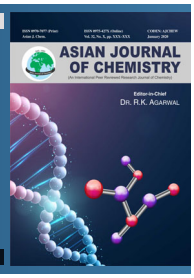
Asian Journal of Chemistry; Vol. 32, No. 4 (2020), 912-922

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22501



Copper Electropolishing in Phosphoric Acid under Normal and Forced Convection Conditions in Presence of Some Pharmaceutical Drugs

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Received: 16 October 2019; *Accepted*: 9 December 2019; *Published online*: 25 February 2020; AJC-19812

Some pharmaceutical drugs namely valsartan, hydrocholorothiazide, erythromycin thiocynate and diclofenac potassium were studied as chemical additions for enhancing the finished copper surface attained. Anode potential-limiting current relationship was measured and comparing of gradually increasing pharmaceutical compound concentrations (from 1×10^{-4} to 7×10^{-4} M). Copper dissolution behaviour in presence of pharmaceutical compounds was studied under natural convection [rotating cylinder (RCE) and rotating disc electrode (RDE)] as forced convection. The limiting current was found to diminish with enlarging additives concentration and increase with increasing temperature (293-313 K). Activation energies values confirm that reaction rate was diffusion controlled. The results showed that the improvement produced in electropolishing in presence of pharmaceutical compounds occurs through adsorption of their molecules above metal surface. All the pharmaceutical compounds adsorption process obey kinetic-thermodynamic model. The data under different conditions were controlled by dimensionless correlations *viz*. Sherwood, Schmidt and Reynolds numbers. Surface morphology also confirmed that an addition of pharmaceutical compound to copper dissolution bath enhance surface appearance and its texture quality to great extent.

Keywords: Copper, Electropolishing, Scanning electron microscope, Pharmaceutical compounds.

INTRODUCTION

Electropolishing (EP) is extensively used procedure in manufacturing, useful to a great metals and alloys figures for debarring in addition to removal of tarnishing and brightening. Electropolishing which is achieved *via* metal surface anodic dissolution which controlled in appropriate electrolyte and can improve planarization efficacy of metal surface [1,2], where the peaks and valleys depth differences are reduced [3,4]. It classically arises at the limiting current of mass transfer process, where the surface of metal become silky and even. Concurrently, throughout electropolishing, several etched pits and defects over the metal surface can be formed owing to oxygen gases evolution adjoining to the anode surface at a potential elevated than the limiting current plateau [5-7]. To reduce the incidence of surface defects formed on copper during electropolishing different additives were added to polishing bath [8-12].

But so far we are aware this is the first report on the use of pharmaceutical compounds as additives during electropolishing process. Recently pharmaceutical compounds have been used as corrosion restrainers [13]. The use of pharmaceutical compounds for the inhibition of the metal corrosions has some advantages over the use of some organic/inorganic inhibitors because they are non-toxic, cheap and environmental friendly. They can easily produce and purified. Generally many authors [14-17] agree that drugs are inhibitors that can compete favourably with green eco-friendly restrainers and most drugs can be synthesized from natural product. Hence the aim of this research is to examine the copper dissolution behaviour in presence of pharmaceutical compounds. The investigated compounds are of interest because their solubility in water, safe use, also high molecular size and containing electronegative atoms such as N, S and O in their molecules. These compounds can be easily synthesized from relatively cheap raw materials and are biodegradable and might accommodate at least some of the environmental restriction.

EXPERIMENTAL

Chemical composition of copper is Sn: 0.005, Pb: 0.003, Ag: 0.011, Cd: 0.001 and Cu: 99.98, H_3PO_4 (85 % w/w), completed by BDH. The chosen pharmaceutical compounds of pure quality (> 97 %) were Fluka products and used without purification. De-ionized water with > 18 MΩ cm as measured resistivity was used in solutions preparation. The concentrations of pharmaceutical compounds cover a range from 1×10^{-4} to 7×10^{-4} mol/L.

Galvanostatic polarization

Natural convection: The cell used consists of rectangular plexi glass container with a base of 15 × 5 and a height of 10 cm with copper sheets electrodes. Electrode separation was 15 cm. The construction of electrical circuit was as follows: power supply (6V DC), multi range ammeter, voltammeter high impedance with and variable resistance were connected in a sequence through cell. Temperature regulation (20, 30, 40 and 50 °C) ± 0.5 °C was achieved *via* thermostatic water bath containing cell.

Forced convection: Cylindrical plexi glass container consists of 20 cm height and 15 cm diameter. Rotating copper rod of 2 cm diameter acts as anode which is isolated by epoxy resin [disc: working area (bottom of the metal cylinder is exposed to electrolyte) is 3.14 cm^2] and steel rod of 2 cm diameter and 2 cm working height (cylinder: working area is 12.56 cm^2) connected to the shaft of a variable speed through a plastic sleeve. Metal cylindrical cathode have 5 cm diameter. The back of the cathode were coated by epoxy resin. Motor rotation speed ranged from 125 to 750 rpm was controlled with optical tachometer.

Surface characterization *via* scanning electron microscopy (SEM): Images of scanning electron microscope were taken using (JEOL, JSM-5300, scanning microscope, OXFORD instrument). The sample was of 1 cm × 1 cm.

Physical properties of the solutions: The physical properties, density (ρ) and viscosity (μ) of the solutions were determined experimentally using typical methods. The diffusion coefficient of Cu^{2+} in different H_3PO_4 concentrations was determined by measuring the limiting current of the copper rotating disc anodic dissolution in H_3PO_4 through applying Levich equation [18].

$$i_L = 0.62\ ZFD^{0.667}\ \nu^{-0.167}\ C_{Fe^{3+}}\omega^{0.5} \quad (1)$$

while diffusion coefficient for copper dissolution using rotating cylinder electrode [18].

$$i_L = 0.079\ ZFD^{0.644}\ d^{-0.3}\nu^{-0.344}\ C_{Fe^{3+}}\omega^{0.7} \quad (2)$$

where i_L is the limiting current density and represented as $i_L = i_L/A$ (A cm^{-2}), where A is the cross-sectional area of copper disc or cylinder, z is the number of electrons involved in the reaction, F is Faraday constant, D is the diffusion coefficient of dissolving species, ν is the kinematic viscosity, ω is the electrode rotation rate ($\omega = 2\pi$ rpm/60), $C_{Cu^{2+}}$ is the saturation solubility of copper phosphate in H_3PO_4 which determined by using Perkin Elemer 2380 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Leveling process in H_3PO_4: A typical polarization curve is obtained for an electrolyte consisting of orthophosphoric acid of concentrations ranged from 6 M to 14 M (Table-1). The curve (Fig. 1) is divided into three parts which are electrolytic etching, polishing and gas (O_2) evolution with pitting occurs. The influence of H_3PO_4 concentration on the i_L values can be clarified based on the mass transfer eqn. 3 [18-20].

TABLE-1
H_3PO_4 CONCENTRATION EFFECT ON THE COPPER ANODIC DISSOLUTION AT 20 °C

H_3PO_4 conc. (mol/L)	i_L (A)	$10^3\ C_{Cu^{2+}}$ (mol cm^{-3})	10^6 D ($cm^2\ s^{-1}$)	η (g $cm^{-1}\ s^{-1}$)
6	0.600	0.98	4.10	1.879
8	0.460	0.95	3.55	4.203
10	0.280	0.85	3.33	5.732
12	0.180	0.78	1.01	6.196
14	0.120	0.70	0.89	14.326

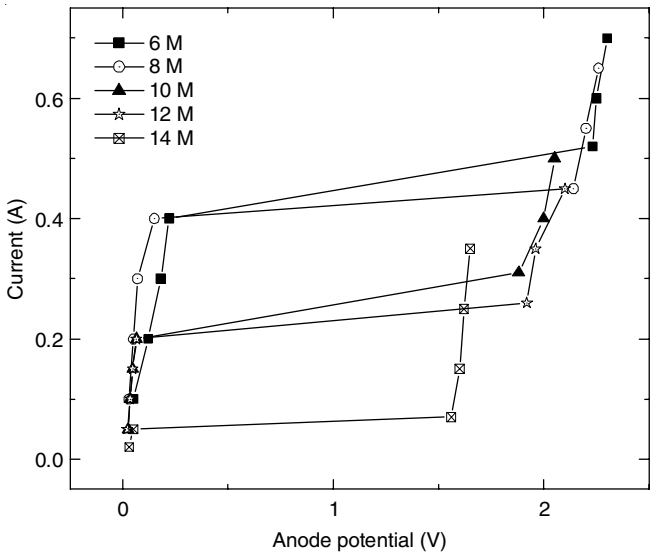

Fig. 1. Polarization curve for vertical copper plate electro-dissolution at 20 °C in the presence of different H_3PO_4 concentrations

$$i_L = \frac{ZFD}{\delta} C_{Cu^{2+}} \quad (3)$$

The saturation solubility of $Cu_3(PO_4)_2$ decreases as H_3PO_4 concentration increases (Table-1) resulting in reduction in i_L. Also, increasing H_3PO_4 concentration lead to increase in solution viscosity (η) so diffusivity of Cu^{2+} ion (D) will decrease and an diffusion layer thickness (δ) will increase resulting in diminish in i_L values. The limiting current performance through electropolishing of copper in H_3PO_4 (Fig. 1) is owing to the certainty that metal dissolution is controlled by mass transport [8,9], during the process, reaction products diffusion is limited and is considered as the rate determine step of overall reaction rate. The mechanism of precipitated salt-film engages diffusion rate limiting of dissolving metal cations from the anode surface into solution bulk [18,19]. At the i_L value, a saturated concentration of metallic cation thin salt film is in presence on the surface of anode and determine the rate at which metal ions depart the anode surface.

Electropolishing of copper in H_3PO_4 electrolyte in the presence of pharmaceutical compounds: The galvanostatic polarization curves of variable pharmaceutical compounds concentrations on behaviour of copper in 8 M H_3PO_4 solution

are presented in Fig. 2 and the limiting current (i_L) was obtained from the graph. The rate of metal dissolution (i_L) and efficiency percentage of retardation (IE %) for the investigated pharmaceutical compound with (1×10^{-4} to 7×10^{-4} mol/L) concentration range and temperatures ranged from 20 to 50 °C are given in Table-2.

In presence of valsartan (different concentrations) as an example of pharmaceutical compounds, the curve (Fig. 2) show a characteristic i_L plateau broaden above wide range of potential, which evidences that mass transport process controlled in existence of pharmaceutical compounds.

If the limiting current in absence of pharmaceutical compounds is $(i_L)_{blank}$ and in the presence of pharmaceutical compounds is $(i_L)_{Ph.cpds}$, then IE % can be estimated from the subsequent equation:

$$IE\ (\%) = \frac{I_{L(blank)} - I_{L(Ph.Cpds)}}{I_{L(blank)}} \times 100 \quad (4)$$

The addition of valsartan, hydrochlorothiazide, erythromycin thiocyanate and diclofenac potassium leads to decrease in i_L of copper dissolution process and increase in IE % value (Table-2).

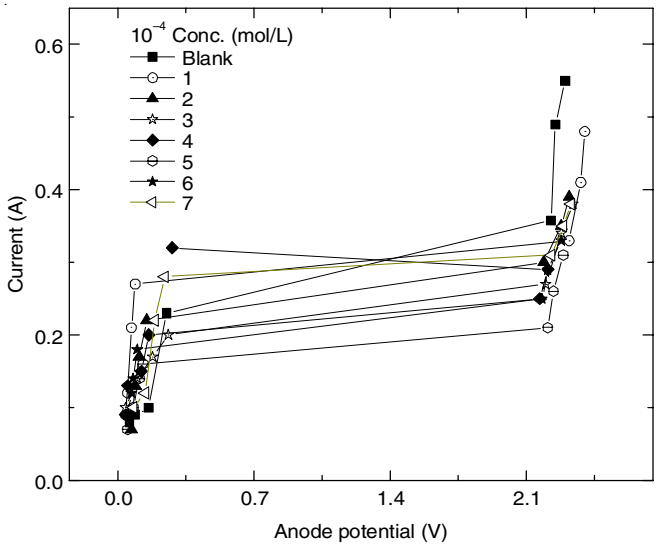

Fig. 2. Electropolishing polarization curves for of vertical copper plates in 8 M H_3PO_4 solution containing different concentrations of valsartan at 20 °C

Table-2 and Fig. 3 show that % IE increases as the studied pharmaceutical compounds concentration increases and tem-

TABLE-2
VALUES OF LIMITING CURRENT OF DISSOLUTION OF COPPER IN 8 M H_3PO_4 ACID IN THE ABSENCE AND PRESENCE OF PHARMACEUTICAL COMPOUNDS AT DIFFERENT TEMPERATURES

Pharmaceutical compounds	Conc. (mol/L)	20 °C	IE (%)	30 °C	IE (%)	40 °C	IE (%)	50 °C	IE (%)
Valsartan	0.0	0.50	–	0.64	–	0.76	–	0.85	–
	1.0×10^{-4}	0.39	22.00	0.55	14.06	0.69	9.21	0.79	7.06
	2.0×10^{-4}	0.37	26.00	0.52	18.75	0.66	13.16	0.77	9.41
	3.0×10^{-4}	0.36	28.00	0.49	23.44	0.64	15.79	0.74	12.94
	4.0×10^{-4}	0.34	32.00	0.46	28.13	0.61	19.74	0.72	15.29
	5.0×10^{-4}	0.32	36.00	0.44	31.25	0.58	23.68	0.69	18.82
	6.0×10^{-4}	0.30	40.00	0.42	34.38	0.56	26.32	0.67	21.18
	7.0×10^{-4}	0.28	44.00	0.40	37.50	0.51	32.89	0.63	25.88
Hydrochlorothiazide	0.0	0.50	–	0.64	–	0.76	–	0.85	–
	1.0×10^{-4}	0.4	20.00	0.54	15.63	0.66	13.16	0.77	9.41
	2.0×10^{-4}	0.39	22.00	0.51	20.31	0.64	15.79	0.75	11.76
	3.0×10^{-4}	0.36	28.00	0.48	25.00	0.61	19.74	0.73	14.12
	4.0×10^{-4}	0.33	34.00	0.46	28.13	0.57	25.00	0.71	16.47
	5.0×10^{-4}	0.32	36.00	0.45	29.69	0.55	27.63	0.69	18.82
	6.0×10^{-4}	0.3	40.00	0.41	35.94	0.51	32.89	0.67	21.18
	7.0×10^{-4}	0.41	18.00	0.55	14.06	0.67	11.84	0.76	10.59
Erythromycin thiocyanate	0.0	0.50	–	0.64	–	0.76	–	0.85	–
	1.0×10^{-4}	0.42	16.00	0.56	12.5	0.67	11.84	0.77	9.41
	2.0×10^{-4}	0.40	20.00	0.54	15.62	0.66	13.16	0.74	12.94
	3.0×10^{-4}	0.39	22.00	0.52	18.75	0.63	17.11	0.72	15.29
	4.0×10^{-4}	0.37	26.00	0.51	20.31	0.61	19.74	0.70	17.65
	5.0×10^{-4}	0.36	28.00	0.48	25.00	0.60	21.05	0.68	20.00
	6.0×10^{-4}	0.35	32.00	0.47	29.69	0.58	25.00	0.67	22.35
	7.0×10^{-4}	0.42	16.00	0.56	14.06	0.69	11.84	0.78	9.41
Diclofenac potassium	0.0	0.50	–	0.64	–	0.76	–	0.85	–
	1.0×10^{-4}	0.44	12.00	0.58	9.38	0.70	7.89	0.80	5.88
	2.0×10^{-4}	0.41	18.00	0.56	12.50	0.68	10.53	0.78	8.24
	3.0×10^{-4}	0.40	20.00	0.54	15.63	0.66	13.16	0.76	10.59
	4.0×10^{-4}	0.38	24.00	0.51	20.31	0.63	17.11	0.72	15.29
	5.0×10^{-4}	0.36	28.00	0.48	25.00	0.60	21.05	0.69	18.82
	6.0×10^{-4}	0.34	30.00	0.45	26.56	0.57	23.68	0.66	21.18
	7.0×10^{-4}	0.42	16.00	0.55	12.50	0.67	9.21	0.77	8.24

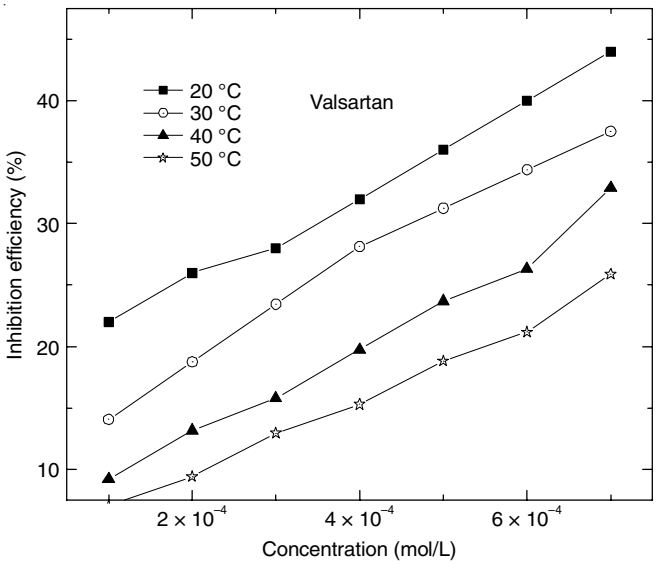

Fig. 3. Inhibition efficiency (%) and pharmaceutical drugs concentration

perature decrease. And % IE caused by pharmaceutical compounds ranged from (5.88-44) depending on their concentration and type. IE % is a function of several aspects including the charged metal and charged inhibitor molecules electrostatic attraction, existence of extra heterocyclic ring, several active adsorption centers, inhibitor molecular size or a mixture of all the previous factors.

Among the studied pharmaceutical compounds valsartan and hydrocholoro thiazide exhibit the most retardation performance relative to the others. This is possible since the several nitrogen atoms and aromatic rings are present in valsartan, so the adsorption of molecules on metal surface will increase. Valsartan might be adsorbed on copper surface as a single molecules or through the configuration of coat, polymeric in nature with a "bidentate structure" where valsartan particles are ordered in horizontal crisscross sequences and attached *via* N-Cu^{2+}-N bond [17], since it contains heterocyclic triazole ring while valsartan contains tetrazole ring. On the other hand, regarding the orientation of valsartan, it is probable that valsartan didn't recline horizontal through the surface, other than lone-pair of nitrogen link to the surface of metal atom.

Hydrochlorothiazide has N atoms (which have lone pair of electrons) (2 N of azine six membered ring in addition to NH_2 group) and π electrons in the benzene. These characteristic would affect the compound adsorption ability on the metal/acid solution interface with one or more of the subsequent methods *via* interaction between free pairs of electron on nitrogen heteroatoms and unoccupied *d*-orbital on copper surface, and/or donor-acceptor interaction between π electrons of aromatic ring and vacant *d*-orbital on copper surface. With respect to erythromycin thiocyanate has a polycentric adsorption sites including (S, N, O), since the presence of highly releasing character -OH groups present five adsorption sites to the molecule. Also due to the electron donating effect of the two methyl groups attached to N (in erythromycin thiocyanate) electron density at this adsorption site will be high. In case of erythromycin thiocyanate sulpher atom can increase the interaction of the molecules with metal surface. One more opportunity is that, as valsartan is huge particle, their coverage capability will be greater.

Diclofenac potassium offer :N and π electrons in the benzene rings as a possible adsorption centers. The introduction of electron attracting groups such as chloro at the *ortho* positions of benzene ring results in the electron density reduction of phenyl group. A reduction in electron density makes the electron transfer between the adsorption center and the metal further complicated which in revolve weaker the binding of diclofenac to copper surface. This leads to least inhibition efficiency of diclofenac potassium. At concentration 6×10^{-4}, hydrochlorothiazide, erythromycin thiocyanate, diclofenac potassium accelerate dissolution rate. The monitored incident resulting in considerable metal dissolution resulting in inhibitor film desorption from surface of metal. So the inhibitor adsorption rate is lower than it's desorption rate [20-22]. Table-2 shows that the % IE caused by pharmaceutical compounds are arranged as follow:

Valsartan > Hydrochlorothiazide > Erythromycin thiocyanate > Diclofenac potassium

Temperature effect on dissolution process and their activation parameters: Temperature is significant consideration in metal dissolution investigation. To calculate the activation energies for metal dissolution reaction, polarization measurements were taken at different temperatures of (20-50 °C) with and without several concentrations of pharmaceutical compounds. Augmentation in temperature lead to amplify dissolution rate (i_L) in 8 M H_3PO_4 free solution and 8 M H_3PO_4 containing pharmaceutical compounds [20,23].

IE % decreases with increasing temperature (Table-2 and Fig. 3) inhibition efficiency (IE %) reduction confirmed that physical adsorption of the pharmaceutical compounds on metal surface [23].

The activated parameters were calculated using Arrhenius and the transition-state equations:

$$\ln i_L = -\left(\frac{E^{\#}}{RT}\right) + \ln A \quad (5)$$

$$i_L = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S^{\#}}{R}\right)\exp\left(-\frac{\Delta H^{\#}}{RT}\right) \quad (6)$$

Fig. 4a illustrates Arrhenius plot for copper in 8 M H_3PO_4 free solution and 8 M H_3PO_4 containing several concentrations of valsartan as an example on plotting of ln i_L (A) against l/T.

Table-3 shows that $E^{\#}$ is lower in the absence than in solution containing pharmaceutical compounds. The higher values of $E^{\#}$ are good evidence for the physical adsorption of pharmaceutical compounds on the copper. Superior $E^{\#}$ values in solution containing pharmaceutical compounds can be associated with enlarging adsorbed layer thickness that improves the $E^{\#}$ of the copper dissolution process [24-26]. Fig. 4b shows the transition state plots obtained for the dissolution of copper in 8 M H_3PO_4 free solution and 8 M H_3PO_4 solution containing valsartan (several concentrations) as an example. By plotting ln i_L/T *vs.* l/T. directly plot are obtained with a slope of $-\Delta H^{\#}/R$ and intercept $\ln(R/Nh) + \Delta S^{\#}/R$. It is observed that lower $\Delta H^{\#}$ values of in absence than in presence of valsartan, erythromycin, hydrochlorothiazide, thiocyanate and diclofenac potassium. This indicate that the pharmaceutical compound adding to dissolution bath enlarges energy barrier height for

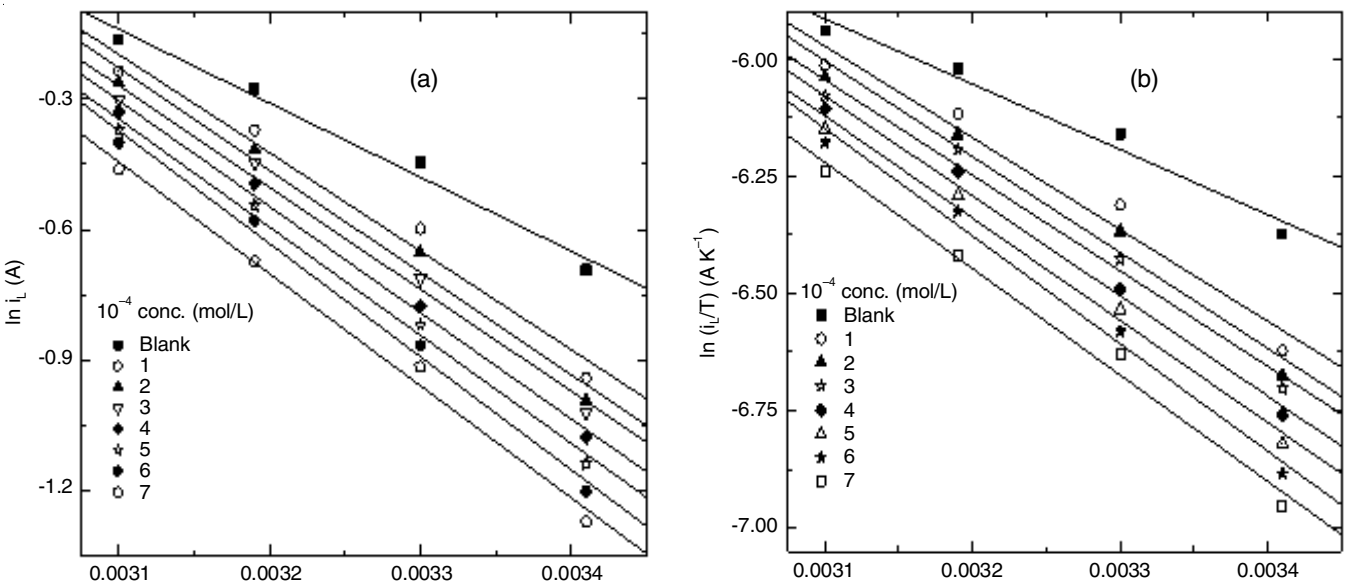

Fig. 4. (a) Arrhenius plot and (b) transition state plot of copper dissolution process in 8 M H_3PO_4 solution containing different concentrations of valsartan

TABLE-3
VALUES OF THERMODYNAMIC ACTIVATED PARAMETERS FOR DISSOLUTION OF COPPER IN 8 M H_3PO_4 IN ABSENCE AND PRESENCE OF PHARMACEUTICAL COMPOUNDS

Drugs	Conc.	$E^{\#}$ (KJ mol^{-1})	A	$\Delta H^{\#}$ (KJ mol^{-1})	$-\Delta S^{\#}$ (J mol^{-1} K^{-1})
Valsartan	0.0	14.17	171.56	11.46	210.83
	1.0×10^{-4}	18.86	929.36	16.06	196.78
	2.0×10^{-4}	19.58	1179.09	16.78	194.80
	3.0×10^{-4}	19.51	1103.19	16.70	195.36
	4.0×10^{-4}	20.33	1444.76	17.51	193.11
	5.0×10^{-4}	20.71	1598.46	17.89	192.27
	6.0×10^{-4}	21.65	1105.33	18.82	189.58
	7.0×10^{-4}	21.44	1902.03	18.64	190.83
Hydrochlorothiazide	0.0	14.17	171.56	11.46	210.83
	1.0×10^{-4}	17.38	513.022	14.625	201.72
	2.0×10^{-4}	17.55	529.53	14.790	201.46
	3.0×10^{-4}	18.91	855.85	16.139	197.47
	4.0×10^{-4}	20.11	1292.58	17.341	194.04
	5.0×10^{-4}	20.05	1225.07	17.286	194.48
	6.0×10^{-4}	20.98	1647.75	10.797	192.02
	7.0×10^{-4}	16.04	311.793	13.307	205.86
Erythromycin thiocyanate	0.0	14.17	171.56	11.46	210.83
	1.0×10^{-4}	16.46	355.26	13.71	204.78
	2.0×10^{-4}	16.31	324.07	13.57	205.54
	3.0×10^{-4}	16.81	380.54	14.06	204.21
	4.0×10^{-4}	17.13	416.82	14.36	203.45
	5.0×10^{-4}	17.33	439.65	14.57	203.00
	6.0×10^{-4}	16.61	393.38	13.85	203.93
	7.0×10^{-4}	15.91	171.56	11.46	210.83
Diclofenac potassium	0.0	14.17	171.56	11.46	210.83
	1.0×10^{-4}	17.06	308.89	13.18	205.94
	2.0×10^{-4}	17.08	465.82	14.88	202.52
	3.0×10^{-4}	17.10	454.59	14.323	202.73
	4.0×10^{-4}	17.46	435.70	14.34	203.08
	5.0×10^{-4}	17.87	477.03	14.70	202.33
	6.0×10^{-4}	16.18	528.87	15.09	193.61
	7.0×10^{-4}	10.51	327.60	13.44	205.45

dissolution procedure [25]. In addition, large and negative $\Delta S^{\#}$ values were both in 8 M H_3PO_4 free solution and 8 M H_3PO_4 solution containing pharmaceutical compounds which reflects that the association for activated complex which formed in the rate determining step also means the conversion of reactants to the activated complex accompanied with increasing in ordering [25].

Arrhenius constant A (pre-exponential factor) for 8 M H_3PO_4 solution containing pharmaceutical compounds (Table-3) is larger than 8 M H_3PO_4 free solution. This indicate that the adsorption of pharmaceutical compounds on the mainly active adsorption sites (having the low energy value) also, the dissolution process takes place generally on higher energy active sites [27].

Adsorption isotherms: Pharmaceutical compounds adsorption mechanism on copper surface was established through fitting θ values to several adsorption isotherms [Langmuir (Fig. 5a) and kinetic thermodynamic adsorption model (Fig. 5b) by eqns. 7 and 8]:

Langmuir isotherm is given as:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{7}$$

the degree of surface coverage, $\theta = (i_{L(blank)} - i_{L(pha.cpds)})/i_{L(blank)}$, the equilibrium constant of adsorption process is K_{ads} and the pharmaceutical compounds bulk solution concentration is C.

The kinetic thermodynamic adsorption model may be written in the form:

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K' + y\log C \tag{8}$$

where inhibitor molecules number occupying one active site is y. y values greater > 1 involve multilayers formation of inhibitor lying on the metal surface; but, y values < 1 point to every inhibitor molecule reside in more than one active site. K′ is a constant related to the binding constant of adsorption process K by the following relationship [19].

$$K = K'^{(1/y)} \tag{9}$$

where 1/y represents, the number of active sites of the surface occupied by one molecule of the inhibitor [13].

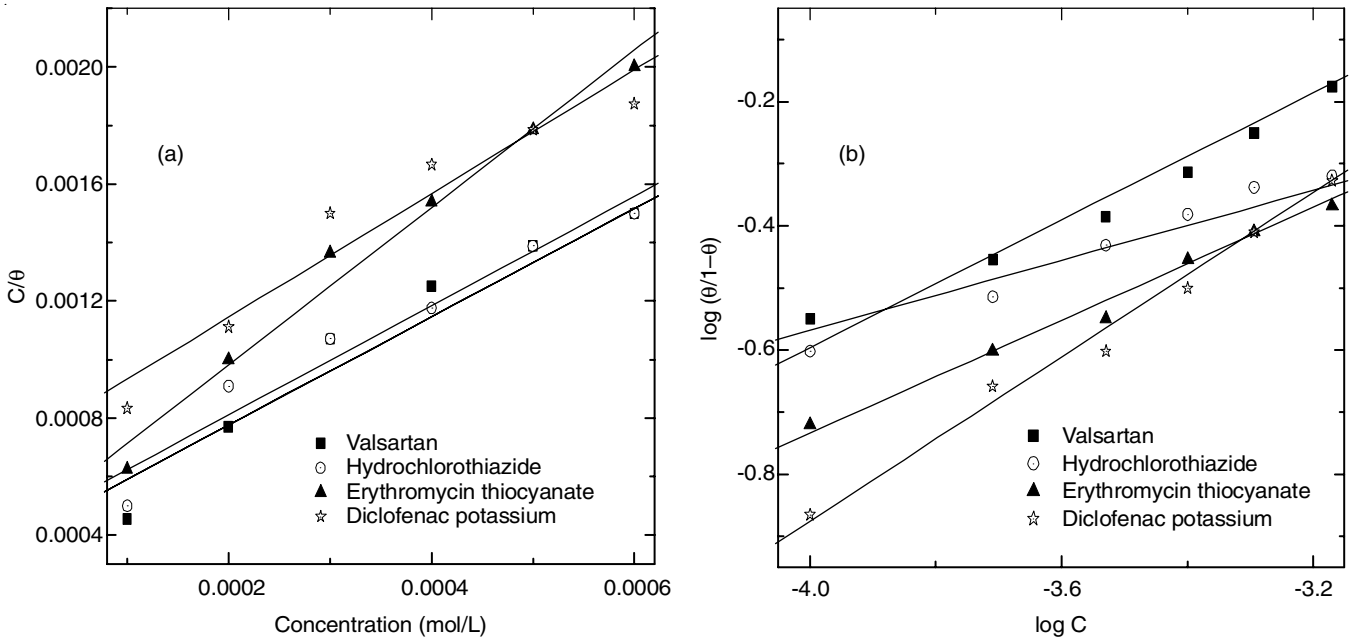

Fig. 5. (a) Langmuir (b) kientic-thermodynmic adsorption isotherm for copper in 8 M H_3PO_4 solution containing different pharmaceutical drugs

The values of 1/y for all pharmaceutical compounds higher than one (Table-4) *i.e*., the given pharmaceutical molecules are attached to more than one active site. y Values are greater one which reflect that pharmaceutical compound will inhibit several active site [26], the elevated K value for valsartan relative to other pharmaceutical compound (hydrochlorothiaizide erythromycin thiocyanate and diclofenac potassium) indicates stronger adsorption of valsartan on carbon steel surface [16].

The standard free energy of adsorption (ΔG°_{ads}) can be expressed:

$$\Delta G^\circ_{ads} = -RT \ln (55.5\ K_{ads}) \quad (10)$$

The universal gas constant is R, absolute temperature is T and the value of 55.5 is the concentration of water molecule in (mol L^{-1}) at metal solution interface in the solution.

The large negative value of ΔG°_{ads} (Table-4) implies that the adsorption of pharmaceutical compounds onto copper surface is allowed from thermodynamics points of view also designates adsorption process is spontaneous and the adsorbed layer on copper surface is stable [28].

The magnitude of ΔG°_{ads} for these pharmaceutical compounds show that $-\Delta G^\circ_{ads}$ are ranging between -20 kJ/mol and -30 kJ/mol indicating that compressive adsorption (physical and chemical adsorption) might be occur [29].

Morphological study by SEM (natural convection): Fig. 6a-j show the SEM images of copper surface morphologies which were polished in 8 M H_3PO_4 free solution and H_3PO_4 containing pharmaceutical compounds. Fig. 6a shows that the surface of raw copper sample was awfully damaged and rough results in the formation of large number of protrusions and pits. After treatment in 8 M H_3PO_4 (Fig. 6b), the surface appeared rough, uneven where protrusions and pits is still represented clearly which reflect dissimilar dissolution of Cu^{2+} ions in 8 M H_3PO_4. In presence of 2×10^{-4} M valsartan (Fig. 6c), the surface appear rough, uneven and improve to great extent in presence of high concentration of valsartan (Fig. 6d), Uniformity, granule borders are totally reduced. The surface is well-polished which is owing to amplify the valsartan molecules adsorption ability resulting in all deep cavities are filling up.

Fig. 6e shows the copper SEM images in 8 M H_3PO_4 containing 2×10^{-4} M hydrochlorothiazide. Simply minor distinction was monitored extra rather than blank, where granule borders are still monitored. This behaviour may be attributed to weak hydrochlorothiazide molecules adsorption at this concentration.

High concentration of hydrochlorothiazide shows that the electropolished surface textile appear regular, even and brilliant relative to its low concentration (Fig. 6f). That behaviour may be attributed to the adsorption of hydrochlorothiazide increases and consequently the grain boundaries are reduced. It is observed that there is gradual enhancement in surface quality after addition low (Fig. 6g) to high concentration rang of erythromycin thiocyanate (Fig. 6h) where brightening and leveling effects were markedly improved for 2×10^{-4} M diclofenac potassium

TABLE-4
LINEAR FITTING PARAMETERS OF PHARMACEUTICAL COMPOUNDS AT 20 °C

Pharmaceutical compounds	Kinetic thermodynamic isotherm			
	y	1/y	K_{ads}	$-\Delta G_{ads}$ (kJ mol^{-1})
Valsartan	0.406	2.463	636.24	25.51
Hydrochlorothiazid	0.441	2.267	405.39	24.42
Erythromycin thiocyanate	0.538	1.858	403.78	24.39
Diclofenac potassium	0.620	1.612	220.38	22.93

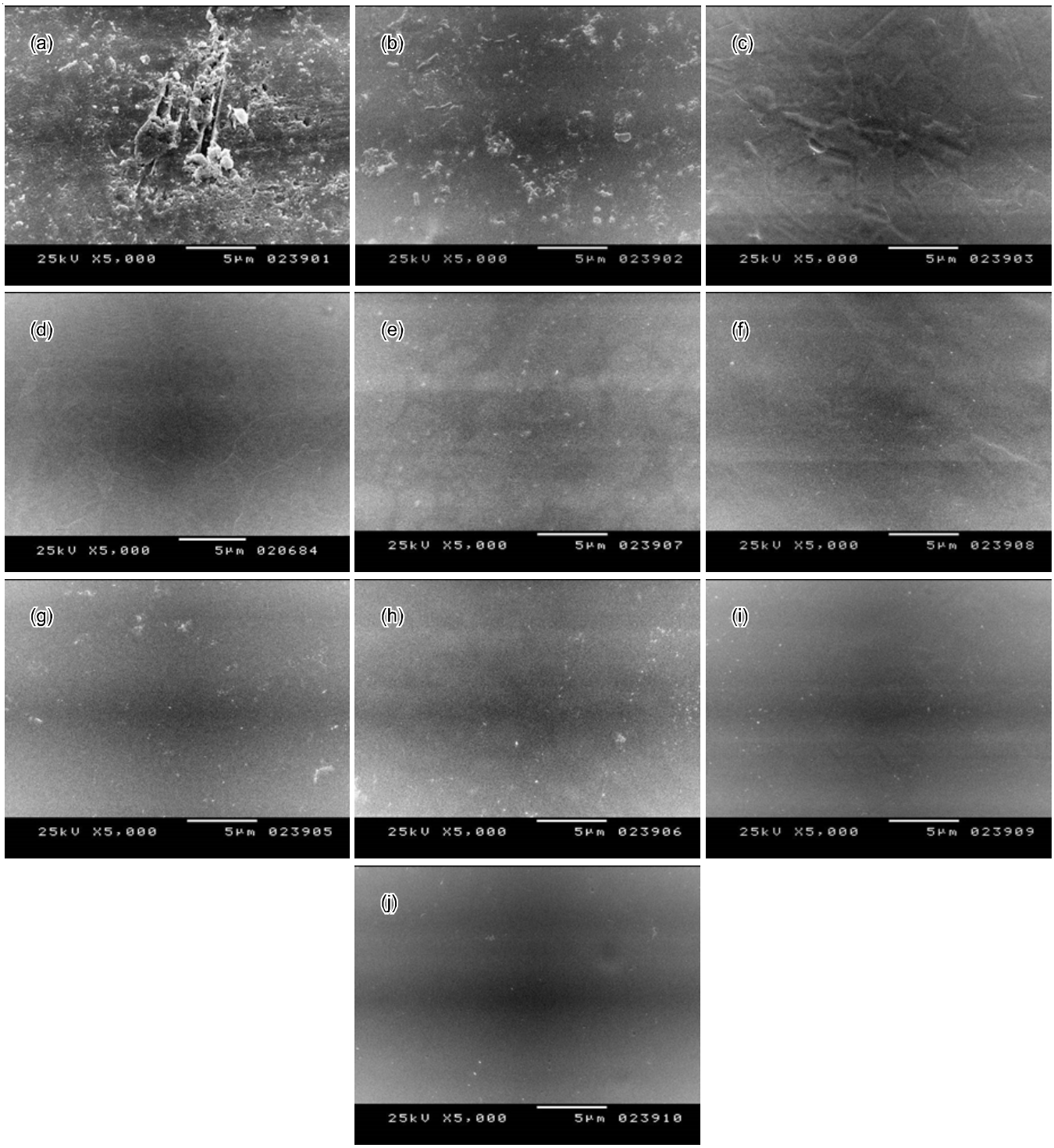

Fig. 6. SEM pictures of (a) raw copper sample before electropolishing; (b) after electropolishing without addition (blank); (c) after electropolishing containing valsartan (2×10^{-4} mol/L) and (d) (7×10^{-4} mol/L); (e) after electropolishing containing hydrochlorothiazide (2×10^{-4} mol/L) and (f) (7×10^{-4} mol/L); (g) after electropolishing containing erythromycin thiocyanate (2×10^{-4} mol/L) and (h) (7×10^{-4} mol/L); (g) after electropolishing containing diclofenac potassium (2×10^{-4} mol/L) and (i) (7×10^{-4} mol/L)

sample image is revealed in (Fig. 6i) leveling and brightening are observed. Just small dissimilarity was noted relative to its absence, where the granule borders are still characterized on metal surface other than it shows consistent greater than its absence.

For high concentration of diclofenac potassium (Fig. 6j), surface brilliance and regularity was enhanced more than image (Fig. 6i) since grain boundaries are totally withdrawal.

Forced convection

Effect of stirring: Fig. 7a-d show polarization curves attained for copper RDE & RCE in 8 M H_3PO_4 free solution and 8 M H_3PO_4 containing 10^{-4} mol/L of valsartan as an example. At 20 °C, plots display good fitting and a broad range of potential for limiting current plateau. The broad limiting current potential range recommend salt film formation, where the dissolved metal ions concentration at electrolyte-the metal interface is

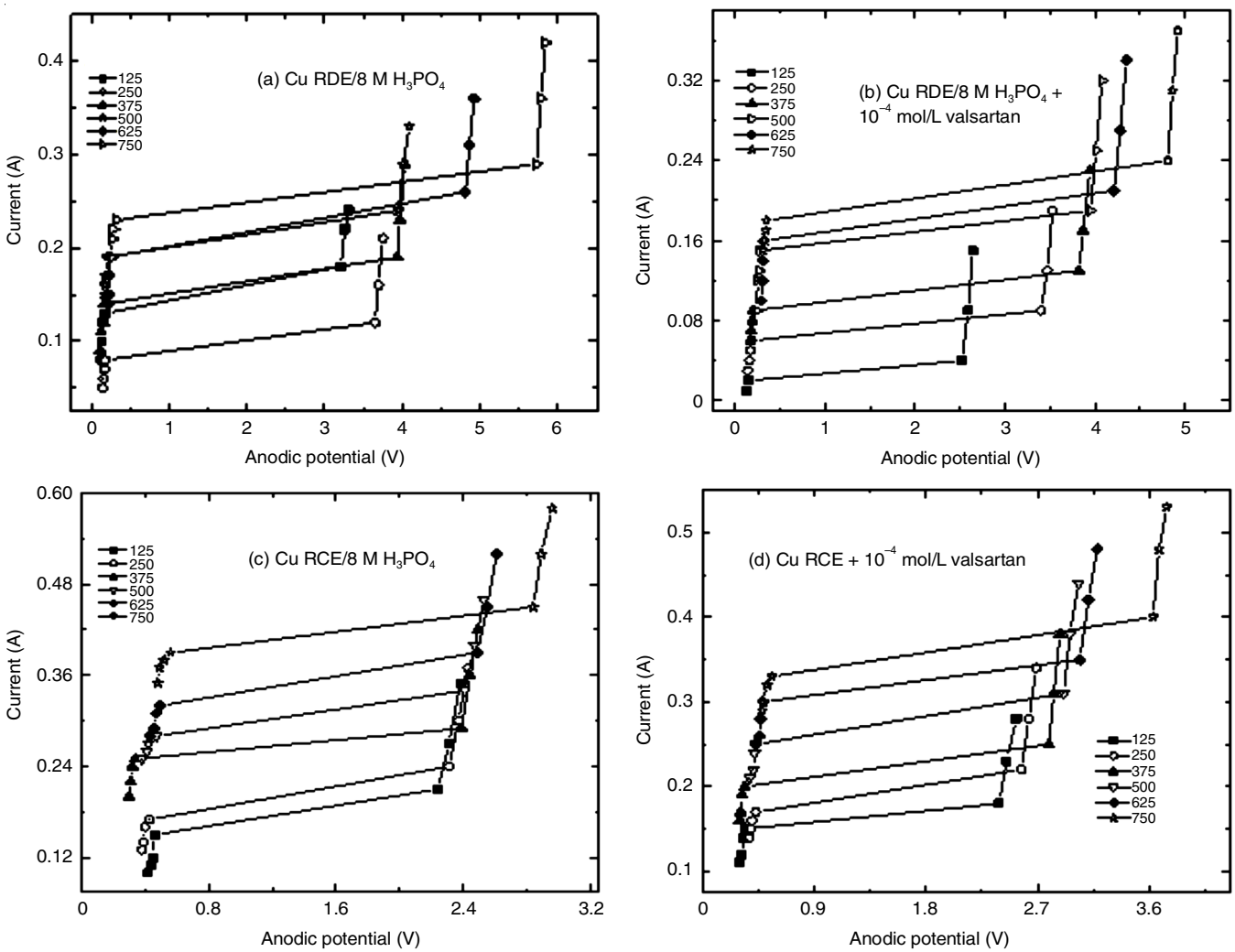

Fig. 7. Anodic polarization curves obtained for copper RDE at different rotation speed in (a) 8 M H_3PO_4 free solution; (b) 8 M H_3PO_4 solution containing 10^{-4} mol/L valsartan; (c) RCE at different rotation speed in 8 M H_3PO_4 free solution; and (d) 8 M H_3PO_4 solution containing 10^{-4} mol/L valsartan

constant and matches to saturated salt film formed between metal cations and electrolyte anions [30]. Dissolution rate is controlled by mass transport and engages metal ions diffusion and migration through a stagnant (Nernst) diffusion layer, the thickness of diffusion layer is rotation rate dependent. It is obvious from the figures that upon augment in rotation rate plateau height (the limiting current magnitude) amplifies. Derived from the above declaration, as rotation rate increase, the thickness of the Nernst diffusion layer magnitude decrease, resulting in shorter diffusion path length for ions therefore the limiting current magnitude become higher *via* electrolyte stirring, the evolved gas bubbles on the anode is blushed away through agitation before it can leave surface pathways, there is a minimum reduction in both thickness and surface roughness while stirring speed is diverse [19]. Stirring effects might begin to amplify the surface roughness after a certain point by removing too much of the thick film which avoids low-lying areas of the surface from being etched.

Mass transport limiting species: Anodic dissolution of copper in 8 M H_3PO_4 containing pharmaceutical compounds solution is controlled *via* Cu^{2+} species transport from dissolution of anode and a concentration incline build up close to anode surface and Cu^{2+} local concentration close to the electrode surface enlarges by means of raise current density.

Fig. 8a shows a Levich plot, that is i_L as a function of $\omega^{0.5}$. It is observed that, i_L values is proportional to $\omega^{0.5}$ at all velocity and in absence and presence of pharmaceutical compounds at 1×10^{-4} mol/L concentrations and at room temperatures reflecting that copper electrode dissolution in 8 M H_3PO_4 free solution and 8 M H_3PO_4 containing pharmaceutical compounds is controlled by mass transfer condition [31].

Fig. 8b shows limiting current density - angular velocity $\omega^{0.7}$ plot in 8 M H_3PO_4 free solution and 8 M H_3PO_4 containing different concentrations of pharmaceutical compounds at 20 °C. It is observed that, i_L values is proportional to $\omega^{0.7}$ at all rotation speed and in 8 M H_3PO free solution and 8 M H_3PO_4 containing different concentrations range of pharmaceutical compounds which studied reflecting that copper electrode dissolution is controlled *via* mass transfer stipulations. The rotating cylinder mass transfer performance have been take place to progress the rotating cylinder reactor performance in demeanor diffusion controlled reaction *via* super imposing axial flow [32].

Surface characterization for rotating cylinder electrode: SEM surface investigation to discover and evaluate the surface

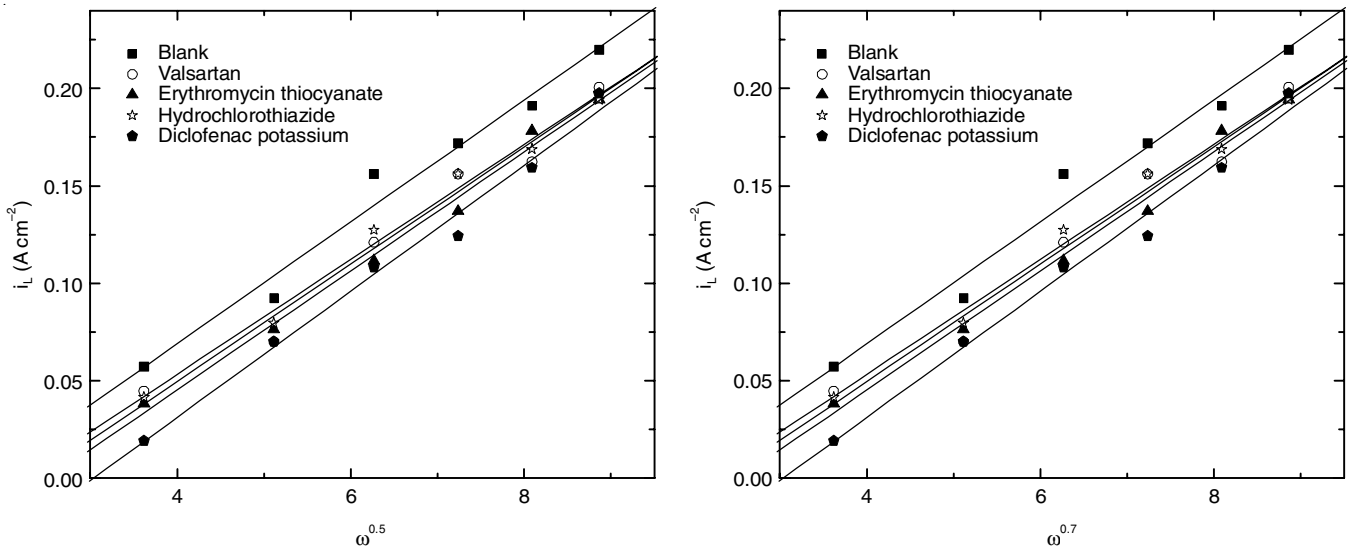

Fig. 8. Relation between limiting current density and angular velocities $\omega^{0.5}$ and $\omega^{0.7}$ in absence and presence of pharmaceutical drugs at 20 °C

morphology development (Fig. 9a-f) demonstrate samples comparison of RCE for copper specimen at 125-500 rpm. At lower rotation speed of rotating copper cylinder (125 rpm) uneven & rough surface was observed where protrusions are represented, which indicate the leveling effect decreases at lower rotation speed when cylinder rotation speed increase to 500 rpm, the leveling effect was improved where protrusions were disappeared so will add pharmaceutical compounds to the electropolishing bath at lower rpm to improve surface quality. Fig. (9c-f) show surface of copper in presence of pharmaceutical compounds. The surface quality improved to great extent and protrusions are diminished completely. we can conclude that pharmaceutical compounds has positive effect in electropolishing bath, presence of pharmaceutical compounds increases the viscosity insulating anodic film which cover the surface and the augment in electric resistance to the elevated speed of ionic movement *via* the diffused layer. The anodic layer coats the minor climaxes and valley avoiding dissolution whilst major climaxes among elevated accuse concentration are protruded beyond the anodic film dissolve extra voluntarily but adsorption of pharmaceutical compounds on higher peaks lead to similar and regular dissolution and subsequently leveling and improvement in surface quality was achieved.

Surface characterization for rotating cylinder electrode: SEM surface investigation to discover and evaluate the surface

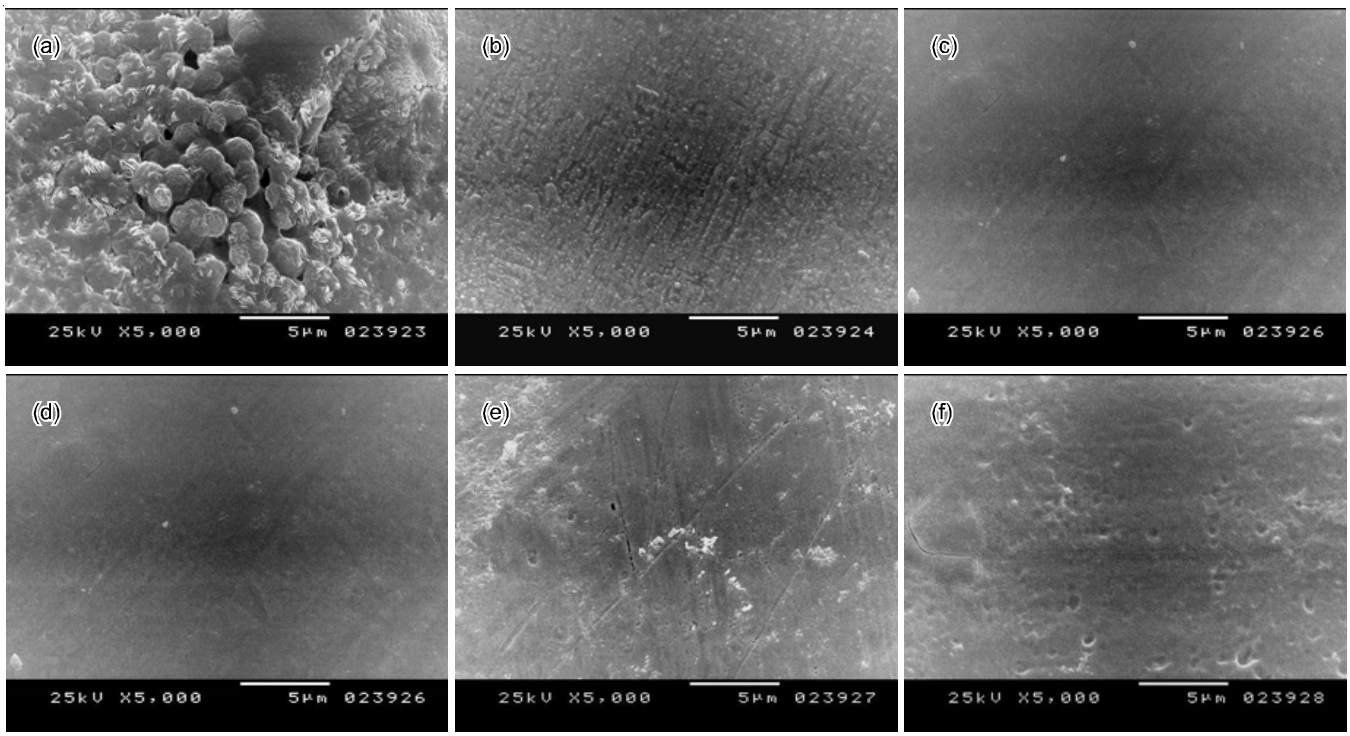

Fig. 9. SEM pictures of copper after electropolishing in 8 M H_3PO_4 at 125 rpm (a); 500 rpm (b); valsartan (2×10^{-4} mol/L) (c); hydrochlorothiazide (2×10^{-4} mol/L) (d); erythromycin thiocyanate (2×10^{-4} mol/L) (e); and diclofenac potassium (2×10^{-4} mol/L) (f) at 125 rpm

morphology development (Fig. 9a-f) demonstrate samples comparison of RCE for copper specimen at 125 to 500 rpm. At lower rotation speed of rotating copper cylinder (125 rpm) uneven & rough surface was observed where protrusions are represented, which indicate the leveling effect decreases at lower rotation speed when cylinder rotation speed increase to 500 rpm, the leveling effect was improved where protrusions were disappeared so will add pharmaceutical compounds to the electropolishing bath at lower rpm to improve surface quality. Fig. (9c-f) show surface of copper in presence of pharmaceutical compounds. The surface quality improved to great extent and protrusions are diminished completely. It is concluded that the pharmaceutical compounds has positive effect in electropolishing bath. The presence of pharmaceutical compounds increases the viscosity insulating anodic film which cover the surface and the augment in electric resistance to the elevated speed of ionic movement *via* the diffused layer. The anodic layer coats the minor climaxes and valley avoiding dissolution whilst senior climaxes among elevated accuse concentration are protruded beyond the anodic film dissolve extra voluntarily but adsorption of pharmaceutical compounds on higher peaks lead to similar and regular dissolution and subsequently leveling and improvement in surface quality was achieved.

Correlation data: Overall mass transfer relationship underneath the current situations *via* using the technique of dimensionless investigation in the form of the following equations:

$$Sh = a\, Re^{b}.\, Sc^{0.33} \qquad (11)$$

where Sh, Re and Sc are the Sherwood (Sh = kl/D), Reynolds (Re = IU/ν) and Schmidt (Sc = ν/D) numbers, correspondingly and a and b are empirical constants, SC = 0.33 (indicating forced convection) *via* scheming log $Sh/Sc^{0.33}$ and log Re a straight line was obtained; its slope gives constant b while intercept give the constant a (Fig. 10) illustrates the mass transfer relationship for all factors used in electropolishing. From this figure, the data can be correlated by the equations given in Table-5.

The exponent in the above equation indicates Laminar stream that concur with the preceding mass transfer investigations in aqueous solvent, also the elevated Sherwood value demonstrate that diffusion layer lie well inside the Laminar sub layer [33].

Conclusion

In this work, some pharmaceutical drugs *viz*. valsartan, hydrocholorothiazide, erythromycin thiocynate and diclofenac potassium were used to retard the copper dissolution effectively in 8 M H_3PO_4 medium. It was found that the concentration of studied drugs inceases the copper dissolution efficiency but decreased through temperature elevation. Pharmaceutical compounds adsorption process on copper surface using 8 M H_3PO_4 obey kinetic-thermodynamic adsorption model. The SEM morphologies also confirmed the adsorption of pharmaceutical compounds on surface of copper which lead to improvement in copper surface texture. Moreover, (ΔG°_{ads}) negative values designates strong and spontaneous adsorption of studied drugs on the copper surface. Under natural convection as forced convection conditions, it was found that when RDE and RCE rotation speed enlarges, dissolution process limiting current also enhanced. Surface morphology of RCE copper surface enhanced at low rotation rate in the presence of studied drugs.

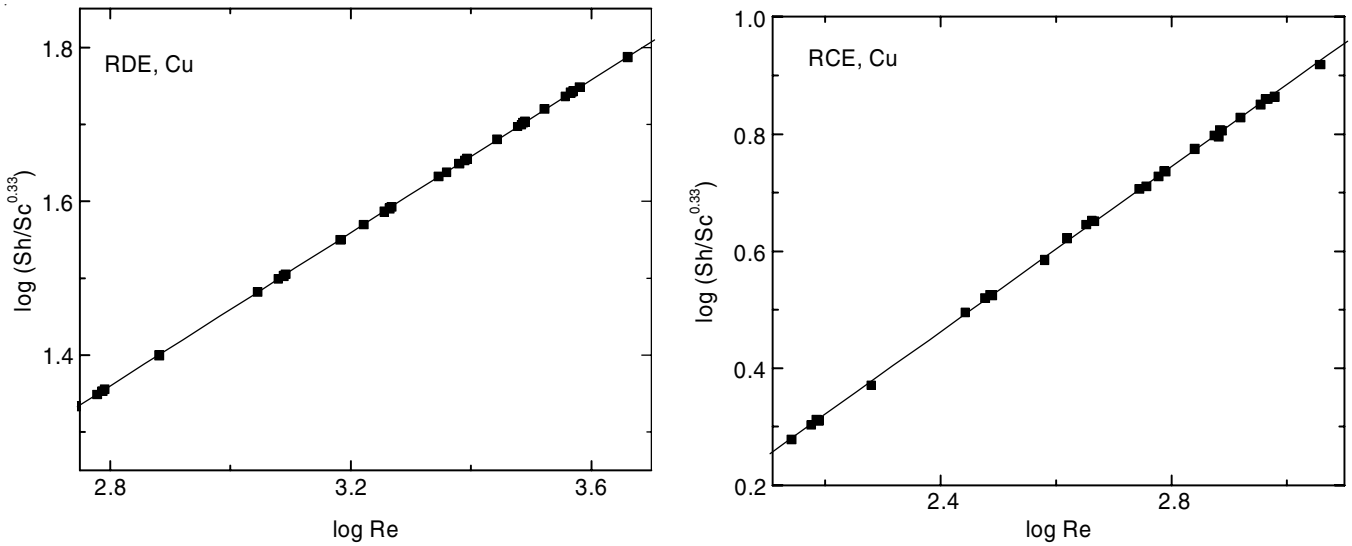

Fig. 10. Overall mass transfer correlation for dissolution process in the absence and presence of pharmaceutical drugs at 20 °C for RCE and RDE

TABLE-5
CORRELATION DATA OF OVERALL MASS TRANSFER RELATIONSHIP

Pharmaceutical compounds	Cylinder	Disc
Blank	$Sh = 0.0581Sc^{0.33}\,Re^{0.70} \pm 0.00272$	$Sh = 0.9170Sc^{0.33}\,Re^{0.50} \pm 1.8655 \times 10^{-4}$
Valsartan	$Sh = 0.0595Sc^{0.33}\,Re^{0.70} \pm 0.00272$	$Sh = 0.9216Sc^{0.33}\,Re^{0.50} \pm 1.9628 \times 10^{-4}$
Erythromycin thiocyanate	$Sh = 0.0588Sc^{0.33}\,Re^{0.70} \pm 0.00182$	$Sh = 0.9220Sc^{0.33}\,Re^{0.50} \pm 1.8280 \times 10^{-4}$
Hydrochlorothiazide	$Sh = 0.0578Sc^{0.33}\,Re^{070} \pm 0.00181$	$Sh = 0.9240Sc^{0.33}\,Re^{050} \pm 9.068 \times 10^{-5}$
Diclofenac potassium	$Sh = 0.0585Sc^{0.33}\,Re^{0.70} \pm 1.23240$	$Sh = 0.9220Sc^{0.33}\,Re^{0.50} \pm 1.8280 \times 10^{-4}$
Overall mass transfer correlation	$Sh = 0.0602Sc^{0.33}\,Re^{0.70} \pm 3.54 \times 10^{-4}$	$Sh = 0.9268Sc^{0.33}\,Re^{0.497} \pm 4.919 \times 10^{-4}$

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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