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Electroplating of Metals in Presence of Benzoic acid Derivatives and their Biological Effect

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Abstract

In this article, copper electroplating in presence of some forms of benzoic acid derivatives was studied. the impact of operational variables, together with organic additives concentrations and temperature on the limiting current were investigated by the potentio-dynamic polarization technique. The adsorption of all inhibitors on copper cathode was found to comply Temkin, Flory-Huggin and kinetic adsorption isotherm. The calculated free energy of adsorption (Δ Gads) of inhibitor on copper surface indicated that the adsorption reactions were spontaneous (Δ Gads<0). The thermodynamic activation parameters (Ea, Δ H^*, Δ S^* and Δ G^*) were also calculated. it had been found that energy of activation values for copper electroplating in inhibited solutions were higher than that for uninhibited solution. The high substance adequacy was discussed in terms of strong adsorption of inhibitor molecules on the copper surface. Also, during this study, biological activities of some synthesized compounds were investigated.

Key words: ***Electroplating; Inhibition; Organic derivatives; Benzoic acid***

Introduction

The properties of copper and its alloys that makes it a significant metal of commerce could also be summarized as follows: High electrical conduction, high thermal conduction, easy casting, extrusion, rolling and drawing to produce wire, conduit and strip, low corrosion rate of copper once used for food preparation, excellent alloying characteristics high esthetic appeal and low toxicity to humans. The occurrence of copper in nature within the metallic form used since early times either as metallic copper or alloyed with tin as bronze [1]. Fire refined copper is adequate for non-critical applications like water conduit, bar stock, or ingots for alloying. Copper intended for electrical uses, however, is produced by electro-refining or typically electro winning techniques. The methods of purifying copper include ionic exchange, vacuum distillation region smelting, low halide and electro-refining. Electro-refining is a very important step in pyrochemical reprocessing, that is non-aqueous technique for reprocessing spent metal fuel. The apseliminary demonstration facility has been erected to demonstrate the varied mechanisms and associate interlocks here the electrolysis of copper within the acidified copper sulphate solution are going to be applied to demonstrate the electrifying method.

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Acid copper solutions containing organic brightening and leveling agents are used extensively to deposit sleek copper rough steel and engraved plastias [2-4]. It is well known that the introduction of small amount of certain substance within the nature of metallic deposits obtained at the cathode. It is well known that small quantities of those substances could stop dendrites growing and improve considerably the smoothness of the cathode surface. In the present work, an attempt was made to examine the effect of different organic compounds such as:

- **Compound I:** 2-{3-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino) acetyl] thioureido}-benzoic acid.
- **Compound II:** 2-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino) acetylcarbamo-thioylthio] acetic acid.
- **Compound III:** 2-Phenyl-3-[(2-phenyl-5-thioxo-2,5-dihydro-1H-1,2,4-triazol-3-yl) methylamino] quinazolin-4(3H)-one.
- **Compound IV:** (S)-N-(2-Mercapto-5-oxooxazolidin-2-yl)-2-(4-oxo-2-phenylquinazolin-3(4H)-ylamino) acetamide.
- **Compound V:** 2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino)-N-(p-tolylcarbamo-thioyl) acetamide.
- **Compound VI :** 3-[(5-Acetyl-6-methyl-4-thioxo-5,6-dihydro-4H-1,3-oxazin-2-yl)methylamino]-2-phenylquinazolin-4(3H) one.

On copper electro-refining from sulfate electrolyte. And investigated the influence of structure of the organic additives related inhibitors on the mechanism and kinetics of inhibition of electroplating process [5,6].

Materials and Methods

Natural convection

The bath solution ($CuSO_4$, H_2SO_4) was placed into a single compartment of two electrode cell. The electro-refining experiments were performed using copper plate (10 cm × 5 cm × 0.2 cm) as cathode and anode. The current was supplied by DC power supply model 34BDCPSC Testronx). All experiments were carried out at 25°C, 30°C, 35°C and 40°C ± 0.1°C. The temperature of the bath remained almost constant during the experiments. The morphological analysis was performed by scanning electron microscope (JEOL, JSM-5300, Scanning microscope, the OXFORD instrument. For this purpose, the copper sheet cathode was (1 cm × 1 cm). Preparation of Solutions: All chemicals were of AnalaR grade and supplied by BDH Chemicals Ltd. The concentration of organic compounds was varied from 1.74×10^{-3} mol/L. the sulphate and sulphuric acid (98%) w/w concentration were 0.15 M and 1.5 M, respectively. For all experiment, copper sulphate concentration was checked iodometry. The total volume of the electrolytic bath solution was made up to 300 ml. Double distilled water with measured resistivity >18 MΩ cm used in preparation of solutions. The organic additives are:

- **Compound I:** 2-{3-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino) acetyl] thioureido}-benzoic acid.
- **Compound II:** 2-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino) acetyl carbamo-thioylthio] acetic acid.
- **Compound III:** 2-Phenyl-3-[(2-phenyl-5-thioxo-2,5-dihydro-1H-1,2,4-triazol-3-yl) methylamino] quinazolin-4(3H)-one.
- **Compound IV:** (S)-N-(2-Mercapto-5-oxooxazolidin-2-yl)-2-(4-oxo-2-phenylquinazolin-3(4H)-ylamino) acetamide.
- **Compound V:** 2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino)-N-(p-tolylcarbamo-thioyl) acetamide
- **Compound VI:** 3-[(5-Acetyl-6-methyl-4-thioxo-5,6-dihydro-4H-1,3-oxazin-2-yl) methylamino]-2-phenylquinazolin-4(3H)-one.

The electrolytic cell and electrical circuit: The limiting current density was measured using the ordinary cell of two vertical parallel plates, one is the cathode (a 99.99% purity rectangular copper plate or analytical highly pure steel plate, 5 cm width and 10 cm height) and the other one is the anode (a 99.99% purity copper with similar dimensions as the cathode). The cell consists of a rectangular plastic container (5.1 cm × 5 cm × 10 cm) with electrodes fitting the whole cross section area. The inter electrode distance was 4 cm. The electrical circuit consists of 6 V d.c. power supply connected in series with the cell and multi-range digital ammeter. A luggin probe is placed where its tip is about 1 mm apart from the bottom one third of the cathode surface. A copper reference electrode is placed in the cup of the luggin probe. A multi-range potentiometer is connected in parallel

with the reference electrode and the cathode.
At the beginning, electrodes were mechanically polished with different grades of silicon carbide papers (120, 800, 1200) and washed with distilled water and degreased by acetone. The backs of the cathode and the anode were coated with Locamit. Polarization curves, from which the limiting current density was determined, were constructed by increasing the current stepwise and measuring the steady state cathode potential against the reference electrode (Figure 1) [7].

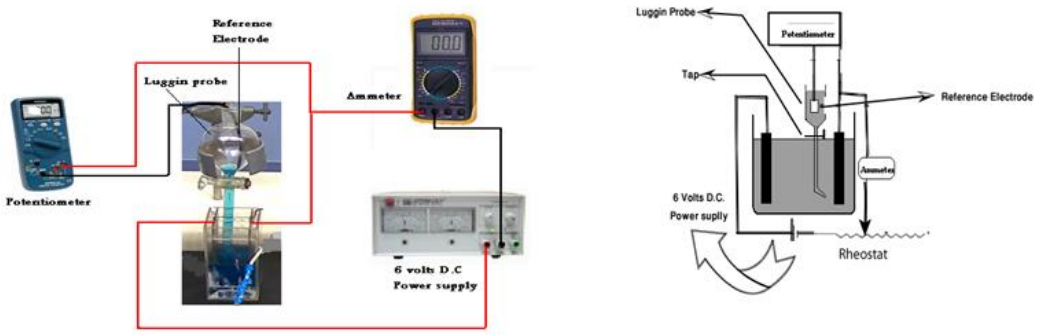

FIG. 1. **The parallel vertical plates electrolytic cell and the electrical circuit.**

Results

Effect of concentration of $CuSO_4$ on the limiting current

The effect of copper sulphate concentration on the limiting current of Cu-Cu, it is obvious that limiting current increases as copper sulphate increases. Increasing the $CuSO_4$ content in the bath decreases the cathodic polarization and increases the limiting current plateau. These results were expected due to an increase in the relative abundance of the uncomplexed Cu^{2+} ions in the solution (Table 1) [8].

TABLE 1. **The effect of different concentration of cuso4 on the limiting current at 298° K in case of cu-cu, using 5 cm height.**

log I	I_l (mA) (Cu-Cu)	log C	$CuSO_4$ C. (Mol l^{-1})
2.2	160	-1.69	0.02
2.3	200	-1.3	0.05
2.44	280	-1	0.1
2.5	320	-0.82	0.15
2.63	430	-0.69	0.2

Potentiodynamic cathodic polarization curves: The observed changes in the cathodic polarization in the presence of organic compound suggest that it must be acting as an inhibitor, which confirmed by the observation that at any given over-potential, the current density for copper deposition from solutions containing organic compound is lower than that found for the corresponding organic free solution. This inhibition of the organic compound in the copper electroplating reaction may be due to the adsorption of organic compound in the cathode surface.

Therefore, the limiting current decreases with increasing organic concentration as shown in due to form complexes with Cu^{2+} ions. Limiting current Values for all solutions at different temperatures using copper anode. Noticeably, that the limiting current decreases with increasing organic additives concentration and increases with temperature [9]. The values of limiting current density Il for all solutions at different temperatures were used to calculate the mass transfer coefficient, K from the equation: K=iL/zFACo. Where, z: Number of

electrons involved in the reaction, F: Faraday constant (A.s. mol^{-1}), Co: Bulk concentration of copper sulphate (mol/cm^3), A: Electrode area.(Figure 2).

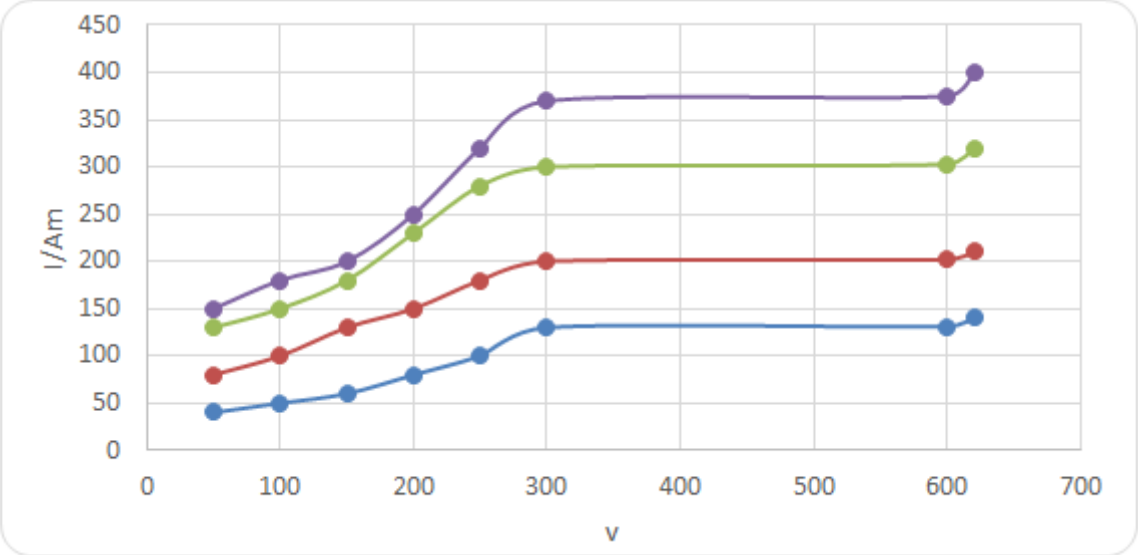

FIG. 2. **Polarization Curves in case of (Cu-Cu) at 298 °K for different Concentration of compound I.**

The percentage of Inhibition can be calculated using the equation: % Inhibition=(I-II/I) × 100

where I and II are electrodeposition limiting current values without and with inhibitor respectively, the addition of organic compounds reduces the limiting current by amount ranging from 6.25% to 76% (Cu-Cu cell).

Under natural convection mass is transferred outside the diffusion layer by natural convection which arises from the density difference between the interfacial solution and the bulk solution while mass is transferred inside the diffusion layer by diffusion only by virtue of the existence of concentration gradient across the diffusion layer [10]. In view of the above mechanism, the adverse effect of organic compounds on the limiting current can explained as follows (Tables 2 and 3)(Figure 3 and 4).

TABLE 2. **Values of limiting current for all solution at different temperatures using copper and stainless-steel anodes.**

Organic additives	**C × 10^6 mol/l**	**Limiting current (mA)**			
		Copper anode			
		25°C	**30°C**	**35°C**	**40°C**
	Blank	340	420	500	600
Compound I	1	300	320	370	420
	5	280	300	340	390
	10	260	280	320	360
	50	240	260	300	340
	100	220	240	280	320
	500	200	220	260	300
	1000	190	200	240	280
Compound II	1	280	320	350	400
	5	260	300	330	370
	10	240	280	310	350
	50	220	260	290	330
	100	200	240	270	310

	500	200	220	250	290
	1000	170	200	230	260
Compound III	1	260	280	320	360
	5	240	260	300	340
	10	220	240	280	320
	50	200	220	240	300
	100	180	200	220	280
	500	170	180	200	260
	1000	160	170	180	230
Compound IV	1	260	340	420	500
	5	240	320	390	470
	10	220	300	360	440
	50	200	270	340	420
	100	180	250	320	400
	500	160	230	300	370
	1000	140	210	280	340
Compound V	1	180	220	250	300
	5	160	200	220	280
	10	140	180	200	260
	50	120	150	180	240
	100	110	130	160	220
	500	100	110	130	200
	1000	90	100	110	150
Compound VI	1	160	190	250	310
	5	140	170	220	280
	10	120	150	200	250
	50	100	130	180	220
	100	90	110	170	200
	500	80	90	140	180

TABLE 3. **Values of % inhibition for all organic compounds at different temperatures.**

Organic additives	**C × 10^6 (mol/l)**	**Percentage inhibition**			
		Copper anode			
		25 °C	**30 °C**	**35 °C**	**40 °C**
Compound I	1	6.25	11.11	7.5	6.67
	5	12.5	16.67	15	13.3
	10	18.75	22.2	20	20
	50	25	27.7	25	24.4
	100	31.25	33.3	30	28.8
	500	37.5	38.8	35	33.3
	1000	40.6	44.4	40	37.7
Compound II	1	12.5	11.11	12.5	11.11
	5	18.7	16.67	17.5	17.8

	10	25	22	22.5	22.2
	50	31.2	27.7	27.5	26.6
	100	37.5	33.3	32.5	31.1
	500	37.5	38.8	37.5	35.5
	1000	46.8	44.4	42.5	42.2
Compound III	1	18.2	22.2	20	20
	5	25	27.7	25	24
	10	31.2	33.3	30	28
	50	37.5	38.8	40	33
	100	43.7	44.4	45	37
	500	46.8	50	50	42
	1000	50	52.7	55	48
Compound IV	1	23.5	19	16	16
	5	29	23	22	21
	10	35	28	28	26
	50	41	35	32	30
	100	47	40	36	33
	500	52	45	40	38
	1000	58	50	44	43
Compound V	1	43	38	37.5	33
	5	50	44	45	37
	10	56	50	50	42
	50	62	58	55	46
	100	65	63	60	51
	500	68	69	67	55
	1000	71	72	72	66
Compound VI	1	52	54	50	48
	5	58	59	56	53
	10	64	64	60	58
	50	70	69	64	63
	100	73	73	66	66
	500	76	78	72	70

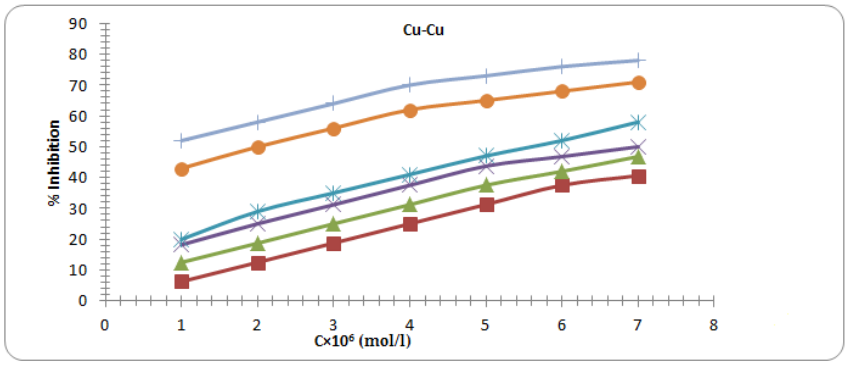

FIG. 3. **The relation between % inhibition and concentration of organic compounds at 298 °K in case of Cu-Cu cell. Note: cpd-1 cpd-2 cpd-3 cpd-4 cpd-5 cpd-6**

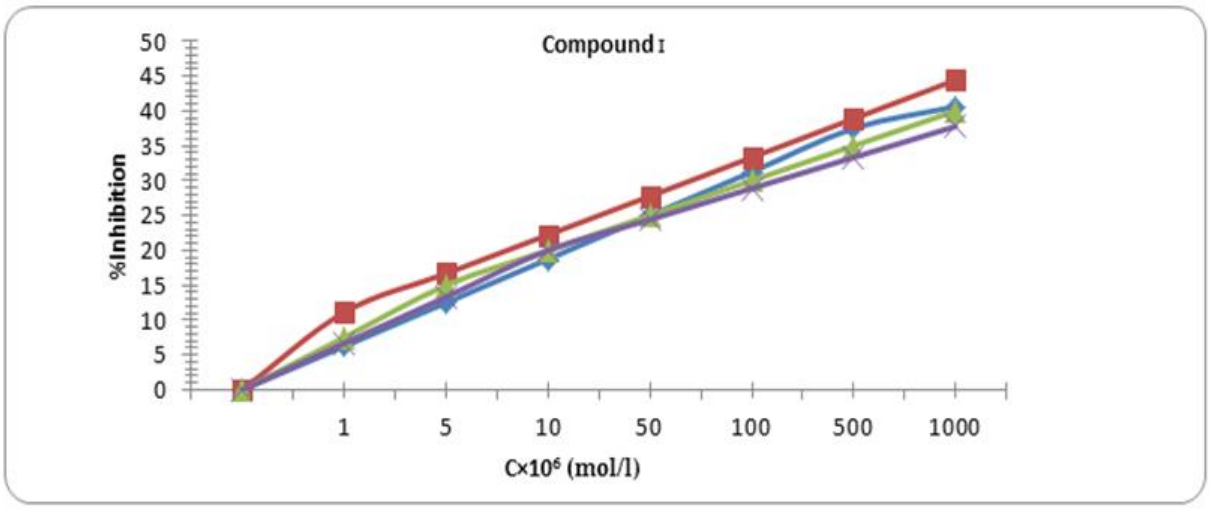

FIG. 4**. The effect of temperature on the % inhibition of limiting current at different temperature for Cu-Cu cell at C=1 × 10^{-6} mol/l. Note: 298 K 303 K 308 K 313 K.**

Adsorption isotherm: Adsorption isotherms are very important for determining the mechanism of organo-electrochemical reactions [11]. The most frequently used isotherms are those of Frumkin, Temkin, Flory-Huggins, Langmiur and Kinetic Isotherm. All these isotherms are of the general form: $f(\theta,x)\exp(-a\theta)=KC$.

Where $f(\theta,x)$ is the configuration factor depends essentially on the physical model and assumptions underlying the derivation of the isotherm. The mechanism of inhibition of electrodeposition is generally believed to be due to the formation and maintenance of a protective film on the metal surface [12-14].

The primary step in the action of organic compounds in acid solution is generally agreed to be adsorbed on to the copper surface. This involves the assumption that the electro deposition reaction is prevented from occurring over the area (or the active sites) of the copper surface covered by adsorbed inhibitors species, whereas the electro deposition reaction occurred normally in the inhibitor free area [15].

Accordingly, the fraction of the surface covered with inhibitor species (θ) can be followed as a function of inhibitor concentration and solution temperature. The part of surface covered with inhibitor lead to decrease of limiting current. When fraction of the surface covered is determined as a function of the concentration at constant temperature, adsorption isotherm could be evaluated at equilibrium conditions. The values of fractional surface coverage (θ) at different concentrations of organic additives and at constant temperature have been used to explain the best isotherm to determine the adsorption process can be determined from (7-11): θ= I-II/I.

The kinetic-thermodynamic model is given by: $\log[\theta/(1-\theta)]=\log K'+y\log C$, where y is the number of inhibitor molecules occupying one active site. The binding constant K is given as

$$K=K'(1/y)$$

If the slope y of the linear relation between $\log \theta/1-\theta$ *vs.* $\log(C)$ for all organic compounds, is greater than unity implies the formation of multi-layers of the additive on the metal surface, while if less than unity, however, it means that the given additive molecule occupied more than one active site. Values of y and number of active sites 1/y of the metal surface that occupied by one molecule of the organic additive under the present conditions have given in obviously, it was concluded from the values in that the number of additive molecules, which occupy one active site, in some cases less than unity and in other cases greater than unit. Also, the efficiency of electro deposition is essentially function of the magnitude of its binding constant K. Larger values of K mean better and strong interaction, whereas small values of K mean that the interaction between the additive molecules and metal surface is weaker (Figures 5-16) [16-18].

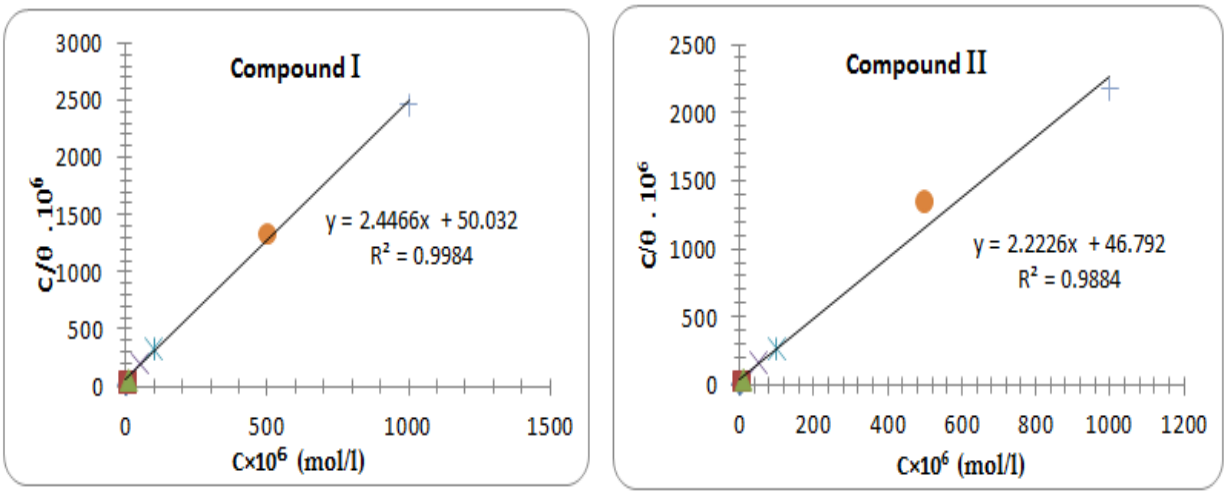

FIG. 5. **Langmiur adsorption isotherm using Cu-Cu cell at 298 °K for compound I and II.**

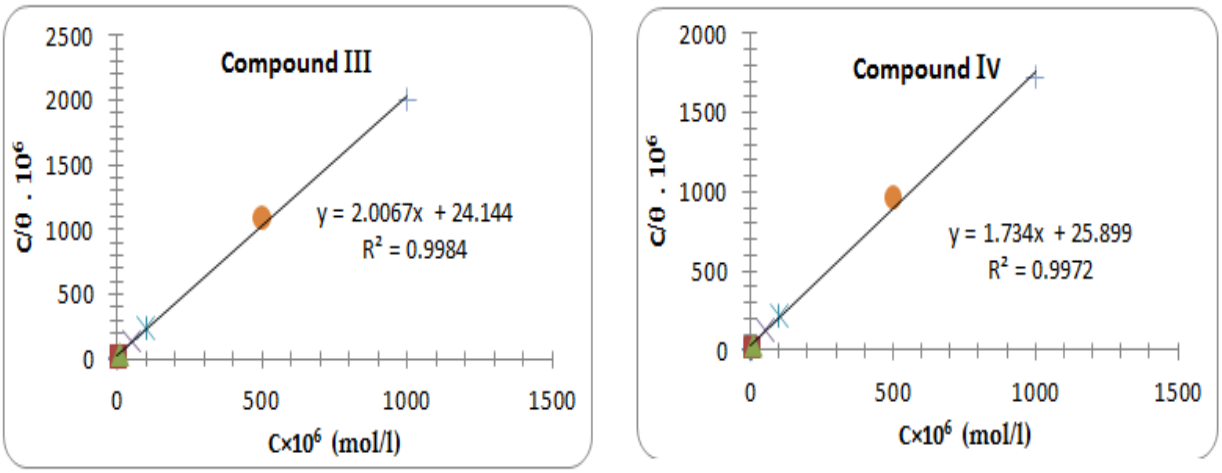

FIG. 6. **Langmiur adsorption isotherm using Cu-Cu cell at 298 °K for compound III and IV.**

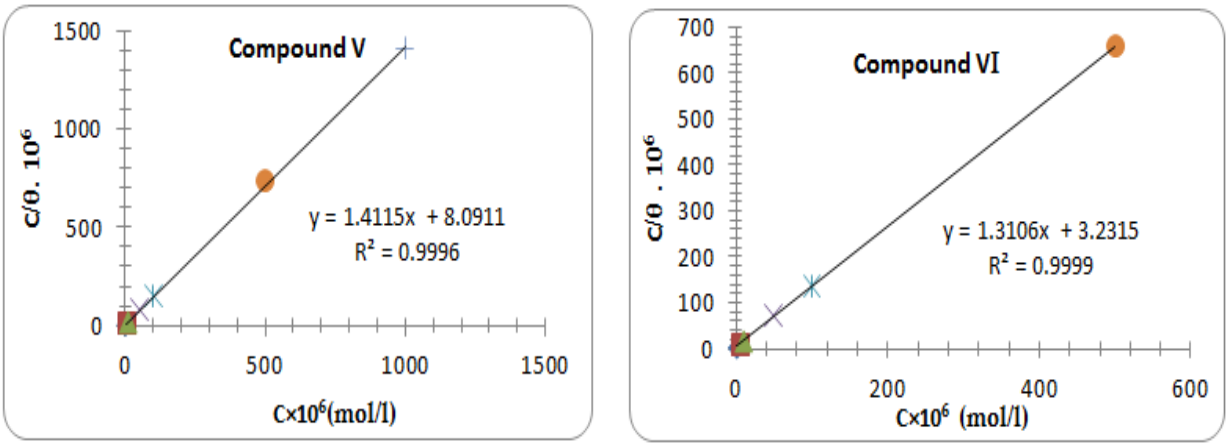

FIG. 7. **Langmiur adsorption isotherm using Cu-Cu cell at 298 °K for compound V and VI.**

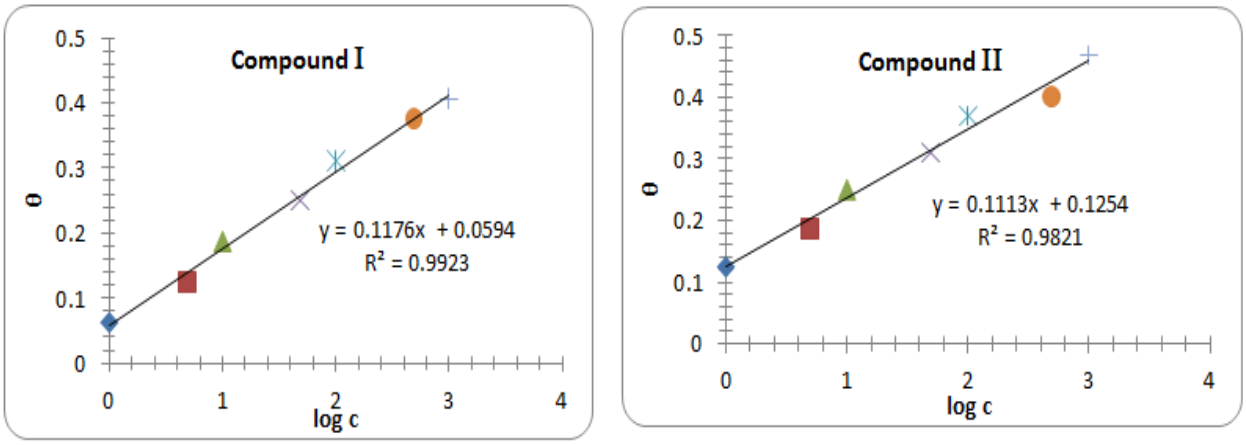

FIG. 8. **Temkin adsorption isotherm using Cu-Cu cell at 298 °K for I and II.**

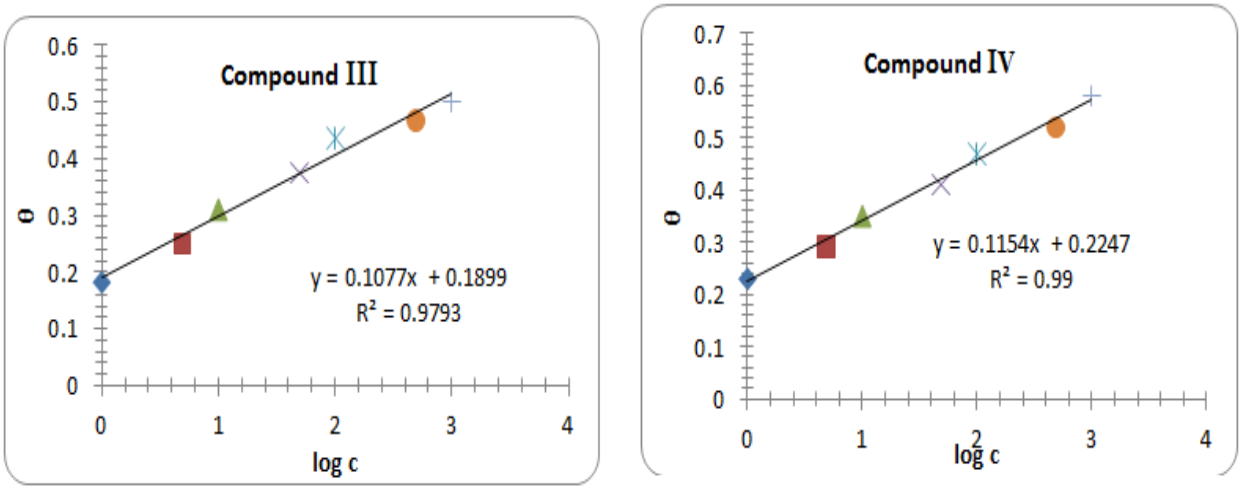

FIG. 9. **Temkin adsorption isotherm using Cu-Cu cell at 298 °K for III and IV.**

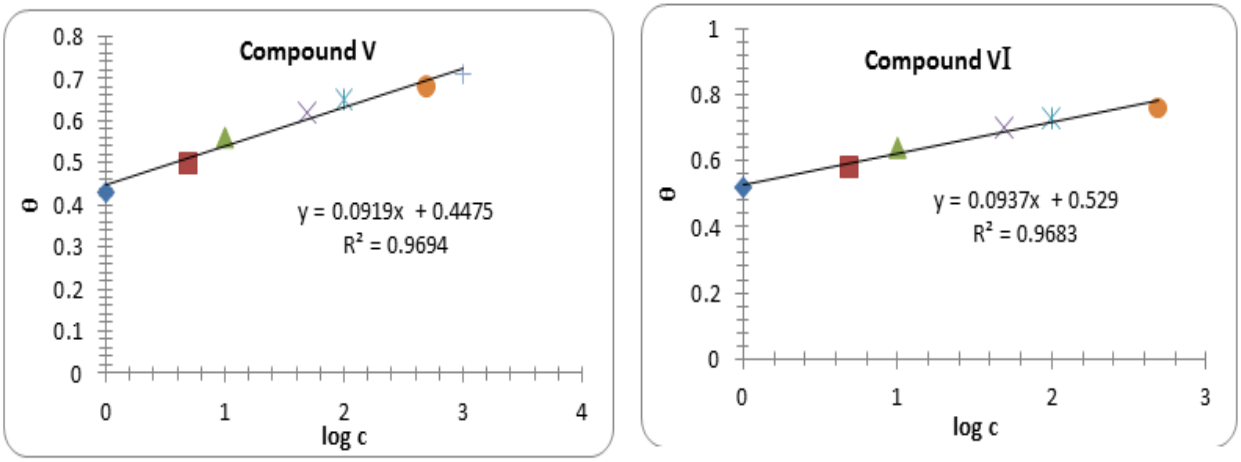

FIG. 10. **Temkin adsorption isotherm using Cu-Cu cell at 298 °K for V and VI.**

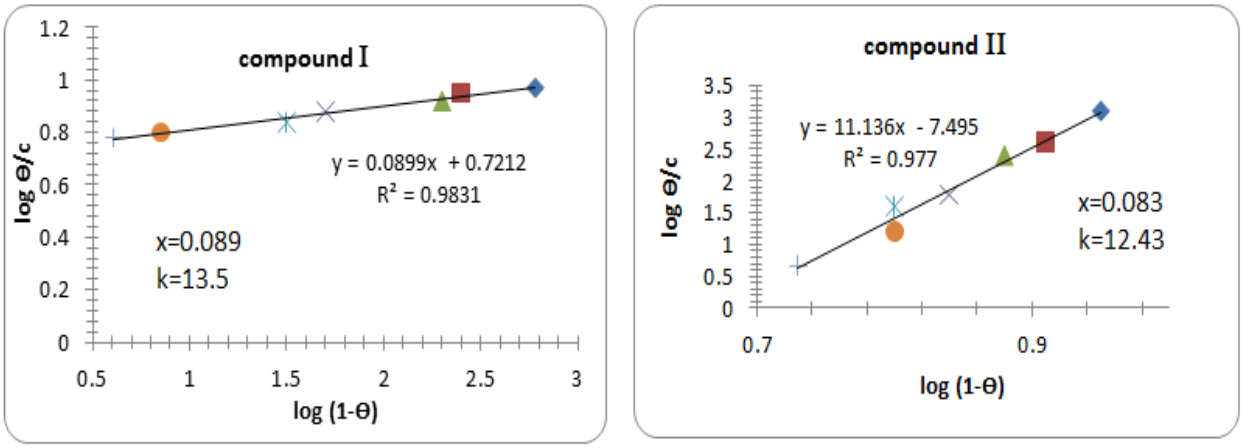

FIG. 11. **Flory-Huggins adsorption isotherm using Cu-Cu cell at 298 °K for I and II.**

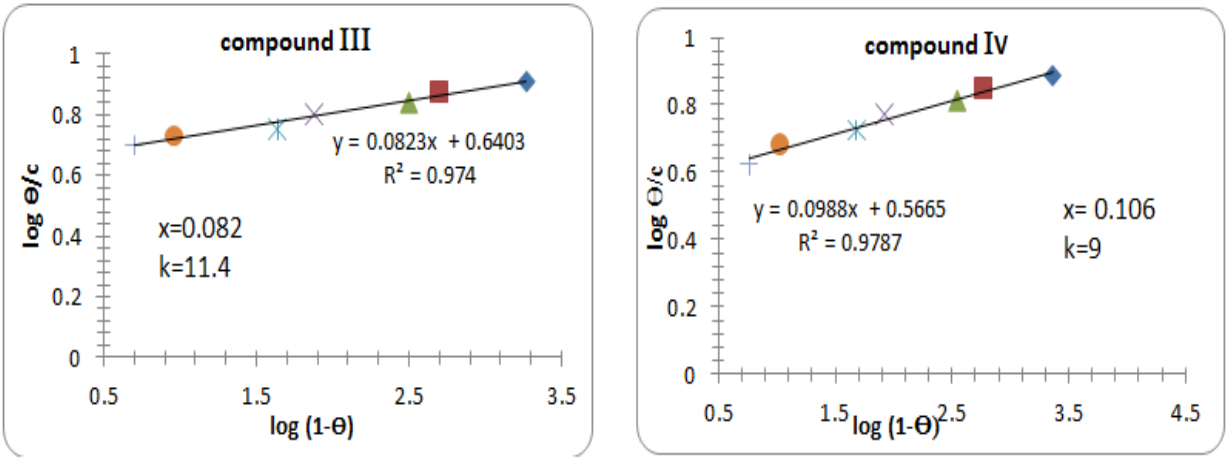

FIG. 12. **Flory-Huggins adsorption isotherm using Cu-Cu cell at 298 °K for III and IV.**

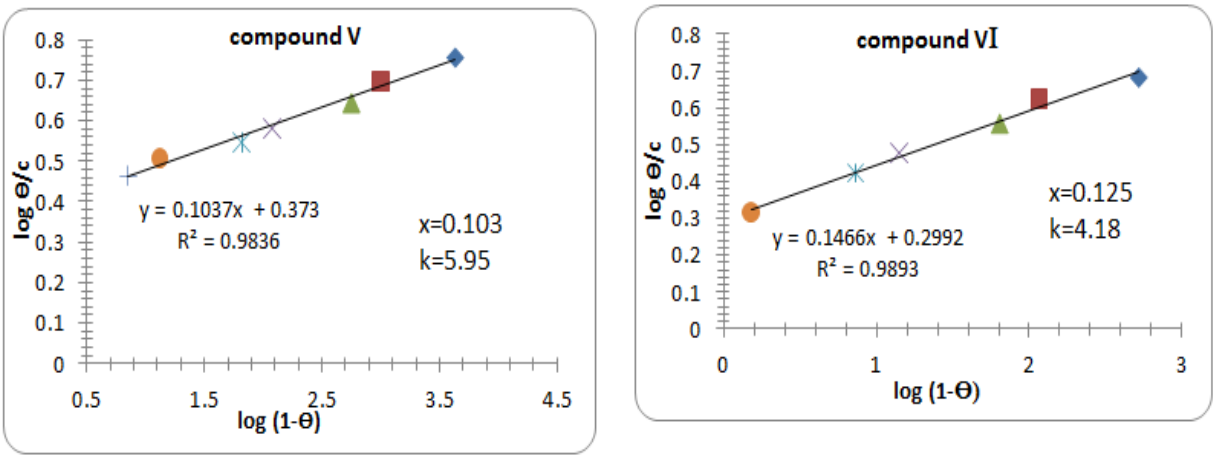

FIG. 13. **Flory-Huggins adsorption isotherm using Cu-Cu cell at 298 °K for V and VI.**

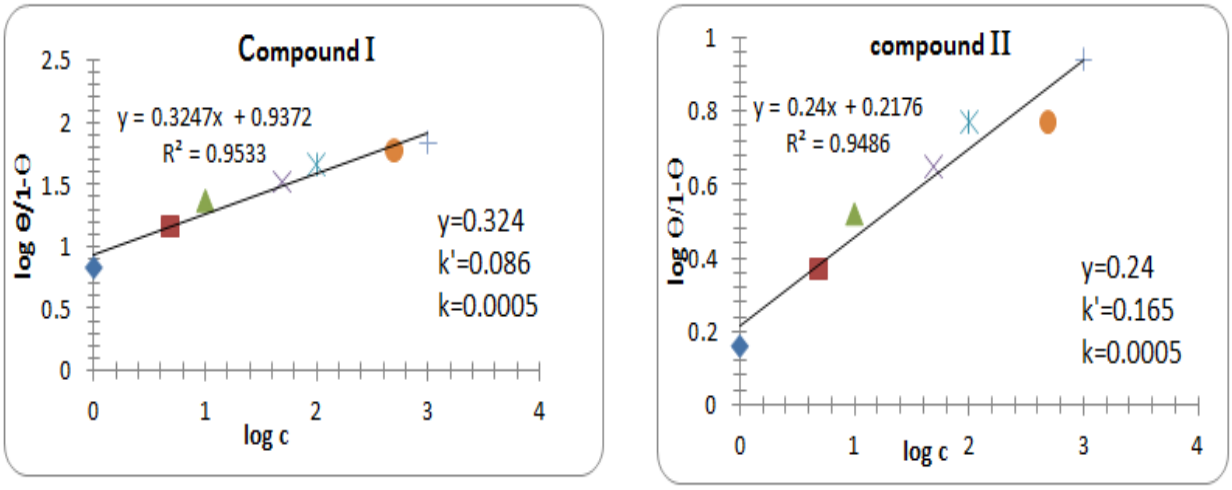

FIG. 14. **Kinetic adsorption isotherm using Cu-Cu cell at 298 °K for I and II.**

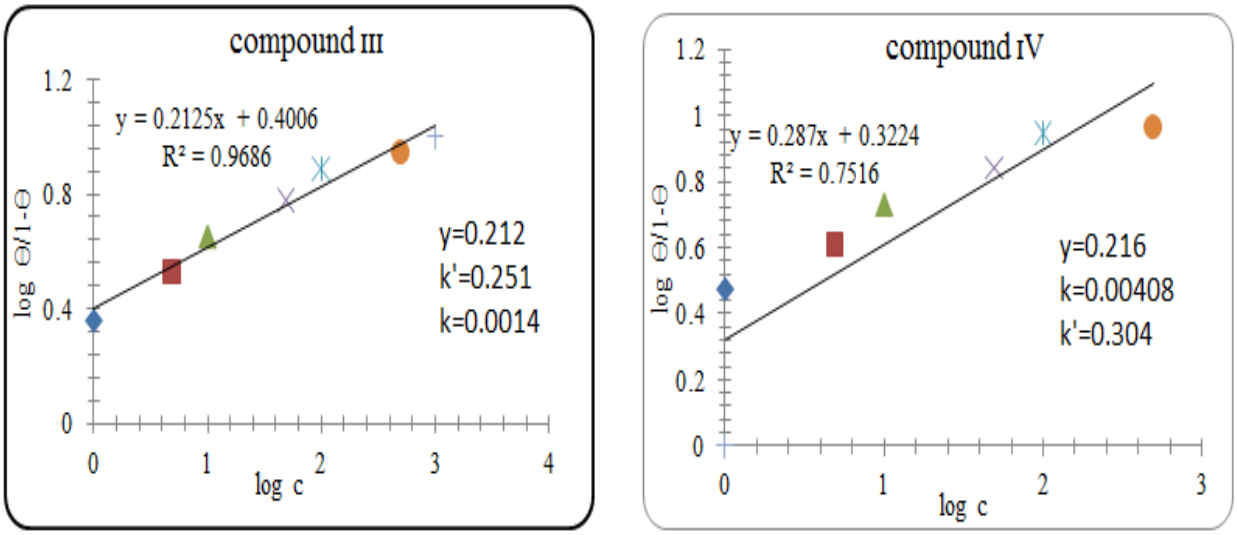

FIG. 15. **Kinetic adsorption isotherm using Cu-Cu cell at 298 °K for III and IV.**

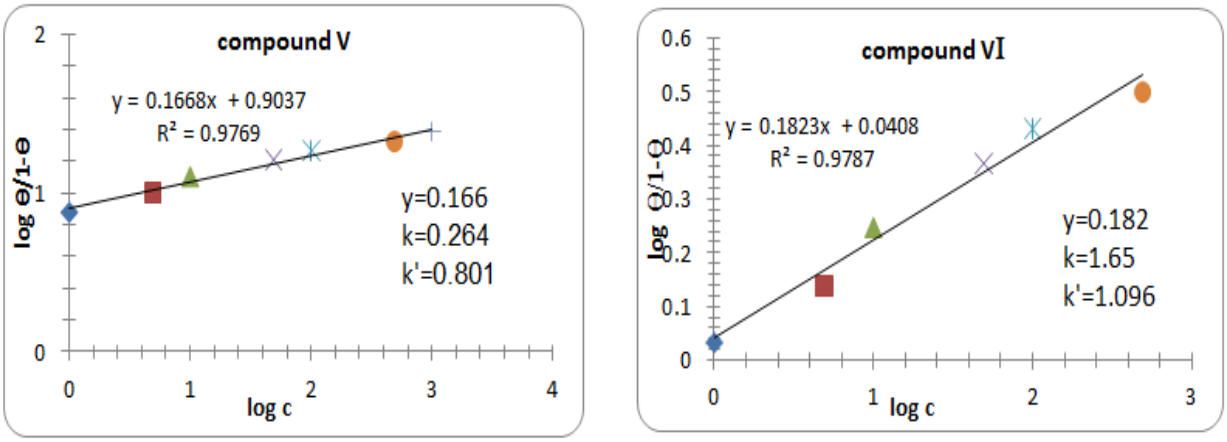

FIG. 16. **Kinetic adsorption isotherm using Cu-Cu cell at 298 °K for V and VI.**

TABLE 4. **Linear fitting parameters of organic compounds additives for (Cu-Cu) at 298 °K.**

Organic compounds	Models parameters						
	Temkin		Flory-Huggins		Kinetic adsorption isotherm		
	-a	K	X	K	y	1/y	K
Compound I	0.0585	1.145	0.089	13.5	0.324	3.086	0.0005
Compound II	0.0555	1.333	0.083	12.43	0.24	4.166	0.0005
Compound III	0.0535	1.545	0.082	11.4	0.212	4.716	0.0014
Compound IV	0.0575	1.674	0.106	9.00	0.216	4.629	4.08E-03
Compound V	0.0455	2.79	0.103	5.95	0.166	6.024	0.264
Compound VI	0.0465	3.38	0.125	4.18	0.182	5.494	1.65

Temperature effect on electrodeposition process: The effect of temperatures on the electrodeposition rate of Cu-Cu cell in absence and presence of all organic additives were studied by measuring the limiting current in the temperature ranges between (298°K-313°K) and illustrated in It observed that the electrodeposition rate increases with temperature for all the studied systems and its extent more pronounced in the uninhibited system, indicating the physical adsorption of additives on the metal surface and desorption, added by increasing the reaction temperature. The variation of II with temperature at different concentration of organic compounds. The electrodeposition reaction can be regarded as an Arrhenius-type process. The activation energy for the studied systems calculated from Arrhenius equation (Tables 4) [19-20].

$\log II = \log A - E_a/2.303\ RT$

Where A is, a pre-exponential factor related to concentration, steric effects, metal surface characteristics, etc., R the molar gas constant and T absolute temperature. Values of E_a that have derived from slopes of the Arrhenius plots (Table 5).

TABLE 5. **Activation energy and thermodynamic parameters for electrodeposition of copper in presence of different organic additives. Note: E_a, ΔH^* and ΔG^* in kJ/mol, ΔS^* in J/mol.Ks**

Organic compound	$C \times 10^6$	Cu-Cu			
	(mol/l)	E_a	ΔH^*	$-\Delta S^*$	ΔG^*
Compound I	Blank	17.49	15.01	146.1	58.71
	1	17.86	15.38	146.05	58.91
	5	17.31	14.84	148.46	59.08
	10	17.18	14.7	149.46	59.24
	50	18.39	15.92	146.05	59.44
	100	19.79	17.31	142.15	59.67
	500	21.42	18.94	137.49	59.91
	1000	20.81	18.33	140.07	60.07
Compound II	Blank	17.49	15.05	146.63	58.71
	1	17.98	15.5	146.05	59.02

	5	17.9	15.42	146.88	59.19
	10	19.14	16.67	143.39	59.4
	50	20.56	18.09	139.32	59.6
	100	22.23	19.75	134.5	59.83
	500	19.23	16.76	144.81	59.91
	1000	21.94	19.47	136.82	60.24
Compound III	Blank	17.49	15.01	146.63	58.71
	1	17.18	14.7	149.46	59.24
	5	18.39	15.92	146.05	59.44
	10	19.79	17.31	142.15	59.67
	50	20.14	17.66	141.81	59.92
	100	21.95	19.48	136.57	60.17
	500	21.29	18.81	139.48	60.38
	1000	17.67	15.19	152.04	60.5
Compound IV	Blank	29.14	26.66	106.98	58.54
	1	33.73	31.26	93.59	59.15
	5	34.37	31.9	92.09	59.34
	10	35.12	32.64	90.27	59.54
	50	38.12	35.65	81.04	59.8
	100	41.03	38.55	72.22	60.07
	500	43.19	40.71	65.82	60.32
	1000	45.84	43.36	57.92	60.62
Compound V	Blank	17.49	15.01	146.63	58.71
	1	25.74	23.27	123.6	60.1
	5	27.5	27.02	118.7	60.39
	10	30.42	27.94	107.97	60.71
	50	35.03	32.55	96	61.16
	100	35.38	32.9	95.75	61.44
	500	34.66	32.18	99.24	61.75
	1000	25.13	22.65	131.84	61.94
Compound VI	Blank	29.14	26.66	106.98	58.46
	1	35.52	32.52	93.76	60.46
	5	36.21	33.73	90.76	60.78
	10	38.6	36.12	84.03	61.16
	50	41.75	39.27	74.8	61.56
	100	43.91	41.43	68.65	61.89
	500	44.5	42.02	67.98	62.28

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

$\Delta H^* = E_a - RT$

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

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

Where B is the Boltzmann constant, e=2.7183, h is Plank constant and other symbols have the definition mentioned above. The values for gradient and intercept are obtained by using the least square method. The results showed positive sign for E_a, reflecting the endothermic nature of electro deposition process. It is

obviously seen that the E_a values for inhibiting systems are higher that Ea for uninhibited system. This indicates that physical adsorption occurred in the first stage, which explains the nature of organic molecules – metal interaction. On the other hand, physical adsorption is related to lower values of E_a (<43 $kJ.mol^{-1}$), also indicating that the diffusion processes are controlling the electro deposition reaction.

The results show positive sign for ΔH^*, reflecting the endothermic nature of the adsorption process. The negative values of ΔS^* pointed to a greater order produced during the process of activation. This can achieve by the formation of activated complex represents association or fixation with consequent loss in the degree of freedom of the system during the process. ΔG^* values show limited increase with a rise in the concentration of organic additives i.e. : ΔG^* values of the inhibited systems were more positive than that for the uninhibited systems revealing that in the cores of inhibitor addition the activated electrodeposition complex becomes less stable as compared to its absence (Figure 17).

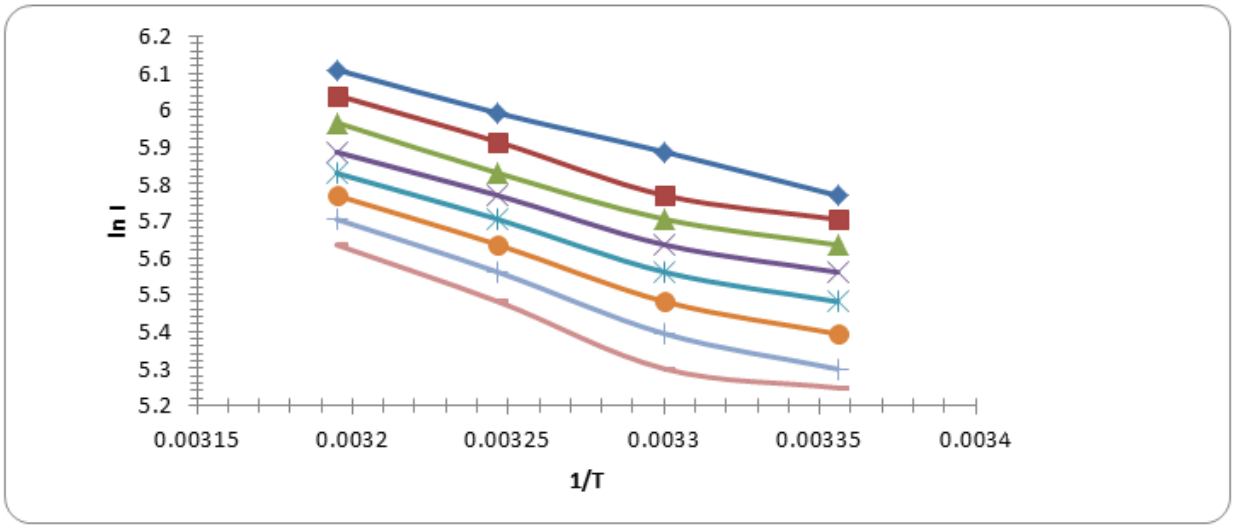

FIG. 17. **Relation between ln Il and 1/T at different concentration of compound I for (Cu-Cu) cell. Note: 0 1.00E-06 5.00E-06 1.00E-05 5.00E-05 1.00E-04 5.00E-04 1.00E-03.**

Biological activity

Antimicrobial activity: The agar diffusion method reported by Cruickshank et al. was used for the screening process. The bacteria and fungi were maintained on nutrient agar and Czapek's-Dox agar media, respectively. The assay medium flasks containing 50 mL of nutrient agar for bacteria and Czapek's-Dox agar medium for fungi respectively were allowed to reach 40°C-50°C to be inoculated with 0.5 mL of the test organism cell suspension.

The flasks were mixed well and poured each into a Petri dish (15 cm × 2 cm) and allowed to solidify. After solidification, holes (0.6 cm diameter) were made in the agar plate by the aid of a sterile cork poorer (diameter 6 mm).

The synthesized target compounds were dissolved each in 2 mL DMSO. In these holes, 100 µl of each compound was placed using an automatic micropipette. The Petri dishes were left at 5°C for 1 h to allow diffusion of the samples through the agar medium and retard the growth of the test organism. Plates were incubated at 30 °C for 24 h for bacteria and 72 h of incubation at 28°C for fungi. DMSO showed no inhibition zones. The diameters of zone of inhibition were measured and compared with that of the standard, the values were tabulated. Ciprofloxacin (50 µg/mL) and fusidic acid (50 µg/mL) were used as standard for antibacterial and antifungal activity respectively. The observed zones of inhibition are presented (Table 6).

TABLE 6. ***In vitro*** **antimicrobial activity by agar diffusion method of the tested compounds.**

Compound No.	Zone of inhibition (mm) of microorganisms			
	Bacillus subtilis	***Escherichia coli***	***Candida albicans***	***Aspergillus flavus***
Penicillin	50	45	17	46

1	30	29	18	35
2	40	30	17	40
3	30	30	14	30
4	27	28	12	35
5	33	37	18	30
6	40	40	14	40

Discussion

The synthesized compounds were screened *in vitro* for their antimicrobial activities against *Escherichia coli* NRRL B-210 (Gram -ve bacteria), Bacillus subtilis NRRL B-543 (Gram +ve bacteria), Aspergillus flavus and Candida albicans NRRL Y-477 (Fungi). The diameters of zone of inhibition were measured and compared with that of the standard, the values were tabulated. Tetracycline was used as standard for the antimicrobial activity and the observed zone of inhibition. The results indicated generally that tested compounds did not show high activity against bacteria under test (*Escherichia coli* and *Bacillus subtilis*) while some compounds revealed high activity against fungi. All new compounds were active against the microorganisms. The antimicrobial activity results and structure activity relationship indicated that the five-membered heterocyclic rings attached to quinazolines moiety resulted in increase of antimicrobial activity.

Antitumor activity

***In vitro* antitumor activity:** Some of the newly synthesized compounds have been evaluated for their potential cytotoxicity testing against breast cancer (MCF7) using the method of skehan and Storeng. Cells were plated in 96-multiwell plate (104 cells/well) for 24 hrs before treatment with the compounds to allow attachment of cell to the wall of the plate. Different concentration of the compound under test (0 µg/ml, 1 µg/ml, 2.5 µg/ml, 5 µg/ml and 10 µg/ml) were added to the cell monolayer triplicate wells were prepared for each individual dose. Monolayer cells were incubated with the compounds for 48 h at 37°C and in atmosphere of 5% CO_2. After 48 h, cells were fixed, washed and stained with Sulfo-Rhodamine-B stain.

Excess stain was washed with acetic acid and attached stain was recovered with Tris EDTA buffer. Color Intensity was measured in an ELISA reader. The relation between surviving fraction and drug concentration is plotted to get the survival curve of each tumour cell line after the specific compound. The IC50 percent control of infected and uninfected response values were calculated for the various active compounds. Doxirubsin (DOX) was used as positive standard. Compounds having IC50<5 µg/ml are considered potentially active and exposed to further *in vivo* studies. Compounds 1-6 possess the highly significant effect against breast cancer cell line (MCF7) and this is might be due to the five-membered heterocyclic rings attached to quinazolines moiety (Table 7).

TABLE 7. **The IC50 (µg/mL) of some of the selected new compounds against breast cancer cell line (MCF7).**

Compound	IC_{50} µg/ml
DOX	2.97
1	4
2	5.5
3	5.88
4	5.5
5	4.9
6	5.1

Telomerase inhibitory: As part of our program to develop new antitumor drugs as small molecules, I (IC_{50}=1.0 µM) was chosen as a lead compound developed by Geron. Co. Ltd. as a telomerase inhibitor.

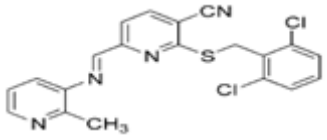

FIG. 18. **Telomeres are DNA-protein complexes at the ends of chromosomes, which play an essential protective role against DNA degradation and aberrant recombination during cell divisions.**

Telomerase activity: The Telomeric Repeat Amplification Protocol (TRAP) assay was performed by a modification of the published method. The telomerase products were resolved by 10% nondenaturing polyacrylamide gel electrophoresis and were visualized by staining with SYBR Green (Molecular Probes, USA). Signal intensity was quantified with a LAS-1000 Plus Image analyzer (Fuji Film, Japan).

The *in vitro* studies: The obtained results revealed that compounds 1-6 were the most active derivatives among the series of tested compounds with telomerase activity (IC_{50} values 25-44 µM). From the telomerase activity results and structure activity relationship, it could be concluded that the triazole, tetrazole, oxadiazole rings attached to quinazolines moiety as well as amino acid derivatives displayed higher activity (Table 8).

TABLE 8. **Telomerase Activity, IC_{50} (µM) of the selected new compounds.**

Compound	Telomerase activity IC_{50} µM
I	1
2	37
4	26
6	44
7	46
8	33
9	33

Hepatitis B activity: Hepatitis B Virus (HBV) is a DNA virus that causes acute hepatitis and lead to chronic hepatitis, liver cirrhosis and hepatocellular carcinoma. Approximately 300 million HBV carriers are infected and more than one million deaths world-wide are reported every year due to HBV-related complications. Although effective vaccination has been successfully used of the prevention of HBV infection, the availability of selective antiviral drug against HBV replication is still needed. A variety of drugs have been evaluated but only alpha interferon has demonstrated some clinical benefit in selected patients.

The potential target for antiviral chemotherapy is the reverse transcription step in HBV life cycle. The minus strand of HBV is synthesized by reverse transcription of the pregenome using the endogenous viral reverse transcriptase. It is shown that reverse transcriptase enzyme leads to incorporate nucleotide analogues more efficiency than cellular DNA polymerase. These nucleotide analogues are competitive inhibitors of the reverse transcriptase with the nucleosides pool in the cell's cytoplasm in minus strand synthesis. The recent development of heterocyclic analogues has represented a breakthrough the research for selective antiviral activities. Among these agents e.g. Lamivudine acts as a retroviral inhibitor. It has activity against HBV replication both *in vitro* and *in vivo*.

Preparation and culture of hep G2 2.2.15 cells: The required cell line was made by transfection of Hep G2-cells with a plasmid containing multiple tandem copies of HBV genome (subtype ayw). The 2.2.15 cell line was maintained in RPMI-1640 (Glutamax) culture media containing 100 IU/ml nystatin and 380 µg/ml G418 (geneticin). The transferred HEP G2-2.2.15 cell line was kept in tissue culture flask at 37°C+5% CO_2. Subcultures were set up after a week by aspiration of the media from culture flask and washing the cells twice by PBS. A 10% versene/trypsin was added, and the cells were incubated for 1 min. at 37°C. The drug Lamivudine which is a potent selective inhibitor of HBV replication has been used as a standard for the comparative studies.

DNA Extraction: HBV-DNA extraction was done by mixing 10 µl of diluted supernatant (1:5 with PBS) in reaction tube with 10 µl of 0.2 M NaOH and incubated at 37°C for one hour. Carefully, 9.6 µl of 0.2 M HCl was added followed by 90 µl of TE buffer solution.

PCR-Elisa: The PCR reaction mixture contained 14 µl extracted supernatant, 4 mmol/l MgCl2, 10 µmol/l DIG-11-dUTP, 190 µmol/l dTTP, 200 µmol/l dATP, dGTP, dCTP, 1.5 U Taq polymerase, 20 mmol/l HCl (pH 8.4), 50 mmol/l KCl, 1 µmol/l HCID-1 primer (5′GGA AAG AAG TCA GAA GGC A3′) and 1 µmol/l HCID-2 (5′TTG GGG GAG GAG ATT AGG TT3′), in total volume 50 µl. PCR reaction conditions were 32 cycles of 1 min. at 94°C, 30 sec. at 58°C and 30 sec. at 72°C+3 sec. for each cycle in a thermal circler as described in literature.

Cytotoxicity assay: A colorimetric assay for living cells utilized the colorless substrate 3-(3,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) that is modified to colored product by any living cells, but not by dead cells or tissue culture medium. The cytotoxic effect of the compounds was accessed by culturing the Hep G2-2.2.15 cells in the presence of compounds using a MTT-assay. The 50% inhibitory concentration of antiviral drugs (IC_{50}) was determined by interpolation from the plots of amount of DNA copies *versus* antiviral drug concentration. The 50% cytotoxic effect (CC_{50}) was calculated from the average viability of the cells with concentration of drugs. The Selective Index (SI) could be calculated as CC_{50}/IC_{50}. Testing. The results of the viral screening against HBV of elected compounds indicated that compounds1- 6 showed moderate spreading replication inhibition and mild cytotoxicity with selective indices 166.6~500.0 (Table 9).

TABLE 9. **Cytotoxic effect (CC_{50}), Inhibitory concentration (IC_{50}), and Selective Index (SI) of compounds FN09-FN46.**

Compound	HBV DNA	Hep G2 2.2.15	SI
No.	IC_{50} (µM)	CC_{50} (µM)	
Lamivudine	0.1	100	1000
2	0.2	100	500
4	0.6	100	166.6
6	0.5	100	200
7	0.2	100	500
8	0.5	100	200
9	0.6	100	166.6

Applications of electroplating

Copper plating on plastic: Over the centuries, copper has been used for many purposes. The ancient romans used copper mined in cyprus for currency. In fact, copper's chemical symbol of Cu was derived from the Latin word "cuprum," which means "from the island of Cyprus." Electroplating copper onto other metals has been a widespread industrial practice for many years. Electroplating can be used for a number of purposes, such as enhancing corrosion and wear resistance, improving electrical and thermal conductivity, adding aesthetic appeal and promoting adhesion. The three basic types of copper electroplating include:

Alkaline cyanide: An alkaline cyanide copper bath provides excellent throwing power and uniform deposit thickness. However, the cyanide component makes this plating solution extremely toxic and must be handled with extreme care.

Alkaline non-cyanide: Non-toxic, cyanide-free plating solutions are now available. However, they may not be as effective as alkaline cyanide baths in all copper plating applications. For instance, using a non-cyanide alkaline solution during rack plating of zinc die castings may produce a non-adhering copper deposit, essentially making the entire procedure ineffective.

Acid copper: An acid copper bath consists of copper ions, additives, acids and either fluoborate or sulfate ions. Advantages of acid copper solutions include low material cost, wide range of composition and relatively easy bath maintenance and control. However, the acidic nature means this type of bath is not compatible for plating directly onto active metals such as zinc and steel due to the lack of proper adhesion.

Plating copper onto non-metallic surfaces: Copper plating is not limited to metal-on-metal applications. It can also be extremely effective when used with non-metallic surfaces, particularly plastics. The copper coating will "metallize" the non-metallic surface, which can make it electrically conductive and provide additional benefits such as strengthening and protecting the substrate. Plating on plastics can also add a metallic shine to the finished product, which is an advantage in manufacturing applications where appearance is important.

Need for copper plating onto plastics

Chemical and corrosion resistance: Effective means of protecting a substrate against the forces of corrosion and make it more resistant to damage from chemicals used in the manufacturing process.

Strength: Some instances, plating on plastic can increase the strength and wear resistance of the substrate.

Conduct electricity: Give a non-conductive plastic surface the ability to conduct electricity, a property that is invaluable to the manufacturers of electronic parts and components used in automobiles, aircraft and a multitude of other products.

UV resistance: Metal coating can also reflect potentially damaging light away from the surface of a plastic substrate.

Conclusion

In conclusion, the antimicrobial screening suggests that all the newly synthesized compounds showed moderate to good activity against the tested organisms. Hence the fact that the compounds prepared in this study are chemically unrelated to the current medication, suggests that further work with similar analogues is clearly warranted.

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