Asian Journal of Chemistry; Vol. 25, No. 3 (2013), 1187-1198

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.11729

Effect of Anodic Mass Transfer in the Electrowinning of Copper in Presence of Organic Compounds

NABILA M. EL-MALLAH[1,*], ABDEL-MONEM M. AHMED[1] and LAMYAA F. GADO[2]

[1]Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426, Alexandria 21321, Egypt
[2]Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Koam, Egypt

*Corresponding author: E-mail: profabdelmonem@gmail.com

(*Received*: 17 June 2011; *Accepted*: 3 September 2012) AJC-12077

The effect of anodic oxygen bubbles on the rate of mass transfer was studied by measuring the limiting current of deposition of copper from acidified $CuSO_4$ solution using parallel plate cell. Different factors studied as types of inhibitors, their concentrations and temperatures. The organic additives used are glucose, fructose, mannose, sucrose, lactose and maltose. The rate of mass transfer was found to decrease over the natural convection value by an amount ranging from 1.8-32.3 % depending on the types of additives and its concentration. Thermodynamic parameters E_a, ΔH*, ΔS*, ΔG* were evaluated and discussed. The adsorption of organic additives was found to obey Langmuir, Temkin, Flory-Huggin and kinetic adsorption isotherm.

Key Words: Electrodeposition, Limiting current, Thermodynamic parameters, Carbohydrates, Adsorption.

INTRODUCTION

Copper is the metal of choice, replacing aluminum in integrated circuit interconnections[1]. This switch are emerged and simulated due to copper advantage characteristics such as low resistivity and high immunity to electromigration, which in turn results in greater circuit reliability and markedly higher cock frequency. Copper dual damascene technology includes two main electrochemical steps. First step is copper electrochemical deposition step[2-7] (or copper electroplating) into trenches and vias. Second electrochemical step utilizes chemical mechanical polishing.

In electrowinning of metals usually an insoluble anode is used where oxygen evolution takes place. Anodic oxygen evolution consumes a considerable portion of the electrical energy provided to the cell and could also adversely affect the performance of the cell by increasing the ohmic drop[8-10] and distributing the uniformity of current distribution[11-14]. On the other hand, anodic oxygen bubbles were found to enhance the rate of mass transfer at the cathode[11-13] to the modest degree in vertical parallel electrode cells to a modest degree. An attempt to maximized the electricians effect of counter electrode, glass bubbles, different cell designs were proposed where the working electrodes was placed up steams of the gas involving counter electrode; an enhancement in the rate of mass transfer to 60 % over the natural convection values obtained. The object of the present work is to study the effect of different carbohydrates on the rate of electrodeposition of copper using lead anode.

EXPERIMENTAL

Fig. 1 shows the cell and the circuit used in the present work. The cell consisted of a rectangular plastic container (5.1 cm × 5 cm × 10 cm) with electrodes fitting the whole cross section area. The cathode was rectangular copper sheet (10 cm height × 5 cm width); the anode was lead sheet with an inter-electrode distance was 5 cm. The cell was placed in 3 L glass container filled with the electrolyte to ensure that the cell is always filled with the electrolyte to minimize the decrease in Cu^{2+} concentration in the cell during polarization.

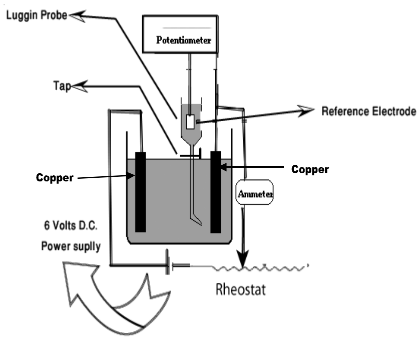


Fig. 1. Electrolytic cell and the electrical circuit showing the position of the two parallel vertical plates and the reference electrode. The ammeter connected in series, while the potentiometer in parallel

The electrical circuit consists of (6 V d.c). Power supply connected in series with the cell along and rheostat and (multi-range digital ammeter). A voltammeter is connected in parallel with the cell to measure the voltage.

Polarization curves from which the limiting current was determined were constructed by increasing the current stepwise and measuring the steady state cathode potential against a copper reference electrode placed in the cup of a luggin tube whose tip was placed at about 1mm from the cathode surface. To make sure that the decrease of Cu^{2+} concentration during polarization was negligible in case of lead anode, the limiting current was measured again potentiostatically using a fresh solution, the galvanostatic and the rapid potentiostatic methods gave almost the same limiting current. Before electrolysis the cathode and anode were isolated from their backs and sides with epoxy resin except at the contact with the feed wires. Electrode treatment was simillar to that used by Wilke *et al.*[14]. Concentrations of $CuSO_4$ were used, namely, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35 M, in all cases 1.5 M H_2SO_4 was used as a supporting electrolyte. All chemicals were of Analar grade. Physical properties of the solution (ρ, μ, D) used to correlate the present data were measured[9]. Temperature was 23 ± 0.5 ºC.

RESULTS AND DISCUSSION

Fig. 2 shows a typical current-potential curve in presence and in absence of compounds at 25 ºC. It is seen that the limiting current decreases with the increase of concentration of organic compounds. Fig. 2 show typical current-potential curves for different carbohydrates at constant concentration. It is seen that, the decrease in limiting current depend on the type of carbohydrate and its structure.

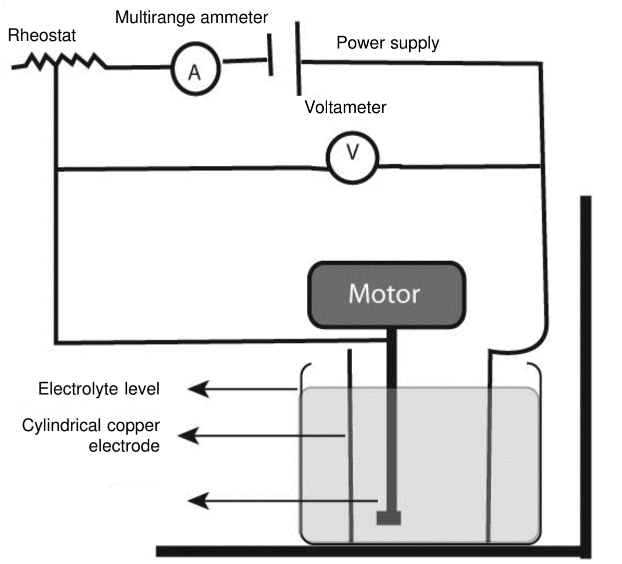


Fig. 2. Electrolytic cell and the electrical circuit using rotating cylinder electrode

These polarization curves are served to determine the limiting current from which the mass transfer coefficient was calculated according to the equation:

$$K = \frac{I_l}{ZFC_b}$$

where K is the mass transfer coefficient, I_l is the limiting current densities under natural convection, Z is the number of electrons involved in the reaction and C_o is the initial concentration of copper ions. Table-1 gives the values of I_l at different temperatures for all additives. Fig. 2 shows that in the absence of carbohydrate, the blank data when we used lead anode fits well into equation which agrees with data derived from the hydrodynamic boundary layer theory[15].

$$J = 1.096\ (Re\ Fr)^{-0.176}$$

J is mass transfer rate (mole $L^{-2}\ s^{-1}$), J is factor (st . $Sc^{0.66}$), St (Stanton number (K/V), Sc (Schmidt number (μ/ρD), Fr is Froude number where $Fr = v^2/hg$, v is oxygen gas discharge velocity (cm s^{-1}), h electrode height, g is the acceleration due to gravity (cm s^{-2}), Re is Reynolds number where Re = ud/ν, U is electrode peripheric velocity cm s^{-1},

$$U = \omega r$$

ω is angular velocity, r the radial distance.

The gas discharge velocity V used in calculating J, Re and Fr were calculated from eqn. 5

$$V = \frac{(IRT)}{(4PF)}$$

I is the current density, R is the gas constant, T is the absolute temperature, P is the pressure and F is Faraday constant.

In presence of organic substance, the following relation was obtained

$$k\alpha(V)^b$$

where "b" is constant depends on organic substances.

Ahmed *et al.*[16] predicted that

$$k\alpha(V)^{0.18}$$

From Table-2 we noticed that the velocity (V) and mass transfer coefficient (k) for all organic compounds are decreased with increase the concentration of the organic compounds.

Plot log k against log V for different organic compounds gave a good straight line as shown in Fig. 3 and Table-2. The values of the slope (b) were found to be constant for all studied additives and its values approximately equal to unity (Table-2), which indicates that the discharge velocity of oxygen gas is affected by the presence of additives compounds with the same extent as the mass transfer coefficient does.

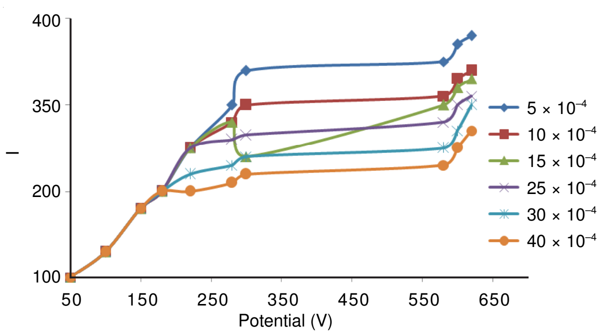


Fig. 3. Current potential curve at different concentrations of compound (**I**) and at 25 ºC

Effect of carbohydrate on the limiting current: If the limiting current in absence of organic compounds (I_b) and in

TABLE-1
LIMITING CURRENT OF DIFFERENT ORGANIC COMPOUNDS (mA) AT DIFFERENT TEMPERATURES

Organic compounds	C × 10^{-4}	Limiting current (I_l) at different temperatures			
		25 °C	30 °C	35 °C	40 °C
Compound (**I**)	5	350	370	390	410
	10	310	330	350	370
	15	300	310	320	330
	25	280	300	310	320
	30	250	260	270	280
	40	230	220	230	340
Compound (**II**)	0	350	370	390	410
	10	300	320	340	350
	15	290	300	310	330
	25	270	280	290	300
	30	240	250	260	270
	40	220	230	240	250
Compound (**III**)	0	350	370	390	410
	10	330	350	370	390
	15	310	330	350	370
	25	300	320	335	350
	30	280	290	310	330
	40	240	260	270	280
Compound (**IV**)	0	350	370	390	410
	10	320	340	360	380
	15	310	325	340	360
	25	290	310	330	350
	30	270	280	290	300
	40	240	250	260	270
Compound (**V**)	0	350	370	390	410
	10	290	310	330	350
	15	260	275	290	310
	25	240	245	260	275
	30	220	230	240	250
	40	210	220	230	240
Compound (**VI**)	0	350	370	390	410
	10	270	280	300	320
	15	250	270	280	290
	25	240	250	260	270
	30	200	220	230	240
	40	200	210	220	230

TABLE 2
RELATION BETWEEN C (mol L^{-1}) AND PERCENTAGE INHIBITION AT 25 °C

C × 10^4 (mol L^{-1})	Inhibition (%) at 25 °C					
	Organic compounds					
	I	**II**	**III**	**IV**	**V**	**VI**
10	11.40	14.20	51.70	8.60	17.40	20.00
15	14.20	17.40	11.20	11.40	25.70	28.57
25	20.20	22.85	14.20	14.20	31.40	31.40
30	25.57	31.40	20.00	22.85	37.10	40.00
40	34.20	37.14	31.40	31.40	40.00	42.80

the presence of organic compounds (I), the percentage inhibition can be calculated from the equation:

$$\text{Inhibition}\ (\%) = \left(\frac{I_b - I}{I_b}\right) \times 100$$

Table-4 and Fig. 4 show the relation between percentage inhibition and concentration of amino acids at 25 °C. Fig. 4 shows that the percentage inhibition caused by carbohydrates ranges from 1.8-33.3 % depending on the type of the carbohydrate and their concentration. The order of decreasing inhibition is as follow:

Fructose > Lactose > Sucrose > Mannose > Maltose > Glucose

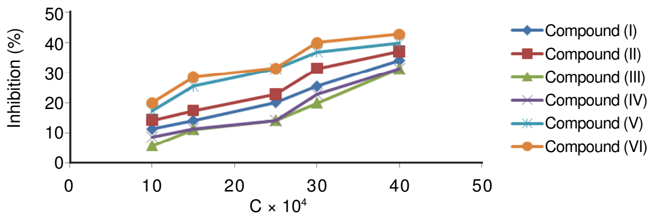


Fig. 4. Relation between C (mol L^{-1}) and % inhibition at 25 °C

The obtained results show that, the presence of organic compounds has an inhibiting effect on the kinetic of the copper discharge process, pointed out by the decrease[17] of the exchange current density. The inhibition enhancing due to

TABLE-3
GENERAL CORRELATION OF FREE CONVECTION MASS TRANSFER FOR DIFFERENT ACIDS SUBSTANCES AT 25 ºC

$C \times 10^4$ (mol L^{-1})	rpm	I_l (mA cm^{-2})	ν (cm^2 s^{-1})	$D \times 10^4$ (cm^2 s^{-1})	Sh	Sc	Re
Compound (**I**)							
Blank	100	380	1.338	7.41	124.00	1805.67	20653.87
10		330	1.311	6.17	129.32	2124.80	21079.24
15		310	1.296	5.62	133.38	2306.05	21323.21
25		290	1.235	5.37	130.58	2299.81	22376.42
30		270	1.222	4.79	136.29	2551.15	22614.47
40		250	1.211	4.37	138.33	2771.17	22819.88
Blank	200	420	1.338	6.03	168.42	2218.91	41307.85
10		360	1.311	4.79	181.73	2736.95	42158.58
15		330	1.296	4.27	186.87	3035.13	42646.53
25		310	1.235	4.07	184.17	3034.40	44752.96
30		290	1.222	3.72	188.50	3284.95	45229.05
40		270	1.211	3.39	192.58	3572.27	45639.88
Blank	300	460	1.338	5.62	197.91	2380.78	61961.77
10		390	1.311	5.50	171.46	2383.64	63237.87
15		350	1.296	4.68	180.83	2769.23	63969.79
25		330	1.235	4.47	178.51	2762.86	67129.43
30		310	1.222	4.17	179.75	2930.46	67843.58
40		300	1.211	3.98	182.26	3042.71	68459.83
Blank	400	490	1.338	5.25	225.68	2548.57	82615.38
10		430	1.311	4.37	237.92	3000.00	84316.84
15		400	1.296	3.98	243.01	3256.28	85292.73
25		360	1.235	3.55	245.20	3478.87	89505.57
30		340	1.222	3.31	248.37	3691.84	90457.76
40		320	1.211	3.02	256.21	4009.93	91279.42
Blank	500	520	1.338	5.13	245.10	2608.19	103269.30
10		460	1.311	4.37	254.52	3000.00	105396.13
15		420	1.296	3.80	267.25	3410.53	106616.00
25		390	1.235	3.55	265.64	3478.87	111882.05
30		360	1.222	3.16	275.46	3867.09	113072.28
40		350	1.211	3.09	273.88	3919.09	114099.36
Blank	700	600	1.338	5.37	270.16	2491.62	144577.15
10		520	1.311	4.37	287.72	3000.00	147554.71
15		510	1.296	4.27	288.80	3035.13	149262.52
25		450	1.235	3.72	292.50	3319.89	156635.00
30		410	1.222	3.24	305.98	3771.60	158301.33
40		400	1.211	3.16	306.07	3832.28	159739.25
Compound (**II**)							
Blank	100	380	1.338	7.41	124.00	1805.67	20653.87
10		340	1.287	6.46	127.26	1992.26	21472.32
15		320	1.272	6.03	128.32	2109.45	21725.53
25		300	1.264	5.50	131.89	2298.18	21863.04
30		280	1.217	5.13	131.97	2372.32	22707.38
40		260	1.183	4.68	134.33	2527.78	23360.00
Blank	200	420	1.338	6.03	168.42	2218.91	41307.85
10		360	1.287	4.90	177.65	2626.53	42944.76
15		340	1.272	4.57	179.89	2783.37	43451.18
25		320	1.264	4.17	185.55	3031.18	43726.19
30		300	1.217	3.98	182.26	3057.79	45414.87
40		280	1.183	4.68	144.66	2527.78	46720.12
Blank	300	460	1.338	5.62	197.91	2380.78	61961.77
10		410	1.287	6.03	164.41	2134.33	64417.13
15		360	1.272	5.01	173.75	2538.92	65176.77
25		340	1.264	4.57	179.89	2765.86	65589.28
30		320	1.217	4.37	177.06	2784.90	68122.31
40		310	1.183	4.27	175.54	2770.49	70080.18
Blank	400	490	1.338	5.25	225.68	2548.57	82615.38
10		430	1.287	4.47	232.60	2879.19	85889.18
15		400	1.272	4.07	237.64	3125.31	86902.03
25		380	1.264	3.80	241.80	3326.32	87452.04
30		360	1.217	3.63	239.80	3352.62	90829.40
40		340	1.183	3.39	242.51	3489.68	93439.88

Blank	500	520	1.338	5.13	245.10	2608.19	103269.30
10		510	1.287	5.13	240.38	2508.77	107361.56
15		450	1.272	4.37	248.99	2910.76	108627.62
25		420	1.264	3.89	261.07	3249.36	109315.13
30		390	1.217	3.63	259.78	3352.62	113536.84
40		370	1.183	3.47	257.82	3409.22	116799.94
Blank	700	600	1.338	5.37	270.16	2491.62	144577.15
10		540	1.287	4.79	272.59	2686.85	150306.32
15		520	1.272	4.57	275.13	2783.37	152078.80
25		480	1.264	3.98	291.61	3175.88	153041.32
30		430	1.217	3.55	292.88	3428.17	158951.71
40		420	1.183	3.55	286.07	3332.39	163520.06
Compound (**III**)							
Blank	100	380	1.338	7.41	124.00	1805.67	20653.87
10		350	1.271	6.92	122.30	1836.71	21742.63
15		330	1.252	6.46	123.52	1938.08	22072.59
25		310	1.244	5.89	127.26	2112.05	22214.53
30		290	1.212	5.50	127.49	2203.64	22801.06
40		270	1.185	5.01	130.31	2365.27	23320.57
Blank	200	420	1.338	6.03	168.42	2218.91	41307.85
10		380	1.271	5.37	171.10	2366.85	43485.37
15		360	1.252	5.13	169.68	2440.55	44145.29
25		340	1.244	4.68	175.66	2658.12	44429.18
30		320	1.212	4.37	177.06	2773.46	45602.23
40		300	1.185	4.07	178.23	2911.55	46641.27
Blank	300	460	1.338	5.62	197.91	2380.78	61961.77
10		430	1.271	6.61	157.30	1922.84	65228.05
15		400	1.252	6.03	160.40	2076.29	66217.93
25		380	1.244	5.50	167.06	2261.82	66643.77
30		360	1.212	5.25	165.80	2308.57	68403.34
40		320	1.185	4.47	173.10	2651.01	69961.90
Blank	400	490	1.338	5.25	225.68	2548.57	82615.38
10		460	1.271	5.01	222.01	2536.93	86970.40
15		420	1.252	4.47	227.19	2800.89	88290.24
25		400	1.244	4.17	231.94	2983.21	88858.02
30		380	1.212	3.98	230.86	3045.23	91204.11
40		340	1.185	3.39	242.51	3495.58	93282.18
Blank	500	520	1.338	5.13	245.10	2608.19	103269.30
10		490	1.271	4.90	241.80	2593.88	108713.08
15		470	1.252	4.68	242.83	2675.21	110362.88
25		440	1.244	4.27	249.16	2913.35	111072.61
30		410	1.212	3.98	249.09	3045.23	114005.22
40		390	1.185	3.72	253.50	3185.48	116602.81
Blank	700	600	1.338	5.37	270.16	2491.62	144577.15
10		570	1.271	5.25	262.52	2420.95	152198.45
15		550	1.252	5.01	265.44	2499.00	154508.17
25		500	1.244	4.37	276.65	2846.68	155501.79
30		460	1.212	3.98	279.46	3045.23	159607.45
40		440	1.185	3.80	279.97	3118.42	163244.08
Compound (**IV**)							
Blank	100	380	1.338	7.41	124.00	1805.67	20653.87
10		330	1.257	6.46	123.52	1945.82	21984.79
15		310	1.244	5.89	127.26	2112.05	22214.53
25		300	1.224	5.62	129.07	2177.94	22577.52
30		290	1.196	5.50	127.49	2174.55	23106.09
40		260	1.157	4.79	131.25	2415.45	23884.94
Blank	200	420	1.338	6.03	168.42	2218.91	41307.85
10		350	1.257	4.79	176.68	2624.22	43969.69
15		330	1.244	4.47	178.51	2783.00	44429.18
25		310	1.224	4.17	179.75	2935.25	45155.15
30		300	1.196	3.98	182.26	3005.03	46212.29
40		280	1.157	3.72	182.00	3110.22	47770.01
Blank	300	460	1.338	5.62	197.91	2380.78	61961.77
10		370	1.257	5.25	170.41	2394.29	65954.53
15		350	1.244	4.90	172.71	2538.78	66643.77
25		330	1.224	4.57	174.60	2678.34	67732.72
30		310	1.196	4.27	175.54	2800.94	69318.44
40		300	1.157	4.17	173.95	2774.58	71655.01

Blank	400	490	1.338	5.25	225.68	2548.57	82615.38
10		390	1.257	3.98	236.94	3158.29	87939.05
15		370	1.244	3.72	240.50	3344.09	88858.02
25		350	1.224	3.47	243.89	3527.38	90309.95
30		330	1.196	3.24	246.27	3691.36	92424.23
40		310	1.157	3.02	248.20	3831.13	95539.65
Blank	500	520	1.338	5.13	245.10	2608.19	103269.30
10		410	1.257	3.80	260.89	3307.89	109923.89
15		390	1.244	3.55	265.64	3504.23	111072.61
25		370	1.224	3.31	270.29	3697.89	112887.52
30		350	1.196	3.16	267.81	3784.81	115530.38
40		330	1.157	2.95	270.48	3922.03	119424.66
Blank	700	600	1.338	5.37	270.16	2491.62	144577.15
10		440	1.257	3.55	299.69	3540.85	153893.58
15		410	1.244	3.24	305.98	3839.51	155501.79
25		400	1.224	3.16	306.07	3873.42	158042.67
30		380	1.196	2.82	325.82	4241.13	161742.67
40		360	1.157	2.82	308.68	4102.84	167194.67
Compound (**V**)							
Blank	100	380	1.338	7.41	124.00	1805.67	20653.87
10		300	1.230	5.62	129.07	2188.61	22467.38
15		280	1.194	5.25	128.96	2274.29	23144.79
25		220	1.161	3.72	143.00	3120.97	23802.65
30		200	1.128	3.31	146.10	3407.85	24499.01
40		180	1.111	2.88	151.12	3857.64	24873.88
Blank	200	420	1.338	6.03	168.42	2218.91	41307.85
10		320	1.230	4.27	181.21	2880.56	44934.88
15		300	1.194	3.98	182.26	3000.00	46289.70
25		240	1.161	2.95	196.72	3935.59	47605.43
30		220	1.128	2.63	202.26	4288.97	48998.14
40		200	1.111	2.34	206.66	4747.86	49747.88
Blank	300	460	1.338	5.62	197.91	2380.78	61961.77
10		340	1.230	4.79	171.63	2567.85	67402.32
15		320	1.194	4.47	173.10	2671.14	69434.55
25		280	1.161	3.72	182.00	3120.97	71408.14
30		260	1.128	3.47	181.17	3250.72	73497.21
40		240	1.111	3.09	187.80	3595.47	74621.83
Blank	400	490	1.338	5.25	225.68	2548.57	82615.38
10		360	1.230	3.55	245.20	3464.79	89869.41
15		340	1.194	3.39	242.51	3522.12	92579.05
25		300	1.161	2.88	251.87	4031.25	95210.49
30		280	1.128	2.63	257.43	4288.97	97995.90
40		260	1.111	2.40	261.95	4629.17	99495.39
Blank	500	520	1.338	5.13	245.10	2608.19	103269.30
10		380	1.230	3.47	264.79	3544.67	112336.85
15		360	1.194	3.31	262.98	3607.25	115723.89
25		310	1.161	2.69	278.65	4315.99	119013.20
30		300	1.128	2.63	275.81	4288.97	122494.97
40		280	1.111	2.40	282.10	4629.17	124369.33
Blank	700	600	1.338	5.37	270.16	2491.62	144577.15
10		400	1.230	3.09	313.00	3980.58	157271.73
15		380	1.194	2.95	311.47	4047.46	162013.59
25		330	1.161	2.45	325.68	4738.78	166618.63
30		310	1.128	2.29	327.32	4925.76	171493.11
40		300	1.111	2.24	323.83	4959.82	174117.22
Compound (**VI**)							
Blank	100	380	1.338	7.41	124.00	1805.67	20653.87
10		280	1.216	5.13	131.97	2370.37	22726.05
15		260	1.188	4.68	134.33	2538.46	23261.68
25		200	1.161	3.24	149.26	3583.33	23802.65
30		180	1.136	2.75	158.27	4130.91	24326.48
40		160	1.098	2.40	161.20	4575.00	25168.38
Blank	200	420	1.338	6.03	168.42	2218.91	41307.85
10		300	1.216	3.98	182.26	3055.28	45452.22
15		280	1.188	3.63	186.51	3272.73	46523.48
25		230	1.161	2.75	202.23	4221.82	47605.43
30		200	1.136	2.24	215.89	5071.43	48653.08
40		180	1.098	2.00	217.62	5490.00	50336.89

Blank		460	1.338	5.62	197.91	2380.78	61961.77
10		320	1.216	4.37	177.06	2782.61	68178.33
15	300	300	1.188	4.07	178.23	2918.92	69785.23
25		240	1.161	2.95	196.72	3935.59	71408.14
30		220	1.136	2.63	202.26	4319.39	72979.62
40		200	1.098	2.34	206.66	4692.31	75505.33
Blank		490	1.338	5.25	225.68	2548.57	82615.38
10		340	1.216	3.31	248.37	3673.72	90904.10
15	400	320	1.188	3.09	250.40	3844.66	93046.62
25		260	1.161	2.29	274.53	5069.87	95210.49
30		240	1.136	2.09	277.66	5435.41	97305.79
40		220	1.098	1.86	286.00	5903.23	100673.39
Blank		520	1.338	5.13	245.10	2608.19	103269.30
10		360	1.216	3.24	268.66	3753.09	113630.21
15	500	340	1.188	3.02	272.22	3933.77	116308.36
25		280	1.161	2.29	295.65	5069.87	119013.20
30		260	1.136	2.09	300.80	5435.41	121632.33
40		240	1.098	1.91	303.83	5748.69	125841.83
Blank		600	1.338	5.37	270.16	2491.62	144577.15
10		380	1.216	2.88	319.04	4222.22	159082.43
15	700	360	1.188	2.75	316.53	4320.00	162831.84
25		300	1.161	2.14	338.97	5425.23	166618.63
30		280	1.136	1.95	347.19	5825.64	170285.41
40		260	1.098	1.82	345.42	6032.97	176178.72

increasing the organic compounds concentration[18] could be related to strong adsorption of organic compound which is in agreement of current density[19] observed on polarization curves. The presence of organic compounds changes the electrodeposition of copper[20] as it can be seen from decreasing the cathodic transfer coefficient.

The decrease in mass transfer coefficient as well as discharge velocity is attributed to: (1) Adsorption of organic substance on the cathode surface where they screen a part of cathode[17] thus is reducing the active cathode area with consequent reduction in the limiting current. (2) The adsorbed organic substance increases the local solution viscosity at the cathode surface with consequent decrease in the diffusivity of copper ions, resulting in a decrease of the mass transfer coefficient k and the limiting current.

Adsorption isotherm: The electrochemical processes on the metal surface are likely to be closely related to the adsorption of the inhibitor and the adsorption is known to depend on the chemical structure of the inhibitor[21-24]. The adsorption of the inhibitor molecules from aqueous solutions can be regarded as (quasi-substitution) process between the organic compound in the aqueous phase, ($org._{(aq)}$) and water molecules at the electrode surface [$H_2O(s)$]

$$(org._{(aq)}) + H_2O = (org._{(s)}) + xH_2O$$

where x (the size ratio) is the number of water molecules displaced by one molecule of organic inhibitor. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions.

The most frequently used isotherms are those of Langmuir, Frumkin, Parson, Temkin, Flory-Huggins and Bockris-Swinkels[25-28]. All these isotherms are of the general form:

$$f(\theta, x) \exp(-a\theta) = kC$$

where f (θ, x) is the configuration factor depends essentially on the physical model and assumptions underlying the derivation of the isotherm[29]. The mechanism of inhibition of reaction is generally believed to be due to the formation ad maintenance of a protective film on the metal surface[30].

Inhibitor adsorption characteristics can be estimated by using Langmuir isotherm given as[31]:

$$KC = \frac{\theta}{1-\theta}$$

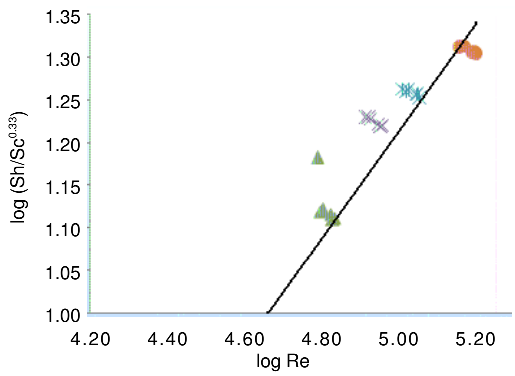
where K is the equilibrium constant of adsorption process, C is the concentration and θ is the surface coverage.

The degree of surface coverage (θ) at constant temperature was determined from[32]

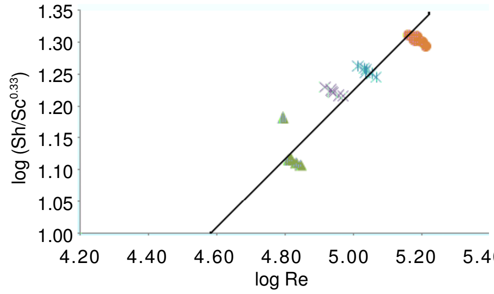
$$\theta = \frac{(I_b - I_{org})}{I_b}$$

A plot of (θ/1 – θ) *vs.* θ should yields straight line, Fig. 4 show straight line indicating that all the inhibitors verify Langmuir adsorption isotherm.

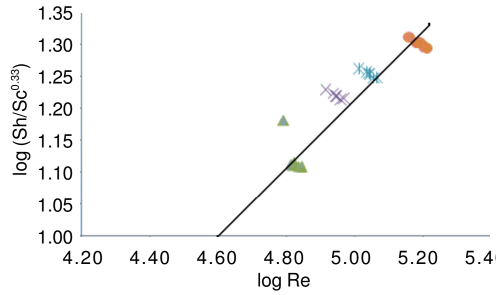
Fig. 6 show the Flory-Huggins adsorption isotherm plotted as log θ/C *vs.* log (1 – θ) for $CuSO_4/H_2SO_4$ organic compounds at 303 K yield a straight line with slope x and intercept log xK. Table-5 shows the values of X and K. The experimental data fits the Flory-Huggins adsorption isotherm which represented by:



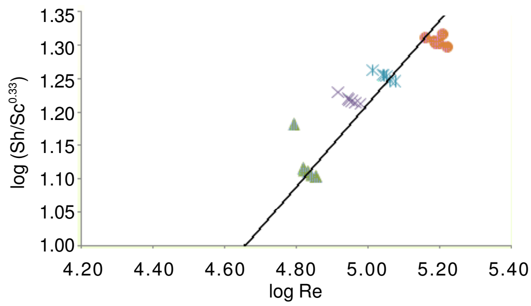
Compound (**I**)



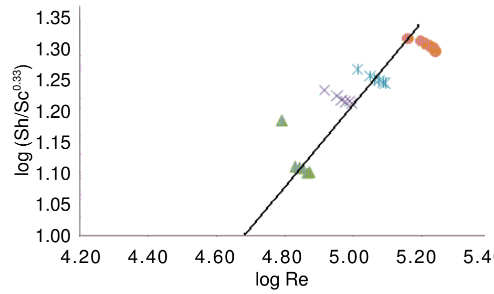
Compound (**II**)



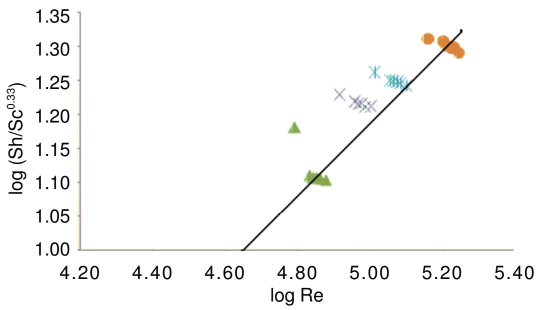
Compound (**III**)



Compound (**IV**)



Compound (**V**)



Compound (**VI**)

Fig. 5. Overall mass transfer correlation for all organic compounds at different rpm

$$\log \frac{\theta}{C} = \log xK + x\log(1-\theta)$$

here x is the number of water molecules replaced by one molecule of the inhibitor. It is clear that the surface coverage data are useful for discussing adsorption characteristics. The adsorption of inhibitors at metal-solution interface may be due to the formation of either electrostatic or covalent bonding between the adsorpates and the metal surface atoms[34].

The free energy of adsorption ΔG_{ads}. At different concentrations was calculated from the equation

$$\Delta G_{ads.} = -RT \ln (55.5k)$$

The value 55.5 is the concentration of water in the solution.

The values of $\Delta G_{ads.}$ are given in Table-5. In all cases; the ($\Delta G_{ads.}$) values are negative and lie in the range of -14.525 to -21.308 kJ/mol. The most efficient inhibitor shows the most negative ($\Delta G_{ads.}$) value. This suggests that they are strongly adsorbed on the metal surface. The negative values of ($\Delta G_{ads.}$) indicate the spontaneous adsorption of the inhibitor. This usually characteristic of strong interaction with metal surface. It is found that the ($\Delta G_{ads.}$) values are more positive than -40 kJ/mol indicating that inhibitors are physically adsorbed on the metal surface. Similar results have also been reported by Talati *et al.*[35].

Effect of temperature: The electrodeposition of copper in presence of different inhibitors was studied by measuring the limiting currents over the temperature ranges between (25-40 ºC). Table-1 shows the limiting currents obtained in presence of organic additives at different temperatures. The results indicate that the rate of electrodeposition increases with increase the temperature. The above behaviour is indicative of the occurrence of the electrodeposition through physical adsorption of additive on the metal surface. Desorption is aided by increasing the reaction temperature.

The values of (I_l) obtained at different temperatures permits the calculation of activation energy, E_a, according to Arrhenius equation:

$$\log I_t = \frac{-E_a}{2.303RT} + \log A$$

The plot of log I against 1/T gave a straight line, where A is pre-exponential factor, R is the gas constant and T is the absolute temperature. The slope of the straight line is proportional to E_a. The activation energy of the process is an important parameter for determining the rate controlling step. If the rate controlling step is a diffusion of species of the species in the boundary layer, E_a is generally ≤ 28 kJ/mol, while E_a values usually > 43 kJ/mol when the reaction is chemically controlled. Table-7 shows that the values of E_a are lower than 43 kJ/mol; characterizing diffusion process to be the controlling electrodeposition reaction.

Thermodynamic treatment of the reaction: The value of the enthalpy of activation ΔH*, entropy of activation ΔS* and free energy of activation ΔG*, can be obtained by using equation:

$$\Delta H^* = E_a - RT$$

$$\frac{\Delta S^*}{R} = \ln A - \ln\left(\frac{BTe}{h}\right)$$

TABLE-4
THERMODYNAMIC PARAMETERS FOR ELECTRODEPOSITION OF COPPER IN PRESENCE OF ORGANIC SUBSTANCE AT 25 ºC

C × 10^{-4}	Thermodynamic parameters	
Compound (**I**)		
5	E_a (kJ mol^{-1})	8194.0517578125 +OR- 51.99991989135742
	ΔH^* (kJ mol^{-1})	5715.232421875 +OR- 51.99991989135742
	ΔS^* (J mol^{-1} k^{-1})	-177.0353088378906 +OR- .1702143996953964
	ΔG^* (kJ mol^{-1})	58498.30859375 +OR- 102.7493438720703
10	E_a (kJ mol^{-1})	9164.4951171875 +OR- 76.20987701416016
	ΔH^* (kJ mol^{-1})	6685.67578125 +OR- 76.20987701416016
	ΔS^* (J mol^{-1} k^{-1})	-174.7875671386719 +OR- .2494622766971588
	ΔG^* (kJ mol^{-1})	58798.58984375 +OR- 150.5870513916016
15	E_a (kJ mol^{-1})	4934.27490234375 +OR- 2.123722791671753
	ΔH^* (kJ mol^{-1})	2455.455810546875 +OR- 2.123722791671753
	ΔS^* (J mol^{-1} k^{-1})	-189.2544403076172 +OR- 6.951706018298864E-003
	ΔG^* (kJ mol^{-1})	58881.66796875 +OR- 4.19637393951416
25	E_a (kJ mol^{-1})	6744.58203125 +OR- 928.3458862304688
	ΔH^* (kJ mol^{-1})	4265.7626953125 +OR- 928.3458862304688
	ΔS^* (J mol^{-1} k^{-1})	-183.6711578369141 +OR- 3.038809061050415
	ΔG^* (kJ mol^{-1})	59027.3203125 +OR- 1834.366821289062
30	E_a (kJ mol^{-1})	5868.66845703125 +OR- 9.804379463195801
	ΔH^* (kJ mol^{-1})	3389.849365234375 +OR- 9.804379463195801
	ΔS^* (J mol^{-1} k^{-1})	-187.6355285644531 +OR- 3.209325298666954E-002
	ΔG^* (kJ mol^{-1})	59333.3828125 +OR- 19.37298202514648
40	E_a (kJ mol^{-1})	18679.205078125 +OR- 11242.025390625
	ΔH^* (kJ mol^{-1})	16200.3857421875 +OR- 11242.025390625
	ΔS^* (J mol^{-1} k^{-1})	-146.1593170166016 +OR- 36.79917907714844
	ΔG^* (kJ mol^{-1})	59777.78515625 +OR- 22213.701171875
Compound (**II**)		
5	E_a (kJ mol^{-1})	8194.0517578125 +OR- 51.99991989135742
	ΔH^* (kJ mol^{-1})	5715.232421875 +OR- 51.99991989135742
	ΔS^* (J mol^{-1} k^{-1})	-177.0353088378906 +OR- .1702143996953964
	ΔG^* (kJ mol^{-1})	58498.30859375 +OR- 102.7493438720703
10	E_a (kJ mol^{-1})	8140.677734375 +OR- 845.6814575195312
	ΔH^* (kJ mol^{-1})	5661.8583984375 +OR- 845.6814575195312
	ΔS^* (J mol^{-1} k^{-1})	-178.4461975097656 +OR- 2.768218755722046
	ΔG^* (kJ mol^{-1})	58865.59375 +OR- 1671.02587890625
15	E_a (kJ mol^{-1})	6516.78759765625 +OR- 840.9186401367188
	ΔH^* (kJ mol^{-1})	4037.968505859375 +OR- 840.9186401367188
	ΔS^* (J mol^{-1} k^{-1})	-184.27978515625 +OR- 2.752628326416016
	ΔG^* (kJ mol^{-1})	58980.98828125 +OR- 1661.61474609375
25	E_a (kJ mol^{-1})	5459.28369140625 +OR- 6.449143886566162
	ΔH^* (kJ mol^{-1})	2980.464599609375 +OR- 6.449143886566162
	ΔS^* (J mol^{-1} k^{-1})	-188.3694458007812 +OR- 2.111036144196987E-002
	ΔG^* (kJ mol^{-1})	59142.81640625 +OR- 12.74319839477539
30	E_a (kJ mol^{-1})	6104.0390625 +OR- 14.07808780670166
	ΔH^* (kJ mol^{-1})	3625.219970703125 +OR- 14.07808780670166
	ΔS^* (J mol^{-1} k^{-1})	-187.1856079101562 +OR- 4.608263447880745E-002
	ΔG^* (kJ mol^{-1})	59434.609375 +OR- 27.81762504577637
40	E_a (kJ mol^{-1})	6618.1416015625 +OR- 20.7771053314209
	ΔH^* (kJ mol^{-1})	4139.322265625 +OR- 20.7771053314209
	ΔS^* (J mol^{-1} k^{-1})	-186.1835479736328 +OR- 6.801091134548187E-002
	ΔG^* (kJ mol^{-1})	59649.9453125 +OR- 41.05455780029297
Compound (**III**)		
5	E_a (kJ mol^{-1})	8194.0517578125 +OR- 51.99991989135742
	ΔH^* (kJ mol^{-1})	5715.232421875 +OR- 51.99991989135742
	ΔS^* (J mol^{-1} k^{-1})	-177.0353088378906 +OR- .1702143996953964
	ΔG^* (kJ mol^{-1})	58498.30859375 +OR- 102.7493438720703
10	E_a (kJ mol^{-1})	8649.8720703125 +OR- 62.83306121826172
	ΔH^* (kJ mol^{-1})	6171.052734375 +OR- 62.83306121826172
	ΔS^* (J mol^{-1} k^{-1})	-175.9946594238281 +OR- .2056751549243927
	ΔG^* (kJ mol^{-1})	58643.859375 +OR- 124.1551055908203

15	E_a (kJ mol^{-1})	9164.4951171875 +OR- 76.20987701416016
	ΔH^* (kJ mol^{-1})	6685.67578125 +OR- 76.20987701416016
	ΔS^* (J mol^{-1} k^{-1})	-174.7875671386719 +OR- .2494622766971588
	ΔG^* (kJ mol^{-1})	58798.58984375 +OR- 150.5870513916016
25	E_a (kJ mol^{-1})	7905.19287109375 +OR- 464.7861633300781
	ΔH^* (kJ mol^{-1})	5426.37353515625 +OR- 464.7861633300781
	ΔS^* (J mol^{-1} k^{-1})	-179.2476806640625 +OR- 1.521411776542664
	ΔG^* (kJ mol^{-1})	58869.0703125 +OR- 918.3950805664062
30	E_a (kJ mol^{-1})	8680.0400390625 +OR- 858.7814331054688
	ΔH^* (kJ mol^{-1})	6201.220703125 +OR- 858.7814331054688
	ΔS^* (J mol^{-1} k^{-1})	-177.3432769775391 +OR- 2.811099529266357
	ΔG^* (kJ mol^{-1})	59076.1171875 +OR- 1696.910766601562
40	E_a (kJ mol^{-1})	7793.81201171875 +OR- 1088.45654296875
	ΔH^* (kJ mol^{-1})	5314.99267578125 +OR- 1088.45654296875
	ΔS^* (J mol^{-1} k^{-1})	-181.4197540283203 +OR- 3.562908887863159
	ΔG^* (kJ mol^{-1})	59405.29296875 +OR- 2150.73779296875
	Compound (**IV**)	
5	E_a (kJ mol^{-1})	8194.0517578125 +OR- 51.99991989135742
	ΔH^* (kJ mol^{-1})	5715.232421875 +OR- 51.99991989135742
	ΔS^* (J mol^{-1} k^{-1})	-177.0353088378906 +OR- .1702143996953964
	ΔG^* (kJ mol^{-1})	58498.30859375 +OR- 102.7493438720703
10	E_a (kJ mol^{-1})	8898.490234375 +OR- 69.14267730712891
	ΔH^* (kJ mol^{-1})	6419.6708984375 +OR- 69.14267730712891
	ΔS^* (J mol^{-1} k^{-1})	-175.4161224365234 +OR- .2263287901878357
	ΔG^* (kJ mol^{-1})	58719.98828125 +OR- 136.6226043701172
15	E_a (kJ mol^{-1})	7661.0380859375 +OR- 357.6551818847656
	ΔH^* (kJ mol^{-1})	5182.21875 +OR- 357.6551818847656
	ΔS^* (J mol^{-1} k^{-1})	-179.8570404052734 +OR- 1.170733690261841
	ΔG^* (kJ mol^{-1})	58806.59375 +OR- 706.7094116210938
25	E_a (kJ mol^{-1})	9737.3330078125 +OR- 92.24694061279297
	ΔH^* (kJ mol^{-1})	7258.513671875 +OR- 92.24694061279297
	ΔS^* (J mol^{-1} k^{-1})	-173.4191436767578 +OR- .3019573390483856
	ΔG^* (kJ mol^{-1})	58963.4296875 +OR- 182.2755279541016
30	E_a (kJ mol^{-1})	5459.28369140625 +OR- 6.449143886566162
	ΔH^* (kJ mol^{-1})	2980.464599609375 +OR- 6.449143886566162
	ΔS^* (J mol^{-1} k^{-1})	-188.3694458007812 +OR- 2.111036144196987E-002
	ΔG^* (kJ mol^{-1})	59142.81640625 +OR- 12.74319839477539
40	E_a (kJ mol^{-1})	6104.0390625 +OR- 14.07808780670166
	ΔH^* (kJ mol^{-1})	3625.219970703125 +OR- 14.07808780670166
	ΔS^* (J mol^{-1} k^{-1})	-187.1856079101562 +OR- 4.608263447880745E-002
	ΔG^* (kJ mol^{-1})	59434.609375 +OR- 27.81762504577637
	Compound (**V**)	
5	E_a (kJ mol^{-1})	8194.0517578125 +OR- 51.99991989135742
	ΔH^* (kJ mol^{-1})	5715.232421875 +OR- 51.99991989135742
	ΔS^* (J mol^{-1} k^{-1})	-177.0353088378906 +OR- .1702143996953964
	ΔG^* (kJ mol^{-1})	58498.30859375 +OR- 102.7493438720703
10	E_a (kJ mol^{-1})	9737.3330078125 +OR- 92.24694061279297
	ΔH^* (kJ mol^{-1})	7258.513671875 +OR- 92.24694061279297
	ΔS^* (J mol^{-1} k^{-1})	-173.4191436767578 +OR- .3019573390483856
	ΔG^* (kJ mol^{-1})	58963.4296875 +OR- 182.2755279541016
15	E_a (kJ mol^{-1})	7509.20068359375 +OR- 500.3245849609375
	ΔH^* (kJ mol^{-1})	5030.38134765625 +OR- 500.3245849609375
	ΔS^* (J mol^{-1} k^{-1})	-181.7763519287109 +OR- 1.637741804122925
	ΔG^* (kJ mol^{-1})	59227 +OR- 988.6173095703125
25	E_a (kJ mol^{-1})	7251.72119140625 +OR- 1053.291015625
	ΔH^* (kJ mol^{-1})	4772.90185546875 +OR- 1053.291015625
	ΔS^* (J mol^{-1} k^{-1})	-183.4333190917969 +OR- 3.447799444198608
	ΔG^* (kJ mol^{-1})	59463.546875 +OR- 2081.25244140625
30	E_a (kJ mol^{-1})	6618.1416015625 +OR- 20.7771053314209
	ΔH^* (kJ mol^{-1})	4139.322265625 +OR- 20.7771053314209
	ΔS^* (J mol^{-1} k^{-1})	-186.1835479736328 +OR- 6.801091134548187E-002
	ΔG^* (kJ mol^{-1})	59649.9453125 +OR- 41.05455780029297

40	E_a (kJ mol^{-1})	6913.685546875 +OR- 25.87574005126953
	ΔH^* (kJ mol^{-1})	4434.8662109375 +OR- 25.87574005126953
	ΔS^* (J mol^{-1} k^{-1})	-185.5786743164062 +OR- 8.47005769610405E-002
	ΔG^* (kJ mol^{-1})	59765.1484375 +OR- 51.12921524047852
	Compound (**VI**)	
5	E_a (kJ mol^{-1})	8194.0517578125 +OR- 51.99991989135742
	ΔH^* (kJ mol^{-1})	5715.232421875 +OR- 51.99991989135742
	ΔS^* (J mol^{-1} k^{-1})	-177.0353088378906 +OR- .1702143996953964
	ΔG^* (kJ mol^{-1})	58498.30859375 +OR- 102.7493438720703
10	E_a (kJ mol^{-1})	8970.958984375 +OR- 884.2886962890625
	ΔH^* (kJ mol^{-1})	6492.1396484375 +OR- 884.2886962890625
	ΔS^* (J mol^{-1} k^{-1})	-176.6717834472656 +OR- 2.894593954086304
	ΔG^* (kJ mol^{-1})	59166.83203125 +OR- 1747.311889648438
15	E_a (kJ mol^{-1})	7497.58349609375 +OR- 1043.4931640625
	ΔH^* (kJ mol^{-1})	5018.76416015625 +OR- 1043.4931640625
	ΔS^* (J mol^{-1} k^{-1})	-182.0774230957031 +OR- 3.415727615356445
	ΔG^* (kJ mol^{-1})	59305.1484375 +OR- 2061.892333984375
25	E_a (kJ mol^{-1})	6618.1416015625 +OR- 20.7771053314209
	ΔH^* (kJ mol^{-1})	4139.322265625 +OR- 20.7771053314209
	ΔS^* (J mol^{-1} k^{-1})	-186.1835479736328 +OR- 6.801091134548187E-002
	ΔG^* (kJ mol^{-1})	59649.9453125 +OR- 41.05455780029297
30	E_a (kJ mol^{-1})	9208.2802734375 +OR- 1314.371948242188
	ΔH^* (kJ mol^{-1})	6729.4609375 +OR- 1314.371948242188
	ΔS^* (J mol^{-1} k^{-1})	-178.1703186035156 +OR- 4.30241060256958
	ΔG^* (kJ mol^{-1})	59850.94140625 +OR- 2597.1357421875
40	E_a (kJ mol^{-1})	9908.6357421875 +OR- 997.0340576171875
	ΔH^* (kJ mol^{-1})	7429.81640625 +OR- 997.0340576171875
	ΔS^* (J mol^{-1} k^{-1})	-175.9748840332031 +OR- 3.263649940490723
	ΔG^* (kJ mol^{-1})	59896.7265625 +OR- 1970.09130859375

TABLE-5
EFFECT OF DIFFERENT CONCENTRATION OF COMPOUND (**I**) ON LIMITING CURRENT AT 25 ºC IN CASE Cu-Cu

V	I_l					
	5×10^{-4}	10×10^{-4}	15×10^{-4}	25×10^{-4}	30×10^{-4}	40×10^{-4}
100	100	100	100	100	100	100
200	130	130	130	130	130	130
300	180	180	180	180	180	180
360	200	200	200	200	200	200
440	250	250	250	250	220	200
580	300	280	280	260	230	210
600	350	320	300	280	250	240
1160	380	340	320	300	280	250
1200	400	350	330	310	300	260
1240	410	350	340	320	310	280

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

Table-8 shows that the entropy ΔS^* posses negative values, indicating a highly ordered organic species in the solution under investigation. It is also noticed that the weak dependence of ΔG^* on the compensation of the organic additives can be attributed largely to the general linear composition between ΔH^* and ΔS^* for the given temperature.

Isokinetic temperature: Variation in the rate within a reaction series may be caused by changes in either or both, the enthalpy or the entropy of activation. The correlation of ΔH^* with ΔS^* is a linear relationship may be stated algebraically;

$$\Delta H^* = \beta\Delta S^* + \text{Constant}$$
$$\delta\Delta H^* = \beta\delta\Delta S^*$$

The operator, δ, concerns difference between any two reactions in the series.

Substituting from $\delta\Delta H^* = \beta\delta\Delta S^*$ into the familiar relationship:

$$\delta\Delta H^* = \delta\Delta G^* + T\delta\Delta S^*$$

We obtain

$$\beta\delta\Delta S^* = \delta\Delta G^* + T\delta\Delta S^*$$

It follows that when $\delta\Delta G^*$ equal zero, β equals T. In other words, the slope in a linear plot of ΔH^* *versus* ΔS^* is the temperature at which all the reactions that conform to the line occur at the same rate. β is therefore known as the isokinetic temperature.

The plots of ΔH^* *versus* ΔS^* in presence of organic additives, the isokinetic temperatures β were 266.7, 280.3, 295.4, 282, 282.9, 285.7 and 277.4 K for mannose, sucrose, lactose and maltose, respectively, these values which are much lower than that of the experimental temperature 298 K indicating that the rate of the reactions is entropy controlled[13], but the value of β which are much higher than 298 K such as 324.6 K for glucose in case of Cu-Pb indicating that the rate of the reaction is enthalpy controlled[36].

Conclusion

The electrode process on copper in acidified $CuSO_4$ was finding to depend on the carbohydrate acids as well as their concentrations. They also depend on the type of the carbohydrate as well as their concentrations. They also depend on the type of the cathode and temperature. The activation energy proves that the reaction is diffusion controlled. The overall mass transfer correlation proves that the electroplating reaction is natural convection which is in accordance with our previous studies.

List of symbols

N	:	Total mass transfer rate, mol cm^{-2} s^{-1}
D	:	Diffusion coefficient of metal ions, cm^2 s^{-1}
[dC/dY]	:	Concentration gradient at the interface
i	:	Current density, A cm^{-2}
n_c	:	Transference number of the deposited cation
z or n	:	Number of the transferred electrons = 2 in case of Cu^{2+} ions
F	:	Faraday's constant = 96485 A s mol^{-1}
δ_N	:	is often named as the effective diffusion layer thickness, cm
j	:	Mass transfer rate, mol cm^{-2} s^{-1}
C_o or C_b	:	Bulk concentration, mol cm^{-3}
C_e	:	Interfacial concentration, mol cm^{-3}
K	:	Mass transfer coefficient, cm s^{-1}
Sh	:	Sherwood number, Sh = kd/D
d	:	Cylinder diameter, cm
Gr	:	Grashoff number, $Gr = g\alpha(C_o - C_b)I^3/\nu^2$
l	:	Cathode height, cm
ν	:	Kinematic viscosity, cm^2 sec^{-1}
Sc	:	Schmidt number, Sc = ν/D
Re	:	Reynolds number, Re = Ud/ν
U	:	Electrode peripheric velocity or characteristic flow velocity, cm s^{-1}, U = ωr, cm rad s^{-1}
ω	:	Angular velocity, rad s^{-1}
r	:	Radial distance, cm
Fr	:	Froude number, $Fr = V^2/hg$
V	:	Oxygen gas discharge velocity, cm s^{-1}
h	:	Electrode height, cm
g	:	Acceleration gravity, cm s^{-2}
Θ	:	Surface coverage
i_L	:	Limiting current density, A cm^{-2}
η	:	Absolute viscosity of solution, centipoises
ρ	:	Density of solution, g cm^{-3}
ΔH*	:	Enthalpy of activation, kJ mol^{-1}
ΔS*	:	Entropy of activation, J mol^{-1} K^{-1}
ΔG*	:	Net free-energy change, kJ mol^{-1}
R	:	Universal gas constant = 8.314 J mol^{-1} K^{-1}
T	:	Absolute temperature, K
E_a	:	Activation energy, kJ mol^{-1}
A	:	Arrhenius constant
RCE	:	Rotating cylinder electrode
RDE	:	Rotating disk electrode
δ	:	Difference between any two reactions in the series
β	:	Isokinetic temperature K
B	:	Boltzmann constant
h	:	Plank's constant

REFERENCES

1. N. Ibl, P. Delahary and C.W. Tobias, Advances in Electrochemistry and Electrochemical Engineering, edn. 2, p. 49 (1962).
2. N. Ibl, P.H. Javet and F. Stonel, *Electrochim. Acta*, **17**, 733 (1972).
3. J. Lipkowski and P.N. Ross, Adsorption of Molecules at Metal Electrodes, VCH Publishers, New York, Weinheim, Cambridge (1992).
4. W. Plieth, *Electrochim. Acta*, **37**, 2115 (1992).
5. L. Oniciu and L. Muresan, *J. Appl. Electrochem*., **21**, 565 (1991).
6. T.C. Franklin, *Plat. Surf. Finish*., **4**, 62 (1994).
7. S. Trasatti, *Electrochim. Acta*, **37**, 2137 (1992).
8. L. Bonou, M. Eyraud, R. Denoyel and Y. Massiani, *Electrochim. Acta*, **47**, 4139 (2002).
9. A.M. Ahmed and S.M. Zourab, *Z. Metalkide*, **74**, 476 (1988).
10. A.M. Ahmed, *Bull. Electrochem. (India)*, **5**, 212 (1989).
11. A.M. Ahmed, *Bull. Electrochem. (India)*, **6**, 528 (1990).
12. A.M. Ahmed, N.H. EI-Hammamy, E.A. Hamed and H.M. Abdelfattah, *J. Alex. Eng*., **30**, 81 (1991).
13. A.M. Ahmed and H.M. Faid-allah, *Bull. Electrochem. (India)*, **3**, 255 (1987).
14. S.S. Abd El-Rehim, S.M. Sayyah and M.M. EI-Deeb, *Appl. Surf, Sci.*, **165**, 249 (2000).
15. A.-M.M. Ahmed, A.A.-H. Abdel-Rahman and A.F. El-Adl, *J. Dispersion Sci. Technol.*, **31**, 3 (2010).
16. S. Vurvara, L. Muresan, A. Nicoara, G. Maurin and I.C. Popescu, *Mater. Chem. Phys*., **72**, 332 (2001).
17. N. Hackerman, *Corrosion*, **18**, 3321 (1962).
18. B.G. Atya, B.E. EI-Anadouli and F.M. EI-Nizamy, *Corros. Sci.*, **24**, 321 (1984).
19. X.L. Cheng, H.Y. Ma, S.H. Chen, R. Yu, X. Chen and Z.M. Yao, *Corros. Sci.*, **41**, 321 (1999).
20. M. Bouayed, H. Rabaa, A. Srhiri, J.Y. Saillard, A.B. Bachirand and A.L. Beuze, *Corros. Sci*., **41**, 501 (1999).
21. A.N. Frumkin, *Z. Phys. Chem*., **116**, 446 (1925).
22. O. lkeda, H. Jimbo and H. Jaumura, *J. Electroanal. Chem*., **137**, 127 (1982).
23. R. Parsons, *J. Electroanal. Chem*., **7**, 136 (1964).
24. J.O.M. Bockris and D.A.J. Swinkels, *J. Electrochem. Soc*., **111**, 736 (1964).
25. B.G. Ateya, B.E. El-Anadouli and F.M. El-Nizamy, *Corros. Sci*., **24**, 509 (1984).
26. V. Chandradrase and K. Kannan, *Bull. Electrochem. (India)*, **20**, 471 (2004)
27. E.E. Oguize, B.N. Okolue, C.E. Ogukwe, A.I. Onuchukwu and C. Unaegbu, *Bull. Electrochem*., **20**, 421 (2004).
28. E.E. Ebenso, U.J. Ekpe, B.I. Ita, O.E. Offiong and U.J. Ibok, *Mater. Chem. Phys*., **60**, 79 (1999).
29. E.E. Ebenso, *Bull. EIectrochem*., **19**, 209 (2003).
30. M.A. Quraishi and R. Sardar, *Bull. Electrochem*., **18**, 515 (2002).
31. D.R. Russev, *J. Appl. Electrochem.*, **11**, 177 (1980).
32. Y. Ogata, K. Yamakawa and S. Yoshizawa, *J. Appl. Electrochim*., **13**, 611 (1983).
33. M.I. Ismmail and T.Z. Fahidy, *J. Appl. Electrochem*., **11**, 543 (1981).
34. P.H. Strickland and F. Lawson, *Proc. Aust. Inst. Min-Met*., **236**, 25 (1970).
35. J.D. Talati and J.M. Darji, *J. Indian Chem. Soc*., **65**, 94 (1988).
36. M. Mousa, M.M. EI-Banna and I.A.S. Monsour, *Bull. Electrochem*., **7**, 164 (1991).