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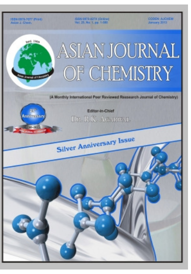

Copper Electropolishing in the Presence of Purine Derivatives

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The electropolishing settings for inhibiting the rate of anodic corrosion of copper plates in phosphoric acid were achieved using potentiodynamic studies including different factors such as plate height, phosphoric acid concentration, type and concentration of purines as well as temperature. The results reveal that purines have strongest inhibitive effect ranging from 9.7 to 80.1 % that provides good protection to copper surface against corrosion in phosphoric acid solutions. Its adsorption obeys Langmuir, Flory-Huggins and kinetic adsorption isotherm. Thermodynamic functions computed and discussed.

Key Words: Anodic corrosion, Purine derivatives, Adsorption isotherm, Thermodynamic functions.

INTRODUCTION

Chemical, physical and mechanical properties of copper make it the third most widely used metal after iron and aluminum. It is used in essential fields such as electronically applications, building construction, industrial machinery, equipment, transportation and consumer products[1]. The corrosion of metals is common phenomenon in industry and it has received a considerable amount of attention. The use of inhibitors is one of the most practical methods for protection against corrosion. Usually, organic compounds are widely used in industry for preventing corrosion in acidic environments[2-8]. To improve the protective efficiency of copper corrosion in corrosive environment, great efforts have been put into the investigation and many technologies have been used[9-11]. The inhibitive power of the organic inhibitors has been interpret in term of many different characteristics such as molecular size, molecular weight, molecular structure, nature of heteroatom present in the molecule, *etc*.[2]. Nitrogen containing compounds have been found to serve as good inhibitors of corrosion[12] and their inhibiting action has been explained in term of the number of mobile electron pairs[13], the π orbital character of free electron and the electron density around the nitrogen atom[2]. Among numerous inhibitors that have been tested and are applied industrially as corrosion inhibitors, those that are non-toxic or low toxic are now far more strategic than in the recent past[14]. Purines are known to be effective non-toxic inhibitors for metal and alloys in different corrosion media. The process is diffusion controlled, depending on the concentration gradient forming a selective electrochemical dissolution of copper. The limiting current value that determines the corrosion efficiency depends on the rate of mass transfer of Cu^{2+} ions from the diffusion layer to the bulk of the solution. The rate of mass transfer depends on the relative ionic movement, geometry of anode, temperature, the type and the physical properties of the electrolyte[1,15]. The novelty of the present work is to study the effects of purines derivatives on the inhibition of copper corrosion in H_3PO_4 solution at different conditions. The study has been carried out using potentiodynamic polarization and the rate of corrosion is determined by measuring the anodic limiting current.

EXPERIMENTAL

Analar grade H_3PO_4 (98 % w/w), supplied by BDH chemicals Ltd., were used for the preparation of the electrolyte. Different solutions of H_3PO_4 with different concentrations 6, 8, 10, 12 and 14 mol were used.

Solution composition: Blank solution consists of 8 M H_3PO_4 and different concentrations of purine compounds. The concentrations of organic additives cover range from 0.5×10^{-3}-5×10^{-4} M.

Apparatus and procedure [Fig. 1]: The cell consists of a rectangular plastic container having the dimensions (5.1 cm × 5 cm × 10 cm) with electrodes fitting the whole cross section area. The electrodes were rectangular copper sheets of 10 cm height and 5 cm width, were located 5.1 cm apart. A porous

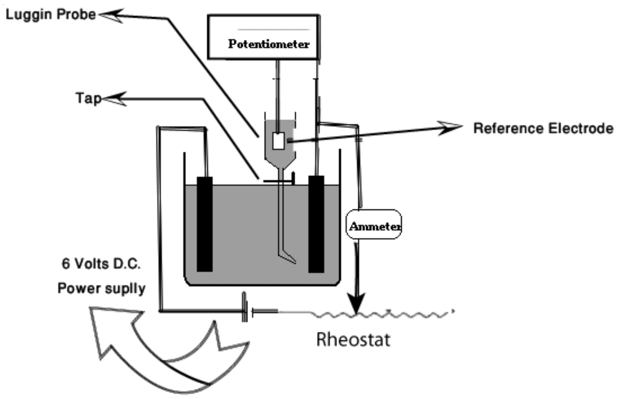


Fig. 1. Cell and electrical circuit

PCV diaphragm was use to prevent the effect due to H_2 bubbles. The electrical circuit consists of 6 V D.C. power supply connected in parallel with the cell to measure the voltage and multi-range digital ammeter connected in series with the cell to measure the current. Reference electrode consists of a copper wire immersed in a cup of luggin tube filled with the phosphoric acid concentration similar to that in the cell. The tip of the luggin tube was place 0.5-1.0 mm from the anode. The potential difference between the anode and the reference electrode was measured by potentiometer. Phosphoric acid concentration prepared from the Analar grade orthophosphoric acid and distilled water. The anode height was 1, 2, 3, 4 and 5 cm and before each run, the back part of the anode insulated with polystyrene lacquers and the active surface of the anode was polished with fin emery paper, degreased with trichloroethylene, washed with alcohol and finally rinsed with distilled water. Electrode treatment was similar to that used by Wilkes[16]. The rate of copper corrosion under different conditions is determined by measuring the limiting current at 25 ºC.

Purine derivatives were synthesized and used as inhibitors

Melting points were determined using a Buchi apparatus: ^{1}H NMR spectra were recorded with a Varian Gemini spectrometer at 300 MHz in DMSO-d_6 with TMS as internal standard. Chemical shifts were reported in δ scale (ppm) relative to TMS as a standard and the coupling constants (J values) are given in Hz.The progress of the reactions was monitored by TLC using aluminum silica gel plates 60 F_{245}. EIMS spectra were recorded with a HP D5988 A 1000 MHz (Hewlett. Packard, Palo Alto, CA, USA). Elemental analyses (C, H and N) were carried out at the Microanalytical Center of Cairo Univ., Giza, Egypt.

General procedure for the preparation of purine derivatives (I-VI): 6-Chloro-9*H*-purine (A) (1.54 g, 10 mmol) was treated with excess of secondary amines (about 10 mL) under reflux for 3-4 h. The excess of the solvent was removed under reduced pressure. The residue was co-evaporated with ethanol (3 mL × 5 mL) and then recrystallized from ethanol to afford **I-VI** in 70-78 % yields, as a pale yellow powder.

6-(Pyrrolidin-1-yl)-9*H*-purine (I): Yield 75 %; m.p. 180-182 ºC. ^{1}H NMR (DMSO-d_6): δ = 1.90 (t, 4H, J = 5.5 Hz, 2 × CH_2), 3.45 (t, 4H, J = 5.5 Hz, 2 × NCH_2), 7.85 (s, 1H, H-8), 8.15 (s, 1H, H-2), 11.03 (brs, 1H, NH). Mass spectrum, m/z: 189 [M^+]. Found (%): C, 57.00; H, 5.44; N, 36.88. $C_9H_{11}N_5$. Calcd. (%): C, 57.13; H, 5.86; N, 37.01.

6-(Piperidin-1-yl)-9*H*-purine (II): Yield 78 %; m.p. 192-194 ºC. ^{1}H NMR (DMSO-d_6): δ = 1.53-1.59 (m, 6H, 3 × CH_2), 4.05 (t, 4H, J = 5.8 Hz, 2 × NCH_2), 7.88 (s, 1H, H-8), 8.10 (s, 1H, H-2), 11.12 (brs, 1H, NH). Mass spectrum, m/z: 203 [M^+]. Found (%): C, 58.89; H, 6.32; N, 34.21. $C_{10}H_{13}N_5$. Calcd. (%): C, 59.10; H, 6.45; N, 34.46.

6-(Morphin-1-yl)-9*H*-purine (III): Yield 77 %; m.p. 233-235 ºC. ^{1}H NMR (DMSO-d_6): δ = 3.50 (t, 4H, J = 5.6 Hz, 2 × NCH_2), 3.75 (t, 4H, J = 5.6 Hz, 2 × OCH_2), 7.85 (s, 1H, H-8), 8.13 (s, 1H, H-2), 11.09 (brs, 1H, NH). Mass spectrum, m/z: 205 [M^+]. Found (%) C, 52.44; H, 5.30; N, 34.03. $C_9H_{11}N_5O$. Calcd. (%): C, 52.67; H, 5.40; N, 34.13.

6-(N,N-Dimethylamin-1-yl)-9*H*-purine (IV): Yield 73 %; m.p. 245-247 ºC. ^{1}H NMR (DMSO-d_6): δ = 3.15 (s, 6H, 2 × NCH_3), 7.80 (s, 1H, H-8), 8.07 (s, 1H, H-2), 11.03 (brs, 1H, NH). Mass spectrum, m/z: 163 [M^+]. Found (%): C, 51.23; H, 5.37; N, 42.66. $C_7H_9N_5$. Calcd. (%): C, 51.52; H, 5.56; N, 42.92.

6-(N,N-Diethylamin-1-yl)-9*H*-purine (V): Yield 72 %; m.p. 190-192 ºC. ^{1}H NMR (DMSO-d_6): δ = 1.05 (t, 6H, J = 3.5 Hz, 2 × CH_3CH_2N), 3.85 (q, 4H, J = 3.5 Hz, 2 × CH_3CH_2N), 7.82 (s, 1H, H-8), 8.11 (s, 1H, H-2), 11.00 (brs, 1H, NH). Mass spectrum, m/z: 191 [M^+]. Found (%): C, 56.40; H, 6.67; N, 36.45. $C_9H_{13}N_5$. Calcd. (%): C, 56.53; H, 6.85; N, 36.62.

6-(N,N-Dipropylamin-1-yl)-9*H*-purine (VI): Yield 70 %; m.p. 211-213 ºC. ^{1}H NMR (DMSO-d_6): δ = 0.90 (t, 6H, J = 3.5 Hz, 2 × $CH_3CH_2CH_2N$), 1.60 (m, 4H, 2 × $CH_3CH_2CH_2N$), 3.45 (t, 4H, J = 3.5 Hz, 2 × $CH_3CH_2CH_2N$), 7.88 (s, 1H, H-8), 8.10 (s, 1H, H-2), 11.04 (brs, 1H, NH). Mass spectrum, m/z: 219 [M^+]. Found (%): C, 60.05; H, 7.67; N, 31.83. $C_{11}H_{17}N_5$. Calcd. (%): C, 60.25; H, 7.81; N, 31.94.

RESULTS AND DISCUSSION

Leveling process: Table-1 and Figs. 2 and 3 showed a typical polarization curves obtained by using different concentration of **I** and **II** using divided and undivided cell at 25 ºC and 8 M H_3PO_4. The limiting current at which polishing take place was determined from those polarization curves and used to calculate the mass transfer coefficient (K) of copper polishing in H_3PO_4 from the equation:

$$K = \frac{I}{ZFC_o} \qquad (1)$$

I: limiting current, F: Faraday constant, C_o: concentration of saturated copper phosphate, z: valency. The values of the limiting current for all compounds at different temperature were given in Table-1. Leveling is the principle process in electropolishing[17]. Mayer *et al.*[18] explained the necessity to separate between anode and cathode by non-conductive slit to prevent the gas bubbles transfer to the anode surface and enhance the homogenous distribution of electric current[2]. The study of leveling based on the classical current voltage curves of electropolishing as shown in Figs. 2 and 3, a typical polarogram obtained in this study for purine derivatives in case of divided and undivided cell. The curve divided into three parts: in the first part, the current density (c.d.) is proportional to the voltage. At the second part of the curve, the metal undergoes electropolishing. In the first part, etching takes place and in the last part, some localized pitting occurs[19].

TABLE-1
VALUES OF LIMITING CURRENT AT DIFFERENT TEMPERATURES FOR ALL COMPOUNDS USED IN CASE OF DIVIDED CELL

Conc. M × 10^6	Compound **I**				Conc. M × 10^6	Compound **II**			
	25 °C	30 °C	35 °C	40 °C		25 °C	30 °C	35 °C	40 °C
0.0	710	750	800	860	0.0	710	750	800	860
0.5	650	670	720	730	0.5	620	640	660	680
1.0	580	600	630	640	1.0	565	585	600	620
1.5	550	570	590	610	1.5	530	545	560	580
2.0	510	530	540	550	2.0	485	500	515	570
2.5	470	485	500	530	2.5	460	470	480	490
3.0	430	445	460	500	3.0	425	440	455	470
5.0	405	420	435	450	5.0	385	400	410	420
	Compound **III**					Compound **IV**			
0.0	710	750	800	850	0.0	710	750	800	860
0.5	590	610	630	650	0.5	570	585	600	620
1.0	550	470	580	600	1.0	540	540	555	570
1.5	510	525	540	550	1.5	490	510	530	545
2.0	470	480	490	500	2.0	460	480	500	520
2.5	450	460	470	480	2.5	420	435	450	470
3.0	400	410	420	440	3.0	390	405	420	430
5.0	350	370	385	400	5.0	275	290	310	330
	Compound **V**					Compound **VI**			
0.0	710	750	800	860	0.0	710	750	800	860
0.5	550	570	585	600	0.5	510	530	550	570
1.0	520	540	555	570	1.0	480	495	510	530
1.5	490	500	510	520	1.5	420	435	450	470
2.0	430	445	450	465	2.0	370	385	400	420
2.5	410	425	440	450	2.5	300	320	340	350
3.0	370	380	390	405	3.0	240	260	280	300
5.0	210	230	250	280	5.0	145	160	180	200

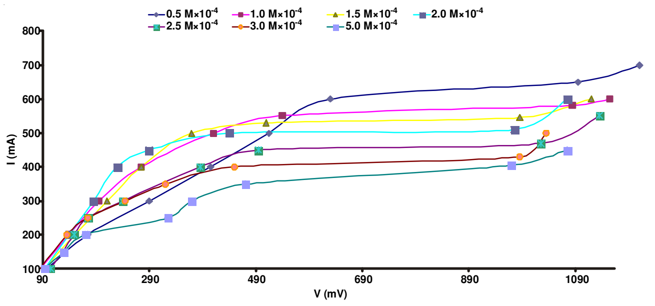


Fig. 2. Relation between **I** (mA) and **V** (mV) in presence of compound **I** at 25 °C and 8 M H_3PO_4 for divided cell at 1 cm height

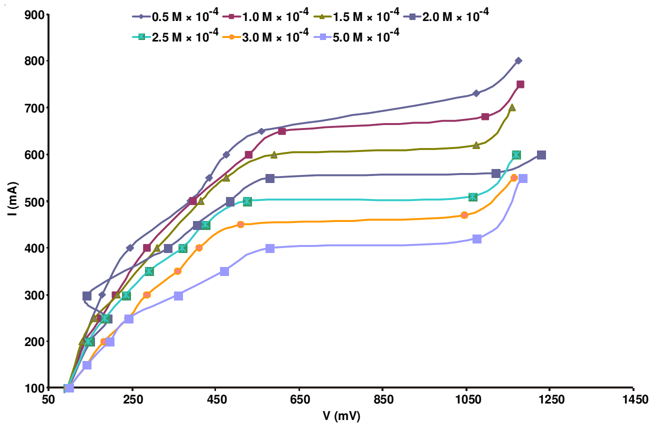


Fig. 3. Relation between **I** (mA) and **V** (mV) in presence of compound **II** at 25 °C and 8 M H_3PO_4 for undivided cell

TABLE-2
LIMITING CURRENT IN PRESENCE OF DIVIDED AND UNDIVIDED CELL AT DIFFERENT TEMPERATURES

1 cm height at different temperatures for blank solution at				
	25 °C	30 °C	35 °C	40 °C
Divided cell	710	750	800	860
Undivided cell	760	820	870	920

Effect of electrode height on limiting current: Table-2 and Fig. 4 showed that, the limiting current density decreases with the increase in height. In electro-polishing and 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 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 parts at the limiting current region. This was confirming by visual observation during Electropolishing. The average limiting current density decreases with increase in the height according to the equation[20]:

$$I_L = \frac{C}{H^a} \qquad (2)$$

where C is constant, H is the height of electrode, a is constant depends on the type of solution, [a = 0.502 for undivided cell].

Effect of organic compounds concentration on the limiting current: The rate of electropolishing which represent by anodic limiting current decrease with increasing the concentration of organic additives as shown in Table-4. We can recommended on the basis of results that, it may use in this range of concentration to inhibit the corrosion of copper metal in 8 M H_3PO_4 acid in all type of organic compounds to be used in this work[21]. The mass transfer coefficient of polishing process, which used in data correlation, calculated from the limiting current using the equation:

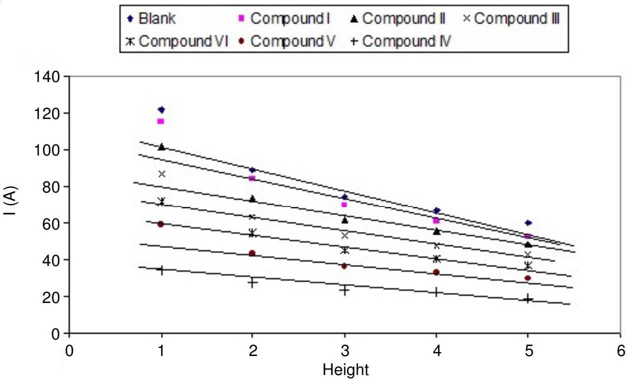


Fig. 4. Relation between current density and height for blank solution and in presence of all compounds

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

Compounds	I (mA) at different electrode height (cm)				
	1	2	3	4	5
Blank	122.00	89.00	74.35	66.75	60.00
I	115.00	84.00	70.00	60.30	52.00
II	102.00	73.50	61.35	55.50	48.00
III	87.00	63.00	52.66	47.30	42.40
IV	72.00	54.00	45.00	40.40	36.60
V	59.00	43.00	36.00	32.30	29.20
VI	34.00	27.50	23.00	22.00	18.60

$$K = \frac{I}{zFAC_s} \quad (3)$$

The above equation based on the finding of previous studies[22]. If the limiting current in absence of compound (**I**) and in the presence of organic compounds (I_L), the percentage of inhibition can be calculated from the following equation:

$$IE\ (\%) = \frac{I - I_L}{I} \times 100 \quad (4)$$

Table-3 and Fig. 5 showed that the per cent inhibition caused by organic compounds ranges from 13.04 to 80.01 % depending on the organic compounds and their concentrations. The limiting current decreases with increasing the concentration of organic compounds this agree with the finding of other authors[23]. The deceasing in the limiting current with increasing the concentration of organic compounds is attributing to: (a) The solubility of 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 purine derivatives concentration with consequence decrease in the diffusivity of Cu^{2+} according to Stokes-Einstein equation[24].

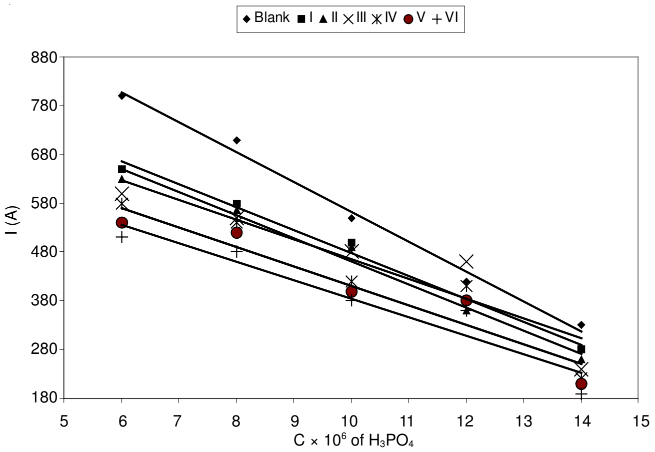


Fig. 5. Relation between current limiting and concentrations of phosphoric acid at different temperatures

Effect of temperature: The effect of temperature on the Cu electropolishing rate in absence and presence of purine compounds was determined at 25, 30, 35, 40 ºC (Table-1). It observed that the electropolishing rate increases with temperature for different concentrations of organic compounds.

Effect of electrolyte concentration on the polishing current: Table-5 (Fig. 5) showed the dependence of the polishing current on the bulk concentration of phosphoric acid. The limiting current decreases with increasing phosphoric acid concentration. Table-5 (Fig. 5) suggests that, the limiting current decreases with increasing H_3PO_4 concentration within the range (6-14 M) in the presence of 2.5×10^{-4} M organic inhibitors. This is in agreement with the findings of the other authors[17,19,20].

The decrease in the limiting current with H_3PO_4 concentration attributed to two effects: (a) The solubility of dissolved copper phosphate in ortho phosphoric acid, which is responsible for the limiting current, decreases with increasing the phosphoric acid concentration. (b) The viscosity of the solution increases with increasing organic compounds concentration with a consequence decrease in the diffusivity of Cu^{2+} according to Stokes-Einstein equation[24]:

$$\frac{D\eta}{T} = \text{Constant} \quad (5)$$

where, D is the diffusivity of Cu^{2+} ($cm^2\ s^{-1}$). η is the viscosity of the solution (poise). T is the absolute temperature.

In addition, the increase in solution viscosity with increasing phosphoric acid, organic derivatives 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 the bulk solution.

TABLE-4
RELATION BETWEEN PERCENTAGE INHIBITION AND CONCENTRATION OF ALL COMPOUNDS AT 25 ºC

$C \times 10^5$ (mol L^{-1})	Inhibition (%)					
	Compound **I**	Compound **II**	Compound **III**	Compound **IV**	Compound **V**	Compound **VI**
0.5	9.7	13.9	18.1	20.8	23.6	29.2
1.0	19.4	21.5	23.6	25.0	27.8	33.3
1.5	23.1	26.4	29.2	31.9	40.3	48.6
2.0	29.2	32.6	34.7	36.1	40.3	48.6
2.5	34.7	36.1	37.5	41.7	43.1	58.3
3.0	40.2	40.9	41.7	45.8	48	66.7
5.0	43.8	46.5	51.4	61.8	70.8	80.1

TABLE-5
EFFECT OF H_3PO_4 ACID CONCENTRATION AND 1 cm HEIGHT IN PRESENCE OF 1×10^{-6} mL OF COMPOUNDS

Compounds	H_3PO_4 (M)				
	6	8	10	12	14
Blank	800	710	550	420	330
I	650	580	500	380	280
II	630	565	490	360	260
III	600	550	480	460	240
IV	580	540	420	410	220
V	540	520	400	380	210
VI	510	480	380	360	190

Adsorption isotherm: It generally assumed that the adsorption isotherm of the inhibitor at the metal solution interface is the first main role in the mechanism of inhibitors action in aggressive acid media. Four types of adsorption may takes place in the inhibiting phenomena involving organic molecules at the metal-solution interface, namely: (a) Electrostatic attraction between charged molecules and the charged metal. (b) Interaction of lone pairs of electron in the molecules with the metal. (c) Interaction of electron with metal. (d) A combination of the above[25].

Chemisorptions involves sharing or charge transfer from the inhibitor molecule to the metal surface in order to from coordinate bond. In fact, electron transfer is typical for transition metals having vacant low energy electron orbital. Concerning inhibitors, electron transfer can expect with compounds have relatively loosely bound electron. This situation may arise because of the presence (in the adsorbed inhibitor) of multiple bonds or aromatic rings of a π character[26-35]. The inhibition efficiency of homologous series of organic substances, differing only in the heteroatom, is usually in the following sequence:

$$P > Se > S > N > O$$

The electrochemical processes on the metal surface are likely to be closely related to the adsorption of the inhibitor and the adsorption is known to depend on the chemical structure of the inhibitor[35]. The adsorption of the inhibitor molecules from aqueous solutions can be regard as substitution adsorption process between the organic compound in the aqueous phase, [org.(aq.)] and water molecules adsorbed on the electrode surface [$H_2O(s)$][36-38].

$$\text{Org(aq)} + xH_2O\text{ (s)} = \text{Org(s)} + (H_2O)$$

where x (the size ratio) is the number of water molecules displaced by one molecule of organic inhibitor. The above process reaches equilibrium when the chemical potential on the left hand equal to that of the right hand side. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used isotherms are those of Langmuir, Frumkin, Parsons, Temkin, Flory-Huggins and Bockris-Swinkels[39-42].

These entire isotherms are of the general form:

$$f(\Theta, x)\exp^{(-a\Theta)} = KC \qquad (6)$$

where f (Θ, x) is the configuration factor which depends essentially on the physical model and assumption underlying the derivation of the isotherm[43]. The mechanism of inhibition is generally believed to be due to the formation and maintenance of a protective film on the metal surface[44-48].

Application of Langmuir isotherm: Inhibitor adsorption characteristics can estimated by using the Langmuir isotherm given by the following equation[46]:

$$KC = \frac{\Theta}{1-\Theta} \qquad (7)$$

$$\Theta = \frac{I_{Blank} - I_{Organic}}{I_{Blank}} \qquad (8)$$

Plot of log Θ/(1-Θ) against log C should yield a straight line with slope ≈ 1. Table-6 give the data of Θ, log Θ/(1-Θ) and log C for all purines and the surface coverage with concentration variation. From above, it is concluded that all compounds verify Langmuir Isotherm.The Flory-Huggins adsorption isotherm for electropolishing in H_3PO_4 plotted as log Θ/C against log (1-Θ) at 25 ºC. A straight line is obtained with a slope x and intercept log xK. The experimental data fits the Flory-Huggins adsorption isotherm which represented by:

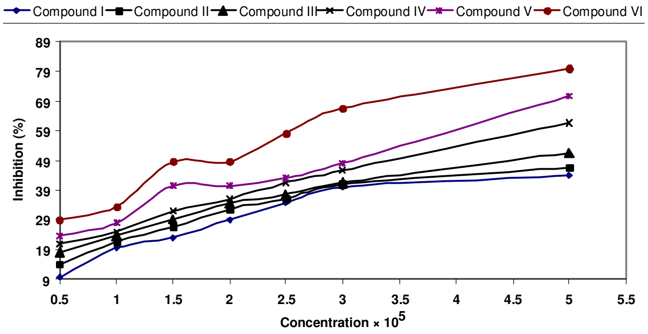


Fig. 6. Relation between % inhibition and concentration of all the compounds at 25 ºC

$$\log\frac{\Theta}{C} = \log xK + x\log(1-\Theta) \qquad (9)$$

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. The adsorption of inhibitors at metal solution interface may be due to the formation of either electrostatic or covalent bonding between the adsorbents and the metal surface atoms[47]. The kinetic adsorption isotherm may be written in the form[48]:

$$\log\frac{\Theta}{1-\Theta} = \log k' + y\log C \qquad (10)$$

where y is the number of inhibitor molecules occupy one active site. The binding constant of adsorption $K = k'^{1/y}$, where 1/y is the number of the surface active sites occupied by one molecule of the inhibitor and k is the binding constant. The linear relation of the inhibitor molecules between log Θ/1-Θ and log C at 25 ºC and the calculated values of 1/y and K given in Table-6. The values of 1/y depend on the type of Purine derivatives. From Table-6 it is obvious that, the value of 1/y for purine derivatives is *ca.* 1. It is suggested that the compound attached to one active site per inhibitor molecule. For other inhibitors the values of 1/y higher than one, indicating that, the given inhibitors molecules are attached to more one active site. The free energy of adsorption (ΔG_{ads}) at different concentration was calculated from the following equation:

TABLE-6
LIMITING CURRENT AND SURFACE COVERAGE OF 8 M PHOSPHORIC ACID WITH DIFFERENT ORGANIC ADDITIVES CONCENTRATIONS

Conc. M × 10^4	Inh. (%)	log C	Θ	Θ/1-Θ	log (Θ/1-Θ)	1-Θ	log (1-Θ)	log Θ/C
Compound **I**								
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
Compound **II**								
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	-3.80	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
Compound **III**								
0.5	18.06	-4.30	0.181	0.220	-0.66	0.18	-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
Compound **IV**								
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
Compound **V**								
0.5	23.61	-4.30	0.236	0.309	-0.51	0.76	-0.12	3.67
1.0	27.78	-4.00	0.278	0.385	-0.41	0.72	-0.14	3.44
1.5	34.72	-3.82	0.347	0.532	-0.27	0.65	-0.19	3.36
2.0	40.28	-3.70	0.403	0.674	-0.17	0.60	-0.22	3.30
2.5	43.06	-3.60	0.431	0.756	-0.12	0.58	-0.24	3.27
3.0	48.61	-3.52	0.486	0.946	-0.02	0.51	-0.29	3.21
5.0	70.83	-3.30	0.708	2.429	0.39	0.30	-0.53	3.15
Compound **VI**								
0.5	29.17	-4.30	0.292	0.412	-0.39	0.71	-0.15	3.76
1.0	33.33	-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

$$\Delta G_{ads} = -RT \ln (55.5\ K) \qquad (11)$$

The value 55.5 is the concentration of water in the solution mol/1. The values of ΔG_{ads} are given in Table-7. In all cases, the ΔG_{ads} values are negative and lie in the rank of 26.56-31.31 KJ/mol. the most efficient inhibitor shows the most negative value. This suggests that, they strongly adsorbed on the metal surface. The negative values of ΔG_{ads} indicate that, the spontaneous adsorption of the inhibitor. It's found that, the ΔG_{ads} values are more positive than -40 K J/mol indicating that the inhibitors are physically adsorbed on the metal surface. Similar results have also been reported[49].

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

$$\ln I = -\frac{E_a}{RT} + \ln A \qquad (12)$$

where R is the gas constant (8.314 kJ mol^{-1}), E_a is the activation energy and A is the frequency factor. It can be seen that, the gradient is given by -E_a/R and the intercept by ln A. Table-8 gave the values of E for the compounds used. The values for enthalpy of activation ΔH*, entropy of activation ΔS* and free energy of activation ΔG* can be obtaining by using equations and are given in Table-8.

TABLE-7
VALUES OF K, X AND 1/Y OF PHOSPHORIC ACID IN PRESENCE OF DIFFERENT ORGANIC ADDITIVES TO LANGMUIR, FLORY-HUGGINS AND KINETIC ADSORPTION ISOTHERM

Compounds	Flory-Huggins		Kinetic adsorption isotherm		
	X	K	Y	1/Y	K
I	1.4396	1669.39	0.8918	1.12	810.59
II	2.1706	1721.95	0.7572	1.32	294.04
III	1.8727	2027.83	0.6903	1.45	188.93
IV	1.4195	2913.83	0.7810	1.28	491.81
V	2.3713	2980.67	0.8425	1.19	997.01
VI	0.6374	2682.53	0.9858	1.01	5640.09

TABLE-8
THE CALCULATED VALUES OF FREE ENERGY OF ADSORPTION (kJ mol^{-1}) OF PHOSPHORIC ACID IN PRESENCE OF DIFFERENT ORGANIC ADDITIVES USING DIFFERENT METHODS

Compounds	Flory-Huggins	Kinetic adsorption isotherm
	$-\Delta G_{ads}$	$-\Delta G_{ads}$
I	28.35	26.56
II	28.42	24.04
III	28.83	22.95
IV	29.73	25.32
V	29.78	27.07
VI	29.52	31.36

$$\Delta H^* = E_a - RT \quad (13)$$

$$\frac{\Delta S^*}{R} = \ln A - \ln\left(\frac{kTe}{h}\right) \quad (14)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (15)$$

where k is Boltzmann's constant, e = 2.7183, h is Plank's constant, A is Arrhenius constant, T is absolute temperature and R is the universal gas constant. The adsorption is usually followed by liberation of heat of adsorption, so that $E_a < 0$, consequently the rate of adsorption decreases with temperature and as a result, the surface coverage at given concentration decreases with increasing temperature. It is known that an increase in the heat of adsorption leads to an increase in the energy of adsorption forces, however rising of the temperature acts in the reverse direction, increasing the kinetic energy of the molecules, facilitating disruption (consequently in the physical adsorption). In absence of organic substance, the results fit a straight line with an activation energy equals to 31.935 kJ mol^{-1} which is higher than the values obtained when organic substance was used as inhibitor. Thus, the low values of activation energy show that: The rate of electropolishing of copper from phosphoric acid decreased by adding small amounts of the organic substances at temperature above 25 ºC. The adsorption process is physical adsorption and molecules of organic substance disrupted at temperature above 30 ºC completely.

Table-9 shows that, the entropy ΔS^* possess height negative values indicating a highly ordered organic species in the solution under investigation. These values found to be independent on the type of purines.

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

$$\Delta H^* = \beta\Delta S^* + \text{Constant} \quad (16)$$

$$\delta\Delta H^* = \beta\delta\Delta S^* \quad (17)$$

The operator, δ, concerns difference between any two reactions in the series. Substituting from $\delta\Delta H^* = \beta\delta\Delta S^*$ into the familiar relationship:

$$\delta\Delta H^* = \Delta\delta\Delta G^* + T\Delta\delta\Delta S^* \quad (18)$$

$$\Delta\beta\delta\Delta S^* = \delta\Delta G^* + T\delta\Delta S^* \quad (19)$$

it follows that when $\delta\Delta G^*$ equal zero then β equal T *i.e.*, the slope in a linear plot of ΔH^* *versus* ΔS^* is the temperature at which all the reactions that conform to the line occur at the same rate. β is therefore known as the isokinetic temperature. The plots of ΔH^* *versus* ΔS^* for the dissolution reaction of copper in presence of different purines with different compositions show the isokinetic relationship for all the compounds. The obtained value of β for compound **II**, **IV** and enthalpy controlled for others compounds **I-VI** are 306 for **I**, 93 for **II**, 380 for **III**, 259 for **IV**, 347 for **V** and 450 for **VI**. The value of β indicating that, these reactions are entropic controlled processes where the solute- solvent interactions play an important role in the rate-determining step.

Structural effect: Most organic inhibitors are compounds with at least one polar unit having of nitrogen, sulphur, oxygen and in some cases selenium and phosphorus. The polar unit is usually regards as the reaction center. In such a case, the adsorption bond strength is determined by the electron density on the atom acting as the reaction center and by Polarisability of the unit. According to Hackerman[49,50] amine type inhibition as purine derivatives have electron, donating ability and their action attributed to adsorption of the inhibitor molecules on the metal surface through unshared pair belonging to nitrogen atom. The same is applicable to sulphur and oxygen atoms. Purine derivatives in aqueous acidic solution may exist as neutral molecules or in the form of cations NH^+ depending on the concentration of H^+ ion in solution[51]. In acidic solution, they predominantly exist as cations adsorb through electrostatic interaction between the positively charged anilinium cations and cathode. The inhibition action of organic inhibitors increased with increase of number of active centers[52-53]. From above, it is obvious that the inhibition efficiency of a given compound depends on the number of centers of adsorption and on the charge density of the inhibitor. All the studied compounds have the same centers of adsorption. In the metal organic additives system; reaction can occurs at the interface (strong interaction between additives and the metal surface) or at the interphase (formation of weakly soluble corrosion products between the metal and the electrolyte). Generally, the first step of the reaction is the adsorption of organic compound on metal surface; this displaces the adsorbed molecule, according to the reaction suggested by Bochris and Swinkels[54].

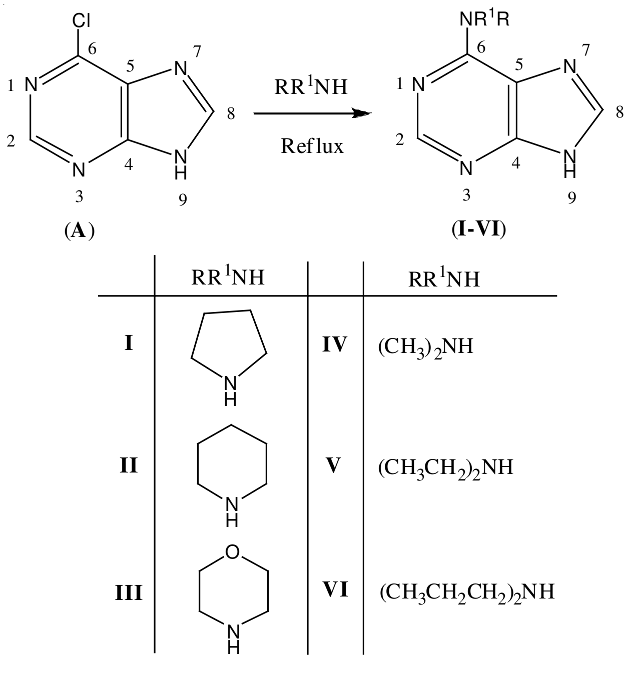
$$\text{Org}_{(sol.)} + n\text{H}_2\text{O}_{(ads.)} \longrightarrow \text{Org}_{(ads.)} + n\text{H}_2\text{O}_{(sol.)} \quad (20)$$

where, n is the number of water molecules removed from the metal surface. Physical adsorption[55] is the way of adsorption, which results from electrostatic attraction forces between organic molecules and metal surface. Physical adsorption process shows ($E_{act} < 10\text{-}15$ K cal mol^{-1}) that are low in comparison with those of chemisorptions ($E_{act} > 15$ K cal mol^{-1}) and relatively independent of temperature. Moreover, the interaction

TABLE-9
VALUES OF ACTIVATION ENERGY AND THERMODYNAMIC PARAMETERS FOR ALL COMPOUNDS

Organic substances	$C \times 10^5$ (mol L^{-1})	Thermodynamic Parameters			
		E_a (kJ mol^{-1})	ΔH* (kJ mol^{-1})	ΔG* (kJ mol^{-1})	-ΔS* (J mol^{-1} k^{-1})
(I)	0.5	5.358 ± 0.003	2.88 ± 0.003	5.74± 0.006	182± 10
	1.0	8.538 ± 0.002	3.17 ± 0.006	57.5 ± 0.012	182 ± 2.1
	1.5	7.240 ± 0.288	4.77 ± 0.023	57.8 ± 0.57	177 ± 0.9
	2.0	6.780 ± 0.023	4.30 ± 0.0023	57.9 ± 0.075	180 ± 7.8
	3.0	9.033 ± 0.002	7.78 ± 0.0042	58.4 ± 0.084	178 ± 14
	5.0	18.460 ± 0.501	16.00 ± 0.501	59.75 ± 0.991	141.8 ± 1.64
(II)	0.5	4.78 ± 0.034	2.303 ± 0.034	57.1± 0.006	183.7 ± 1.1
	1.0	4.85 ± 0.023	2.37 ± 0.023	53.3 ± 0.46	184± 7.6
	1.5	9.521 ± 0.04	3.13 ± 0.04	57.17 ± 0.9	211 ± 15.5
	2.0	5.61 ± 0.272	3.13 ± 0.21	57.17 ± 0.518	180± 8.5
	3.0	10.92 ± 2.9	8.44 ± 2.9	58.1 ± 0.55	166 ± 9.5
	5.0	6.67 ± 0.299	4.164 ± 0.299	58.2 ± 0.591	181 ± 9.6
(III)	0.5	9.2 ± 0.023	6.71 ± 0.23	57.36± 4.6	176 ± 7.6
	1.0	6.62 ± 0.02	6.141 ± 0.02	58.38 ± 0.04	178.5± 6.8
	1.5	5.71 ± 0.008	3.281± 0.08	57.6 ± 0.017	182 ± 2.8
	2.0	7.93 ± 0.09	5.45 ± 0.09	57.9 ± 0.032	181 ± 2.8
	3.0	7.41± 0.95	4.93 ± 0.033	58.3 ± 0.07	179 ± 11.1
	5.0	9.78 ± 0.98	7.3 ± 0.98	59 ± 3.5	173 ± 5.6
(IV)	0.5	8.88 ± 0.048	4.083 ± 0.048	57.574± 0.925	179 ± 1.53
	1.0	6.10 ± 0.013	3.621± 0.013	57.71 ± 0.026	181.4 ± 4
	1.5	1.621 ± 0.02	0.857 ± 0.02	57.86 ± 5.8	196.9 ± 9
	2.0	8.85 ± 0.741	6.371 ± 0.741	58.86 ± 5.1	162 ± 14
	3.0	11.554 ± 0.152	9.08± 0.152	59.43 ± 0.30	168 ± 4.9
	5.0	14.67± 0.81	12.196 ± 0.8	59.7 ± 2.7	159 ± 4.6
(V)	0.5	4.58± 0.006	2.1 ± 0.006	57± 0.013	184 ± 2.1
	1.0	5.1 ± 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	183.0 ± 10
	2.0	5.76 ± 0.008	3.28 ± 0.008	57.6 ± 0.0017	182.0 ± 2.8
	3.0	11.16 ± 0.21	8.68 ± 0.21	57.8 ± 0.57	164.8 ± 9.55
	5.0	6.65 ± 0.3	4.17± 0.3	58.2 ± 0.59	181± 9
(VI)	0.5	5.915 ± 0.416	2.98 ± 0.0416	57.278± 0.90	182.6 ± 1.5
	1.0	5.459 ± 0.006	2.98 ± 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
	2.0	6.347 ± 0.016	4.483 ± 0.016	57.821 ± 0.032	181 ± 5.39
	3.0	7.411 ± 0.035	4.932 ± 0.035	58.2 ± 0.115	178.7 ± 0.11
	5.0	9.778 ± 1.77	7.299 ±1.77	59.063± 3.513	173.6 ± 5.8

and removal of surface molecules occur very quickly. Table-4 showed that the percentage inhibition caused by organic compounds ranges from 9.7-80.1 % for all compounds. The percentage inhibition calculated from equation 3.8 depending on the concentration and type of inhibitor. It is observable that the percentage inhibition increases as concentration increases. The order of inhibition as follow: compound (**VI**) > compound (**V**) > compound (**IV**) > compound (**III**) > compound (**II**) > compound (**I**). The obtained results show that the presence of organic compounds has an inhibiting effect on the kinetics of the copper discharge process, pointed out by decreasing of the limiting current density. The inhibition, enhances by increasing the organic compounds concentration, could related to the strong adsorption of the organic compounds constituents on the copper electrode surface, which is in agreement with the decay of the current intensity observed on the polarization curves. The presence of organic compounds changes the mechanism of the copper corrosion, as it can be seeing from the decreasing of anodic transfer coefficient. A possible explanation for this fact consists in the increasing role of an additional reaction that produces the same chemical species (Cu^+) as those involved in the rate determining



Scheme-I

reaction[56,57]. All investigated compounds inhibited the rate of corrosion. Compound (**VI**) consider the better inhibitor because it contain besides 4 nitrogen reaction center an oxygen reaction center and steric hindrance effect of morphine.

Conclusion

Electroplating treatment of copper surface influenced by type of cell divided or undivided cell, electrode height, temperature, type and concentrations of purine compounds and rpm of rotating copper cylinder. Purine compounds acts as strong inhibitor for copper corrosion in phosphoric acid and its adsorption obey Langmuir, Flory-Huggins and kinetic adsorption isotherm. By increasing concentration of purine compounds the inhibition increases.

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