www.sphinxsai.com

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.5, pp 2432-2438, 2014-2015

Quantum mechanical investigations for auto catalytic copper plating process

K.Raja, P.A.Jeeva, S.Karthikeyan*

**School of Mechanical and Building Sciences, VIT University,
Vellore- 632014, India**

Abstract: A high speed auto catalytic copper plating bath has been developed with Naficillin and Oxacillinantibiotics as accelerators for auto catalytic copper plating process. The acceleration effect of the compounds was determined by weight gain and electrochemical method. Both compounds improved the rate of deposition to considerable extent by adsorbing strongly on the steel surface. The adsorption of the accelerators was found to obey Langmuir adsorption isotherm. The quantum mechanical parameters further justified the impressive performance of accelerators through their effective adsorption on metal surface.

Keywords: Accelerators; Adsorption; Electroless; Polarisation; Quantum.

1.Introduction:

It is found on many occasions that the rate of electrolesscopper with hypophosphite as the reducing agent is below 8 μ/hr and so for a viable industrial process high speed electroless copper plating is a subject of practical interest. It is known that the additives have an important role in the plating process for they can act as accelerator – inhibitors, partial accelerators and accelerators only besides their complexing ability for the metal ion. Sulphur bearing organic compounds are some of the potential additives often tried in plating, battery electrolyte and pickling baths[1-8] but, they are toxic. From the detailed literature survey it is obvious that no significant publications are available for antibiotics tried as a accelerators in particular to antibiotics Viz., Naficillin (NAFI) and Oxacillin (OXAC) for Electroless copper plating plating [9-13]. Hence there is good scope to study the structural aspects of these additives related to their performance as the accelerators. Also the mode of action of additives can be understood from techniques such as weight gain metod,anodic and cathodictafel polarization and impedance measurements.

2. Methods and Materials

Evaluation of accelerators by different techniques

The bath used in the present study had the following composition [14-16].

Copper sulphatepentahydrate	0.13M
Sodium hypophosphite	0.2M
Sodium potassium Tartarate	0.4M
Glycine	0.1M
pH	11 ± 0.1
Temperature	40 ± 0.1°C

Table 1 .Effect of Naficillin(NAFI) on rate of deposition by weight gain studies pH 11 ±0.1 Temp. 40°C

Concentration of NAFI x10^{-}3 mM	Rate of deposition (μ/hr)
0	2.00
0.55	6.32
1.11	16.00
2.22	9.72
3.33	5.31
4.44	2.2
5.55	2.2
6.66	2.2
7.77	2.2

Table 2 :Effect of Oxaccillin (OXAC) on rate of deposition by weight gain studies pH 11 ±0.1 Temp. 40oC

Concentration of Oxac x 10^{-3}mM	Rate of deposition (μ/hr)
0	2.00
0.98	4.2
1.96	12.00
2.94	15.20
3.91	10.02
4.89	6.75
5.87	4.31
6.85	2.1
7.83	2.1
8.81	1.2
9.79	0.2

Table 1 gives the values of electrolesscopper deposition rate in the presence of various concentrations of NAFI. It is seen from the table that the acceleration effect starts even at 0.55 x 10-3mM of NAFI. Above this concentration, NAFI inhibits the deposition rate. The maximum plating rate of 16μ/hr is achieved with even trace amounts of (1.11 x 10-3mM) the compound. This is a most welcome feature of a good accelerator. Among two compounds used in the present work, NAFI is seen to give the highest deposition rate. The compound is classified as accelerator-inhibitor [3].

Table 2 indicates the influence of OXAC on the rate of electroless copper deposition. From the table it is clear that a maximum plating rate of 15.2 μ/hr is achievable with an optimum concentration of 2.94 x 10-3 mM. As in the earlier cases here also the plating rate is found to decrease with increase in concentration of the accelerator beyond the optimum concentration and the rate of decrease is found to be much pronounced. With 9.79 x 10-3 mM of the compound the rate is found to be almost nil. Hence this compound could also be grouped under accelerator – inhibitor. [3].

Electrochemical polarisation studies

Two types of polarisation studies have been carried out using electrolessly deposited copper as the working electrode. In this measurement , the anodic and cathodicpolarisations over a wide range of potentials are performed separately from the rest potential, varying the bath constituents with a view to fix the role of accelerators as anodic or cathodicdepolarisers.

According to Paunovic theory [4], the electroless plating of metal can be viewed as the anodic oxidation of the reducing agent and the cathodic deposition of metal.

It has been widely accepted that the overall reaction of electroless copper plating comprises of two kinds of simultaneous reaction [5].

(i) The cathodic reduction of Cu^{2+}, H^+ and $H_2PO_2^-$ or the deposition of Cu-P alloy and the formation of hydrogen, that is,

(ii) The anodic oxidation of the reducing agent, i.e., $H_2PO_2^-$.

In light of the above mechanism of electroless copper deposition with sodium hypophosphite as the reducing agent, the role of the sulphur compounds as accelerators is to be probed through the above anodic and cathodicpolarisation measurements. This will help to fix the additives as either anodic or cathodicdepolariser or both.

(a) Anodic polarisation studies

The bath formulation for the anodic polarisation studies is as follows.

Sodium hypophosphite	0.2M
Sodium potassium Tartarate	0.4M
Glycine	0.1M
pH	11 ± 0.1
Temperature	40 ± 0.1°C

It is to be noted that the above bath is devoid of any Cu2+ ions. The potential window selected is wide from 0 to 1000mV to ensure the complete oxidation of hypophosphite. Anodic polarisation experiments have been done with the above bath with and without the presence of accelerators with electrolessly plated copper alloy as the working electrode at a fixed scan rate of 10 mV/sec. The choice of this scan rate is to get reproducible results. The results are shown in Table 3. For each accelerator three discrete concentrations have been chosen from lower values up to the optimum concentration.

In all the cases the oxidation current of H_2PO_2- is found to increase with increase in concentrations of the accelerators and reach the maximum value at their respective optimum concentration. Among the derivatives of antibiotics studied, NAFI gives the highest oxidation current of 39.81mA, while OXAC gives the lowest oxidation current of 15.84mA. The order of oxidation currents in the above studies is in line with the performance trend in weight gain studies. Thus it is clear that these compounds act as anodic depolarizers in enhancing the oxidation of H2PO2-.

Table 3. Anodic polarisation results for the electroless plating of nickel in the presence and absence of the accelerators

S.No	Accelerator and Concentration x 10-3 mM	Oxidation current of hypophosphite (in mA)
1	No accelerator	7.88
2	Naficilin (NAFI)	
	0.28	6.99
	0.55	7.94
	1.11	39.81
3	Oxacillin (Oxac)	
	0.98	5.54
	1.96	17.01
	2.94	30.69

(b) Cathodic polarization studies.

To clarify the role of the accelerators whether they are directly involved in the reduction of Ni2+ ions, the above polarisation studies were carried out with the same above-mentioned electrode in the following bath.

Copper sulphatepentahydrate	0.1 M

Sodium potassium Tartarate	0.4 M
Glycine	0.1 M
pH	11 ± 0.1
Temperature	40 ± 0.1°C

Again it is to be noted that H2PO2- is substituted with Cu2+ ions here in contrast to the anodic polarisation studies. The polarisation is carried out with and without the presence of all the accelerators. The results are presented in table 4. It is evident from the results that the influence of the accelerators on the reduction of Cu2+ is negligible indicating that the compounds cannot accelerate the reduction of Cu2+ ions directly in the absence of any H2PO2- ions. Haruyama et.al [6] have estimated that the rate of electroless plating of Co bath by partial polarisation curves in the bath removing either H2PO2- or cobalt sulphate from the standard bath and concluded on the same lines as in the present study. Han et al [7] in their experiments with electroless nickel plating using sodium hypophosphite as the reducing agent have also concluded in a similar way. Further Fang et al [8] in their studies with the thioglycolic acid as the accelerator in EN bath in presence of hypophosphite has come to the decisive conclusion on the role of accelerators as only indirectly assisting the nickel reduction via hypophosphite oxidation.

As the compounds are not directly involved in the reduction of Cu2+ ions, their performance variations is not reflected in the cathodicpolarisation studies unlike in their anodic polarisationbehaviour.

Table 4 Cathodic polaization results for the electroless plating of copper in the presence and absence of the accelerators.

S. No	Accelerator and Concentration x 10-3 mM	Cathodic limiting current (mA)
1	Bath (without H2PO2- &	10
2	accelerators)	
	NAFI	10.0
	0.28	8.9
	0.555	7.0
3	1.11	
	OXAC	12.5
	0.98	10.0
	1.96	7.5
	2.94	

Impedance Measurements

The A.C impedance spectra obtained during the electroless copper deposition and simultaneous oxidation of the hypophosphite in the presence and absence of the accelerators in their optimum concentration at room temperature are in table 5.

In this experiment the A.C voltage is superimposed on the rest potential on electrolessly deposited Cu-P alloy electrode immersed in the bath. The rest potential or the mixed potential is one at which two different electrochemical reactions occur simultaneously on the Ni-P surface in the metal / solution interface. Thus the overall reaction in the electrolesscopper plating system is as follows:

Cu2+ + H2PO2- +H2O Ni + H2PO3- +2H+ (4.7)

Using the Nyquist plots the charge transfer resistance values of the above reaction is calculated as the X intercept of the semicircle where the x-axis represents the real part of the impedance. Perfect semicircles are encountered, in case where the electrochemical reaction of interest is under charge transfer control. Where the reactions are partially under charge transfer and mass transport control there is a drag noted in the semicircular plot. When the reaction is under diffusion control a rising portion is noted in the low frequency end of the plot. Also any looping at the tail – end of the plot is attributed to the contribution of the Warburg impedance.

In the present case the situation is similar as it corresponds to a highly resistive condition for the above charge transfer reactions reflected in their high Rtvalues. Impedance studies have been adapted to understand the behaviour of thiourea function as accelerator in electrolessCu bath [17]. The decreased Rt value is claimed to reflect on the accelerating affect on the additives during plating process

Table 5 Values of charge transfer resistance and double layer capacitance obtained from the impedance measurements in the presence and absence of all additives

Accelerator	Rt K.ohm.cm2	Cdl μF. cm-2
No accelerator	15.00	39
NAFI	1.10	977
OXAC	1.50	790

3 Application of adsorption isotherms

In the present study the values of fractional surface coverage (θ) were obtained using values of rates of deposition in the presence and absence of additives (ro) from weight gain method. The fractional surface coverage is written as

$$\theta = 1- (ro / rt) \qquad (1)$$

Suppose that the adsorption of all the additives on the metal surface follows the Langumuir isotherm; then the fractional surface coverage is given by

$$\theta = KC_0/ 1+KC_0 \qquad (2)$$

Where C_0 denotes the bulk concentrations of the additives and K is the adsorption constant. Equations 4.15 and 4.16 can be combined and rearranged to give.

$$(1 / rt) = (1 / r_o) + (K / r_o)\ C_o \qquad (3)$$

The Langumuir isotherm was tested by plotting 1/rt Vs C0 for all the compounds. A straight-line relationship was obtained in all the cases thereby confirming that the adsorption process obeys Langumuir adsorption isotherm[18-20]. The results are presented in figure 1 - 2.

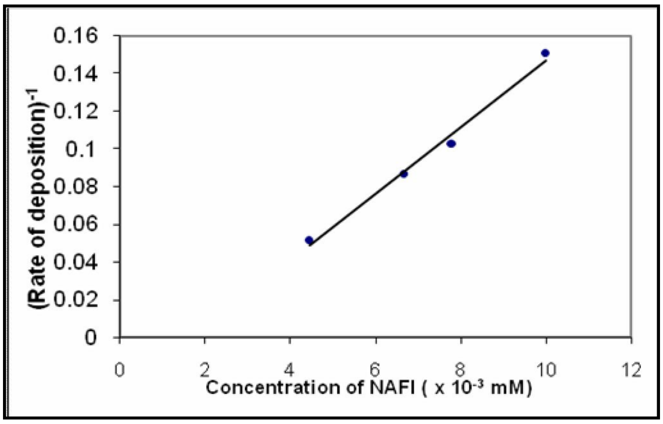


Fig 1.Langumuir isotherm plot for electroless copper plating process in the presence of different concentrations of NAFI

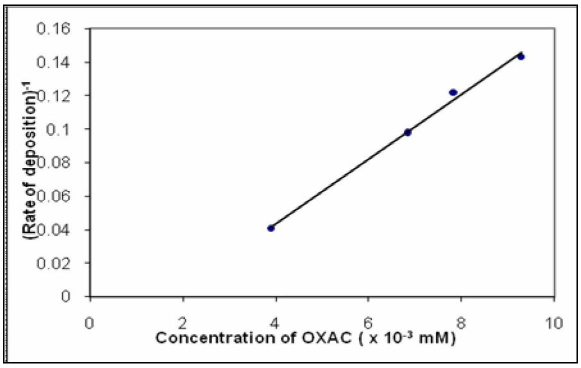
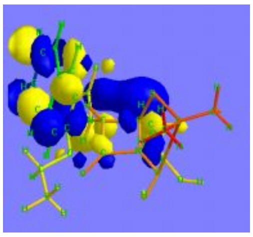


Fig 1.Langumuir isotherm plot for electroless copper plating process in the presence of different concentrations of OXAC.

Quantum mechanical calculations



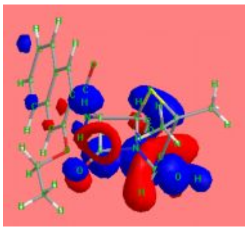


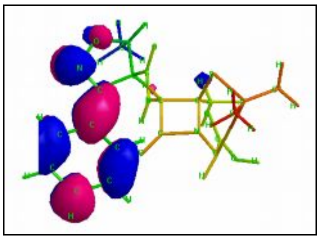
Fig 3.HOMO Of Naficillin **Fig 4. LUMO Of Naficillin**

Quantum chemical calculations were carried out to investigate the adsorption and inhibition mechanism of the inhibitorsThe values of calculated quantum chemical parameters i.e. E_{HOMO} (highest occupied molecular orbital), E_{LUMO} (lowest unoccupied molecular orbital), ΔE (energy gap) and μ (dipole moment), are summarized in table-6.

E_{HOMO} is associated with the electron-donating ability of the molecule. Several researchers have shown that the adsorption of an inhibitor on metal surface can occur on the basis of donor-acceptor interactions between the π-electrons of heterocyclic atoms and the vacant d-orbitals of the metal surface atoms. A high value of E_{HOMO} indicates a tendency of a molecule to donate electrons to acceptor molecules with low energy empty molecular orbital. Increasing values of E_{HOMO} facilitates the adsorption and increases the inhibition efficiency by influencing the transport process through the adsorbed layer . E_{LUMO} indicates the ability of the molecule to accept the electrons, hence these are acceptor states. The lower the value of E_{LUMO}, the more probable is that the molecule can accept electrons and increase the inhibition efficiency. Regarding ΔE (E_{LUMO}-E_{HOMO}) lower values of energy difference will cause higher inhibition efficiency because energy to release electron from last occupied orbital will be low. When dipole moment is concerned higher values of μ, will favours a strong interaction of inhibitor molecule with the metal surface.

Table 6: Quantum mechanical parameters for the thio compounds

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol-1)	Dipole moment (Debye)
Naficillin	0.597018	-8.13957	8.737	4.9493
Oxcillin	0.173069	-8.02091	8.914	4.8621



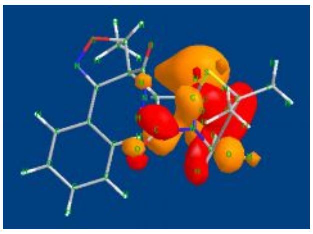


Fig 5.HOMO Of Oxacillin **Fig 6. LUMO Of Oxacillin**

Conclusion:

An attempt has been made to utilize quantum mechanical approach using simulation technique for substantiating the acceleration effects of antibiotics in electroless copper plating. The performance of exaltation by these compounds follows the order:

Naficillin>Oxacillin

References

1. Clara de Minjer and Brenner, Plating , Dec, 1297 (1957)
2. Brenner and Riddell, J.Research NBS, 37, 31 (1946); Proc. American Electroplaters Soc., 33, 16 (1946).
3. N.Fieldstein and T.S.Lancsek, J.Eleectrochem. Soc., June, 869 (1971)
4. M.Paunovic, J.Electroanalchem, 14, 447 (1967)
5. M.Paunovic, Plating 55, 1161 (1968)
6. S.Haruyama et al, Metal Finishing Soc. of Japan 137,918 (1990)
7. K.P. Hand and J.L.Fang, Metal Finish, Feb, 73 (1997)
8. J.L.Fang, Y.Lu and K.P.Han, Plating and Surf. Finish, Sep, 91 (1997)
9. El. Raghy and Aho-Solama, J.Electrochem.Soc, 126, 171 (1979)
10. F.M.Donahue and C.U.Yu, ElectrochimActa, 15, 237 (1970)
11. F.M. Donahue and F.L.Shippey, Plating, 60, 135 (1970)
12. A.Molenaar, F.E.Holdrinet and L.K.H.VanBeck, Plating, 61, 238 (1974)
13. C.K.Mital, P.B.Srivastava and R.G.Dhaneswar, Metal Finishing, 88, June (1987)
14. Potentiodynamic polarization and cyclic voltammetric studies of electroless nickel Plating process, S.Karthikeyan, Electroplating and Finishing, China **,**Vol No10,Oct (2008).1.
15. Impedance measurements for electroless nickel plating procesm S.Karthikeyan**,** K.N. Srinivasan, T.Vasudevan, S. John., *.Port. Electrochim. Acta* , 2006, vol.24, no.4, p.405-413.
16. Hydrogen permeation measurements for electroless nickel plating process, K.N. Srinivasan S.Karthikeyan, T.Vasudevan and S.John, Electroplating and Finishing, CHINA,Vol No 23,Feb(2004),1
17. K.P.Han and J.L Fang, J.Appl.Eleectrochem, 26, 1273 (1996).
18. B.Donnelly, T.C. Downie, R.Grezeskowiak, H.R.Hamburg and D.Short, Corrosion Science, 14, 597 (1974)
19. R.G.Pearson, J.Am.Chem.Soc, 85, 3533 (1963).
20. K.Madhavan, S.Muralidharan and S.V.K.Iyer, Proc. Tenth National Cong. on Corrosion control, Sep. 6-8, 207 (2000).

*****