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Kinetics of Corrosion of Copper Metal in Presence of Benzoic Acid Derivatives

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The rate of copper corrosion in presence of phosphoric acid were studied using weight loss method and by measuring the anodic limiting current in case of anodic corrosion. The rate of corrosion is measured in presence and in absence of benzoic acid, *p*-toluic acid, phthalic acid and salicylic acid. The factors studied are types of organic acid and its concentration, concentration of H_3PO_4, viscosity of solution, density, diffusion coefficient and the rate of rotation. In presence of these acids, it has been found that the rate of corrosion and anodic corrosion decrease. The percentage inhibition ranged from 9.72-60.14 % in case of anodic dissolution and from 9.62-65.38 in case of weight loss method. Flory-Huggery kinetic isotherm was applied. It is found that, the rate of corrosion decreases in order salicylic acid > phthalic acid > *p*-toluic acid > benzoic acid. The rate of corrosion depends on phosphoric acid concentration and electrode height. Increasing the speed of rotating electrode was found to increase the rate of corrosion. The dimensionless groups were calculated for the different acids.

Key Words: Kinetics, Copper, Corrosion, Benzoic acid.

INTRODUCTION

Inhibitors are widely used in the corrosion protection of materials in several environments[1]. Corrosion inhibitors are needed to reduce corrosion rates of metallic materials in such corrosive media as chloride solutions.

The corrosion inhibition efficiency of organic compounds is connected with their adsorption properties. The adsorbed inhibitor accounts for protecting the metal from corrosive medium and/or modifying electrode reactions in the dissolution of the metal. Furthermore, the adsorption of organic compounds on electrode surfaces provides information on the structure of electrical double layer, the kinetics of electron transfer and the role of intermediates in the mechanism of such electrode processes as electro organic synthesis and electroplating.

It has been observed that adsorption depends mainly on certain physico-chemical properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and π-orbital character of donating electrons[2-4] as well as on the electronic structure of the molecules[5,6].

Adsorption of inhibitors at the metal/solution interface is usually associated with the formation of electrostatic or covalent bonding between the metal surface atoms and the adsorbates[7]. Compared with common inhibitors, adsorption of surfactants on the metal surface seems to be much more complicated. In aqueous solutions, the surfactant molecules may adsorb on the solid surface through electrostatic attraction or chemisorptions depending on the charge of the solid surface and the free energy change of transferring hydrocarbon chains from water to the solid surface[7].

The relationship between the adsorption of organic inhibitors and their molecular structure has attracted the attention of many investigators[8-13]. The inhibition of localized corrosion by organic compounds usually involves chemical adsorption on the oxide covered metal surface as a primary step, but the exact mechanism of adsorption of inhibitor molecules or ions is not clear.

The determination of the type of adsorption isotherm corresponding to the adsorption on the metal-electrolyte phase boundary gives a lot of information on the adsorption process because it contributes to defining quantities and the standard free energy of adsorption, its dependence on the degree of surface coverage, the character of the adsorption layer on the metal-electrolyte phase boundary, the magnitude and character of interactions between the molecules of the adsorbed substance or between these molecules and the surface atoms of the metal. Therefore, the accurate determination of the type of adsorption isotherm corresponding to investigated adsorption process is the primary importance[14].

Many organic molecules are used to inhibit copper corrosion[15-17]. Heterocyclic compounds containing nitrogen

and sulphur are known to be good corrosion inhibitors of copper and alloys in various aggressive media. Benzotriazole is one of the most important inhibitors for copper and copper alloy corrosion in the environments of the wide temperature and pH ranges. However, the most serious drawback in benzotriazole is its toxicity[18]. The aim of present work is to study the effect of some organic acids on the corrosion of copper in phosphoric acid.

EXPERIMENTAL

Fig. 1 shows the cell and electrical circuit used in the present work. The cell consists of rectangular plastic container having dimensions 5.1 cm × 5 cm × 10 cm with electrodes filling the whole cross section. The electrodes were rectangular copper sheets of 10 cm height and 5 cm width. Electrode separation (5 cm porous PVC diaphragm) was used to prevent the effect due to H_2 bubbles. The electrical circuit consists of 6V D.C. power supply, while a voltmeter is connected in parallel with the cell to measure the voltage and multirange ammeter is connected in series with the cell to measure the current.
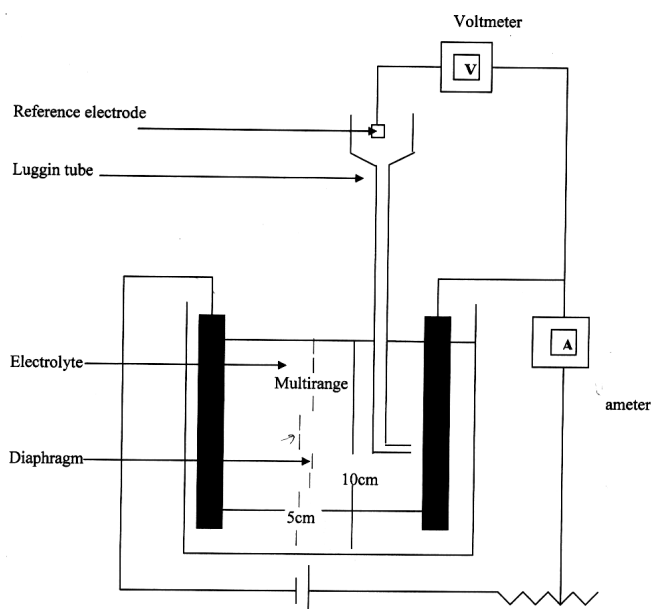

Fig. 1. Electrolytic cell and electrical circuit

Measurements of the limiting reagent: Polarization curves were obtained by increasing the cell current stepwise and measure the steady state anode potential against reference electrode consisted of a copper wire immersed in a cup of a Luggin tube filled with phosphoric acid with concentration similar to that in a cell. The tip of the Luggin tube was placed 0.5-1.0 mm from anode wall. The potential difference between the anode and the reference electrode was measured by high impedance potentiometer. Four phosphoric acid concentrations (6, 8, 10, 12 M) were prepared from analar grade phosphoric acid and distilled water. The anode height varied from 1-5 cm.

Before each run, the back part of the anode was insulated with polystyrene lacquers and the active surface of the anode was polished with fine emery paper, degreased with trichloro-

ethylene, washed with alcohol and finally rinsed in distilled water. The rate of electro- polishing of copper was determined at 25 ºC.

Rotating cylinder electrode (RCE) cell and circuit: Fig 2 shows the apparatus outlines which permits the rotation of the cylinder at accurately controlled angular velocities. The shaft is driven by a variable speed motor. The frequency of rotation, recorded per minute, was counted by an optical tachometer. The glass vessel which holds the electrode is 13 cm in diameter. The electrical circuit (Fig. 2) consists of 6 V D.C. power supply, a multirange ammeter connected in series with the cell to measure the current and a voltmeter connected in parallel with the cell to measure its voltage.
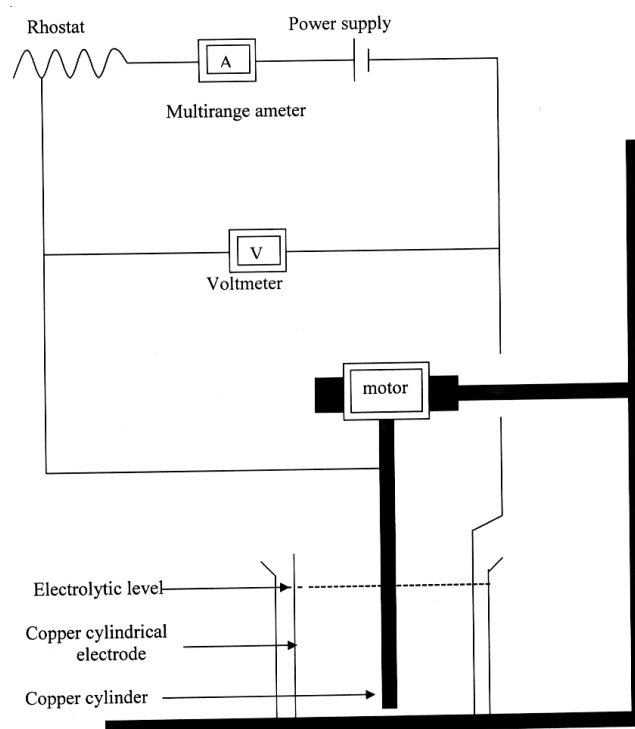

Fig. 2. Electrolytic cell and electrical circuit

The anode consists of a copper metal cylinder 0.98 cm diameter and 2 cm length. The sides and back of the cylinder as well as the drive shaft are insulated by epoxy resin. The cathode is made of a cylinder of copper metal electrode of 12 cm diameter. It also acted as the reference electrode by virtue of its high surface area compared to that of the anode.

Weight loss method: The weight loss experiments were carried out using 200 mL capacity glass beaker placed in thermostat water bath. The solution volume was 100 mL. The used copper sample (99.99 %) had a rectangular form with the following dimensions: length = 5 cm, width = 1 cm and thickness = 0.025 cm.

Prior to all measurements, the samples were polished, then washed with distilled water, degreased with ethanol, washed again with distilled water and finally dried at room temperature. The samples were weighted and suspended in 100 mL of aerated 8M H_3PO_4 solution containing organic acids at the desired concentrations for exposure time (3 day) at 25 ºC. At the end of the tests, the samples were taken out, washed

with distilled water, dried and then weighed using an analytic balance.

RESULTS AND DISCUSSION

Weight loss measurements: The free dissolution of copper in 8M H_3PO_4 with and without addition agents such as benzoic acid (BA), p-toluic acid, salicylic acid (SA) and phthalic acid (PA) was carried out for 3 days at 30 ℃. From weight loss data the corrosion rate (mg cm^2 h^{-1}) was calculated for different concentrations (0.5-5.0 × 10^{-4} M) of addition agents. The corrosion inhibition of copper in H_3PO_4 increases appreciably in the presence of traces of benzoic acid. Table-1 shows the variation of corrosion inhibition with inhibitor concentration. The extent of inhibition of corrosion was found to depend on the nature and concentration of inhibitor. The dependence of corrosion inhibition was the same for all inhibitors.

TABLE-1
RELATION BETWEEN PERCENTAGE INHIBITION
AND CONCENTRATION IN PRESENCE OF DIFFERENT
CARBOXYLIC ACIDS CONCENTRATIONS AT 25 ℃

Conc. M × 10^4	Weight loss (g)	Corrosion rate	Inhibition (%)
Benzoic acid			
0.5	0.0473	0.57	9.62
1.0	0.0415	0.51	20.15
1.5	0.0391	0.48	24.35
2.0	0.0372	0.45	28.85
2.5	0.0342	0.41	34.60
3.0	0.0312	0.38	40.38
5.0	0.0283	0.34	46.15
p-Toluic acid			
0.5	0.0453	0.55	13.45
1.0	0.0402	0.48	23.08
1.5	0.0382	0.46	26.08
2.0	0.0351	0.42	32.69
2.5	0.0332	0.40	36.54
3.0	0.0302	0.36	42.31
5.0	0.0262	0.32	50.0
Phthalic acid			
0.5	0.0422	0.51	19.23
1.0	0.0392	0.47	25.00
1.5	0.0361	0.44	30.77
2.0	0.0334	0.46	36.38
2.5	0.0292	0.35	44.23
3.0	0.0251	0.30	51.92
5.0	0.0231	0.28	55.77
Salicylic acid			
0.5	0.0402	0.48	23.08
1.0	0.0372	0.45	28.85
1.5	0.0341	0.41	34.62
2.0	0.0293	0.35	44.23
2.5	0.0251	0.30	51.92
3.0	0.0221	0.27	57.69
5.0	0.0182	0.22	65.38

The inhibitor efficiency (γ) of each inhibitor on the copper surface at different concentrations was calculated using the equation:

$$\gamma = \frac{(W_0 - W)}{W_0} \times 100$$

where W_0 and W are the corrosion rates of copper without and with inhibitor, respectively. The values of γ at different concentrations of inhibitors are given in Table-1. It is clear from Table-1 that salicylic acid and phthalic acid are more effective acid corrosion inhibitors for copper than others. The γ of inhibitors at a given concentration was in the following order: salicylic acid > phthalic acid > p-toluic acid > benzoic acid.

Leveling process: Leveling is the principle process in electro-polishing[19]. It can be explained by mass transfer mechanism[20]. A cell with a diaphragm is used for this study. The use of this cell eliminates the effect of hydrogen gas evolved at the cathode from affecting the rate of mass transfer at the anode *i.e.*, mass transfer by convection.

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. The study of leveling is based on the rate of mass transfer at the anode and the classical current-voltages curves of electro-polishing as shown in Table-2 and Fig. 3. A typical polarogram is obtained in this study for acid in case of divided and undivided cell. The curve is divided into three parts. In the first part of the curve, the current density (c.d) is proportional to the voltage. In the second part, the metal undergoes electro- polishing. In the first part, etching takes place and in the last part, some localized pitting occurs[21].
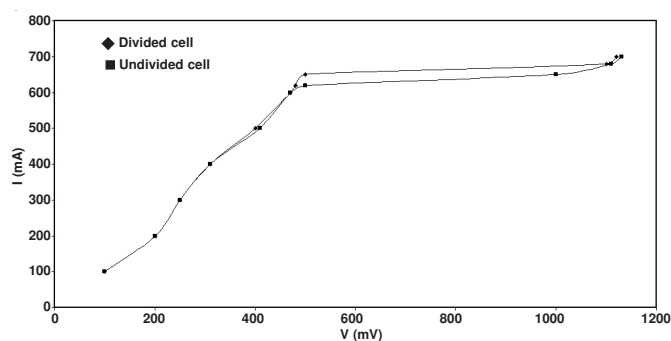

Fig. 3. Typical polarization curves obtained for carboxylic acid derivatives at 25 ℃. (1) divided cell (2) undivided cell

Effect of electrode height on limiting current: Table-3 shows that, the limiting current density decreases with the increase in height in electro polishing. Generally for anodic dissolution of metal, the direction of flow of the thermodynamic boundary layer and the diffusion layer increase in the downward direction, *i.e.*, the resistance to mass transfer increases in up-ward direction of the anode. This explains why polishing is attained at the upper parts of the electrode before the lower parts at the limiting current region. This was confirmed by visual observation during electro-polishing. The average limiting current density decreases with increase in the height according to the equation:

$$I_l = \frac{C}{(H)^a} \tag{1}$$

where 'C' is constant, 'H' is the height of electrode and 'a' is constant depends on type of solution used where a = 0.33 for 8 M H_3PO_4 as example.

Effect of the concentration of organic acids on limiting current: The observed limiting current, which represents

TABLE-2
CHANGE OF CELL VOLTAGE WITH CURRENT OF Cu ANODE IN H$_3$PO$_4$ (8M)
IN PRESENCE OF DIFFERENT CONCENTRATIONS OF BENZOIC ACID AT 25 ºC

Divided cell									
Conc. (M × 10^4)	Change of the cell voltage with current								
0.5	I (mA)	100	200	300	400	500	600	650	700
	V (mV)	98	175	290	405	515	630	1095	1210
1.0	I (mA)	100	200	300	400	500	550	580	600
	V (mV)	85	140	195	275	410	540	1085	1155
1.5	I (mA)	100	200	300	400	500	530	545	600
	V (mV)	93	150	211	275	370	510	985	1120
2.0	I (mA)	100	200	300	400	450	500	510	600
	V (mV)	95	140	185	230	290	440	975	1075
2.5	I (mA)	100	200	250	300	400	450	470	550
	V (mV)	105	149	175	240	385	495	1025	1135
3.0	I (mA)	100	200	250	300	350	400	430	500
	V (mV)	85	135	175	245	320	450	985	1035
5.0	I (mA)	100	150	200	250	300	350	405	450
	V (mV)	93	130	170	325	370	470	970	1075
Undivided cell										
0.5	I (mA)	100	200	300	400	500	550	600	650	730	800
	V (mV)	95	135	178	245	390	435	475	560	1075	1175
1.0	I (mA)	100	200	250	300	400	500	600	650	680	750
	V (mV)	97	138	175	210	285	395	530	610	1095	1180
1.5	I (mA)	100	200	250	300	400	500	550	600	620	700
	V (mV)	95	130	160	215	310	415	475	590	1075	1160
2.0	I (mA)	100	200	250	300	400	450	500	550	560	600
	V (mV)	97	150	190	240	335	405	485	580	1120	1230
2.5	I (mA)	100	200	250	300	350	400	450	500	510	600
	V (mV)	95	145	185	235	290	370	425	525	1065	1170
3.0	I (mA)	100	150	200	250	300	350	400	450	470	550
	V (mV)	97	140	183	240	285	360	410	510	1045	1165
5.0	I (mA)	50	100	150	200	250	300	350	400	420	550
	V (mV)	45	98	140	195	240	360	470	580	1075	1185

TABLE-3
LIMITING CURRENT OF COPPER AT DIFFERENT ELECTRODE
HEIGHT USING 8M PHOSPHORIC ACID IN PRESENCE OF 2.5 ×
10^{-4} M ORGANIC ADDITIVES AT 25 ºC

Compounds	I (mA) at different height (cm)				
	1	2	3	4	5
Blank	610	890	1115	1335	1500
Benzoic acid	580	840	1050	1255	1410
p-Toluic acid	510	735	920	1105	1240
Phthalic acid	435	630	790	945	1060
Salicylic acid	370	540	675	808	915

TABLE-4
EFFECT OF PHOSPHORIC ACID CONCENTRATION
ON THE LIMITING CURRENT AT 25 ºC

Conc. H$_3$PO$_4$ (m L^{-1})	I$_1$
6	1000
8	580
12	500
14	320

the rate of copper metal corrosion in the phosphoric acid at 250ºC, is found to decrease with increasing the concentration of organic acids as shown in Tables 4 and 5. These tables show the dependence of limiting current on the bulk concentration in the absence and in the presence of organic acids. It's found that the limiting current decreases with increasing the concentration of acids. From the practical point of view, we can recommend on the basis of results that, it may use in this range of concentration to inhibit the corrosion of copper metal in 8M H$_3$PO$_4$ in all type of organic acids to be used in this work[22,23].

If the limiting current in absence of organic acids (I) and in presence of organic acids (I$_L$), the percentage of inhibition can be calculated from the following equation:

$$\text{Inhibition (\%)} = \frac{I - I_1}{I_1} \times 100 \qquad (2)$$

Figs. 4 and 5 and Tables 6 and 7 show that the inhibition per cent that is caused by organic acids, using electrode deposition method and weight loss method, ranges from 9.72-61.81 % depending on the acid type and its concentration. The limiting current decreases with increasing the concentration of acids. This agrees with the finding of other authors who worked within the same range of concentration using other anode geometries[24,25]. The decrease in the limiting current with increasing the concentration of acids is attributed to: (a) The solubility of the dissolved copper phosphate in orthophosphoric acid, which is responsible for the limiting current, decreases with increasing phosphoric acid concentration. (b) The viscosity of the solution increases with increasing H$_3$PO$_4$ concentration with consequent decrease in the diffusivity of Cu^{2+} according to Stokes-Einstein equation[26].

The limiting current decreases as the organic acid is added to phosphoric acid, with different concentrations. This is explained on the basis that, the viscosity of organic acids-water-H$_3$PO$_4$ mixture is higher than water-H$_3$PO$_4$ mixture. This led

TABLE-5
EFFECT OF DIFFERENT CARBOXYLIC ACIDS ON THE
PERCENTAGE INHIBITION OF COPPER DISSOLUTION
IN PRESENCE OF H_3PO_4 (8M) AT 25 ºC

| Conc. M. × 10⁴	I_1 (mA)	Inhibition (%)
Benzoic acid		
0.5	650	9.72
1.0	580	19.44
1.5	550	23.61
2.0	510	29.17
2.5	470	34.72
3.0	430	40.28
5.0	405	43.75
p-Toluic acid		
0.5	620	13.89
1.0	565	21.53
1.5	530	26.39
2.0	485	32.64
2.5	460	36.11
3.0	425	40.97
5.0	385	46.53
Phthalic acid		
0.5	590	18.08
1.0	550	23.61
1.5	510	29.17
2.0	470	34.72
2.5	450	37.50
3.0	420	41.67
5.0	350	51.39
Salicylic acid		
0.5	570	20.53
1.0	540	25.00
1.5	510	31.94
2.0	460	36.11
2.5	390	41.67
3.0	375	45.83
5.0	325	61.81
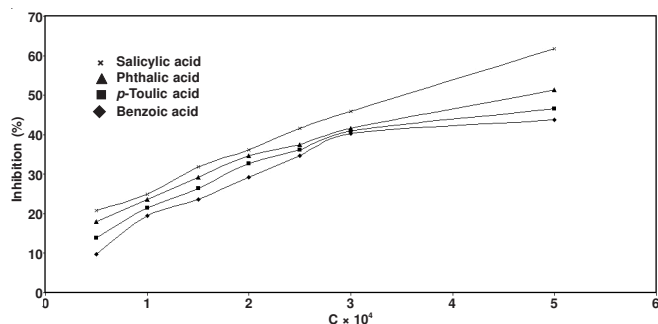
Fig. 4. Relation between % inhibition and concentration for all carboxylic acid derivatives at 25 ºC using electroplating method
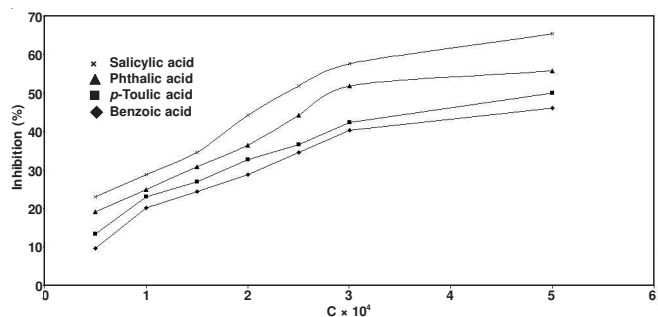

Fig. 5. Relation between % inhibition and concentration for all carboxylic acid derivatives at 25 ºC using weight loss method

to: (a) Decrease in the diffusivity of Cu^{2+}. (b) Quick saturation of copper phosphate in organic acids mixture and consequently the limiting current decreased.

Adsorption isotherm: It is generally assumed that the adsorption isotherm of the inhibitor at the metal solution interface is the first step in the action mechanism of inhibitors in aggressive acid media. Four types of adsorption may take place in the inhibiting phenomena involving organic molecules at the metal- solution interface, namely: (a) Electrostatic attraction between charged molecules and charged metal. (b) Interaction of uncharged electron pairs in the molecules with the metal. (c) Interaction of electron with metal. (d) A combination of the above[27].

The electrochemical processes on the metal surface are likely to be closely related to the adsorption of the inhibitor[28-36] and the adsorption is known to depend on the chemical structure of the inhibitor[37-39]. 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.

$$Org._{(aq.)} + xH_2O \rightarrow Org._{(S)} + xH_2O \qquad (3)$$
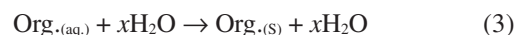
where x is the number of water molecules displaced by one molecule of organic inhibitor.

Adsorption isotherms are very important in determining the mechanism of organo- electrochemical reactions. The most frequently used isotherms are those of Langmuir, Frumkin, Parrsons, Temkin, Flory-Huggins and Bockris-Swinkels[40-43]. These entire isotherms follow the general form:

$$f(\theta, x)\exp^{(-a\theta)} = KC \qquad (4)$$

where $f(\theta, x)$, is the configuration factor which depends essentially on the physical model and the assumption underlying the derivation of the isotherm[44]. The mechanism of inhibition is generally believed to be due to the formation and maintenance of a protective film on the metal surface[45].

Inhibitor adsorption characteristics can be estimated[46] by using the Langmuir isotherm given by.

$$KC = \frac{\theta}{1-\theta} \qquad (5)$$

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

The degree of surface coverage (T) at constant temperature was determined[47] from the eqn. 6

$$\theta = \frac{(I - I_1)}{I} \qquad (6)$$

From eqn. 5 a plot of log $\theta/(1-\theta)$ against log C should yields a straight line with intercept of log K. Tables 6 and 7 give the data between $\theta/1-\theta$ against log C for all organic acids and the surfaces coverage with concentration in case of weight loss and electro-polishing. Figs. 5 and 6 show the Flory-Huggins adsorption isotherm for copper electrode in H_3PO_4 acid plotted as log θ/C against log $(1-\theta)$ at 25 ºC. A straight line obtained with slope X and intercept log xK. The experimental data fits the Flory-Huggins adsorption isotherm which is represented by:

TABLE-6
LIMITING CURRENT AND SURFACE COVERAGE OF H_3PO_4 (8M) IN
PRESENCE OF DIFFERENT CARBOXYLIC ACIDS CONCENTRATIONS

Conc. (M × 10⁴)	Inhibition (%)	log C	θ	θ/(1-θ)	log θ/(1- θ)	(1 - θ)	log (1- θ)	log θ/C
			Benzoic acid					
0.5	9.72	-4.30	0.097	0.106	-0.97	0.92	-0.04	3.29
1.0	19.44	-4.00	0.241	0.252	-0. 60	0.81	-0.09	3.28
1.5	23.61	-3.82	0.309	0.322	-0.49	0.76	-0.12	3.20
2.0	29.17	-3.70	0.412	0.405	-0.39	0.71	-0.15	3.16
2.5	34.72	-3.60	0.532	0.529	-0.28	0.65	-0.19	3.14
3.0	40.28	-3.52	0.674	0.677	-0.17	0.60	-0.22	3.13
5.0	43.75	-3.30	0.778	0.857	-0.07	0.56	-0.25	2.94
			p-Toluic acid					
0.5	13.89	-4.30	0.139	0.161	-0.79	0.85	-0.07	3.44
1.0	21.53	-4.00	0.215	0.274	-0.56	0.78	-0.11	3.33
1.5	26.39	-3.82	0.264	0.358	-0.45	0.74	-0.13	3.25
2.0	32.64	-3.70	0.326	0.485	-0.315	0.68	-0.17	3.21
2.5	36.11	-3.60	0.361	0.565	-0.25	0.65	-0.19	3.16
3.0	42.97	-3.52	0.409	0.694	-0.16	0.60	-0.22	3.13
5.0	46.53	-3.30	0.465	0.870	-0.06	0.54	-0.27	2.97
			Phthalic acid					
0.5	18.06	-4.30	0.181	0.220	-0.66	0.81	-0.09	3.56
1.0	23.61	-4.00	0.236	0.309	-0.51	0.76	-0.12	3.37
1.5	29.17	-3.82	0.292	0.412	-0.39	0.71	-0.15	3.29
2.0	34.72	-3.70	0.347	0.532	-0.27	0.65	-0.19	3.24
2.5	73.50	-3.60	0.375	0.600	-0.22	0.63	-0.20	3.18
3.0	41.67	-3.52	0.417	0.417	-0.15	0.59	-0.23	3.14
5.0	51.39	-3.30	0.514	1.057	-0.02	0.49	-0.31	3.01
			Salicylic acid					
0.5	20. 83	-4.30	0.208	0.263	-0.58	0.79	-0.10	3.62
1.0	25.00	-4.00	0.250	0.333	-0.48	0.76	-0.12	3.40
1.5	31.94	-3.82	0.319	0. 469	-0.33	0.68	-0.17	3.33
2.0	36.11	-3.70	0.361	0. 565	-0.25	0.65	-0.19	3.26
2.5	41.67	-3.60	0.417	0.417	-0.15	0.59	-0.23	3.22
3.0	45.83	-3.52	0.458	0.846	-0.07	0.54	-0.27	3.18
5.0	61. 81	-3.30	0.618	1.518	-0.21	0.38	-0.42	3.09

TABLE-7
PERCENTAGE INHIBITION AND SURFACE COVERAGE OF H_3PO_4 (8M) IN PRESENCE OF
DIFFERENT CARBOXYLIC ACIDS CONCENTRATIONS (IN CASE OF WEIGHT LOSS METHOD)

| Conc. (M × 10⁴)	Inhibition (%)	log C	θ	θ/(1- θ)	log θ/(1- θ)
		Benzoic acid			
0.5	9.62	-4.30	0.096	0.106	-0.97
1.0	20.15	-4.00	0.202	0.252	-0. 60
1.5	24.35	-3.82	0.244	0.322	-0.49
2.0	28.85	-3.70	0.289	0.405	-0.39
2.5	34.60	-3.60	0.346	0.529	-0.28
3.0	40.38	-3.52	0.404	0.677	-0.17
5.0	46.15	-3.30	0.462	0.857	-0.07
		p-Toluic acid			
0.5	13.45	-4.30	0.135	0.155	-0.81
1.0	23.08	-4.00	0.231	0.300	-0.52
1.5	26.92	-3.82	0.269	0.368	-0.43
2.0	32.69	-3.70	0.327	0.486	-0.31
2.5	36.54	-3.60	0.365	0.576	-0.24
3.0	42.31	-3.52	0.423	0.733	-0.13
5.0	50.00	-3.30	0.500	1.00	-0.00
		Phthalic acid			
0.5	19.23	-4.30	0.192	0.328	-0.66
1.0	25.00	-4.00	0.250	0.334	-0.51
1.5	30.77	-3.82	0.308	0.444	-0.39
2.0	36.38	-3.70	0.364	0.572	-0.27
2.5	44.23	-3.60	0.442	0.793	-0.22
3.0	51.92	-3.52	0.519	1.079	0.15
5.0	55.77	-3.30	0.558	1.261	0.02
		Salicylic acid			
0.5	23.08	-4.30	0.231	0.300	-0.52
1.0	28.85	-4.00	0.289	0.405	-0.39
1.5	34.62	-3.82	0.364	0. 530	-0.28
2.0	44.23	-3.70	0.442	0. 793	-0.10
2.5	51.92	-3.60	0.519	1.080	-0.03
3.0	57.69	-3.52	0.577	1.364	0.13
5.0	65.38	-3.30	0.654	1.887	0.28
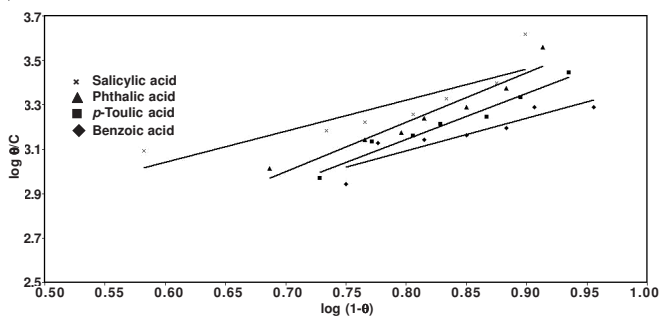
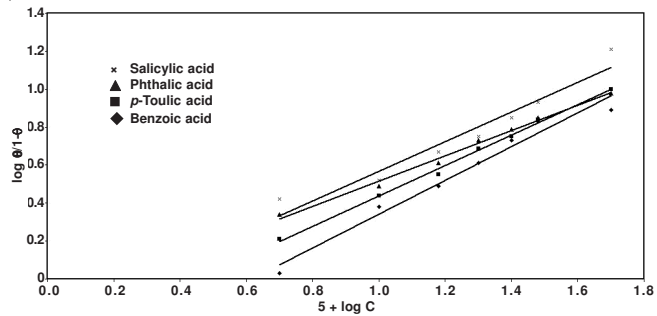Fig. 6. Relation between log θ/C and log (1-θ) for all carboxylic acid derivatives using electroplating method
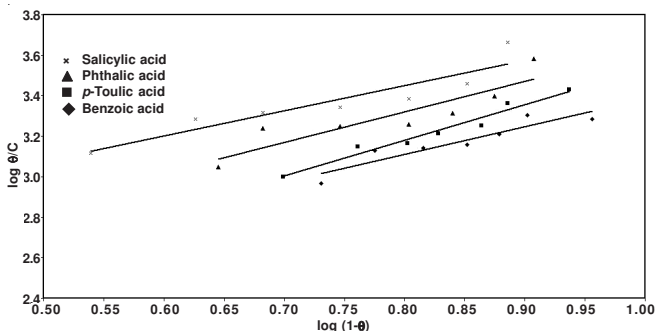
Fig. 7. Relation between log θ/C and log (1-θ) for all carboxylic acid derivatives using weight loss method

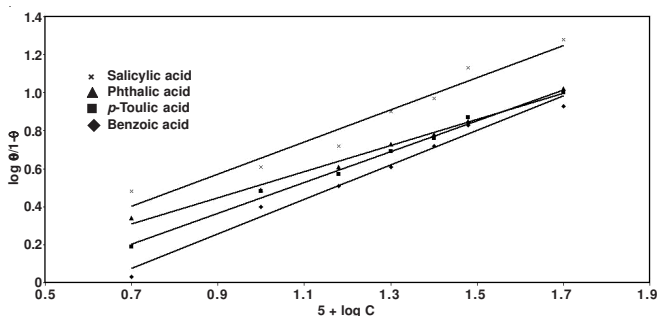$$\log \frac{\theta}{C} = \log xK + x \log(1-\theta) \qquad (7)$$

where 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 and the electrostatic or covalent bonding between the adsorbates and the metal surface atoms[48]. The kinetic adsorption isotherm[49] may be written in the form.

$$\log \frac{\theta}{(1-\theta)} = \log k + y \log C \qquad (8)$$

where y is the number of inhibitor molecules occupying one active site. The binding constant of the adsorption K is the number of the surface active sites occupied by one molecule of the inhibitor ($K = k^{(1/y)}$). Figs. 8 and 9 show the linear relation between log θ/(1-θ) and log C at 25 ℃ and the calculated values of 1/y and K are given in Tables 8 and 9. The values of 1/y depend on the type of organic acid. From Tables 8 and 9 it is obvious that the value of 1/y for phthalic acid is approximately one, suggesting that the compound is attached to one active site per inhibitor molecule. For other inhibitors, the value of 1/y is higher than one, indicating that the given inhibitors molecules are attached to more than one active site. The free energy of adsorption can be obtained from eqn. 9.

$$(\Delta G_{ads}) = -RT \ln (55.5K) \qquad (9)$$

The value 55.5 is the concentration of water in the solution (mol/L). The values of ΔG_{ads} are given in Tables 10 and 11. In all cases the ΔG_{ads} values are negative and lie in the range of 26.56-30.49 kJ/mol. The most efficient inhibitor shows the most negative (ΔG_{ads}) value. This suggests that, they are strongly adsorbed on the metal surface. The negative values of (ΔG_{ads}) indicate the spontaneous adsorption of the

Fig. 8. Relation between log (θ/1-θ) and log C for all carboxylic acid derivatives using electroplating method

Fig. 9. Relation between log (θ/1-θ) and log C for all carboxylic acid derivatives using weight loss method

TABLE-8
VALUES OF K, X AND 1/y OF H_3PO_4 IN PRESENCE OF DIFFERENT CARBOXYLIC ACIDS IN CASE OF ELECTRODISSOLUTION

Acids	Flory-Huggins isotherm		Kinetic adsorption isotherm		
	X	K	Y	1/y	K
Benzoic acid	1.439	1669	0.890	1.12	810.6
p-Toluic acid	2.170	1721	0.757	1.32	294.0
Salicylic acid	1.873	2028	0.696	1.41	189.0
Phthalic acid	1.419	2912	0.780	1.28	491.0

TABLE-9
VALUES OF K, X AND 1/Y OF H_3PO_4 IN PRESENCE OF DIFFERENT CARBOXYLIC ACIDS TO KINETIC ADSORPTION ISOTHERM (IN CASE OF WEIGHT LOSS)

Compound	Flory-Huggins		Kinetic adsorption isotherm		
	X	k	Y	1/Y	K
Benzoic acid	1.355	1969	0.9056	1.10	931.97
p-Toluic acid	1.746	1941	0.8108	1.23	490.23
Salicylic acid	1.197	3970	0.7885	1.27	523.24
Phthalic acid	1.494	2762	0.8607	1.16	1273.50

TABLE-10
CALCULATED VALUES OF FREE ENERGY OF ADSORPTION IN kJ/mol IN PRESENCE OF CARBOXYLIC ACIDS IN CASE OF ELECTRODISSOLUTION

| Acids	Flory-Huggins isotherm	Kinetic adsorption isotherm
	$-\Delta G_{ads}$	$-\Delta G_{ads}$
Benzoic acid	28.35	26.56
p-Toluic acid	28.42	24.04
Salicylic acid	28.83	22.95
Phthalic acid	29.73	22.32

TABLE-11
CALCULATED VALUES OF FREE ENERGY OF ADSORPTION
IN kJ/mol IN PRESENCE OF ORGANIC ACIDS USING
WEIGHT LOSS METHOD

| Acids	Flory-Huggins isotherm	Kinetic adsorption isotherm
	$-\Delta G_{ads}$	$-\Delta G_{ads}$
Benzoic acid	28.49	26.90
p-Toluic acid	28.72	25.10
Salicylic acid	29.59	25.47
Phthalic acid	30.49	27.67

inhibitor. It is found that the (ΔG_{ads}) values are more positive than -40 kJ/mol. This indicates that the inhibitors are physically adsorbed on the metal surface. Similar results also been reported by Talati *et al.*[50].

Structure effect of the metallic surface: The instability of the metallic surface in the given environment is due to the presence of surface defects which initiate the corrosion process. The corrosion of copper in aerated acidic solution is a result of the following reactions[51,52]:
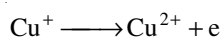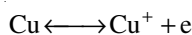
Anodic

$$2Cu \longrightarrow Cu^{2+} + 2e$$

Cathodic

$$2Cu^{2+} + O_2 + 4H^+ + 2e \longrightarrow 2Cu^{2+} + H_2O$$
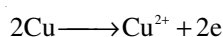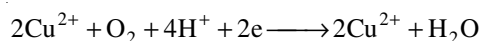
where the cathodic reaction in the presence of inhibitor is more consistent with the slow formation of Cu^+ as an intermediate in the anodic reaction, followed by the rate controlling oxidation of Cu^+ to Cu^{2+}

$$Cu \longleftrightarrow Cu^+ + e$$

$$Cu^+ \longrightarrow Cu^{2+} + e$$

It is known that many additives are usually capable of adsorption on the anodic substrate and even might trap in the corrosion over potential. This may be due to either the need for the electron transfer to occur through the adsorbed layer or to a complex formation at the electrode surface. A complexation of the metal cation in the solution is also proposed. In many cases, the use of additives is still done in an empirical way. Indeed, the number of these organic or non- organic substances is very large. Moreover, their action could be different in function of the substrate, the ion to reduce and the electrolytic conditions. For example, additives re-orientation on the electrode surface has been observed depending on the surface coverage or as a function of pH.

A complex in solution between acid derivatives and Cu^+ or Cu^{2+} cation is formed as a result of transport of copper ions from the interface to the bulk and the discharge of the copper complex ion increases. The effect of organic acids on the corrosion processes is revealed by the adsorption curves. The observed corrosion data in presence of inhibitors (Fig. 2 and 3) and the decrease of anodic limiting current in presence of inhibitors (Tables 1 and 2) indicate that acid corrosion inhibitor of copper is by adsorption of these inhibitors in molecular form[53,54] at the electrode solution interface. The nature of inhibitor interaction on the metal surface during corrosion inhibitor has been deduced in terms of its adsorption charac-

teristics[55]. The metal surface in aqueous solution is always covered with adsorbed water dipoles; therefore the adsorption of inhibitor molecules from aqueous solution is a quasi-substitution process.

Experiments with constant concentration of benzoic acid derivatives revealed that the benzene ring attached to the carboxyl group is also the effective portion for corrosion inhibition. In benzoic acid, oxygen atom of the carboxyl group may conjugate with the orbital system of benzene ring, there by assuming some degree of π orbital character between the carbonyl carbon atom and benzene ring. The degree of participation of unshared pair of electrons of oxygen with the π-ring system may depend on *para*-substituent. The same efficiency was given in case of weight loss or electro-polishing process. Salicylic acid is more inhibitor because it has OH group in the *ortho* position of carboxylic group which is more linked with metal. The value of ΔG_{ads} was calculated for various inhibitors. Tables 10 and 11 show ΔG_{ads} values for salicylic and phthalic acid. The efficiency of inhibition decreases in the order: salicylic acid > phthalic acid > *p*-toluic acid > benzoic acid. In the acidic medium, oxygen atom becomes protonated to form complex at the anode copper surface.

Effect of stirring and applications of dimensional analysis: The effect of the speed of rotation on the rate of electro-polishing can also be used to determine whether the electro-polishing process is diffusion or chemically controlled process. If the rate of electro- polishing increase by increasing the speed of rotation, then the reaction is diffusion controlled. However, if the rate of electro-polishing is independent of the rotation, it is likely to be chemically controlled.

The angular velocity ω is given by:

$$\omega = 2\pi \text{ rpm} \tag{10}$$

Fig. 10 shows the relation between the limiting current and the angular velocity ω at different composition of organic acids at 25 ºC. Straight lines were obtained. The limiting current increases with increasing rotation, which indicate that the electro-polishing is diffusion controlled process.

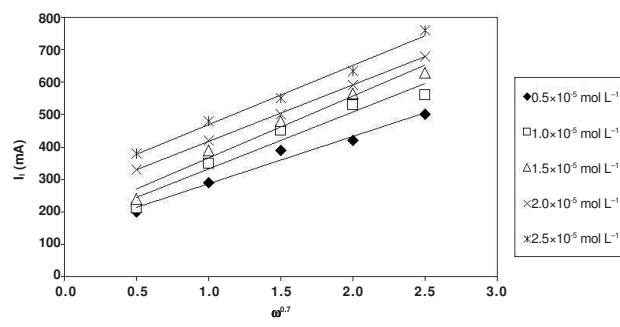Fig. 10. Relation between the limiting current and the angular velocity $\omega^{0.7}$ for phthalic acid at 25 ºC

Tables 12-15 show the effect of speed of rotation on the limiting current density in presence of organic acids. The data satisfied the Eisenberg equation. The diffusion coefficient of Cu^{2+} ions (D) in the different solutions was determined from the values of limiting current densities using Eisenberg equation:

TABLE-12
OVERALL CORRELATION OF PHTHALIC ACID

Conc. (M × 10⁴)	r.p.m	IL (mA cm⁻²)	V (cm² s⁻¹)	K × 10² (cm s⁻¹)	D × 10⁵ (cm² s⁻¹)	Sh	Sc	Re
0.5	100	106.383		3.1	3.19	1943.57	1097.18	293.14
	200	120.188		3.6	1.82	3956.04	1923.08	586.29
	300	148.611	0.0350	4.4	1.63	5398.77	2147.24	879.43
	400	175.410		5.2	1.54	6753.25	2272.73	1173.14
	500	201.398		6.0	1.50	8000	2333.34	1437.71
1.0	100	100.698		3.0	2.63	2047.78	1201.37	291.48
	200	109.631		3.2	2.19	4076.43	2242.04	582.95
	300	124.574	0.0342	3.7	225	6016.26	2861.79	874.43
	400	154.783		4.8	2.36	7619.05	2793.65	1166.48
	500	181.420		5.4	2.20	8503.94	2771.65	1429.55
1.5	100	93.390		2.8	3.37	2187.50	1421.88	281.87
	200	101.510		3.0	1.92	4379.56	2656.93	563.74
	300	114.504	0.0340	3.4	2.05	6415.09	3433.96	845.60
	400	145.850		4.3	1.99	7610.62	3221.24	1128.02
	500	169.238		5.0	2.12	8928.57	325.00	1382.42
2.0	100	85.688		2.5	2.58	2232.14	1629.46	281.10
	200	95.176		2.8	1.81	4516.13	2943.55	562.19
	300	112.230	0.0337	3.3	1.64	6407.77	3543.69	843.29
	400	132.694		3.9	1.54	7959.18	3724.49	1124.93
	500	152.347		4.5	1.34	9473.68	3842.11	1378.63
3.0	100	71.788		2.1	1.99	2470.59	2152.94	280.33
	200	82.183		2.4	1.52	4897.96	3734.69	560.66
	300	79.937	0.03360	2.9	1.42	6987.95	4409.64	840.98
	400	118.077		3.5	1.31	8641.98	4518.52	1121.86
	500	134.643		4.0	1.12	10256.41	4692.31	1374.86
5.0	100	59.282		1.8	1.84	2880.00	2968.00	276.55
	200	69.027		2.0	1.27	5333.31	4946.67	553.10
	300	84.619	0.03350	2.5	1.11	7575.76	5621.21	829.64
	400	99.399		2.9	0.97	9354.84	5983.87	1106.74
	500	117.102		3.5	0.95	10952.38	5904.76	1356.33

TABLE-13
OVERALL CORRELATION OF SALICYLIC ACID

Conc. (M × 10⁴)	r.p.m	IL (mA cm⁻²)	V (cm² s⁻¹)	K × 10² (cm s⁻¹)	D × 10⁵ (cm² s⁻¹)	Sh	Sc	Re
0.5	100	99.886		3.0	2.99	2006.69	1153.84	297.39
	200	111.255		3.3	1.66	3975.90	2078.31	594.78
	300	128.309	0.0345	3.8	1.34	5671.64	2574.63	892.17
	400	151.860		4.6	1.27	7244.09	2716.54	1190.15
	500	176.222		5.3	1.26	8412.70	2738.09	1458.55
1.0	100	95.014		2.9	2.76	2101.45	1253.62	296.53
	200	102.323		3.1	1.50	4133.31	2306.67	593.06
	300	113.367	0.0346	3.4	1.10	6181.82	3145.45	889.59
	400	134.156		4.0	1.05	7619.05	3295.24	1186.71
	500	158.519		4.8	1.06	9056.60	3264.15	1454.34
1.5	100	86.406		2.6	2.34	2222.23	1534.19	285.79
	200	93.877		2.8	1.25	4480.00	2872.00	571.58
	300	104.272	0.0359	3.1	0.95	6526.32	3778.95	857.38
	400	125.061		3.8	0.92	8260.87	3902.17	1143.73
	500	147.150		4.4	0.93	9462.37	3860.22	1401.67
2.0	100	80.559		2.4	2.08	1923.08	1754.81	281.09
	200	88.030		2.6	1.12	4642.86	3258.93	562.19
	300	100.211	0.0365	3.0	0.88	6818.18	4147.73	843.28
	400	115.641		3.5	0.81	8641.98	4506.17	1124.93
	500	134.319		4.0	0.80	10125.00	4562.50	1378.63
3.0	100	67.728		2.0	1.58	2531.65	2322.78	279.56
	200	75.037		2.3	0.87	5287.36	4218.39	559.13
	300	87.055	0.0367	2.6	0.71	7323.94	5169.01	838.69
	400	102.485		3.1	0.67	9253.73	5477.61	1118.80
	500	116.128		3.5	0.64	10937.50	5734.38	1371.12
5.0	100	51.161		1.5	1.03	2912.62	3553.40	280.33
	200	59.282		1.8	0.61	5901.64	6000.00	560.66
	300	69.027	0.0366	2.1	0.49	8571.43	7469.39	840.98
	400	85.756		2.6	0.51	10196.08	7176.47	1121.86
	500	99.399		3.0	0.49	12244.90	7469.39	1374.86

TABLE-14
OVERALL CORRELATION OF *p*-TOLUIC ACID

Conc. (M × 10⁴)	r.p.m	IL (mA cm⁻²)	V (cm² s⁻¹)	K × 10² (cm s⁻¹)	D × 10⁵ (cm² s⁻¹)	Sh	Sc	Re
0.5	100	116.128		3.4	3.65	1863.01	956.16	293.98
	200	136.430		4.0	2.21	3636.36	1586.36	587.97
	300	170.538	0.0349	5.0	2.01	4975.12	1736.32	881.95
	400	203.021		6.0	1.93	6212.62	1808.29	1176.51
	500	227.383		6.7	1.80	7944.45	1938.89	1441.83
1.0	100	108.819		3.2	3.31	1939.39	1054.55	294.83
	200	118.564		3.5	1.78	3932.58	1955.06	589.66
	300	155.920	0.0348	4.6	1.75	5257.14	1988.57	884.48
	400	185.155		5.5	1.67	6586.83	2083.83	1179.89
	500	207.893		6.1	1.57	7770.71	2216.56	1445.98
1.5	100	97.450		2.9	2.80	2071.43	1235.71	296.53
	200	112.676		3.3	1.65	4000.25	2096.97	593.06
	300	143.739	0.0346	4.2	1.55	5419.36	2232.26	889.60
	400	177.359		5.2	1.57	6624.20	2203.82	1186.71
	500	192.626		5.7	1.40	8142.86	2471.43	1454.34
2.0	100	88.517		2.6	2.40	2166.67	1454.17	293.98
	200	105.083		3.1	1.47	4217.69	2374.15	587.97
	300	129.121	0.0349	3.8	1.31	5801.53	2664.12	881.95
	400	153.483		4.5	1.25	7200	2792.00	1176.51
	500	171.999		5.1	1.17	8717.95	2982.91	1441.83
3.0	100	76.011		2.2	1.86	2365.59	1935.84	285.00
	200	92.415		2.7	1.19	4537.82	3025.21	570.00
	300	115.316	0.0360	3.4	1.08	6296.29	3333.34	855.00
	400	137.242		4.0	1.03	7766.66	3495.15	1140.56
	500	151.372		4.5	0.94	9574.47	3829.79	1397.87
5.0	100	67.403		2.0	1.54	2597.40	2363.64	281.87
	200	80.721		2.4	0.96	5000.00	3791.67	563.74
	300	99.886	0.0364	2.9	0.85	6823.53	4282.35	845.60
	400	114.991		3.4	0.78	8717.95	4666.67	1128.02
	500	134.319		4.0	0.77	10389.61	4727.27	1382.42

TABLE-15
OVERALL CORRELATION OF BENZOIC ACID

Conc. (M × 10⁴)	r.p.m	IL (mA cm⁻²)	V (cm² s⁻¹)	K × 10² (cm s⁻¹)	D × 10⁵ (cm² s⁻¹)	Sh	Sc	Re
0.5	100	137.242		3.9	4.61	1691.97	739.70	300.88
	200	149.423		4.3	2.47	3481.78	1380.57	601.76
	300	199.773	0.0341	5.7	2.50	4560.00	1364.57	902.64
	400	246.873		7.1	2.54	5590.55	1342.52	1204.11
	500	284.229		8.2	2.48	6612.90	1375.00	1475.66
1.0	100	117.752		3.4	2.63	1873.28	942.15	300.00
	200	138.054		4.0	2.19	3652.97	1561.64	600.00
	300	186.779	0.0342	5.4	225	4800.00	1520.00	900.00
	400	235.504		6.8	2.36	5762.71	1449.15	1200.58
	500	263.115		7.6	2.20	6909.09	1554.54	1471.35
1.5	100	112.068		3.2	3.37	1899.11	1008.90	301.76
	200	126.685		3.6	1.92	3789.47	1789.47	603.53
	300	175.410	0.0340	5.0	2.05	4878.47	1658.54	905.29
	400	211.142		6.1	1.99	6130.65	1789.47	1207.65
	500	256.618		7.4	2.12	6981.13	1603.77	1480.00
2.0	100	94.202		2.7	2.58	2093.02	1306.20	304.45
	200	121.813		3.5	1.81	3867.40	1861.20	608.90
	300	151.860	0.0337	4.4	1.64	5365.85	2054.87	913.35
	400	177.846		5.1	1.54	6623.38	2188.31	1218.39
	500	190.515		5.5	1.34	8208.96	2514.93	1493.18
3.0	100	79.548		2.3	1.99	2311.56	1688.44	305.36
	200	108.819		3.1	1.52	4078.95	2210.53	610.71
	300	138.054	0.03360	4.0	1.42	5633.80	2366.19	916.07
	400	160.793		4.6	1.31	7022.90	2564.89	1222.02
	500	169.726		4.9	1.12	8750.00	3000.00	1497.62
5.0	100	75.524		2.2	1.84	2391.30	1820.65	306.27
	200	96.638		2.8	1.27	4409.45	2637.79	612.54
	300	117.752	0.03350	3.4	1.11	6126.13	3018.02	918.81
	400	132.370		3.8	0.97	7835.05	3453.61	1225.67
	500	152.672		4.4	0.95	9263.16	3526.61	1502.09

$$I_L = 0.079 nFC_b v^{0.7} d^{-0.3} U^{-0.344} D^{0.644} \qquad (11)$$

where n is the number of exchanged electrons, F is Faraday's constant (nF called "Faraday's equivalence"), C_b is the bulk concentration (mol cm^{-3}), U is the peripheral velocity = wr (cm rad S^{-1}) where w is the angular velocity (rad S^{-1}), r is the radial distance in cm or U = 2πwr in cm S^{-1}, d is the characteristic length for the rotating cylinder = the diameter of the electrode in cm^2 S^{-1} and v is the kinematic viscosity in stoke (γ = π/p). Values of D and γ for all solutions under different conditions are also recorded in Tables 12-15.

The diffusion coefficient D of Cu^{2+} ions in solutions containing organic acids decreases due to the increase in the viscosity π[55] according to Stockes-Einstein equation:

$$\frac{\pi D}{T} = const$$

where: π is the viscosity of the solution (g cm^{-1} S^{-1}). D is the diffusion coefficient of Cu^{2+} (cm^2 S^{-1}) and T is the absolute temperature (K$_0$).

The dimensionless groups most often used in convection mass transfer were[56]:

Sherwood number　$Sh = kd/D$ 　　(13)
Schmidt number　　$Sc = v/D$ 　　(14)
Reynolds number　$Re = ud/v$ 　　(15)

where k is mass transfer coefficient, D diffusion coefficient, V is kinamitic viscosity and, d is distance from the entrance or leading edge. Reynolds number was used in forced convection problem, while Groasshof number was used in the case of dimensional analysis. To obtain an overall mass transfer correlation under the present conditions by using the method of dimensional analysis, we suppose:

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

where (a, b) are constants. By plotting log {Sh/(Sc)$^{0.33}$} against log (Re) a straight line is obtained. Its slope gives the constant b while the intercept gives the constant a and c = 0.33 (indicating forced convection).

Figs. 11-14 show the overall mass transfer correlations for all carboxylic acids derivatives used. Tables 10-13 summarize the values of dimensional groups Sh, Sc and Re used in the correlation.
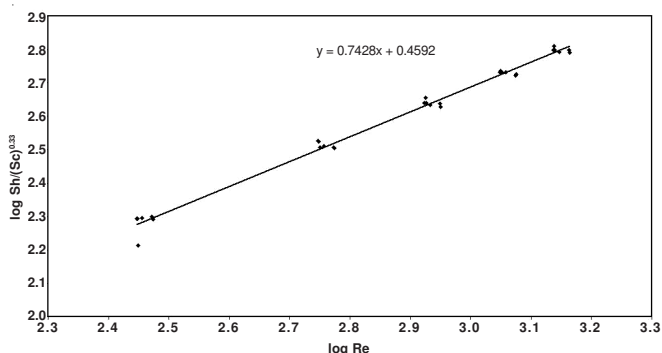
Fig. 11. Overall correlation of salicylic acid

$Sh = 0.5046\, Re^{0.7201}(Sc)^{0.33}$ for benzoic acid
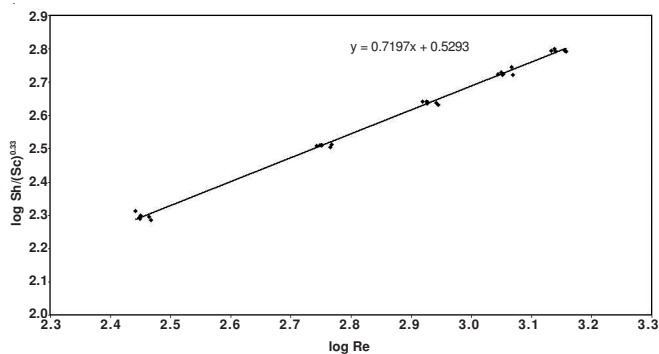$Sh = 0.5381\, Re^{0.7157}(Sc)^{0.33}$ for p-toluic acid
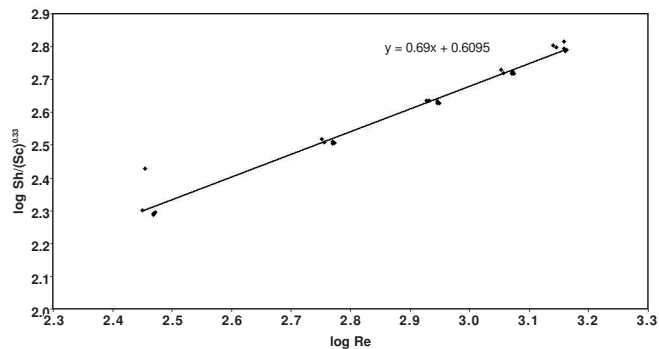
Fig. 12. Overall correlation of phthalic acid
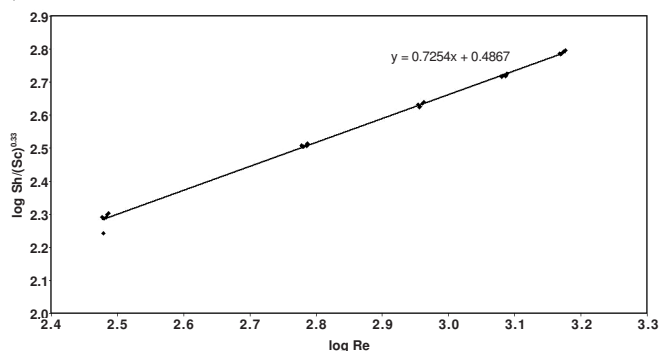
Fig. 13. Overall correlation of p-toluic acid

Fig. 14. Overall correlation of benzoic acid

$Sh = 0.4887\, Re^{0.7356}(Sc)^{0.33}$ for salicylic acid
$Sh = 0.5167\, Re^{0.7207}(Sc)^{0.33}$ for phthalic acid

Conclusion

The study of the effect of different carboxylic acids on copper corrosion led to the following important conclusions: Rate of copper corrosion decrease by adding the different carboxylic acids in both cases of weight loss and electropolishing. Rate of copper corrosion depend on the type and concentration of the carboxylic acid. The rate of corrosion decrease in the following order: salicylic acid > phthalic acid > p-toluic acid > benzoic acid. The rate of corrosion of copper increases by increasing the speed of the rotating electrode.

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