Int. J. Electrochem. Sci., 11 **(2016)** 7269 – 7281, doi: 10.20964/2016.08.20

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Comparison Between Electropolishing Behavior of Copper and Mild Steel in the Presence of Lactic and Mandolic Acid

Fatma.M.Abouzeid

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
*E-mail: fatmaabouzeid44@yahoo.com;

Received: 20 July 2015 / *Accepted:* 27 May 2016 / *Published:* 7 July 2015

Addition of lactic and mandolic acid to electropolishing bath of copper and steel was examined using potentiodynamic polarization, weight loss method and scanning electron microscopic studies. Addition of different concentrations of lactic and mandolic acid gave a clear reduction in electropolishing rate. Scanning electron microscopic studies supplied the assenting proof of get better surface condition after addition of lactic and mandolic to electropolishing bath. The kinetic and activated parameters were computed for the dissolution process. Addition of lactic and mandolic acid to electropolishing bath made the solution appeared hopeful, a diverse development in the finish was noted where surface roughness ,Ra decreases to a great extent by addition of lactic and mandolic acid.

Keywords: copper; steel; electropolishing; scanning electron microscopic; surface roughness

1. INTRODUCTION

The chief commercial use of copper is based on its electrical conductivity (second only to that of silver); about half the total annual output of copper is employed in the manufacture of electrical equipment and wire. Copper is also used widely as roofing, in making copper tools, and for coins and metalwork. Copper tubing is used in plumbing, and, because of its high heat conductivity, in heat-exchanging plans such as refrigerator and air-conditioner coils. [1,2]

Steel is one of the mainly broadly used metals in our current planet, building all from our homes to skyscrapers, transportation, and bridges. Its adaptability, toughness, and potency make it a well-liked alternative for many different applications and it is also a reasonable and environmentally-friendly option for contractors all over the world. In addition, it is one of the strongest materials that contractors can use, forming the backbone for even the largest structures in modern society, such as roads that support millions of tons of vehicles every year, and buildings that must withstand both everyday stresses and the danger of potential disasters [3, 4]

Polishing eliminates tarnishes, surface corrosion, and scratches are removed to create a smoother, shinier finish[5,6].

In the present investigation, an attempt has been made to study the morphology of electropolished copper and steel in H_3PO_4 acid solution using potentiodynamic polarization and weight loss measurements. The extent of polishing copper and steel were evaluated through a detailed study relating the influence of the attendance of different concentration of the mandolic and lactic acid .The resulting surface morphology (examined by SEM), surface roughness (explored by Profilometer) .

2. EXPERIMENTAL

2.1 .Solution and material

8M orthophosphoric acid was set up from analar grade H_3PO_4 (85 %) . Seven concentrations of organic acid (lactic and mandolin) with 8 M H_3PO_4 are used, ranging from 1 X10^{-4} to 7 X10^{-4} M. The steel sheet [0.0257% S, 0.07% P, 0.4% Mn, 0.1% C and the rest iron] while the copper used is 99.98was submerged into the corner of a rectangular cell with the 100 mL EP solution.Doubly distilled water with a resistivity > 18 mΩ was used in the preparation of solutions

2.2 .Electrochemical measurements

Electrochemical trials were performed in a cell with a capacity of 100 mL. The electropolishing trials were performed using copper and steel plate (10x5 x0.2 cm) as cathode and anode. The potentiodynamic current–potential curves were evidenced by varying the electrode potential and measuring the corresponding current. Before each run, the back of anode was insulated with polystyrene lacquer and the active surface was washed with alcohol and bathed in distilled water. The temperature was controled by placing the cell in thermostatic water bath (± 1 ^oC)at different temperatures (20, 30, 40 and 50^o C).

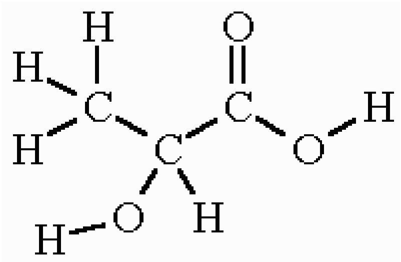
2.3. Scanning electron microscope (SEM)

The scanning electron microscope images were taken using (JEOL, JSM-5300, scanning microscope, OXFORD instrument). For this purpose the copper and steel sheet anode was (1cm ×1 cm).

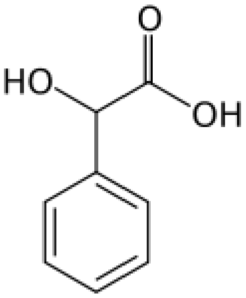
2.4. Profilometer

The quantitative roughness was measured by means of stylus profilometers (Talysurf i60). The long cutoff wavelength (sampling) and the short cutoff wavelength were 0.25 mm and 0.025 mm, respectively. The evaluation length was 5 mm (five sampling lengths). Approximately150 measuring lines were used, and thus the mean roughness values could be obtained.

The structure of the organic acid is given below.



lactic acid



mandolic acid

3. RESULTS AND DISCUSSION

3.1. Polarization measurements and mechanism

Fig. 1a shows the anodic polarization behavior of copper and steel recorded in 8 M phosphoric acid solution at a constant temperature of 293 K.The curves show a characteristic limiting current density plateau enlarging over a confident potential range, which establishes the mass transport controlled process [7].

Mass transport plays a leading role in anodic metal dissolution for influential and surface structuring [8]. Mass transport controlled dissolution results in surface smoothing because peaks of a rough surface diffuse at higher rates than recesses, resulting in surface leveling of the metal. In literature it is widespread to differentiate anodic leveling or smoothing from anodic brightening. The former refers to the removal of surface unevenness of height > 1 μm and the later to the elimination of surface unevenness comparable to the wave lengths of light [9] resulting in surface brightening [8,10].

The chemical phenomena which have been postulated to occur at the metal/solution interface are briefly: (a) the formation of a thin solid film at the beginning of the I=f(Vt) curve ; (b) the formation of a viscous layer along the plateau region; and (c) the evolution of oxygen above a certain voltage, the evolution becoming more vigorous as the current and voltage are increased. The chemistry of the anodic process is thus seen to be multifaceted. It is complicated to study because one cannot forever,be sure the compounds found by analysis of the solutions are true representations of the products present during electropolishing. Any explanation of the mechanism of the electrolytic processes taking place must include not only electrical but chemical phenomena. [11]

As mentioned in the mass transport section, diffusion is an important factor in understanding electropolishing. Therefore a model for diffusion is needed: Fick`s First and Second Laws of Diffusion.

Since the reaction is considered to be heterogeneous(reaction occurs at the electrode surface only), an electroactive species being consumed decreases as it approaches the anode and creates a concentration profile with respect to distance. If the concentration becomes zero at the surface, which happens when the electric potential exceeds the current limiting voltage, more electroactive species must diffuse to the electrode in order for the reaction to proceed. This causes an almost linear decrease in the concentration profile of the species. The Nernst diffusion layer is defined as the distance at which the bulk concentration line and the derivative of the concentration profile at the surface meet and is usually represented in literature by the symbol "δ". It then becomes obvious that at high voltages, the rate of electron transfer at the electrode is much faster than the rate at which the electroactive species reaches the electrode: the process is mass transport controlled under these conditions. Also, at these voltages, the concentration of the electroactive species at the electrode surface is zero for a species that is being consumed.

It has been observed that the issues which tend to obliterate the layer of anolyte (electrolyte in immediate vicinity of the anode) result in uneven polishing or etching of the surface [12, 13]. If one, however, alters the conditions (increases temperature, adjusts agitation, moves the anode from a horizontal to a vertical position) such as to return the current density to its maximum value on the plateau of the curve, micropolishing resumes [14]. These observations led Elmore [15, 16]to postulate the importance of diffusion in the mechanism of electropolishing. The basic assumptions of Elmore1s theory of electropolishing are: (a) Ions of the metal are scattered from the anode by diffusion and convection rather than by electrolytic migration; and (b) the anolyte layer is saturated with the products of solution. Thus, Elmore believes that in the case of copper polished electrolytically in orthophosphoric acid, the concentration of copper ions in the electrolyte at the anode surface increases with current density up to a maximum value. Dissolution of the metal continues beyond this point only to the extent that copper ions are allowed to diffuse into the bulk electrolyte from the boundary layer. The rate of this diffusion is greatest at the asperities where the concentration gradient is the highest, thus they will dissolve first

3.2. Influence of organic acid addition

The changes in dissolution rate after the addition of the organic acid are a useful indication of whether the anodic reaction of metal dissolution is retarded or accelerated. To estimate the outcome of the organic acid on the electrochemical performances of mild steel and copper, polarization trials were carried out. The Potentiodynamic curves are shown in the Fig.1

The dissolution rate (I_L values) and embarrassment efficiency percentage (IE %) for the organic acid at a concentration variety from 1×10^{-4} to 7×10^{-4} Mol/l is given in Table 1. It is obvious (Table 1) that I_L diminishes and IE % enlarges by increasing organic acid concentration(Fig.2).

If $(I_L)_{\text{blank}}$ is the limiting current in the absence of organic acid and $(I_L)_{\text{O.A}}$ in the presence of organic acid , then IE % can be calculated from the following equation

$$IE\% = \frac{I_{L(blank)} - I_{L(O.A)}}{I_{L(blank)}} \text{X100} \qquad (1)$$

According to Hackerman [17], the retarding properties of many compounds are established by the electron density at the reaction center. With an augment in the electron density at the reaction center, the chemisorption bonds between the inhibitor and the metal are strengthened

Table 1. Values of limiting current, % inhibition for dissolution of steel & copper in 8M H_3PO4 in presence of different concentration of organic acid and weight loss measurements

I_L(A)		Copper			Steel		
Conc. (mol/l)		I_L(A)	*Wloss*	IE%	I_L(A)	*Wloss*	IE%
0.0	Lactic acid	0.485	0.048		0.512	0.029	
1.0×10^{-4}		0.410	0.040	15.46	0.422	0.024	17.57
$2.\ 0\times10^{-4}$		0.372	0.036	23.30	0.377	0.022	26.36
$3.0\ \times10^{-4}$		0.351	0.034	27.63	0.355	0.020	30.66
4.0×10^{-4}		0.333	0.032	31.34	0.333	0.019	34.96
5.0×10^{-4}		0.312	0.030	35.67	0.300	0.017	41.41
6.0×10^{-4}		0.295	0.028	39.18	0.281	0.016	45.12
7.0×10^{-4}		0.277	0.027	42.89	0.255	0.014	50.20
0.0	Mandolic acid	0.485	0.048		0.512	0.029	
1.0×10^{-4}		0.420	0.041	13.40	0.440	0.025	14.06
$2.\ 0\times10^{-4}$		0.392	0.038	19.18	0.382	0.022	25.39
$3.0\ \times10^{-4}$		0.365	0.035	24.74	0.361	0.021	29.49
4.0×10^{-4}		0.343	0.033	29.28	0.344	0.020	32.81
5.0×10^{-4}		0.325	0.032	32.99	0.321	0.018	37.30
6.0×10^{-4}		0.305	0.030	37.11	0.295	0.017	42.38
7.0×10^{-4}		0.287	0.028	40.82	0.263	0.015	48.63

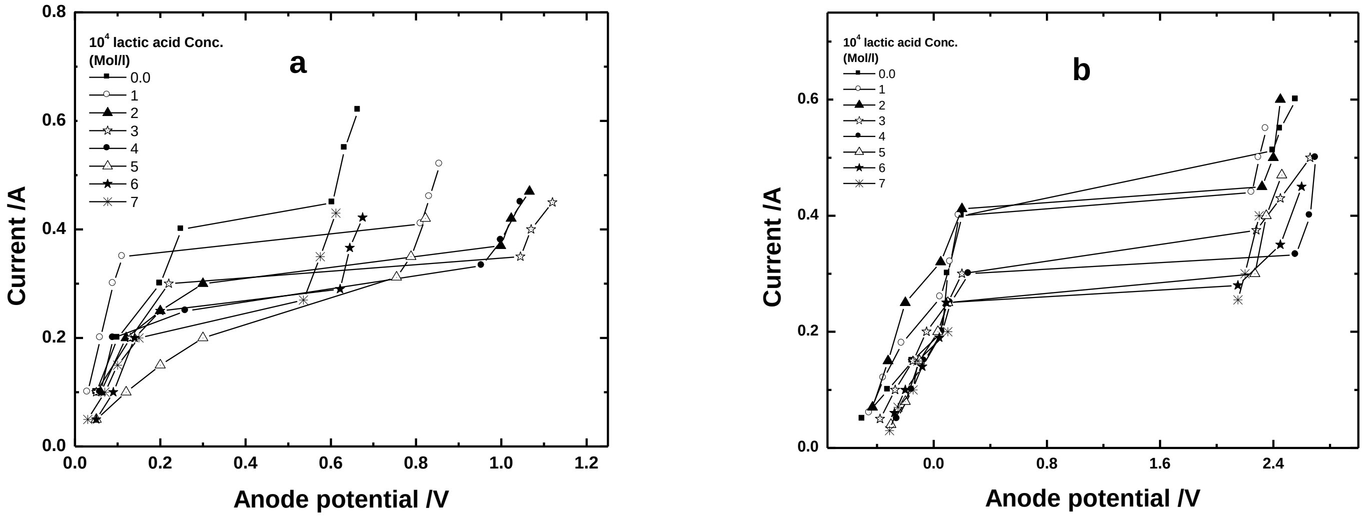


Figure 1. polarization curves acquired for dissolution of (a) copper and (b) steel electrode in 8 M H_3PO_4 in the absence and presence of different concentrations (1×10^{-4} -7 $\times10^{-4}$ mol/l) of the lactic acid

It is assumed that for organic compounds during the first ionization one of the electrons of the unshared pair is disengaged, then the ionization potential can provide as a measure of the electron density at the nitrogen atom. Hackerman et al [17, 18] have been studied the adsorption of organic substances with a long hydrocarbon chain from organic solvents. Theses studies showed that the better the substance is adsorbed, the more effectively it protects the surface.

The dissolution inhibition process is promoted by the adsorption of non-dissociated organic acid molecules onto the copper and mild steel electrode surface. On the other hand, dissociated species are involved in complexing reactions

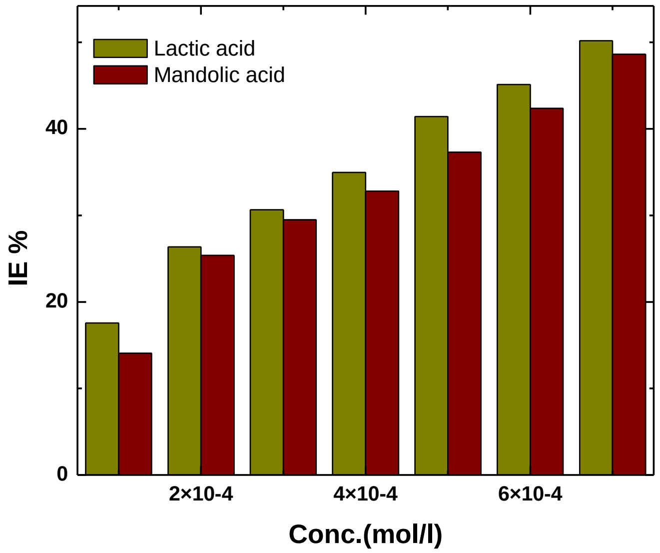


Figure 2. Relation between inhibition efficiency percentage and concentration at 20°C for the studied organic acid for copper dissolution

3.3.Electropolishing Rate Calculation

Electropolishing rates were calculated for each set of parameters. The weight of the specimen was measured before and after electropolishing. The electropolishing rate was calculated according to Equation 2

$$EP_{\text{rate}} = \left[\frac{WbeforeEP - WafterEP}{area}\right] \Big/ Time \qquad (2)$$

where WeightbeforeEP is the weight of the test specimen before electropolishing and after surface preparation and WeightafterEP is the weight after electropolishing and post

cleaning. Area is the total area of the test specimen (2 cm x 2 cm) and Time is the electropolishing time in s (seconds). The units of the EP rate were gram/cm^2 min. The EP rate was calculated using Equation 2

Table 2. Values of electopolishing rate of copper and steel in 8M H_3PO4 in presence of different concentration of organic acid

Metal	**copper**			**steel**		
Conc. (mol/l)	W_{before}	W_{after}	EP $_{rate}$	W_{before}	W_{after}	EP $_{rate}$
0.0	4.54	4.12	0.021	4.66	4.00	0.033
Lactic acid						
2.0×10^{-4}	4.44	4.18	0.013	4.64	4.12	0.026
4.0×10^{-4}	4.33	4.10	0.011	4.55	4.23	0.016
6.0×10^{-4}	4.36	4.16	0.01	4.58	4.29	0.014
Mandolic acid						
2.0×10^{-4}	4.56	4.26	0.015	4.72	4.16	0.028
4.0×10^{-4}	4.44	4.20	0.012	4.56	4.18	0.019
6.0×10^{-4}	4.46	4.23	0.011	4.63	4.30	0.016

The electropolishing rate (EP rate) decreased with an increase in the organic acid concentration. The test specimens were electropolished at a 20°C bath temperature for 5 min. the decrease in the electropolishing rate can be deduced from Faraday's Law of Electrolysis, shown in Equation 3.

$$Wloss = \frac{ItM}{nF} \qquad (3)$$

where Wioss is the total material loss, *n* is the valence of the metal ion, F is Faraday's constant (96,500 Columnb), M is the molecular weight of the anode, I is the process current, and t is the EP time. M, *n,* and F are constants.. The electropolishing rate (Table1) was measured by the total material removed over EP time, and is shown in Equation 3

Weight loss measurements (Table 1) and electropolishing rate measurements (Table 2) confirmed the data obtained from potentiodynamic measurements , where addition of organic acid retards the dissolution rate and retardation behavior increase by increasing organic acid concentration.

3.4. Temperature influence

The dissolution of copper and mild steel in phosphoric acid enlarges with augment in temperature . The retardation efficiency, reduces with growing temperature. The reducion in the retardation efficiency could be due to amplify the dissolution of copper and mild steel with mounting temperatures and desorption of the adsorbed inhibitor molecules from the metal surface [20]. The activation energy (E_a) for the dissolution process in the presence and the absence of organic acid was calculated using the Arrhenius equation.

$$\ln I_L = - (Ea/RT) + \ln A \qquad (4)$$

where E_a is activation energy, R is the gas constant, A is the Arrhenius pre-exponential factor and T is temperature. Fig.3 demonstrates the Arrhenius plots for the copper and mild steel in 8 M phosphoric acid with and without 7×10^{-4} of lactic and mandolic acid. The augment in E_a with the retardation of organic acid may be due to the enlarged energy barrier of the dissolution reaction [21]. When the retardation efficiency, reduces with increasing temperature and the E_a in the presence of inhibitor is superior than the

Ea in the absence of inhibitor, then the adsorptive film formed on the surface of the metal is believed to be due to physical adsorption [22-26].

$$I_L = (RT/Nh) \exp (\Delta S_a/R) \exp (-\Delta H_a/RT) \quad (5)$$

To investigate the system thermodynamics further the enthalpy of activation (ΔH_a) ,entropy of activation (ΔS_a) for the system was calculated using the transition state equation from the results of the potentiodynamic experiments at different temperatures with and without of 7 × 10 $^{-4}$ mol/l organic acid [27-30].

Table 3. Values of limiting current for copper and steel anodes dissolution in 8 M H_3PO4 in the absence and presence of 7× 10^{-4} mol/l organic acid at different temperatures and activated parameters for process

Conc. (mol/l)	20 °C		30 °C		40 °C		50 °C		Activated parameters			
	I_L(A)	IE%	I_L(A)	IE%	I_L(A)	IE%	I_L(A)	IE%	Ea kj.mol^{-1}	A	ΔHa kj.mol^{-1}	-ΔSa J.mol^{-1}.K^{-1}
Copper												
0.0	0.485		0.563		0.646		0.732		10.81	40.85	8.33	222.33
7.0× 10^{-4}lactic acid	0.277	42.88	0.333	40.85	0.412	36.22	0.500	31.69	15.61	167.33	13.13	210.71
7.0× 10^{-4}Mandolic acid	0.287	40.82	0.353	37.30	0.432	33.12	0.517	29.37	15.50	164.02	13.02	210.72
Steel												
Conc. (mol/l)	20 °C		30 °C		40 °C		50 °C		Activated parameters			
	I_L(A)	IE%	I_L(A)	IE%	I_L(A)	IE%	I_L(A)	IE%	Ea kj.mol^{-1}	A	ΔHa kj.mol^{-1}	-ΔSa J.mol^{-1}.K^{-1}
0.0	0.512		0.600		0.693		0.777		11.00	46.52	8.52	221.20
7.0× 10^{-4}lactic acid	0.255	50.19	0.322	46.33	0.400	42.27	0.466	40.00	15.98	208.51	13.50	209.96
7.0× 10^{-4}Mandolic acid	0.263	48.63	0.335	44.16	0.412	40.54	0.488	37.19	16.26	181.25	13.73	208.76

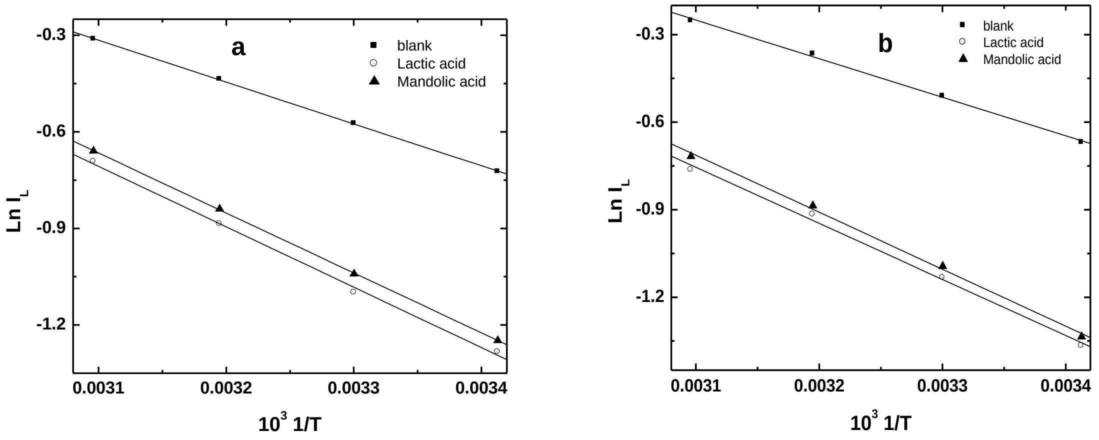


Figure 3. Arrhenius plot of the dissolution process for (a) copper (b) steel in presence of 7 × 10 $^{-4}$ mol/l of lactic and mandolic acid.

In equation 5, N is the Avogadro's number and h is the Planck's constant. The values of ΔH_a and ΔS_a in the presence and absence organic acid are shown in the Table 1. The ΔH_a increases with the addition of organic acid. A positive value of ΔH_a shows that the dissolution process is endothermic and that the dissolution in the presence of organic acid. [30]

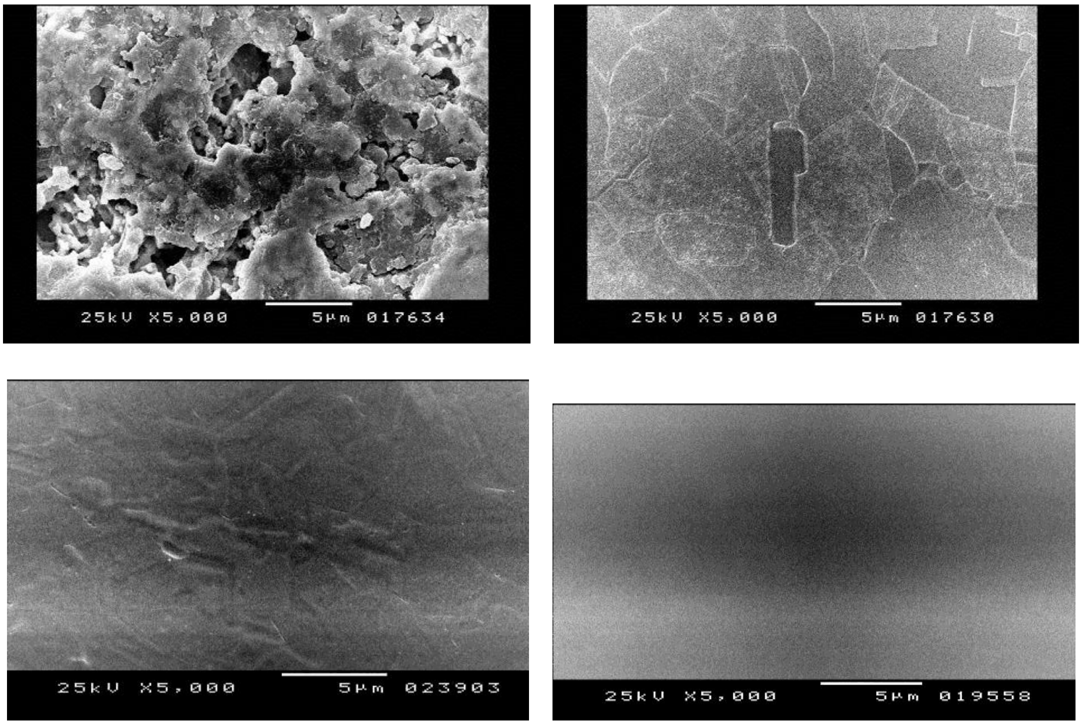
The ΔS_a is negative in both cases .A negative ΔS_a is an indication that the dissolution process is controlled by activation complex [30, 31].

3.5. Surface characterization

3.5.1. Scanning electron microscope (copper)

Visual observation of the sample used in the present work revealed that polishing (leveling and brightening) was obtained, but quality of the surface represented obviously by scanning electron microscope images. After electropolishing , the copper and steel surface was examined by SEM to discover and contrast the development of surface morphology . Fig4a-9f demonstrates an assessment between samples before and after electropolishing of copper samples in 8 M H_3PO_4 while Fig5a-9f shows a comparison between samples before and after electropolishing of steel samples in 8 M H_3PO_4.

A rough, matt and uneven surface was seen before electropolishing where a large deep cavities and small pits are distributed over the surface (fig.4a). At 8 M H_3PO_4(fig.4b), uneven and rough surface was observed to some extent where large grain boundaries are represented .When organic acid added , the leveling effect improved to some extent where large protrusions are disappeared and large grain boundaries which diminished at lower concentration of organic acid (fig 4c &4e).



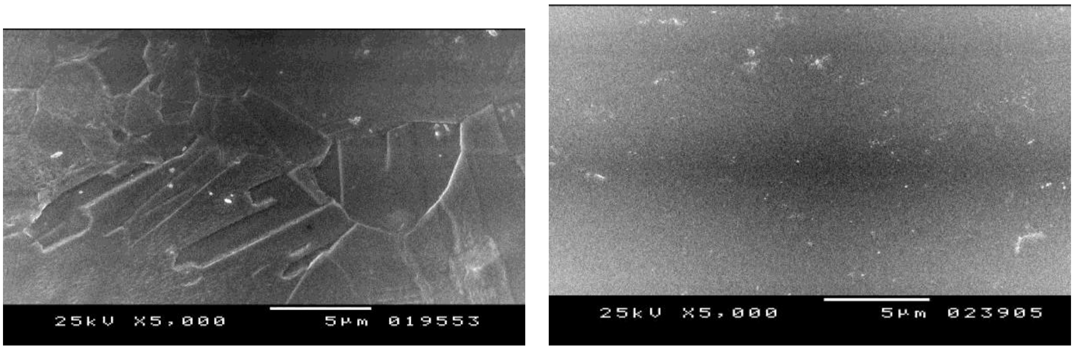
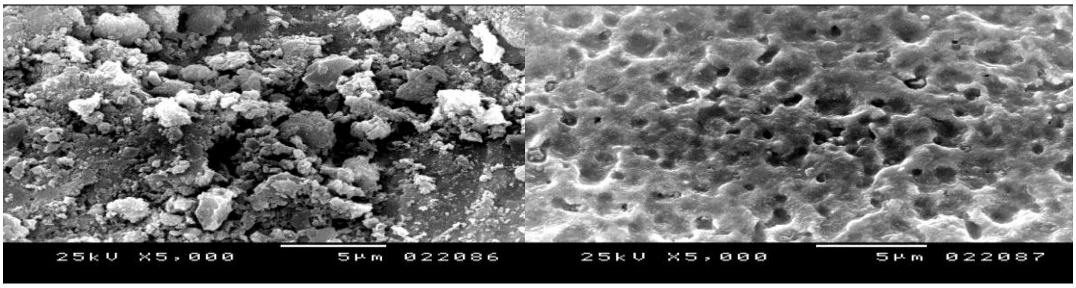
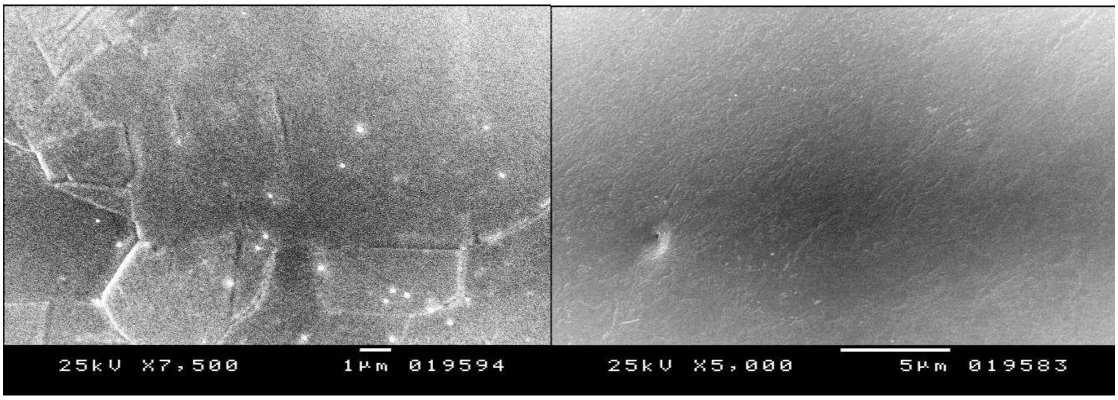


Figure 4 a. Raw sample before polishing; b. After electropolishing without addition (blank); c. After EP +2 × 10 $^{-4}$ mol/l of lactic acid.; d. After EP +7 × 10 $^{-4}$ mol/l of lactic acid.; e. After EP +2 × 10 $^{-4}$ mol/l of mandolic acid.; f. After EP +7 × 10 $^{-4}$ mol/l of l mandolic acid.

At higher concentration of organic acid (fig 4d &4f), a well polished surface was obtained where grain boundaries are completely disappeared and a smooth and completely uniform surface was obtained.

In order to study the electropolishing behavior of steel in the absence and presence of organic acid , Raw sample (Fig.5a) looked bumpy and appeared to have holes .A large number of lowest point with large size and high depth distributed over the surface are seen. But, after the EP in 8M H_3PO_4, only a slim difference was monitored more than raw sample, where some numbers of pits are still observed. The specimen surface was smooth to some extent, where levelling and brightening occur and some deep cavities were filled up (Fig. 5b).





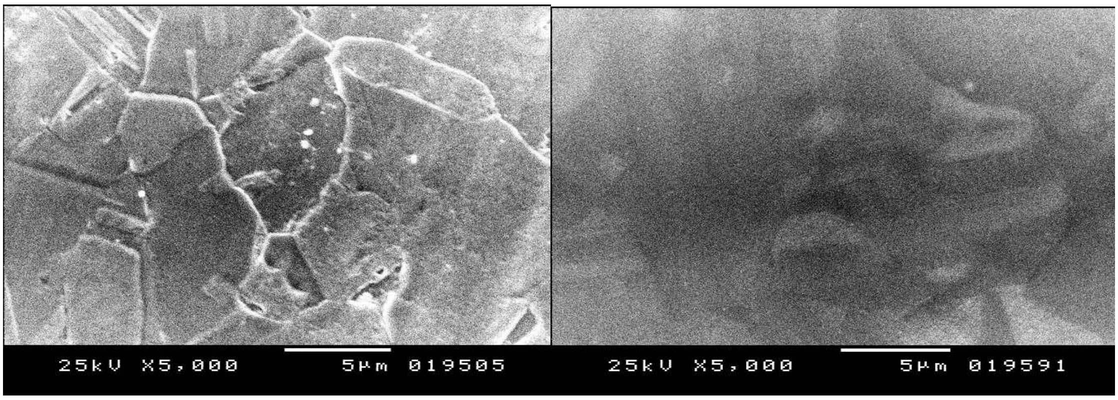


Figure 5 a. Raw sample before polishing. b. After electropolishing without addition (blank). c. After EP +2 × 10 $^{-4}$ mol/l of lactic acid. d. After EP +7 × 10 $^{-4}$ mol/l of lactic acid. e. After EP +2 × 10 $^{-4}$ mol/l of mandolic acid. f. After EP +7 × 10 $^{-4}$ mol/l of l mandolic acid.

After addition of low concentration of organic acid (fig.5c &5e) .Only a slight difference was observed compared to blank, where the pits decrease gradually and some protrusions are still represented on the surface of steel but it appears uniform more than blank. As represented in fig 5d&5f obviously the leveling and brightening effects were markedly get better by the adding of high concentration of organic acid where high concentration of organic acid are filling up the grooves and grain boundaries, also etching effect are eliminated.

3.5.2. Surface roughness

Table 4. Measured roughness (Ra) , Rq(RMS) , Rz and Peak - valley ratio of copper and steel samples

Copper						
			mandolic acid		lactic acid	
ASE Conc.(mol/l)	**Raw sample**	**0.00**	2 × 10 $^{-4}$	7 × 10 $^{-4}$	2 × 10 $^{-4}$	7× 10 $^{-4}$
Ra (µm)	**0.92**	**0.66**	**0.44**	**0.13**	**0.38**	**0.05**
Rq (µm)	**2.50**	**0.87**	**0.64**	**0.42**	**0.56**	**0.35**
Rz (µm)	**3.66**	**2.00**	**1.67**	**1.32**	**1.45**	**1.23**
PV (µm)	**27.6**	**8.26**	**7.52**	**5.53**	**6.45**	**4.22**
Steel						
			mandolic acid		lactic acid	
ASE Conc.(mol/l)	**Raw sample**	**0.00**	2 × 10 $^{-4}$	7 × 10 $^{-4}$	2 × 10 $^{-4}$	7× 10 $^{-4}$
Ra (µm)	**1.32**	**0.92**	**0.57**	**0.30**	**0.41**	**0.14**
Rq (µm)	**3.1**	**1.25**	**0.79**	**0.54**	**0.61**	**0.41**
Rz (µm)	**4.22**	**2.36**	**1.88**	**1.53**	**1.53**	**1.30**
PV (µm)	**32.55**	**11.56**	**8.92**	**6.42**	**7.32**	**5.36**

As a quantitative characterization of the surface finish, Table 4 summarizes the average roughness (R_a) measured on the copper and steel surface electropolished under the designated conditions resulted in a roughness on the level of a few microns. From the Table 4, the surface roughness will be reduced by the addition of different type of organic acid. Since the trends of Ra and RMS are almost the same, only Ra values are provided for the following discussion.

It is observed that the average roughness (R_a) is reduced by adding of organic acid particularly at higher concentration at both steel and copper samples.

This result is related to the differences in dissolution rate across grains,significant EP development is found under the conditions. According to the $R_{a\ values}$ results in not only a smoother surface at macroscopic scale ,but also a more homogeneous polishing across grains.

3.6. Comparasion between copper and steel in polishing and dissolution behavior

Organic acid recorded higher inhibition percentage for steel dissolution more than copper dissolution , organic acid has more positive effect on surface morphology of copper more than steel ,in the presence of organic acid, the surface roughness of copper decrease to a great extent more than steel sample. No preferential dissolution is observed at grain boundaries for copper samples due to the crystal orientation , also , The sharp grain boundaries may be related to etching or macrosmoothing is observed for steel samples[32,33].

4. CONCLUSION

- Lactic and manodolic acid have retardation, behavior in dissolution bath for copper and steel in 8M H_3PO_4.
- The retardation behavior of lactic and manodolic acid confirmed by weight loss measurements.
- The enhancement of the surface morphology and decrease in surface roughness was achieved by the addition of Lactic and manodolic acid to the electrolytic solution.
- Improvement produced in EP by the studied compounds was due to the adsorption of such molecules on the anode surface

References

1. K.P Rajurkr, S.C Tam. *J. Mater*. Process. *Technol*, *35*(6) (*1992) 83*
2. R. Sautebin, H. Froidevaux, D. Landolt, *J. Electrochem. Soc*. 127 (1980) 1096.
3. *F*.M.Abouzeid,*asian journal of chemistry*, 27(12)(2015)4337.
4. A.A.Taha ,H.H. Abdel Rahman,A.M.Ahmed, F.M.Abouzeid, *Int. J. Electrochem. Sci.,* 8 (2013) 9041 .
5. A.A.Taha, H.H. Abdel Rahman, F.M.Abouzeid , *Int. J. Electrochem. Sci*., 8 (2013) 6744 .
6. M. M .Lohrengel. and C.Rosenkranz, *Corros. Sci*, 47 (2005) 785.
7. O. Piotrowski, C. Madore, D. Landolt, *J. Electrochem. Soc*. 145 (1998) 2362.

8. C. Trepanier, M. Tabrizian, L.H .Yahia, L. Bilodeau and D. L. Piron. *J. Biomed Mater Res*, 43(4) (1998) 433.
9. O. Cisse, O. Savadogo, M. Wu and L. Yahia, . J Biomed Mater Res, 61(3) (2002) 339.
10. C. Trepanier, T.K. Leung, M. Tabrizian, L.H. Yahia, J.-G. Bienvenu, J.-F. Taguay, D.L. Piron and L. Bilodeau, . *J Biomed Mater Res*, 48(2) (1999)165.
11. P. A. Jacquet, *Bull. Soc. Chim. France*, 3(1936)705.
12. L .Capdecomme and M.Ortiac, *Comt. rend*., 213(1941)383.
13. H. P.Walton, *J. Electrochem. Soc.*, 97(1950) 219
14. P. A. Jacquet, *Compt. rend*., 202(1936) 402.
15. J. Elmore, J.*Appl. Physics*, 11 (1950)797
16. J. Elmore, *J. Appl. Physics*, 10 (1940)727.
17. R.R. Annand, R.M. Hurd, N. Hackerman, *J.Electrochem. Soc*., 112 (1965) 1968.
18. E.Z. Cook, N. Hackerman, J. *Phys. Chem*., 55 (1951) 549
19. J. Bordeaux, N. Hackerman, *J. Phys. Chem*., 61 (1957)1329
20. A. Singh, I. Ahamad, V.K. Singh, M.A. Quraishi, *J. Solid State Electrochem*., 15 (2011) 1087
21. M.H. Hussin, M.J. Kassim, *Mater. Chem. Phys*., 125 (2011) 461
22. E.E. Oguzie, *Corros. Sci*., 50 (2008) 2993.
23. I. Ahamad, R. Prasad, M.A. Quraishi, *J. Solid State Electrochem*., 14 (2010) 2095.
24. G. Gunasekaran, L.R. Chauhan, *Electrochim. Acta*., 49 (2004) 4387.
25. M.S.S. Morad, A. El-Hagag, A. Hermas, M.A.S. Aal, *J. Chem. Technol. Biotechnol*., 77 (2002) 486.
26. A.K. Singh, M.A. Quraishi, *Corros. Sci*., 52 (2010) 152.
27. R. Solmaz, *Corros. Sci*., 79 (2014) 169.
28. M. Bouklah, B. Hammouti, M. Lagren'ee, F. Bentiss, *Corros. Sci*., 48 (2006) 2831
29. I. Ahamad, R. Prasad, M.A. Quraishi, *Corros. Sci*., 52 (2010) 933
30. N.O. Eddy, E.E. Ebenso, U.J. Ibok, *J. Argent. Chem. Soc*., 97 (2009) 178
31. K.M. Ismail, *Electrochim. Acta*, 52 (2007) 7811
32. A.A. Taha, A.M. Ahmed, H.H. Abdel Rahman, F.M. Abouzeid, *Applied Surface Science* 277 (2013) 155.
33. *F*.M.Abouzeid, *Asian journal of chemistry*, 28(4)(2016)743.