

Effect of new amide additives on rate and qualities of steel deposition

Mervette El Batouti*, Abdel-Moneim M.Ahmed
Chemistry Department, Faculty of Science, Alexandria University, (EGYPT)
E-mail: mervette_b@yahoo.com

ABSTRACT

The most important effects of additives, such as the grain refinement of the deposit, polarization of the cathode, incorporation of additives in the deposit, the change of the orientation of crystals and the synergism of additives are presented.

Current efficiency of steel deposition ranged from 6.45% to 41.94% depending on the operating conditions while energy consumption ranged from 3.66 kJ mol⁻¹ to 11.66 kJ mol⁻¹ depending on the operating conditions. The mechanism of action of different amides has been discussed. Possible application of the present results in different electrometallurgical processes involving steel deposition such as electrowining, recovery of steel from waste solutions, electroforming, electrofining and electroplating was noted.

The present work is concerned with studying the effect of some new aliphatic and aromatic amides as additives with the effect of other parameters such as current density, temperature on the rate of electrodeposition, and energy consumption. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Limiting current;
Steel;
Thermodynamic parameters;
Electrodeposition;
Acceleration.

INTRODUCTION

Electrodeposition process is known to be diffusion controlled reaction whose rate may be affected by organic additives. The process involves metal deposition from an electrolyte onto a conduction electrode by application of an electromotive force.

Copper is an intermediate metal^[1], which has medium exchange current densities (10⁻³ to 10⁻⁸ Acm⁻²) and deposits at medium polarization. It deposits in very rough or powdery form when electrodeposition is carried out at in at the limiting current by means density, which is the case for many metals. The possibility of preventing such a powder formation at the limiting current by means of suitable additive is of great interest and represents a significant activity in electroplating^[2].

An addition agent is defined^[3] as any material, which is added to an electroplating bath for the specific purpose of modifying the physical properties of the deposit. Relatively large effect on the physical properties of deposits such as brightness, smoothness, hardness and ductility. Most addition agents are organic^[4,5] compounds but occasionally inorganic^[6] materials are employed.

The goal of the present work is to study the effect of medium composition on the electrodeposition process of steel from acidified solutions of copper sulfate. The effect of amide additives in combination with the effect of other parameters such as temperature, current density on the quality of the electrodeposit such as brightness and rate of steel deposition expressed in terms of the current efficiency has been studied in the present

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work. To assist in the economic evaluation of the present additives, their effect on electrical energy consumed in steel deposition was studied. Thermodynamic parameters of the deposits formed on the cathode surface have also been discussed to shed more lights on the mechanism of the electrodeposition process.

EXPERIMENTAL

The electrolytic cell and electrical circuit

Vertical parallel plates cell

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, 5cm width and 10cm height) and the other one is the anode (99.99% purity copper with similar dimensions as the cathode).

The cell consists of a rectangular plastic container (5.1* 5*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 small amounts of addition agent have the limiting current was determined, were constructed by increasing the current stepwise and measuring the steady state cathode potential against the reference electrode.

The rotating cylinder electrode (RCE)

The voltmeter is connected in parallel with the cell to measure its voltage. The cathode consisted of Cu metal cylinder 1 cm diameter and 7 cm length. The disk is insulated by epoxy resin. The anode is made of cylindrical copper metal counter electrode of 12 cm diameter; it's also acted as the reference electrode by virtue

of its high surface area compared to that of cathode.

Organic additives

Analar grade Compound I benzamide, Compound II urea, Compound III formamide, Compound IV propionamide, and Compound V acetamide, Compound VI dimethylformamide, Compound VII and ethylene diamine tetra acetic acid (disodium salt) supplied by BDH Chemicals Ltd., were used as organic additives.

RESULTS AND DISCUSSION

Potentiodynamic cathodic polarization curves

The cathodic polarization curve for copper electrodeposition from sulphate solution under the influence of adding increasing concentrations of Compound I. It is obvious that in the organic free solution, the current, at first, increases linearly, then tends to exhibit limiting current plateau with increases in the cathodic potential. It is generally accepted that electrodeposition of Cu^{2+} ions takes place through two steps^[7]:



It was assumed that the first step in this process occurred slowly and the rate was controlled by the equilibrium between Cu^{2+} and Cu^+ at the electrode surface. However, addition of organic additives to the sulphate solution increases the cathodic polarization and decreases the value of limiting current density. The observed changes in the cathodic polarization in the presence of organic additive suggest that it may be acting as an accelerator, which is confirmed by the observation that at any given overpotential, the current density for copper deposition from solutions containing organic additive is higher than that found for the corresponding organic free solution. This acceleration of the rate of the reaction in the presence of organic additive on the copper electroplating reaction may be due to the formation of NH^+ ion in acidic medium in case of which repel with Cu^{++} i.e. the mobility of ions increase and rate of reaction increase^[8]

Therefore, the current plateau increases with increasing organic concentration as predicted due to the increasing in Cu^{2+} ions mobility.

In modern electroplating practice, it is well known

that the addition of even small amounts of certain additives in the plating bath leads to significant changes in the properties and aspect of the deposit. Recent reviews have tried to summarize their different effects^[9-14]. Values of limiting current for all solutions using copper cathode and in another case using steel cathode are given in TABLE 1. Noticeably, the limiting current increases with increasing organic Amide derivative concentration.

Polarization curves used to determine the values of the limiting current in absence and in presence of Compound I when copper cathode was used.

The limiting current density i_L obtained from polarization curves was used to calculate the mass transfer coefficient, k from the equation:

$$k = i_L / zFC_o \quad (1)$$

Where z : number of electrons involved in the reaction;
 F : Faraday constant; C_o : bulk concentration of copper

sulphate (mol l^{-1}).

Effect of organic additives on the limiting current

If $(I_L)_{\text{blank}}$ is the limiting current in absence of organic additive and $(I_L)_{\text{org}}$ in presence of organic additive then is the percentage acceleration can be calculated according to equation (2), where

$$\% \text{ Acceleration} = \frac{(I_L)_{\text{org}} (I_L)_{\text{blank}}}{(I_L)_{\text{blank}}} \times 100 \quad (2)$$

Figures 1-3 and TABLE 2 show that the percentage acceleration caused by organic additives ranges from 6.45% to 41.94% for cell using steel cathode.

The percentage of acceleration was calculated from equation (2) depending on the concentration and type of organic additive as well as anode and cathode. It is observable that percentage acceleration increased as concentration increased.

The order of acceleration in case of Cu-S is as

TABLE 1 : Limiting current (mA) and mass transfer coefficient (cm sec^{-1}) for different organic additives.

Organic additive	$C \times 10^3 \text{ Mol l}^{-1}$	$I_L \text{ mA}$	$k \times 10^4 \text{ cm sec}^{-1}$	Organic additive	$C \times 10^3 \text{ Mol l}^{-1}$	$I_L \text{ mA}$	$k \times 10^4 \text{ cm sec}^{-1}$
Blank	0	300	4.15	Compound IV	0.956	310	4.28
					1.912	320	4.42
					2.868	330	4.56
					4.78	365	5.04
					6.692	380	5.25
Compound I	3	330	4.56	Compound V	9.56	400	5.53
					1.38	320	4.42
					2.76	330	4.56
					4.14	350	4.84
					6.9	370	5.11
					9.66	380	5.25
Compound II	6	350	4.84	Compound VI	13.8	390	5.39
					2.038	320	4.42
					4.076	330	4.56
					6.114	350	4.84
					10.19	370	5.11
					14.27	390	5.39
Compound III	9	360	4.97	EDTA	20.38	410	5.66
					1.289	315	4.35
					2.579	325	4.49
					3.867	335	4.63
					6.445	370	5.11
					9.023	390	5.39
Compound IV	15	380	5.25	EDTA	12.89	410	5.66
					0.505	330	4.56
					1.01	340	4.70
					1.515	350	4.84
					2.525	360	4.97
Compound V	21	400	5.53	EDTA	2.525	360	4.97
					3.535	380	5.25
					5.05	400	5.53
Compound VI	30	420	5.80	EDTA	5.05	400	5.53
					5.05	400	5.53

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follow:

EDTA>dimethylformamide>propionamide>acetamide
formamide> urea> benzamide.

The obtained results showed that the presence of organic additives has an accelerating effect on the kinetics of the copper discharge process, pointed out by the increase of the limiting current. The observed enhancement in the rate of Cu deposition in presence of increasing concentration of organic additives may be due to:

- (A) Those additives act as carriers of (Cu^{2+}) and led to increase the mobility of (Cu^{2+}), therefore the mass transfer coefficient will increase and the rate of electrodeposition increases.
- (B) The presence of organic additive changes the mechanism of the copper electrodeposition as it can be seen from increasing the cathodic mass 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 reaction^[15]

Effect of temperature on the reaction

The electrodeposition of copper and steel in presence of different additives was studied by measuring the limiting current over the temperature ranges between (25-40 °C). TABLES 3 show the limiting current obtained in the presence of organic additives at different temperatures. The results indicate that the rate of electroplating increases with increasing the temperature.

The values of I_1 obtained at different temperatures permits the calculation of activation energy E_a according to Arrhenius equation:

$$\log I_1 = \log A - E_a / 2.303RT \quad (3)$$

where A is a pre-exponential factor, R is the universal gas constant and T is the absolute temperature. The activation energy of the process is an important

TABLE 2 : Relation between percentage acceleration and concentration (mol l^{-1}) at 30 °C.

Organic additive	$C \times 10^3 \text{ Mol l}^{-1}$	$I_1 \text{ mA}$	% Acceleration	Organic additive	$C \times 10^3 \text{ Mol l}^{-1}$	$I_1 \text{ mA}$	% Acceleration
Blank		310		Compound IV	0.956	330	6.45
					1.912	335	8.06
					2.868	350	12.90
					4.78	360	16.13
					6.692	380	22.58
Compound I	3	350	12.90	Compound V	9.56	400	29.03
	6	360	16.13		1.38	340	9.68
	9	380	22.58		2.76	350	12.90
	15	400	29.03		4.14	360	16.13
	21	420	35.48		6.9	380	22.58
	30	440	41.94		9.66	395	27.42
Compound II	2.038	340	9.68	Compound VI	13.8	410	32.26
	4.076	350	12.90		1	335	8.06
	6.114	360	16.13		2	345	11.29
	10.19	385	24.19		3	365	17.74
	14.27	410	32.26		5	375	20.97
	20.38	415	33.87		7	390	25.81
Compound III	1.289	330	6.45	EDTA	10	405	30.65
	2.579	340	9.68		0.505	350	12.90
	3.867	350	12.90		1.01	360	16.13
	6.445	370	19.35		1.515	370	19.35
	9.023	380	22.58		2.525	380	22.58
	12.89	400	29.03		3.535	395	27.42
				5.05	405	30.65	

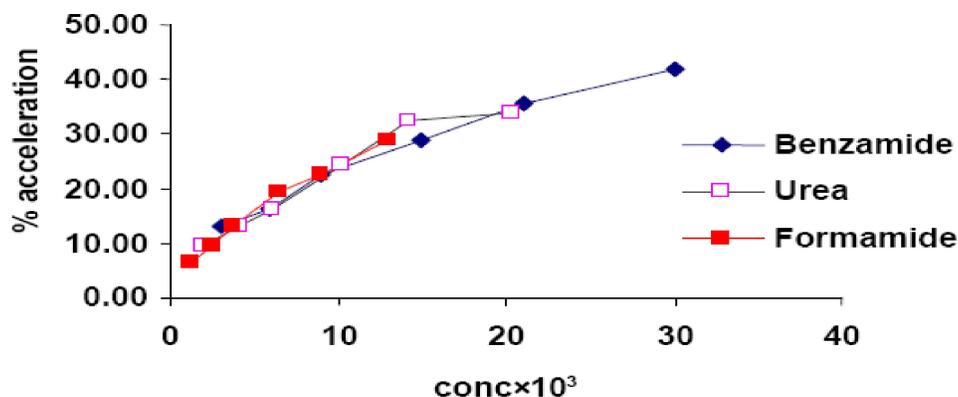


Figure 1 : The relation between percentage acceleration and concentration (mol l⁻¹) of compound I, compound II and compound III at 30 °C.

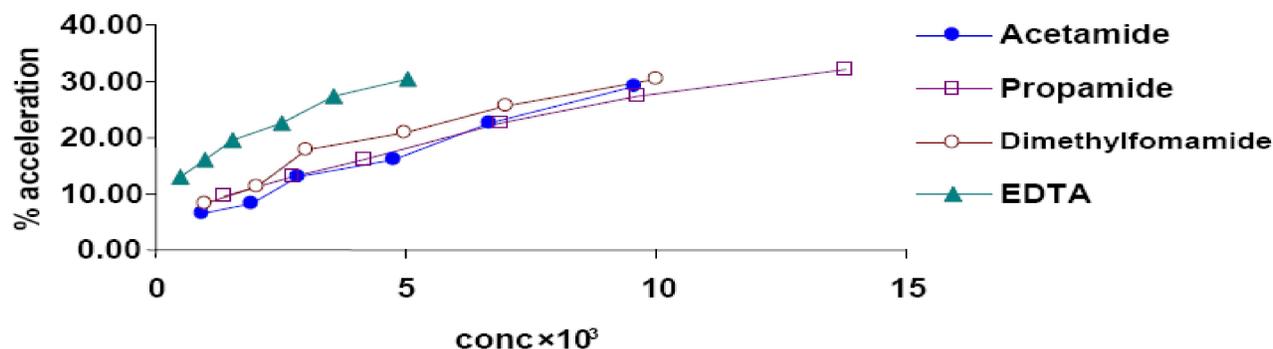


Figure 2 : The relation between percentage acceleration and concentration (mol l⁻¹) of compound IV, compound V, dimethylformamide and EDTA at 30°C.

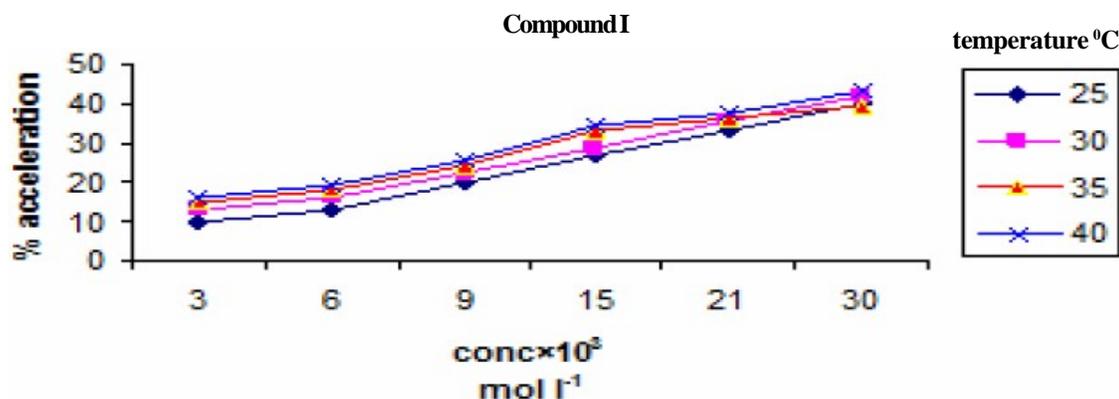


Figure 3 : The relation between percentage acceleration and concentration (mol l⁻¹) of organic additives at different temperatures (°C).

parameter for determining the rate controlling step. If the rate controlling step is the diffusion of species in the boundary layer then E_a is generally ≤ 28 kJ/mol, while E_a values usually > 43 kJ mol⁻¹ when adsorption of species on the reaction surface and subsequent chemical reaction takes place.

From TABLE 3, it is obvious that the values of E_a are lower than 28 KJ mol⁻¹; characterizing diffusion processes are controlling the reaction.

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:

$$\Delta H^* = E_a - RT \quad (4)$$

$$\Delta S^* = \ln A - \ln (B T e/h) \quad (5)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (6)$$

where B is the Boltzman constant, $e = 2.7183$, h is

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TABLE 3 : The limiting current (mA) obtained in the presence of organic additives at different temperatures ($^{\circ}\text{C}$).

$C \times 10^3$ Mol l^{-1}	Temp. $^{\circ}\text{C}$			
	25	30	35	40
Compound I				
3	330	350	380	390
6	340	360	390	400
9	360	380	410	420
15	380	400	440	450
21	400	420	450	460
30	420	440	460	480
Compound II				
2.038	325	340	370	390
4.076	335	350	380	395
6.114	350	360	390	405
10.19	365	385	410	420
14.27	380	410	425	435
20.38	395	415	445	460
Compound III				
1.289	315	330	365	385
2.579	325	340	375	390
3.867	335	350	380	395
6.445	350	370	400	410
9.023	365	380	410	420
12.89	385	400	430	440
Compound IV				
0.956	315	330	365	380
1.912	320	335	370	385
2.868	330	350	375	390
4.78	345	360	390	410
6.692	365	380	410	420
9.56	380	400	430	440
Compound V				
1.38	325	340	365	380
2.76	335	350	380	390
4.14	345	360	395	410
6.9	365	380	410	420
9.66	380	395	425	435
13.8	390	410	435	450
Compound VI				
1	315	335	375	390
2	330	345	385	400
3	350	365	400	410
5	360	375	410	425
7	375	390	425	435
10	390	405	440	450
EDTA				
0.505	330	350	380	390
1.01	345	360	390	405
1.515	355	370	400	410
2.525	365	380	410	420
3.535	380	395	425	435
5.05	390	405	435	450

TABLE 4 : The thermodynamic parameters for the solution in the presence of different concentrations of organic additive.

$C \times 10^3$ mol l^{-1}	E_a kJ mol^{-1}	ΔH^* kJ mol^{-1}	$-\Delta S^*$ $\text{J mol}^{-1} \text{K}^{-1}$	ΔG^* kJ mol^{-1}
Compound I				
3	10.24 \pm 0.60	7.76 \pm 0.60	170.66 \pm 1.97	58.65 \pm 1.19
6	9.70 \pm 0.57	7.23 \pm 0.57	171.97 \pm 1.86	58.50 \pm 1.12
9	9.46 \pm 0.556	6.98 \pm 0.55	172.56 \pm 1.82	58.43 \pm 1.09
15	9.00 \pm 1.31	6.52 \pm 1.31	173.56 \pm 4.28	58.27 \pm 2.58
21	7.60 \pm 0.94	5.12 \pm 0.94	177.89 \pm 3.07	58.16 \pm 1.85
30	5.94 \pm 0.59	3.46 \pm 0.59	183.04 \pm 1.95	58.03 \pm 1.18
Compound II				
2.038	10.53 \pm 0.62	8.05 \pm 0.62	169.95 \pm 2.03	58.72 \pm 1.22
4.076	9.66 \pm 0.83	7.18 \pm 0.83	172.59 \pm 2.73	58.64 \pm 1.65
6.114	7.46 \pm 1.17	4.98 \pm 1.17	179.53 \pm 3.83	58.51 \pm 2.31
10.19	6.89 \pm 0.75	4.41 \pm 0.75	180.93 \pm 2.45	58.36 \pm 1.48
14.27	5.66 \pm 0.59	3.18 \pm 0.59	184.59 \pm 1.95	58.21 \pm 1.18
20.38	5.89 \pm 0.32	3.42 \pm 0.32	183.39 \pm 1.05	58.09 \pm 0.63
Compound III				
1.289	10.91 \pm 1.15	8.43 \pm 1.15	168.86 \pm 3.77	58.78 \pm 2.28
2.579	10.02 \pm 1.23	7.54 \pm 1.23	171.58 \pm 4.01	58.69 \pm 2.42
3.867	8.96 \pm 0.90	6.48 \pm 0.90	174.87 \pm 2.95	58.61 \pm 1.78
6.445	5.98 \pm 1.59	3.50 \pm 1.59	184.11 \pm 5.20	58.39 \pm 3.14
9.023	3.84 \pm 0.01	1.36 \pm 0.01	190.74 \pm 0.03	58.23 \pm 0.02
12.89	3.66 \pm 0.01	1.18 \pm 0.01	190.93 \pm 0.04	58.10 \pm 0.02
Compound IV				
0.956	11.66 \pm 0.95	9.18 \pm 0.94	166.43 \pm 3.10	58.80 \pm 1.87
1.912	10.76 \pm 1.14	8.27 \pm 1.13	169.25 \pm 3.72	58.74 \pm 2.25
2.868	10.46 \pm 1.47	7.98 \pm 1.47	170.03 \pm 4.82	58.68 \pm 2.91
4.78	5.82 \pm 0.52	3.34 \pm 0.51	184.67 \pm 1.69	58.39 \pm 1.02
6.692	5.44 \pm 0.55	2.96 \pm 0.55	185.61 \pm 1.79	58.30 \pm 1.08
9.56	3.74 \pm 0.01	1.27 \pm 0.01	190.84 \pm 0.04	58.17 \pm 0.02
Compound V				
1.38	11.19 \pm 2.06	8.71 \pm 2.06	167.82 \pm 6.76	58.75 \pm 4.08
2.76	10.64 \pm 2.44	8.16 \pm 2.44	169.19 \pm 7.98	58.61 \pm 4.82
4.14	9.31 \pm 2.00	6.83 \pm 2.00	173.11 \pm 6.54	58.44 \pm 3.95
6.9	8.47 \pm 1.70	5.99 \pm 1.70	175.47 \pm 5.56	58.31 \pm 3.36
9.66	8.26 \pm 1.26	5.78 \pm 1.26	176.02 \pm 4.14	58.26 \pm 2.50
13.8	8.26 \pm 1.26	5.78 \pm 1.26	176.02 \pm 4.14	58.26 \pm 2.50
Compound VI				
1	11.27 \pm 0.64	8.79 \pm 0.64	167.56 \pm 2.10	58.75 \pm 1.26
2	8.83 \pm 1.12	6.35 \pm 1.12	175.22 \pm 3.68	58.59 \pm 2.22
3	6.86 \pm 0.69	4.38 \pm 0.69	181.32 \pm 2.28	58.44 \pm 1.37
5	6.61 \pm 0.67	4.13 \pm 0.67	181.84 \pm 2.20	58.34 \pm 1.33
7	6.26 \pm 0.31	3.78 \pm 0.31	182.75 \pm 1.01	58.26 \pm 0.61
10	6.22 \pm 0.63	3.74 \pm 0.62	182.49 \pm 2.05	58.15 \pm 1.24
EDTA				
0.505	10.65 \pm 1.96	8.17 \pm 1.96	169.23 \pm 6.43	58.62 \pm 3.88
1.01	9.40 \pm 0.81	6.92 \pm 0.81	173.21 \pm 2.65	58.57 \pm 1.60
1.515	8.39 \pm 0.55	5.92 \pm 0.55	176.34 \pm 1.81	58.49 \pm 1.09
2.525	7.98 \pm 0.05	5.50 \pm 0.05	177.52 \pm 0.15	58.42 \pm 0.09
3.535	6.14 \pm 0.54	3.66 \pm 0.54	183.20 \pm 1.78	58.28 \pm 1.07
5.05	4.81 \pm 0.64	2.33 \pm 0.63	187.32 \pm 2.08	58.18 \pm 1.25

Plank constant and other symbols have the definition mentioned above. The values for gradient and intercept are obtained by using the least square method.

Results are applied using a simple microprocessor program and applied to all the individual values of the rate. TABLE 4 give the values of thermodynamic parameters.

Although the change in free energy of the activation ΔG^* with the studied organic additives concentrations used is only small as shown in TABLE 4 and variations occur in the enthalpy of activation ΔH^* and the entropy of the activation ΔS^* with the organic additives concentrations where, in all cases ΔH^* and ΔS^* compensate each other to produce little change in ΔG^* . It is noticed that all the values of ΔS^* are highly negative, indicating a more ordered system and non-random distribution of ions^[16-18].

Effect of rotation

The present results agree with the polarographic studies⁽⁹⁶⁻⁹⁸⁾ conducted in solutions containing organic additives where it was found that the diffusion current increases in the presence of organic additives.

Conventional RCE system is designed so that the inner cylinder rotates and creates a turbulent flow in the field. When the inner cylinder is rotated slowly, a laminar flow pattern can be maintained, however, in laminar flow fluid moves in circular pattern about the axis with no radial component. Thus, there is no convection in the radial direction, and no enhancement of mass transport due to fluid flow. Consequently, an RCE is rarely operated in the laminar flow regime in electrochemical studies. Eisenberg et al^[20] correlated their data for the conditions $10^2 < Re < 10^5$. Figures 4 show the relation between rpm and I_l

$$\omega \propto (I_l)^n \quad (7)$$

It is found that the limiting current increases with increasing rpm. This may be attributed to break down a hydrodynamic boundary layer and diffusion layer are formed. The higher rpm, the higher solution flow and thinner the diffusion layer; thus giving a higher rate of transfer of copper ions to the metal surface and, at the same time, through the porous deposit layer formed on the metal which, in turn, enhances the rate of deposit.

The effect of the speed of rotation on the rate of metal deposition can also be used to determine whether

the electrodeposition process is diffusion or chemically controlled process. If the rate of deposition increases by increasing the speed of rotation, then the reaction is diffusion controlled. However, if the rate of deposition is independent of rotation, so the reaction is likely to be chemically controlled. The angular velocity ω is given by:

$$\omega = (2\pi \text{ rpm}) / 60 \quad (8)$$

TABLES 5 and Figure 4 give the relation between the limiting current and the angular velocity, ω , to the power 0.7 at different concentrations of organic additive at 25 C°. Straight lines were obtained and the limiting current increases by increasing the rotation which indicates that electrodeposition reaction of copper is diffusion controlled reaction^[20].

Data correlation

To obtain an over all mass transfer correlation under the present conditions where a rotating cylinder is used the method of dimensional analysis was used. To identify the variables which affect the rate of mass transfer in the electroplating reaction, the mechanism of forced convection mass transfer should be recalled first. Forced convection takes place as a result of cylinder rotation. The thickness of this hydrodynamic boundary layer determines the thickness of the diffusion layer across which diffusion of Cu^{++} from the bulk solution to surface of steel takes place. The thickness of the hydrodynamic boundary layer at the rotating cylinder and the diffusion layer are determined by the physical properties of the solution, the geometry of the system (cylinder diameter) and cylinder rotation speed. This picture leads to the equation:

$$k = f(\rho, \eta, D, U, d) \quad (9)$$

Where k = mass transfer coefficient, cm sec^{-1} ; ρ = is density of bulk, g cm^{-3} ; η = is viscosity of bulk, $\text{cm}^2 \text{sec}^{-1}$; D = diffusion coefficient, $\text{cm}^2 \text{sec}^{-1}$; U = cylinder linear velocity ($U = \omega r$); ω = angular velocity; d = diameter of cylinder, cm .

Figure 5 gives the overall correlation for all organic additives which correlates by the equation:

$$\log \text{Sh}/(\text{Sc})^{0.33} = \log a + b \log \text{Re} \quad (10)$$

The exponents in TABLE 6 denote a highly turbulent flow, which agree with the previous mass transfer study in aqueous media.

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TABLE 5 : The effect of the speed of rotation on the limiting current for different concentrations of organic additives.

	rpm	$\omega^{0.7}$	I_l	$C \times 10^3$					$C \times 10^3$						
				3	9	15	21	30	1.38	4.14	6.9	9.66	13.8		
Blank	125	6.05	340						125	6.05	330	340	360	400	410
	250	9.83	380						250	9.83	360	380	400	430	460
	375	13.05	400						375	13.05	410	420	440	480	500
	500	15.96	480						500	15.96	450	480	500	540	580
	700	20.20	560						700	20.20	520	580	600	620	640
	900	24.09	600						900	24.09	620	640	660	680	700
Compound I	125	6.05	360	380	400	420	440		125	6.05	320	330	340	360	380
	250	9.83	400	420	440	460	500		250	9.83	340	360	380	410	440
	375	13.05	460	480	500	520	570		375	13.05	380	400	420	440	480
	500	15.96	500	520	540	560	620		500	15.96	430	460	480	520	560
	700	20.20	580	600	620	640	660		700	20.20	500	560	580	600	620
	900	24.09	620	640	660	680	710		900	24.09	600	620	640	660	680
Compound II	125	6.05	350	370	400	410	435		125	6.05	315	325	335	350	370
	250	9.83	390	410	430	470	500		250	9.83	330	350	360	390	420
	375	13.05	450	480	500	510	530		375	13.05	360	380	400	420	460
	500	15.96	500	520	560	600	625		500	15.96	400	440	460	500	520
	700	20.20	560	600	620	640	660		700	20.20	460	520	560	580	600
	900	24.09	620	640	680	700	710		900	24.09	580	600	620	640	660
Compound III	125	6.05	340	360	380	410	430		125	6.05	310	315	325	340	360
	250	9.83	380	400	420	450	480		250	9.83	320	330	340	370	400
	375	13.05	430	460	480	520	530		375	13.05	340	360	380	400	440
	500	15.96	480	500	520	580	610		500	15.96	380	420	440	480	500
	700	20.20	560	600	620	640	650		700	20.20	440	500	540	560	580
	900	24.09	640	660	680	690	700		900	24.09	540	560	580	600	620
Compound IV	125	6.05	340	360	380	410	430		125	6.05	310	315	325	340	360
	250	9.83	380	400	420	450	480		250	9.83	320	330	340	370	400
	375	13.05	430	460	480	520	530		375	13.05	340	360	380	400	440
	500	15.96	480	500	520	580	610		500	15.96	380	420	440	480	500
	700	20.20	560	600	620	640	650		700	20.20	440	500	540	560	580
	900	24.09	640	660	680	690	700		900	24.09	540	560	580	600	620
Compound V	125	6.05	360	380	400	420	440		125	6.05	320	330	340	360	380
	250	9.83	400	420	440	460	500		250	9.83	340	360	380	410	440
	375	13.05	460	480	500	520	570		375	13.05	380	400	420	440	480
	500	15.96	500	520	540	560	620		500	15.96	430	460	480	520	560
	700	20.20	580	600	620	640	660		700	20.20	500	560	580	600	620
	900	24.09	620	640	660	680	710		900	24.09	600	620	640	660	680
Compound VI	125	6.05	350	370	400	410	435		125	6.05	315	325	335	350	370
	250	9.83	390	410	430	470	500		250	9.83	330	350	360	390	420
	375	13.05	450	480	500	510	530		375	13.05	360	380	400	420	460
	500	15.96	500	520	560	600	625		500	15.96	400	440	460	500	520
	700	20.20	560	600	620	640	660		700	20.20	460	520	560	580	600
	900	24.09	620	640	680	700	710		900	24.09	580	600	620	640	660
EDTA	125	6.05	340	360	380	410	430		125	6.05	310	315	325	340	360
	250	9.83	380	400	420	450	480		250	9.83	320	330	340	370	400
	375	13.05	430	460	480	520	530		375	13.05	340	360	380	400	440
	500	15.96	480	500	520	580	610		500	15.96	380	420	440	480	500
	700	20.20	560	600	620	640	650		700	20.20	440	500	540	560	580
	900	24.09	640	660	680	690	700		900	24.09	540	560	580	600	620

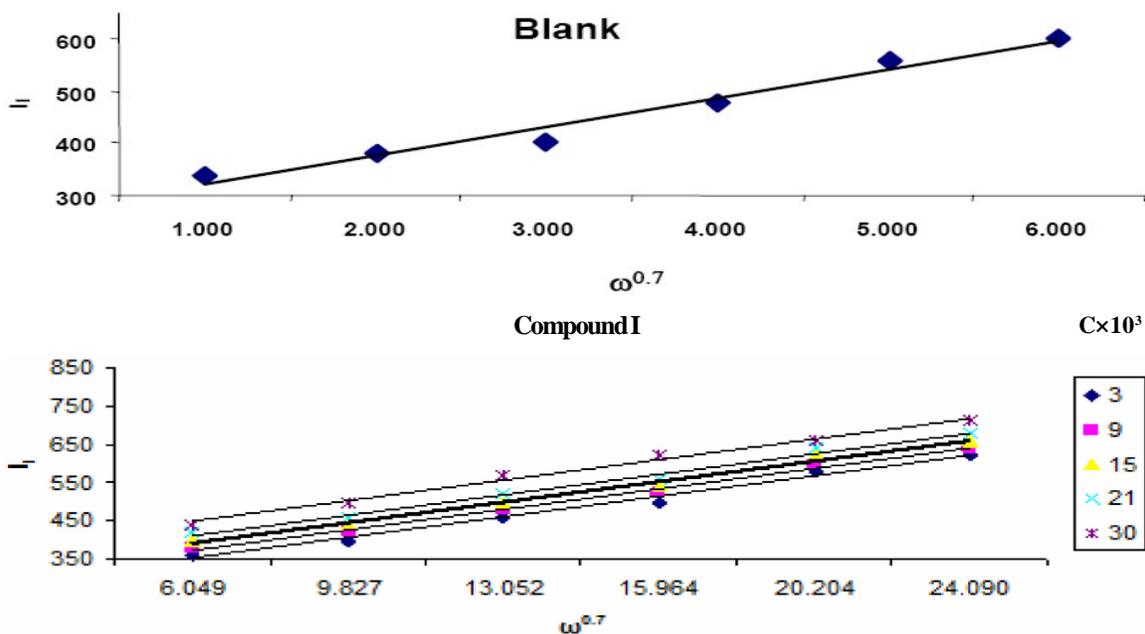
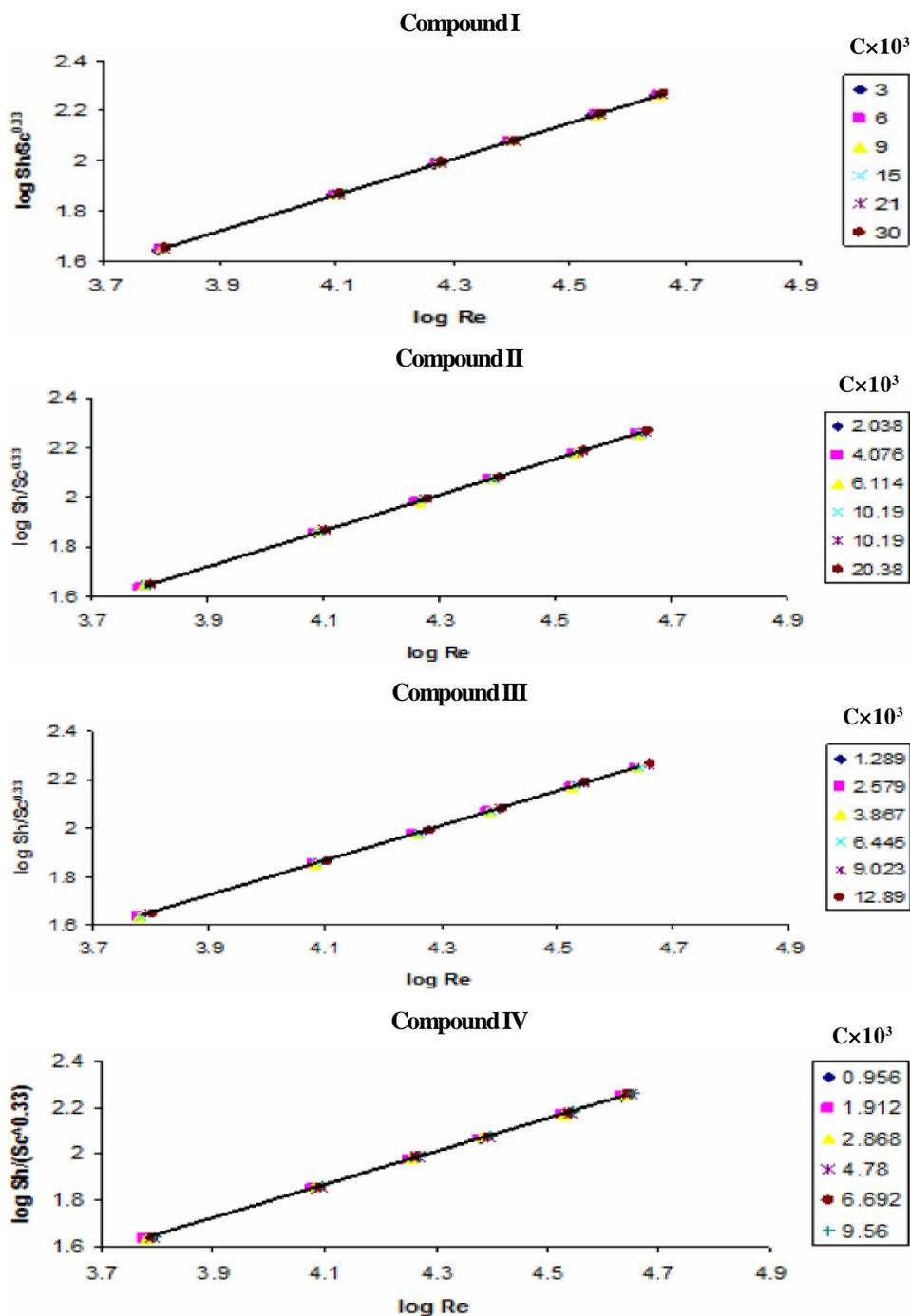

Figure 4 : The relation between limiting current (mA) and angular velocity (rad. sec⁻¹) for different additives.

TABLE 6 : The equation of Sh, Sc, Re and the average deviation

Organic additive	Steel Cylinder
Compound I	$Sh = 0.088 Re^{0.718} Sc^{0.33}$ With an average deviation : $\pm 0.064\%$
Compound II	$Sh = 0.09 Re^{0.717} Sc^{0.33}$ With an average deviation : $\pm 0.072\%$
Compound III	$Sh = 0.09 Re^{0.716} Sc^{0.33}$ With an average deviation : $\pm 0.089\%$
Compound IV	$Sh = 0.092 Re^{0.715} Sc^{0.33}$ With an average deviation : $\pm 0.11\%$
Compound V	$Sh = 0.092 Re^{0.715} Sc^{0.33}$ With an average deviation : $\pm 0.12\%$
Compound VI	$Sh = 0.092 Re^{0.716} Sc^{0.33}$ With an average deviation : $\pm 0.142\%$
EDTA	$Sh = 0.091 Re^{0.716} Sc^{0.33}$ With an average deviation : $\pm 0.148\%$



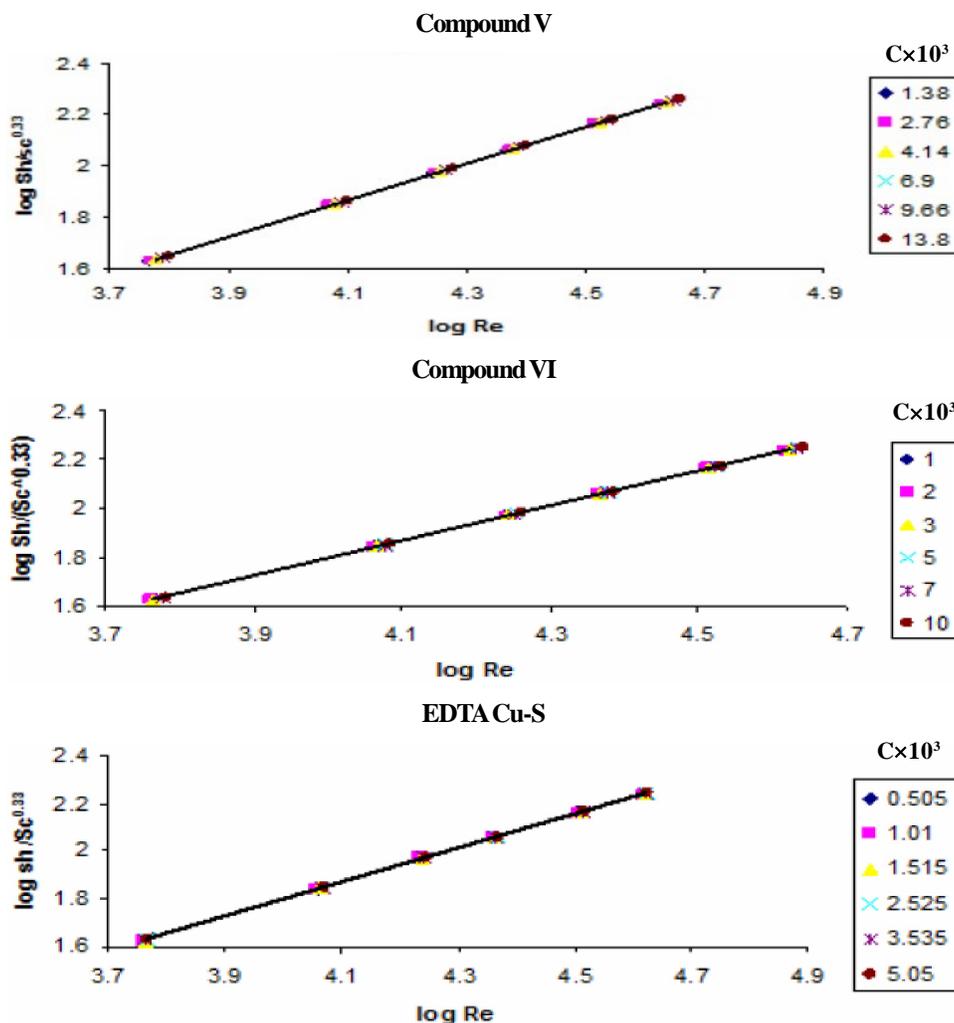


Figure 5 : The relation between $\log Sh/Sc^{0.33}$ and $\log Re$ for different concentrations (mol l^{-1}) of organic additives at 25 °C.

In our present study, a forced convection mechanism^[21] is obtained which agree very well with the relationship:

$$Sh = 0.0791 Re^{0.7} Sc^{0.356} \quad (11)$$

Given by Eisenberg et al^[20] for mass transfer to a rotating cylinder in turbulent flow system.

Also, our results agree excellently with:

$$Sh = 1.581 Re^{0.725} Sc^{0.33} \quad (12)$$

given by Nasser et al. ⁽¹²¹⁾ for mass transfer during cementation using rotating cylinder in an aqueous medium as well as with the equation given by Ahmed et al^[23] for mass transfer during copper cementation from alcoholic water mixtures using rotating cylinder in turbulent system.

$$Sh = 0.061 Re^{0.833} Sc^{0.33} \quad (13)$$

given by Ahmed et al^[23] for mass transfer during copper cementation from alcoholic water mixtures using

rotating cylinder in turbulent system.

CONCLUSION

1. By increasing the temperature, the deposition rate increases and thus current efficiency (CE) increases and energy consumption (EC) decreases.
2. Also, by increasing the applied current density, the rate of deposition increases and CE increases by a small amount. It seems that increasing the CE, the rate of nucleation becomes higher than that of crystal growth ; accordingly a fine deposit is obtained at high current density.
3. Amides play an important role in the deposition process of steel from a Watt bath; a small concentration of these amides can act as brighteners for the steel deposit not only becomes bright but it also compact and adherent. The presence of amides was found to

increase the current efficiency and decrease energy consumption.

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