

## Kinetic Study of the Effect of Selected Surfactants on Corrosion of Copper

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**Abstract:** The rates of copper corrosion were determined by measuring the limiting current of anodic dissolution of copper in phosphoric acid in presence and in absence of cetyl trimethyl ammonium bromide (CTAB) and cetyl pyridinium bromide (CPYB). The rate of corrosion is found to decrease by increasing the concentration of the surfactant. The percentage of inhibition ranged from 1.85 to 33.97% depending on the type of surfactant and its concentration. Increasing the copper electrode height, and concentration of  $H_3PO_4$  decreases the rate of copper corrosion. The investigated adsorption isotherms indicate that the two surfactants fit Langmuir and Flory Huggins isotherm. The thermodynamic parameters show that corrosion is a diffusion controlled process. The dimensional analysis method was used to obtain the overall mass transfer correlations under the study conditions.

**Keywords:** corrosion, surface active substance, ammonium salts, mass transfer in electrolysis.

### INTRODUCTION

Copper is one of the preferred metals in industry owing to its excellent electrical and thermal conductivities, good mechanical workability and its relatively noble properties<sup>[1-3]</sup>. Corrosion inhibition of copper in a wide variety of media has attracted the attention of a number of investigators<sup>[4-8]</sup>. In general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure, and the type of the electrolyte solution<sup>[9]</sup>. It has been accepted that the corrosion inhibition process results from the formation of organic inhibitor films on the metal surface<sup>[10]</sup>. The anodic dissolution of copper in organic solvent environments is influenced by its concentration<sup>[11]</sup>. In the present work, a study of the inhibiting effect of some inhibitors in case of copper corrosion in different concentrations of phosphoric acid solution was carried out. The aim is to discuss the mechanism of protection given by these organic additives as CPYB and CTAB on the electro-dissolution of copper in  $H_3PO_4$  and the factors that affect corrosion process.

### MATERIALS AND METHODS

All of the reagents and chemicals were of analytical grade and used without further purification. Double distilled de-ionized water was used in the preparation of solutions.

The cell used in the present work consists of rectangular container having the dimensions of 5 x 5x 10 cm with electrodes fitting the whole cross section. The electrodes were rectangular copper sheets of 10 cm height and 5cm width. Electrode separation was 5 cm; a porous PVC diaphragm was used to prevent the stirring effect due to  $H_2$  bubbling. The electric circuit consisted of a 6v D.C. power supply, a variable resistance and a multirange ammeter connected in series with the cell. A high impedance voltmeter was connected in parallel with the cell to measure its potential. Five concentrations (6, 8, 10, 12 and 14 M) of phosphoric acid were used. The steady state anode potential was measured against a reference electrode consisted of copper wire immersed in a cup of luggin tube filled with phosphoric acid organic additives solution similar to that in the cell; the tip of the luggin tube was placed 0.5-1 mm from the anode wall. Polarization curves, from which the limiting current was determined, were plotted by increasing the applied current stepwise and measuring the corresponding steady state potential. Before each run, the back of the anode was insulated with polystyrene lacquer and the active surface was polished with fine emery paper, degreased with trichloroethylene, washed with alcohol and finally rinsed in distilled water. The temperature was regulated by placing the cell in a thermostated water bath. The apparatus, which permits the rotation of camping cylinder assembly, is arranged so that, the anode consists of copper metal disk of 2 cm diameter and 2mm thickness. The sides and back of the disk as well

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as the drive shaft are insulated by epoxy resin. The cathode is made of cylindrical copper electrode of 12 cm diameter. It also acts as a reference electrode because its surface area is very large compared to that of the anode.

### RESULTS AND DISCUSSION

Leveling is the principle process in electropolishing [12] and can be explained in terms of mass transfer mechanism [13]. The study of leveling is based on the classical current voltage curves of corrosion. Cell with and without a diaphragm were used to study the effect of hydrogen gas evolved at the cathode on the limiting current. While a cell without diaphragm is used to study the effect of hydrogen gas evolved at the cathode on the rate of mass transfer at the anode i.e. forced convection. Fig. 1 shows the limiting current,  $I_l$  currents with and without a diaphragm.

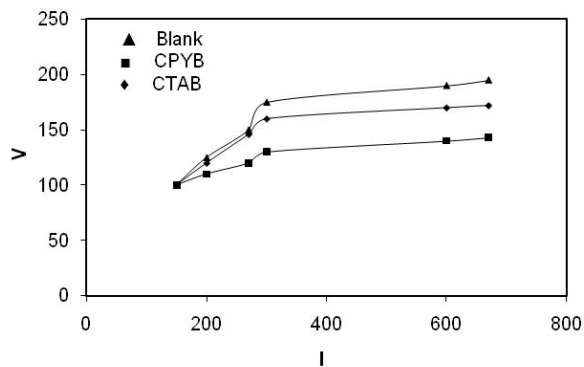


Fig. 1a: The relation between current and voltage at 298K and 4cm height in 8M  $H_3PO_4$

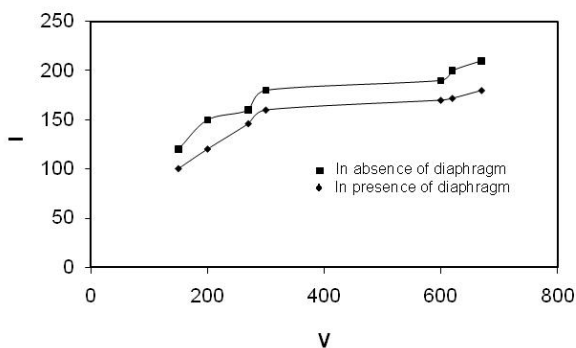


Fig. 1b: The relation between current and voltage at 298K and 4cm height, 8 M  $H_3PO_4$  in absence and presence of diaphragm

**Effect of electrolyte concentration on the polishing current:** Fig. 2 shows the dependence of the polishing current on the bulk concentration of phosphoric acid. The limiting current density decreases with the increase of phosphoric acid concentration but the values of limiting current in acid-additives mixtures is less than in water-acid mixtures. This is in agreement with the finding of other authors who worked within the same range of concentration using other anode geometries [14-16]. From the practical point of view, we can recommend on the basis of above result that it is preferable to use relatively high organic additives percentage to inhibit polishing or dissolution of metal at the same phosphoric acid concentration.

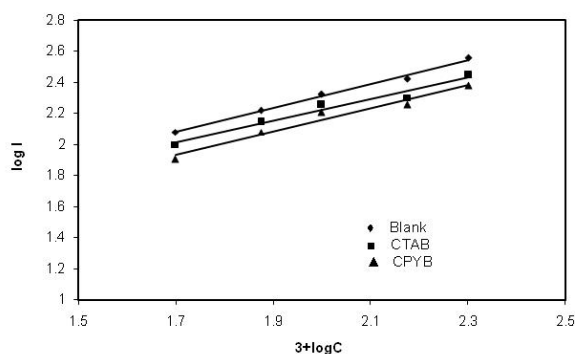


Fig. 2: The relation between  $\log I_l$  and phosphoric acid concentration at 298K

The decrease in the limiting current with increasing  $H_3PO_4$  concentration is attributed to two effects:

1. The solubility of the dissolved copper phosphate in  $H_3PO_4$ , which makes the onset of the limiting current, decreases with increasing  $H_3PO_4$  concentration.
2. The viscosity of the solution increases with increasing  $H_3PO_4$  concentration with consequence decrease in the diffusivity of  $Cu^{2+}$  according to Stokes-Einstein equation:

$$D\eta/T = \text{constant} \quad (1)$$

where  $D$  = diffusivity of  $Cu^{2+}$  in  $cm^2s^{-1}$ ,  $\eta$  = viscosity of solution in poise,  $T$  = absolute temperature and  $\nu = \eta/\rho$  (where  $\nu$  is the kinematic viscosity in stoke and  $\rho$  is density in  $gm\ cm^{-3}$ ).

Also, the increase in solution viscosity with increasing phosphoric acid concentration results in an increase in the diffusion layer thickness which represents the resistance to the rate of mass transfer of  $Cu^{2+}$  from anode surface to bulk solution.

On adding organic additives of different concentrations to phosphoric acid, the limiting current decreases. This may be explained on the basis that viscosity of organic

additives-water- H<sub>3</sub>PO<sub>4</sub> mixture is higher than for water- H<sub>3</sub>PO<sub>4</sub> mixture and this led to:

1. Decrease in diffusivity of Cu<sup>2+</sup>.
2. The solubility of copper phosphate in this solvent is lower than in water phosphoric acid medium so saturation of solution is attained quickly and the limiting current is small.

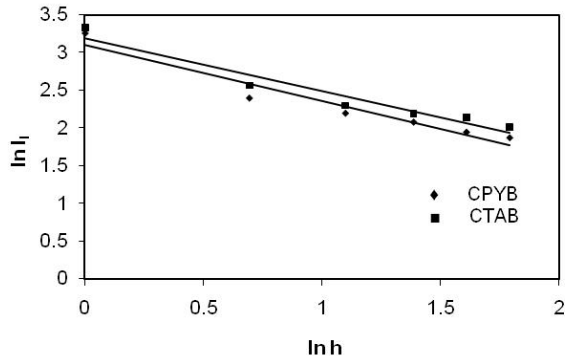


Fig. 3: The relation between I<sub>1</sub> and height of electrode at 298K and 8MH<sub>3</sub>PO<sub>4</sub>

Table 1: Effect of different height of copper electrode on limiting current (mA) in presence of organic substances (C=11x10<sup>-4</sup> mol l<sup>-1</sup> at 298K and 12M H<sub>3</sub>PO<sub>4</sub>)

h cm	I <sub>1</sub> blank	I <sub>1</sub> /A blank	I <sub>1</sub> /A CPYB	I <sub>1</sub> /A CTAB
1	170	30	26	28
2	150	15	11	13
3	180	12	9	10
4	210	10.5	8	9
5	260	10.4	7	8.5
6	280	9.33	6.5	7.5

**Effect of electrode height on polishing current:** Table 1 and Fig. 3 show that the limiting current density decreases with the increase in height. In electropolishing and generally for anodic dissolution of metals, the direction of flow of the hydrodynamic boundary layer and the diffusion layer increases in the downward direction. Accordingly, the local limiting current density increases in the upward direction of the anode. This explains why polishing is attained at the upper parts of the electrode before the lower part at the limiting current region. This was confirmed by the visual observation during electropolishing. The average limiting current density decreases with the increase in the height according to the equation:

$$I_1 = \frac{C}{(H)^a} \quad (2)$$

where C is constant, H is the height, a is constant depends on type of solution used, where a = 0.31 for 8 M H<sub>3</sub>PO<sub>4</sub> as example.

**Effect of organic additives concentrations:** If the limiting current in the absence of SAS is (I<sub>1</sub>) and in the presence of SAS is (I), the percentage inhibition can be calculated from:

$$\% \text{ inhibition} = \frac{I_1 - I}{I_1} \times 100 \quad (3)$$

Table 2: Effect of concentration of organic additives on the percentage inhibition at 298K

Cx 10 <sup>4</sup> mol l <sup>-1</sup>	I <sub>1</sub>	CTAB %inhibition	I <sub>1</sub>	CPYB %inhibition
0.0	265			
5.50	230	13.21	265	1.852
11.0	225	15.10	260	3.704
21.78	200	24.53	245	9.259
32.36	190	28.34	235	12.96
47.73	180	32.08	230	14.82
52.91	175	33.97	220	18.2

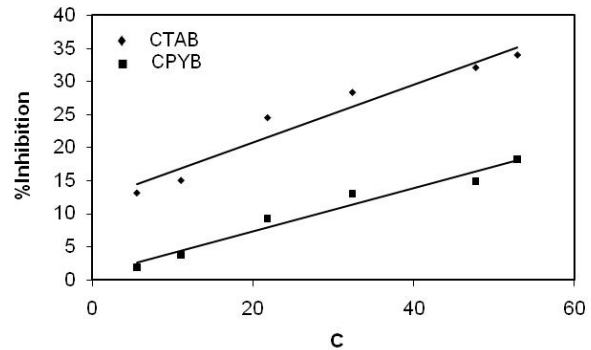


Fig. 4: The relation between percentage inhibition and concentration at 298K

Table (2) and Fig. (4) show that % inhibition depends on the type of SAS and its concentration. The values are ranged from 13.21% to 33.97 % depending on the type of SAS and its concentration. From table (1) and Fig. (3), the order of increasing the rate of corrosion is as follow:

$$CTAB > CPYB$$

Fig. 3 shows that as T increases the rate of the corrosion increases. Cationic SAS adsorbed strongly on the surface of copper metal. The above results are discussed as:

1. SAS may form a thin film on the metal surface; which leads to decrease the rate of corrosion. Also,

adsorption of SAS on copper surface depends mainly on its structure.

2. The decrease in the diffusion coefficient (D) of Cu<sup>2+</sup> ion solutions containing surfactants which is due to the increase in the interfacial viscosity (η) is in accordance with Stokes-Einstein equation as shown in table (8). The increase in interfacial viscosity in table (8) is caused by the adsorption of surfactant molecules at the copper surface with their polar end direction towards the solution and the non polar end directed to the copper surface. The present results agree with polarographic studies conducted in solutions containing surfactants where it was found that the diffusion current decreases in the presence of surfactants.

3. SAS not only decrease the limiting current through lowering surface tension but also through other effects such as adsorption on the cathode surface. The cationic SAS repels from the anode<sup>[17, 18]</sup>.

4. Adsorption of SAS on the Cu-anode may lower the limiting current through increasing the interfacial viscosity owing to displacement of adsorbed H<sub>2</sub>O molecules on the Cu-surface by surfactant molecules which is supported by adsorption isotherm.

**Adsorption isotherm:** The value of (ΔI<sub>l</sub>) (the decrease of the limiting current with respect to the I<sub>l</sub> value in absence of SAS) at a given concentration was determined and the degree of surface coverage θ was calculated by the relation:

$$\theta = \frac{I_l - I}{I_l} \quad (4)$$

The adsorption of SAS was found to obey a Langmuir isotherm which is given by equation (5):

$$\frac{\theta}{1-\theta} = K(C)^y \quad (5)$$

or  $\log \frac{\theta}{1-\theta} = \log K + y \log C \quad (6)$

Table 3: Adsorption isotherm data using 8 M H<sub>3</sub>PO<sub>4</sub> at 298K

Cx 10 <sup>4</sup> mol l <sup>-1</sup>	I <sub>l</sub> mA	θ	1-θ	θ/(1-θ)	-log(1-θ)	-Logθ/C
(a) CTAB						
0.0	265					
5.50	230	0.13	0.87	0.15	0.06	2.38
11.0	225	0.15	0.85	0.18	0.07	2.14
21.78	200	0.25	0.71	0.33	0.12	2.05
32.36	190	0.28	0.72	0.39	0.14	1.94
47.73	180	0.32	0.68	0.47	0.17	1.88
52.91	175	0.34	0.66	0.51	0.18	1.80
0.0	265					
5.50	260	0.02	0.98	0.02	0.01	1.54
11.0	250	0.08	0.94	0.06	0.03	1.71
21.78	240	0.09	0.91	0.10	0.04	1.64
32.36	230	0.13	0.87	0.15	0.06	1.61
47.73	225	0.15	0.85	0.18	0.06	1.55
52.91	215	0.19	0.81	0.25	0.09	1.55

Table 3 shows adsorption isotherm data using 8 M H<sub>3</sub>PO<sub>4</sub> at 298K. A plot of (θ/1-θ) vs. C would give a straight line for both organic additives as in figure (5) indicating that the inhibitor verifies Langmuir adsorption isotherm. Fig. (6) shows the Flory Huggins adsorption isotherm plotted as log θ/C vs. log (1-θ) yielded straight line with slope x and intercept log xk. The experimental data fits Flory Huggins adsorption isotherm which is represented by equation

$$\log \frac{\theta}{C} = \log xk + \log (1-\theta) \quad (7)$$

where x is the number of water molecules replaced by one molecule of inhibitor.

The free energy of adsorption ΔG<sub>ads</sub> was calculated from the equation

$$\Delta G_{ads} = -RT \ln (55.5k) \quad (8)$$

The values of ΔG<sub>ads</sub> are given in table (4). ΔG<sub>ads</sub> values are negative and lie in range 19.24 to 20.97. The most efficient inhibitor shows the most negative ΔG<sub>ads</sub>. This suggests that they are strongly adsorbed on metal surface. The negative values ΔG<sub>ads</sub> indicate the spontaneous adsorption of inhibitors. This is usually characteristic of strong interaction with metal surface. It is found that ΔG<sub>ads</sub> are more positive than 46 KJ/mol indicating that inhibitors are physically adsorbed on metal surface. Similar results have also been reported<sup>[19]</sup>.

**Effect of temperature:** The corrosion of copper in phosphoric acid in the presence of inhibitors was studied by measuring the limiting current over the temperature range 298-313K. The data is shown in Table (5). It is found that the rate of copper corrosion increases as temperature increases. Table (6) shows the values of E<sub>a</sub> obtained at different temperatures permitted the calculation of the activation energy E<sub>a</sub> according Arrhenius equation:

$$\log I = [-E_a/(2.303RT)] + C \quad (9)$$

where R is gas constant = 8.32 x 10<sup>7</sup> erg mole<sup>-1</sup> degree<sup>-1</sup> and T is the absolute temperature. Plotting log K vs. 1/T gives a straight line.

The activation energy values are given in table (7). Such values indicate that the presence of inhibitor decreases the activation energy of the reaction.

Table 4: The values of ΔG in case of two inhibitors

Organic compound	Langmuir		Flory Huggins		
	-ΔG	K	-ΔG	X	K
CTAB	20.823	80.49	20.972	3.99	84.81
CPYB	19.2442	42.54	20.972	2.52	22.79

Table 5: Limiting current of different organic compounds (mA)

	Cx 10 <sup>4</sup> mol l <sup>-1</sup>	298K	303K	308K	313K
CPYB	0.00	190	265	300	330
	5.50	185	260	295	325
	11.00	175	250	280	290
	21.78	166	240	265	270
	32.76	140	230	250	255
	47.73	130	225	235	240
CTAB	52.91	130	215	220	225
	0.00	190	265	300	330
	5.50	188	230	265	300
	11.00	185	225	250	280
	21.78	180	200	230	260
	32.76	170	196	220	245
	47.73	165	180	215	230
	52.91	155	175	200	210

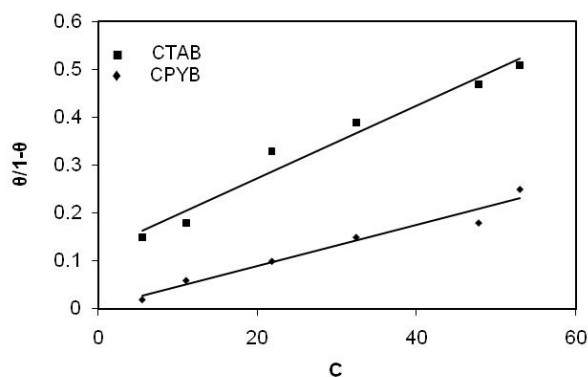


Fig. 5: The relation between  $\theta/1-\theta$  vs C at 298K

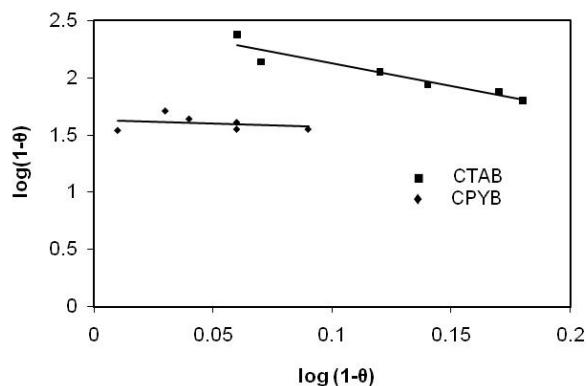


Fig 6: The relation between  $\log \theta/C$  vs  $\log (1-\theta)$  at 298K

**Thermodynamic treatment of the results:** From the integrated form of Arrhenius equation:

$$\ln I = -E/RT + \ln A \quad (10)$$

where I is the limiting current (mA), R is the gas constant (8.314 KJ mole<sup>-1</sup>), E is the activation energy and A is the frequency factor. The values of E are given in table (6). These values for the enthalpy of activation  $\Delta H^*$ , entropy of activation  $\Delta S^*$  and free energy of activation  $\Delta G^*$  can be obtained by using equations:

$$\Delta H^* = E - RT \quad (11)$$

$$\Delta S^*/R = \ln A - \ln (BTe/h) \quad (12)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (13)$$

Where B is the Boltzmann constant, e is 2.7183, h is Plank's constant. The increase in the heat of adsorption led to an increase in the energy of adsorption forces, however raising of the temperature acts in the reverse direction increasing the kinetic energy of the molecules facilitating desorption (consequently in physical adsorption). In absence of SAS the activation energy = 27 KJ mole<sup>-1</sup> which is larger than when SAS is used as an inhibitor. Thus the values of activation energies show that:

1. The rate of corrosion of copper is increased by addition of SAS at temperature above 298K.

2. The adsorption process is physical adsorption.

However, the value of  $\Delta E$  of corrosion reaction is smaller in presence of SAS than in its absence. This is explained by the fact that these compounds partly formed some chemical bond with copper [18], and consequently a part of the electrode remains covered even at higher temperature.

Table (6) shows that the entropy  $\Delta S^*$  posses negative values, indicating a highly ordered organic species in the solution under investigation. These are found to be independent on the type of electrode and the type of SAS.

The variability of  $\Delta H^*$  values and similarities of  $\Delta S^*$  indicate that the mass transfer process is enthalpy and not entropic controlled process.

**Effect of rotation:** It is found that the limiting current density increases with increasing rpm. This may be attributed to break down a hydrodynamic boundary layer and a diffusion layer is formed. It is, also, observed that the higher the rpm, the higher the solution flow and the thinner the diffusion layer. This gives a higher rate of transfer of copper ions to the metal surface and, consequently, through the porous deposit layer formed on the metal which, in turn, enhances the rate of deposit. The limiting current density increases by increasing the rotation which indicates that corrosion reaction of copper is a diffusion controlled reaction. Table (7) shows the relation between rpm and  $I_L$ .

**Data correlation:** It was noted that mass transport to an inner RCE in turbulent flow system may be described by empirical dimensionless correlations of them from:

Table 6: Thermodynamic parameters for electrodeposition of copper at 298K

Cx 10 <sup>4</sup> mol l <sup>-1</sup>	E <sub>a</sub> kJmol <sup>-1</sup>	ΔH* kJmol <sup>-1</sup>	ΔG* kJmol <sup>-1</sup>	-ΔS* Jmol <sup>-1</sup> K <sup>-1</sup>
<b>(a) CTAB</b>				
0.0	19.33±0.88	16.852±0.67	59.436±1.76	142.83±2.890
5.50	20.230±3.4	17.760±1.39	59.630±6.23	140.45±1.166
11.0	18.60±3.88	16.123±3.01	59.720±5.97	146.22±1.912
21.78	19.35±3.88	16.870±3.80	59.880±1.75	144.25±1.212
32.36	18.942±4.7	16.640±4.70	59.990±2.31	145.99±1.350
47.73	16.692±4.75	14.310±4.70	66.092±6.40	153.88±1.530
52.91	16.55±3.165	14.08±3.160	66.235±4.21	154.81±1.013
<b>(b) CPYB</b>				
0.0	19.331±0.880	11.552±0.870	59.436±1.74	142.83±2.983
5.50	20.679±0.976	18.200±0.967	59.520±1.915	138.60±3.180
11.0	22.054±1.240	19.575±1.240	59.671±2.46	134.50±4.083
21.78	21.174±1.240	18.695±4.140	59.90±8.203	138.189±1.36
32.36	24.049±5.460	21.570±4.140	60.128±3.21	129.320±4.20
47.73	22.099±6.290	19.620±6.290	60.223±4.20	136.180±3.82
52.91	22.510±0.575	20.040±0.560	60.320±5.30	135.114±3.98

Table 7a: Overall mass transfer correlation for CTAB

Temp	Rpm	U (cmS <sup>-1</sup> )	(v= η/ρ) (cm <sup>2</sup> s <sup>-1</sup> )	I <sub>l</sub> mAm <sup>-2</sup>	(D) cm <sup>2</sup> s <sup>-1</sup>	K (mA)	Sh	Sc	Re
298	50	2.617	1.138E-02	12.73885	5.05E-06	9.67E-02	1915.98	2253.31	230.02
	100	5.233	1.138E-02	14.55869	3.67E-06	1.11E-02	3014.17	3101.75	460.03
	200	10.467	1.138E-02	15.92357	2.49E-06	1.21E-02	4847.09	4560.39	920.07
	300	15.700	1.138E-02	17.28844	2.08E-06	1.31E-02	6305.10	5463.82	1380.10
	500	26.167	1.138E-02	18.19836	1.53E-06	1.38E-02	9014.47	7421.11	2300.16
303	50	2.617	1.065E-02	14.559	6.07E-06	1.11E-02	1821.86	1755.80	245.6042
	100	5.233	1.065E-02	15.469	3.95E-06	1.17E-02	2972.50	2696.22	491.2083
	200	10.467	1.065E-02	17.288	2.78E-06	1.31E-02	4728.71	3837.70	982.4166
	300	15.700	1.065E-02	18.198	2.21E-06	1.38E-02	6247.02	4816.42	1473.625
	500	26.167	1.065E-02	19.108	1.62E-06	1.45E-02	8942.62	6566.40	2456.042
308	50	2.617	8.96E-03	15.924	6.65E-06	1.21E-02	1818.99	1348.27	291.97
	100	5.233	8.96E-03	16.379	4.12E-06	1.24E-02	3016.37	2173.68	583.93
	200	10.467	8.96 E-03	17.971	2.82E-06	1.36E-02	4842.95	3180.73	1167.87
	300	15.700	8.96E-03	19.563	2.36E-06	1.49E-02	6291.34	3795.67	1751.80
	500	26.167	8.96E-03	20.473	1.72E-06	1.55E-02	9021.06	5200.66	2919.67
313	50	2.617	8.93E-03	17.288	7.51E-06	1.31E-02	1747.18	1188.78	292.92
	100	5.233	8.93E-03	18.653	5.01E-06	1.42E-02	2828.86	1783.92	585.91
	200	10.467	8.93E-03	20.018	3.31E-06	1.52E-02	4592.50	2698.63	1171.82
	300	15.700	8.93E-03	20.928	2.61E-06	1.59E-02	6087.86	3421.80	1757.73
	500	26.167	8.93E-03	22.748	2.02E-06	1.73E-02	8565.35	4429.18	2929.54

Table 7b: Overall mass transfer correlation for CPYB

Temp	Rpm	U (cmS <sup>-1</sup> )	(v= η/ρ) (cm <sup>2</sup> s <sup>-1</sup> )	I <sub>l</sub> mAm <sup>-2</sup>	(D) cm <sup>2</sup> s <sup>-1</sup>	K (mA)	Sh	Sc	Re
298	50	2.617	1.13E-02	11.83	4.51E-06	8.98E-03	1991.82	2504.96	231.65
	100	5.233	1.13E-02	13.65	3.32E-06	1.04E-02	3118.52	3399.00	463.29
	200	10.467	1.13E-02	15.01	2.28E-06	1.14E-02	5000.62	4954.89	926.58
	300	15.700	1.13E-02	16.38	1.92E-06	1.24E-02	6489.31	5894.13	1389.87
	500	26.167	1.13E-02	17.29	1.42E-06	1.31E-02	9264.98	7972.32	2316.45
303	50	2.617	1.028E-02	12.97	5.05E-06	9.85E-03	1947.81	2033.73	254.54
	100	5.233	1.028E-02	15.47	3.92E-06	1.17E-02	2999.18	2624.92	509.08
	200	10.467	1.028E-02	16.38	2.54E-06	1.24E-02	4901.88	4051.84	1018.16
	300	15.700	1.028E-02	17.29	2.03E-06	1.31E-02	6466.82	5064.07	1527.24
	500	26.167	1.028E-02	18.65	1.55E-06	1.42E-02	9132.24	6628.05	2545.40
308	50	2.617	9.24E-03	14.56	5.855E-06	1.11E-02	1887.98	1577.70	283.25
	100	5.233	9.24E-03	16.38	4.154E-06	1.24E-02	2993.60	2223.66	566.50
	200	10.467	9.24E-03	17.74	2.785E-06	1.35E-02	4837.11	3316.64	1133.00
	300	15.700	9.24E-03	18.65	2.215E-06	1.42E-02	6394.32	4170.49	1699.50
	500	26.167	9.24E-03	20.02	1.679E-06	1.52E-02	9054.13	5502.64	2832.50
313	50	2.617	8.73E-03	15.47	6.32E-06	1.17E-02	1857.96	1380314	299.90
	100	5.233	8.73E-03	18.20	4.80E-06	1.38E-02	2880.84	1818.96	599.81
	200	10.467	8.73E-03	19.11	3.07E-06	1.45E-02	4728.21	2843.23	1199.62
	300	15.700	8.73E-03	20.02	2.43E-06	1.52E-02	6264.28	3593.97	1799.43
	500	26.167	8.73E-03	20.93	1.77E-06	1.59E-02	8982.50	4931.78	2999.04

$$Sh = a Sc^b Re^c \quad (14)$$

Where Sh, Re and Sc are Sherwood ( $Sh = kd/D$ ), where k is the mass transfer coefficient  $k = I_p/zFC_{Cu^{2+}}$  where  $C_{Cu^{2+}}$  is the saturation solubility of copper phosphate, Reynolds ( $Re = dU/v$ ) and Schmidt ( $Sc = v/D$ ) numbers respectively and a, b and c are empirical constants,  $c = 0.33$  indicating forced convection [20]. By plotting  $\log Sh/Sc^{0.33}$  and  $\log Re$ , a straight line was obtained; its slope gives constant c and intercept gives the constant a. Figures (7, 8) give the above relations for two substances used. The general equations were

$$Sh = 9.784 Re^{0.52} Sc^{0.33} \quad (15)$$

With average deviation  $\pm 1.29\%$  for CTAB

$$Sh = 9.79 Re^{0.51} Sc^{0.33} \quad (16)$$

With average deviation  $\pm 2.7\%$  for CPYB

The exponent in the above equation denotes a highly turbulent flow which agrees with the previous mass transfer studies in aqueous media. In our present study forced convection mechanism is obtained, which agree very well with similar relationships reported before [21-25].

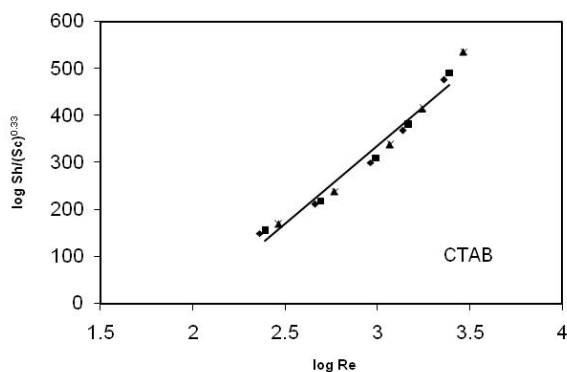


Fig. 7: Mass transfer correlation of CTAB

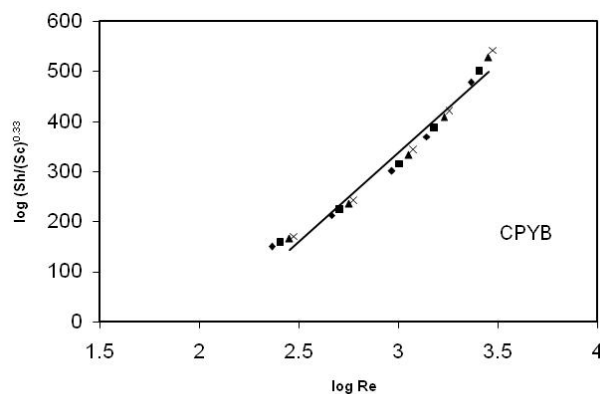


Fig. 8: Mass transfer correlation of CPYB

## CONCLUSION

The present study of copper corrosion in presence of phosphoric acid and surfactants led to the following important conclusions:

1. The rate of copper corrosion decreases by increase of phosphoric acid concentration. The addition of to surfactant acid enhances the decrease.
2. The rate of copper corrosion decreases by the increase of surfactant concentration.
3. The decrease in the copper corrosion depends on the type of surfactant.
4. The rate of copper corrosion decreases by the increase of the height of copper electrode.
5. The rate of copper corrosion increases by the increase of temperature.

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