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Inhibition of Aluminum Corrosion in Hydrochloric Acid Using Hexadecyltrimethyl Ammonium Bromide (Ctabr)

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ABSTRACT

The corrosion inhibition of aluminum in (1M) hydrochloric acid solution in the presence of Hexadecyltrimethyl ammonium bromide (CTABr) at temperature range of 30^o – 50 $C^o$was studied using galvanostatic polarization techniques. The results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. The inhibition efficiency (%IE)was found to increase with increasing inhibitor concentration ($2*10^{-6}$ M – $12*10^{-6}$ M) and decreased with increasing temperature. The behavior of these compounds on the metal surface was found to obey Temkin adsorption isotherm. Thermodynamic parameters for adsorption and activation processes were determined. Galvanostatic polarization data indicated that these compounds act as mixed- type inhibitors. Phenomenon of physical adsorption is deduced from the obtained values of Ea^*andΔG_{ads}.

Keywords: Hcl , Al , CTABr , Inhibition

تثبيـط تأكل الالمنيوم في حامض الهيدوركلوريك باستخدام المثبط هيكساديل تراي مثيل امونيوم برومايد (CTABr)

الخلاصة

تمت دراسة تثبيط تاكل الالمنيوم في محلول (1 مولاري) من حامض الهيدروليك بوجود المثبط (CTABr) في نطاق درجات الحرارة (من 30 الى 50 درجة سيليزية) باستخدام تقنيات الاستقطاب. اظهرت النتائج ان التثبيط يحدث عن طريق امتزاز جزيئات المثبط على السطح المعدني. وجد ان كفاءة التثبيط تزداد مع الزيادة في تركيز المثبط المستخدم ($2*10^{-6}$ مولاري - $12*10^{-6}$ مولاري) وتتناقص مع زيادة درجات الحرارة. وجد ان سلوك هذه المواد ينطبق مع موديل
(Isotherm) الخاص بالعالم (Temkin). تم حساب المعامل الثرموديناميكية للامتزاز و التنشيط حيث اشارت البيانات المأخوذة من جهاز الاستقطاب (الكلفانوستات) ان هذه المكونات تؤثر كمثبطات مزدوجة و ان القيم المستخلصة لطاقة التنشيط Ea^* و الطاقة الحرة ΔG_{ads} يثبت بان الامتزاز الذي يحدث هو امتزاز فيزيائي .

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INTRODUCTION

Aluminum and its alloys have a remarkable economic and attractive materials for engineering applications owing to its low cost, light weight high thermal conductivity[1]. The interest of the materials arises from their importance in recent civilization. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface form a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition the mode of adsorption, the chemical structure of the inhibitor and the type of corrosion media. To prevent the attack of acid, it is used to add a corrosion inhibitor to decrease the rate of Al dissolution in the solutions. Thus, many studies concerning the inhibition of Al corrosion using organic substances are conducted in acidic and basic solutions[2]. The present study aims to investigate theinhibition efficiencyof Hexadecyltrimethyl ammonium bromide CTABr for Al in HCL.It is also aimed to investigate the effects of the concentration and temperature on the inhibition efficiency of the studied inhibitor.

EXPERIMENTAL WORK

The experiments were performed on Aluminum of 99.2 % purity. The aluminum metal has the chemical composition given in Table (1).

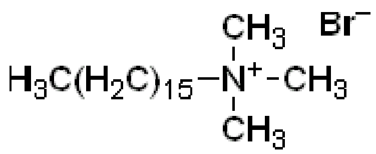
Table(1) The chemical composition of Aluminum (weight%)[3].

Aluminum Al 1100				
Fe	Cu	Mn	Zn	Al
0.45	0.05-0.20	0.05	0.10	99.2

The measurements were performed in 1M HCl without and with inhibitor (CTABr)in the concentration values of $2*10^{-6}$, $4*10^{-6}$, $8*10^{-6}$, $12*10^{-6}$ M.

Aluminum sheets with surface area 1.0 cm^2 were used for galvanostatic polarization experiments. For anodic and cathodicTafel polarization measurements. Prior to each experiment, the surface of Al was mechanically polished with different grades of emery paper in order to obtain a smooth surface followed by ultrasonically degreasing with ethanol, then rinsed with distilled water and finally dried. The temperature was controlled at 30±0.1 ^{O}C. Polarization curves were obtainedgalvanostatically using (parstat2273)galvanostate.

Three compartment cell with a saturated calomel reference electrode (SCE), working electrode and copper as coupled electrode was used. The molecular structure of inhibitor is:



Hexadecyltrimethyl ammonium bromide (4)

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The inhibition efficiency was calculated from galvanostatic polarization techniques by the following relation(5,6):

$$\%IE = \left(\frac{Ifree - I\,inh}{Ifree}\right) * 100 \text{-} \ldots\ldots\ldots\ldots(1)$$

$$\theta = \left(\frac{Ifree - I\,inh}{Ifree}\right) \text{-} \qquad \ldots\ldots\ldots\ldots(2)$$

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

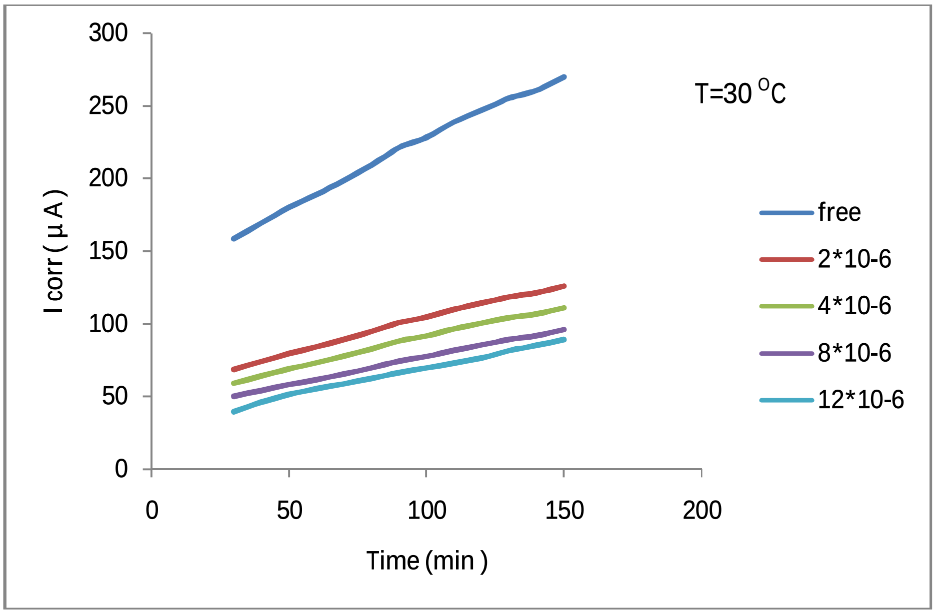

Figure (1)Current DensityVersusTime Curve for Al Corrosion in 1M Hcl with different Concentration of the Inhibitor CTABr.

RESULTS AND DISCUSSION

Figure (1) shows the data of corrosion current density – time curves for Al corrosion in 1M HCl in absence and in the presence of inhibitor. It is clear that by increasing the concentration of this compound the corrosion current density of Al samples are decreased. This means that the presence of this organic compound retards the corrosion. In absence of any surface films, the inhibitor is first adsorbed , into the

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metal surface and there after impede corrosion either by merely blocking the reaction sites (anodic and cathodic)or by altering the mechanism of the anodic and cathodic partial processes(5). The %IE was calculated and represented in Table (2). Table (2) reveals that CTABr 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 (2). From the data of Table (2) reveals that θ increases as the inhibitor concentration (C) increases(7).

Table (2)Effect of CTABr concentration on the %IE and θ for Al corrosion in 1M HCl at 30 C^{o}.

Inhibitor Conc. (M)	T= 30 ^{o}C.	
	%IE	θ
$2*10^{-6}$	54.64	0.5464
$4*10^{-6}$	60.31	0.6031
$8*10^{-6}$	66.32	0.6632
$12*10^{-6}$	70.03	0.7003

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 CTABr was found to follow the substitutional isotherm of Timken given by(7,8):

$$\exp (-2a\theta) = KC \qquad \text{......(3)}$$

Where \`a\` is molecules interaction parameter , \`θ\` is the degree of surface coverage, \`K\` is the equilibrium constant of adsorption process and \`C\` is the concentration of the inhibitor. The free energy of adsorption is related to the equilibrium constant of adsorption , K by the following equation:

$$K = \frac{1}{55.5} * (\frac{-\Delta G_{ads}}{RT}) \qquad \text{...... (4)}$$

The plot of θ versus logC for Timken isotherm gives a straight line for Al in 1M HCl in the presence of CTABr as shown in Figure (2).

The free energy of adsorption ΔG_{ads}, is associated with water adsorption equilibrium. ΔG_{ads} was calculated from above relation. The obtained value of ΔG_{ads} at 30C^{o} is -11.615 KJ.mol^{-1}. The negative value of ΔG_{ads} here indicates that the adsorption process on Al surface is spontaneous.

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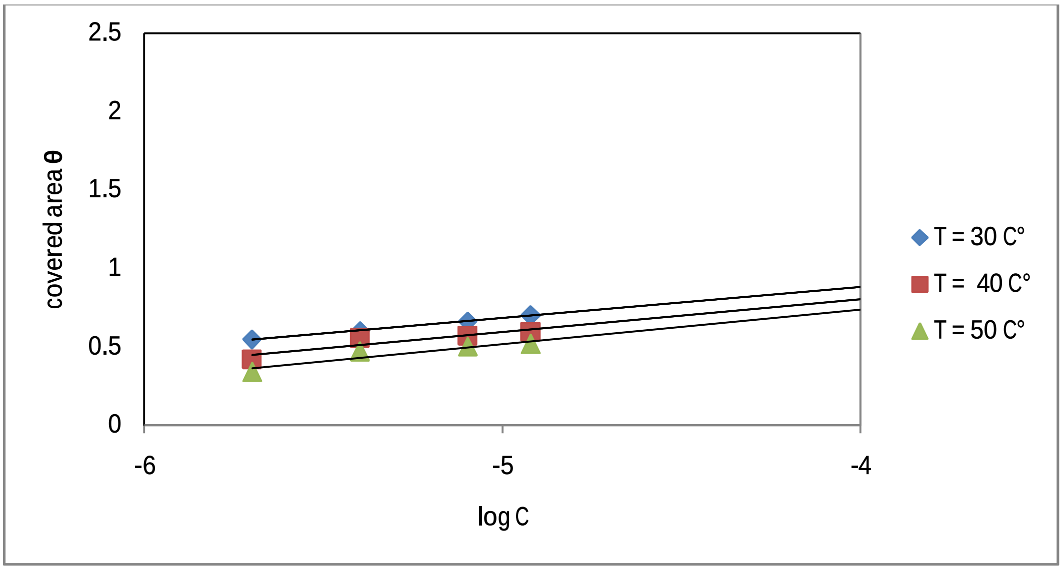

Figure (2)The Relationship Between Covered Area and CTABr Inhibitor Concentration at Different Temperatures.

The influence of temperature on the corrosion rate of Al in 1M HCl in absence and in the presence of different concentration of the used inhibitor was investigated for temperature range30 to 50C°. From the calculated values of %IE at 30, 40 and 50 C° shown in Table (3). It is obvious that the inhibition efficiency increases by increasing the concentration of inhibitor and decreases by increasing the temperature. The decrease in %IE is due to the desorption of the molecules from the surface of the Al 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(8).

Table (3)Effect of CTABr concentration on the %IE and θ for Al corrosion in 1M Hcl at 30, 40 and 50 °C.

Inhibitor Conc. (M)	T = 30 °C		T = 40°C		T = 50°C	
	%IE	θ	%IE	θ	%IE	θ
$2*10^{-6}$	54.64	0.5464	42.01	0.4201	34.01	0.3401
$4*10^{-6}$	60.31	0.6031	55.42	0.5542	47.11	0.4711
$8*10^{-6}$	66.32	0.6632	57.09	0.5709	50.27	0.5027
$12*10^{-6}$	70.03	0.7003	59.37	0.5937	51.74	0.5174

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The value of ΔG(kJ/mole) change with the range of temperature, these values are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption) these values are negative in all cases and lie in the range of -11.297 to -12.380 (kJ/mole)as shown in Table (4).

Table (4)Isotherm parameters.

Temp. C^o	Isotherm parameter	
	ΔG kJ/mole	K_{ads}
30	11.297	1.811
40	11.992	1.807
50	12.380	1.810

The apparent activation energy (Ea^*) for the corrosion process in absence and presence of CTABr were evaluated from Arrhenius equation [9,10].

$$\log R\ corr = logA - \frac{E_a^*}{2.303\ RT} \qquad .... (5)$$

whereR_{corr} is the corrosion rate ($mg/cm^2.min$), A is the frequency factor, Ea^* is the apparent acivitation energy and R is gas constant (8.314 J/mole. K), that by plot of log (corrosion rate)Vs (1/T)as shown in Figure (3).

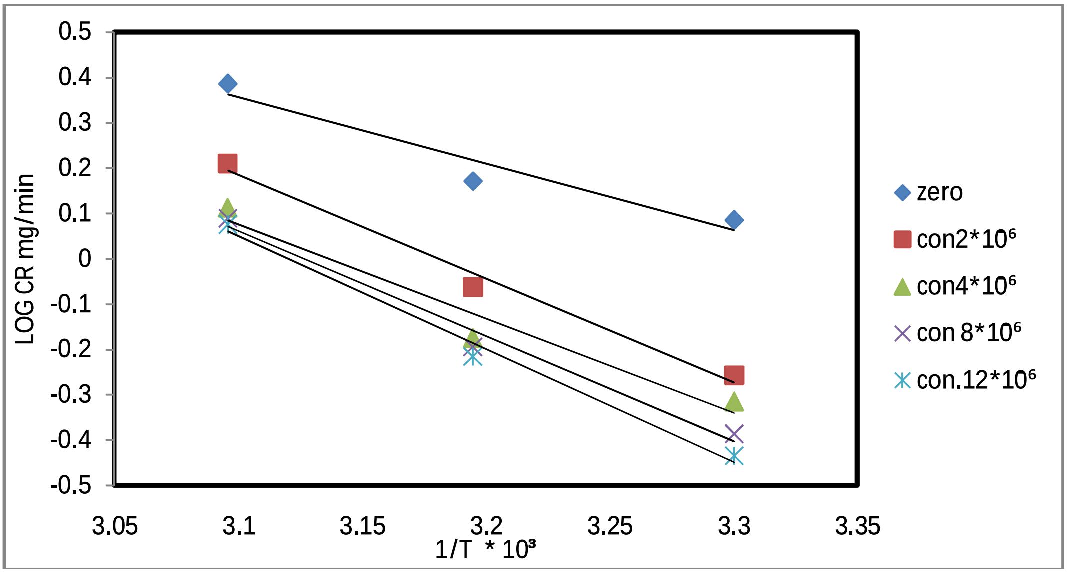

Figure (3)Corrosion rate versus reciprocal temp. fitting for Arrhenius equation for couple metals with different concentrations of CTABr.

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The addition of CTABr modified the values of Ea^*. This is attributed to the adsorption on Al surface.

Table (5)Activation energy for different CTABr concentration.

CTABr conc (M).	Ea^*(kJ)
$2*10^{-6}$	-40.1116
$4*10^{-6}$	-43.8392
$8*10^{-6}$	-44.545
$12*10^{-6}$	-47.7764

The activation energy values shown in Table (5) for HCl-inhibitor systems support the fact that the inhibitors are physically adsorbed on Al surface. This is in agreement with G.Y. Elewady[1] and E. E. Ebenso[11].

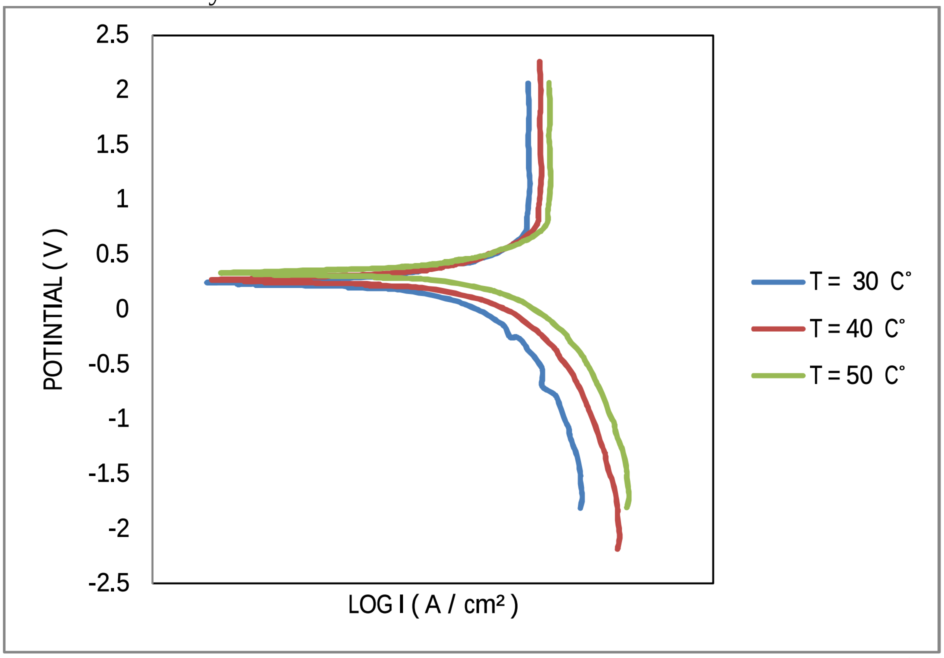

Figure (4) Polarization curve for Al with CTABr inhibitor conc.($2*10^{-6}$) at different temperatures.

Figure (4).shows the galvanostatic polarization curves for Al in 1M HCl solution for ($2*10^{-6}$ M)inhibitor concentration at different temperature . The numerical values of the variation of corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel slopes

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(Ba and Bc), with the concentration of the inhibitor are given in Table (6). This indicates that(7):

1- 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.
2- 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.
3- The values of corrosion potential (E_{corr}) shifted to less negative values by increasing the concentration of the inhibitor.

Table (6) Effect of CTABr concentration on the corrosion potential (E_{corr}), corrosion current density (I_{corr}), Tafel slopes (Ba and Bc) for ($2*10^{-6}$ M) concentration of inhibitor at 30 C^{o}.

Inhi. Conc.	**E corr.**	**I corr.**	**Ba**	**Bc**
$0*10^{-6}$	-945.32	217.501	221	91
$2*10^{-6}$	-943.93	98.983	204	111
$4*10^{-6}$	-942.42	86.682	199	112.4
$8*10^{-6}$	-939.02	73.629	196	113
$12*10^{-6}$	-937.87	65.816	194	115

CONCLUSIONS

1- The corrosion rate of Al increases with rise in temperature.
2- The corrosion rate decreases with increase in CTABr concentration and the inhibition efficiency increase with increasing the inhibitor concentration.
3- CTABr gives a good inhibition for Al corrosion in hydrochloric acid solution.
4- The CTABr inhibitor increases the value of activation energy of corrosion and consequently decrease the rate of dissolution of Al in Hcl solution.
5- The inhibitor molecules are physically adsorbed on Al surface following Temkin adsorption isotherm.
6- Polarization measurements revealed that CTABr act as mixed type inhibitor.

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