE	θ
1.0×10^{-6}	77.0	0.77	59.8	0.60	58.8	0.59
3.0×10^{-6}	78.7	0.79	60.6	0.61	60.1	0.60
5.0×10^{-6}	81.0	0.81	71.1	0.71	68.2	0.68
7.0×10^{-6}	82.1	0.82	72.1	0.72	69.0	0.69
9.0×10^{-6}	83.2	0.83	73.2	0.73	70.6	0.71
1.1×10^{-5}	85.0	0.85	75.0	0.75	73.1	0.73

Table 3. Synergism parameter (S_{θ}) for different concentrations of the cationic compound with addition of 1.0×10^{-2} M anion for corrosion of Al in 1M HCl after 2h immersion at 30°C.

Concentration M	Synergism parameter S_{θ}		
	I ⁻	SCN ⁻	Br ⁻
1.0×10^{-6}	0.91	0.90	0.90
3.0×10^{-6}	0.94	0.93	0.91
5.0×10^{-6}	0.97	0.93	0.93
7.0×10^{-6}	0.99	0.96	0.93
9.0×10^{-6}	1.01	0.99	0.95
1.1×10^{-5}	1.02	1.00	0.96

Further more the organic cation it self ETMA⁺ is weakly adsorbed on aluminum, since the metal surface is positively charged in hydrochloric acid solution (18,19). However, when the anions (I⁻, SCN⁻, Br⁻) are adsorbed onto the surface, they decrease the positive charge of Al, due to the formation of Al-anion surface bond, which produce a negative pole, facilitating the adsorption of the organic cation (ETMA⁺). Therefore, the inhibitor film is assumed to be Al-anion-ETMA complex, which has a greater inhibiting effect so it has a protective and compact nature.

The inhibition efficiency caused by addition of anions to ETMAB in the order I⁻ > SCN⁻ < Br⁻. This observation is in good agreement with the adsorption ability on the aluminum surfaces was in the order I⁻ > SCN⁻ > Br⁻ (20).

3.3. Adsorption consideration

The adsorption of an organic inhibitor on the surface of a corroding aluminum specimen may be regarded as a substitution process between the organic compound in the aqueous phase and water

molecules adsorbed on the metal surface. Indeed, the adsorption of ETMAB was found to follow the substitutional isotherm of Freundlich, given by

$$\log \theta = \log K + n \log C \quad 1 < n > 1 \quad (6)$$

where θ is the degree of surface coverage, C the inhibitor concentration, n the number of water molecules replaced by one inhibitor molecule and K is the equilibrium constant for the adsorption process.

The plot of $\log \theta$ versus $\log C$ for Freundlich isotherm gave a straight line for Al in 1M HCl in the presence of ETMAB as shown in Figure (3). The intercept of the straight line is $\log K$ and its slope is n indicating that Freundlich adsorption isotherm is valid for this inhibition. The calculated value of K amounts to 52.0×10^{-2} .

The free energy of adsorption, ΔG_{ads} , is associated with water adsorption equilibrium. ΔG_{ads} was calculated from the relation

$$K = \frac{1}{55.5} \exp^{(-\Delta G_{\text{ads}}/RT)} \quad (7)$$

The obtained value of ΔG_{ads} is $-3.74 \text{ KJ.mol}^{-1}$. The negative value of ΔG_{ads} , here indicate that the adsorption process on Al surface is spontaneous.

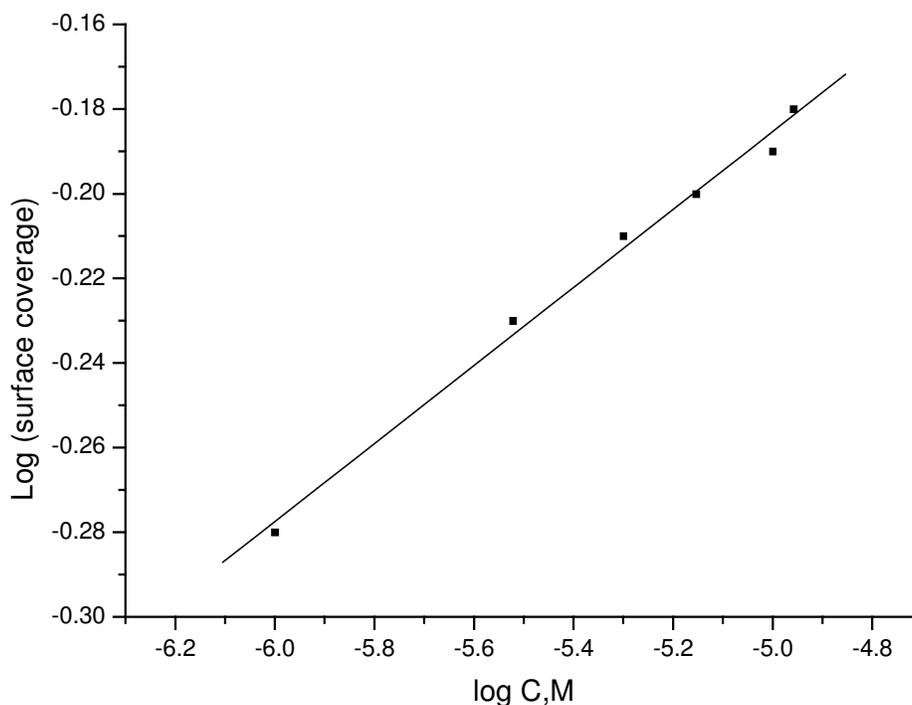


Figure 3. Curve fitting of corrosion data for Al in 1M HCl in presence of different concentration of ETMAB to Freundlich adsorption isotherm at 30 °C

3.4. Effect of temperature

The influence of temperature on the corrosion rate of aluminum in 1M HCl is absence and in the presence of different concentration of the used cationic inhibitor was investigated by weight loss technique in the temperature range (30 to 50°C). From the calculated values of %IE at 35, 40, 45 and 50°C (Table 4). It is obvious that the inhibition efficiency increases with increasing the concentration of the compound and decreases by increasing the temperature. The decrease in %IE is due to the desorption of the molecules from the surface of the aluminum by increasing the temperature. This indicates that the inhibitor is physically adsorbed on Al surface. This suggests that the adsorbed molecules mechanically screen the coated part of the metal surface from the action of the corrodent.

Table 4. Inhibition efficiency %IE of Al corrosion in 1M HCl at different temperature in the presence of different concentration of the inhibitor after 2h immersion.

Conc. M Temp.	%IE			
	35°C	40°C	45°C	50°C
1.0 x 10 ⁻⁶	10.9	10.4	9.2	9.0
3.0 x 10 ⁻⁶	18.6	18.0	12.5	11.0
5.0 x 10 ⁻⁶	23.9	23.4	21.9	21.1
7.0 x 10 ⁻⁶	27.1	26.6	24.5	23.9
9.0 x 10 ⁻⁶	36.2	29.2	27.4	26.2
1.1 x 10 ⁻⁵	41.3	30.3	29.3	27.3

Plots of logarithm of corrosion rate ($\log k$), with the reciprocal of absolute temperature $\left(\frac{1}{T}\right)$ for aluminum in 1M HCl in absence and in the presence of 7.0x10⁻⁶M ETMAB and after 120 min. immersion is shown in Figure 4. As shown from this Figure, straight line with slope of $-E_a^*/2.303 R$ and intercept of A was obtained according to Arrhenius-type equation

$$k = A \exp^{-\left(E_a^*/RT\right)} \quad (8)$$

where k is the corrosion rate ($\text{mg cm}^{-2} \text{ min}^{-1}$), A is a constant depends on the metal type and electrolyte, E_a^* is the apparent activation energy, R is the universal gas constant and T is the absolute temperature.

Plots of $\log(\text{corrosion rate}/T)$ vs. $\frac{1}{T}$ (Figure 5) give a straight line with slope of $(-\Delta H^*/2.303 R)$ and intercept of $[\log(R/Nh + \Delta S^*/2.303 R)]$ was obtained according to the transition state equation

$$\text{Rate of corrosion} = RT/Nh \exp^{(\Delta S^*/R)} \exp^{-(\Delta H^*/RT)} \quad (9)$$

where h is the Planck's constant, N is Avogadro's number, ΔH^* is the activation enthalpy and ΔS^* is the activation entropy. The calculated values of the apparent activation energy, E_a^* , activation

enthalpy, ΔH^* , and activation entropy ΔS^* in absence and in the presence of 7.0×10^{-6} ETMAB are given in Table (5). The increase in activation energy indicates that the adsorption of the inhibitor molecules on Al surface form an energy barrier. The increase in the activation enthalpy ΔH^* in the presence of the inhibitor in the acid solution increases the height of the energy barrier of the corrosion reaction, the activation entropy ΔS^* in the absence and in the presence of the inhibitor is large and negative indicating that the activated complex is the rate determining step and represents association rather than dissociation (21,22).

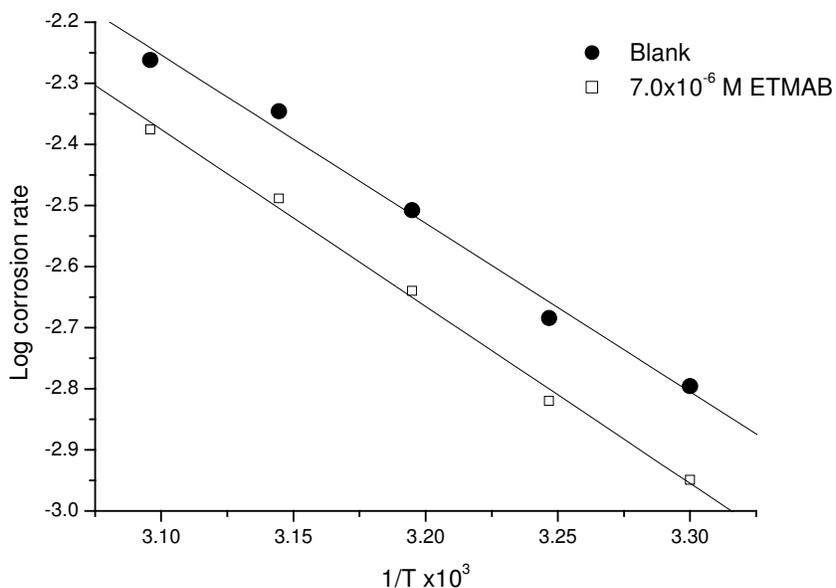


Figure 4. log corrosion rate – 1/T for the corrosion of Al in 1 M HCl in absence and in the presence of 7.0×10^{-6} M ETMAB

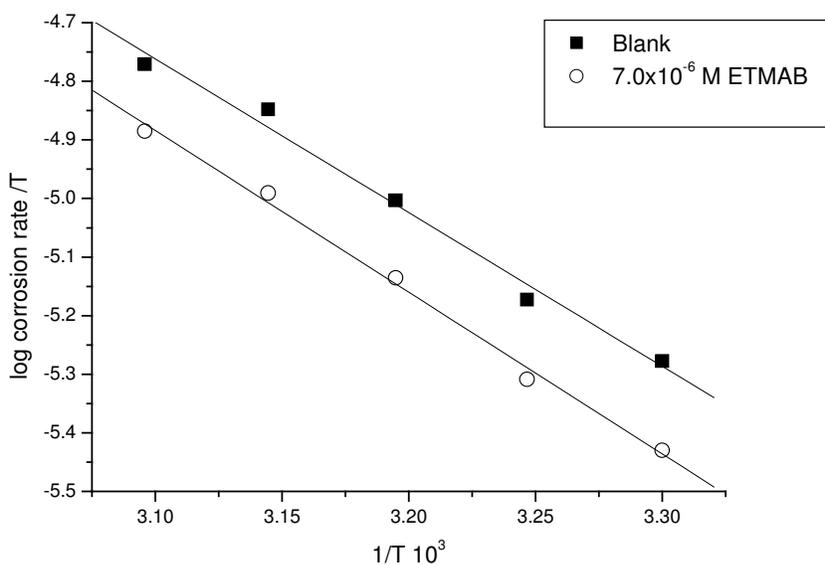


Figure 5. log corrosion rate/T - 1/T for the corrosion of Al in 1 M HCl in absence and in the presence of 7.0×10^{-6} M ETMAB

Table 5. Activation parameters of aluminum corrosion in 1M HCl in absence and in the presence of 7.0×10^{-6} M ETMAB.

Concentration	Activation		
	E_a^* , KJ mol ⁻¹	ΔH^* , KJ mol ⁻¹	$-\Delta S^*$, J mol ⁻¹ K ⁻¹
0.0	58.48	56.20	163.20
7.0×10^{-6} M	62.60	58.70	159.50

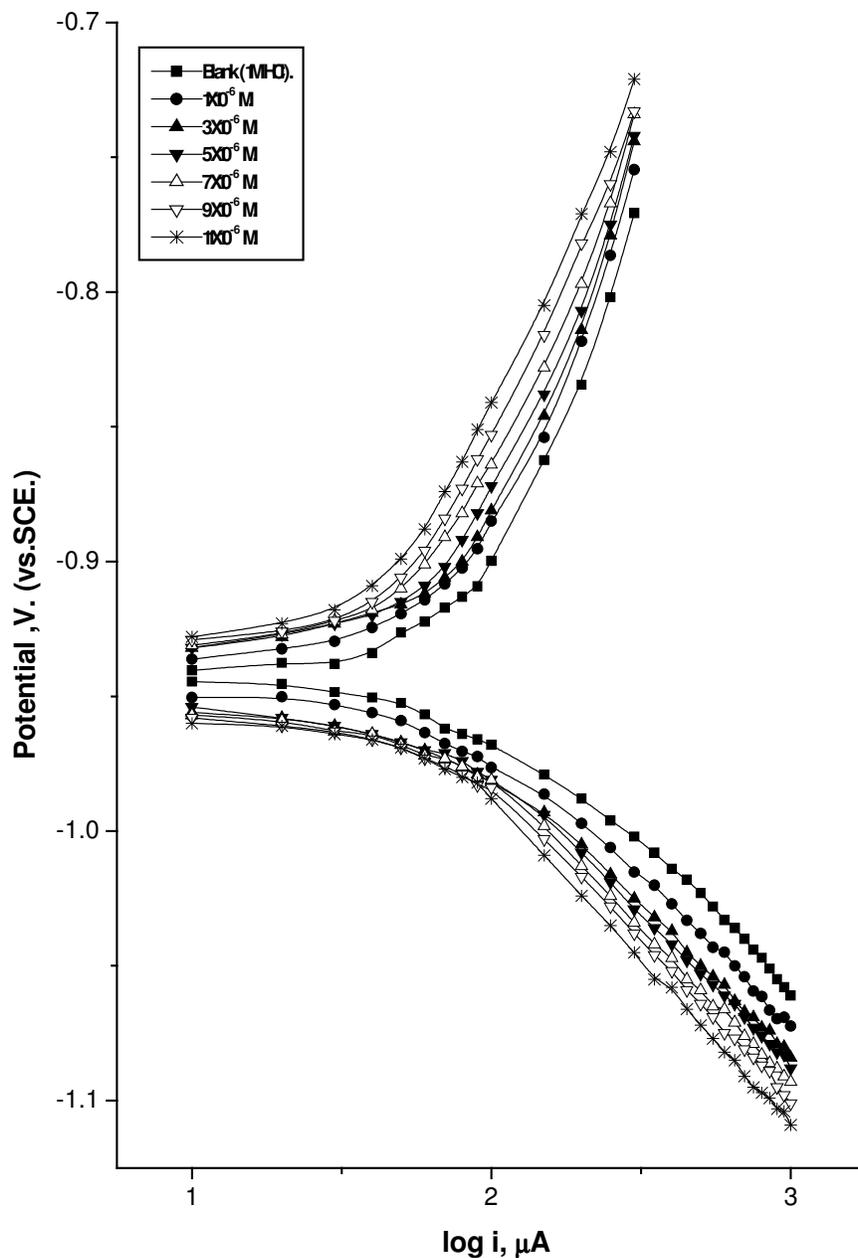


Figure 6. Polarization curves for Al dissolution in 1M HCl in the presence of different concentrations of ETMAB at 30 °C.

3.5. Polarization measurements

Figure (6) shows the galvanostatic polarization curves for aluminum in 1M HCl solution at 30°C in the absence and presence of different concentrations of ETMAB. The numerical values of the variation of corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel slopes (β_a and β_c), degree of surface coverage (θ), and inhibition efficiency (%IE) with the concentration of the inhibitor are given in Table (6). This indicates that:

1. The cathodic and anodic curves obtained exhibit Tafel-type behavior. Addition of ETMAB increases both cathodic and anodic over potentials and caused mainly parallel displacement to the more negative and positive values, respectively.

2. The corrosion current density (i_{corr}) decreases with increasing the concentration of the additive, which indicates that the presence of this inhibitor retards the dissolution of Al in 1M HCl and the degree of inhibition depends on the concentration of the inhibitor.

3. The data suggest that this compound act as mixed type inhibitor because it enhances both the anodic and cathodic processes but the anode is more polarized.

4. The values of corrosion potential (E_{corr}) shifted to less negative values by increasing the concentration of the inhibitor.

5. The values of %IE and the degree of surface coverage θ obtained from polarization measurements are in good agreement with those obtained from weight loss technique.

Table 6. Effect of ETMAB concentration on the corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), inhibition efficiency (%IE), and degree of surface coverage (θ) for the corrosion of aluminum in 1M HCl at 30°C.

Concentration M	$-E_{\text{corr}}$ mV	i_{corr} $\mu\text{A cm}^{-2}$	β_a mV dec ⁻¹	β_c mV dec ⁻¹	%IE	θ
0.0	942	62.0	217	89	-	-
1.0×10^{-6}	941	52.9	202	10.7	52.90	0.53
3.0×10^{-6}	940	51.6	204	109	60.50	0.61
5.0×10^{-6}	939	47.0	205	111	61.8	0.62
7.0×10^{-6}	938	43.5	206	113	62.7	0.63
9.0×10^{-6}	937	39.8	209	115	64.5	0.65
1.1×10^{-5}	936	36.4	211	117	68.4	0.68

4. CONCLUSIONS

1. ETMAB inhibits aluminum corrosion in hydrochloric acid solution.
2. The inhibitor molecules are physically adsorbed on Al surface following freundlich adsorption isotherm.
3. Synergistic affects increased the inhibition efficiency of ETMAB in the presence of Γ^- , SCN^- and Br^- anions.
4. Polarization measurements suggest that ETMAB act as mixed type Inhibitor.
5. In the presence of anions, the protective film is assumed to be Al- anion -ETMA complex.

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