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Electrochemical Behavior of Ti – Alloy in the Mixture of Formic and Phosphoric Acid in the Presence of Organic Compound

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The effect of dimethyl 2-(2–hydroxyphenyl amino)–3-(triphenyl phosphoranylidene) butanedioate, (L–OH), an organic compound on the corrosion parameters of Ti-6Al-4V in the mixture of concentrated phosphoric and formic acid at different temperatures (20, 30, 40 and 50±1°C) were investigated by potentiodynamic method. It is observed that the cathodic current density values increased with increasing cathodic potential (more negative) at each concentration but these values decreased with increasing L-OH concentration. However, the nature of the curves was identical. The values of cathodic Tafel slopes derived from the curves were found to be in the range of 90 – 135 mV per decade of current vs. SCE which is indicative of hydrogen evolution reaction (h.e.r). Corrosion potential (E_{corr}) shifted toward noble direction with increasing the concentration of L-OH, whereas corrosion current density (i_{corr}), critical current density (i_{cr}) and passive current density (i_p) decreased. Corrosion potential shifted toward more active potential (-ve) and current densities (i_{corr}, i_{cr}, i_p) increased significantly with increasing temperature from 20 to 50±1°C

Keywords: Corrosion, Electrochemical behavior; Inhibitor; Ti-alloy, L-OH

1. INTRODUCTION

Titanium and its alloys are being used in many areas: food industry [1], desalination plant [2], restorative surgery such as dental and orthopedic prostheses pacemakers and heart valves [3], biological fluids and biocompatibility [4], landing gears blades of gas turbines, nuclear power plants and prosthetic implants [5]**.** Phosphoric acid and their mixtures are also frequently used as pickling solutions or for the purpose of cleaning and electropolishing [6]. These wide range uses is due to of their appropriate mechanical properties and excellent corrosion resistance. Titanium and its alloys have been subjected to several investigations of corrosion behavior and the nature of passive film [7-10]. The electrochemical behavior of titanium was interpreted in terms of a two layer structure of the passive film. A barrier film, next to the metal, inhibits the metal dissolution due to its low cationic conductivity and a porous outer layer [11]. The active dissolution and passive behavior of titanium in solution of mineral acids such as sulfuric, hydrochloric, phosphoric and perchloric acids has been investigated by many research groups [12-17]. On the other hand the instability and frequent failure of Ti and its alloys in reducing acid solution have been identified and have drawn the attention of researchers to study the electrochemical behavior of Ti in such a media [18-21]. It has been reported that corrosion inhibitors for titanium materials are not significant, probably because of good corrosion resistance of Ti and its alloys in aqueous environments. Brynza and Gerasyutina [22, 23], being concerned with the corrosion resistance of Ti in certain applications in the chemical industry, and have studied organic inhibitors in sulfuric acid and hydrochloric acid. Most organic inhibitors used to protect titanium against corrosion function as oxidizers which are principally reduced on the metal surface and then enhance the effectiveness of the cathodic process [24]. Chemisorption on the positively charged surface of titanium is often suggested, but has not been actually proved. It seems that some additives take part in the passive film growth by directly oxidizing the metal. So fare, it is still difficult to draw a classification of the various molecules investigated, based on the inhibition mechanism. Therefore it is advisable to describe the effect of organic oxidizing molecules on the corrosion of titanium on the basis of chemical families [24]. Although titanium-based alloys exhibit good corrosion resistance due to the formation of titana on its surface, the nature, composition and thickness of the protective oxide scales depend on environmental conditions. Furthermore Ti-6Al-4V is an α-β alloy having been developed to optimize the desirable properties of both phases [25, 26]. Aluminum stabilizes the α-phase and raises the α→β conversion temperature while the vanadium stabilizes the β phase and raises the β→α temperature. Very few corrosion studies in acid solution, containing inhibitor, have been reported for the alloy Ti-6Al-4V. In spite of its commercial importance in various industries. Since it meets the strength requirement it is used to replace Ti. In the present work, the corrosion inhibition property of L-OH [27] (Fig.1) against Ti-alloy in the mixture of concentrated phosphoric and formic acid have been investigated.

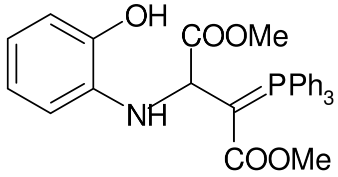

Figure 1. Structure of L-OH

2. EXPERIMENTAL PART

A cylinder made of Ti-6Al-4V, was cut in to pieces, each with a surface area of 2 cm^2, and used as working electrodes. Prior to immersion in the electrolyte, the individual specimens were mechanically polished with graded emery paper in the order as (400, 800, 1200, and 1500 grit). After polishing, the specimens were etched in an aqueous mixture of two volumes HF and four volumes HNO_3 for a few seconds at ambient temperature to remove any possible oxide film, and then washed with double distilled water. The specimens were finally degreased with acetone. A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrode respectively. The electrochemical measurements were performed using a potentiostat CG, CV &PG system model DPSWx. Prior to polarization measurement, the Ti-alloy working electrode was immersed in the experimental solution for ~30 min to attain a stable OCP value. Potentiodynamic polarization studies were performed in the mixture of concentrated H_3PO_4 and HCOOH containing various concentrations (20, 40 and 60 ppm) of L-OH. Polarization was performed moving from negative to positive potentials in the range of -800 to 1600 mV, with a scan rate of 1 mV S^{-1}, at constant temperatures (within $\pm 1^{\circ}C$ of the target value). The influence of temperature was investigated at 20, 30, 40 and $50 \pm 1^{\circ}C$ for each concentration of inhibitor. All potentials were measured against the SCE. The corrosion parameters, including the corrosion potential (E_{corr}), corrosion current densities (i_{corr}), critical current density (i_{cr}), passive current density (i_p) and inhibition efficiency (η %), were used to evaluate the corrosion behavior of the alloy in the test solution.

3. RESULTS AND DISCUSSION

The cathodic and anodic polarization curves of Ti-alloy in binary solution mixtures of phosphoric acid and formic acid (1:1) with different concentrations of L-OH at 20 to $50 \pm 1^{\circ}C$ are shown in Figs. 2-5 and related corrosion parameters are listed in Tables 1-4. It is seen that the cathodic current density increased with increasing cathodic potential in all of the experimental solution containing L-OH at different temperatures, but decreased as the amount of L-OH increased. An investigation of these curves reveals that the cathodic polarization curves are linear and almost overlap each other. Evolution of gas was observed during these experiments especially at higher temperatures. The cathodic Tafel slopes derived from the cathodic curves were found to be in the range of 90 - 135 mV per decade of current vs. SCE. These values are consistent with previously reported values for the hydrogen evolution reaction [28-30]. Anodic polarization curves show active–to-passive behavior for the alloy in acidic solution. It is observed that the corrosion potential (E_{corr}) shifts toward the noble direction (increase) in the present of the inhibitor. The corrosion current density (i_{corr}), critical current density (i_{cr}) and passive potential (E_p) decrease as the concentration of L-OH increases. The passive current density (i_p) followed a similar pattern to that of the I_{cr} in the binary solution mixtures containing different concentrations of L-OH. The corrosion current densities (I_{corr}) obtained by extrapolation of the Tafel lines.

The percentage inhibition efficiency (η %) and surface coverage degree (θ) are obtained from the following equations [29] :

$$\eta = \left(\frac{i_0 - i_1}{i_0} \right) \times 100\%$$

$$\theta = \left(\frac{i_0 - i_1}{i_0} \right)$$

where i_0 and i_1 are the corrosion current densities obtained in the absence and in the presence of the inhibitor.

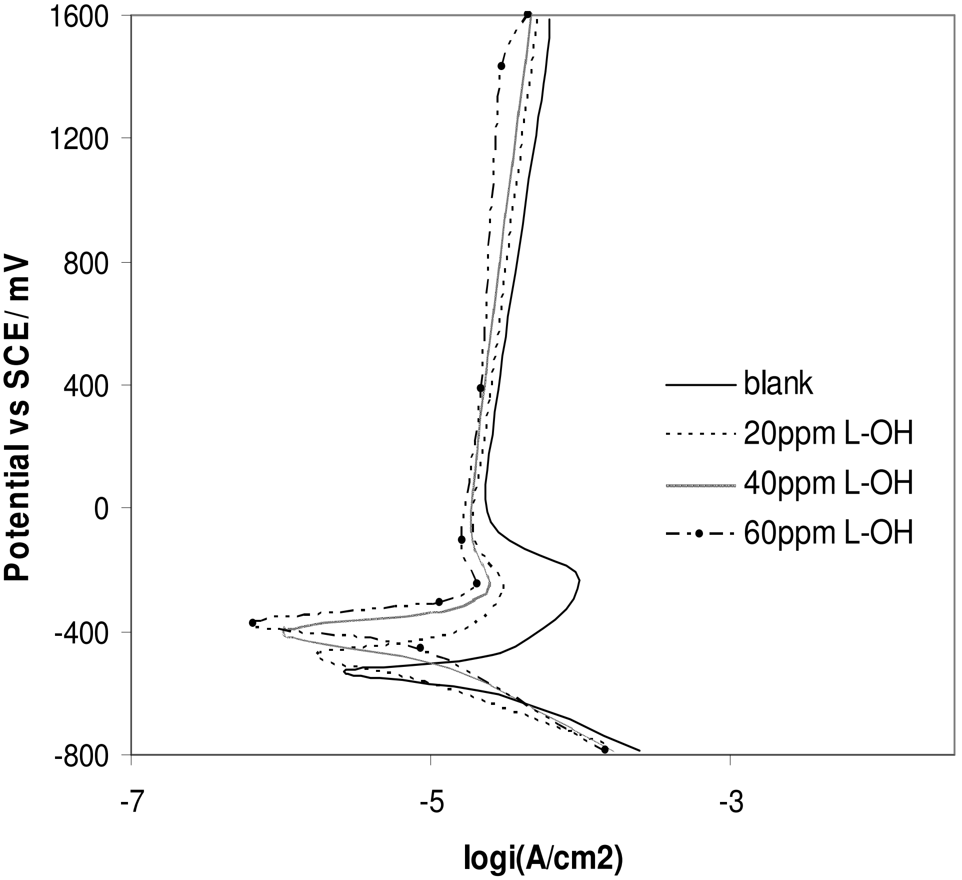

Figure 2. Polarization curves for Ti-6Al-4V in the mixture of phosphoric acid and formic acid + L-OH at 20 ± 1°C.

Table 1. Effect of L-OH concentration on the corrosion parameters of Ti-alloy at 20 ±1°C.

Concentrations of (L-OH) / ppm	E_{corr} (mV vs SCE)	log i_{corr} (A/cm^2)	log i_{cr} (A/cm^2)	E_p (mV vs SCE)	log i_p (A/cm^2)	Inhibition efficiency η %	θ
0	-611	-5.58	-4.00	-27	-4.60		
20	-579	-5.76	-4.50	-35	-4.71	34%	0.34
40	-524	-5.99	-4.61	-66	-4.74	61%	0.61
60	-475	-6.185	-4.650	-89	-4.80	73%	0.73

Passivation is evident over a wide range of potential, with low values of passive current density in all concentrations of the inhibitor. Most likely the nitro-group of the additives is being reduced on the surface of the alloy which consequently is polarized to more noble potentials. For metals which show an active to passive transition in their anodic polarization into the passive region or to increase corrosion due to polarization in the active region, which case will be found depends on the cathodic current generated by the reduction of the nitro-group in a given metal / electrolyte system [31].

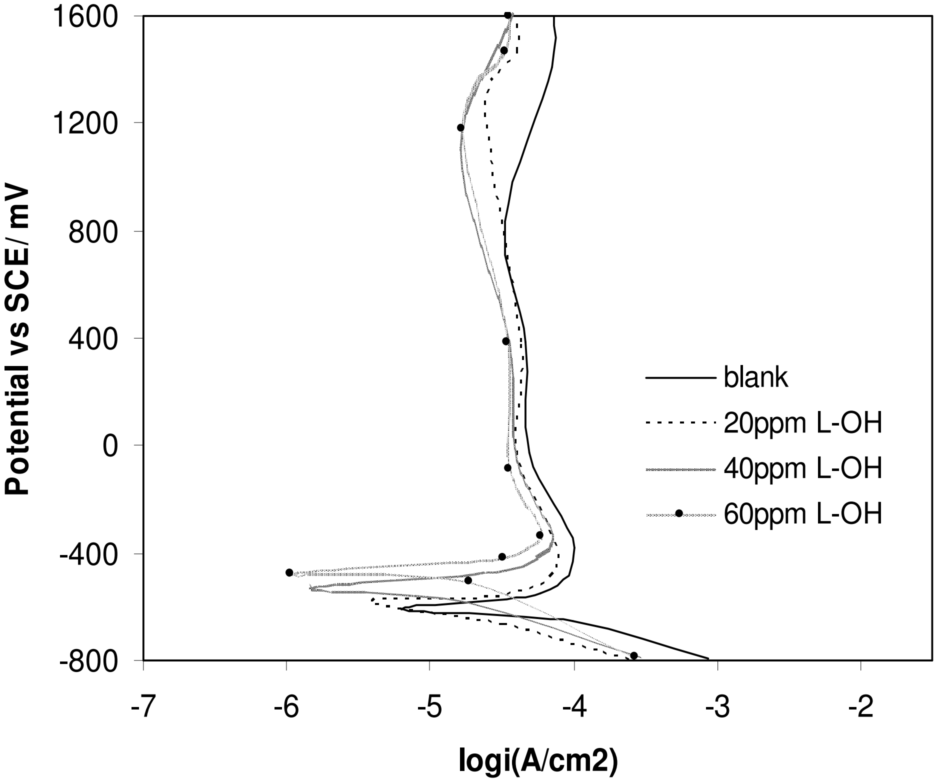

Figure 3. Polarization curves for Ti-6Al-4V in the mixture of phosphoric acid and formic acid + L-OH at 30 ± 1°C.

Table 2. Effect of L-OH on the corrosion parameters of Ti-alloy (Ti-6Al-4V) at 30±1° C.

Concentrations of (L-OH) / ppm	E_{corr} (mV vs SCE)	log i_{corr} (A/cm^2)	log i_{cr} (A/cm^2)	E_p (mV vs SCE)	log i_p (A/cm^2)	Inhibition efficiency η %	θ
0	-530	-5.21	-3.90	-44	-4.31	....	
20	-476	-5.42	-4.10	-64	-4.40	40%	0.40
40	-400	-5.90	-4.15	-76	-4.45	80%	0.80
60	-37	-6.0	-4.2	-104	-4.50	84%	0.84

The effect of temperature on cathodic and anodic curves for the alloy is shown in Fig 6. The nature of anodic curves at different temperatures in 60 ppm of L-OH is similar, however the effect of the temperature clearly has been observed on different corrosion parameters. Corrosion potential shifted toward more active potential (-ve) and current densities (i_{corr}, i_{cr}, i_p) increased significantly as the temperature rise from 20 to 50 ± 1°C. An overall examination of the polarization curves (Figs 2-6) of the alloy in the acid mixture containing different amounts of L-OH at various temperatures indicate that similar reaction is taking place on the surface of the alloy but with different rates as the corrosion parameters differed. The shape and nature of these curves are approximately similar to those reported for Ti and its alloys in reducing acids [30, 32]. There is an appreciable decrease in the inhibition efficiency as the temperature is raised from 30 to 50 ± 1°C. Critical current density in acid solution containing 20 ppm of L-OH increased (~ 13 time) whereas passive current density decreased (~ 0.5 time) when temperature rise from 20 to 50 ± 1°C. The decrease in i_p at 50 ± 1°C compared to 20 ± 1° C is possibly due to the nature of passive film formed at the surface of the sample.

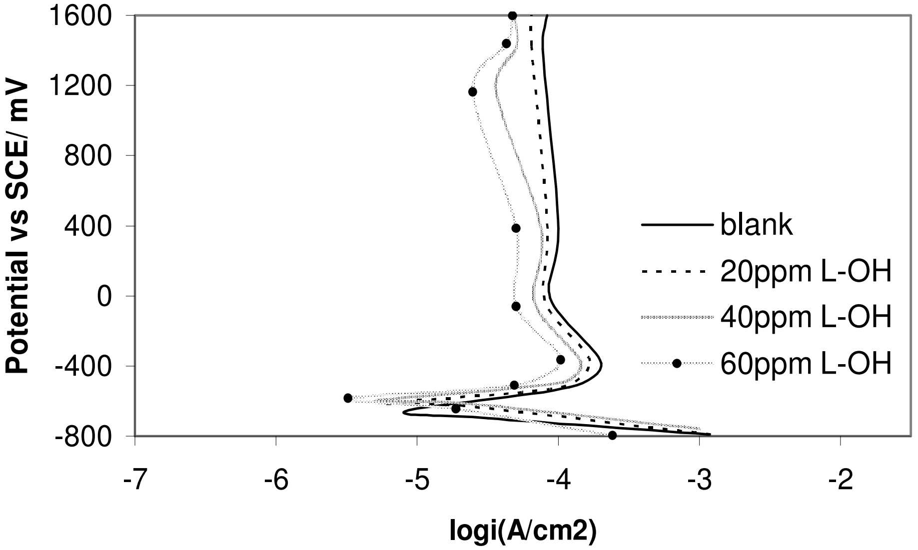

Figure 4. Polarization curves for Ti-6Al-4V in the mixture of phosphoric acid and formic acid +L-OH at 40 ±1°C.

Table3. Effect of L-OH on the corrosion parameters of Ti-alloy (Ti-6Al-4V) at 40±1°C.

Concentration of (L-OH) / ppm	E_{corr} (mV vs SCE)	log i_{corr} (A/cm^2)	log i_{cr} (A/cm^2)	E_p (mVvs SCE)	log i_p (A/cm^2)	Inhibition efficiency η %	θ
0	-685	-5.10	-3.70	-13	-4.00		
20	-611	-5.21	-3.80	-27	-4.10	20%	0.20
40	-600	-5.30	-3.84	-43	-4.20	36%	0.36
60	-586	-5.50	-4.00	-62	-4.30	60%	0.60

The percentage inhibition efficiency (η %) and surface coverage degree (θ) increased with increasing inhibitor concentration, that implies very good adsorption of this inhibitor on the surface of alloy. The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals and alloys has been deduced in terms of adsorption characteristics of the inhibitor [33]. Adsorption inhibitors are usually organic substances containing polar functions with nitrogen, sulfur and/or oxygen in the conjugated system [34]. Such substances have been reported to function by adherence to the metal surface through metal ions still in place in the lattice and thereby retard metal dissolution by virtue of adsorption, with the polar group acting as the reaction centre for the adsorption process [35, 36].The adsorption bond strength is dependent on the composition of the metal and corrodent, inhibitors structure and concentration as well as temperature [37]. Generally, inhibitor molecules either

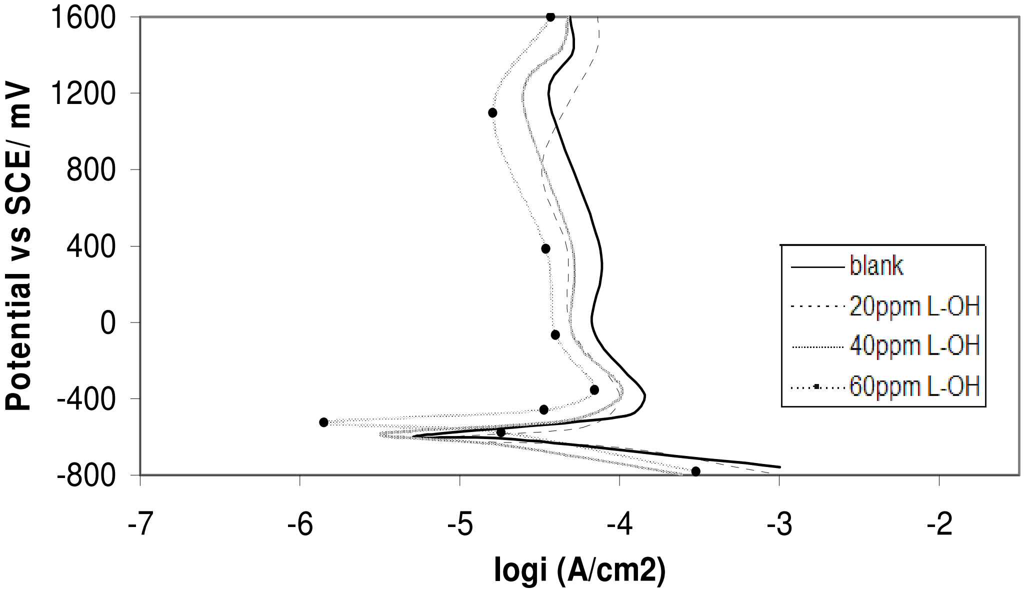

Figure 5. Polarization curves for Ti-6Al-4V in the mixture of phosphoric acid and formic acid +L-OH at 50 ±1°C.

Table 4. Effect of L-OH on the corrosion parameters of Ti-alloy (Ti-6Al-4V) at 50±1°C.

Concentration of (L-OH) / ppm	E_{corr} (mV vs SCE)	log i_{corr} (A/cm^2)	log i_{cr} (A/cm^2)	E_p (mV vs SCE)	log i_p (A/cm^2)	Inhibition efficiency η %	θ
0	-696	-5.00	-3.50	-43	-3.90		
20	-624	-5.064	-3.426	-50	-3.96	14%	0.14
40	-600	-5.127	-3.652	-56	-3.82	30%	0.30
60	-594	-5.320	-3.752	-66	-3.80	53%	0.53

physically or chemically adsorb on a corroding metal surface. It has been suggested [38,39] that physisorbed molecules are attached to the metal at local cathodes and essentially retard metal dissolution by stifling the cathodic reaction, whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. According to Ebenso [40] and Al mayouf [41] a decrease in inhibition efficiency with rise in temperature suggests that inhibitor molecules are physically absorbed on the metal surface, while the reverse behavior suggests chemisorption. Accordingly, the trend of inhibition efficiency with temperature (30-50±1°C) as illustrated in Figure 7 and Table 5 suggests that L-OH molecules were physically adsorbed at different concentrations on the metal surface. The reason for this behavior is still not quite clear and several factors may possibly play a role for this behavior. The increase in inhibition efficiency from 20-30±1°C is possibility due to the kind of film and its absorption on the surface of the alloy. The orientation of adsorbed aromatics is a function of several variables, among which are adsorbate molecular structure and solute concentration, and the reactivity of these adsorbed intermediates is a sensitive function of their orientation [42]. Generally, the mechanism by which a given inhibitor may attach to metal depends on the functional group present in its molecule. Some functional groups are normally held more firmly than others [43]. According to Fragnani and Trabanelli [44], sulfur-containing substances easily chemisorb onto the surface of metal in acid media, whereas nitrogen-containing compounds tend to favor physisorption. These suggestions have been corroborated by the results of other investigators [45]. Thus L-OH having nitrogen atom, physisorption on the metal surface, functions by a data inhibitory mechanism and, depending on the concentration, inhibits both cathodic and anodic reactions.

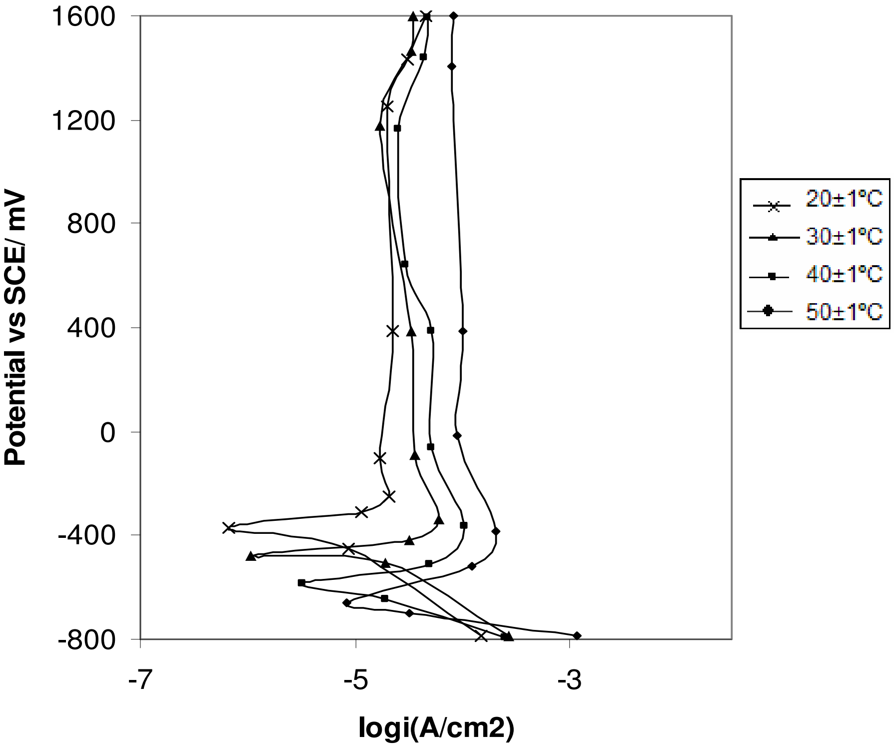

Figure 6. Polarization curves for Ti-6Al-4V at different temperatures in the Presence of 60 ppm L-OH.

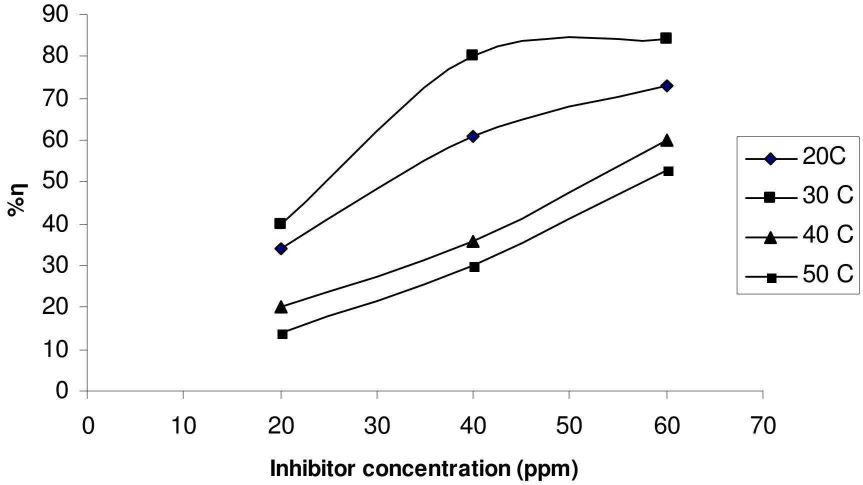

Figure 7. Variation of inhibition efficiency with inhibitor concentration at different temperatures.

Table 5. The effect of temperature on the inhibition efficiency of L-OH.

Inhibitor Concentration (ppm)	Inhibition efficiency (%)			
	20±1°C	30±1°C	40±1°C	50±1°C
20	34.0	40.0	20.0	14.0
40	61.0	80.0	36.0	30.0
60	73.0	84.0	60.0	53.0

For the blank solution, the OCP of the sample before polarization ranged between -530 to -680 mV vs. SCE at different temperatures. Note that in acid solution containing 20, 40 and 60 ppm of L-OH at 30 ±1°C, before polarization the OCP were between -280 and -100 mV vs. SCE. However, after polarization the OCP value in the presence of 60 ppm L-OH was 380 mV vs. SCE. The increase in the value of the OCP after polarization is due to the passive formation of a film on the surface of the samples. From Fig. 8, the measurement of the OCP value over time reveals that after polarization the film remained protective during the prolonged exposure to the acid solution containing 60 ppm of L-OH at 30 ±1°C. The OCP value decreased gradually after further exposure and thereafter attained stable value. This suggests that the insulating properties of the film formed on the surface did not change, even if the anodic film has been dissolved to some extent at OCP.

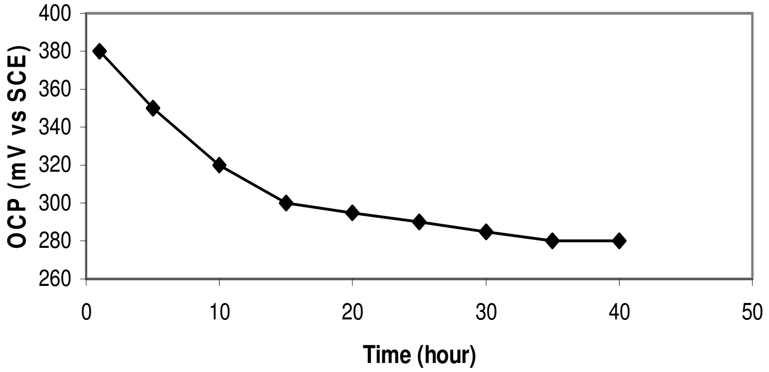

Figure 8. OCP values vs. time

The corrosion reaction occurring at the surface of passive film of the alloy appears to be dissolution/formation reaction during the exposure and polarization in acidic media and the film formed on the surface may be composed of two layers which differ in their chemical composition. A two stage dissolution process of the oxide film on titanium has been reported [46].

The corrosion reaction may be regarded as an Arrhenius-type process and its rate is given by:

$$I_{corr} = k \exp(-E_a/RT)$$

where k is the Arrehenius pre-exponential constant, and E_a is the activation energy for the corrosion process. The E_a values were determined from the slopes of these curves (log I vs 1/T) (Fig.9) and are calculated to be Ea =19.6 kJmol^{-1} in the blank solution and Ea = 26.6 kJmol^{-1} in the presence of 60 ppm L-OH in passive region for Ti-alloy. The apparent activation energy obtained for the alloy in this media may be considered to be associated with the complex process/ mechanism/ resistance/dissolution that occur in this region [30]. Arrhenius plots in critical region for Ti-alloy (0 and 60 ppm) are shown in Fig.10. The Ea= 13.3 kJmol^{-1} in the blank solution and E_a= 24.1 kJmol^{-1} for 60 ppm L-OH. These values may be attributed to the formation of passive film on the surface of samples.

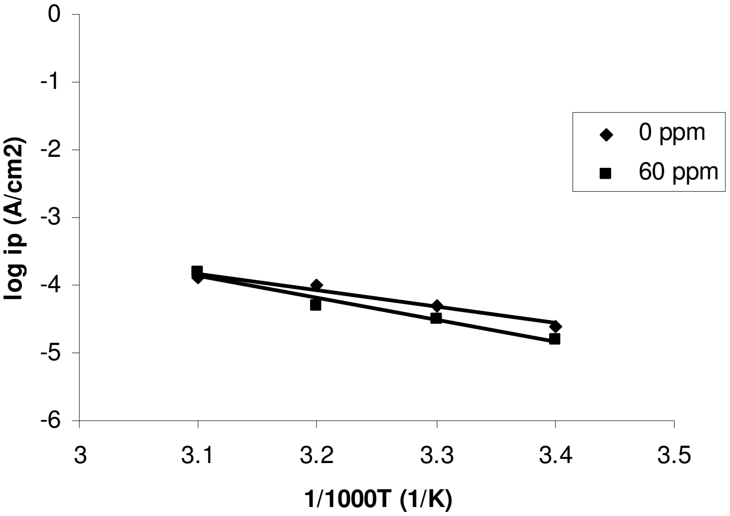

Figure 9. Arrhenius plot in passive region for Ti-alloy in the absence and presence of L-OH.

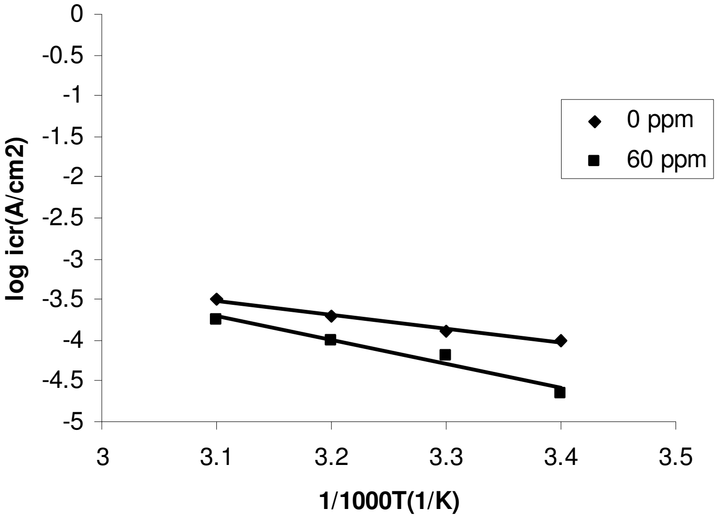

Figure 10. Arrhenius plot in critical region for Ti-alloy in the absence and presence of L-OH.

The corrosion inhibitors adsorb to the metal surface atoms at the metal/solution interface through electrostatic or covalent bonding. The planarity (π) and lone pair of electrons present on heteroatom are the important structured features that determine the adsorption of these molecules on the metal surface. The π -electrons of the double bond form a chemical bond with the d-orbital of transition metals [47] inhibiting corrosion. At the same time, both π-electrons and lone pair of electrons present on nitrogen and oxygen of L-OH play an important role in the adsorption of inhibitor on to the metal surface.

4. CONCLUSIONS

- The potentiodynamic polarization curves of Ti-6Al-4V in the mixture of concentrated phosphoric and formic acids in the presence of L-OH at different temperatures exhibited an active-to-passive transition state.
- Corrosion potential (E_{corr}) decrease (moved toward cathodic potential) with increasing temperature while corrosion current density (i_{corr}) critical current density (i_{cr}) and passive current density (ip) increase.
- The decrease in corrosion and critical current density is significant in comparison to passive current density with increase in the inhibitor concentration.
- L-OH affects as a cathodic and anodic inhibitor on the corrosion of Ti-6Al-4V in the mixture of formic and phosphoric acids media.
- Inhibition efficiency increase with increasing the concentration of inhibitor (L-OH) at all temperatures studied.
- The organic inhibitor studied belongs to the group of inhibitors classified as passivators. Its amino-group is being reduced at the Ti surface which enhances the passivation of the Ti alloy.
- The inhibition of corrosion of the Ti-alloy in acidic media is attributed to the adsorption of this inhibitor on to the alloy surface via double bonding of carbon atoms and lone pair electrons present on the nitrogen and oxygen in the conjugated system. The decrease in the inhibition efficiency with arise in temperature suggests the L-OH molecules are physically adsorbed on the metal surface.

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