

A kinetic study of the electropolishing Of cubiform surfaces under natural convection conditions
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Receiving Date: 14-02-2011 - **Accept Date:** 14-06-2011

Abstract

The rates of electropolishing copper cubiform surfaces in H_3PO_4 were studied under natural convection conditions in a two-compartment cell. The following variables were studied : anode shape and its dimensions (cubiform) , H_3PO_4 concentration, temperature and viscosity of polishing solution.

The dimensions of cubiform of the anode were found to have no effect on the polishing current density. Also it was found that the polishing current density to increase with decreasing H_3PO_4 concentration and to increase with increasing temperature. The effect of the temperature on the polishing current density was found to obey the Arrhenius equation with an activation energy of $4.9 \text{ kcal mol}^{-1}$. The polishing current density was found to decrease with increasing viscosity of electropolishing solution.

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Introduction

Electropolishing is widely used in industry and research. In such processes the metal to be polished forms the anode in an electrolytic cell. When the current passes the dissolution of the metal in its solution occurs in such a way that irregularities on the surface are removed and the surface becomes smooth and bright.

A machined surface of a metal may be considered to consist of series of hills and valleys. In order to produce a truly flat surface, the irregularities must be removed by using electropolishing process.

In mechanism of electropolishing it was found that the loss of metal (anode) from peak areas through the diffusion layer at a faster rate than metal loss from the valleys. Jacquet [1] supposed that the current density over elevated spots of the anode would be greater than that over the depressed regions, because the electrolytic resistance across the diffusion layer is greater adjacent to these latter areas owing to the greater width of the layer [2,3]. Hickling and Higgins [4,5] suggested that diffusion of metal salt out a scratch or cavity is slow compared with that over a ridge or peak. As a result, provided enough current passes, the scratches and pores become plugged by salt, but the peaks continue to dissolve a way. On this view, the anode initially dissolves uniformly, then non-uniformly when the pores are plugged and finally uniformly after the peaks have disappeared.

If do comparison between electrolytic and mechanical polishing found; with a little practice the progressive smoothing of a metal may be achieved by mechanical polishing, but considerable dexterity is often required to avoid surface distortion of the metal structure resulted from the generation of heat by friction. The amorphous Beilby layer which is created at and just below the surface of a mechanically polished metal is avoided by the technique of electrolytic polishing. In this process the metal to be polished is made the anode in suitable electrolyte, dissolution takes place preferentially from the raised portions of the surface, and after a short time any scratches would have disappeared. An electropolished surface is very smooth and some times has a mirror finish[2].

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Electropolishing finds considerable use in metallographic examination for not only is the grain structure at the polished surface undistorted but voids, fissures, and inclusions are much more readily identified. In contrast, mechanical polishing often either disguises voids by flowing the metal over them, or may fill them with polishing powder and other debris so that they appear as inclusions. Large and irregularly shaped articles are more quickly and efficiently polished electrolytically [2].

The final preparation of surfaces before electroplating may be carried out by electropolishing. It is found that the plating adheres better to an electropolished surface. This is probably a result of the undistorted structure of the electropolished metal surface.

Electropolishing is quicker and involves less labour than mechanical polishing, and produces a surface which is free from stress [6].

Electropolishing as a diffusion-controlled electrochemical process which takes place at the limiting current density (polishing current density) [1,7,8] whose value is determined by the rate of transfer of Cu^{+2} from the diffusion layer to the bulk of the solution [1,9]. In an unstirred solution the transfer of Cu^{+2} from the anode surface to the solution bulk takes place mainly by diffusion and by natural convection arising from a density difference between the interfacial solution (saturated with copper phosphate) and the bulk solution (H_3PO_4). The intensity of the natural convection depends on the electrode geometry and dimensions as well as on the physical properties of the solution.

The rate of electropolishing depends on the geometry of the surface to be polished [10]. Previous studies have covered geometries such as vertical plates [11], horizontal plates [12], ring discs [13,14], vertical cylinders [15], horizontal cylinders [16,17] and horizontal tubes [18]. To date, no work has been reported on the polishing rates of cubiform surfaces (cubic shape) despite the importance of this geometry in the engineering field, which that shape is considered as one of the complicated shapes. The aim of the present work was to investigate the rates of electropolishing of such surfaces as a function of the acid concentration, dimensions of cubiform anode, solution temperature and solution viscosity. To

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this end the electropolishing of cubiform surfaces of copper in H_3PO_4 was chosen for the present study.

Experimental technique

The cell used in the present work consisted of a cylindrical glass container 11 cm in diameter and 15 cm high divided into two compartments by a cylindrical porous poly vinyl chloride diaphragm 9 cm in diameter. The diaphragm served to prevent the stirring caused by the hydrogen bubbles evolved at the cathode from interfering with the natural convection process at the anode. The cathode comprised a cylindrical copper sheet 10 cm in diameter and 14 cm high placed in the outer compartment of the cell. By virtue of the large cathode area compared with the anode, the cathode also acted as a reference electrode against which the anode potential was measured. The anode consisted of a copper cubiform ($2 \times 2 \times 2$) cm , ($3 \times 3 \times 3$) cm and ($4 \times 4 \times 4$) cm in dimensions. The electrical circuit consisted of a 6 volt d.c., power supply, a variable resistance and a multi range ammeter connected in series with the cell. A high impedance voltmeter was connected in parallel with the cell to measure the cell potential. The three concentration of H_3PO_4 used were 5,7 and 9M; all solution were prepared from AnalaR grade H_3PO_4 acid. Polarization curves from which the limiting current density (polishing current density) was determined were plotted by increasing the applied current stepwise and by measuring the corresponding steady state potential. Before each run the anode was degreased with trichloroethylene, treated with fine emery paper, washed with alcohol and rinsed in distillate water. The anode was positioned half-way between the top and the bottom of the electrolyte which almost filled the container. An insulated copper wire (2 mm in diameter) brazed to the cubic copper acted to hold the anode in position and to feed it with current. To regulate the demand temperature (20,30,40) C° , the cell was placed in a thermostat controlled water bath. Each run was carried out using a fresh solution and a new anode to avoid any error which might arise from the slight change in the dimensions of cubiform during electropolishing. The dimensions of cubiform (cubic shape) were measured before and after each experiment to check that no significant dimensional change had taken place. Each experiment was repeated twice and needed thirty minutes to carry out. All the cubic shapes were made of electrolytically pure copper.

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Results and Discussion

Figure (1) shows a set of typical polarization curves of current density versus potential obtained at various H_3PO_4 concentrations. These curves with well-defined limiting current density plateau where polishing process takes place at various concentration of H_3PO_4 . Figure (2) Shows that the limiting current density at which the polishing takes place decreases with increasing H_3PO_4 concentration with in the range studied (5-9) M ; this is in agreement with the findings of other workers who studied the same range of concentration using different anode geometries [4,19]. The effect of the H_3PO_4 concentration on the value of the limiting current density (polishing current density) can be explained on the basis of the mass transfer equation [10]:

$$J_L = \frac{ZFD}{s} C_{Cu^{+2}} \text{ -----(1)}$$

An increase in H_3PO_4 concentration decreases the saturation solubility of copper phosphate ($C_{Cu^{+2}}$) with a consequent decrease in the limiting current density (polishing current density), according to equ.(1). An increase in H_3PO_4 concentration also increase the viscosity of the solution, shows figure (7,8); this results in decrease in the diffusivity D of the $C_{Cu^{+2}}$ ions and an increase in the diffusion layer thickness with consequent decrease in the limiting current density value according to the equ.(1). To relate the limiting current density quantitatively to the H_3PO_4 concentration, two approaches are possible:

(i) The first approach is a theoretical approach based on the application of the theory of mass transfer [10] to the polishing process to derive an equation which relates to the polishing current density to the physical properties of the solution and to other variables. The disadvantage of the resulting equation is that it includes many parameters which should be determined before hand, such as the solution viscosity, the density in the bulk and at the interface, the saturation solubility of copper phosphate in H_3PO_4 and the diffusivity of the copper ions in H_3PO_4 .

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(ii) The second approach, which is followed here, is a simple empirical approach which relates the polishing current density directly to the H_3PO_4 concentration. Figure (5) shows that the polishing current density (limiting current density) can be related to the acid concentration by the equation:

$$J_L = a C^{-1.8} \quad \text{-----}(2)$$

Figure (3,6) shows that the effect of the temperature on the polishing current density

$$J_L = J_o \exp \left(- \frac{E}{RT} \right) \quad \text{-----}(3)$$

The activation energy E for the electropolishing process was found to be $4.9 \text{ kcal mol}^{-1}$. This value is of the same order of magnitude as the values determined by other workers [13,20,21]. The value of the activation energy and the shape of the polarization curves(Fig.1) confirm the fact that electropolishing is a diffusion-controlled process [22].

Figure (4) shows the effect of dimensions of cubiform surface (anode) on the value of the polishing current density; it is found that the dimensions of cubic shape (anode) has almost no effect on the polishing current density with in the range studied in this work. This behaviour suggests that copper ions are transferred a way from the anode surface during electropolishing by a natural convection turbulent flow mechanism. According to the boundary layer theory, when the flow is turbulent the diffusion layer thickness and the limiting current density (polishing current density) are independent of the characteristics length of the electrode [10]. Also it is found due to the boundary layer theory; when the natural convection flow created by a density difference between the electrode surface and the bulk solution is turbulent, the electrode dimensions (height or diameter) do not affect the rate of mass transfer or the polishing current density [10]. Therefore it is concluded that the flow in the present work or experiments is turbulent.

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The surface products from that electropolishing process is found very smoothing and brightening. These properties can be related to:

(i) The formation of relatively thick viscous layer of reaction products around the anode. This layer controls the smoothing action.

(ii) The formation of thin oxide film on the surface of the anode. This film controls the brightening action.

These processes are related to the well-known anodic phenomena of concentration over potential and passivity [2,6,7].

Conclusion

- 1- The polishing current density increases as the concentration of H_3PO_4 decreases at the range studied (5-9) M .
- 2- The polishing current density increases as the temperature increases at the range temperature studied (20 – 40) °C.
- 3- Cubiform dimensions of the anode range between (2*2*2 – 4*4*4) cm or the volume of Cubiform of the anode range between (8-64) cm^3 have no effect on the polishing current density.
- 4- The polishing current density decreases with increase in the kinematic viscosity of solution.
- 5- The effect of temperature on the polishing current density was found to obey the Arrhenius equation. The activation energy for the electropolishing process was calculated and found to be (4.9) Kcal mol^{-1} .

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Nomenclature

- E : activation energy (cal mol⁻¹).
- C : H₃PO₄ concentration (mol l⁻¹).
- J_L : limiting current density (mA cm⁻²).
- J_o : constant.
- a : constant.
- R : gas constant (cal mol⁻¹ K⁻¹).
- T : temperature (K).
- C_{Cu+2} : copper ion concentration (mol cm⁻³).

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D : diffusivity of copper ions ($\text{cm}^2 \text{s}^{-1}$).

F : Faraday constant (96500 c).

δ : diffusion layer thickness (cm).

Z : number of electrons involved in the reaction.

Cubiform dimensions(cm)	Temperature C°	Concentration M	Polishing current density mA/cm ²
2 * 2 * 2	20	5	68
2 * 2 * 2	20	7	36
2 * 2 * 2	20	9	24
2 * 2 * 2	30	5	76
2 * 2 * 2	30	7	54
2 * 2 * 2	30	9	28
2 * 2 * 2	40	5	120
2 * 2 * 2	40	7	65
2 * 2 * 2	40	9	42
3 * 3 * 3	20	5	67
3 * 3 * 3	20	7	35
3 * 3 * 3	20	9	26
3 * 3 * 3	30	5	78
3 * 3 * 3	30	7	59
3 * 3 * 3	30	9	30
3 * 3 * 3	40	5	125
3 * 3 * 3	40	7	64
3 * 3 * 3	40	9	40
4 * 4 * 4	20	5	70
4 * 4 * 4	20	7	34
4 * 4 * 4	20	9	26
4 * 4 * 4	30	5	75
4 * 4 * 4	30	7	57

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4 * 4 * 4	30	9	32
4 * 4 * 4	40	5	118
4 * 4 * 4	40	7	68
4 * 4 * 4	40	9	38

Table (1) The effect of concentration, temperature and the dimensions of anode Cubiform on the polishing current density.

Temperature C°	Concentration M	Kinematic viscosity mm ² /sec
20	5	2.48
20	7	4.02
20	9	6.34
30	5	1.27
30	7	3.32
30	9	5.41
40	5	0.78
40	7	2.94
40	9	4.48

Table (2) Kinematic viscosity of H₃PO₄ at various concentrations and temperatures

Concentration=5 M		Concentration=7 M		Concentration=9 M	
Current density mA/cm ²	Cell potential mv	Current density mA/cm ²	Cell potential mv	Current density mA/cm ²	Cell potential mv
9	450	15	640	5	600
37	750	38	760	17	850
55	1050	40	1000	27	1150
71	1250	52	1140	38	1250
83	1480	65	1250	28	1620

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76	1750	54	1730	28	2125
76	2000	53	2150	28	2480
75	2250	54	2500	30	2750
76	2680	62	2750	40	2830
85	2820	75	3040	50	3050
96	3150			62	3250

Table (3) Cubiform dimensions (2*2*2) cm , Temperature = 30 C°

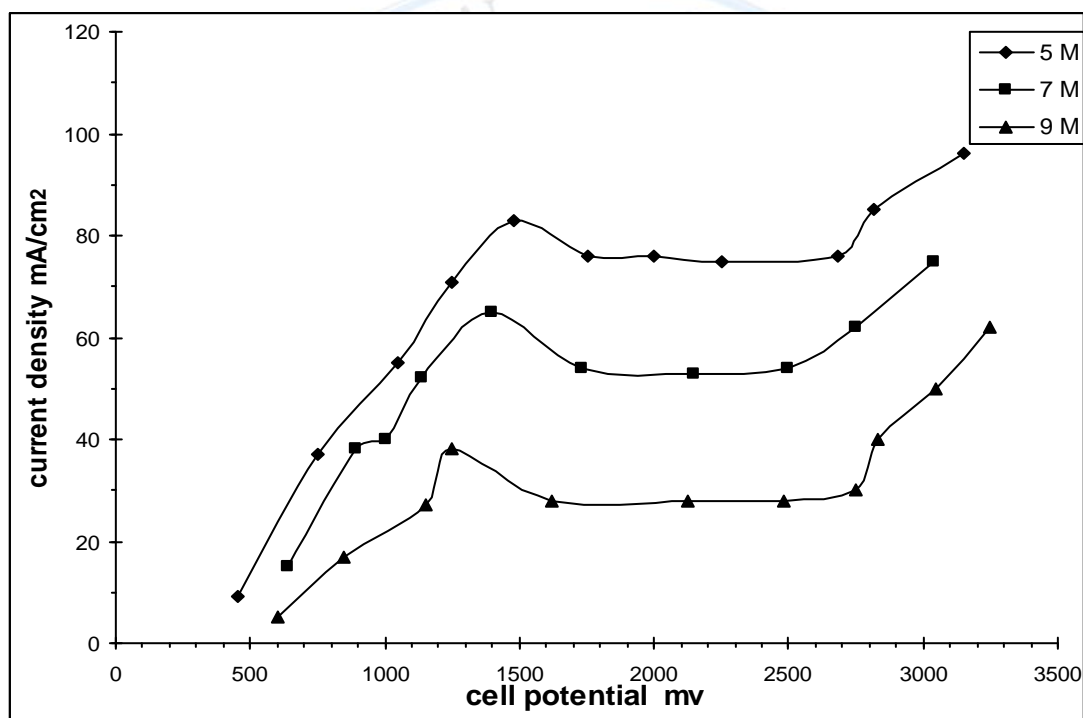


Fig. (1) Typical polarization curves obtained for various concentration of H₃PO₄ (cubiform dimension 2*2*2 cm, temperature 30C°)

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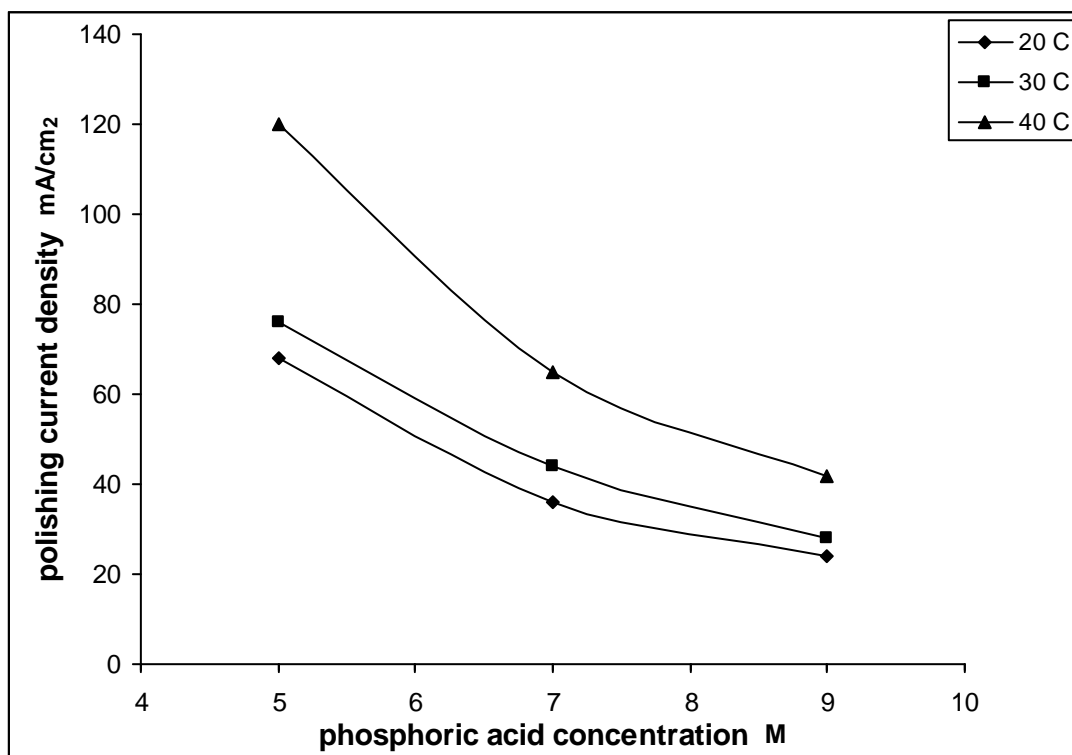


Fig.(2) Effect of phosphoric acid concentration on the polishing current (cubiform dimension 2*2*2 cm) for various temperatures.

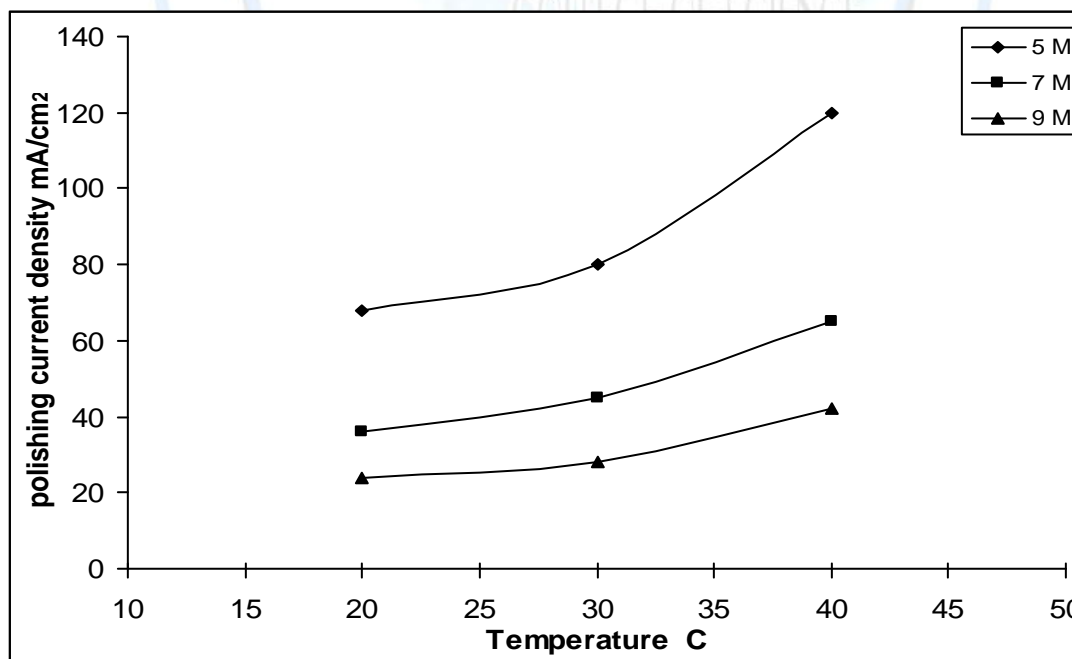


Fig.(3) Effect of temperature on the polishing current (cubiform dimension 2*2*2 cm) for various H₃PO₄ concentrations

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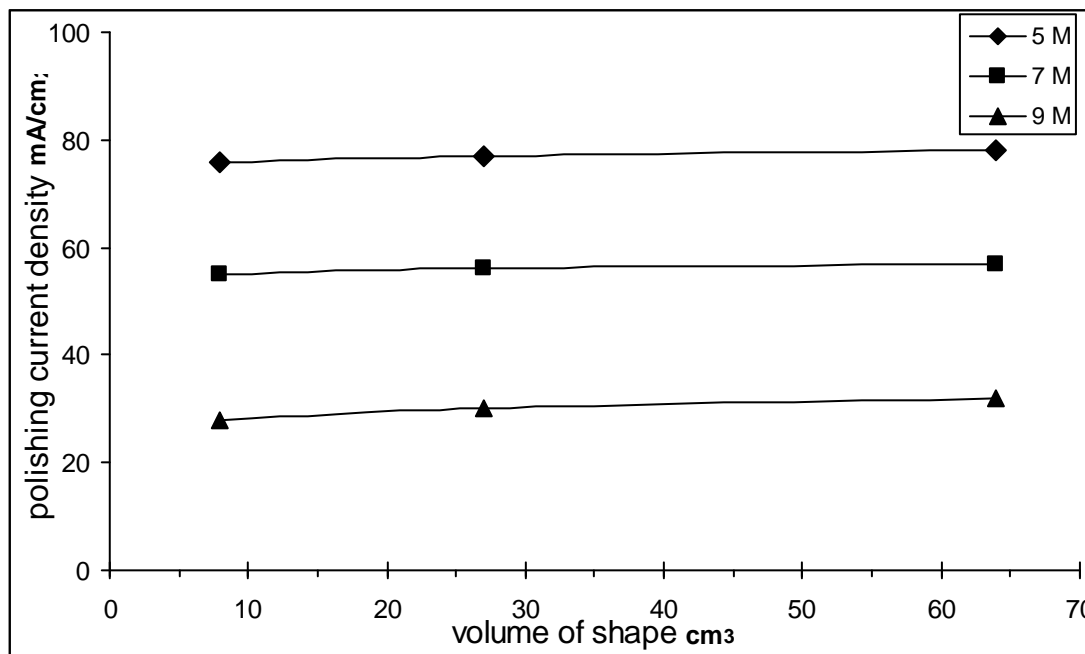


Fig.(4) Effect of cubiform dimensions (volume shape) on the polishing current (temperature 30C°) for various H₃PO₄ concentrations

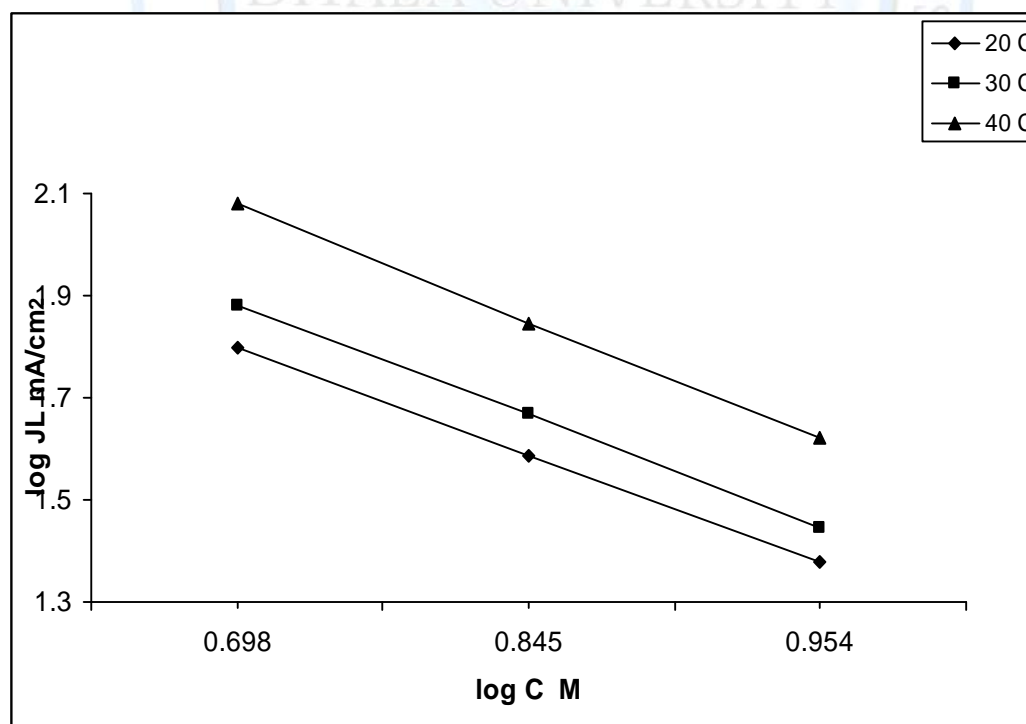


Fig.(5) Log J_L vs LogC for various temperatures (cubiform dimensions 2*2*2 cm)

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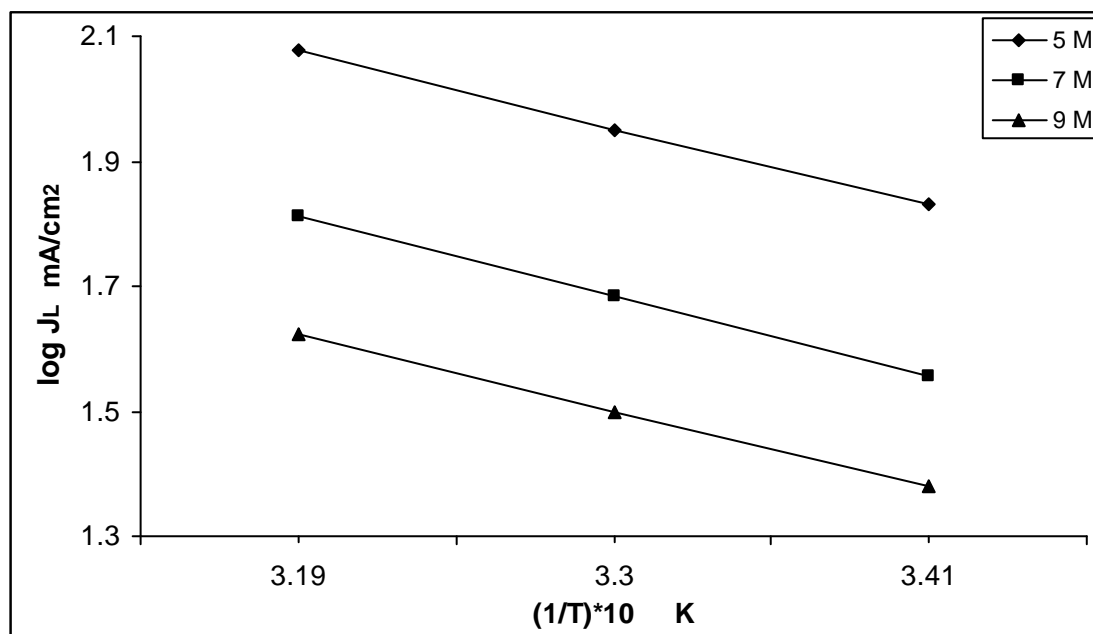


Fig.(6) Arrhenius activation energy plot (cubiform dimensions 2*2*2 cm) for various H₃PO₄ concentrations

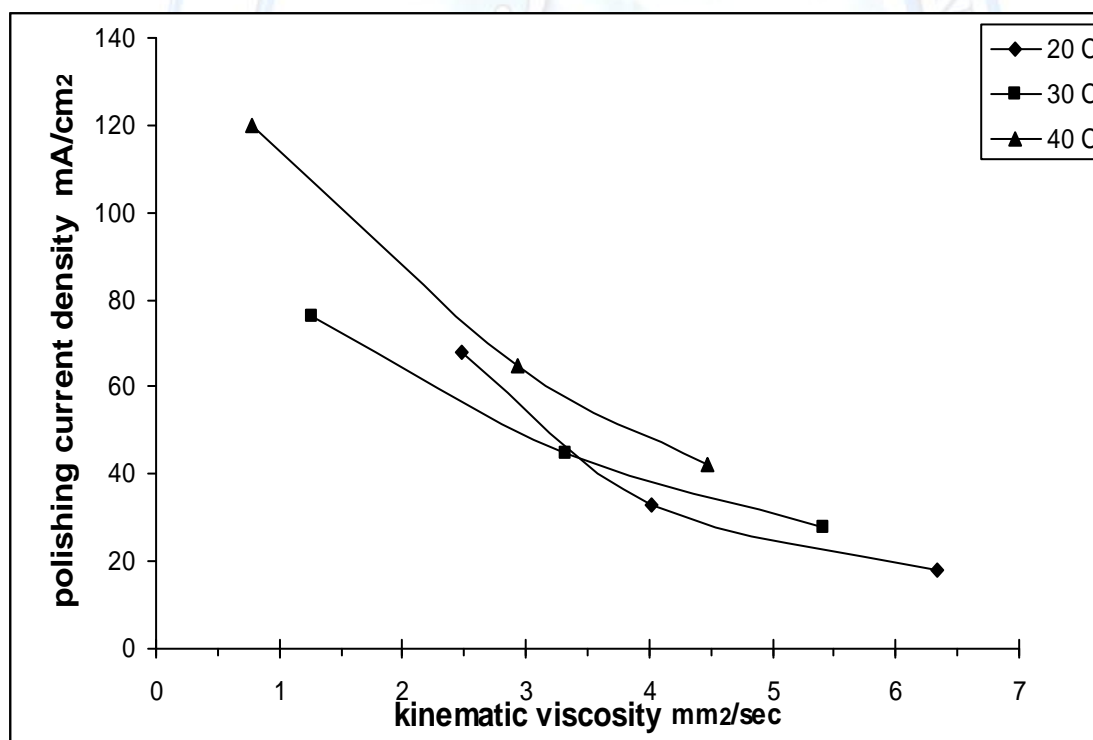


Fig.(7) Effect of kinematic viscosity of solution on the polishing current (cubiform dimensions 2*2*2 cm) for various temperatures

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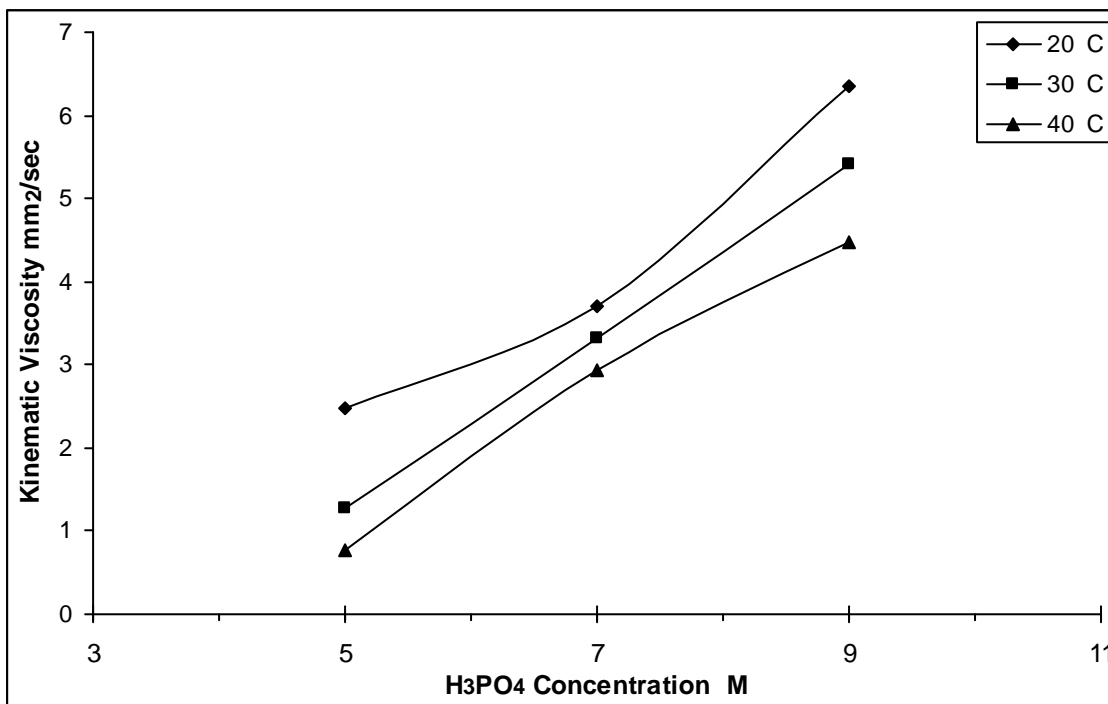


Fig.(8) Kinematic viscosity of solution vs H₃PO₄ concentration at various temperatures

