CHAPTER - IV

KINETICS OF ELECTRODE PROCESSES DURING ELECTRODEPOSITION OF NICKEL

CHAPTER IV
KINETICS OF ELECTRODE PROCESSES DURING ELECTRO -
DEPOSITION OF NICKEL

4.1 INTRODUCTION;

Even a brief exposition of all the methods presently employed for studying the kinetics of electrode processes is outside the scope of our research work. We are discussing here. a basic method used for investigating the kinetics of electrochemical reactions.

The method gives more stress on Plotting curves. relating current density to electrode − polarisation curves. The curves are plotted. in the present work, by direct compensation method. In this method, a constant current is applied to the cathode and the stationary or steady state potential is measured. The magnitude of the cathodic polarisation is then determined by the equation −

$$\Delta E = E_1 - E_s$$

were, E_1 is the electrode potential for given C.D. and E S is the electrode potential when no current is flowing. ΔE is then cathodic polarisation. The different polarisation curves of C.D. v·s. cathodic polarisation are plotted. Analysis of the shape of polarisation curves and study of their dependence on the solution composition. temperature and other physicochemical parameters enabled us to obtain sufficiently detailed information about the nature of the particular electrode process (46-48).

The high response of electrode potential during a passage of current. change in the solution composition. the presence even of negligible amount of surface active substance and catalytic poisons call for special care in preparing solutions and electrodes for studies of electrochemical kinetics. This was over looked in early works and in many old data on chemical polarisation and cannot therefore be trust. A special procedure is therefore employed during our work for preparing solution and electrodes.

The history of study of electrode kinetics begin with the classical research undertaking by Tafel, who in 1905 established the linear dependence between the current logarithm and the overvoltage. It is given as

$$\eta = a + b \log i$$

where η = electrochemical polarisation.

a and b are constants and i the current density.

For $i = 1$ A/sq.dm. $\eta = a$

The constant 'a' depends substantially on the electrode material and the solution composition. while the constant 'b' is determined by the electrode reaction mechanism . For Tafel's equation it becomes obvious that polarisation increase with increase in C.D.

Further any electrode process in complex heterogeneous reaction involving a number of consecutive steps as discussed in chapter I (section 1.2.5).

To establish the number, nature and sequence of steps making up an electrode process, is one of the main task of electrode kinetics. From chemical kinetics it is known that the rate of a multistep consecutive reaction is govern by the rate of the slowest of its step and that out of number of parallel path, the most probable is the one that is least inhibited.

The same principle applies to electrochemical process. The occurrence of the electrode polarisation is therefore directly associated with the step that determines the rate of the overall process i.e. the slowest step. The elucidation of the nature of the slowest step (Rate determining step) constitutes another principal task of electrochemical kinetics. On the other hand, the occurrence of a new path, which increases reaction rate, may reduce the electrode potential. This fall of electrode potential and the process responsible for it is called depolarisation.

The slow rate of any step is directly responsible for electrode polarisation.. If the nature of the inhibited step, which is the cause of polarisation is known, the term electrode overpotential (η) or simply overpotential is preferred to polarisation.

As discussed in chapter –I. there are various types of overpotentials.

1) Concentration overpotential

2) Activation overpotential

3) Ohmic overpotential

Concentration overpotential is reduced to negligible extent by agitation. In order to avoid ohmic overpotential to negligible extent. Luggin capillary (Vide Supra sec. 2.8 and Fig. 2.2) is used. Now activation overpotential is further classified into electrochemical overpotential and phase overpotential. Any electrode process involves at least one step associated with the transfer of charges across the electrode – electroyte interface. The electrode polarisation caused by the slow rate of this step is called as electrochemical overpotential (η_c) because it is precisely this charge – transfer process which is the electrochemical act proper. This overpotential is also named as retarded discharge or transition overpotential. The overpotential observed. when the inhibited step is the incorporation of metallicions into the crystal lattice. and also when the slow step is the transformation of one modification (less stable) into another (more stable). may be called the phase overpotential (η_{ph})

The subdivision of polarisation into concentration and activation polarisations is somewhat arbitrary. Thus. the phase overpotential referred to activation polarisation. is essentially dependent on the concentration of intermediate particles and in this sense. it may be related to concentration polarisation. Finally the rate of the purely chemical reaction step is also determined by the corresponding value of the activation energy.

4.2 Electrode Kinetics during electrodeposition of nickel from Ammonical Acetate bath :

The electrode kinetics during electrodeposition of nickel is studied, using direct compensation method (Sec.4.1). The electrical set – up used for this purpose is illustrated in Fig. 2.2 and discussed in detail in sec. 2.8 (Chapter –II).

The subject of special interest is the study of electrode kinetics and the roll of cathodic polarization which affects the character of deposits .during electrodeposition of nickel. Recently number of workers are showing keen interest in this field(49-53)

Experimental investigation of the kinetics of the cathodic deposition of metals is complicated. The cathode surface does not remain intact during electrolysis : it changes all the times as the metal is being deposited. The growth of

the deposit is essentially dependent on the nature of the metal and electrolysis conditions. Study of the kinetics of electrodeposition of metals is also associated with difficulties due to the time variation of the cathode potential. Therefore in the usual procedure of tracing polarisation curves, the potentials are measured after a certain lapse of time i.e. when the values are constant (steady state potentials). Because of these difficulties it makes the data of different workers incomparable, during measurements of polarisation.

In spite of serious difficulties encountered in experiments and in theoretical interpretation of the results obtained, definite conceptions have emerged, concerning the nature of these processes, by using accurate experimental technique and taking special care in preparing solutions and electrodes.

Following physico – chemical parameters are selected for polarisation studies.

1) Concentration of complexing agent.

2) pH of the bath solution.

3) Temperature of the bath solution.
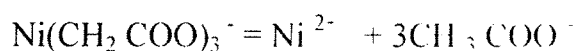
4) Addition agents.

Cathodic polarisation measurements are done and from the analysis of shape of polarisation curves, the definite conclusions regarding dependence of cathodic polarisation on these variables have been drawn. The attempts have also been made to correlate the cathodic polarisation with the nature of deposits.

1. Concentration of complexing agent

During formation of nickel ammoniacal acetate complex, ammonium acetate acts as a complexing agent as discussed in (sec.3.3   ). under the mechanism. By the formation of complex, the course of the cathodic process is changed markedly. It is seen that with 2% nickel sulphate (simple bath) the cathodic polarisation is comparatively small (cf. Table 4.2.3) and the deposits obtained are non – adherent and black. However on switching from simple to complex bath, it is observed that the cathodic polarisation increases to considerable extent (cf. Graph 4.2.4) and the deposits are smoth and fine grained.
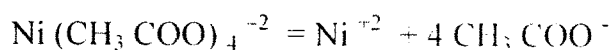
The above mentioned effect of complexing agent can be explained as follows–

Our results indicate that the formation of complex in the solution shifts the equilibrium potential of the metal in the negative direction, by reducing the concentration of its free lions. Here the instability constant for the complex can be given as

$$Ni(CH_2 COO)_3{}^- = Ni^{2-} + 3CH_3 COO^-$$

$$Kinst(1) = \frac{a_{Ni}{}^{-2} \times a^3{}_{CH_3COO}}{a_{Ni(CH_3COO)}{}^3}$$

OR

$$Ni(CH_3 COO)_4{}^{-2} = Ni^{-2} + 4 CH_3 COO^-$$

$$Kinst(2) = \frac{a_{Ni}{}^{+2} \times a^4{}_{CH_3COO}{}^-}{a_{Ni(CH_3COO)}{}^{-2}}$$

The instability constant characterizes the ability of the complex to dissociate with recovery of the intial ions Ni^{+2} and thus determines their equilibrium concentration.

$$a_{Ni}{}^{+2} = Kinst(1) \times \frac{a_{Ni(CH_3COO)}{}^3}{a^3{}_{CH_3(COO)}{}^-}$$

OR

$$a_{Ni}{}^{+2} \quad Kinst(2) \times \frac{a_{Ni(CH_3COO)}{}^{-2}}{a^4{}_{CH_3COO}}$$

The fraction of Ni^{+2} ions present in the solution depends on the value of instability constant. Lower the instability constant, lower will be the fraction of free Ni^{+2} ions present in the solution. Consequently lower the free Ni^{+2} ions concentration in solution, shift of reversible electrode potential in the negative direction will be greater. As a result more voltage is necessary to deposit metal ions or in short cathode polarisation increases.

It is observed that the appearance of nickel complexes in solution affects not only the magnitude of overpotential, but also the nature of the deposit.
On switching from simple to complex electrolyte, the overpotential increases which results in decrease of grain size of the deposits. The tendency towards the formations and growth of densities in suppressed and the deposits obtained are fine grained, smooth and quite satisfactory.

Further our observations (of Graph 4.2.3) indicate that for a given CD (1 A / sq. dm), cathodic polarisation increases with increase in concentration of complexing agent.(ammonium acetate). It may be because, with increase in concentration of ammonium

acetate, the concentration of ions in the solution increases. Thus, the dissociation of the complex is suppressed, which further lowers free metal ion concentration (common ion effect).

$$a_{Ni}^{+2} = Kinst\,(1)\ X\ \frac{a_{Ni\,(CH_3COO)_2}}{a^3_{CH_3COO}}$$

or

$$a_{Ni}^{+2} = Kinst\,(2)\ X\ \frac{a_{Ni\,(CH_3COO)_4}^{-2}}{a^4_{CH_3COO}}$$

TABLE NO.4.2.1 <u>CATHODIC POLARISATION</u>

OPTIMUM CONDITION BATH: –VIDE –SUPRA-TABLE NO. 3.6

OBS. NO.	C.D. A/Sq.dm.	CATHODIC POLARISATION Volt
1	0.00	0.000
2	0.25	0.710
3	0.5	0.742
4	1.0	0.812
5	1.5	0.878
6	2.0	0.920
7	2.5	0.960
8	3.0	1.060
9	3.5	1.120

TABLE NO.4.2.2 <u>CATHODIC POLARISATION</u>

2% NICKEL SULPHATE (SIMPLE BATH)

TEMPERATURE-25 ^{0}C

OBS. NO.	C.D. A/Sq.dm.	CATHODIC POLARISATION Volt
1	0.0	0.000
2	0.25	0.543
3	0.5	0.575
4	1.0	0.590
5	1.5	0.648
6	2.0	0.700
7	2.5	0.730
8	3.0	0.808
9	3.5	0.850

CATHODIC POLARISATION OF
SIMPLE BATH & OPTIMUM CONDITION
GRAPH NO.4.2.1
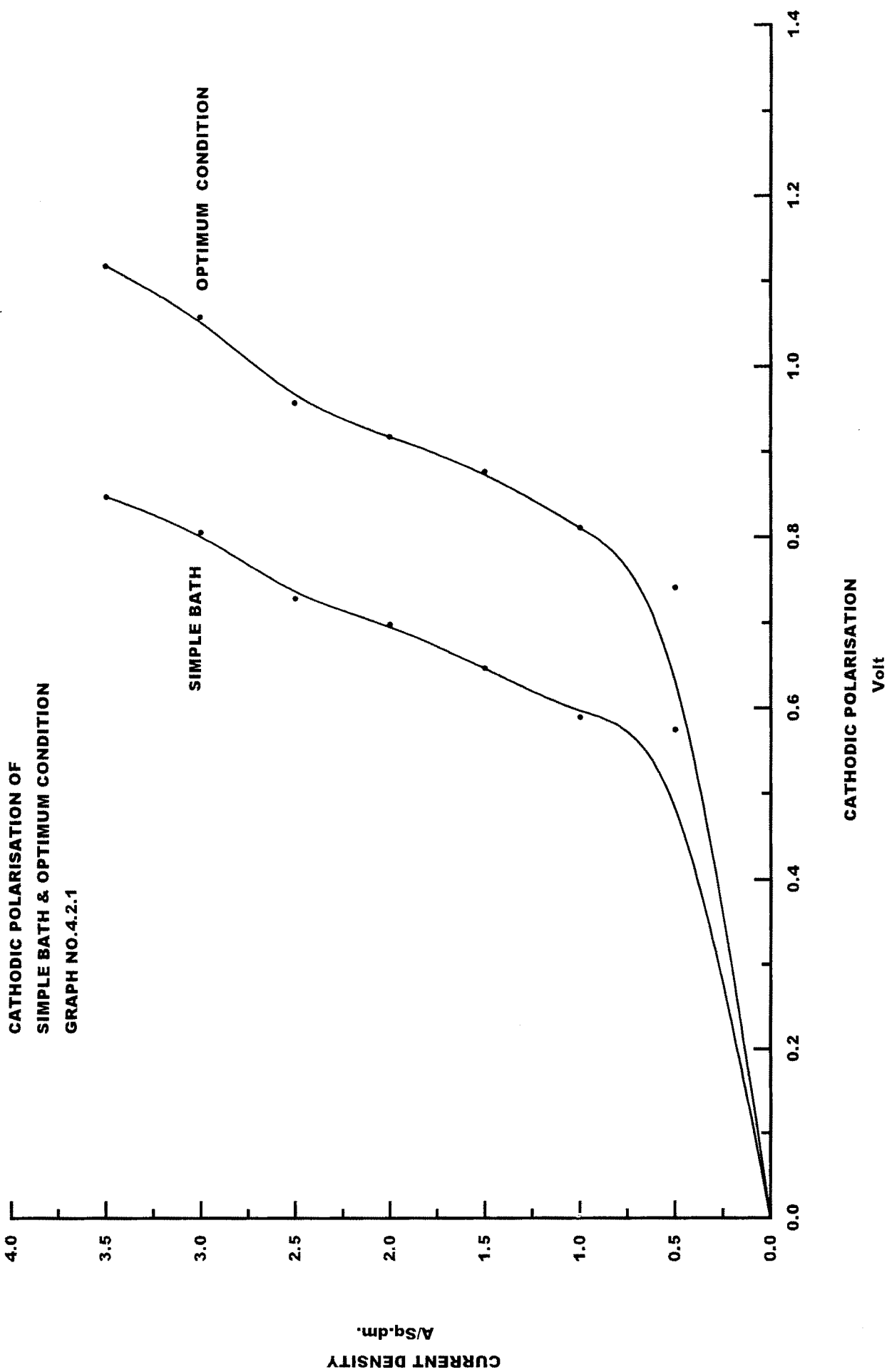
The equilibrium potential thus shifts again in the negative direction. increasing cathode overpotential.

From our observations (Table No.3.2 Graph No.3.2) it is clear that with increase in the concentration of ammonium acetate, nature of the deposit improves. It may be because cathode polarisation increases with increase in the concentration of ammonium acetate. It affects the throwing power of the bath in such a way that greater the slope of the polarisation curve (i.e. the more nearly horizotal), better is the throwing power, which results in the production of finer grained deposits. The quantitative test for throwing power has been carried out. as described in sec. 2.10 (Chapter – II).

However. at very high concentration of complexing agent (36%). although cathodic polarisation is high. the deposits obtained are not satisfactory.

At high concentration of ammonium acetate, the cathode polarisation is also high hence there is impoverishment of metal ions near the cathode at high concentration of ammonium acetate, as a result no depoits are obtained at very high concentration of ammonium acetate (33%). The overall process results in obtaining black, non – satisfactory deposit. with evolution of gas.
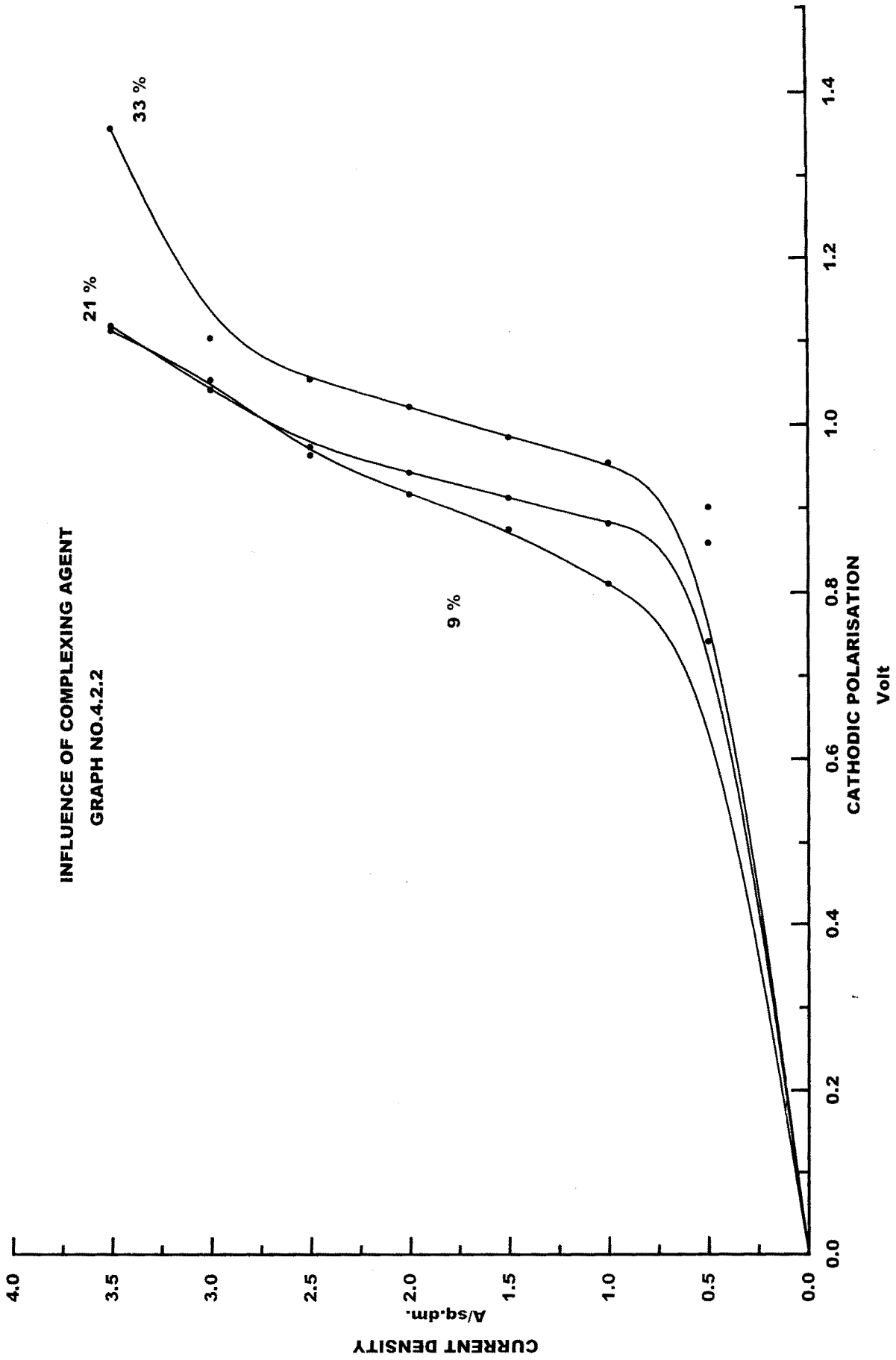
In the past, it was supposed that deposits from complex baths had finer grain structure than those from simple salt baths: because the concentration of free ions is low. But it is now known that fine grained deposits from complex baths are mainly due to the effect of adsorbed complex ion on the cathode. during deposition process (54 - 56). Further due to the adsorbed free ligand on the cathode, the cathode polarisation increases.

The same theory may be extended further. The complex formed is negatively charged (Ni $(CH_3 COO)_3$ $^-$ or Ni $(CH_3 COO)_4$ $^{-2}$ as a result a diffusion layer rapidly builds up during cathodic deposition. so that there is significant contribution of concentration overpotential to the total overpotential. All these effects raise activation overpotential and in particular. the concentration overpotential. as observed in the electrodeposition from this complex bath.
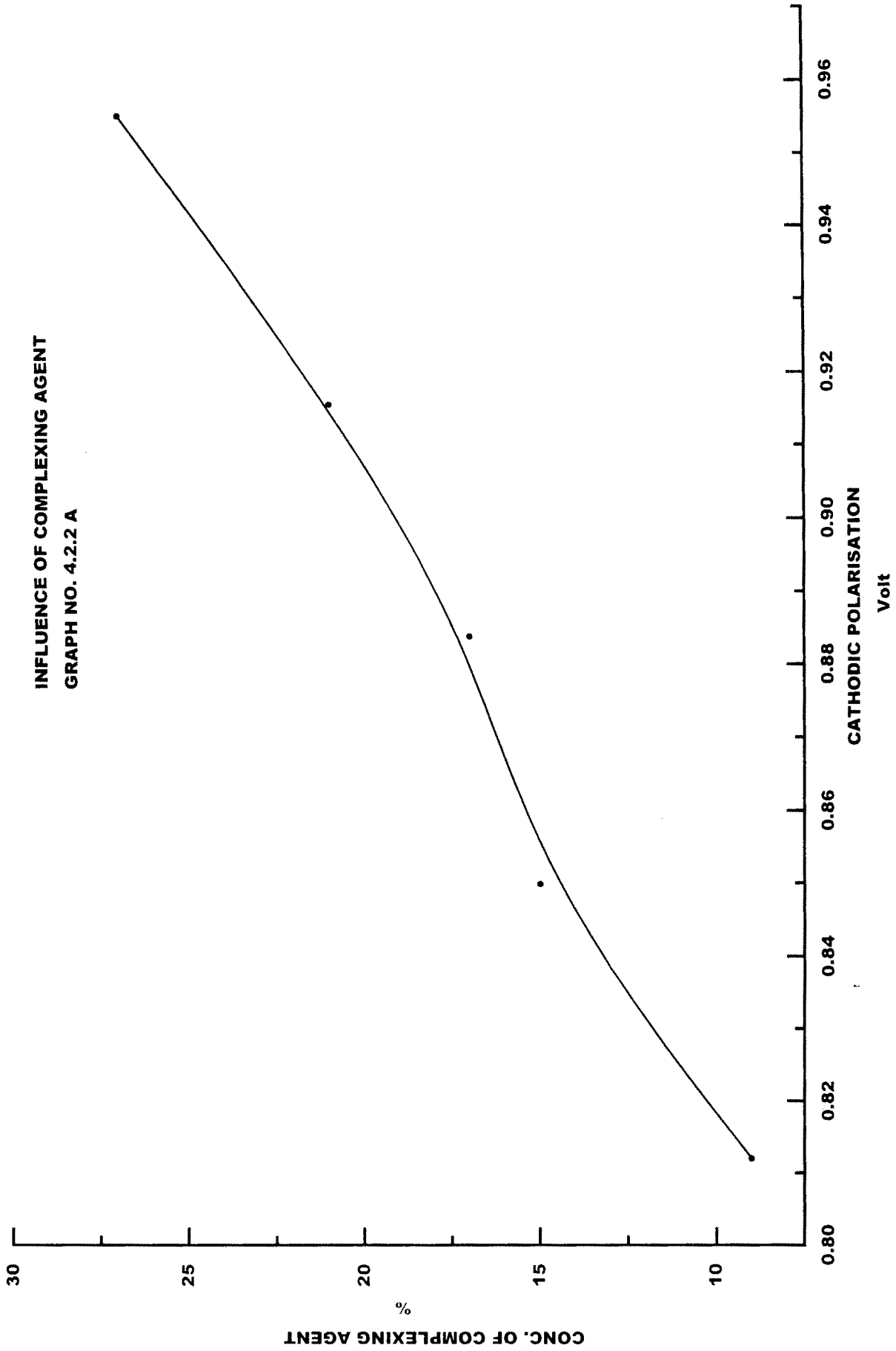
TABLE NO.4.2.3 CATHODIC POLARISATION

INFLUENCE OF COMPLEXING AGENT (AMMONIUM ACETATE)

OBS.	C.D.	CATHODIC POLARISATION Volt				
NO.	A/Sq.dm.	CONC. OF COMPLEXING AGENT %				
		9	15	21	27	33
1	0.0	0.000	0.000	0.000	0.000	0.000
2	0.5	0.742	0.812	0.860	0.880	0.902
3	1.0*	0.812	0.850	0.884	0.916	0.956
4	1.5	0.878	0.892	0.915	0.950	0.998
5	2.0	0.920	0.936	0.946	0.992	1.026
6	2.5	0.968	0.980	0.990	1.038	1.066
7	3.0	1.060	1.056	1.065	1.080	1.120
8	3.5	1.120	1.122	1.135	1.150	1.165

* OPTIMUM CONDITION

INFLUENCE OF COMPLEXING AGENT
GRAPH NO.4.2.2

33 %

21 %

9 %

CATHODIC POLARISATION
Volt

CURRENT DENSITY
A/sq.dm.

4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4

INFLUENCE OF COMPLEXING AGENT
GRAPH NO. 4.2.2 A

CONC. OF COMPLEXING AGENT

%

CATHODIC POLARISATION

Volt

From the aforesaid discussion. it appears doubtful to accept the adsorption of a negatively charged ligand $(CH_3COO)^-$ on the – vely charged cathode : however it may be justified. if we suppose. that the – vely charged ligand. in the form of an ion – pair with the +ve metal ion. which holds the former. may get adsorbed as a hole.

2) pH –

The pH of the bath solution is varied from 6 to 8. The results are presented in Table No.4.2.4 and graphically shown in Figs. 4.2.3 and 4.2.3 A .it is seen that CCE is less than hundred percent. This clearly shows that the current is used in processes other than metal deposition. In aqueous solution. simultaneous discharge of H^+ ions along with the metal ions leads to decrease the H^+ ion concentration near the cathode and thus the pH on the cathode film becomes higher compared to that in the body of the solution.

With variation in pH of the solution from 6.0 to 8.0 the pH near the cathode film becomes less. hence the CCE should increase. This is observed upto the pH 7.00, above which the CCE decreases to considerable extent.
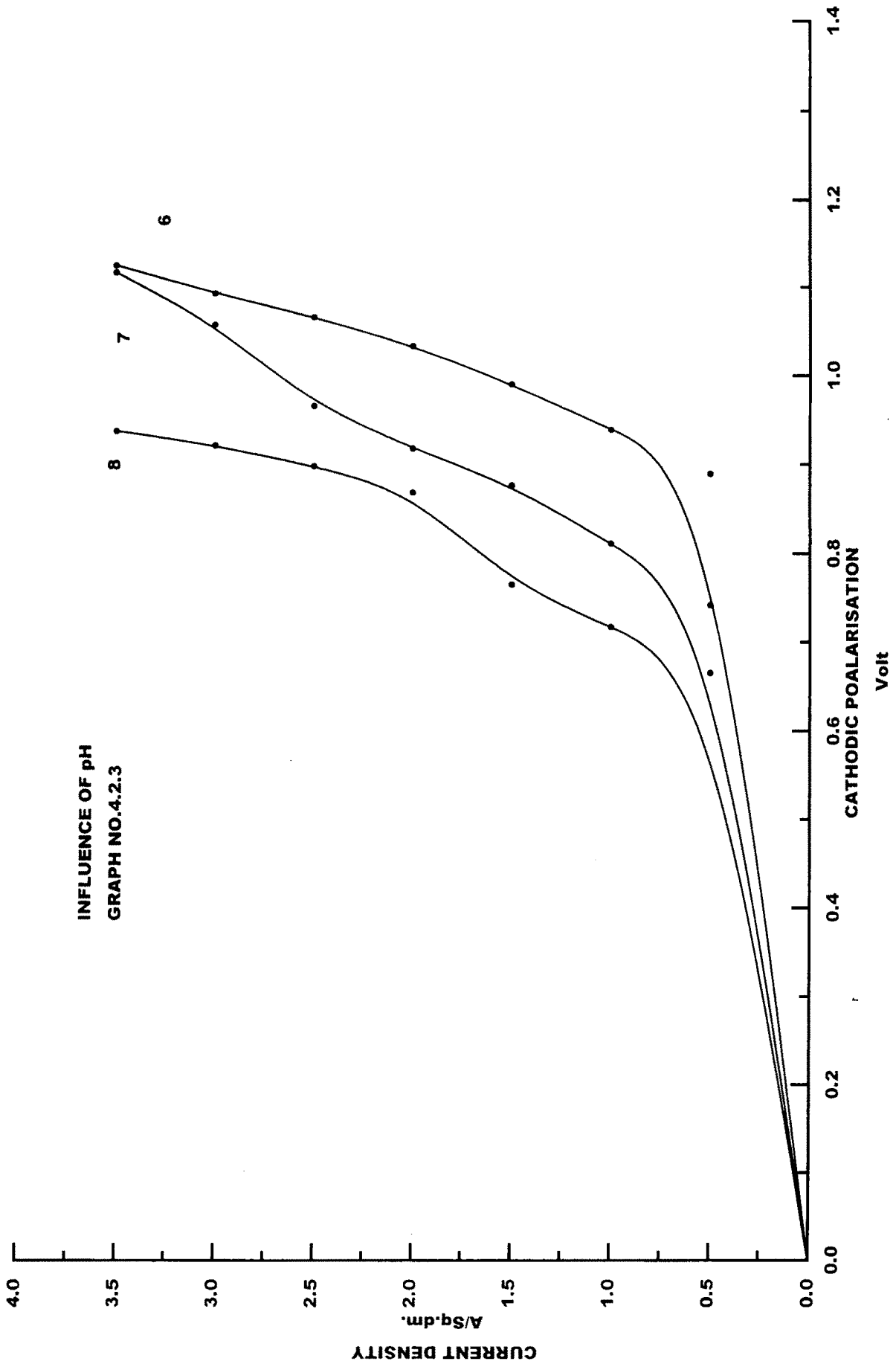
At constant C.D. viz. the optimum value for deposition (1.00 A/sq. dm.) the polarisation is seen to decrease from 0.940 at pH of 6.00 to 0.718 at the pH of 8.00. This becomes obvious from aforesaid reason viz. decrease in H^+ ion concentration near the cathode film affects its simultaneous discharge. Alternatively. the decrease in polarisation may be attributed to the adsorbed acetate ion with the metal ion, on the cathode as postulated in sec. 3.3 . In absense of the adsorbed ions, the polarisation would have remained the same in line with observations of S. Glasstone (57).

The result in Table No.3.3 for a sudden drop in C.C.E. from about 73.07 to 54.12 of special interest.This may be attributed to simultaneous discharge of NH_4^{4+} ions in the form of ammonia gas near the cathode as bath is more basic along with metal deposition.The deposits are also unsatisfactory.The decrease in polarisation from 0.726 to 0.718 at constant C.D. may be due to reasons other than simultaneous gas evolution .such as deposition of subsequently formed acetate ions ,a process using part of the energy.
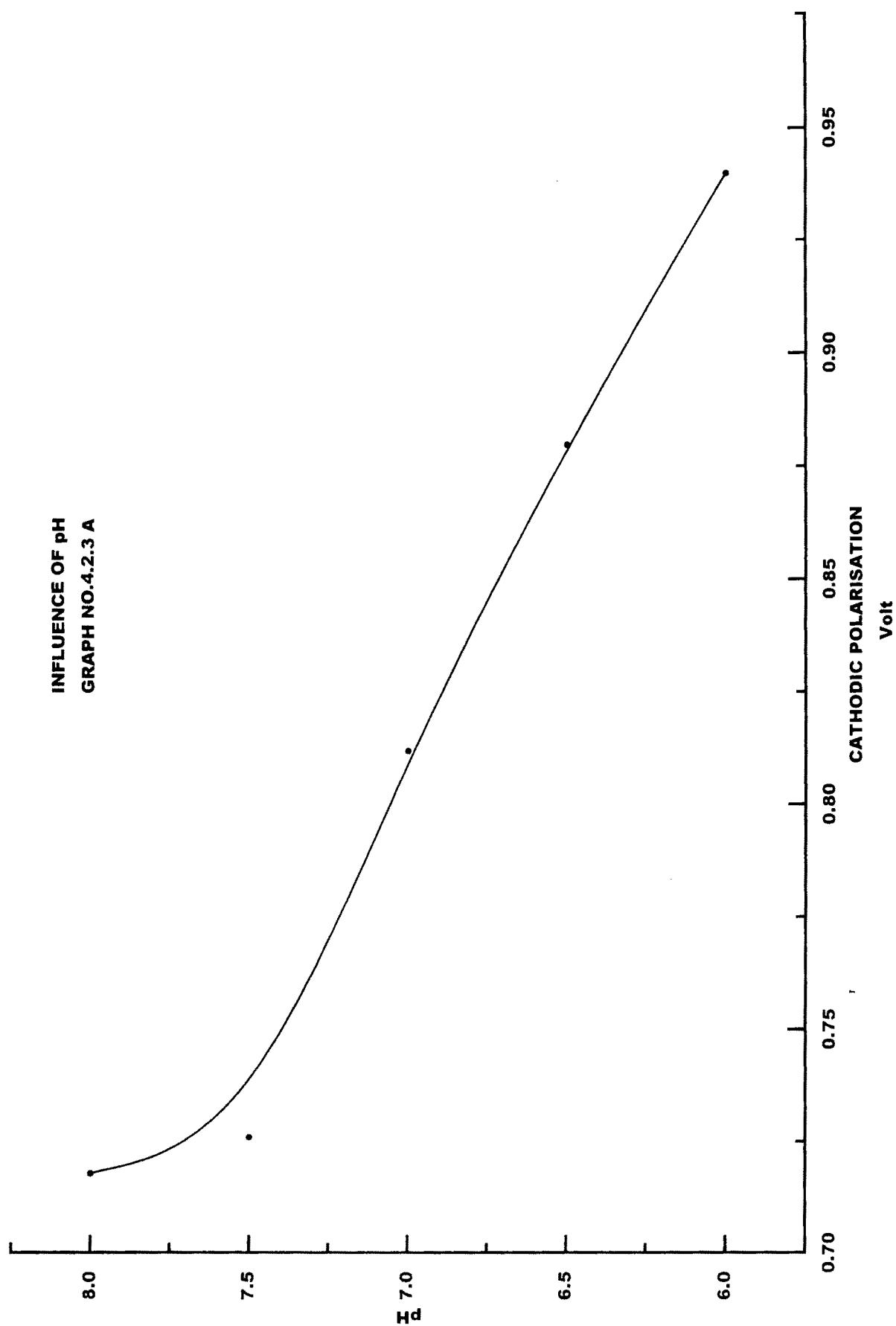
TABLE NO.4.2.4   <u>CATHODIC POLARISATION</u>

<u>INFLUENCE OF pH</u>

OBS.	C.D.	CATHODIC POLARISATION				Volt
NO.	A/Sq.dm.	pH OF BATH SOLUTION				
		6.0	6.5	7.0	7.5	8.0
1	0.0	0.000	0.000	0.000	0.000	0.000
2	0.5	0.890	0.824	0.742	0.694	0.666
3	1.0*	0.940	0.880	0.812	0.726	0.718
4	1.5	0.992	0.926	0.878	0.788	0.766
5	2.0	1.035	0.952	0.920	0.844	0.870
6	2.5	1.068	0.978	0.968	0.890	0.900
7	3.0	1.096	0.992	1.060	0.900	0.924
8	3.5	1.128	1.026	1.120	0.938	0.940

* OPTIMUM CONDITION

INFLUENCE OF pH
GRAPH NO.4.2.3

CURRENT DENSITY
A/Sq.dm.

CATHODIC POALARISATION
Volt

INFLUENCE OF pH
GRAPH NO.4.2.3 A

CATHODIC POLARISATION
Volt

pH

3) Temperature –

The temperature of the bath was varied from 5^0 to 45^0 c. to study the effect of temperature on cathodic polarisation. The results are summerised in Table No. 4.2.5 and graphically shown in Figs.4.2.4 and 4.2.4 A. From the results it is seen that, with increasing temperature from 5^0 to 45^0 C. the cathodic polarisation is decreased from 0.830 to 0.690 at an operating C. D. viz. 1 A/sq. dm., which was kept constant.

Temperature in general. has two opposing effects. In the first place, it increases the C.C.E. with improvement in nature of the deposit and in the second place, it gives a course and rough deposit at higher temperatures. Polarisation is decreased with increase in temperature.
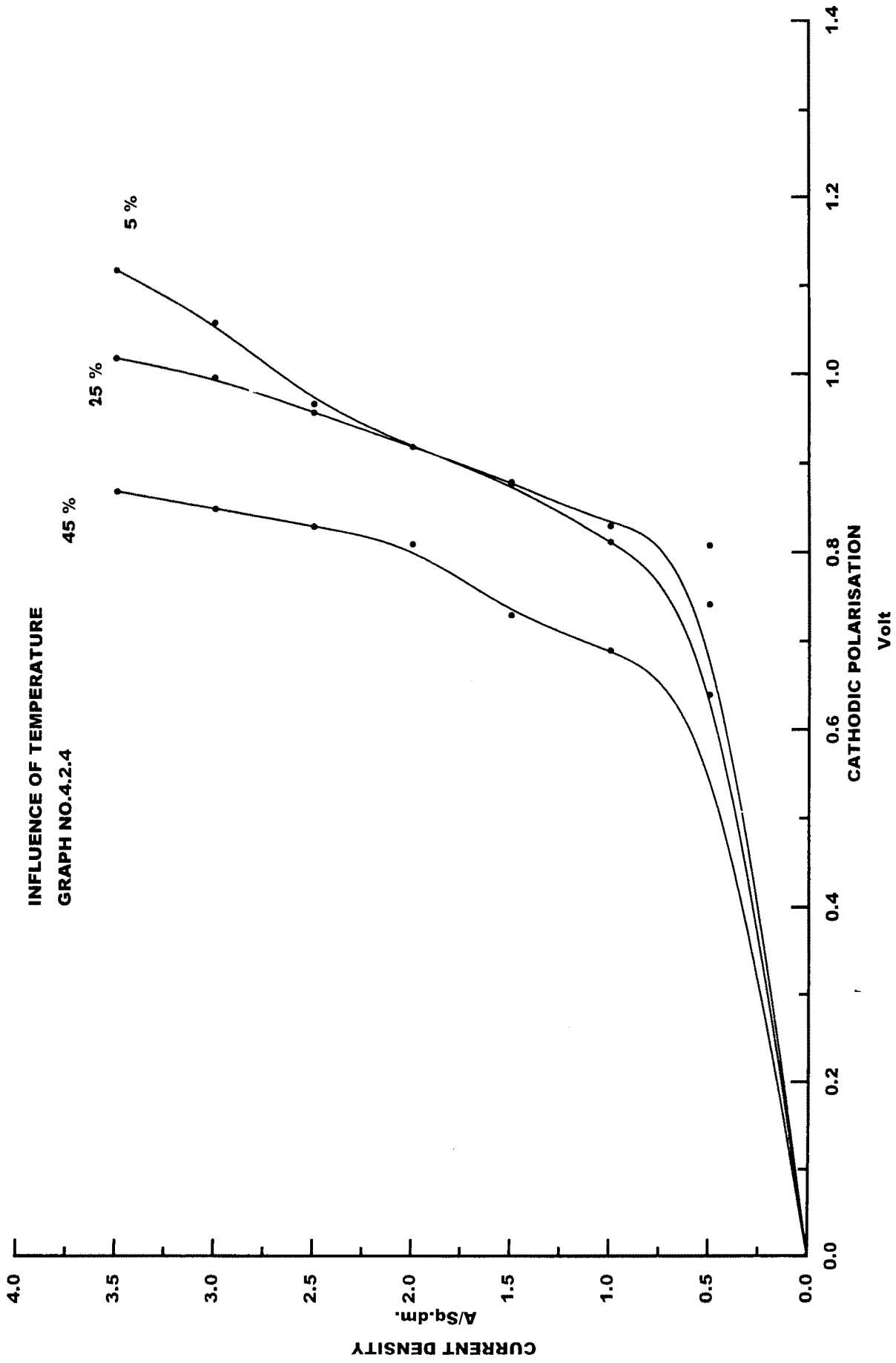
In electroplating. one has to make a compromise between the desired CCE of the process and the nature of the deposit. The latter is governed by two process viz., the rate of nucleation and the velocity of crystallisation, both of which are temperature dependent. Tmax for the rate of nucleation is lower than that for the crystal growth. Hence at lower or moderate temperatures. the rate of nucleation exceeds the rate of crystal growth. So that fine grained deposits are obtained. whereas at high temperatures the rate of nucleation drops and the velocity of crystallisation of a few nuclei is favoured. So that rough and coarse deposits result. Also the fact that polarisation decreases. seems to affect the nature of the deposit. which becomes unsatisfactory in line with general observations.
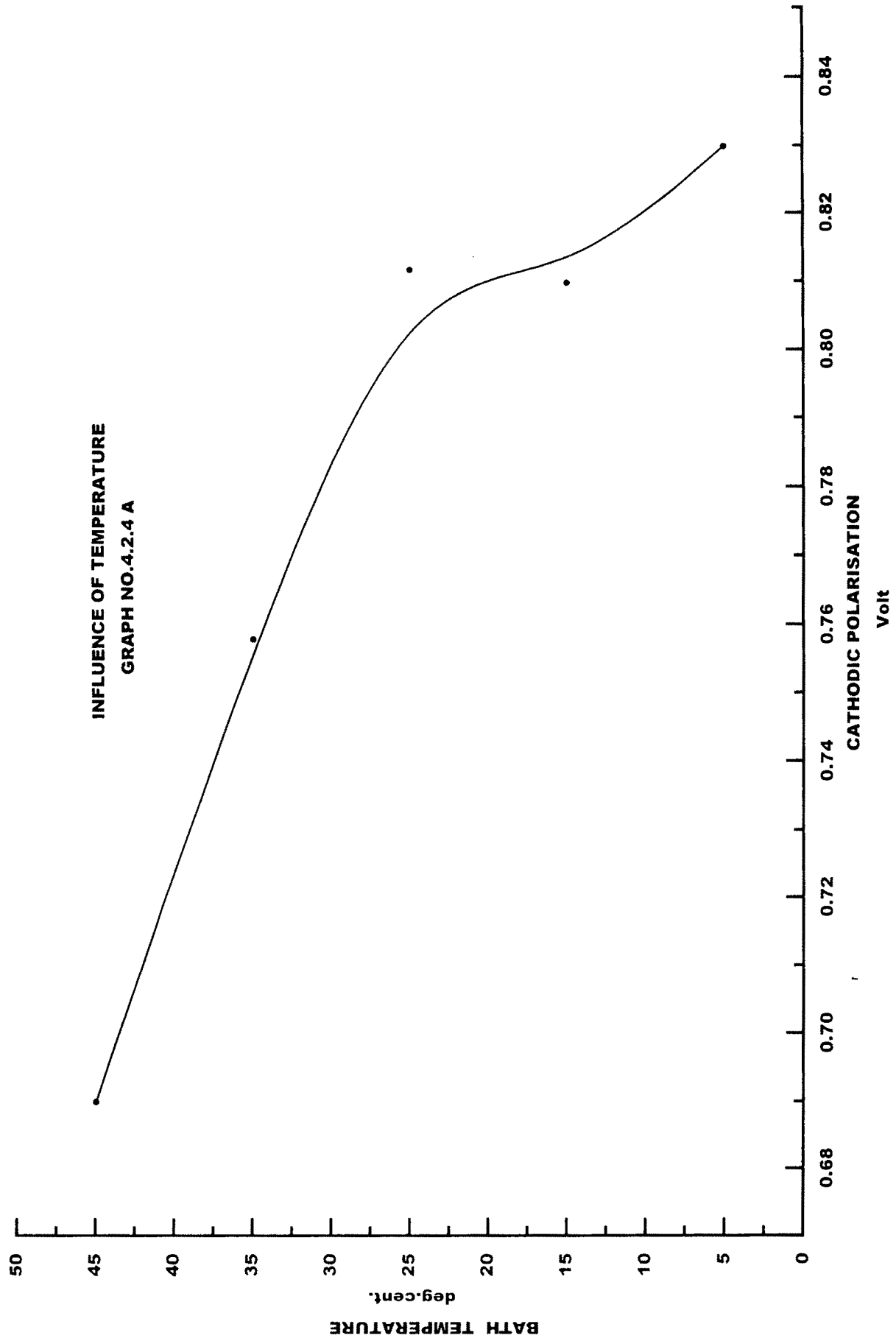
The decrease in polarisation and subsequent increase in CCE with increase in temperature may be ascribed to increase in ionic mobilities. which increases the rate of diffusion of metal ions. Polarisation is regarded as an irreversible phenomenon and as such the laws of thermodynamics may be ignored and the electrode processes may be explained on the basis of laws of chemical kinetics. Thus. with increase in temperature. the rate of deposition increases with subsequent increase in CCE, Decrease in polarisation with temperature, also favours the rate of deposition i.e. CCE. Again the conspicuous feature of the bath is % CCE as well as polarisation remains same at 15^0 C. and 25^0 C. The nature of deposit is also moreover less same. Hence the bath can be operated over a wide range of temp. i.e. 15 to 25^0 C.

TABLE NO. 4.2.5 <u>CATHODIC POLARISATION</u>

<u>INFLUENCE OF TEMPERATURE</u>

OBS. NO.	C.D. A/Sq.dm.	CATHODIC POLARISATION Volt				
		TEMPERATURE ^{o}C				
		5	15	25	35	45
1	0.00	0.000	0.000	0.000	0.000	0.000
2	0.50	0.808	0.750	0.742	0.690	0.640
3	1.00 *	0.830	0.810	0.812	0.758	0.690
4	1.50	0.880	0.898	0.878	0.818	0.730
5	2.00	0.920	0.920	0.920	0.870	0.810
6	2.50	0.958	1.010	0.986	0.920	0.830
7	3.00	0.998	1.030	1.060	0.950	0.850
8	3.50	1.02	1.100	1.120	0930	0.870

* OPTIMUM CONDITION

INFLUENCE OF TEMPERATURE

GRAPH NO.4.2.4

5 %

25 %

45 %

CATHODIC POLARISATION

Volt

CURRENT DENSITY

A/Sq.dm.

INFLUENCE OF TEMPERATURE

GRAPH NO.4.2.4 A

BATH TEMPERATURE
deg.cent.

CATHODIC POLARISATION
Volt

5) Addition agents –

Various addition agents (Organic, Inorganic and Colloidal), listed in Table3.7, are added in traces in the bath. The effect of these addition agents on cathodic polarisation and on the nature of the deposits is studied in greater details. (Table 4.2.6 Graphs 4.2.5& 4.2.5 A)

The amounts of addition agents used in deposition work, are generally very small. A molecule of an addition agent, is sufficient, to affect many thousands of metal ions. In order to be effective, the additive must, in some way be adsorbed or be otherwise included in the deposit. The mechanism by which they exert their effect is not clear and in spite of much fundemental research, the development of an effective addition agent for a particular bath remains a purely empirical search. Recently, polarisatoin studies have shown that the elctro-crystallisation of nickel, apparently occurs in several steps and that on adsorbed species of nickel hydroxide is   formed as an intermediate and is consumed during electrodeposition (58,59). Addition agents appear to modify the rates of the electron transfer reactions.
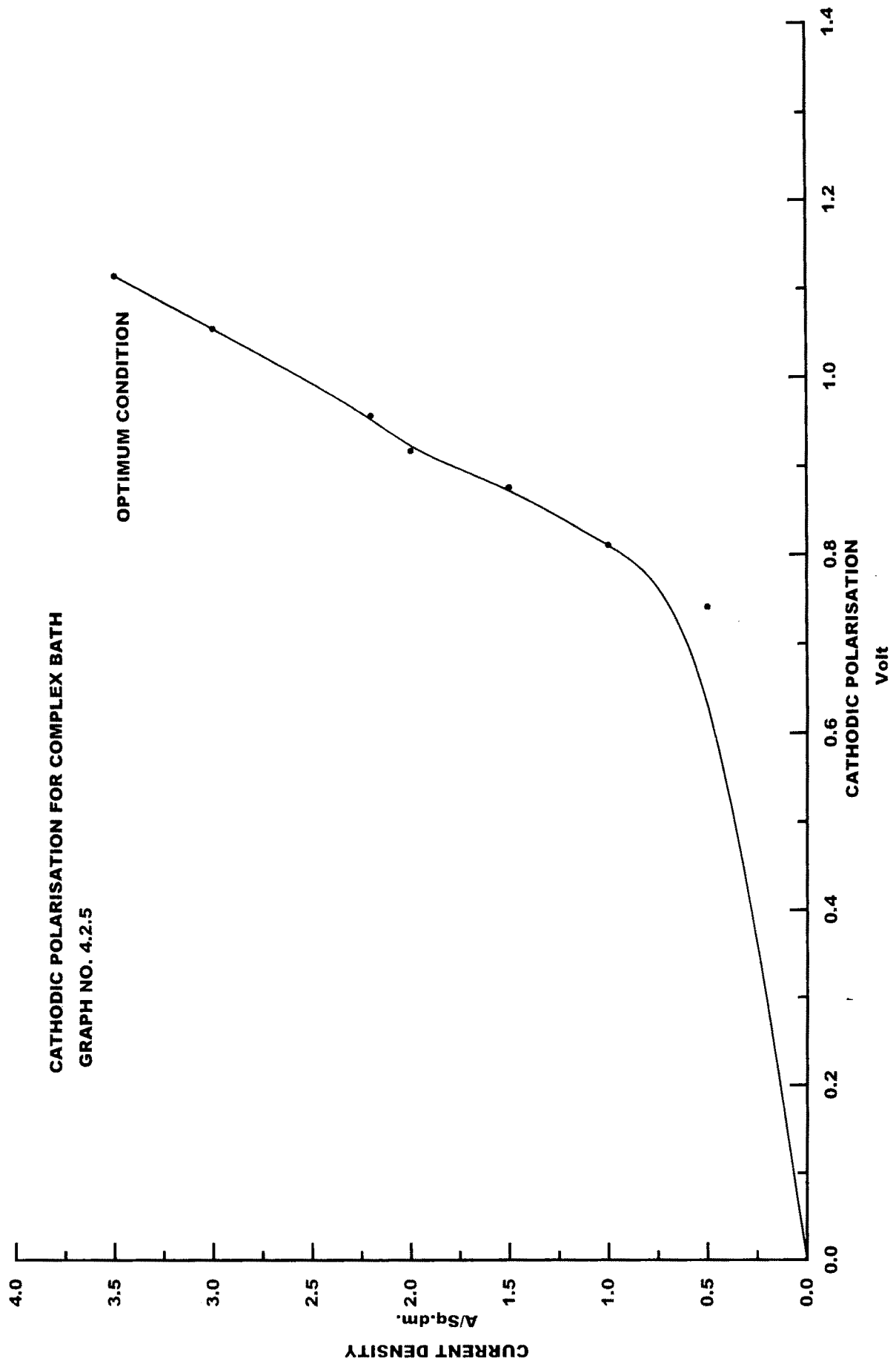
Addition agents have found rather wide use in plating industry. However, few comprehensive researches of a fundamental nature have been reported in this regard. Meyer and Phillips (6) made an electrochemical and crystallographic study of the effects of a number of foreign metal ions upon electrodeposition of copper. They found that where there was an increase in brightness, there was also an increase in cathode polarisation. Conversely depolarisation was coincident with a large crystal size in the plate. They also found that some of the cations that did not codeposit, had a decided effect on the structure of the plate and on the cathode polarisation.

Much work has been done on beneficial action of Organic and colloidal addition agents (60-62). The general conclusions drawn are that, these agents induce a finer grained deposit and that they increase polarisation in the process. Data obtained by us on this work indicate that number of addition agents give results in accordance with these conclusions.
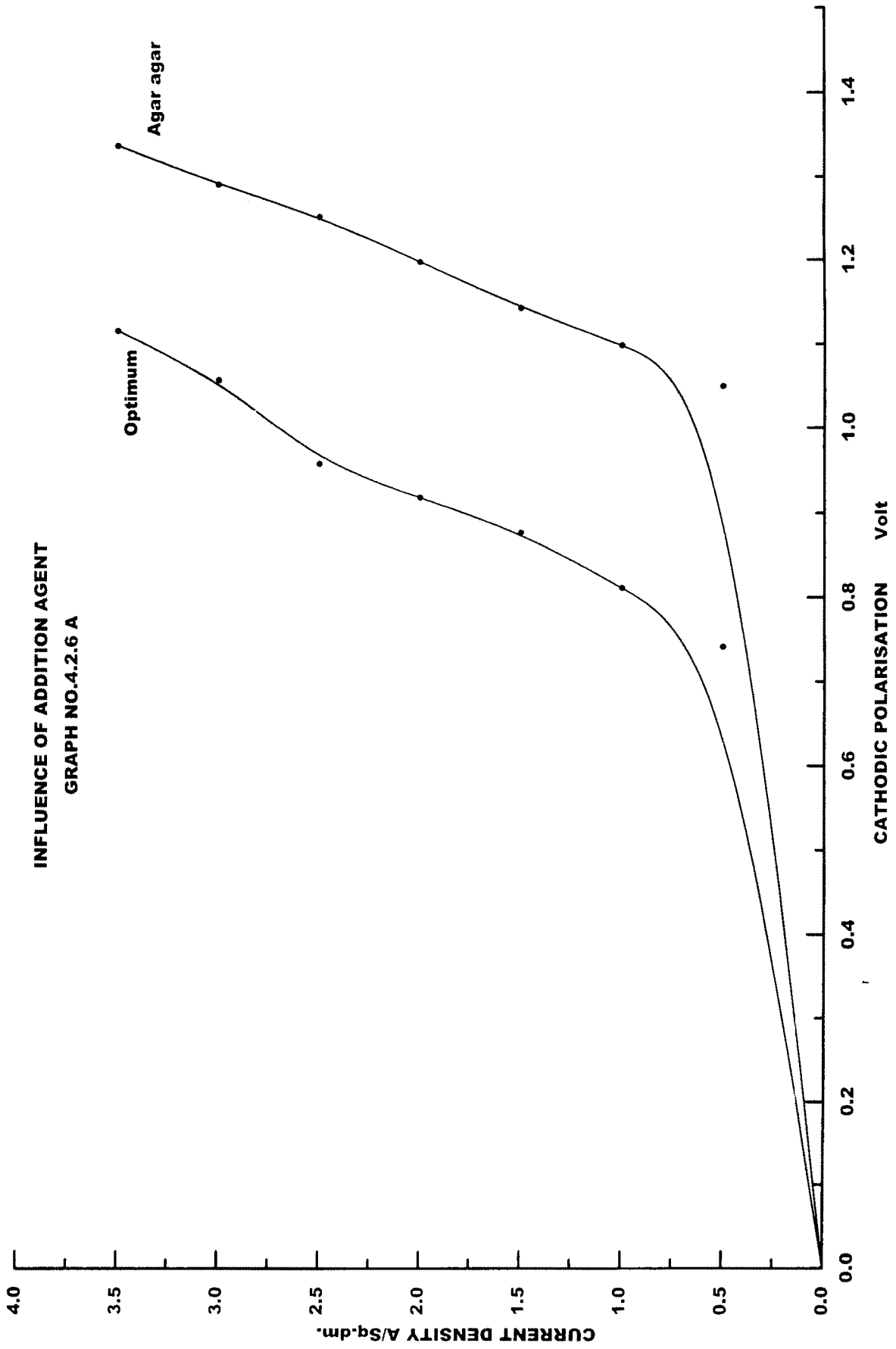
During our experiments, the values of cathodic polarisation versus current density were compared with the curve obtained in absence of the agent.

TABLE NO 4.2.6 CATHODIC POLARISATION
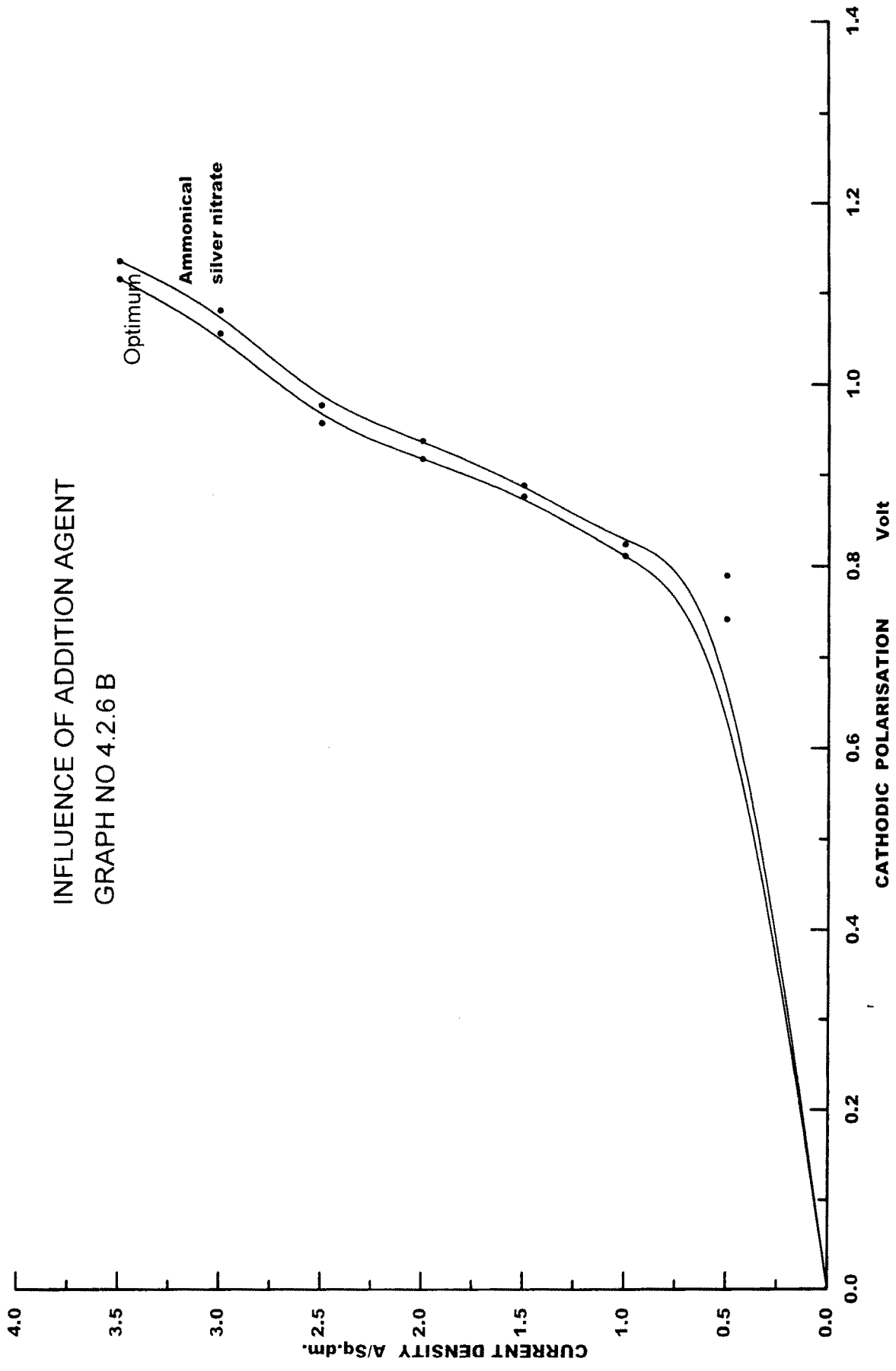## INFLUENCE OF ADDITION AGENTS
OPTIMUM CONDITION :-VIDE SUPRA TABLE NO. 3.6

Ob No	C.D A/sq. dm	CATHODIC POLARISATION VOLT						
		ADDITION AGENTS						
		Reference plate	Agar agar	Ammonical Silver nitrate	Ammonical salicylate	Urea	Glucose	Ammmo nical molybda te
1	0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	0.50	0.742	1.050	0.790	0.720	0.910	0.910	0.694
3	1.0	0.812	1.100	0.825	0.728	0.970	1.030	0.732
4	1.5	0.878	1.145	0.890	0.745	0.995	1.080	0.773
5	2.0	0.920	1.200	0.940	0.770	1.045	1.140	0.804
6	2.5	0.960	1.255	0.980	0.787	1.090	1.178	0.850
7	3	1.060	1.295	1.085	0.798	1.169	1.210	0.880
8	3.5	1.120	1.342	1.140	0.820	1.180	1.270	0.910

CATHODIC POLARISATION FOR COMPLEX BATH

GRAPH NO. 4.2.5

OPTIMUM CONDITION
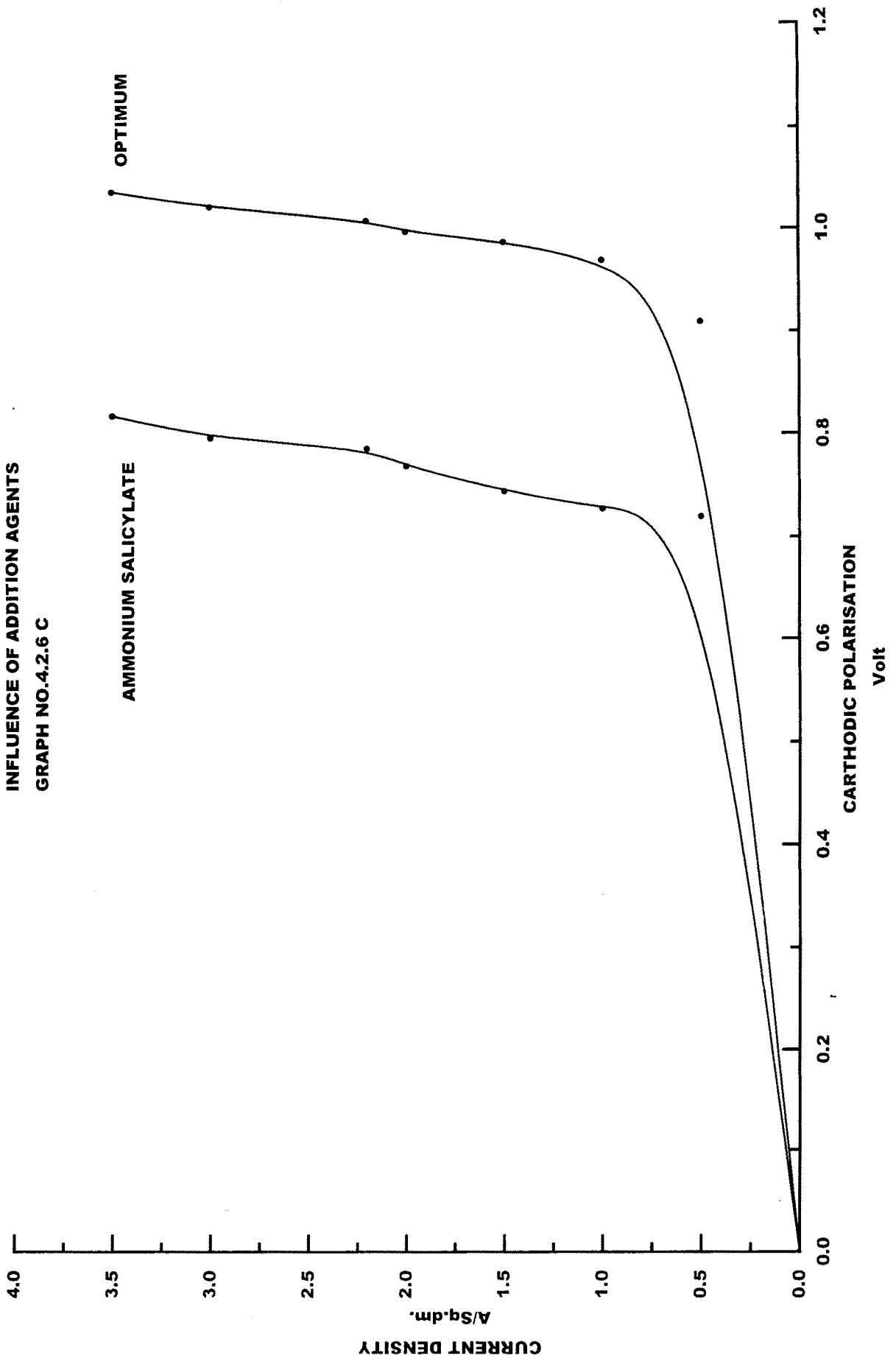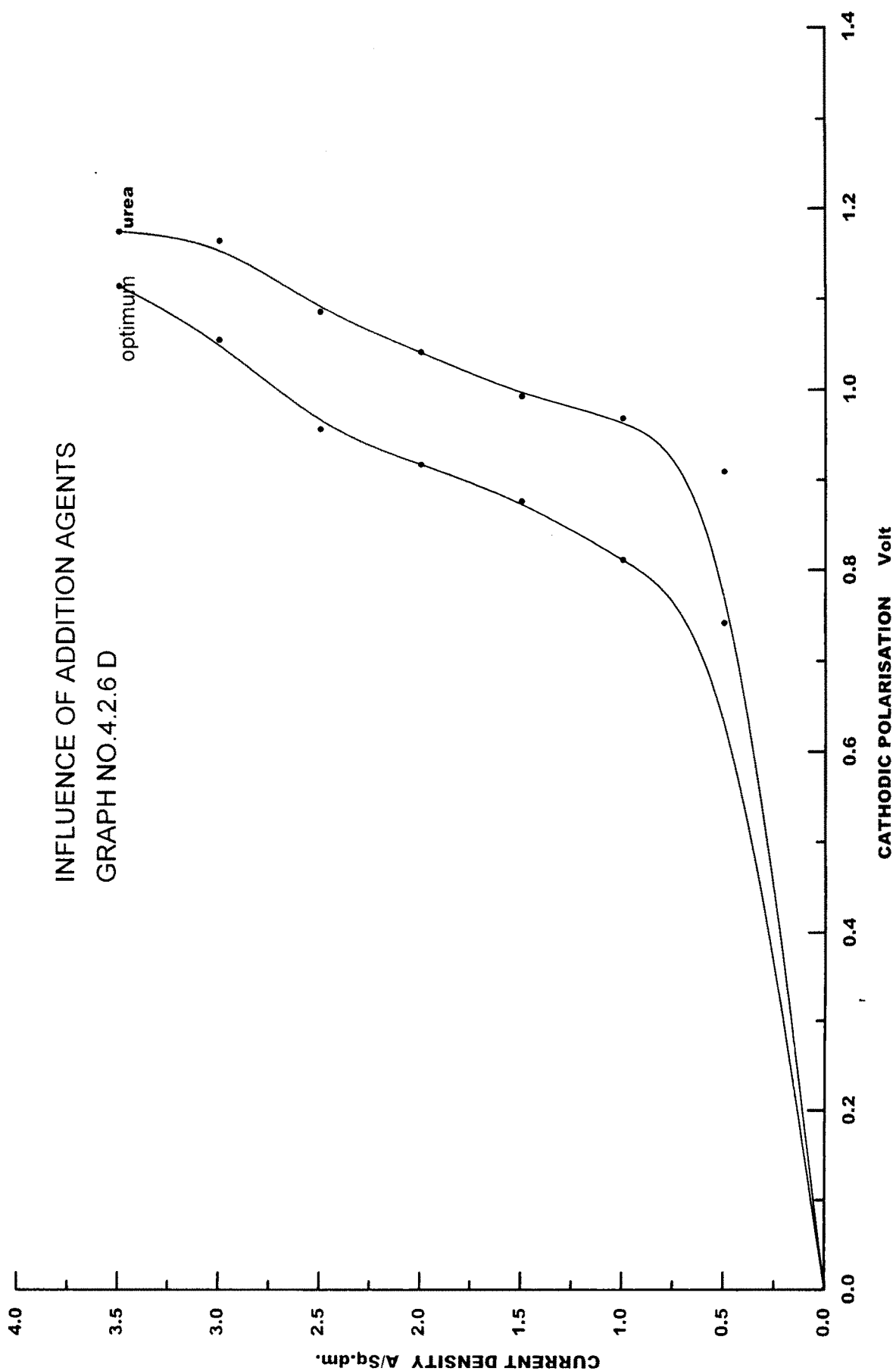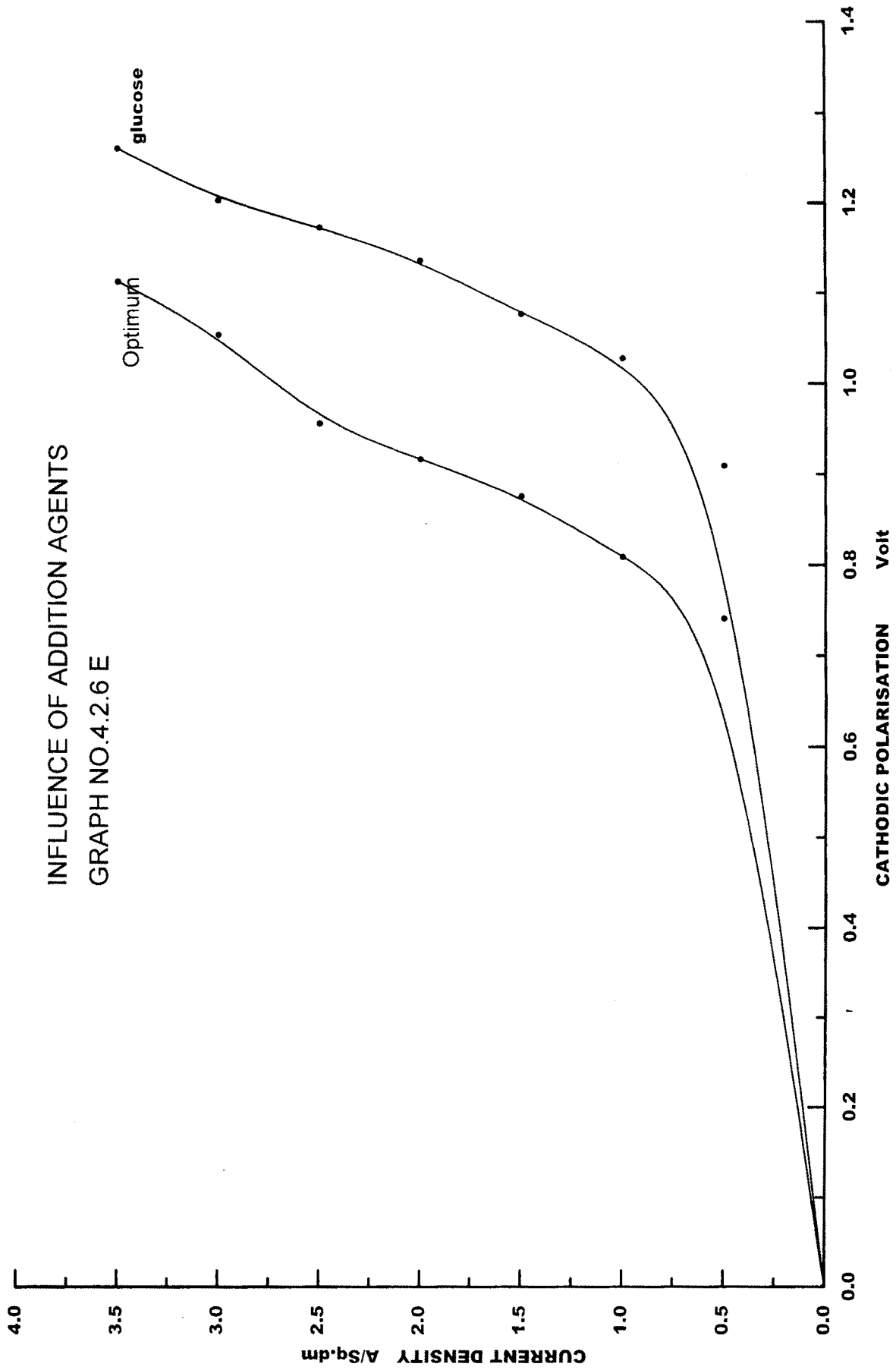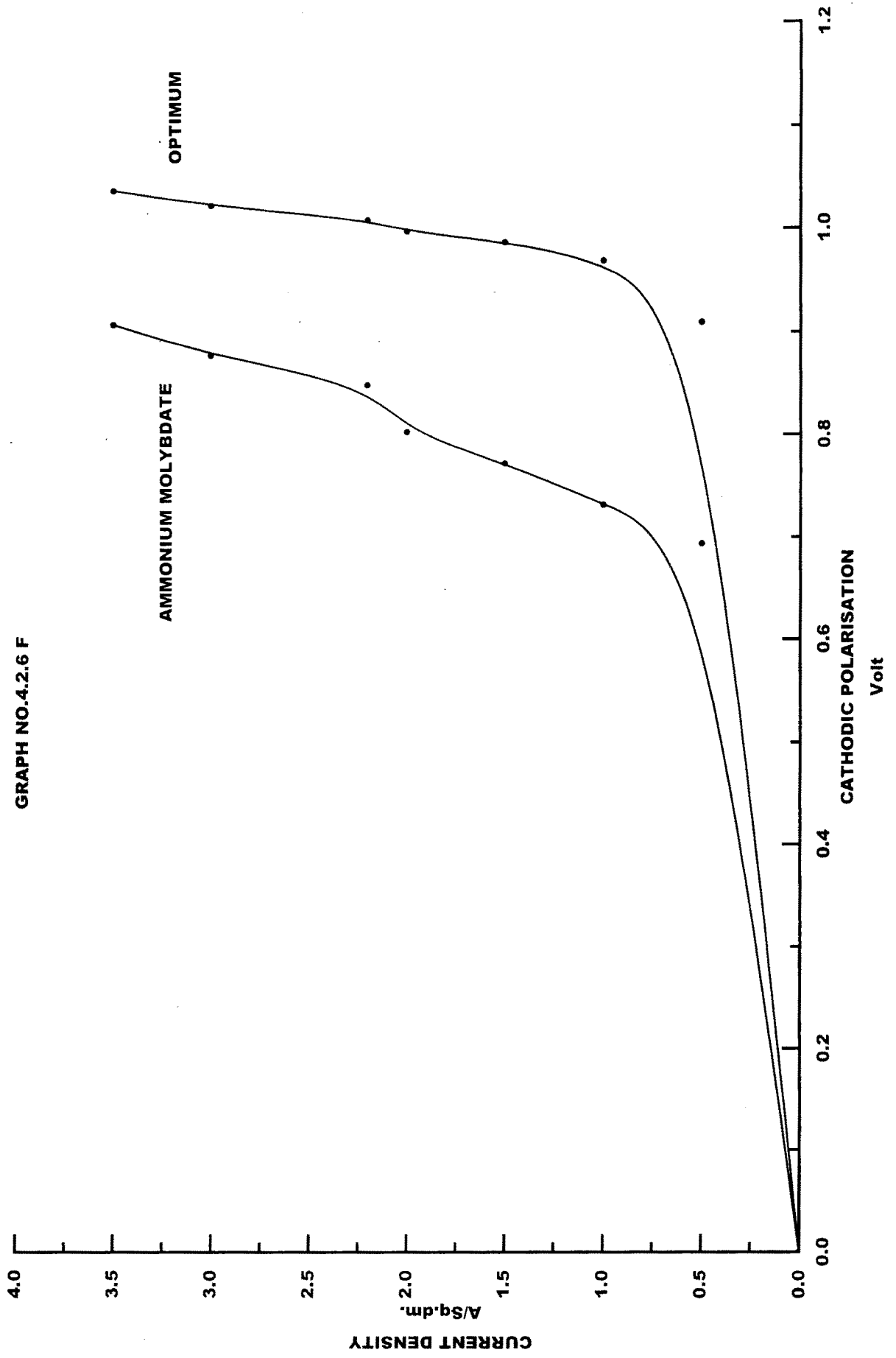
CATHODIC POLARISATION
Volt

CURRENT DENSITY

A/Sq.dm.

INFLUENCE OF ADDITION AGENT
GRAPH NO.4.2.6 A

INFLUENCE OF ADDITION AGENT
GRAPH NO 4.2.6 B

65

INFLUENCE OF ADDITION AGENTS
GRAPH NO.4.2.6 C

OPTIMUM

AMMONIUM SALICYLATE

CURRENT DENSITY
A/Sq.dm.

CARTHODIC POLARISATION
Volt

INFLUENCE OF ADDITION AGENTS

GRAPH NO.4.2.6 D

CATHODIC POLARISATION   Volt

CURRENT DENSITY A/sq.dm.

INFLUENCE OF ADDITION AGENTS
GRAPH NO.4.2.6 E

INFLUENCE OF ADDITION AGENTS
GRAPH NO.4.2.6 F

OPTIMUM

AMMONIUM MOLYBDATE

CATHODIC POLARISATION

Volt

CURRENT DENSITY

A/Sq.dm.

On the basis of the effect of addition agents on cathodic polarisation, they may be divided into four classes.

Class – 1 : It includes those addition agents which have no effect or very little effect on the polarisation curve as examplified by Ammonium silver nitrate. However although cathodic polarisation remains the same, throwing power of the bath solution increase to some extent as confirmed by the test (sec.2.10)

Class – 2 : The class contains those addition agents which displace the polarisation curves to moderate extent. Urea is included in this class. These addition agents usually make their own contribution to levelling. Further on the atomic scale, they may inhibit crystallographic growth. either by adsoption or by blanketing the whole surface. Thus, it favours the formation of new crystal nuclei on the metal surface, leading to deposit. ion with finer crystal structure.

Class – 3 : The addition agents such as Agar – Agar and glucose are included in this class. From our observations it is clear that Agar – Agar and glucose changes the slope of the polarisation curve to maximum. The large deviation in polarisation may be attributed to a change in the path of electrodeposition process from the normal one or a different step not known as yet, may be slowing down the rate of deposition.

Class – 4 : The addition agent. Ammonium – Molybdate and Ammonium salicylate are included in this class. It is observed that cathodic polarisation decreases considerably due to addition of these substances. Hence, instead of calling them as addition agents, they may be regarded as contaminants, Decrease in polarisation accelarates the growth of the nuclei which are already formed, and thus coarse deposits are obtained.

From the afored said discussion. it may be concluded that the action of addition agents is specific, depending on the nature of the bath solution.

4.3 CONCLUDING REMARKS ON ELECTRODEPOSITION OF NICKEL AND CATHODIC POLARISATION

The formation of complexes in solution affects not only the magnitude of overpotential but also the nature of cathodically formed deposits. Therefore deposits Obtained from simple bath (sulphate) are black non adherent for

nickel(Table no 4.2.2). However. on switching from simple to complex bath (ammonical acetate), the nature of deposits improved to marked extent with increase in cathode polarization (Table 4.2.6).

In the past. it was supposed that deposits from complex baths had finer grained structure than those from simple baths because ,the concentration of the free metal ions is low concept. the fine grained deposits from complex bath are due mainly to the effect of adsorbed complex ions on the cathode. during deposition process .Again from the mechanism of deposition ,it is seen that the complex formed is usually negetively charged .As a result there is a formation of a ionic sheet. It retards the discharging of metal ions near cathode. Therefore a higher overpotential is required for discharge process to occur.

Experimental data further indicates that the overpotentials also depends on the nature of the metal to be deposited .Threfore nickel gets deposited from ammonical acetate bath,comparitavely with higher overpotential. The reason may be hidden in the electrode-kinetics of this metal .The large value of overpotential for nickel is predominately caused by slow rate of the electrochemical step. From these points of view. all factors responsible for slow rate of the discharge step must diminished the relative roll of crystallisatior phenomenon and encourage the formation of uniform and fine grained deposits .