

Anodic corrosion of copper in presence of aniline derivatives

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The rates of anodic corrosion of copper plates in different concentrations of phosphoric acid (6, 8, 10, 12 and 14 mol) have been studied by measuring the limiting current of anodic dissolution. The rates of corrosion are measured in absence and presence of aniline derivatives, such as aniline, *p*-bromoaniline, *m*-chlororaniline, *o*-chlororaniline, *p*-chlororaniline and *p*-methyl aniline. It is found that the rate of corrosion depends on the type of inhibitor and its concentration. The rate of corrosion decreases by increasing the amount of inorganic additives from 9.72% to 80.14 %, depending on organic compounds and their concentrations. These compounds verify Langmuir and Flory-Huggins isotherm. Thermodynamic parameters are also reported.

Keywords: Aniline derivative, Corrosion inhibition, Electropolishing, Limiting current, Mass transfer, Thermodynamic parameters

Due to its excellent electrical and thermal conductivities and good mechanical workability, copper is a material commonly used in heating and cooling systems. Scale and corrosion products have negative effect on heat transfer and cause decrease in the heating efficiency of equipment, which requires periodic descaling and cleaning in hydrochloric acid pickling solution.

Most corrosion inhibitors can eliminate the undesirable destructive effect and prevent metal dissolution. Copper normally doesn't displace hydrogen from acid solutions and therefore, is virtually not attacked in non-oxidizing conditions. In fact, if hydrogen bubble is passed through a solution of copper salt, it reduces copper as fast as the process occurs¹. Copper dissolution in acidic medium has been studied by several researchers²⁻⁷. Corrosion inhibitors can be used to prevent copper dissolution. Benzotriazole is found to have excellent inhibition properties in several corrosion environments⁸. The molecules contain nitrogen atoms and it usually prevents copper by staining and tarnishing⁹.

One of the most important methods in the protection of copper against corrosion is the use of organic inhibitors¹⁰. Organic compounds containing polar groups including nitrogen, sulfur, oxygen¹¹⁻¹⁷

and heterocyclic compounds with polar functional groups and conjugated double bonds have been reported to inhibit copper corrosion¹⁸⁻²⁰. The inhibiting action of these organic compounds is usually attributed to their interactions with the copper surface via their adsorption. Polar functional groups are regarded as the reaction center that stabilizes the adsorption process²¹. 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 electrolyte solution. Among various nitrogen containing organic compounds, anilines are known to be very effective inhibitors for metal and alloys in different corrosion media.

In this study, the effect of some amine derivatives on the inhibition of copper corrosion in 8M H₃PO₄ at different condition has been investigated. The rate of copper corrosion is determined by measuring the anodic limiting current, i.e at which polishing take place.

Experimental Procedure

Materials

Aniline, *p*-bromoaniline, *m*-chlororaniline, *o*-chlororaniline, *p*-chlororaniline, *p*-methyl aniline, all of BDH, were used as corrosion inhibitors. Chemically pure H₃PO₄ and double distilled water were used to prepare solutions. Electrode treatment as reported by Wilke²² was used in the study. The rate of

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copper corrosion under different conditions is determined by measuring the limiting current at 25°C. Seven different concentrations of analar organic compound with 8M H₃PO₄ were used ranging from 0.5×10^{-4} M to 5.0×10^{-4} M.

Apparatus and procedure

Figure 1 shows the cell and electrical circuit used in the study. The cell consists of a rectangular plastic container having the dimensions $5.1 \times 5.0 \times 10.0$ cm with electrodes fitting the whole section. Two electrodes, each as rectangular copper plate of 10 cm height and 5 cm width, are located 5.1 cm apart. A porous poly vinyl chloride diaphragm is used to prevent the effect of H₂ bubble. The electrical circuit consists of 6 volt D.C. power supply with a voltage regulator and multi-range ammeter, was connected in series with cell. Potential differences were obtained by increasing the cell current stepwise and measuring the steady state anode potential against a reference electrode. The reference electrode consisted of a copper wire immersed in a cup of Luggin probe filled with phosphoric acid solution containing organic compound at concentration similar to that in the cell, the tip of Luggin probe was placed 0.5-1 mm tube from the anode surface. The potential difference between the anode and the reference electrode was measured by high impedance potentiometer. Ortho-phosphoric acid solution was prepared from Analar ortho-phosphoric acid and distilled water. The anode height was 2 cm and before each run the block part of the anode was insulated with poly-styrene lacquers and the active surface of the anode was polished with fine emery paper, degreased with trichloroethylene, washed with alcohols and finally rinsed in distilled water. Electrode treatment was done as per the procedure reported by Wilke²². The rate of copper corrosion under different conditions was determined by measuring the limiting current at 25°C.

Leveling process

Leveling is the principle process in electro-polishing^{23,24}. It can be explained by mass transfer mechanism²³. A cell with a diaphragm was used for this study in order to eliminate the effect of hydrogen gas evolved at the cathode from affecting the rate of mass transfer at the anode. A cell without diaphragm was 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 classical current voltage curves of

electro-polishing (Fig. 2). A typical polarogram is obtained in this study for aniline in case of divided and undivided cell.

The curve is divided into three parts. In the first part, the current density (c.d.) is proportional to the voltage. In the second part of the curve, the metal undergoes electro-polishing. In the first part, etching takes place and in the third part, some localized pitting occurs²⁴.

Results and Discussion

Effect of electrode height on limiting current

Figure 3 shows that the limiting current decreases with the increase in height. In electro-polishing and

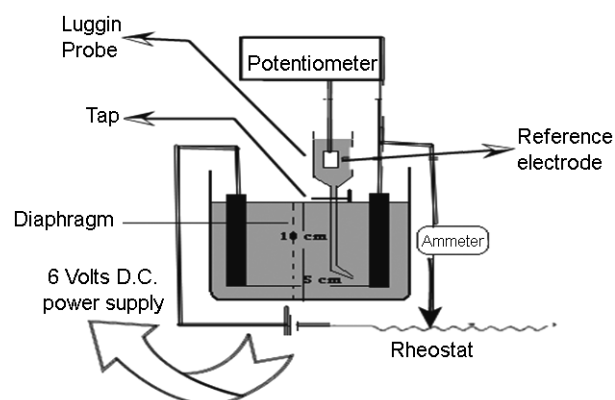


Fig. 1—Electrolytic cell and electrical circuit

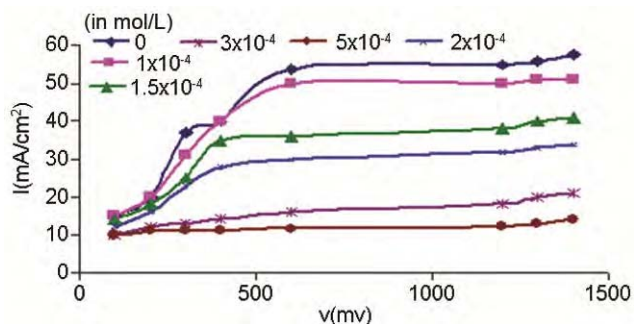


Fig. 2—Current-potential curves in presence and absence of aniline (NaOH, h = 5 cm, 8M H₃PO₄ and 25°C)

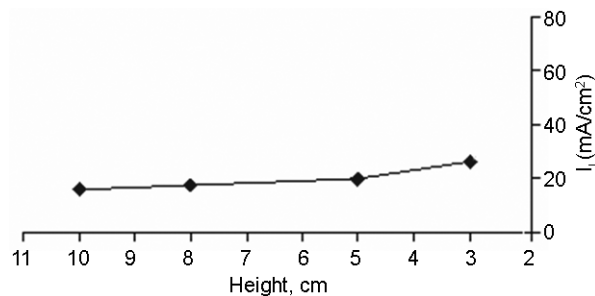


Fig. 3—Relationship between limiting current density and height at 25°C for 8M H₃PO₄

generally for anodic dissolution of metal, the current flow in the thermodynamic boundary layer and the diffusion layer increases in the downward direction, i.e. the resistance to mass transfer increases in the downward direction. Accordingly, the local limiting current density increases in the up-ward direction of the anode. This explains why polishing is attained in the upper parts of the electrode before it occurs in the lower parts at the limiting current region. This is also confirmed by visual observation during electro-polishing. The average limiting current density decreases with the increase in the height, according to the following equation²⁵:

$$I_l = C/H^{0.33} \quad \dots (1)$$

where C is the constant; H , the height of electrode; and I_l , the limiting current.

Effect of aniline concentration on limiting current at anode

The observed limiting current, represents the rate of anodic copper metal dissolution in Ortho-phosphoric acid at 25°C. It is found that the limiting current decreases with increasing the concentration of organic compound additives. Table 1 shows the dependence of limiting current on the bulk concentration in absence and presence of organic compound additives. It is found that the limiting current decreases with increasing the concentration of organic compound. From the practical point of view, it is inferred that the finding indicating the decrease in I_l (mit) by organic test-additives could be extended to suggest similar inhibition of corrosion rate in 8M H_3PO_4 by the type of organic additives under study. If the limiting current values in absence and presence of organic compound are I and I_l respectively, the percentage of inhibition can be calculated from the following equation:

$$\% \text{ Inhibition} = \frac{I - I_l}{I_l} \quad \dots (2)$$

Results in Table 1 and plots, correlating additives concentration with per cent inhibition (Fig. 4), show

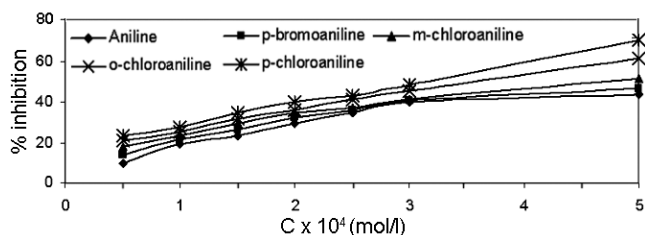


Fig. 4—Relationship between percentage inhibition and concentration of organic compounds at 25°C

Table 1—Effect of concentration of organic additives on % inhibition in presence of 8M H_3PO_4 at 25°C

$C \times 10^4$ mol.L ⁻¹	Aniline		p-bromoaniline		m-chloroaniline		o-chloroaniline		p-chloroaniline		p-methyl aniline	
	I_l , mA	% Inhibition	I_l , mA	% Inhibition	I_l , mA	% Inhibition	I_l , mA	% Inhibition	I_l , mA	% Inhibition	I_l , mA	% Inhibition
0.5	650	9.72	620	13.89	590	18.08	570	20.83	550	23.61	510	29.17
1.0	580	19.44	565	21.53	550	23.61	540	25.00	520	27.78	480	29.17
1.5	550	23.61	530	26.39	510	29.17	490	31.94	470	34.72	420	41.67
2.0	510	29.17	485	32.64	470	34.72	460	36.11	430	40.28	370	48.61
2.5	470	34.72	460	36.11	450	37.50	420	41.67	410	43.06	300	58.33
3.0	430	40.28	425	40.97	420	41.67	390	45.83	370	48.61	240	66.67
5.0	405	43.75	585	46.53	350	51.39	275	61.83	210	70.83	143	80.14

that the per cent inhibition caused by organic compound ranges from 9.72 to 80.14, depending on the type of organic compounds. These results are in agreement with the finding of other researchers²⁶ who used same range of concentration for other anode geometries. The decrease in limiting current with increasing the concentration of aniline derivatives could be attributed to the following facts:

(i) The decreasing solubility of dissolved copper phosphate in *o*-phosphoric acid and organic compound mixture is responsible for decreasing the limiting current.

(ii) The increasing viscosity of the test solution in presence of aniline derivatives consequently decreases the diffusivity of Cu^{2+} according to stokes-Einstein equation²⁷.

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

The viscosity of organic additives water- H_3PO_4 mixture is found to be higher than the water- H_3PO_4 mixture, possibly resulting in decrease in diffusivity of Cu^{2+} . Also, the solubility of copper phosphate in test solutions with organic additives is found to be lower than the water phosphoric acid mixture, and hence the saturation of solution could be attained quickly, thereby decreasing the limiting current.

Adsorption isotherm

It is generally assumed that the adsorption isotherm of the inhibitor at the metal solution interface is the first step to be considered for the mechanism of organic compounds in aggressive acid media. Four types of adsorption may take place in the inhibiting phenomena involving organic molecules at the metal-solution interface, as shown below:

- (i) Electrostatic attraction between charged molecules and charged metal
- (ii) Interaction of uncharged electron pairs in the molecules with the metal
- (iii) Interaction of electron with metal
- (iv) A combination of the above²⁸.

Chemisorptions involve sharing or charge transfer from the inhibitor molecule to the surface in order to form coordinate bond. In fact, electron transfer is typical for transition metals having vacant low energy electron orbital. Concerning inhibitors, electron transfer can be expected with compounds having

relatively loosely bound electron. This situation may arise because of the presence (in the adsorbed inhibitor) of multiple bonds or aromatic rings with a π character^{29,30}. The inhibition efficiency of homogenous series of organic substances, differing only in the hetero atom, is usually in the sequence $\text{P} > \text{Se} > \text{S} > \text{N} > \text{O}$. The Langmuir adsorption isotherm is donated by

$$KC = \theta/(1-\theta) \quad \dots (3)$$

$$\text{or } \log \theta/(1-\theta) = k \log C \quad \dots (4)$$

where K is the equilibrium constant of adsorption process; C , the concentration; and θ , the surface coverage. The degree of surface coverage (θ) at constant temperature was determined from following expression as reported elsewhere³¹.

$$\theta = \frac{I - I_l}{I_l} \quad \dots (5)$$

From Eq. (4), a plot of $\log (\theta/1-\theta)$ against $\log C$ should yield a straight line with intercept of $\log K$. Table 2 gives the data between $\log (\theta/1-\theta)$ against $\log C$ for all aniline derivatives of the surface coverage with concentration variation. Figure 5 shows the Flory-Huggins adsorption isotherm for copper electrode in H_3PO_4 plotted as $\log (\theta/C)$ against $\log (1-\theta)$ at 25°C. A straight line is obtained with slope x and intercept $\log xk$. The experimental data fits the Flory-Huggins adsorption isotherm which is represented as shown below:

$$\log \theta/C = \log xk + x \log (1-\theta) \quad \dots (6)$$

where x is the number of water molecules replaced by one molecule of the inhibitor. The adsorption of inhibitors at metal-solution interface might be due to the formation of either electrostatic or covalent bonding between the adsorbate and the metal surface atoms³². The kinetic adsorption isotherm may be written in the following form³³:

$$\log \theta/1-\theta = \log k' + y \log C \quad \dots (7)$$

where y is the number of inhibitor molecules that occupy one active site. The binding constant of adsorption $K = k^{1/y}$, where $1/y$ is the number of surface active sites occupied by one molecule of the inhibitor;

Table 2—Limiting current and surface coverage of 8M H₃PO₄ in presence of different aniline derivatives concentration

$C \times 10^4, \text{mol.L}^{-1}$	% Inhibition	$-\log C$	θ	$\theta/1-\theta$	$\log(\theta/1-\theta)$	$1-\theta$	$\log(1-\theta)$	$\log(\theta/C)$
Aniline								
0.5	9.72	4.30	0.097	0.108	-0.97	0.92	-0.04	3.29
1.0	19.44	4.00	0.194	0.241	-0.62	0.81	-0.09	3.28
1.5	23.61	3.82	0.236	0.309	-0.51	0.76	-0.12	3.20
2.0	29.17	3.70	0.292	0.412	-0.39	0.71	-0.15	3.16
2.5	34.72	3.60	0.347	0.532	-0.27	0.65	-0.19	3.14
3.0	40.28	3.52	0.402	0.674	-0.17	0.60	-0.22	3.13
5.0	43.75	3.30	0.438	0.778	-0.11	0.56	-0.25	2.94
p-bromoaniline								
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	40.97	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
m-chloroaniline								
0.5	18.08	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	37.50	3.60	0.375	0.600	-0.22	0.63	-0.20	3.18
3.0	41.67	3.52	0.417	0.714	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
o-chloroaniline								
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	0.714	-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
p-chloroaniline								
0.5	29.17	4.30	0.236	0.309	-0.51	0.76	-0.12	3.67
1.0	33.34	4.00	0.278	0.385	-0.41	0.72	-0.14	3.44
1.5	41.67	3.82	0.347	0.532	-0.27	0.65	-0.19	3.36
2.0	48.61	3.70	0.403	0.674	-0.17	0.60	-0.22	3.30
2.5	58.33	3.60	0.431	0.756	-0.12	0.58	-0.24	3.27
3.0	66.67	3.52	0.486	0.946	-0.02	0.51	-0.29	3.21
5.0	80.14	3.30	0.708	2.429	0.39	0.30	-0.53	3.15
p-methylaniline								
0.5	29.17	4.30	0.292	0.412	-0.39	0.71	-0.15	3.76
1.0	33.34	4.00	0.333	0.500	-0.30	0.66	-0.18	3.47
1.5	41.67	3.82	0.417	0.714	-0.15	0.59	-0.23	3.32
2.0	48.61	3.70	0.486	0.946	-0.02	0.52	-0.28	3.38
2.5	58.33	3.60	0.583	1.400	0.15	0.42	-0.38	3.36
3.0	66.67	3.52	0.667	2.000	0.30	0.33	-0.48	3.35
5.0	80.14	3.30	0.801	4.035	0.61	0.19	-0.71	3.20

and k , the binding constant³³. Figure 6 shows linear relation of the inhibitor molecules between $\log \theta/(1-\theta)$ and $\log C$ at 25°C, and the calculated values of $1/y$ and K are given in Table 3. The values of $1/y$ depend on the type of aniline derivative. From Table 3, it is obvious that the value of $1/y$ for p -methyl aniline is approximately one, suggesting that the compound is attached to one active site per inhibitor molecule.

For other inhibitors (aniline, p -bromoaniline, m -chloroaniline, o -chloroaniline, p -chloroaniline), the values of $1/y$ are higher than one, indicating that, the given inhibitors molecules are attached to more than one active site. The free energy of adsorption (ΔG_{ads}) at different concentration was calculated from the following equation:

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

The value 55.5 is the concentration of water in the solution (mol L^{-1}). The values of ΔG_{ads} are given in Table 4. In all cases, the ΔG_{ads} values are found to be negative and remains in the range 26.56-31.31 kJ mol^{-1} . The most efficient inhibitor shows the most negative value. This suggests that they are strongly adsorbed on the metal surface. The negative values of ΔG_{ads} indicate the spontaneous adsorption of the inhibitor. It

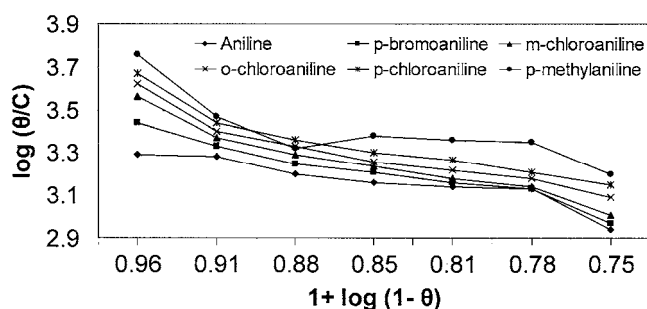


Fig. 5—Relationship between $\log (\theta / C)$ against $\log (1-\theta)$ for all compounds at 25°C

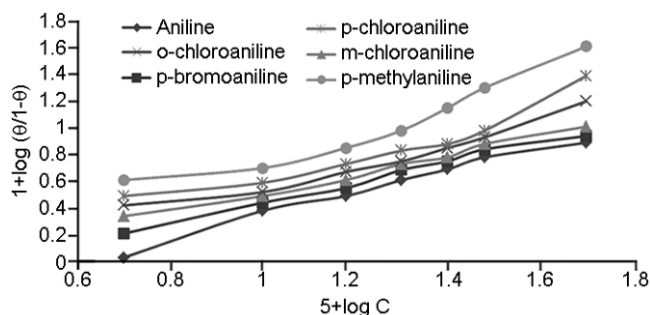


Fig. 6—Kinetic isotherm for all compounds used

is found that the ΔG_{ads} values are more positive than -40 kJ mol^{-1} , indicating that the inhibitors are physically adsorbed on the metal surface. Similar results have also been reported by Talati *et al.*³⁴.

Structure effect of organic additives

It is known that many additives are usually capable of being adsorbed on the anodic substrate and even might get trapped within metal/solution interference. 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 such organic or non-organic substances is very large. Moreover, their action could be different for different functions of substrates, the ions to reduce and the electrolytic conditions. For example, additive re-orientation on the electrode surface has been observed, depending on the functions of surface coverage or as a function of pH .

In the case of copper, a complex in solution between aniline derivative and Cu^+ or Cu^{2+} cation is formed as a result of transport of copper ions from the interlace to the bulk and the work for the discharge of copper complex ion increases. The effect of inhibitor concentration on the inhibition efficiency of various aniline derivatives in 8 M H_3PO_4 is shown in Fig. 4

Table 3— k , x and $1/y$ of H_3PO_4 in presence of different organic additives to Flory-Huggins and kinetic adsorption

Compound	Flory-Huggins		Kinetic adsorption isotherm		
	x	k	y	$1/y$	k
Aniline	1.4396	1669.39	0.8918	1.12	810.59
p -bromoaniline	2.1706	1721.95	0.7572	1.32	294.04
m -chlororaniline	1.8727	2027.83	0.6903	1.45	188.93
o -chlororaniline	1.4195	2913.83	0.7810	1.28	491.81
p -chlororaniline	2.3713	2980.67	0.84250	1.19	997.01
p -methylaniline	0.6374	2682.53	0.9858	1.01	5640.09

Table 4—Calculated values of free energy of adsorption of H_3PO_4 in presence of different organic additives using different methods

Compound	$-\Delta G_{ads}, \text{kJ mol.l}^{-1}$	
	Flory-Huggins	Kinetic adsorption isotherm
Aniline	28.35	26.56
p -bromoaniline	28.42	24.04
m -chlororaniline	28.83	22.95
o -chlororaniline	29.73	25.32
p -chlororaniline	29.78	27.07
p -methylaniline	29.52	31.36

the order of decrease in inhibition efficiency of inhibitors is found to be *p*-methyl aniline > *p*-chloro aniline > *m*-chloro aniline > *p*-bromo aniline > aniline. All inhibitors has amino group which is the effective group of adsorption on copper surface. Aniline has less steric hindrance than other, so it has small efficiency. CH₃ is electron releasing group which stabilizes -NH₂ to be adsorbed on copper surface.

Effect of temperature

The effect of temperature on the Cu electropolishing rate in absence and presence of all aniline additives was determined in the temperature range 25-40°C (Table 5). It is observed that the electropolishing rate increases with temperature for different concentrations of organic additives. Table 2 gives the variation in %IE with temperature. Values of E_a that have been derived from the slopes of Arrhenius plots³⁵ are given in Table 6.

It is obviously seen that the E_a values in absence and presence of organic additives are <28 k J mol⁻¹, indicating that the diffusion processes are controlling the electrodeposition reaction³⁶. The thermodynamic parameters such as change in free energy ΔG*, enthalpy ΔH* and entropy ΔS* were calculated in the same way as reported by other researches³⁷. Table 6 summarizes the values of these thermodynamic properties. From transition state equation³⁸, a straight line is obtained, from which ΔH* and ΔS* can be calculated from the slope and intercept respectively.

The findings indicate that the tested compounds act as inhibitors through adsorption on copper surface, which results in formation of a barrier to mass and charge transfer. The values of ΔH* reflect the strong adsorption of these compounds on copper surface. The negative values of ΔS* point out a greater order produced during the process of activation. This can be achieved by the formation of activated complex representing the association or fixation with consequent loss in the degree of freedom of the system during the process. ΔG* values show limited increase with the increase in the concentration of organic additives, revealing that weak dependence of ΔG* on the composition of the organic additives can be attributed largely to the general linear composition between ΔH* and ΔS* for the given temperature^{39,40}.

Table 5—Effect of temperature on limiting current in presence of organic additives and 8M H₃PO₄

$C \times 10^4$ mol.L ⁻¹	Limiting current, mA			
	25°C	30°C	35°C	40°C
Aniline				
0.5	650	670	690	710
1.0	580	600	620	640
1.5	550	570	590	610
2.0	510	530	550	570
2.5	470	490	510	590
3.0	430	450	470	490
5.0	405	420	440	460
<i>p</i>-bromoaniline				
0.5	620	640	660	680
1.0	565	580	600	620
1.5	530	545	560	580
2.0	485	500	520	540
2.5	460	480	500	515
3.0	425	440	460	530
5.0	405	420	440	460
<i>m</i>-chloroaniline				
0.5	540	610	630	650
1.0	550	575	600	625
1.5	510	530	550	570
2.0	470	490	510	550
2.5	450	470	490	510
3.0	420	425	450	470
5.0	350	370	390	410
<i>o</i>-chloroaniline				
0.5	570	600	620	640
1.0	540	560	580	600
1.5	490	515	540	560
2.0	460	480	500	520
2.5	420	440	440	460
3.0	390	410	430	450
5.0	275	300	325	330
<i>p</i>-chloroaniline				
0.5	550	570	590	610
1.0	520	540	560	580
1.5	470	495	520	540
2.0	430	450	470	490
2.5	410	430	450	470
3.0	370	390	410	430
5.0	210	240	270	300
<i>p</i>-methylaniline				
0.5	510	530	550	580
1.0	480	500	520	540
1.5	470	440	460	480
2.0	370	400	420	440
2.5	300	320	390	370
3.0	240	260	280	300
5.0	210	240	260	280

Table 6—Activation energy and thermodynamic parameters for all compounds

$C \times 10^5$ mol.L ⁻¹	E^* J.mol ⁻¹ K ⁻¹	ΔH^* J.mol ⁻¹ K ⁻¹	ΔG^* J.mol ⁻¹ K ⁻¹	$-\Delta S^*$ J.mol ⁻¹ K ⁻¹
Aniline				
0.5	5.358 ± 0.003	2.88 ± 0.003	5.74 ± 0.006	182 ± 10
1	8.530 ± 0.002	3.17 ± 0.006	57.5 ± 0.012	182 ± 2.1
1.5	7.240 ± 0.288	4.76 ± 0.023	57.8 ± 0.57	177 ± 0.9
2	6.780 ± 0.023	4.3 ± 0.023	57.985 ± 0.078	180 ± 78
3	9.033 ± 0.002	7.782 ± 0.042	58.4 ± 0.084	178 ± 14
5	18.46 ± 0.501	16 ± 0.501	59.75 ± 0.991	141.8 ± 1.64
m-chloroaniline				
0.5	9.2 ± 0.023	6.71 ± 0.23	57.36 ± 4.6	170 ± 7.6
1	6.62 ± 0.02	4.141 ± 0.02	57.38 ± 0.041	178.5 ± 6.8
1.5	5.76 ± 0.008	3.281 ± 0.008	57.6 ± 0.017	182 ± 2.8
2	7.93 ± 0.09	5.45 ± 0.09	57.86 ± 0.032	181 ± 5.4
3	4.24 ± 0.08	1.76 ± 0.08	58 ± 1.9	188 ± 3.26
5	7.41 ± 0.035	4.93 ± 0.035	58.23 ± 0.069	179 ± 11.1
p-bromoaniline				
0.5	4.78 ± 0.034	2.303 ± 0.034	57.1 ± 0.006	183.7 ± 1.1
1	4.85 ± 0.233	2.37 ± 0.23	57.3 ± 0.46	184 ± 7.6
1.5	9.521 ± 0.04	6 ± 0.004	57.17 ± 0.9	211 ± 15.5
2	5.61 ± 0.262	3.13 ± 0.21	57.7 ± 0.518	180 ± 8.5
3	5.9 ± 0.272	3.43 ± 0.272	57.812 ± 0.551	182 ± 9.1
5	10.92 ± 2.9	8.446 ± 2.9	58.1 ± 5.5	166 ± 9.5
p-methylaniline				
0.5	8.88 ± 0.048	4.083 ± 0.048	57.574 ± 0.925	179 ± 1.53
1	6.100 ± 0.013	3.621 ± 0.013	57.71 ± 0.026	181.4 ± 4
1.5	1.621 ± 0.02	0.857 ± 0.02	57.85 ± 5.8	196.9 ± 9
2	8.85 ± 0.741	6.371 ± 0.741	58.86 ± 5.1	162 ± 14
3	11.554 ± 0.152	9.08 ± 0.152	59.43 ± 0.30	168 ± 4.9
5	14.67 ± 0.81	12.196 ± 0.8	59.7 ± 2.7	159.4 ± 4.6
p-chloroaniline				
0.5	4.58 ± 0.006	2.10 ± 0.006	57 ± 0.013	184 ± 2.1
1	5.100 ± 0.044	2.621 ± 0.044	57.2 ± 0.0087	183.2 ± 1.4
1.5	5.36 ± 0.003	2.88 ± 0.003	57.4 ± 0.006	183 ± 10
2	5.76 ± 0.008	3.28 ± 0.008	57.6 ± 0.017	182 ± 2.8
3	11.16 ± 0.21	8.68 ± 0.21	57.8 ± 0.57	164.8 ± 9.55
5	6.65 ± 0.3	4.17 ± 0.3	58.2 ± 0.59	181 ± 9
o-chloroaniline				
0.5	5.915 ± 0.416	2.98 ± 0.0416	57.278 ± 0.90	182.6 ± 1.5
1	5.439 ± 0.006	2.980 ± 0.006	57.42 ± 0.013	182.6 ± 2.15
1.5	6.96 ± 0.247	4.482 ± 0.0247	57.66 ± 0.541	178.3 ± 0.89
2	6.347 ± 0.016	4.483 ± 0.016	57.821 ± 0.032	181 ± 5.39
3	7.411 ± 0.035	4.932 ± 0.035	58.2 ± 0.115	178.7 ± 0.11
5	9.778 ± 0.77	7.299 ± 1.77	59.063 ± 3.513	173.6 ± 5.8

Conclusion

The rate of electropolishing of anodic dissolution is determined by measuring limiting current. It is found that the rate of anodic corrosion decreases in presence of aniline derivatives. Rate of inhibition depends on concentration of organic substance and the rate of corrosion increases by increasing temperature.

References

- Gilber P T & Shreir L L, Copper and Copper Alloy in *Corrosion*, 2nd edn (Newnes Butterworths, London, UK), 1976, 436.
- Weeks J R & Hill G R , *J Electrochem Soc*, 103 (1956) 203.
- Gregory D P & Riddiford A C , *J Electrochem Soc*, 107 (1960) 950.
- Bumbulis J & Graydon W F, *J Electrochem So* , 109 (1962) 1130.
- Otsuka R & Uda M , *Corrosion Sci* , 9 (1969) 703.
- Schumacher R, Muller A & Stockel W , *J Electroanal Chem*, 219 (1987) 311.
- Moreira A H, Benedetti A V, Calo P L & Sumodjo P T A, *Electrochim Acta*, 38 (1993) 981.
- Moretti G, Molokanov V V, Quartarone G & Zingales A, *Corrosion*, 54 (1998) 135.
- Khaled K F & lackerman N I, *Electrochim Acta*, 49 (2004) 485.
- Zhang D Q, Gao L X & Zhou G D, *Corrosion Sci*, 46 (2004) 3031.
- Christy A G, Lowe A, Otieno-Alego V, Stoll M & Webster R D , *J Appl Electrochem*, 34 (2004) 225.
- Otmacic H & Telegdi I & Papp K & Stupnisek-Lisac E, *J Appl Electrochem*, 34, 545 (2004)
- Ma H, Chen S, Niu L, Zhao S, Li S & Li D 1, *J Appl Electrochem*, 32 (2002) 65.
- Wang C, Chen S & Zhao S, *J Electrochem Soc*, 151 (2004) B11.
- Kendig M & Jeanjaquet S, *J Electrochem Soc*, 149 (2002) B11.
- Ma H Y, Yang C, Yin B S, Li G Y, Chen H S & Luo J L, *J Appl Surf Sci*, 218 (2003)143.
- Khled K F & Lackerman N , *Electrochem Acta*, 49 (2004)485.
- Otnlacic H & Stupnisek-Lisac E , *Electrochim Acta*, 48 (2002)985.
- Scendo M, Poddebniak D & Malyszko J, *J Appl Electrochem*, 33 (2003) 287.
- Dalali A, Hammouti B, Touzani R, Kertit S, Ramdai A, El & Kacemi K , *Anti-corros Methods Mater*, 49 (2002) 96.
- Fontana M G, Staehle K W, *Advances in Corros Sci and Technology*, Vol. 1 (Plenum Press, New York), 1970.
- Jaquet P A, *Electrochem Trans Soc*, 69 (1936) 629.
- Fouad M G, Zein F N & Ismail M I , *Electrochem Acta*, 9 (1972) 150.
- El-Subruiti G M & Kawana A L, *J Appl Sci*,10 (1995) 318.
- Hacerman N & Maki-ides A C, *Ind Eng Chem*, 39 (1954) 790.
- Taha A A, *Bull Electrochem*, 9 (2&3) (1993)80.
- Ahmed A M & Mohamed G B, *J Chin Chem Soc (Taiwan)*, 42 (1989) 78.

- 28 Donnue F & Nobe K, *J Electrochem Soc*, 112 (1965) 886.
29 Atega Bi, *J Electroanal Chem*, 76 (1977) 191.
30 Al-Anadouli B, Eltaib F & El-Nizami F, *Extended Abstracts* (Electrochemical Soc Fall Meeting, Chigco), 1988, 188.
31 Ebenso E E, Ekpe U J, Ita B I, Offioing O E & Ibok U J, *Mater Chem Phys*, 60 (1999) 79.
32 Ebenso E E, *Bull Electrochem*, 19 (2003) 209.
33 EL-Awady A, Abd EL-Nabey B & Aziz J, *J Electrochem Soc*, 139 (1992) 2150.
34 Talati J D & Darji J M, *Ind Chem Soc*, 65 (1988) 94.
35 Poling G, *J Electrochem Soc*, 114 (1967) 1209.
36 Murhawa T, Kato T, Nagura S & Ilackerman N, *Corrosion Sci*, 8 (1958) 341.
37 Mat' Ioa Y, Kinuhata Y, Okahara M, Komari S & Tamura H, *Corrosion*, 10 (1973) 557.
38 Kaminiski M & Szharska-Simiallowska Z, *Corrosion Sci*, 13 (1973) 557.
39 Taha A A, Sal lam S H & Ahmed A M, *Anti Corrosion*, 41 (1994) 10.
40 Ahmed A M & Mohamed G B, *J Chin Chem Soc (Taiwan)*, 2 (1989) 78.