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ELECTRO-OXIDATION OF SILVER(I) SALTS IN THE PRESENCE OF POLYPYRIDYLS IN ACETONITRILE

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by

Mohammad Abu Anwer Usmani

The thesis is in submission for the degree of Doctor of Philosophy in The City University

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ABSTRACT

The electrochemical oxidation of solutions of silver(I) nitrate and silver(I) perchlorate in the presence of various polypyridyl ligands in acetonitrile was studied using the techniques of polarography and controlled potential coulometry. Tetra-n-butylammonium perchlorate was used as the supporting electrolyte. In the absence of ligand, silver(I) nitrate gave single oxidation wave which was found to correspond to the one-electron oxidation of the nitrate ion. In the presence of ligand, two oxidation waves were observed, the first of which corresponded to the one electron oxidation of silver(I) complex; this was confirmed by coulometric determinations. The second wave was thought to be associated with the catalytic oxidation of the ligand molecule.

A detailed polarographic study of the silver(I) nitrate/ 2,2'-bipyridyl system showed that the limiting current of the Ag(I)/Ag(II) wave was proportional to the concentration of the intermediate complex, $Ag(bipy)^+$; this was interpreted in terms of a kinetically controlled wave involving $Ag(bipy)^+$ as the precursor of the electroactive species.

Preparative scale electrolyses at controlled potentials corresponding to the first anodic wave of the silver(I)/polypyridyl systems were carried out, and several silver(II) complexes were isolated. In the case of silver(I) nitrate in the presence of 2,2'-bipyridyl and 4,4'-dimethyl 2,2'-bipyridyl, silver(II) complexes of the type $[AgL_2]NO_3.ClO_4$ were obtained. These ligands gave complexes of the type $[AgL_2](ClO_4)_2$ when silver (II) perchlorate was used as the source

of Ag(I). Silver(I)/2,2',2''-terpyridyl systems yielded a silver(II) complex of the type $[AgL_2](ClO_4)_2$ irrespective of which silver(I) salt was used. Although coulometric studies established a one electron change for the first wave of the silver(I)/5,5'-dibutyl 2,2'-bipyridyl system, the resulting silver(II) was not isolated.

A preliminary study of electro-oxidation of Cu(II)/2,2'-bipyridyl and Ni(II)/2,2'-bipyridyl systems indicated that, in the case of Ni(II) oxidation to a higher oxidation state occurred. However, attempts to isolate the complex were unsuccessful.

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1. INTRODUCTION

The aim of the present work was to attempt to develop a method for the preparation of higher oxidation state complexes of transition metals using electrochemical techniques. Methods which have been employed successfully for organic electrochemical oxidations in non-aqueous solvents are reviewed by Weinberg and Weinberg;[1] these include controlled potential electrolysis at potentials corresponding to specific oxidation steps determined by anodic polarography. In the present work this technique has been applied to the oxidation of transition metal salts in the presence of complexing ligands.

A particular advantage of electrochemical oxidation processes compared to conventional chemical methods is that, in principle, they are highly specific. Further, the maximum anodic potential which can be used in a particular system is limited only by the oxidation potentials of the electrode material, the solvent system, and the supporting electrolyte. Isolation of the products of an electrochemical oxidation requires only the removal of the solvent and supporting electrolyte, whereas in a chemical oxidation, any excess of oxidant and its reduction products are also present.

Anodic polarography in the present work was carried out using a rotating platinum electrode (R.P.E.) first described by Nernst and Merriam[2] and further investigated by Laitinen and Kolthoff.[3] This indicator electrode has many advantages over the dropping mercury electrode normally used in conventional polarography. The standard reduction poltential of the Hg_2^{2+} / Hg couple in aqueous solution is 0.79 V vs. S.H.E. which severely limits its anodic range; whilst the value of 1.20 V vs. S.H.E. for the standard reduction potential of the

Pt^{2+}/ Pt couple would appear to offer no great advantage in this respect, the rate of oxidation of platinum is very slow, and the electrode can be satisfactorily used at potentials well in excess of 3.00 V in acetonitrile. The R.P.E. provides a very thin diffusion layer as a result of rapid rotation and gives about a twenty-fold increase in diffusion current compared to the D.M.E. and stationary electrodes, hence reliable data can be obtained at low concentrations of electroactive species. Furthermore, stable diffusion conditions are far more rapidly attained at the R.P.E. Although the R.P.E. has the disadvantage that it often gives less well defined and less reproducible polarographic waves than the D.M.E., this is out-weighed by the advantages it offers, particularly with regard to its application to anodic polarography. A comparative study of platinum and graphite electrodes has been reported by Lord and Rogers[4] where it was observed that graphite electrodes generally gave less well-defined waves, especially when the electrodes were rotated. However stationary graphite electrodes did offer an advantage over platinum electrodes for studying the oxidation of organic compounds which form inert, non-conducting films.

The solvent system chosen for the present study was acetonitrile, which is extremely resistant to oxidation, with tetra-n-butylammonium perchlorate as the supporting electrolyte. The anodic limit of this system is of the order of 3.2 V vs S.H.E. The use of this solvent system as a preparative medium for higher oxidation state species has obvious advantages over an aqueous medium for which the anodic limit is only of the order of 1.0 V. Anodic polarographic studies of iron (II) and copper (I) at a R.P.E. in acetonitrile have been reported by Kolthoff and Coetzee.[5]

Controlled potential electrolysis in the present work was carried out at a rotating macro-platinum anode using a three compartment cell [6] in which the electrolysis products were contained in separate compartments. The rotating macro-electrode reproduced as near as possible the conditions in the polarographic cell in which the rotating micro-electrode was used. The quantity of electricity passing during electrolysis could be measured to give the number of electrons per molecule involved in the anodic reaction.

Ideally, a useful procedure for studying the electrochemical oxidation of a particular transition metal compound is to determine, first, by polarography the number of oxidation steps which occur within the anodic range of the solvent system. The electron change per molecule in each step can then be determined by controlled potential coulometry at the half-wave potential corresponding to each step, thus providing information which might help to identify the electrode reactions taking place. In principle, controlled potential electrolysis can then be carried out on a preparative scale to give the required product. In order to develop this technique it was decided to study the electrochemical oxidation of silver (I) salts in the presence of polypyridyls, since these ligands are known to give well characterised complexes of silver (II). Further, there was the possibility that silver (II) might be oxidised to the less common silver (III) at high anodic potentials. Although electrochemical preparations (as well as chemical oxidation methods) have been described for silver (II) polypyridyl complexes, controlled potential methods have not been employed and no polarographic data are available.

It was hoped to extend the study to the electrochemical oxidation of nickel (II) and copper (II) complexes where oxidation to the (III) state is extremely difficult to achieve. However, because of the detailed study which the silver (I) polypyridyl systems required, it was possible to carry out only a preliminary investigation of the electro-oxidation of certain nickel (II) and copper (II) complexes. The literature survey, therefore, has been restricted to a discussion of studies of higher oxidation compounds of silver.

2. LITERATURE SURVEY

Higher Oxidation State Compounds of Silver

Silver, an element of the second transition series and member of group IB of the Periodic Table, has the outer ground state electronic configuration $4d^{10}5s^{1}$. Although copper ($3d^{10}4s^{1}$) and gold ($5d^{10}6s^{1}$) of the same group have similar electronic configurations and ionisation potentials to silver, there are few similarities between the three elements and no simple explanations for many of the differences. Thus, whereas silver (I) is the most stable and common oxidation state of silver and silver (I) ions are stable in aqueous solution, the dipositive oxidation state is the most important for copper, copper (I) ions being unstable in aqueous-solution (disproportionating into metallic copper and stable copper (II) ions). Unlike copper (II), silver (II) exists mainly in complex compounds, only one binary silver (II) compound (silver difluoride) having been characterised. The aquated silver (II) ion is unstable. The chemistry of gold, on the other hand, is quite dissimilar to that of copper and silver; gold (II) is virtually unknown and in aqueous solution gold (I) disproportionates into metallic gold and gold (III), an oxidation state common for gold but difficult to achieve in copper and silver.

Interest in higher oxidation state compounds of silver was first centered on oxide systems. As early as 1804, Ritter[7] obtained a black crystalline powder at the anode when an electric current was passed through a neutral aqueous solution of silver nitrate. It was considered to be a peroxide of silver since oxygen was evolved on heating. Analysis of the product by several workers[8 - 12] established the stoichiometry of

the compound as Ag_7NO_{11} which was formulated $2Ag_3O_4AgNO_3$ by Tanatar[9] and given the name, "silver peroxynitrate". The decomposition of "silver peroxynitrate" was found to yield oxygen, silver nitrate and an oxide of composition AgO, formulated as silver peroxide (Ag_2O_2) by Watson.[10] The reaction was written

$$Ag_7NO_{11} \longrightarrow 3Ag_2O_2 + AgNO_3 + O_2 \qquad (1)$$

Other so-called peroxy-salts such as "silver peroxysulphate"[8] and two "peroxyfluorides" of different composition[9] were also prepared by the same electrolytic method. It was soon realised[12] that "silver peroxide" was not, in fact, a peroxide since it did not reduce lead dioxide, manganese dioxide or potassium permanganate, nor did it give hydrogen peroxide with acids. Consequently, it was considered to be silver (II) oxide, AgO, until its more recent formulation by McMillan[13] as a silver (I) - silver (III) mixed oxide ($Ag_2O\ Ag_2O_3$). The "peroxy-salts" are now described as argentic oxysalts and formulated[13] as $Ag(Ag_3O_4)_2\ X$ ($X = NO_3$, ClO_4, F etc.) in which the Ag_3O_4 structure is regarded as a silver (II) - silver (III) mixed oxide system.

Silver (II) oxide has been prepared directly by chemical oxidation of silver (I) salts by potassium peroxodisulphate[14 - 17] or sodium hypochlorite[18,19] in an alkaline medium. It has also been prepared by oxidation of silver (I) salts by fluorine[20] and ozone[21] and by treatment of silver (II) complexes with boiling water.[22] Oxidation in neutral or acid solution generally gives rise to argentic oxysalts.[23, 24]

Physicochemical investigations have also been used to establish the existence of higher oxidation states of silver. Luther and Pokorny[25] determined current-voltage curves for the oxidation of a silver anode in

both alkaline and acidic solutions. In alkaline solution, it was found that silver was oxidised in two steps, first to Ag_2O, and, then to AgO, whereas in acid solution it was claimed that the oxidation proceeded to silver (III) oxide, Ag_2O_3; the reduction potentials for the Ag (III)/Ag (II), Ag(II)/Ag(I) and Ag(I)/Ag(O) couples were quoted as 1.57 V, 1.41 V and 1.17 V respectively. These results have been confirmed by many subsequent workers.[26 - 28] Luther and Pokorny[25] also observed three steps in the reduction of argentic oxynitrate and inferred that the Ag_2O_3 was probably present in this compound.

An extensive study of the oxidation of silver nitrate with ozone in concentrated nitric acid solution has been carried out by Noyes et al.[21] The oxidation led to the formation of a black soluble argentic nitrate which attained a steady concentration. Kinetic data for the oxidation reaction at 0^oC suggested the formation of an oxygenated silver (III) species (AgO^+) as an intermediate according to the following scheme.

$$Ag^+ + O_3 \longrightarrow AgO^+ + O_2 \text{ (slow)} \qquad (2)$$

$$AgO^+ + Ag^+ + 2H^+ \rightleftharpoons 2Ag^{2+} + H_2O \text{ (rapid equilibrium)} \qquad (3)$$

This reaction scheme accounts for the establishment of a steady concentration of Ag^{+2}, further evidence of a silver (III) intermediate resulting from the precipitation of a mixture of AgO and argentic oxynitrate, when solutions of Ag^{+2} were neutralised. The standard reduction potential of the system Ag(II)/Ag(I) was determined by Noyes et al.[29] from measurements of the potential of a platinum electrode in a solution of silver (I) and silver (II) nitrates in 1 - 2N nitric acid against a standard hydrogen electrode; it was found to be 1.914 ± 0.002 volts. The high value of

this standard potential compared to that of the H_2O_2/H_2O couple was used by Noyes to support his hypothesis that the decomposition of bipositive silver by water with the evolution of oxygen proceeds by the slow formation of H_2O_2 and its instantaneous reaction with Ag^{+2} according to the equation

$$H_2O_2 + 2Ag^{2+} \longrightarrow O_2 + 2Ag^{+} + 2H^{+} \qquad (4)$$

Since the standard reduction potential of the Ag^{2+}/Ag^{+} couple is 1.91 V and that of H_2O_2/H_2O in acid solution is 1.77 V, the reaction

$$2H_2O + 2Ag^{2+} \longrightarrow 2Ag^{+} + H_2O_2 + 2H^{+} \qquad (5)$$

is thermodynamically feasible.

The standard reduction potential for the system Ag(II)/Ag(I) was found to be 2.0 volts in 4N $HClO_4$.[30] Which is slightly higher than the value in nitric acid solution. Further, the colour of Ag^{2+} solutions in a perchloric acid medium is pink whereas nitric acid solutions are black-brown; in sulphuric acid and condensed phosphoric acid solutions, the colours are greenish black[10] and pink-purple[31] respectively. These observations can be explained on the assumption that bipositive silver exists in solution mainly in the form of an anionic complex. The formation of anionic complexes of Ag^{2+} in strongly acid media is further supported by the fact that silver was shown to migrate to the anode when solutions of silver (II) oxynitrate in concentrated nitric acid were electrolysed.[32] Later workers have demonstrated that silver (II) is stable in strongly acid solutions but disproportionates into Ag(I) and Ag(III) in alkaline solutions in agreement with equation (3). McMillan and Smaller[33] have shown that when AgO is dissolved in nitric acid

solution, all the silver is present in the bipositive oxidation state, whilst although AgO is only slightly soluble in alkaline solution,[34] it reacts, in the presence of coordinating ligands such as periodate,[35] to form stable silver (III) complexes.

Oxidation of silver (I) in condensed phosphoric acid, studied by chronopotentiometry and cyclic voltammetry,[31] has shown that Ag (II) and possibly Ag (III) are produced. It was found that, in this medium, the Ag (II) was much more stable than in other acidic media and a reduction potential for the Ag(II)/Ag(I) couple was determined as 2.01 V (vs. S.H.E.)

More recent work on silver oxide systems has stemmed from their use in storage batteries. Casey and Moroz[37] reported the electrochemical formation of Ag_2O_3 when sheet silver metal was anodically oxidized at 15 mA/Cm^2 at - 40°C in a KOH - H_2O eutectic mixture. If the temperature was higher or if a lower current desnity was used, only AgO was obtained. Kazakevich et al.[38] also obtained Ag_2O_3 at a relatively high current density. Dirkse[36] has shown that the anodic oxidation of silver in alkaline solution gave first Ag_2O and then AgO followed by the formation of Ag_2O_3 when excess of charge was passed.

Anodic oxidation of smooth silver metal in 12 M potassium hydroxide solution at a current density of 70 mA/Cm^2, resulted in the formation of a soluble silver (III) species,[39] which was shown to be $Ag(OH)_4^-$ by a polarographic method involving the variation of half-wave potential with ligand concentration.

Takehara[40] has studied the anodic oxidation of silver in alkaline solution at constant current density by observing the impedence and

potential changes after opening the cell circuit. It was concluded that the rate at which Ag_2O was formed during the first stage of the reaction was controlled by the rate of diffusion of Ag^+ and/or O^{2-} in the oxide layer, and that the rate of formation of AgO in the second stage was controlled by the crystallisation process of AgO on the Ag_2O surface.

The structure and composition of silver (II) oxide remained unresolved for many years. Several workers[41-43] showed that silver (II) oxide was weakly diamagnetic, a fact not in accordance with the expected d^9 arrangement for silver (II) and in contrast to the paramagnetism observed in other compounds containing silver (II) such as argentic oxynitrate[43] and many silver (II) complexes. This anomaly was first explained[43] in terms of silver-silver bonding in which the unpaired electrons of two silver atoms were paired together. McMillan[44, 13] finally resolved the problem of the structure of AgO by x-ray analysis which indicated that the compound was, in fact, a mixed oxide of silver (I) and silver (III), the coordination numbers of Ag^+ and Ag^{3+} being respectively 2 (linear) and 4 (planar). The existence of two kinds of silver atoms as well as their positions has been confirmed by Graff and Stadelmaier[45] and the neutron diffraction study of Scatturin et al.[46] McMillan[13] has also demonstrated that the crystal structure of argentic oxynitrate is consistent with the formulation $Ag(Ag_3O_4)_2\ NO_3$ where the silver atoms of the Ag_3O_4 structure are coordinated with four oxygens, in a square planar configuration, there being one Ag^{2+} ion and two Ag^{3+} ions per Ag_3O_4 occupying the same set of equivalent positions.

The only binary compound known in which silver is bipositive is silver (II) fluoride, AgF_2. It has been prepared as a dark-brown or black

solid by direct combination of the elements at 150° - 1300°C and by the action of fluorine or chlorine trifluoride on silver (I) chloride at 200°C.[47-50] The compound has also been obtained[51] as a yellow solid by heating powdered silver in a current of fluorine at 250°C. Silver (II) fluoride presents an interesting property of being ferromagnetic below 163°C and is the only magnetically dense argentic compound known. The heat of formation of AgF_2 was found to be 84.5 K cal./mole and its thermal stability is shown by the fact that it melts at 690°C without decomposition.[52]

Although binary compounds of silver (II) are rare, silver (II) exists in many complex compounds, particularly with ligands capable of π-bonding. Such complexes are commonly four-coordinated with the square planar arrangement expected for a d^9 system. In this respect, silver (II) resembles copper (II) although distorted octahedral complexes, which are common for copper (II) are rare in silver (II). The increase in stability of silver (II) when complexing takes place is reflected in the lowering of the reduction potential of the silver (II)/silver (I) couple from 1.91 volts (vs. S.H.E.) in nitric acid solution[29] to 1.45 volts in the presence of 2,2-bipyridyl.[53]

A number of silver (II) complexes with 2, 2-bipyridyl (bipy.) have been prepared[54] in the form of red crystals by oxidation of hot aqueous alcohlic solutions of silver nitrate with potassium peroxodisulphate. The following types of silver(II)/bipy. complexes were isolated, one having a coordination number of four and the other six

$[Ag(bipy)_2]X_2$ ($X = S_2O_8$ or $(HSO_4)_2$)

and $[Ag(bipy)_3]X_2$ ($X = NO_3$, ClO_3 or ClO_4)

A binuclear compound $[Ag_2(bipy)_5](S_2O_8)_2$ was also described.

Recently it has been suggested by Thorpe and Kochi[55] that the reported tris(bipy) silver (II) complexes[54] are in fact bis(bipy) complexes. These workers also isolated bis(bipy) silver (II) trifluoromethanesulphonate, $[Ag(bipy)_2](O_3SCF_3)_2$, by anodic oxidation of $[Ag(bipy)_2](O_3SCF_3)$ which was dissolved in water in the presence of excess trifluoromethanesulphonic acid, a current of 1 amp being passed for 20 minutes. The yield was 40% and the silver (II) complex decomposed at 200 - 210°C. Oxidation of the corresponding silver (I) complex was also carried out using AgO in aqueous acetonitrile solution at 0°C, the solution turning deep red in less than 1 minute.

In the preparation of silver (II) complexes, oxidizing agents such as lead dioxide, barium dioxide, and ceric oxide, which are not effective in oxidizing Ag (I) to Ag (II) in the absence of suitable ligand, have been used[56] as alternatives to potassium peroxodisulphate. A variety of silver (II) complexes of the type $[Ag(bipy)_2]X_2$ (X = NO_3, ClO_3 or ClO_4) have been prepared[57] by treating with ozone a solution containing bis(bipyridyl) silver (I) nitrate, $Ag(bipy)_2NO_3$, in the presence of the acid corresponding to the particular anion required and its sodium salt. The oxidation reaction was written

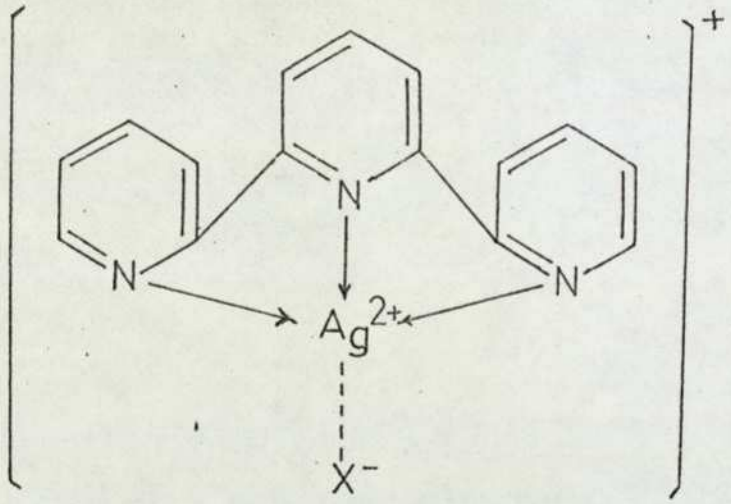
$$2\left[Ag(bipy)_2\right]^+ + 2H^+ + O_3 \longrightarrow 2\left[Ag(bipy)_2\right]^{2+} + H_2O + O_2 \qquad (6)$$

Barbieri[58] isolated $[Ag(bipy)_2]X_2$ (X = NO_3, ClO_4 or HSO_4) by anodic oxidation of the corresponding silver (I) compound at a current of 2 - 4 amp. in a divided cell.

The ligand, o-phenanthroline complexes strongly with silver (II). $[Ag(o\text{-}phen)_2]S_2O_8$ has been obtained[59] in quantitative yield from a solution of silver nitrate by oxidation with ammonium peroxodisulphate

in the presence of an excess of o-phenanthroline. From a solution of the complex peroxodisulphate in 64% nitric acid, the corresponding chlorate, perchlorate, nitrate, and bisulphate complexes were obtained by treatment with the appropriate alkali salt.

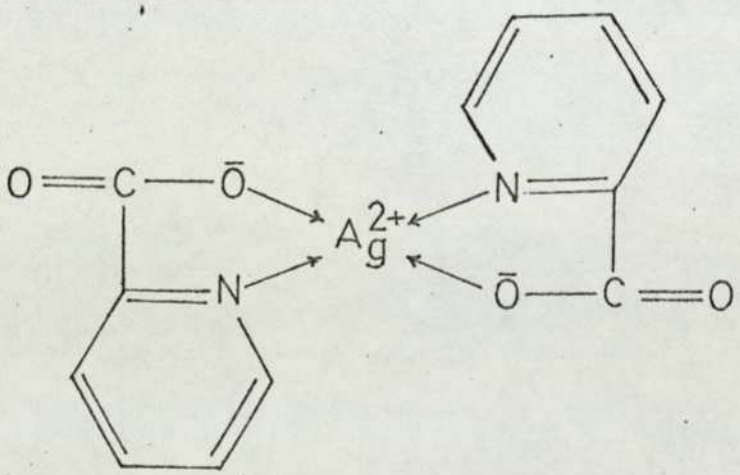
In the presence of dilute nitric acid, terpyridyl silver (I) nitrate, $Ag(terpy)NO_3$ is oxidized readily at the anode of an electrolytic cell with the formation of the corresponding silver (II) complex $[Ag(terpy)NO_3]NO_3$.[60] Aqueous solutions of this complex react by double decomposition with the corresponding anions, to yield the compounds $[Ag(terpy)X]X$ ($X = ClO_3$ or ClO_4) and $Ag(terpy)S_2O_8$. The structure of complexes of the type $[Ag(terpy)X]X$ was given as



Barbieri[61] isolated $[Ag(py)_4]S_2O_8$ by oxidizing an aqueous solution of silver (I) nitrate in pyridine using potassium peroxodisulphate as the oxidant, while the corresponding silver (II) complex containing the nitrate anion was prepared electrolytically from an aqueous pyridine solution. The compound was also obtained[62] in a small yield from an

anolyte composed of 8 - 10% silver nitrate and 40% pryidine. The persulphate complex of silver(II) crystallises as orange-coloured prismatic crystals, while the nitrate is reported to form orange-red needle shaped crystals.[61]

A very stable chelate complex of bipositive silver of the "inner metallic" type with picolinic acid (pyridine-2-carboxylic acid), $[Ag(C_6H_4NO_2)_2]$, was obtained by Barbieri[63] when silver nitrate solution was oxidized with potassium peroxodisulphate in the presence of excess of picolinic acid. The complex separated as sparingly soluble orange-red needles when the solution was rendered alkaline with sodium carbonate. It was also prepared by electrolytic oxidation. The complex is decomposed by hydrochloric acid with the evolution of chlorine and precipitation of silver chloride, whilst ammonia and hydrogen peroxide are oxidized with the evolution of N_2 and O_2 respectively. Cox et al.[64] have shown by x-ray analysis that the compound has a square planar configuration and is isomorphous with the copper (II) complex of the same ligand and is represented as

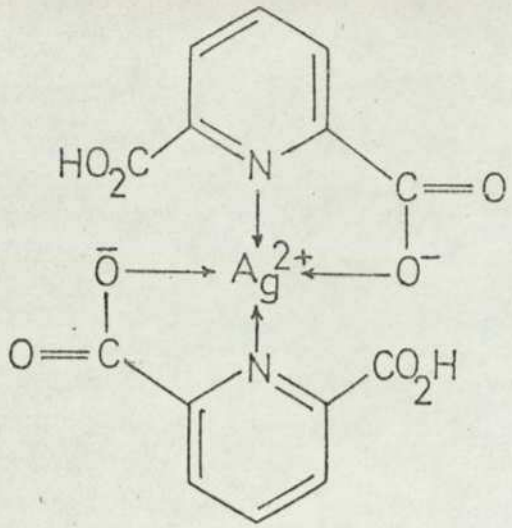


Banerjee and Ray[65] prepared silver (II) complexes of nicotinic acid (pyridine-3-carboxylic acid) and isonicotinic acid (pyridine-4-carboxylic acid) by oxidizing cold aqueous solutions of the ligand and silver nitrate with potassium peroxodisulphate. The compounds are more or less decomposed by mineral acids and alkalies, and are isomorphous with the corresponding copper (II) compounds.[66] Little is known of the structure of these compounds although two models, one dimeric and the other polymeric, have been suggested.[65]

Five complexes of silver (II) with the pyridine dicarboxylic acids have also been prepared,[67] namely: quinolinate (2, 3), cinchomeronate (3,4), isocinchomeronate (2,5), lutidinate (2,4), and dipicolinate (2,6). The dipicolinate complex was isolated in two modifications, dark-red (with $2H_2O$), and green (with $4H_2O$).

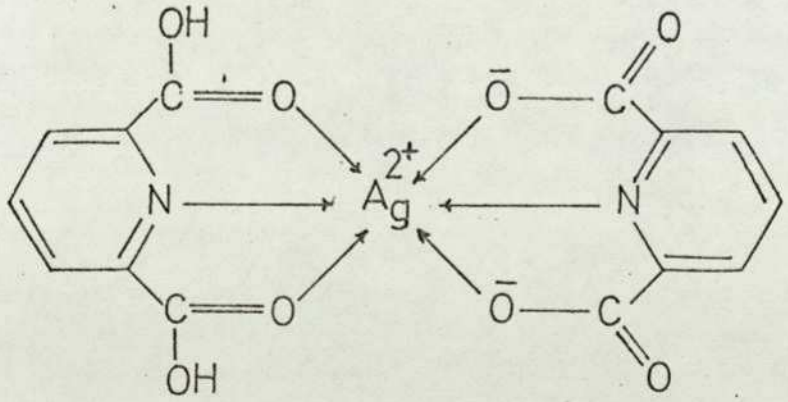
Fowles et al.[68] have recently studied the magnetic and spectral properties of silver (II) complexes with pyridine carboxylic acids. Infra-red spectra of silver (II) complexes with monocarboxylic acids revealed the absence of free carboxylic acid groups. However in the case of the silver (II) complexes with pyridine dicarboxylic acids, similar i.r. data showed the presence of free and coordinated carboxylate groups which indicates that only one of the two possible carboxylic acid groups is bonded to silver (II). Although the magnetic data were not diagnostic of stereochemistry the diffuse reflectance spectra indicated that, with the exception of silver (II) dipicolinate tetrahydrate, the complexes were square planar; this was deduced from the presence of d - d transition bands near 25,000 Cm^{-1}, characteristic of square planar silver (II) complexes.[69, 70] The reflectance spectrum of silver (II) dipicolinate tetrahydrate showed a distinct absorption at 15,600 Cm^{-1}

indicative of pseudo-tetrahedral structure. This indeed is what might be expected since a structure



in which the free carboxylic acid groups are adjacent to the pyridine nitrogen atoms is likely to distort so that the coplanarity is lost.

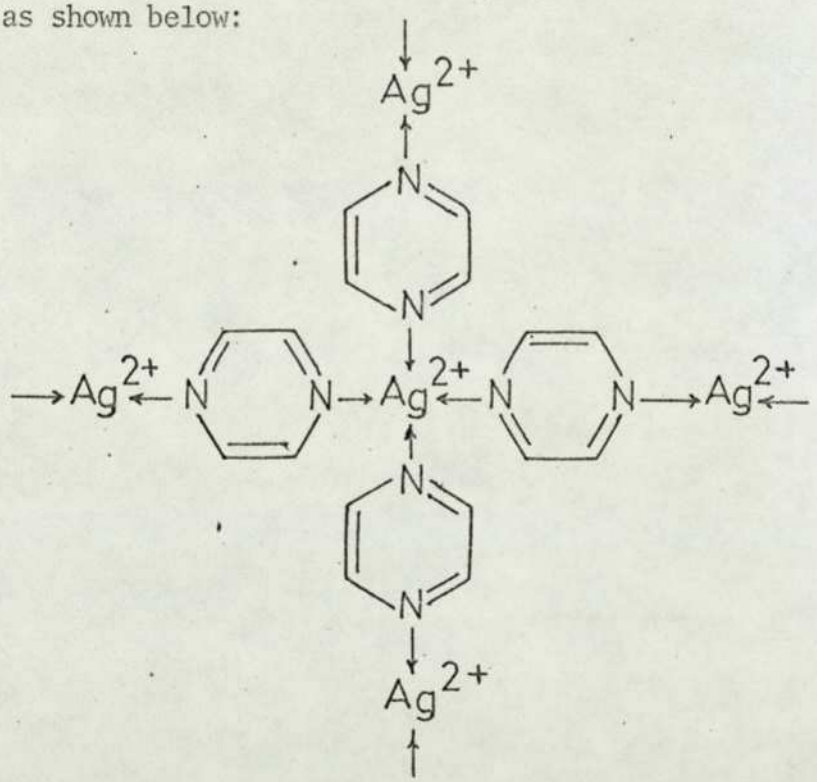
A three-dimensional x-ray analysis[71] of silver (II) dipicolinate monohydrate has shown it to have a distorted octahedral structure in which each ligand is tridentate. An unusual feature is that the two ligands are coordinated differently, one as an ionic ligand the other neutral viz:



Banerjee and Ray[72] have described the preparation of silver (II) complexes of some pyridine tricarboxylic acids, namely pyridine 2,3,6-,

2, 4, 5-, and 2, 4, 6-carboxylic acids by oxidation of cold aqueous silver nitrate solutions containing the ligand concerned. The composition of the complexes can be represented $[Ag(LH_2)_2]$ where LH_3 represents the tricarboxylic acid; it appears, therefore, that only one carboxylic acid group of each ligand is involved in coordination to the silver (II).

The preparation of bis(pyrazine) silver (II) peroxodisulphate and bis(pyrazine-2-carboxylato) silver (II) has been reported recently by Matthews et al.[73] Silver nitrate was oxidized by sodium or ammonium peroxodisulphates in the presence of the ligand. The pyrazine complex is thought to involve a square planar arrangement of nitrogen atoms around the silver (II) with bridging pyrazine molecules to give a polymeric structure as shown below:



This is supported by diffuse reflectance spectra and infra-red studies. Unlike pyridine complexes, pyrazine complexes are unstable at room temperature, their successful preparation and storage requiring a temperature less than $5^{o}C$.

Silver (III) compounds are much less common than those of silver (II) and, with the possible exception of the oxide, Ag_2O_3, no simple binary compounds are known. However, the (III) oxidation state can be stabilized by certain inorganic anions, namely fluoride, periodate and tellurate and by chelating organic ligands containing N donor groups.

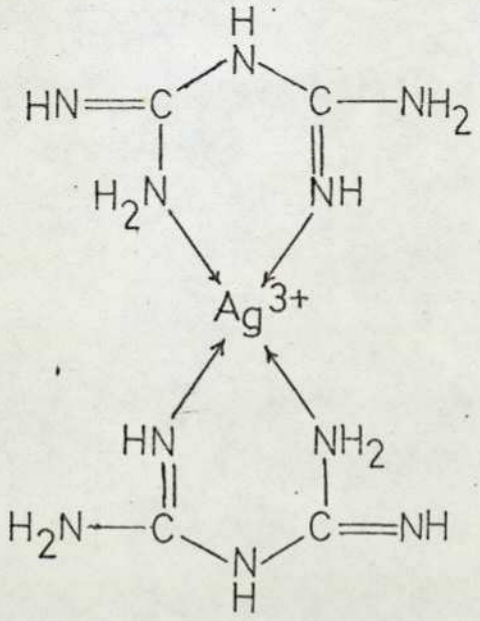
Silver (III) compounds of the type of $KAgF_4$ have been isolated and found to be diamagnetic[74] which is consistent with a spin-paired d^8 configuration and indicative of a square planar structure. $KAgF_4$ was obtained by treating an equimolecular mixture of silver nitrate and potassium chloride or potassium nitrate with fluorine at 200° - 400°C; it is a yellow compound which darkens in a fluorine atmosphere at high temperatures. $CsAgF_4$ and $BaAgF_5$ have also been prepared.[75] These complex fluorides are very unstable, reacting vigourously with water and decomposing by the action of atmospheric moisture. $BaAgF_5$ on heating at 200°C yields the more stable $BaAgF_4$.[75]

Malatesta[76] has prepared a number of strongly coloured complexes of the general formula $M_7[Ag(IO_6)_2] \times H_2O$ by oxidation of a mixture of Ag_2SO_4, KIO_4 and KOH with potassium peroxodisulphate in boiling aqueous solutions. The compounds are all diamagnetic and thought to be square planar with each IO_6^{5-} ion acting as a bidentate ligand. Similar preparations[76,77] using TeO_2 in place of KIO_4 yielded complex tellurates of composition $M_9^{I}[Ag(TeO_6)_2] \times H_2O$. Again the diamagnetism of the complexes indicates a square planar configuration, although six coordination of the silver (III) with each TeO_6^{6-} ion acting as a tridentate ligand cannot be ruled out.

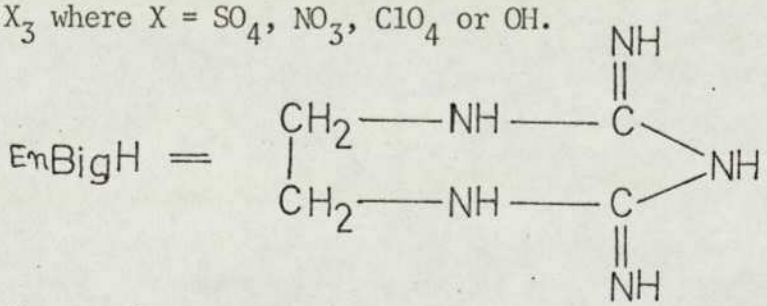
Nakatsuka et al.[78] have reported the preparation of a silver (III) complex with 8-hydroxy quinoline by the action of silver (II) and silver (III) oxides on 8-hydroxy quinoline in cold pyridine solution. It is an unstable yellowish brown compound, insoluble in water but highly soluble in pyridine.

The most stable silver (III) compounds are those in which the silver (III) is complexed with the ligands biguanide,[79] ethylene biguanide,[80] and ethylene bisbiguanide.[81]

Silver (III) biguanide sulphate is formed when a cold aqueous solution of a mixture of biguanide sulphate and silver nitrate at pH 6.5-7.0 is oxidised with potassium peroxodisulphate. The complex separates as sparingly soluble crystals of composition $[Ag\ (C_2H_7N_5)_2]\ (OH)\ SO_4 \cdot 7H_2O$ which can be converted to $[Ag(C_2H_7N_5)_2]\ (NO_3)\ (SO_4) \cdot 6H_2O$ by treatment with a solution of 1 N nitric acid. The suggested structure of the cation is:-

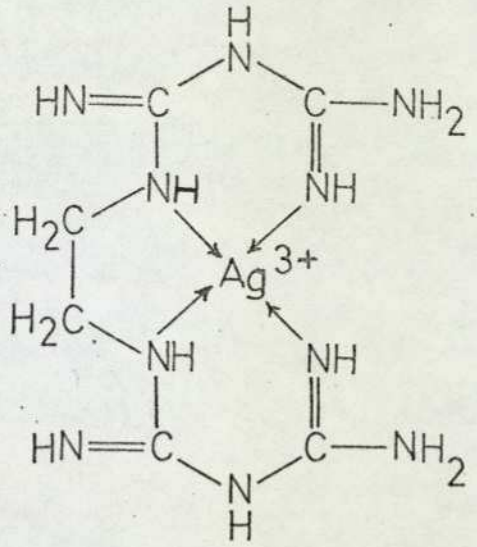


Ethylene biguanide has been found to give complexes of the type $[Ag(EnBigH)_2]\ X_3$ where X = SO_4, NO_3, ClO_4 or OH.



The salts form needle-shaped prismatic crystals of a deep-red colour and are quite stable at ordinary temperatures (20° - 24°C), while the colour of the base is mentioned to be dark violet-red. No other physical data are available.

Silver (III) ethylene bisbiguanide complexes are readily prepared[81] by oxidation of silver (I) salts by potassium peroxodisulphate in the presence of the ligand. Complexes of the type $[AgEn(BigH)_2]X_3$ where $X = HSO_4$, NO_3, ClO_4, or OH and $En(BigH)_2$ is ethylene bisbiguanide have been isolated. The cation has the structure



The molecular conductivity of ethylene bisbiguanide silver (III) was found to be 518 mho at 20°C,[81] in keeping with a complex yielding four ions in solution and supporting the silver (III) formulation. The complex nitrate is moderately soluble in water while the perchlorate is highly soluble; both these compounds are diamagnetic corresponding to a spin paired d^8 configuration. The rate of decomposition of ethylene bisbiguanide silver (III) nitrate as a function of the pH at 25, 35, and 45°C also has been studied.[82] The extreme stability of this silver (III)

complexes is indicated by the value of the stability constant of the complex cation which has been determined as 10^{52} at $32^{o}C$.[83]

The kinetics of formation of the silver (II) bipyridyl and the silver (III) - ethylene bisbiguanide complexes by peroxodisulphate oxidation of the corresponding silver (I) complexes have been investigated.[84] It was found that the silver (II) complex was formed in a reaction which was first order in both reactants while the silver (III) complex was formed in two consecutive reactions, each of first order in both reactants; this evidence suggested that the reaction between silver (I) and the peroxodisulphate anion involved one electron processes.

3. EXPERIMENTAL

3.1. Chemicals

3.1.1. Acetonitrile

Electrochemical studies were carried out in acetonitrile as the solvent medium. Spectrograde acetonitrile was supplied by Eastman Kodak, Co., Rochester, New York and used after drying for several days over type 3A molecular sieve (supplied by B.D.H.) without further purification. The solvent supplied was found to contain about 600 p.p.m. water as determined by Karl Fischer method; this was reduced to less than 50 p.p.m. by treatment with 3A molecular sieve.

3.1.2. Supporting Electrolytes

Tetra-n-butylammonium perchlorate

Tetra-n-butylammonium perchlorate was prepared by the following method.

200 cm^3 40% tetra-n-butylammonium hydroxide (B.D.H. Lab. Grade) was diluted to about 400 cm^3 with distilled water and neutrallized carefully with 71% w/w perchloric acid (B.D.H. General Purpose Reagent). The final stage of the neutralisation was completed by adding a dilute solution of perchloric acid (71% w/w diluted five times with distilled water) from a burette until the acid was slightly in excess. The mixture, from which some of the salt had separated was left to cool and then extracted with five 100 ml portions of chloroform. The combined chloroform extracts were reduced in bulk to about 200 cm^3 on a heating mantle at 80^{o}C. After the addition of 200 cm^3 ethyl acetate (B.D.H., Analar), the bulk was again reduced to 200 cm^3. Ether was added dropwise to the hot holution until the salt just started to crystallise. The solution was then cooled

in an ice bath when fine white crystals separated. The product was filtered and washed with 150 cm^3 ether; it was recrystallised three times from a mixed solvent of 90% ethyl acetate and 10% ether. The product was dried for two hours in a vacuum oven at 80°C; after crushing the crystals, drying was continued for a further two hours. This procedure was effective in removing trace of both water and ethyl acetate.

yield 90 gms. m.p. 212-213°C

Literature values[85,86] 207° and 213°C respectively.

Tetra-n-butylammonium nitrate

Tetra-n-butylammonium nitrate was prepared by the same method as for tetra-n-butylammonium perchlorate by neutralising tetra-n-butylammonium hydroxide with nitric acid. The product was recrystallised twice from a mixed solvent of 90% ethyl acetate and 10% ether and was dried at 60°C for three hours under vacuum.

m.p. = 118.5°C (literature[87] value 120°C)

Tetra-n-butylammonium tetrafluoroborate

Tetra-n-butylammonium tetrafluoroborate was prepared[87] as follows.

100 cm^3 tetra-n-butylammonium hydroxide (B.D.H. Technical Grade 40%) was neutralised with fluoroboric acid (B.D.H. Technical Grade) until the solution was faintly acid. The solution was extracted four times with 100 cm^3 aliquots of chloroform.[88] After removing the chloroform under vacuum, the residue was recrystallised twice from water followed, after drying under reduced pressure at 60°C, by a final recrystallization from dry ethyl acetate. The product was filtered and washed thoroughly with dry ether and dried at 60°C under reduced pressure.

m.p. 158 - 159°C (literature[87,88] m.p. 161.8°C 153 - 155°C).

3.1.3. Ligands

2,2′- Bipyridyl

2,2′- Bipyridyl (puriss), was supplied by Koch-Light Lab. Ltd., Colnbrook, Bucks, England. It was recrystallised twice from an ethanol/water mixture and dried under reduced pressure at 50°C.

m.p. 69°C

2,2′,2″- Terpyridyl

2,2′,2″-Terpyridyl (puriss) was used as supplied by Koch-Light Ltd.

4,4′-Dimethyl 2,2′-bipyridyl

4,4′-Dimethyl 2,2′-bipyridyl (puriss A.R.), was used as supplied by Koch-Light Ltd.

1,10-Phenanthroline

1,10-Phenanthroline (Research Chemical) was supplied by Ralph N. Emanuel Ltd., Wembly, England. It was twice recrystallised from an ethanol/water mixture.

Pyridine

Pyridine (Analar grade supplied by Hopkin and William Ltd.) was redistilled and the fraction boiling at 115.5°C was collected over sodium hydroxide and stored in the dry-box.

Quinoline

Quinoline (G.P.R. grade supplied by Hopkin and Williams Ltd.) was twice distilled and the fraction boiling at 238°C was collected and stored in the dry-box.

5,5′-Dibutyl - 2,2′-bipyridyl

5,5′-Dibutyl - 2,2′-bipyridyl was used as prepared by Mr. T. Rahman, The City University.

3.1.4. Metal Salts and Complexes

Silver (I) perchlorate

Silver perchlorate (Laboratory Reagent) supplied by B.D.H. was recrystallised twice from benzene and dried at 60°C under vacuum.

Silver (I) nitrate

Silver nitrate (A.R.) supplied by B.D.H. was vacuum dried at about 80°C and stored in dry-box.

Nickel (II) perchlorate $6H_2O$

Nickel (II) perchlorate $6H_2O$ (pure grade) was used as supplied by K & K, U.K. distributors Kodak Ltd., Kirkby, Liverpool.

Copper (II) perchlorate $6H_2O$

Copper perchlorate hexahydrate was used as supplied by K & K, (U.K. distributors, Kodak Ltd., Kirkby, Liverpool.)

Copper (II) nitrate $3H_2O$

Copper nitrate trihydrate (Analar grade) was used as supplied by B.D.H. Ltd.

Bis(quinoline) silver (I) nitrate

Bis(quinoline) silver (I) nitrate was prepared according to the method described by Peard et al.,[89] by mixing an aqueous silver nitrate solution with a solution of quinoline in ethanol.

An excess of a 0.1M aqueous solution of silver nitrate (B.D.H. Analytical Reagent) was added with constant stirring to 50 cm^3 of a 5% ethanolic solution of quinoline contained in a beaker immersed in ice-bath. The light pink product which separated was filtered on a sintered filter funnel, washed with two 40 cm^3 aliquots of distilled water, and recrystallised twice from a 50% ethanol/water solution. It was dried over phosphorous

pentoxide in a vacuum desiccator.

m.p. 105 - 110°C (literature[89] 106 - 111°C).

Bis (2,2′- bipyridyl) silver (I) nitrate

Bis (2,2′- bipyridyl) silver (I) nitrate was prepared by the same procedure as for bis (quinoline) silver (I) nitrate by the addition of an excess of a 0.1M aqueous solution of silver nitrate to 50 cm^3 of a 3% ethanolic solution of 2,2′-bipyridyl. The yellow-green needle shaped crystals after purification gave melting point of 134°C.

Literature m.p.[89] 135°C.

Bis (o-phen) silver (I) perchlorate

Bis-(o-phen) silver (I) perchlorate was prepared on adding an excess of a 5% solution of silver perchlorate in acetonitrile to 20 cm^3 acetonitrile containing about o.2 g of o-phenanthroline with constant stirring. The yellow precipitate was filtered through sintered funnel and washed with acetonitrile to remove excess of silver perchlorate. The complex was dried for two hours at 40°C under vacuum.

C, H, N analysis:

Found C 50.41% , H 2.71% , N 9.60%

Theoretical C 50.77% , H 2.84% , N 9.87%

Bis (2,2′ -biquinolyl) copper (II) perchlorate

Bis (2,2′ -biquinolyl) copper (II) perchlorate was prepared by a method based on the procedure described by Harris et al.[90] A hot solution of cuperic perchlorate, hexahydrate (0.185 g) in methanol (5 cm^3) was added with constant stirring to a hot methanol (2.5 cm^3)-benzene (5 cm^3) mixture containing 2,2′-biquinolyl (0.25 g.). The reddish-brown leaflets which

separated were filtered from the cooled reaction mixture and washed with hot benezene and cold methanol. The product was dried over phosphoric acid in a vacuum desiccator, since the anhydrous complex is known to readily absorb water to form a green monohydrate. It was stored and handled in the dry box.

3.2 Apparatus

3.2.1 Polarograph and Controlled Potential Coulometer

Basic Equipment

The apparatus used for both the polarographic and controlled potential coulometric studies was basically the same and comprised a potentiostat, a reference voltage scanner, a potentiometric recorder and one of two electrolysis cells depending on the mode of operation. The potentiostat controlled the potential between a reference electrode and the working electrode of the electrolysis cell at a value fixed by the reference voltage source, the current flowing through the cell being measured by observing the potential drop across a resistance in series with the cell using a potentiometric recorder.

The potentiostat employed was a W.E. Potentiostat, Mark I" supplied by Witton Electronic Ltd., Birmingham, the circuit being based on a design described by Hickling.[91] Its specifications included control of the working electrode to within $\pm$ 10 mV of a reference voltage, and a maximum current output of 300 mA.

An "Electrochemical Voltage Scanning Unit (Model E.C. 232)" supplied by Witton Electronic Ltd. was used as the reference voltage source. This instrument was capable of scanning between any two voltages in the range + 5.0 V to - 5.0 V in either direction at rates of scan varying between 1 mV $min.^{-1}$ and 1.5 V $min.^{-1}$.

The potentiometric recorder was a "Speedomax W" model supplied by Leeds and Northrup Ltd., Birmingham. Sensitivity ranges of 1 mV, 10 mV and 100 mV for a full scale deflection were available with chart speeds ranging from 0.6 to 600 inches per hour.

The series resistance, across which the recorder was connected, was a decade box of range 0.1 Ω to 100,000 Ω, type RBBG, supplied by the Croydon Precision Instrument Co. Ltd., England.

The external circuit of the potentiostat is shown in Fig. 1, p.53 The potentiostat functions in such a way that the voltage developed across the control terminals is maintained at 0.000 $\pm$ 0.010 V. If the potential between the reference electrode and the working electrode (anode) is not equal to that of the reference voltage source, the resulting potential drop across the control terminals is amplified and used to control the output voltage; this changes the current passing through the cell such that the potential at the working electrode becomes equal to that of the reference voltage source. At this point, the potential at the working electrode lies within 10 mV. of the reference voltage.

The ganged switches S_1, S_2 provided a means of isolating the electrolysis cell and introducing the resistances R_1 and R_2 which simulated the resistance paths with the electrolysis cell, R_1 corresponding to the resistance between the reference electrode and the working electrode, and R_2 to that between the auxiliary electrode and reference electrode. This arrangement enabled checks to be readily made that the potentiostat was properly adjusted and functioning correctly. Before each experiment, the potentiostat was checked by the following procedure.

With the resistance network in circuit (switches S_1 and S_2 in positions B) and with R_1 and R_2 set at about 5K Ω and 50K Ω respectively, a high impedance voltmeter was used to fix the reference voltage at, say, 1.00 V. (The voltmeter used was a "D.C. Differential Voltmeter, Model 871A"

supplied by John Fluke Manufacturing Co., Inc., Seatle, Washington). The voltmeter was then placed across R_1, and a potentiometer in the control circuit of the potentiostat was adjusted so that the potential developed across R_1 was equal to that set up on the voltage scanner. The reference voltage was then set at a higher value, say 1.50 v., and a check was made that the voltage across R_1 was within 10 mV of this value without further adjustment of the potentiostat. Further checks were made over the voltage range to be used. On completing the initial adjustments to the potentiostat and switching the electrolysis cell into the circuit (switches S_1 and S_2 in position A) any potential set up at the reference source then appeared between the reference electrode and the working electrode.

The modes of operation of the apparatus, as a polarograph and as a controlled potential coulometer are now described.

Polarograph

The electrolysis cell used in the polarographic mode of operation is shown in Fig. 2, p.54 . It had a capacity of about 40 cm^3 and was fitted with a P.T.F.E. stopper, in which three holes were bored. One hole held the auxiliary electrode, the other two holes providing access for the rotating platinum electrode (R.P.E.) and the bridge of the saturated calomel electrode (S.C.E.).

The micro-platinum electrode was formed by sealing a piece of 38 S.W.G. bright platinum wire into the side of a soda glass tube about 6 mm. in diameter and 25 cm. long to leave only the tip of the wire protruding from the outside surface, the tube being sealed about 1 cm. from the wire. The electrode was rotated at 700 r.p.m. by a constant speed motor (Type S/700/R,

supplied by Voss Instruments Ltd., Maldon, Essex, England) mounted above the cell. Electrical contact between the platinum electrode and potentiostat was made via a column of mercury which filled the rotating tube.

The saturated calomel electrode (S.C.E.) was clamped so that the tip of the Agar/KCl bridge, which was drawn to a fine capillary (about 0.5 mm. diameter) and packed with asbestos fibres, was about 0.5 mm. from the micro-electrode.

A square of 26 S.W.G. platinum, 2.5 cm x 2.5 cm, welded to a piece of 22 S.W.G.bright platinum wire sealed into the bottom of a 6 mm. diameter and 15 cm. long soda-glass tube, formed the auxiliary electrode. Electrical connection to the electrode was made by a piece of copper wire welded to the platinum wire on the inside of the tube.

The electrodes of the polarographic cell were connected to the potentiostat as in the circuit diagram previously described (Fig. 1, p.53). After filling the cell with the solution under investigation, a polarogram was obtained in the following way.

The potential at the R.P.E. was first adjusted to the required starting value, say, 1.00 V. The reference voltage scan rate and chart recorder speed were then selected to give the desired voltage calibration for the time axis of the chart recorder. (For example, if the scan rate was adjusted to 0.2 V/min. and the chart speed was set at 60 inch/hr. then the time axis of the chart paper corresponded to 0.2 V/inch.). Synchronisation between the voltage scanner and the recorder was obtained by first starting the chart recorder motor and starting the scanner when the pen of the recorder coincided with one of the main division lines on

the paper; this line then corresponded to the starting potential (1.00 V).

In many of the polarographic experiments, the series resistance in the cell circuit (Fig. 1, p.53) was chosen as 1000 Ω; with a recorder sensitivity of 10 mV. f.s.d., this corresponded to a cell current of 10 μA for a full scale deflection.

The complete polarographic cell assembly, including the constant speed motor, was housed in a nitrogen-filled dry box maintained at a relative humidity of 5% to 8% at a temperature of 20 $\pm$ 1 °C.

Controlled Potential Coulometer.

The electrolysis cell used for the controlled potential coulometric mode of operation, shown in Fig. 3, p.55 , had separate anode and cathode compartments, each of about 40 cm^3 capacity, connected by a wide bore tube fitted with No. 4 sintered discs at each end.

A pool of mercury formed the cathode of the electrolysis cell, electrical connection to the potentiostat circuit being made by a piece of 22 S.W.G. platinum wire sealed into the base of the cathode compartment. The surface of the mercury pool was continually renewed by a magnetic stirrer.

The anode was a macro-platimum electrode which consisted of 50 cm. of 22 S.W.G. platimum wire, sealed into, and would round, a 25 cm. long soda-glass tube of about 6 mm. diameter. The tube was filled with mercury for electrical contact and was rotated at 700 r.p.m. using the constant speed motor already described.

The S.C.E. was positioned so that the tip of the Agar/KCl bridge (previously described on p. 44) was about half way down the length, and as close as possible to the platimum coil.

After filling the anode compartment with a solution containing the supporting electrolyte and the substance to be oxidised (the cathode and centre compartments being filled with a solution of the supporting electrolyte only), a current-time curve at a constant potential was obtained in the following way.

The coulometric cell was connected to the potentiostat circuit as described in Fig. 1, p.53 , and the reference voltage source was adjusted to give the required potential (switches S_1 and S_2 in positions B). The series resistance was selected so that expected initial current would give a chart reading of about 90% f.s.d.; for an anticipated initial current of about 50 mA, and with a recorder sensitivity of 10 mV f.s.d., a series resistance of 0.2 Ω would be required. The chart recorder speed was set at a suitable value, say 30 inch/hr. and the electrolysis was started by switching S_1 and S_2 to positions A, when the recorder pen coincided with one of the main division lines on the chart paper. When the current had fallen to about 10% of its initial value, the series resistance was increased ten times; the series resistance was increased a further ten times when the current had dropped to 1% of its initial value. Electrolysis was taken as complete when the current had reached about 0.1% of its initial value. The area under the current time curve was measured by cutting out each section of the curve and comparing its weight with that of a known number of squares. Calculations of the total number of coulombs dissipated during electrolysis and the number of electrons per mole of the electrolysed species were then made.

As in the polarographic studies, the whole coulometric cell assembly, including the constant speed motor and the magnetic stirrer was housed

in the nitrogen-filled dry box. In the case of purely preparative electrolyses at constant potential, the same experimental set-up and procedure was used as for the coulometric studies, but a full current-time was not obtained, only the initial and final currents being noted.

3.2.2 Sweep polarograph

Triangular voltage sweep polarography was carried out using a Tektronix "Storage Oscilloscope, Type 564" incorporating a polarographic amplifier (Type 300) giving sensitivity ranges of 0.01 μA div^{-1} to 100 μA div^{-1}, and polarographic time base (Type 205) providing sweeptimes of 0.01 sec. div^{-1} to 10 $sec.div^{-1}$ with a voltage scan of 2V. For sweep rates of 0.2 V. sec^{-1} and less, a "Model 27000" chart recorder supplied by Bryans Ltd., Mitcham, Surrey, was used to record polarograms. This instrument became available towards the end of the present work and was only used for a limited number of experiments involving the silver (I) nitrate/bipy system.

3.2.3 Spectrophotometers

Visible-UV-spectrophotometer

A "Recording Spectrophotometer Model EPS-3T" by Hitachi Perkin-Elmer was used for the solid reflectance spectra study of silver (II) complexes.

Infra-red spectrophotometer

An "Infracord spectrophotometer" and a "Grating infra-red spectrophotometer Model 457" supplied by Perkin-Elmer were used for infra-red studies of silver and other compounds.

3.3 Details of Procedure for Polarographic and Coulometric Experiments

The procedure for carrying out a polarographic or coulometric experiment falls into four main stages: cleaning the electrodes, making up the solutions required, assembling the electrolysis cell, and adjusting and operating the potentiostat in the mode required (already described in section 3.2.1). For a coulometric experiment there is the additional stage of calculating the area under the current-time curve to give the number of coulombs which have passed during electrolysis. All electrochemical studies were carried out at the ambient temperature of the dry box ($20 \pm 1^{\circ}C.$)

Experimental details for the first three stages and the method of calculating the number of coulombs are now described.

3.3.1 Method of cleaning electrodes

The platinum micro-electrode and the platinum macro-electrode were cleaned by the following method.

The electrode was suspended in boiling nitric acid (33% v/v) vapour for ten minutes after which it was rinsed several times with distilled water. Any oxide coating on electrode was then removed by immersing the electrode in a saturated solution of ferrous ammonium sulphate, acidified with dilute sulphuric acid, for about half an hour. The electrode was then washed repeatedly with distilled water and finally rinsed several times with acetonitrile.

The auxiliary electrode (platinum foil), used in the polarographic cell, was cleaned first with acetone, rinsed with tap water, and then left

in concentrated nitric acid for about two hours. It was finally washed thoroughly with distilled water and dried at 120°C.

The bridge of the S.C.E. which was immersed in a saturated solution of potassium chloride when not in use, was thoroughly rinsed with distilled water, dried with tissue paper, and finally rinsed with acetonitrile. The bridge was immersed in acetonitrile solution for about ten minutes before use.

After cleaning, the electrodes were transferred to the nitrogen-filled dry-box.

3.3.2. Solutions for polarographic and coulometric experiments.

All weighing operations and the making up of solutions were carried out in the dry-box.

The supporting electrolyte solution, 0.1 M tetra-n-butylammonium perchlorate in acetoniltrile was made up by dissolving the calculated amount of salt in dry spectrograde acetonitrile, and making up to the mark in a 100 cm^3 measuring flask. Metal salt and/or ligand solutions were made up in this medium, a fresh solution of supporting electrolyte being used for each experiment.

In the case of polarographic experiments, calculated amounts of metal salt and/or ligand were weighed and transferred to a 50 cm^3 measuring flask which was filled to the mark with supporting electrolyte solution. Approximately 25 cm^3 of this solution was required for the polarographic cell (Fig. 2, p.54).

In coulometric experiments, a different procedure was used for making up the metal and/or ligand solutions. Since in coulometry it is necessary

to know only the weight of metal salt undergoing electrolysis and not its concentration, the three compartment cell (Fig. 3, p 55) was first filled with the supporting electrolyte solution and the required quantities of metal salt and ligand were then dissolved directly in the solution in the anode compartment.

3.3.3 Assembly of electrolysis cells

The electrolysis cells after cleaning and drying were introduced into the dry box together with the cleaned electrodes.

The polarography cell was assembled as shown in Fig. 2, p. 54 ; after introducing about 25 cm^3 of the solution under investigation, connections were made to the potentiostat as described in section 3.2.1.

In the assembly of the coulometric cell (Fig. 3, p55) each of the three compartments was filled with a solution of the supporting electrolyte. About 5 cm^3 of mercury and the magnetic stirrer were then introduced into the cathode compartment which was positioned over the centre of the magnetic stirrer motor, and the rotating macro-electrode was positioned in the anode compartment. Connections were made to the potentiostat as described in section 3.2.1. When the levels of the supporting electrolyte in the cathode and anode compartments had attained equilibrium and there was no movement of solution through the sintered discs weighed amounts of metal salts and ligand were introduced into the anode compartment and the rotating electrode motor was switched on. The coulometric determination was started when the metal salt and ligand had completely dissolved.

In cases where controlled potential electrolysis was used for purely preparative purposes, the anolyte was transferred as quickly as possible, after completion of the electrolysis, to a stoppered flask using a large dropping pipette.

3.3.4. Calculations of the number of electrons involved per molecule in the electrode reaction.

The quantity of electricity passed during the electrolysis of a known weight of oxidisable material was calculated from the area under the current-time curve. The current-time curve usually consisted of three sections corresponding to three different sensitivity ranges for the current co-ordinate, the current calibration of each range being fixed by the sensitvity of the recorder and theseries resistance of the electrolysis cell circuit (cf. section 3.2.1.). The area under curve was determined by cutting out each section of chart paper and comparing its weight with that of a known number of squares of the same chart-paper (usually 100 large squares were taken for comparison); knowing the number of coulombs (amp. x sec.) corresponding to one square, the number of coulombs for each section was deduced and hence the total number of coulombs for the electrolysis was determined. In all coulometric experiments, a small residual current was usually observed for which a correction was made.

The number of electrons involved in the oxidation of one molecule of the oxidisable species in the overall electrode reaction is given by the relationship:

$$n = \frac{Q \cdot M}{F \cdot W} \qquad (7)$$

where Q = the total number of coulombs

W = weight of compound electrolysed

M = the molecular weight of the compound undergoing electrolysis

F = the Faraday (96,493 coulombs).

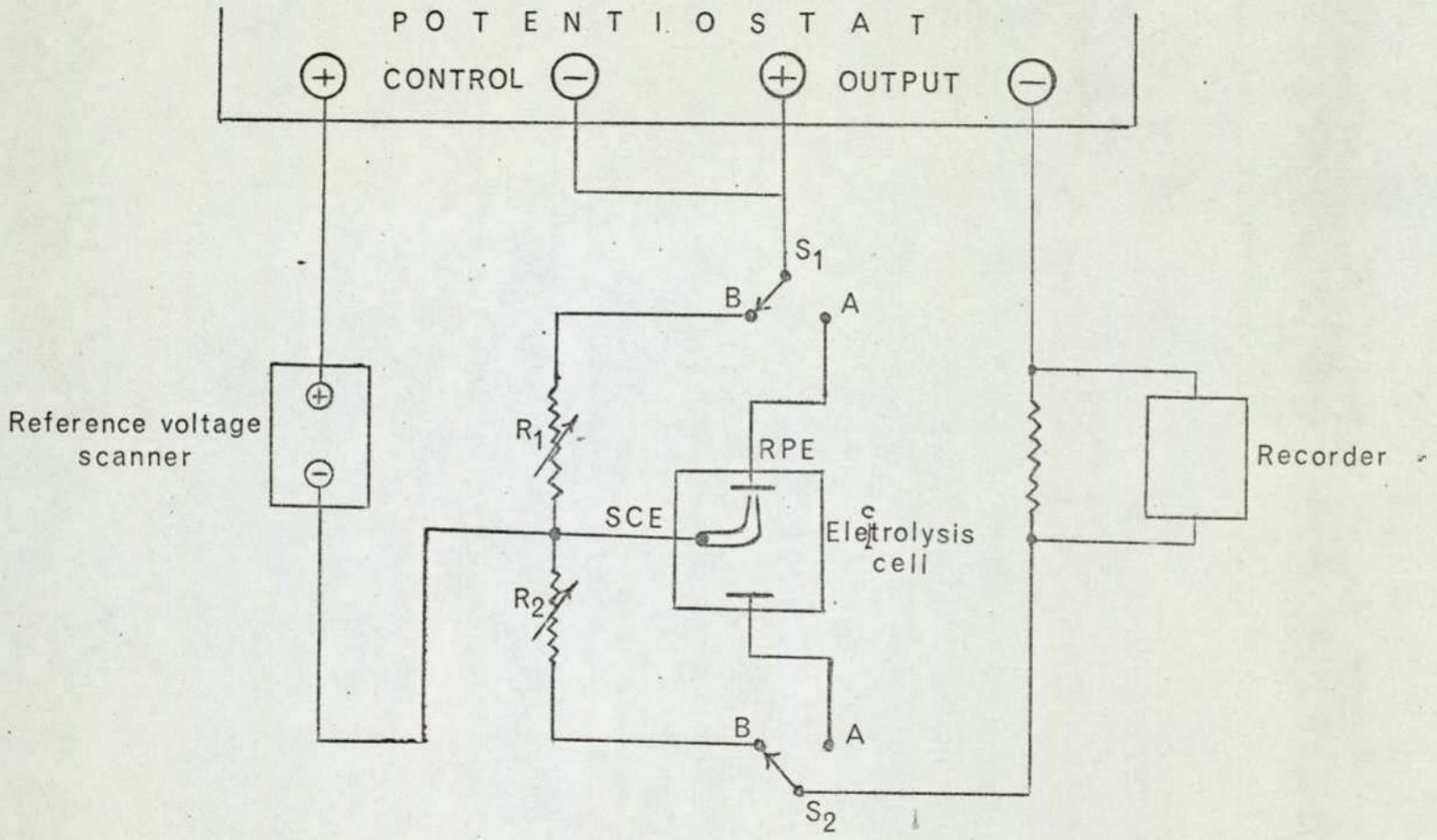


Fig. 1. External Potentiostat Circuit

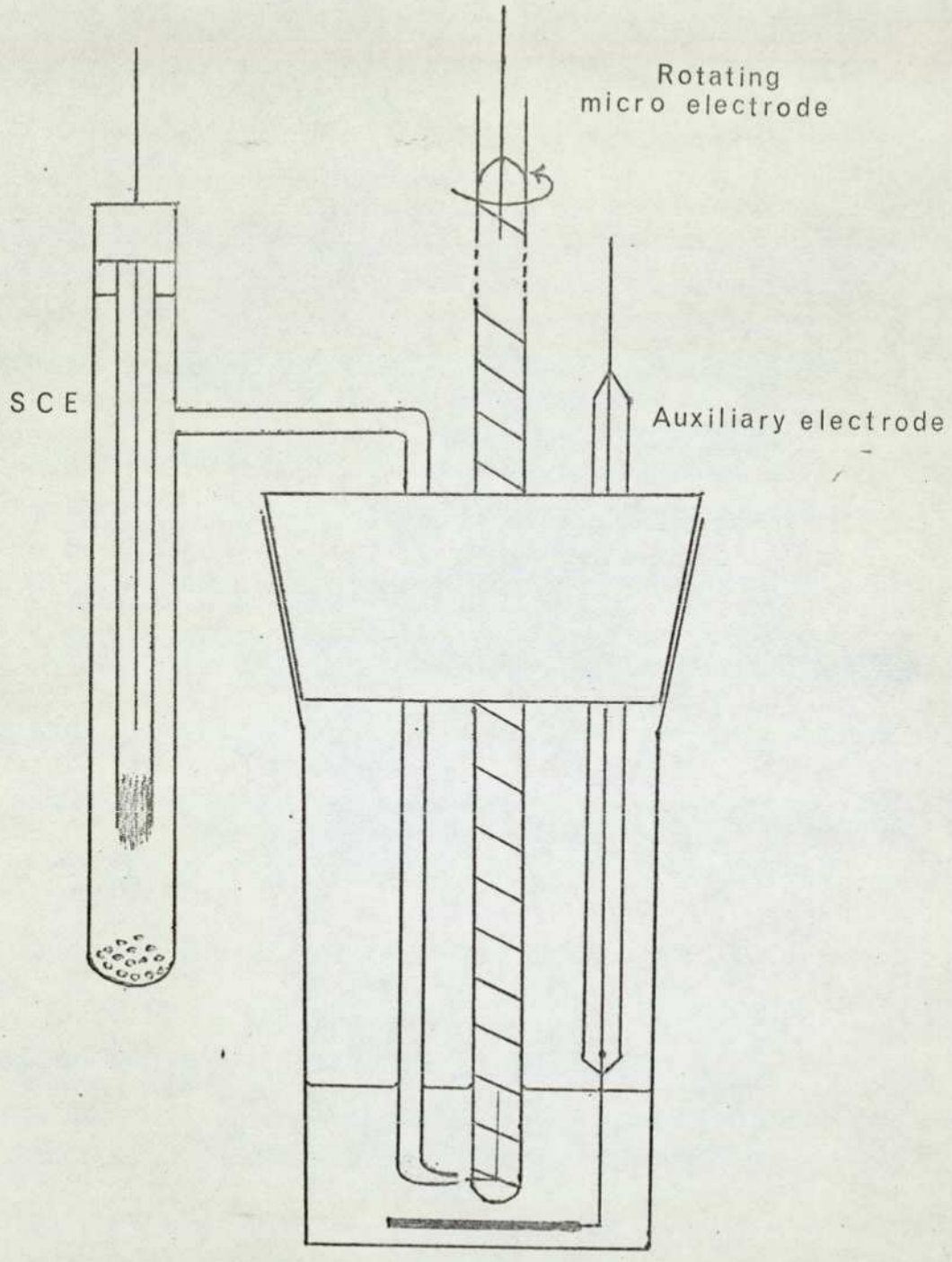


Fig. 2. Polarographic Cell

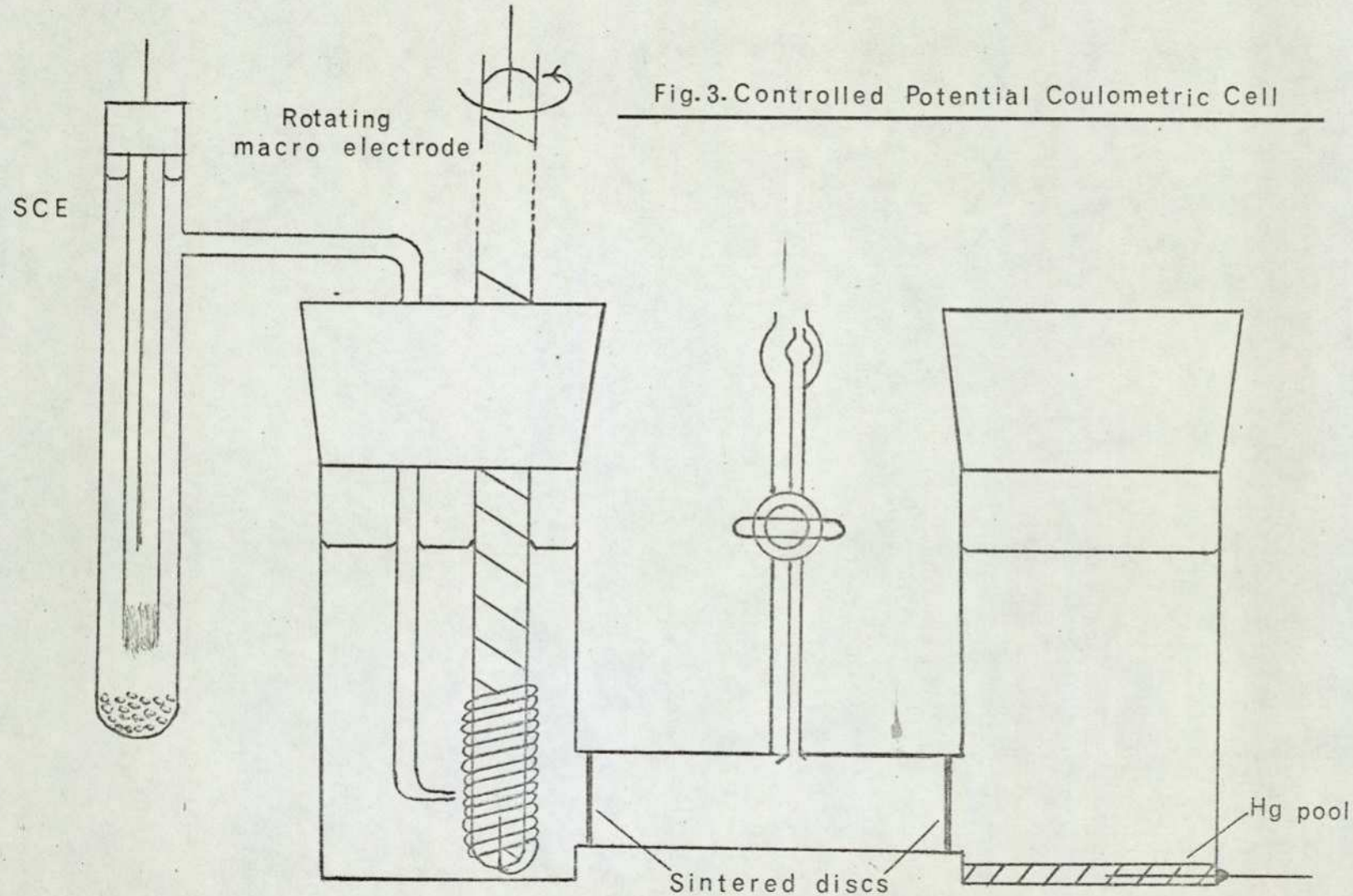


Fig. 3. Controlled Potential Coulometric Cell

3.4. Analytical Determinations

3.4.1. Determination of silver (II)

A novel method was developed for the determination of small amounts of silver (II). The method described by Dutta[19] involving the oxidation of iodine by silver (II) was found to be unsuitable because silver (II) complexes with polypyridyls were found to give an incomplete reaction with potassium iodide solution in the cold. It was thought that this was due to the adsorption of iodine onto the surface of the crystals and that this prevented further reaction. This difficulty was apparently overcome by refluxing the solution; however, using a water condenser, some iodine was lost and further it was difficult to remove all traces of iodine from the condenser. The method described here uses bromide ion as the reductant, the liberated bromine being readily removed from the reaction mixture.

The apparatus is shown in Fig. 4, p. 58 , and consists of a 50 cm^3 pear-shaped distillation flask fitted with a nitrogen inlet and reflux condenser leading to a trap (A) containing potassium iodide solution. A second safety trap contained a solution of potassium iodide to which was added a few drops of starch solution.

An accurately weighed amount of silver (II) complex (usually about 50 mg.) was introduced into the pear-shaped flask together with about 10 cm^3 deoxygenated water and about 100 mg. analar grade potassium bromide. The oxygen free nitrogen supply was switched on and the solution was heated to boiling using a micro-burner and refluxed for about five minutes. At this stage, most of the bromine had passed over into the iodide trap; the last

traces of bromine in the reaction vessel were removed by increasing the nitrogen flow and switching off the water supply to the condenser until steam just began to condense into the delivery tube. With the water supply restored, the nitrogen flow was continued for a further minute.

The iodine solution was transferred to a 100 cm^3 conical flask together with washings from the delivery arm and titrated against a standaridised 0.01 N solution of thiosulphate contained in a weight burette using a starch solution as indicator. The 0.01 N thiosulphate solution was standardised against potassium bromate. A known weight of analar grade potassium bromate was placed in the reaction vessel to which was added an excess of analar potassium bromide and 10 cm^3 0.5 N sulphuric acid. The bromine produced was transferred to the iodide trap by the procedure described above and the resulting iodine titrated by weight against the 0.01 N thiosulphate solution.

The use of 0.01 N solution of thiosulphate together with the weight titration technique allowed small quantities of silver (II) complexes to be accurately analysed.

3.4.2. C, H and N analyses

Carbon, hydrogen and nitrogen analyses were performed using "C, H, N analyser Model 185" supplied by F. & M. Scientific Corporation, Avondale, Penna.

3.4.3. Mass spectrometry

A limited number of mass spectrographic analyses were carried out by the Physico-Chemical Measurements Unit, Harwell, Didcot, Berks.

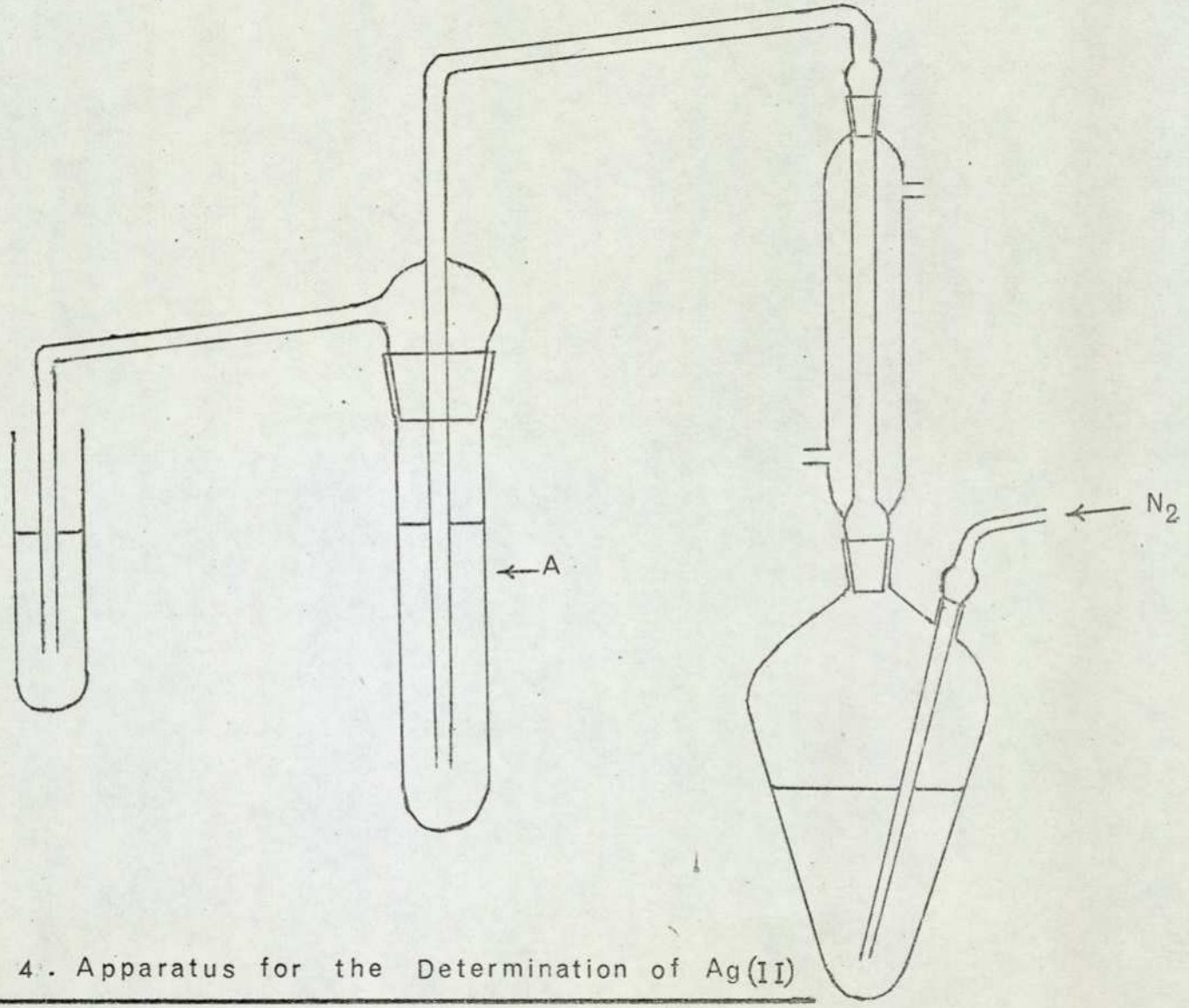


Fig. 4. Apparatus for the Determination of Ag(II)

4. RESULTS AND DISCUSSION

4.1. Preliminary Experiments

4.1.1. Water seepage from the aqueous reference electrode

Since a saturated calomel electrode (S.C.E.) with an Agar/ Potassium chloride bridge was to be used as a reference electrode in acetonitrile, it was deemed necessary to check the rate of water seepage into the system. The acetonitrile used in all polarographic and controlled potential electrolysis work was "Spectro Grade" acetonitrile supplied by Eastman Kodak Co. After drying by the method already described (3.1.1.) the solvent was found to have a water content of 50 p.p.m. as determined by the Karl Fischer method.

Two 25 cm^3 samples of dry (50 p.p.m.) acetonitrile were placed in 100 cm^3 beakers in the dry-box. The tip of the salt bridge of the S.C.E. was immersed in one of these solutions and after three hours the water content of each solution was redetermined. The water content of the control sample was found to have increased to 75 p.p.m. whilst the sample into which the salt bridge had been immersed, increased to 130 p.p.m. It can be seen that the increase in water content of the sample due solely to the presence of S.C.E. was 55 p.p.m., a value of the same order as the water content initially present in the acetonitrile, this increase taking place over a period of three hours. Since the duration of a normal series of experiments was considerably less than three hours, it was concluded that the seepage of water from the S.C.E. was not a serious problem.

The water content of a third 25 cm^3 sample of dry acetonitrile in an open beaker left outside the dry-box increased to about 700 p.p.m. in a period of three hours. This justified the use of a dry box for carrying out all electrochemical experiments involving acetonitrile solutions.

4.1.2. Anodic limits of supporting electrolytes

Results

The anodic polarogram determined over the range 0.0 V to 3.0 V at a scan rate of 0.4 V min^{-1} for a 0.1 M solution of tetra-n-butylammonium perchlorate, prepared and purified as described in section 3.1.2. is presented in Fig. 5, p. 69.

The anodic limit, defined abitrarily[4] as the potential corresponding to a current of 1 μA, was found to be 2.75 V (vs. S.C.E.).

Similar polarograms are also shown in Fig. 5, p.69 for two samples of tetra-n-butylammonium tetrafluoroborate. Fig. 5, p. 69 polarogram 1 refers to a 0.1 M solution of a sample of the electrolyte prepared and purified as described in section 3.1.2. After recrystallising this sample three times, polarogram 2 was obtained which shows an improvement in the anodic limit, from 2.50 V to 2.75 V. Further recrystallisation of electrolyte gave no further increase in the anodic limit.

Discussion

The anodic limits for tetra-n-butylammonium perchlorate and tetra-n-butylammonium tetrafluoroborate (after three additional recrystallisation) are identical (2.75 V) according to the arbitrary definition given above. However, the perchlorate is considered to be a more useful supporting electrolyte since the potential at which the anodic current first starts to increase significantly is about 2.05 V compared to a value of 1.50 V (polarogram 2) for the tetrafluoroborate. This observation does not agree with the claim of Fleischmann[93] that the potential range in acetonitrile can be extended by the use of tetrafluoroborate as supporting

electrolyte. Tetra-n-butylammonium perchlorate was used as the supporting electrolyte in all subsequent electrochemical studies.

The nature of the anodic background reaction of perchlorate salts in acetonitrile solutions is still open to question. The following reaction mechanism for the oxidation of perchlorate ion in acetonitrile was put forward by Schmidt and Noack.[94]

$$ClO_4^- \longrightarrow ClO_4^{\cdot} + e \qquad (8)$$

$$CH_3CN + ClO_4^{\cdot} \longrightarrow {}^{\cdot}CH_2CN + HClO_4 \qquad (9)$$

and $$2.CH_2CN \longrightarrow NCCH_2CH_2CN \qquad (10)$$

several investigations have provided evidence both in support of and against this mechanism. Billon[95] has described a method for the coulometric determination of organic bases in which the bases are neutrallised by hydrogen ions generated by the anodic oxidation of solutions of anhydrous lithium perchlorate in acetonitrile. The electrochemical generation of acid was attributed to the above mechanism; this disputed the claim of Streuli,[120,121] employing a similar technique but using lithium perchlorate trihydrate, that the generation of hydrogen ions arose from the oxidation of water:

$$2H_2O \longrightarrow 4H^+ + O_2 + 4\bar{e} \qquad (11)$$

Koyama[96] et al. were unable to detect the presence of succinonitrile after prolonged electrolysis of perchlorate solutions in acetonitrile, but detected chloride ion in small quantity. Maki and Geske[97] using E.S.R. spectroscopy reported the observation of chlorine containing radicals when a mixed solution of lithium and sodium perchlorates in anhydrous acetonitrile

was oxidised. The spectrum showed a hyperfine structure of four equally spaced lines of approximate equal intensity and this was interpreted as due to the presence of a radical species containing a single chlorine atom, thought to be the perchlorate radical. Although the radical $.CH_2CN$ was not detected, this was attributed to the rapid dimerisation of these radicals to give succinonitrile.

The validity of the first step of the Schmidt and Noack[94] reaction scheme is not disputed by Russell,[98] but it was suggested that this is followed by oxidative attack of the perchlorate radical on the solvent and the degeneration of the perchlorate radical to lower oxidation states of chlorine. A fraction of the perchlorate was, in fact, shown to be reduced all the way to chloride ion, the presence of which was also detected by Koyama.[96] Russell claims further that the E.S.R. data of Maki and Geske[97] are consistent with the spectrum of chlorine dioxide obtained by Cole.[99]

Although the anodic background reaction mechanism for perchlorates in acetonitrile is not yet fully understood, this does not detract from its suitability as a supporting electrolyte since the reaction only interferes at relatively high potentials, the useful anodic limit being 2.75 V.

4.1.3. Anodic polarography of the iodide ion

In order that a check could be made on the proper functioning of the polarograph, it was decided to study first a system for which the polarographic behaviour was well known.

Tetra-n-ethyl-ammonium iodide in acetonitrile has been shown to

give four anodic waves;[102] the overall reaction for the first two well-defined waves corresponding to the one electron oxidation of iodide to iodine. Polarograms of tetra-n-ethyl-ammonium iodide in 0.1M tetra-n-butylammonium perchlorate were obtained in the range 0.00 V to 3.00V vs S.C.E. using a scan rate of 0.4 V min^{-1}.

Results and discussion

The results of three polarographic runs are given in Table I and a representative polarogram (Experiment No. 1) is shown in Fig. 6, p.70 .

Four waves labelled I, II, III and IV are observed, wave III being small and ill-defined. No explanation to account for wave III has been put forward by previous workers[102] (in the study of Dryhurst and Elving,[100] it was ignored completely) and it will not be considered further.

Table I Anodic polarography of Et_4NI

Expt. No.	Wave No.	$E1_{V/2}$ V	$\Delta E1_{V/2}$ V	i_L µA	Iodide Concn. mM	$i_{L/C}$ µA. mM^{-1}	$i_L I / i_L II$	$\frac{i_L I + i_L II}{C}$ µA. mM^{-1}
1	I	0.30	0.35	3.6	3.0	1.20	2.00	1.80
	II	0.65		1.8		0.60		
	IV	2.03		2.2		0.73		
2	I	0.28	0.34	3.9	3.20	1.22	2.05	1.81
	II	0.62		1.9		0.59		
	IV	2.01		2.1		0.66		
3	I	0.32	0.35	3.8	3.20	1.19	1.90	1.81
	II	0.67		2.0		0.62		
	IV	2.00		1.9		0.59		

Concentration of Bu_4NClO_4 is 0.1 M in acetonitrile

Concentration of Et_4NI = C

There is seen to be some variation in the half-wave potentials for waves I, II and IV which is probably due to fluctuations in the liquid junction potential since the differences in half-wave potential for wave I and II and for waves I and IV are much more reproducible. The mean value of the half-wave potentials for waves I and II are 0.30 V and 0.65 V vs. S.C.E. respectively which compare with the values of 0.3 V and 0.6 V obtained by Kolthoff and Coetzee[5] using 0.5 mM sodium iodide; the corresponding sets of value determined by Popov and Geske[102] and Dryhurst and Elving[100] were 0.29 V, 0.61 V, and 0.36 V, 0.71 V, respectively.

The value of $\Delta E_{\frac{1}{2}}$, the difference in half-wave potential for waves I and II is identical with that obtained by Dryhurst and Elving,[100] ($\Delta E_{\frac{1}{2}}$ = 0.35 V), value being somewhat higher than those of Kolthoff and Coetzee[5] (0.30 V), and Popov and Geske[102] (0.32 V).

It has been established[5, 100, 102] that waves I and II correspond to the formation of the tri-iodide ion, I^-_3, and its subsequent oxidation to the free halogen according to the equations,

$$3I^- \longrightarrow I^-_3 + 2e^- \qquad (12)$$

$$2I^-_3 \longrightarrow 3I_2 + 2e^- \qquad (13)$$

the overall diffusion controlled reaction being

$$2I^- \longrightarrow I_2 + 2e^- \qquad (14)$$

This mechanism was supported by the observation that the height of the first-anodic wave was twice the height of the second wave. Further, in the presence of an excess of iodine, when all the iodide was converted to I^-_3, the first wave disappeared and the height of the second

wave was equal to the combined heights of the two waves obtained in the absence of iodine in accordance with the equation (13). The overall reaction has been confirmed as an equivalent one electron process by coulometric studies.[103]

The present data are in agreement with equations (12), (13) and (14). Table I includes values of the ratio of limiting currents for waves I and II, $i_L I/i_L II$; these values fall in the range 2.0 ± 0.1 which is in good agreement with equations (12) and (13). For the particular electrode used in these experiments, the value of i_L/C corresponding to a one electron change per molecule for the overall process was found to be $1.8 \pm 0.1\ \mu A.mM^{-1}$.

It has been suggested[100] that wave IV is also an equivalent one electron process and corresponds to the oxidation of iodine (0) to iodine (I) according to

$$I_2 \longrightarrow 2I^+ + 2e \qquad (15)$$

The unipositive iodine, it is thought, will be present as HOI formed by the reaction

$$OH^- + I^+ \longrightarrow HOI \qquad (16)$$

where the hydroxyl ion comes from the presence of traces of water in the acetonitrile (0.01% water by weight corresponds to a 4.3 mM solution which is appreciable compared to the concentrations of iodide used in the polarographic studies). The height of wave IV is therefore expected to be the same as wave II.

In the present work, there is reasonable agreement with equation (15). Although values of i_L/C for wave IV are somewhat larger and less reproducible than those for wave II, the data for wave IV are less reliable due to the

presence of the maximum associated with wave IV and the proximity of the anodic limit of 0.1 M tetra-n-butylammonium perchlorate. The half-wave potential for wave IV was 2.01 V compared to the value of 2.12 V quoted by Popov and Geske.[102]

It was concluded that, by comparison with published data on the anodic oxidation of the iodide ion, the polarograph was working satisfactorily. For the particular platinum micro-electrode used in this work a calibration value for the limiting current per millimole of 1.8 $\mu A.mM^{-1}$ was obtained for the established diffusion-controlled one electron oxidation of iodide to iodine.

4.1.4. Assessment of ohmic drop between working and reference electrodes

It is well known[92, 101] that the ohmic drop between the working electrode and reference electrode in high resistance systems is not completely compensated for in three-electrode resistance-compensating potentiostats, even though the current flowing in the reference cell is zero. The potential drop arises from the current flowing between the working electrode and the auxiliary electrode and its magnitude increases as the distance between the tip of the reference electrode and the working electrode increases. Although theoretical calculations [92, 104] have been made for the ohmic drop occurring in the vicinity of a D.M.E. the problem is much more complex when a R.P.E. employed and a theoretical solution is not possible.

In an attempt to evaluate the magnitude of this effect for the present cell arrangement using a R.P.E., a purely emperical method was employed. Polarograms were obtained for a 1.76 mM solution of silver nitrate (see section 4.2 for full details of the anodic behaviour of silver nitrate

solutions) where the distance between the tip of the reference electrode and the R.P.E. was varied, other paramaters being kept constant. Curves I II and III, Fig. 7, p.71 are polarograms of a solution of 1.76 mM silver nitrate in acetonitrile (supporting electrolyte 0.1 M Bu_4NClO_4) where the distance between the reference electrode tip and the R.P.E. was approximately 0.5 mm., 1.0 mm. and 2.0 mm respectively. The waves for the first two cases were identical whilst a slight distortion was observed when the distance was increased to 2.0 mm. Since the tip of the reference cell bridge in all cases was kept within 1.0 mm it was concluded that the ohmic drop correction was negligible under the particular cell conditions used.

Fig.5. Anodic Range of Bu_4NClO_4 & Bu_4NBF_4

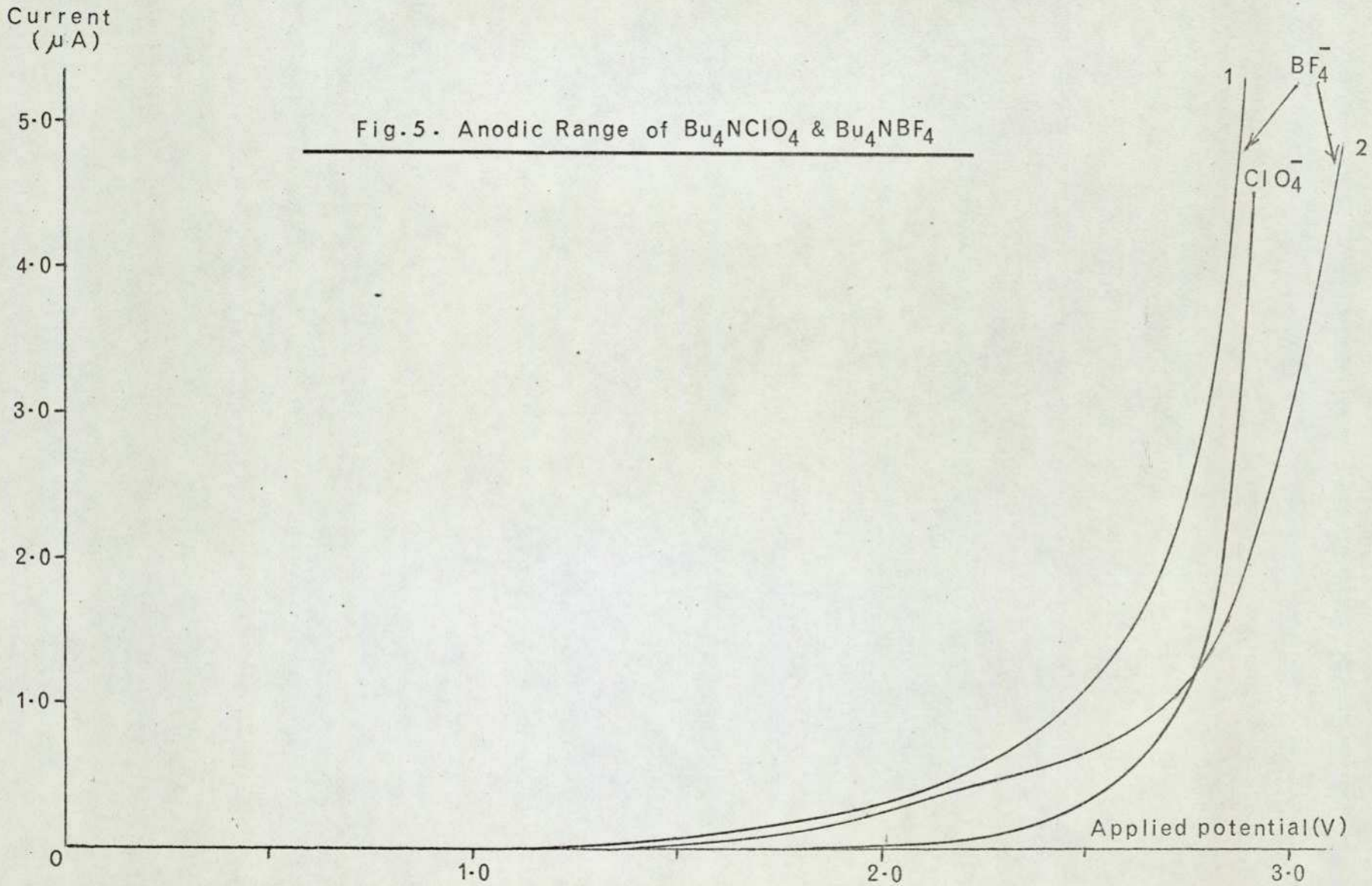


Fig. 6. Anodic Polarography of Et_4NI

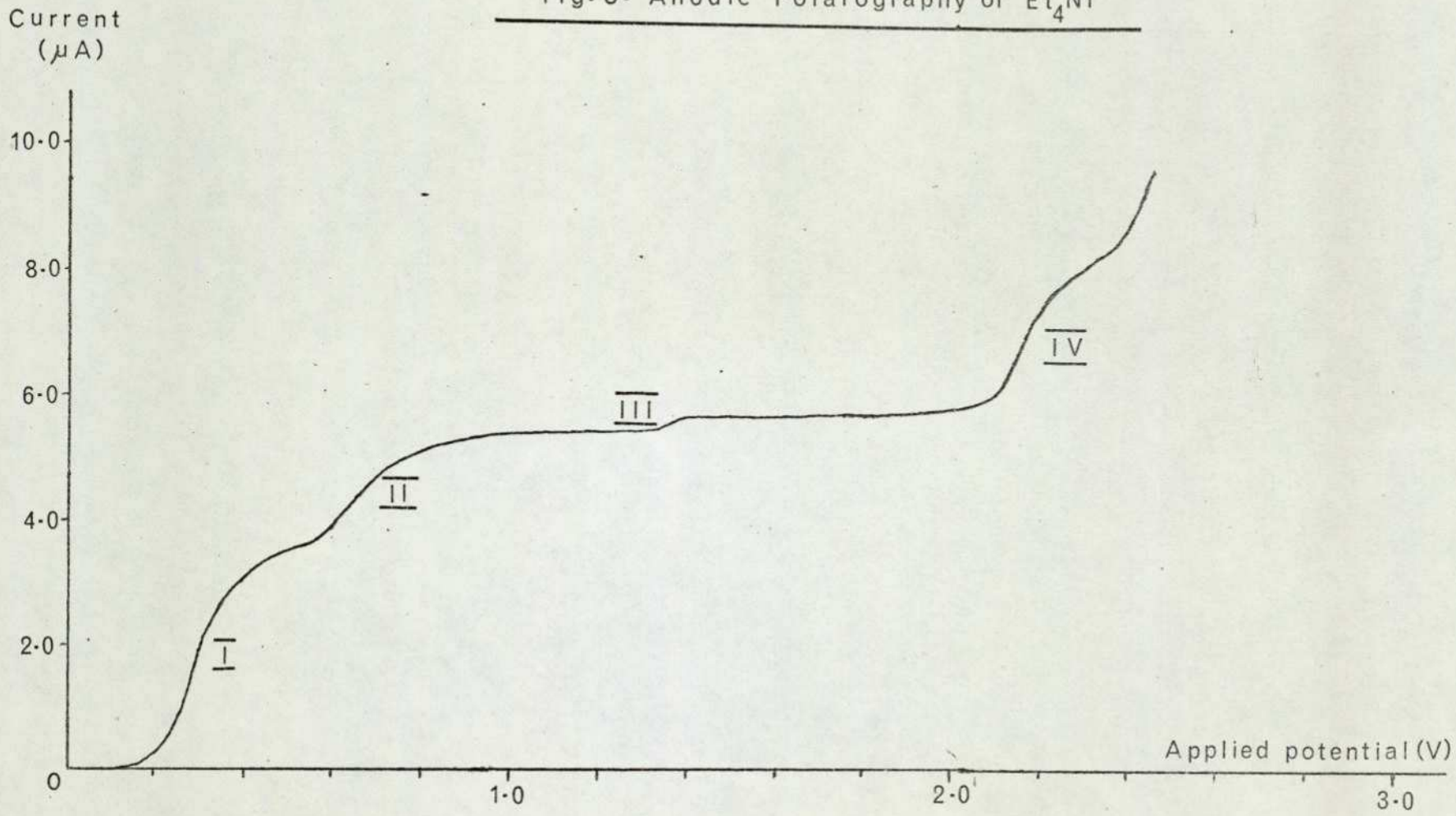
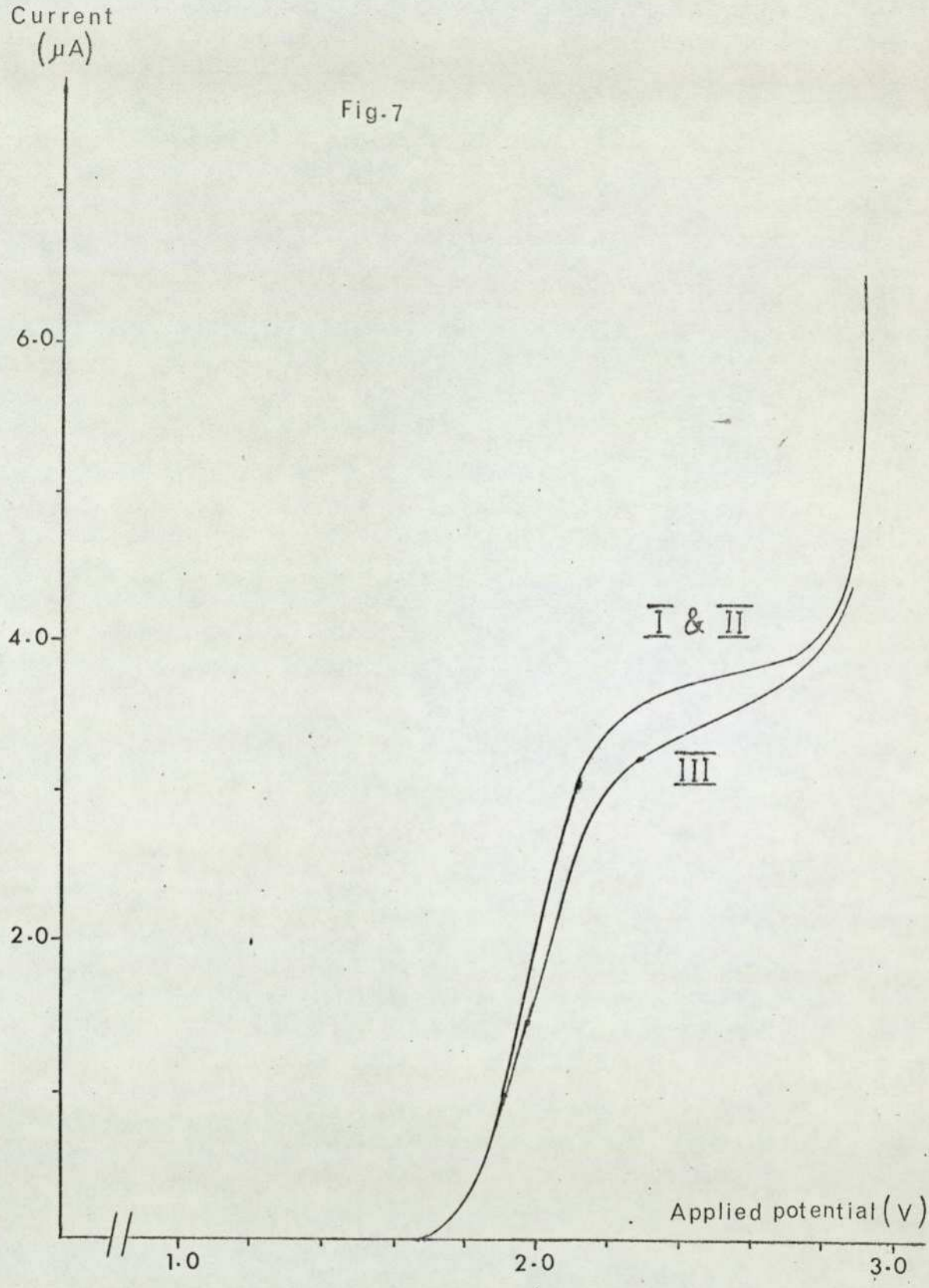


Fig.7



4.2 Anodic Polarography and Coulometry of Silver(I) Nitrate Solutions

A polarographic study of silver(I) nitrate solutions was carried out to ascertain whether a wave for the oxidation of silver(I) to silver(II) existed within the anodic range of the solvent medium. If this oxidation were to occur, then it might provide an ideal route for the preparation of silver(II) complexes via the free silver(II) ion. Although a previous study[105] of the electrolytic oxidation of silver nitrate solutions in acetonitrile did not indicate the oxidation of silver(I) ions but resulted in oxidation of the nitrate ion, these electrolyses were not carried out at a controlled anode potential and were not preceded by polarographic analysis. This evidence was not considered, therefore, to preclude the possibility of the oxidation of silver(I) in acetonitrile.

The oxidation of silver(I) to silver(II) within the anodic limit of the solvent system would appear to be feasible. The strong solvation of silver(I) ions by acetonitrile has been demonstrated by Janz and co-workers[108, 109] who isolated $[Ag.CH_3CN]NO_3$ and $[Ag(CH_3CN)_2]NO_3$ from solutions of silver nitrate in acetonitrile. That silver ions are more strongly solvated in acetonitrile than in water is further indicated by the fact that the standard reduction potential for the silver(I)/silver(0) couple in acetonitrile is some 0.4 V more negative than the corresponding value determined in an aqueous medium.[110]

Although the silver(I) ion is strongly solvated in acetonitrile (a factor which would tend to make the reduction potential of the silver(II)/silver(I) couple more positive) the dipositive silver ion might be expected to be even more strongly solvated as is usually found

for ions of higher charge. If this is the case, then it would be reasonable to anticipate that the standard reduction potential of the silver(II)/ silver(I) couple in acetonitrile would be of the same order as the value determined in an aqueous medium (2.16 V vs. S.C.E.).[29] Since this value is well within the anodic limit of the solvent system (about 3.0 V), an oxidation wave would be expected to be observed within the experimental range available.

Results and discussion

Polarograms for silver(I) nitrate solutions in the concentration range 1 mM to 5 mM were recorded over the range 1.0 V to 3.0 V at a scanning rate of 0.4 V min^{-1}. Initially, the lower limit of the scanning range was selected as 0.0 V but this was changed to 1.0 V since a reduction wave was found to be present at 0.30 V vs. S.C.E. (this wave has been characterised by Kolthoff[5] and Larson et al.[107] as the reduction wave of the silver(I)/ silver(0) couple).

A representative polarogram for the anodic oxidation of silver nitrate is given in Fig. 8, p. 80 and shows a single wave having a half-wave potential of about 2.0 V. Table II, p. 74 gives details of the complete set of results and Fig. 9, p. 81 shows a plot of the limiting current (i_L) versus the concentration of silver nitrate (C) for the oxidation wave.

Table II. Anodic polarography of silver nitrate

S.No.	$AgNO_3$ Concn. mM	Limiting Current μA	Half-wave potential V
1	1.14	2.1	2.05
2	1.20	2.2	2.04
3	1.66	2.8	1.98
4	1.76	3.3	1.99
5	2.00	3.5	2.05
6	2.20	3.9	2.06
7	2.28	4.2	2.05
8	2.47	4.5	2.04
9	2.55	4.6	2.06
10	4.20	7.3	2.04
11	4.70	8.2	2.04

From the slope, (Fig. 9, p. 81) the limiting current for 1 mM silver nitrate is found to be 1.8 ± 0.2 μA.

The oxidation wave has a half-wave potential of 2.00 ± 0.04 V and the limiting current is proportional to the concentration over the experimental range used. The slope of i_L vs C curve was found to be 1.8 ± 0.2 μA mM^{-1} , compares favourably with the value of 1.8 ± 0.1 μA mM^{-1}, obtained for the one-electron iodide ion oxidation wave used to calibrate the electrode system (section 4.1.3, p. 63). It is concluded, therefore, that the oxidation wave for silver(I) nitrate corresponds to a one-electron

process; the wave, however, is not reversible since the plot of $\log i/_{i_L - i}$ against V (Fig. 10, p. 82) for the polarogram shown in Fig. 10, p. 82 gives a slope which corresponds to an electron change of about 0.5 per molecule.

Coulometric studies confirmed that the oxidation wave for silver(I) nitrate corresponded to a one-electron process. Table III gives details of coulometric experiments in which solutions containing silver(I) nitrate in the presence of TBAP as supporting electrolyte were oxidised at a controlled potential in the vicinity of the half-wave potential of the anodic wave (2.00 V) by the method described in section 3.2.1., p. 45 . The values of the electron change per molecule for the three electrolyses were 0.99, 0.94 and 1.02 corresponding to the electrolysis of 9.8 mg., 18.1 mg., and 46.7 mg. of silver nitrate respectively. The anolyte from the last of these experiments was removed for chemical tests.

Table III Coulometry of Silver Nitrate

(A) Wt. of silver nitrate electolysed = 0.0098 g

Bu_4NClO_4 concentration = 0.1 M

Anodic applied potential = 2.05 V

Initial current = 25 mA

Electrolysis time = 84 min

Total quantity of electricity for electrolysis = 5.534 coulombs

$$n = \frac{Q.M}{F.W} = 0.99 \text{ electron/molecule}$$

(B) Wt. of silver nitrate electrolysed = 0.0181 g

Bu_4NClO_4 concentration = 0.1 M

Anodic applied potential = 1.90 V

Initial current = 8.5 mA

Electrolysis time = 66 min.

Total quantity of electricity for electrolysis = 9.649 coulombs.

n = 0.94 electron/molecule

(C) Wt. of silver nitrate electrolysed = 0.0467 g

Bu_4NClO_4 concentration = 0.1 M

Anodic applied potential = 2.05 V

Initial current = 15.5 mA

Electrolysis time = 82 min.

Total quantity of electricity for electrolysis = 26.966 coulombs

n = 1.02 electron/molecule

n = No. of electrons involved per molecule (section 3.3.4)

Although a one-electron change for the oxidation process was established, the product of the reaction did not appear to be Silver(II). In the first place, the oxidised solutions were colourless and, further, oxidsing properties were absent as indicated by the reaction with iodide in which silver iodide was precipatated but no oxidation to iodine occurred. The addition of o-phenanthroline to the oxidised solution gave a yellow precipitate which, after filtration and drying under vacuum over phosphorous pentoxide, did not melt even at 340°C. This compound was similar in colour and gave the same infra-red spectrum as bis(o-phen) silver(I) perchlorate, a complex which also does not melt even at 340°C.

It was concluded, therefore, that the oxidation wave of silver(I) nitrate ($E_{\frac{1}{2}}$ = 2.00 V) corresponded to the one-electron oxidation of the nitrate ion and was not associated with the oxidation of the cation. This conclusion was supported by two further polarographic experiments. The polarogram of a 1.74 mM silver(I) perchlorate solution showed the complete absence of an oxidation wave (Fig. 11, p.83) whilst the polarogram of a 2.7 mM solution of tetra-n-butylammonium nitrate (Fig.8, p.80) showed an oxidation wave ($E_{\frac{1}{2}}$ = 2.01 V) identical with that of silver(I) nitrate.

The polarographic and coulometric data for the oxidation of nitrate ion are not consistent with the scheme below, which is analogous to that proposed by Schmidt and Noack[94] for perchlorate ion oxidation in acetonitrile:

$$NO_3^- \longrightarrow NO_3^{\cdot} + e^- \qquad (17)$$

$$NO_3^{\cdot} + CH_3CN \longrightarrow HNO_3 + \cdot CH_2CN \qquad (17a)$$

$$2 \cdot CH_2CN \longrightarrow CN - CH_2 - CH_2 - CN \qquad (17b)$$

Since the nitrate ion is regenerated in reaction (17a) this scheme corresponds to the catalytic oxidation of the solvent and would simply represent the anodic limit of the solvent system; a limiting current would not be attained.

The data are consistent, however, with the reaction scheme proposed by Schmidt and Strange[105] to account for nitrate ion oxidation in acetonitrile viz.

$$NO_3^- \longrightarrow NO_3^{\cdot} + e^- \qquad (18)$$

$$2NO_3^{\cdot} \longrightarrow N_2O_6 \qquad (18a)$$

$$N_2O_6 \longrightarrow N_2O_5 + \tfrac{1}{2}O_2 \qquad (18b)$$

and also with the reaction scheme

$$NO_3^- \longrightarrow NO_2^+ + \tfrac{1}{2}O_2 + 2e^- \qquad (19)$$

$$NO_2^+ + NO_3^- \longrightarrow N_2O_5 \qquad (19a)$$

proposed by Cauquis et al.[106] to account for nitrate ion oxidation in nitromethane. Although both the above schemes correspond to a one-electron change per molecule in keeping with the present data, a complete analytical investigation of the products and intermediates would be required before the mechanism could be more fully understood.

The absence of a Silver(I)/Silver(II) wave within the anodic limit of the solvent system ($\sim$3.0 V) is somewhat surprising. This implies that the silver(II) ion in acetonitrile is much less strongly solvated than Silver(I) ion, a situation which would not be expected on purely electrostatic grounds. The following argument might be used to explain this anomaly. If the specific solvation of Ag^+ by acetonitrile is attributed to back π-bonding from the silver ion to the NC-group, this effect might be considerably reduced when the silver is in the dipositive

state, the extra positive charge reducing the π-donor properties of the silver ion and thereby reducing the strength of the silver(II)/ acetonitrile bond.

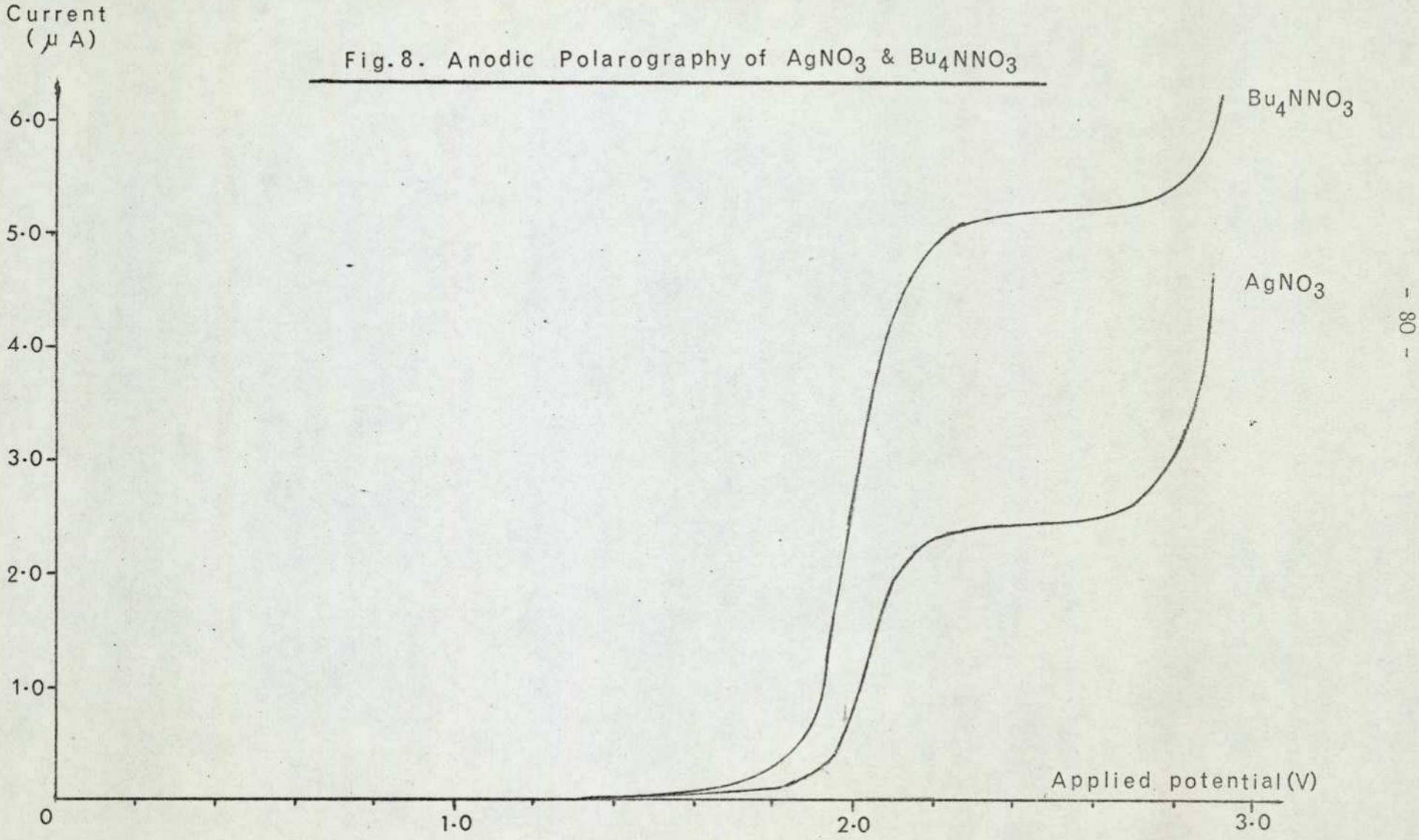
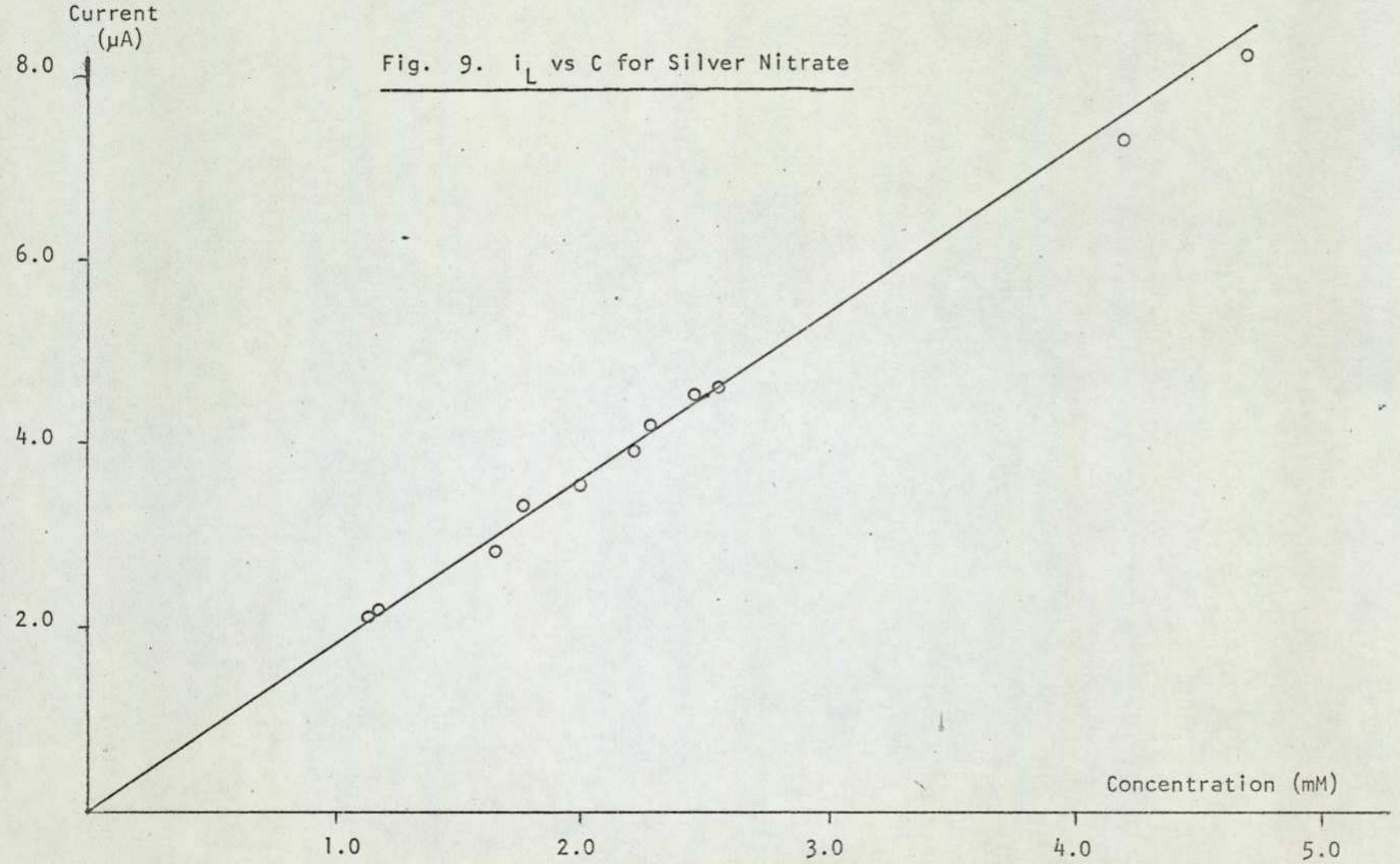


Fig. 8. Anodic Polarography of $AgNO_3$ & Bu_4NNO_3

Fig. 9. i_L vs C for Silver Nitrate



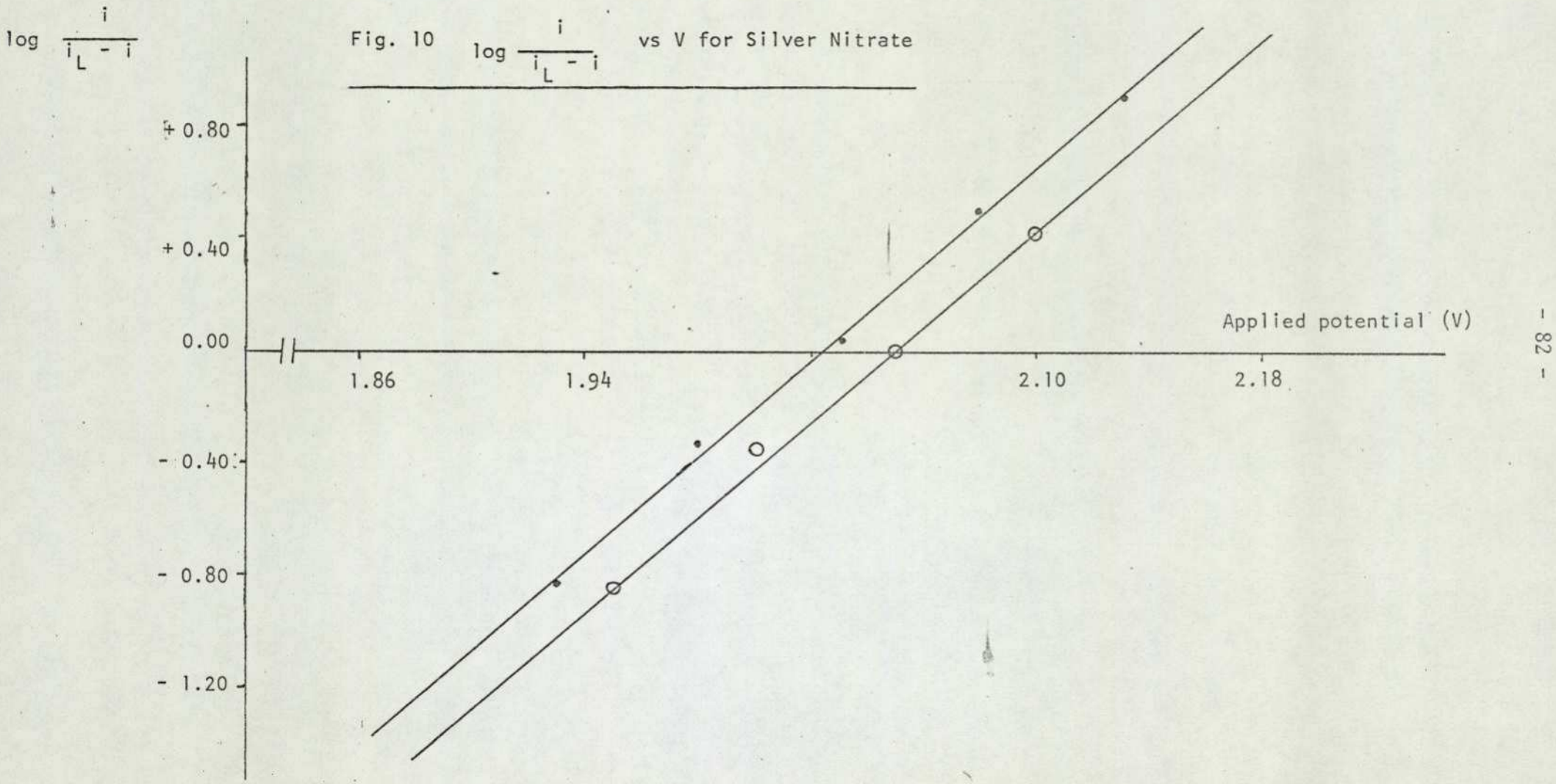
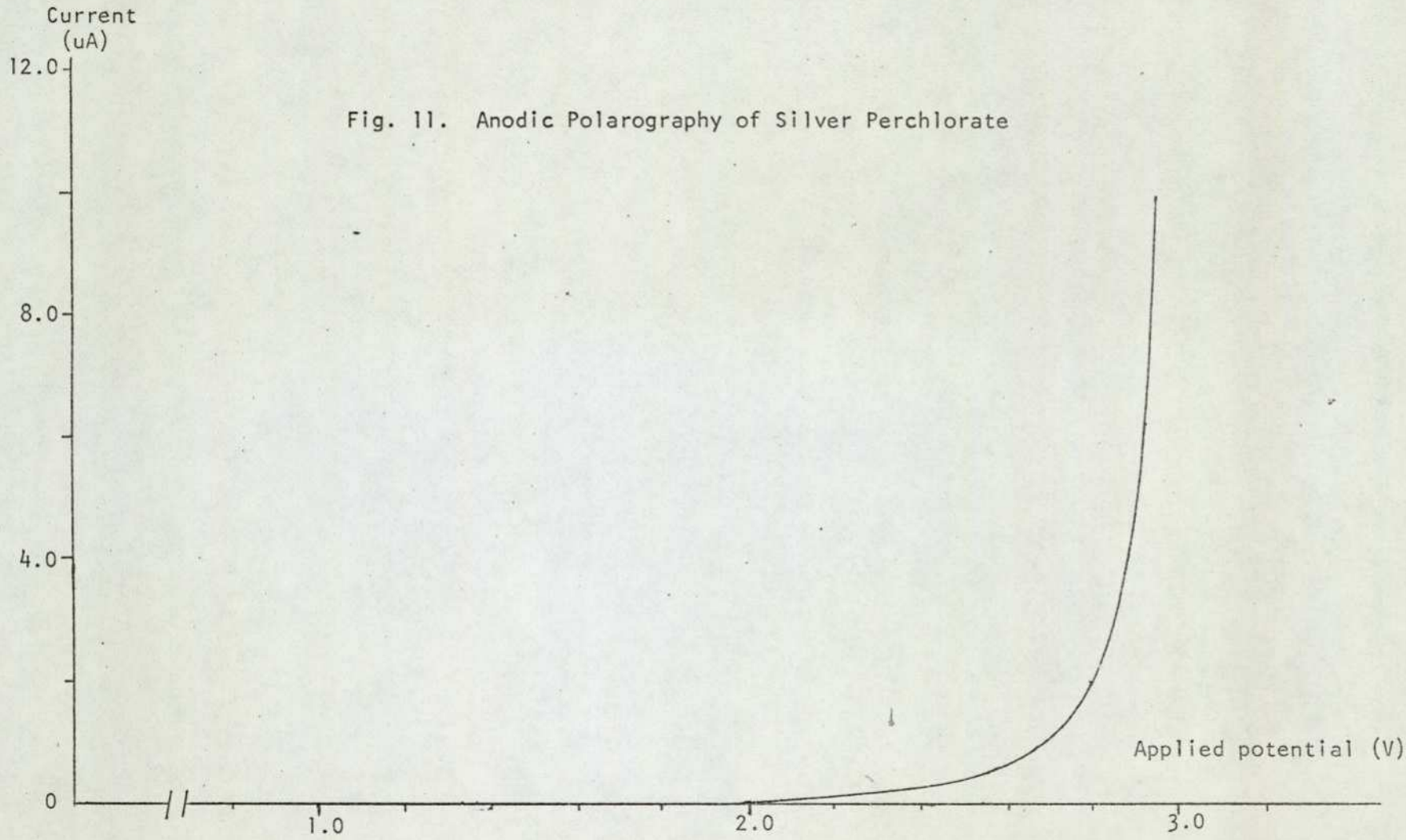


Fig. 10 $\log \frac{i}{i_L - i}$ vs V for Silver Nitrate

Fig. 11. Anodic Polarography of Silver Perchlorate



4.3 Electrochemical Oxidation of Silver(I) Nitrate and Silver(I) Perchlorate in the Presence of 2,2'-Bipyridyl

4.3.1. Preliminary polarographic studies

In the study of the silver(I)/bipy system, it was necessary to establish, first, whether the ligand itself gave an oxidation wave in the absence of silver ions. Fig. 12, p.106 is a polarogram of 2.0 mM 2,2'-bipyridyl in 0.1 M tetra-n-butylammonium perchlorate as supporting electrolyte at a scan rate of 0.4 V min^{-1}. A very small wave ($i_L \sim 0.3$ μA) is observed at a half-wave potential of 2.1 V. Polarograms were also obtained for bipyridyl concentration of 6mM, 10mM and 30mM for which the limiting current was virtually constant at the same value as for the 2mM solution. The consistancy of the limiting current with changes in concentration is difficult to account for. However, as far as the present work is concerned, it is clear that the bipyridyl wave will not interfere at potentials less than 2.0 V and at higher potentials, a correction which is small, can be made for its presence.

Polarograms were next determined for solutions of silver(I) nitrate and siver(I) perchlorate in the presence of bipyridyl. Fig. 13, p.107 shows a representative polarogram for the silver(I) nitrate/bipy system ($[AgNO_3]$ = 1.76 mM, [bipy] = 3.69 mM, $[Bu_4NClO_4]$ = 0.1M) at a scan rate of 0.4 V min^{-1}. A polarogram for the same concentration conditions but using a higher current sensitivity is shown in Fig. 14, p.108 . Fig. 15 is a polarogram of a 1.76 mM silver(I) nitrate solution in the presence of an excess of bipyridyl (86.2 mM).

Fig. 16 curves A and B are polarograms of a 1.6 mM solution of silver(I) perchlorate containing 6.2 mM bipyridyl and 96.8 mM bipyridyl

respectively in the presence of 0.1 M tetra-n-butylammonium perchlorate (scan rate 0.4 V min^{-1}).

Discussion

The silver(I) nitrate/bipy system shows two well defined waves (cf. Fig. 13) the first of which occurs at a potential of 1.44 $\pm$ 0.04 V, the limiting current for this wave being much smaller than expected for a one electron oxidation process. The second wave occurs at the same potential ($\sim$2.0 V) as that of the nitrate ion wave (section 4.2) although the limiting current is much greater than that for a silver nitrate solution of the same concentration in the absence of ligand. The limiting currents of both waves could be measured with a reproducibility of about $\pm$ 0.1 μA. An interesting feature of the system is that the limiting currents of both waves vary with ligand concentration, that of the first wave reducing to zero when the bipyridyl is present in large excess (Fig. 15, p.109).

In contrast to the silver(I) nitrate/bipy system, the silver(I) perchlorate/bipy system shows a poorly defined first wave which is followed by a pronounced maximum at higher potentials, the current falling to a low level before the anodic limit is reached (Fig. 16, Curve A, p.110). The first wave occurs at the same potential as that of the silver(I) nitrate/bipy system (1.44 V); this wave, and the maximum which follows it, disappear when the ligand is present in large excess (Fig. 16, Curve B).

The variation of the limiting current of the first wave of the silver(I)/bipy system with ligand concentration was considered to be of particular interest to justify a more detailed investigation. It is

clear that the silver(I) nitrate/bipy system is better suited to such a detailed study than the silver(I) perchlorate/bipy system because the polarograms are more reproducible and the waves were clearly defined permitting accurate measurements to be made of limiting currents and half-wave potentials. Also, the silver(I) nitrate/bipy system is not complicated by the presence of a maximum. Before this was carried out, however, an attempt was made to characterise the oxidation processes occurring using constant potential coulometry.

4.3.2 Control potential electrolysis of solutions of silver(I) and 2,2'-bipyridyl.

Electrolysis of silver(I) nitrate/bipy solutions at 1.40 - 1.50 V.

Coulometric determinations (cf. section 3.2.1.) for the electrolysis of silver(I) nitrate solutions in the presence of bipyridyl were carried out at a constant potential in the vicinity of the half-wave potential (1.44 V). Initially, solutions have molecular ratios of bipy : silver(I) nitrate of the order of 2 : 1 were electrolysed but it was found that dark red-brown crystals separated from the solution and adhered to the rotating macro-electrode giving a sharp reduction in current and preventing complete electrolysis. When the molar ratio of ligand : metal was increased to about 30 : 1, the product remained in solution (which gradually turned dark brown) and the electrolysis proceeded to completion. Table IV, p. 87 gives the result of three such electrolyses giving electron changes of 1.12, 0.98 and 0.98 per molecule calculated according to the method described in section 3.3.4. The one-electron process was consistant with the oxidation of silver(I) to silver(II).

Table IV Coulometry of silver(I) nitrate/bipy solutions

(A)	Weight of silver nitrate electrolysed	= 0.0101 g
	Bu_4NClO_4 concentration	= 0.1 M
	Anodic applied potential	= 1.40 V
	Initial current	= 2.25 mA
	Electrolysis time	= 150 min
	Total quantity of electricity for electrolysis	= 6.41 coulombs
	Molecular ratio of bipy : $AgNO_3$	= 32 : 1

$$n = \frac{Q \,.\, M}{F \,.\, W} = 1.12 \text{ electron/mole}$$

(B)	Weight of silver nitrate electrolysed	= 0.0109 g
	Bu_4NClO_4 concentration	= 0.1 M
	Anodic applied potential	= 1.45 V
	Initial current	= 3.1 mA
	Electrolysis time	= 118 min
	Total quantity of electricity for electrolysis	= 6.09 coulombs
	Molecular ratio of bipy : $AgNO_3$	= 30 : 1

n = 0.98 electron/mole

(C)	Weight of silver nitrate electrolysed	= 0.0101 g
	Bu_4NClO_4 concentration	= 0.1 M
	Anodic applied potential	= 1.50 V
	Initial current	= 3.7 mA
	Electrolysis time	= 52 min
	Total quantity of electricity for electrolysis	= 5.60 coulombs
	Molecular ratio of bipy : $AgNO_3$	= 30 : 1

n = 0.98 electron/mole

Controlled potential electrolyses (at 1.4 - 1.5 V) were next performed on a larger scale and the oxidation product was separated from the anode solutions. Table V gives details of the product obtained. In these experiments the ratio of bipyridyl to silver(I) nitrate was about 3 : 1. During electrolysis, some of the product separated from solution and coated the electrode producing a rapid fall in current; when this happened, the electrolysis was temporarily stopped to allow the electrode to be cleaned. Because of this effect, the current-time curves were not reliable and were not used for coulometric calculations.

The oxidation product was isolated in the following way. First, the small amount of solid which separated during electrolysis was removed by decantation. Silver(I) nitrate was then added to the dark brown anolyte in small amounts until no more dark red-brown crystals separated and the supernatant liquid was a pale yellow colour. The bulk of the supernatant liquid was removed by pipette and the residue was purified by washing several times with acetone in which silver(I) nitrate, bipyridyl and tetra-n-butylammonium perchlorate were all soluble. After each addition of acetone, the solution was centrifuged and the centrifugate was evaporated to dryness; this was continued until no residue was found in the washings. The dark red-brown crystals were dried in a vacuum oven at 40°C. The needle-shaped crystals, which melted at 198 - 208°C, exhibited oxidising properties, yielding iodine with acqueous potassium iodide solution and bromine with aqueous potassium bromide solution.

Analysis of the product gave:

	C	H	N	Ag^{2+}
Found	40.9%	2.8%	11.9%	17.8%
	40.8%	2.9%	11.7%	17.9%
Theoretical for $[Ag(bipy)_2] NO_3 \cdot ClO_4$	41.29%	2.77%	12.04%	18.54%
Theoretical for $[Ag(bipy)_2] (NO_3)_2$	44.14%	2.96%	15.44%	19.82%
Theoretical for $[Ag(bipy)_2] (ClO_4)_2$	38.80%	2.60%	9.05%	17.42%

The compound had an effective magnetic moment of 1.9 B.M. at 20°C as determined by the Gouy method.

The analysis indicated that the product was $[Ag(bipy)_2] NO_3 \cdot ClO_4$ (Table V giving the percentage yield based on this product).

The infra-red spectrum of the product (in potassium bromide disc) showed a very strong band at 1380 cm^{-1} indicating the presence of ionic nitrate; a broad and very strong ionic perchlorate band was also observed at 1085 - 1145 cm^{-1}. These data support the suggested formulation of the product as a mixed anion silver(II) complex.

The diffuse reflectance spectrum for the silver(II) complex gave a distinct absorption band at 18, 182 cm^{-1}, this compares with the single absorption band (for d^9 arrangement) at 19,048 cm^{-1} reported by Lake and Kennedy[31] for silver(II) in condensed phosphoric acid. Thorpe and Kochi[55] also reported an absorption band at 23,529 cm^{-1} for bis(bipy)silver(II) dinitrate in water.

Table V Preparation of bis(bipy)silver(II) nitrate perchlorate

S.No.	Wt. of $AgNO_3$ g	*Bipy/Silver(I)	Anodic Potential V	% yield
1	0.0212	3.0 : 1	1.50	44.1
2	0.0433	3.1 : 1	1.50	44.5
3	0.0630	3.2 : 1	1.45	39
4	0.0425	3.1 : 1	1.50	47

* Bipy/silver(I) = Molecular ratio

Whilst the possibility of an equimolar mixture of the dinitrate and diperchlorate is not ruled out, the formulation of a mixed salt is not unexpected since in silver(I) nitrate solution in acetonitrile, nitrate ions are known to form ion pairs with silver ions,[109] if this is also the case for unipositive silver(I) complex ions then it is not unreasonable to assume that the nitrate ion will be in the vicinity of the complex species when oxidation takes place and will therefore be associated with the product.

The method of isolation of the product calls for some comment. Although the method was based on the chance observation that the addition of silver(I) nitrate to solutions of silver(II) in the presence of excess ligand caused precipitation of the silver(II) complex, the effect can be explained in rational terms. The addition of silver nitrate to the solution is thought to reduce the concentration of bipyridyl (by complex formation with silver(I)) until a level is reached where the less soluble silver(II) complex precipitates. Since the solubility of bis(bipy)silver(II) complex is increased appreciably in the presence of an excess of bipyridyl, it can be inferred that higher complex species e.g. tris(bipy)silver(II) ions are present in solution.

Electrolysis of silver(I) perchlorate/bipy solution at 1.4 - 1.5 V.

Solutions of silver(I) perchlorate in the presence of bipyridyl were electrolysed at a controlled potential in the vicinity of the half-wave potential of the first wave (1.4 - 1.5 V). For this system, coulometric determinations were incorporated in preparative scale electrolyses. Table VI, p.92 gives details of two coulometric determinations in which a

Table VI Coulometry of silver(I) perchlorate/bipy solutions

(A) Weight of silver perchlorate electrolysed = 0.2011 g.

BU_4NClO_4 concentration = 0.15 M

Anodic applied potential = 1.45 V

Initial current = 40 mA

Electrolysis time = 204 min

Total quantity of electricity for electrolysis = 107.73 coulombs

Molecular ratio of bipy : $AgClO_4$ = 11 : 1

$$n = \frac{Q.M}{F.W} = 1.15 \text{ electron/mole}$$

(B) Weight of silver perchlorate electrolysed = 0.0933 g

BU_4NClO_4 concentration = 0.2 M

Anodic applied potential = 1.50 V

Initial current = 25 mA

Electrolysis time = 196 min

Total quantity of electricity for electrolysis = 46.02 coulombs

Molecular ratio of bipy : $AgClO_4$ = 22.66 : 1

$$n = 1.06 \text{ electron/mole}$$

large excess of bipyridyl was used to prevent precipitation of the silver(II) product and give reliable current-time curves.

These data confirm the one-electron oxidation of silver(I) at the potential of the first polarographic wave.

Because of the large excess of bipyridyl used in these experiments, the method of adding silver(I) salt would have been required thus increasing the problems of purification. Instead, the solvent was simply removed under vacuum at room temperature, the supporting electrolyte and excess of ligand being removed by washing the residue several times with acetone. The product was dried in a vacuum oven at 40°C. The dark brown-red needle shaped crystals had a melting point of 231 - 236°C.

Two further preparative scale electrolyses were carried out using smaller ratios of ligand to metal salt (5 : 1). As in the case of silver(I) nitrate experiments with low bipy/silver(I) ratios, the anode required to be recleaned during electrolysis. The silver(II) complex was precipitated by the addition of silver(I) perchlorate by the method described in the preceding section. The dark brown-red needle-shaped crystals had a melting point of 231 - 235°C. Table VII gives details of the amounts of silver(I) perchlorate and bipyridyl ratio used in the complete set of experiments and includes the percentage yield of the product obtained. Analyses of the product isolated by the two different methods gave

Method of isolation	C%	H%	N%	Ag^{2+}%
Solvent evaporation	38.75	2.69	9.16	16.1
Addition of $AgClO_4$	38.54	2.58	9.01	15.9

Table VII Preparation of bis(bipy) silver(II) diperchlorate

S.No.	Silver Perchlorate g.	*Bipy/Silver(I)	Anodic Potential V	% yield
1	0.0933	22 : 1	1.50	57.4 %
2	0.2011	11 : 1	1.45	65.1 %
3	0.2385	5 : 1	1.40	39.6 %
4	0.3554	5 : 1	1.40	31.1 %

* Bipy/silver(I) = Molecular ratio

These analyses are consistent with the complex $[Ag(bipy)_2](ClO_4)_2$ for which

C = 38.80%, H = 2.60%, N = 9.05%, Ag^{2+} = 17.42%

The infra-red spectrum of the product gave a very strong broad band at 1085 - 1150 cm^{-1} corresponding to the absorption of the perchlorate ions, the ionic nitrate band at 1380 - 1410 cm^{-1} being absent. These data are in accordance with the diperchlorate silver(II) complex. The diffuse reflectance spectrum gave an absorption band at 20,408 cm^{-1} (490 mμ) which is higher than that found for bis(bipy)silver(II) nitrate perchlorate.

The mass spectrum of the product gave a maximum mass number of 156.0687 corresponding to the mass of the 2,2'-bipyridyl molecule. It appears, therefore, that under the conditions used to determine the mass spectrum (ion source temperature 300°C, electron energy 70 eV), the complex was decomposed. However, the mass spectrum is useful in demonstrating that the ligand remains unchanged during the electrochemical oxidation of the silver(I) complex.

Table VII includes values of percentage yield based on the product as bis(bipy)silver(II) diperchlorate. It is noted that using the solvent evaporation method of isolation, higher yields are obtained compared to the precipitation method. This is to be expected on the grounds that in the latter method, precipitation is not complete. However, the precipitation method has the advantage that only two or three washings are required to remove the excess reagents and supporting electrolytes; this compares with about eight washings required for the solvent evaporation method.

Electrolysis of silver(I)nitrate/bipy solutions at 2.0 V.

Electrolysis of a silver nitrate/bipy solution was carried out at an anode potential of 2.0 V i.e. at a potential corresponding to the second polarographic wave. Details of the coulometric determinations are given in Table VIII.

The amount of electricity passed during the electrolysis was extremely large and on the basis of the total silver(I) percentage gave an electron charge/molecule of about 7.3; this indicates that not only the silver(I) but the ligand also is undergoing oxidation. Observations of the colour changes occurring in the anode compartment during electrolysis support this suggestion. The colourless silver(I) solution first turned dark brown corresponding to the oxidation of silver(I) to silver(II); continued electrolysis, however, produced a considerable reduction in the colour intensity, a yellow solution remaining at the end of the experiment. This would occur if the ligand itself were oxidised, its continued removal eventually shifting the silver(II) complex equilibria in favour of the ligand and the unstable silver(II) ion which would be reduced to silver(I) in the absence of ligand. The final solution, in fact, gave a yellow precipitate with o-phenanthroline, (thought to be bis(o-phen)silver(I) perchlorate) which did not exhibit oxidising properties. It seems reasonable to assume, since the second oxidation wave of the system occurs at the same half-wave potential as that of the nitrate ion, that the wave is associated with the oxidation of the nitrate ion to the nitrate radical. This radical might then oxidise the ligand with the regeneration of the nitrate ion giving a catalytic wave. (It will be remembered that the limiting current of the

Table VIII Coulometry of silver(I) nitrate/bipy at 2.0 V

Weight of silver(I) nitrate taken	= 0.0393 g.
Bu_4NClO_4 concentration	= 0.1 M
Anodic applied potential	= 2.0 V
Initial current	= 184 mA
Electrolysis time	= 405 min.
Total quantity of electricity for electrolysis	= 162.08 coulombs
Weight of bipyridyl taken	= 0.3222 g.

$$n = \frac{Q.M}{F.W} = 7.26 \text{ electron/mole}$$

second wave is much greater than expected for the same concentration of silver nitrate in the absence of ligand).

Clearly, the oxidation processes occurring at 2.0 V are extremely complex and although the characterisation of the products and elucidation of the mechanism would be of considerable interest, it was thought to be outside the scope of the present work which was concerned primarily with the oxidation of silver(I) complexes.

4.3.3. Detailed polarographic study of silver(I) nitrate in the presence of 2,2'-bipyridyl.

Anodic polarograms over the voltage range 1.0 V to 3.0 V were obtained for solutions containing different total concentrations of silver(I) nitrate (C_M) and bipyridyl (C_L) in 0.1 M tetra-n-butylammonium perchlorate as supporting electrolyte using a scan rate of 0.4 V min^{-1}. For each set of concentration conditions, two polarograms were obtained at different current sensitivities, the measurement of the limiting current of the smaller first wave requiring a high sensitivity than that for the second wave. The data are recorded in Table IX, p.99 in which the values of the limiting current of the first and second waves are denoted as $i_L(I)$ and $i_L(II)$ respectively. Also included in Table IX are the data of polarograms obtained for solutions of the complex bis(bipy)silver(I) nitrate (these are indicated by an asterisk and in these cases C_L has been taken as equal to $2C_M$).

Discussion

The result of the coulometric experiments established that the first anodic wave corresponds to the oxidation of silver(I) to silver(II). However, since the limiting current is much smaller than would be expected

Table IX Anodic polarography of the silver(I) nitrate/bipy system

S.No.	C_M mM	C_L mM	$i_L(I)$ μA	$E_{\frac{1}{2}}(I)$ V	$i_L(II)$ μA	$E_{\frac{1}{2}}(II)$ V	$[AgL^+]$ mM
1	0.62	31.5	0.3	1.44	4.0	2.02	0.113
2	1.00	5.8	0.7	1.44	4.7	2.05	0.524
3	*1.00	2.0	0.9	1.48	3.1	2.07	0.497
4	1.50	4.41	1.6	1.40	6.6	2.00	0.836
5	1.66	43.7	0.4	1.44	7.2	2.02	0.237
6	1.66	93.7	0.3	1.44	6.1	2.00	0.116
7	1.76	3.69	1.7	1.45	5.2	2.01	0.968
8	1.76	7.13	1.6	1.44	9.0	2.00	0.907
9	1.76	46.3	0.5	1.42	7.5	2.05	0.238
10	1.76	86.2	0.2	1.46	6.5	2.05	0.133
11	2.00	5.80	1.8	1.42	11.0	2.03	1.098
12	*2.00	4.00	1.7	1.47	5.8	1.99	1.104
13	*3.00	6.00	2.7	1.40	8.1	2.04	1.671
14	2.28	2.15	1.4	1.47	5.0	2.08	0.941
15	2.28	4.15	2.0	1.40	6.4	2.05	1.253
16	2.28	6.30	2.2	1.44	8.2	2.04	1.244
17	2.28	8.25	2.2	1.44	11.8	2.05	1.148
18	2.28	9.74	2.0	1.44	8.0	2.04	1.070
19	2.28	10.20	2.0	1.45	13.0	2.08	1.046
20	2.28	18.66	1.4	1.40	9.4	2.09	0.710
21	2.28	27.9	1.1	1.38	10.4	2.02	0.498

* Data for bis(bipy) silver(I) nitrate

on the basis of a one electron change involving the total silver(I), particularly when excess ligand is present, a suitable explanation was sought.

The observation that for a given concentration of silver salt, the limiting current of the first wave, $i_L(I)$, at first increased and then decreased with increasing ligand concentration (C_L), led to the suggestion that $i_L(I)$ might be related to the concentration of one of the complex species present. In the silver(I)/bipy system two complex species, $Ag(bipy)^+$ and $Ag(bipy)_2^+$, will be present, their concentrations depending on the equilibrium constants of the following reactions:

$$Ag^+ + bipy \rightleftharpoons Ag(bipy)^+ \qquad (20)$$

$$Ag(bipy)^+ + bipy \rightleftharpoons Ag(bipy)_2^+ \qquad (20a)$$

Since, at constant C_M, the concentration of $Ag(bipy)^+$ will first increase and then decrease as C_L increases, it seemed likely that there might exist a correlation between $[Ag(bipy)^+]$ and $i_L(I)$. In order to test this hypothesis, calculations were made of the concentration of $Ag(bipy)^+$ in each of the solutions (of known C_M and C_L) used in the polarographic study. This was possible using recently determined values of the overall stability constants for the silver(I)/bipy system in acetonitrile.[111] The procedure was as follows.

For the case in which a metal ion (M) forms two successive complexes ML and ML_2 with a ligand L the overall stability constants for the equilibria are defined as

$$\beta_1 = \frac{[ML]}{[M][L]} \quad \text{and} \quad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

Using the concept of the average ligand number, $\bar{n}$, defined by Bjerrum[112] as

$$\bar{n} = \frac{C_L - [L]}{C_M} \qquad (21)$$

where C_M and C_L are total concentrations of metal and ligand and $[L]$ is the free ligand concentration, it follows that

$$\bar{n} = \frac{[ML] + 2[ML_2]}{[M] + [ML] + [ML_2]}$$

whence

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2} \qquad (22)$$

and $[ML] = C_M \cdot \dfrac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2}$ (23)

the formation curve[112] of the system ($\bar{n}$ vs. $p[L]$) constructed by substituting in equation (22) the values of β_1 and β_2 (determined[111] as 9.37×10^2 mole^{-1} Kg and 1.38×10^5 mole^{-2} Kg^2 respectively) and calculating values of $\bar{n}$ for different values of $[L]$. This curve is shown in Fig. 17, p. 111.

For each experimental value of C_M used, a plot was made of C_L vs. $[L]$ using equation (21) to calculate value of C_L for given pairs of values $\bar{n}$, $[L]$ selected from the formation curve (two such curves are shown in Fig. 18, p. 112 for C_M = 1.76 mM and 2.28 mM). Finally, for each given set of experimental values of C_M and C_L, the value of $[L]$ was interpolated from the appropriate C_L vs $[L]$ curve and $[ML]$ calculated from equation (23). Table IX, p. 99 includes values of $[Ag(bipy)^+]$ and Fig. 19, p. 113 shows the relationship between $[Ag(bipy)^+]$

and $i_L(I)$. Within the experimental error of the limiting current values ($\pm$ 0.15 uA) this relationship is linear.

Two explanations can be put forward to account qualitatively for the linear relationship between $[Ag(bipy)^+]$ and $i_L(I)$. This behaviour would be expected for a diffusion controlled wave assuming $Ag(bipy)^+$ to be the only electroactive silver(I) species present in solution. However, the important assumption would have to be made that the equilibria associated with the silver(I)/bipy system were established extremely slowly, otherwise the other silver(I) species would contribute to the diffusion process giving a limiting current proportional to the total silver(I) present.

A more likely explanation is that the limiting current is kinetically controlled by the conversion of $Ag(bipy)^+$, assumed to be inactive, into some electroactive species at a rate which is slow compared to the rate of diffusion of $Ag(bipy)^+$ to the electrode surface. Thus under such conditions, the concentration of $Ag(bipy)^+$ at the electrode surface will be maintained at the bulk solution concentration; the rate of conversion to the active form and hence the limiting current will be proportional to $[Ag(bipy)^+]$ if the chemical reaction is first order or pseudo first order. This explanation is suppported by the results of a series of cyclic voltammetry experiments on solutions containing silver(I) nitrate and bipyridyl in which the voltage was swept 0.0 V to 2.0 V and back to 0.0 V in order to cover the voltage range of the first wave of the system. These data were obtained using the rapid sweep oscillographic polarograph (section 3.2.2., p. 47) in conjuncture with the micro-platinum electrode already described (section 3.2.1., p. 43). Cyclic polarograms were

obtained with the stationary electrode; Fig. 20, p.114 shows a representative cyclic polarogram for a solution containing 1.9 mM silver(I) nitrate, 7.0 mM bipyridyl in 0.1M tetra-n-butylammonium perchlorate using a stationary electrode and sweep rate of 0.2 V sec^{-1}. The most striking feature of the polarogram is that the usual peaking characteristics of rapid sweep polarograms are absent, the wave appearing as a normal polarogram obtained with a slow rate of scan. Another interesting feature is the almost complete absence of a reduction wave on the reverse scan. Further, the wave-form and wave height were almost completely independent of scan rate even when rates as high as 4 V sec^{-1} were used. These characteristics are consistent with a kinetically controlled wave[113,114] and correspond to the case where the charge transfer process is preceded by a slow chemical reaction producing the depolariser. The depolariser will be formed at a constant rate at the electrode surface if the rate of diffusion of the inactive form is greater than its rate of conversion to the active form; under these conditions the surface layer will not be depleted in the inactive form and the current will remain constant. The absence of a reduction wave on the reverse sweep implies either that the charge transfer process is completely irreversible or that the oxidised form of the depolariser is rapidly converted into an inactive form.

The experimental data available for the silver(I) nitrate/bipy system do not, of course, enable the electroactive species to be identified and any theory put forward must be extremely speculative. It seems probable, however, that the complex species $Ag(bipy)^{+}$ is the precursor

of the active form. Conversion to the active form may involve some change in the solvation sphere of the complex species, a process which has been suggested in the case of the reduction of aquated nickel(II) ions.[115] In the silver(I) nitrate system a tentative suggestion is that the inactive species is in the form of an ion pair, $Ag(bipy)^+.NO_3^-$, conversion to the active form involving the removal of nitrate ion. The rapid recombination of the nitrate ion with the oxidised form, $Ag(bipy)^{2+}$, would then account for the absence of a reduction wave in the reverse sweep of the cyclic polarogram. This idea is supported to some extent by published data[109] on the nature of acetonitrile solutions of silver(I) nitrate in which the presence of $Ag^+.NO_3^-$ ion pairs has been established.

The scheme proposed is

$Ag(bipy)^+.NO_3^-$ ion-pair (inactive)

$\uparrow\downarrow$ $- NO_3^-$ (slow) (24)

$Ag(bipy)^+ \rightleftharpoons Ag(bipy)^{2+}$ (charge transfer, $- e$)

$\uparrow\downarrow$ $+ NO_3^-$ (fast)

$Ag(bipy)^{2+}.NO_3^-$ ion-pair (inactive)

It must be emphasised that although such a scheme is consistent with the experimental data, it is highly speculative. A more detailed study will be required before the processes taking place are more fully understood. In this respect, a cyclic voltammetry study at a stationary planar electrode, for which the mathematical solutions of the electrode processes

have been obtained[114], would allow the electroactive intermediates to be detected and the rate constants of the reaction to be determined.

The detailed polarographic study of the silver(I) nitrate/bipy system did not give any further information regarding the electrode processes associated with the second wave at 2.0 V, there being no apparent correlation between the limiting current $i_L(II)$ and the concentration of any of the species present in solution (cf. Table IX).

Fig. 12. Anodic Polarography of 2.2' Bipyridyl

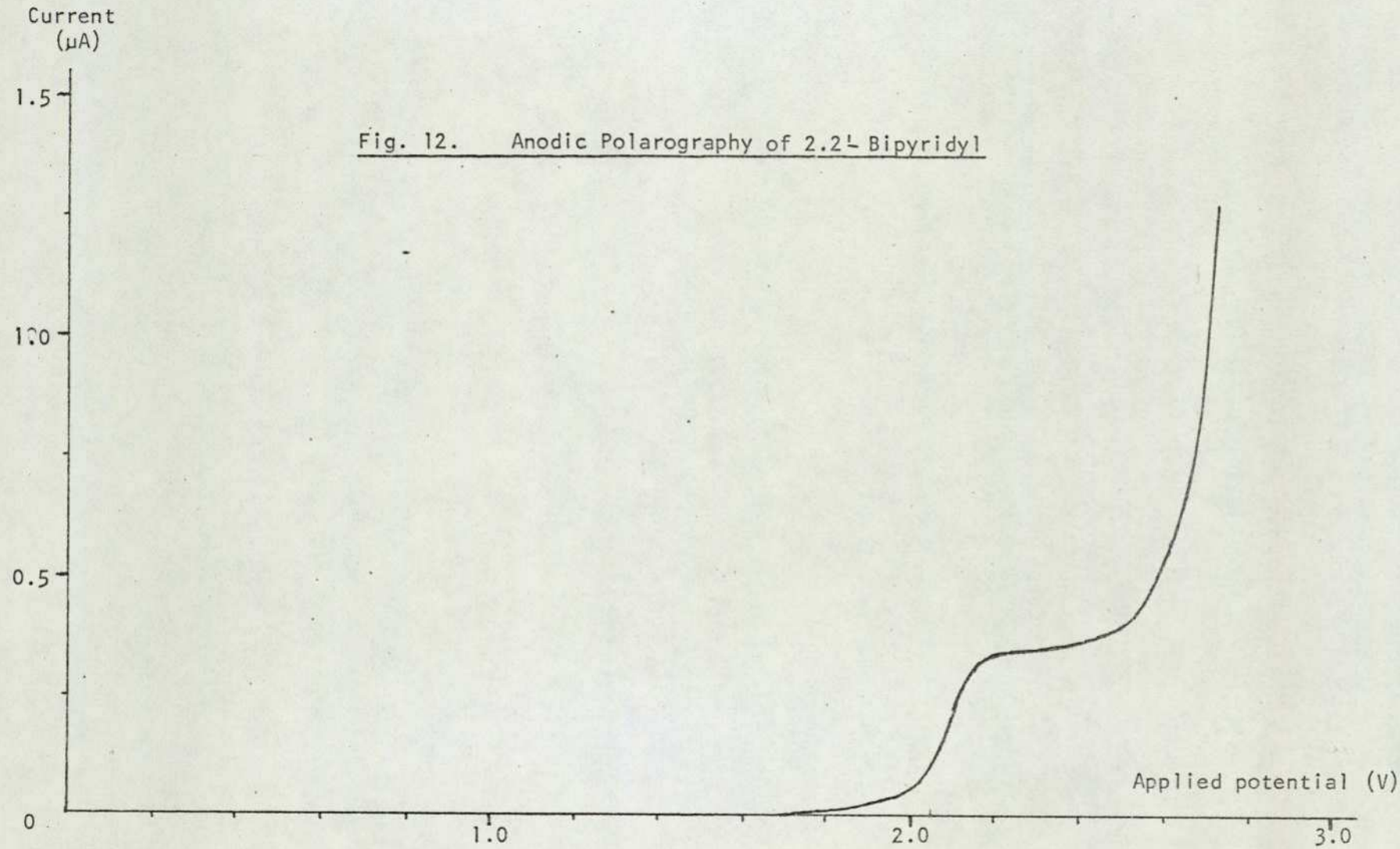
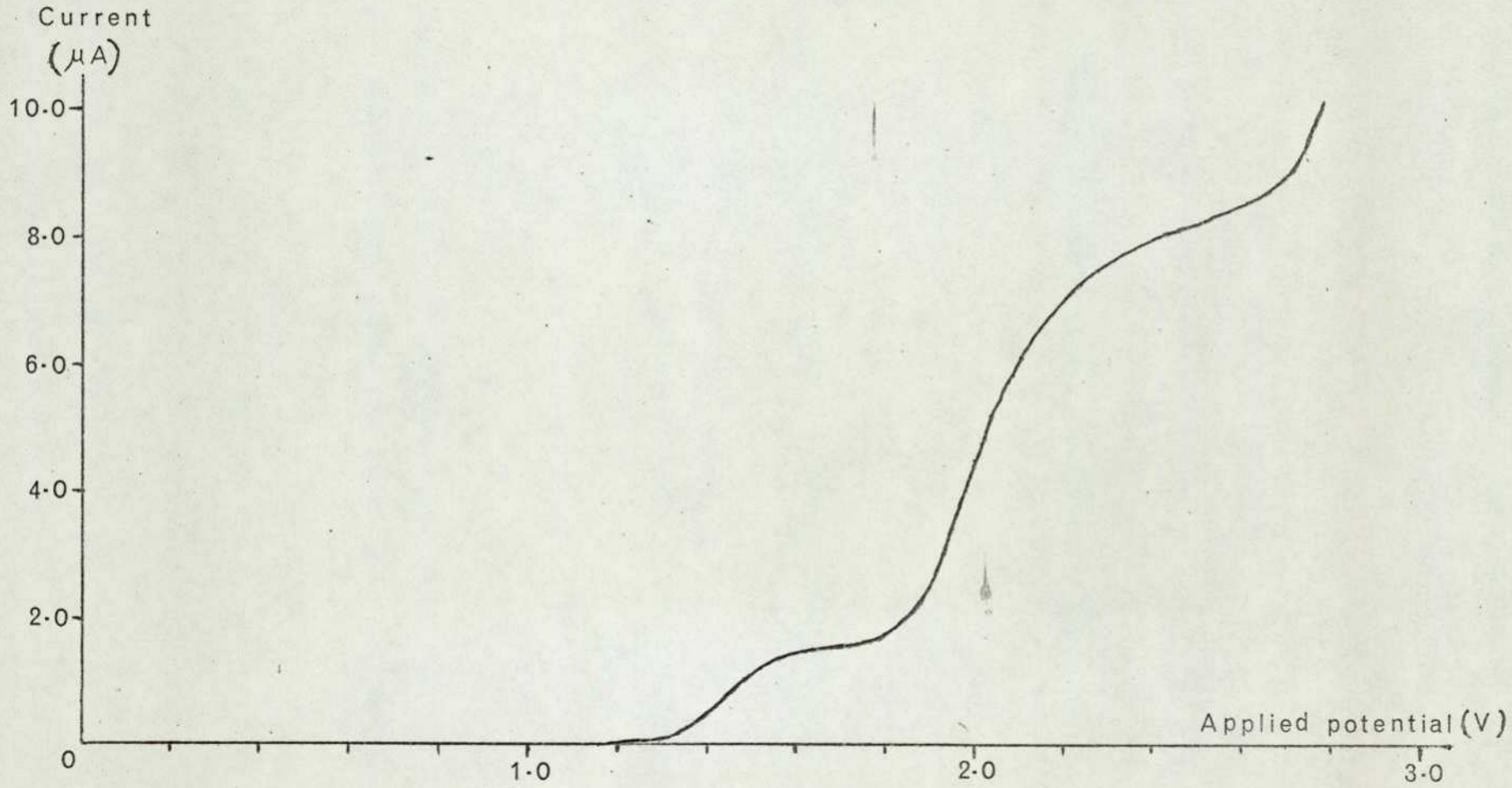


Fig.13. Anodic Polarography of $AgNO_3$ with Bipy.



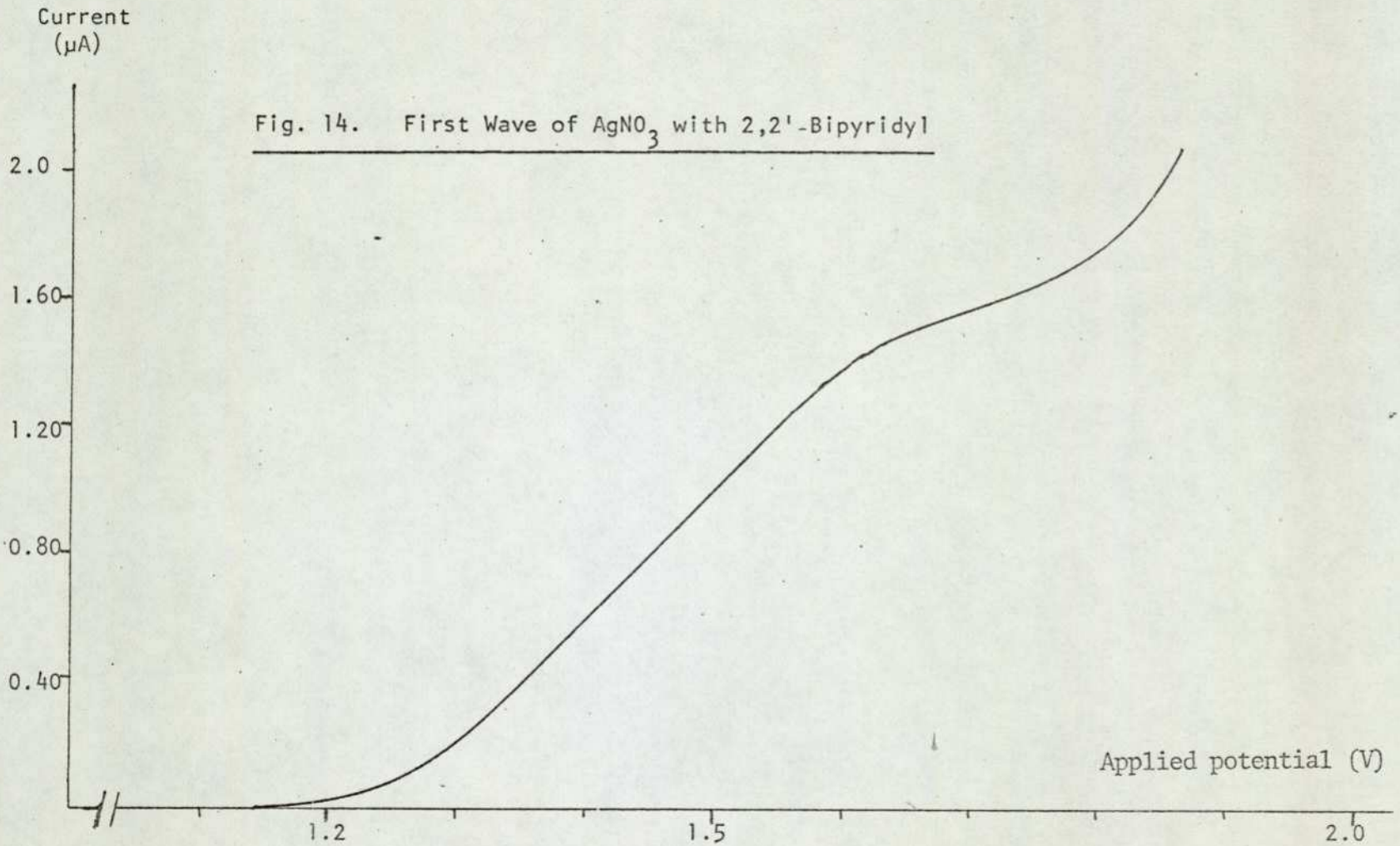


Fig. 14. First Wave of $AgNO_3$ with 2,2'-Bipyridyl

Fig.15. Anodic Polarography of $AgNO_3$ with Excess of Bipy.

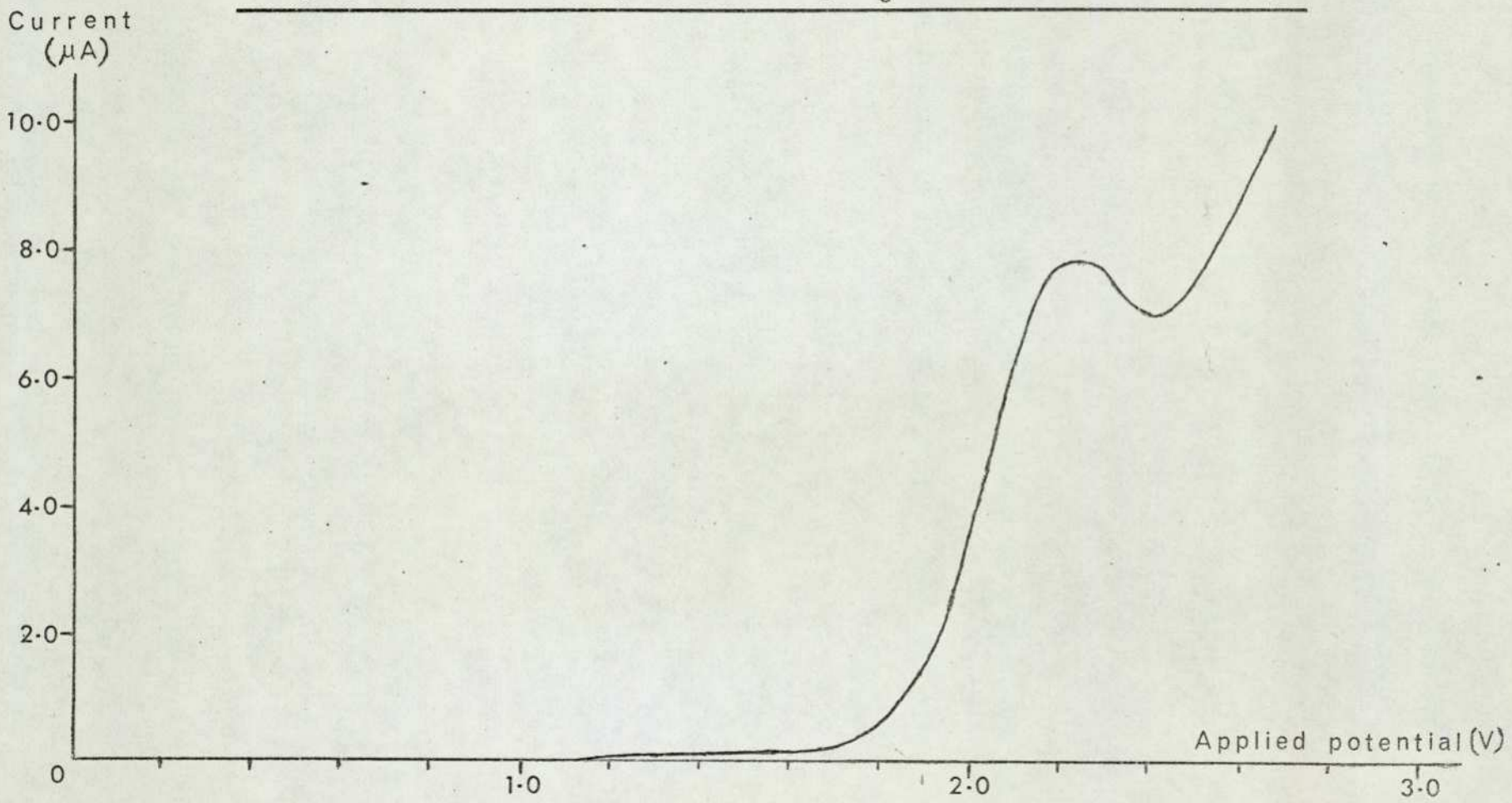


Fig. 16. Anodic Polarography of Silver Perchlorate with Bipy

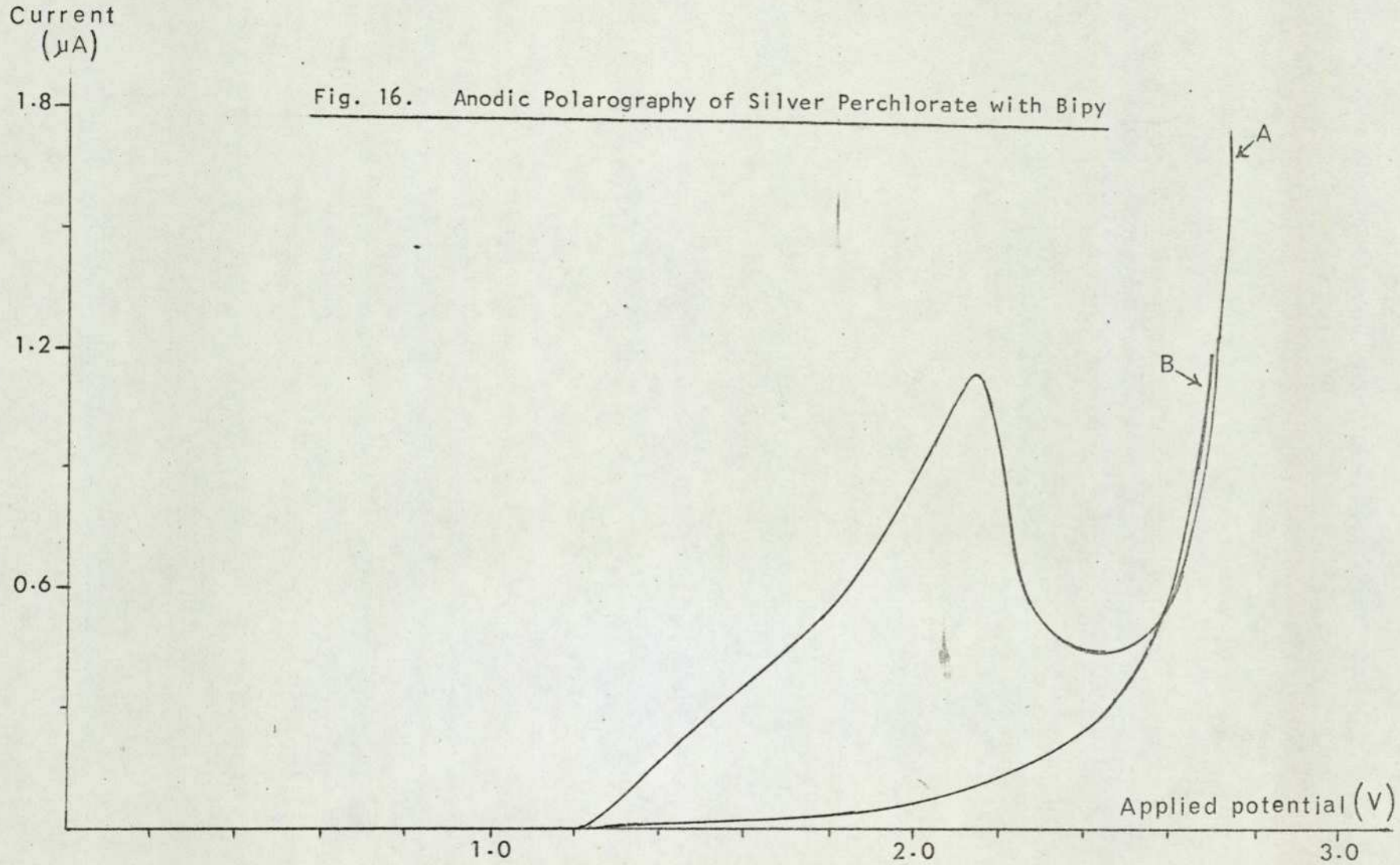


Fig. 17. Formation Curve for Ag^{+}/Bipy System

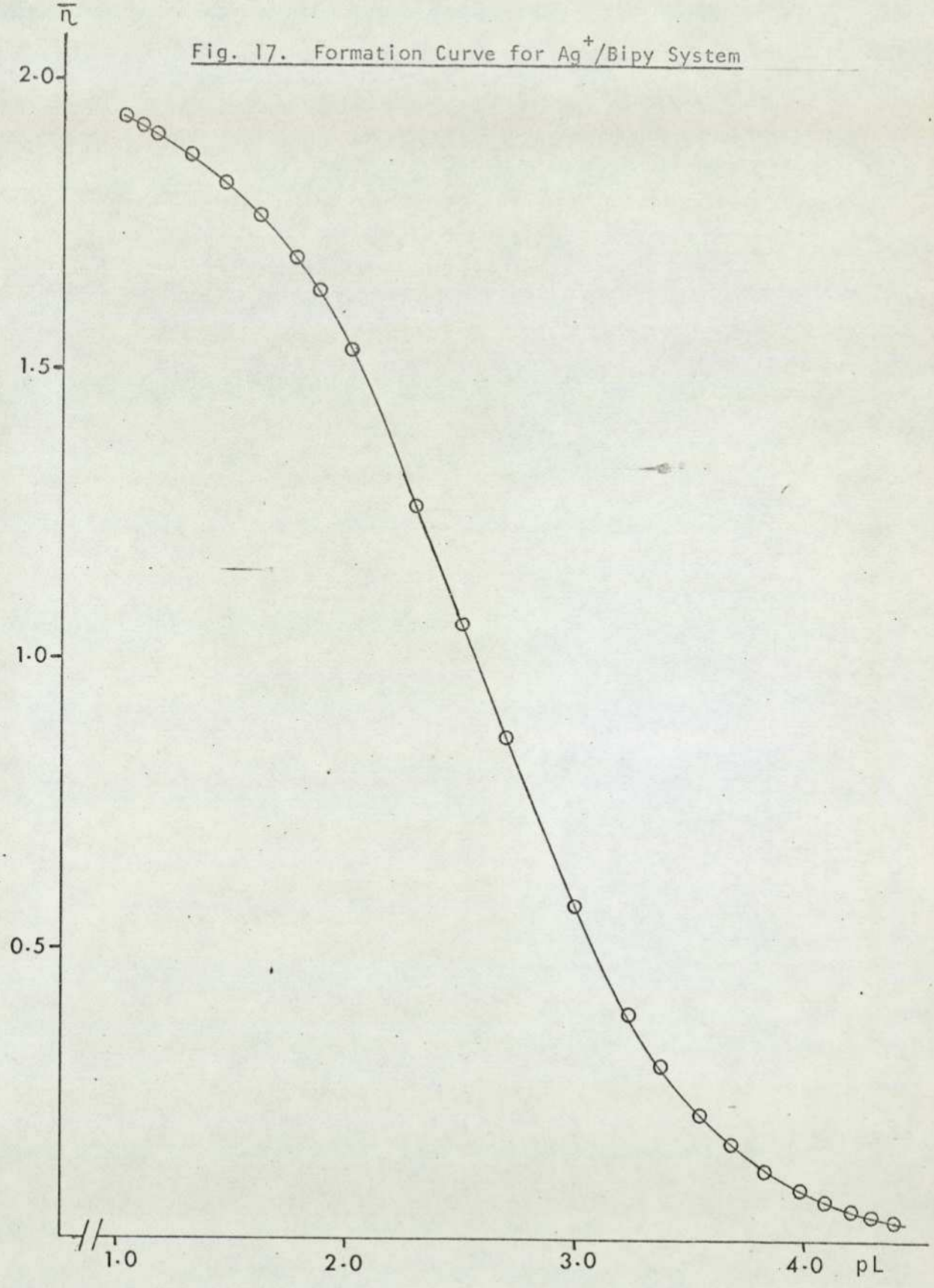
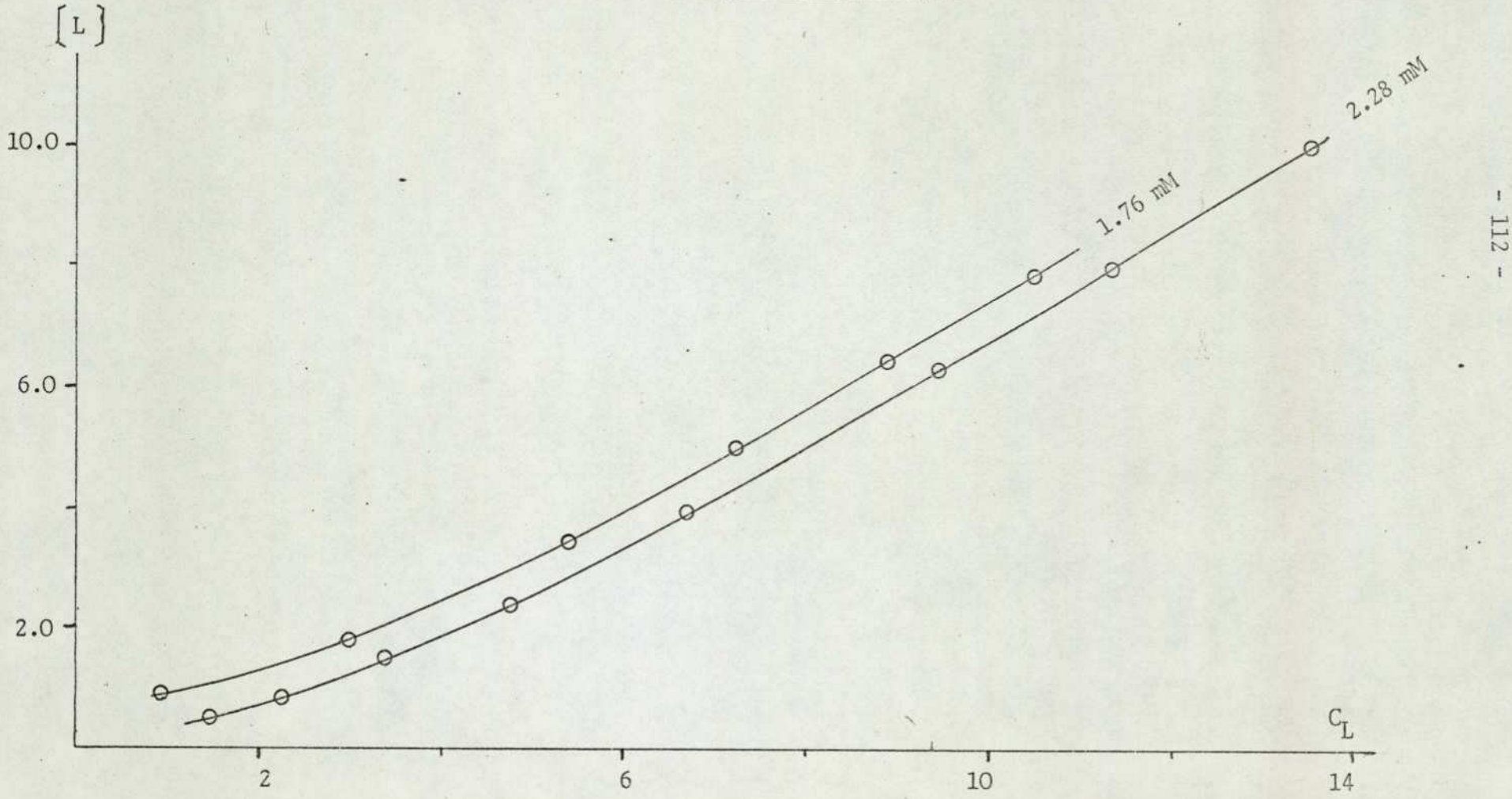


Fig. 18. C_L versus [L] for Ag^+/Bipy System



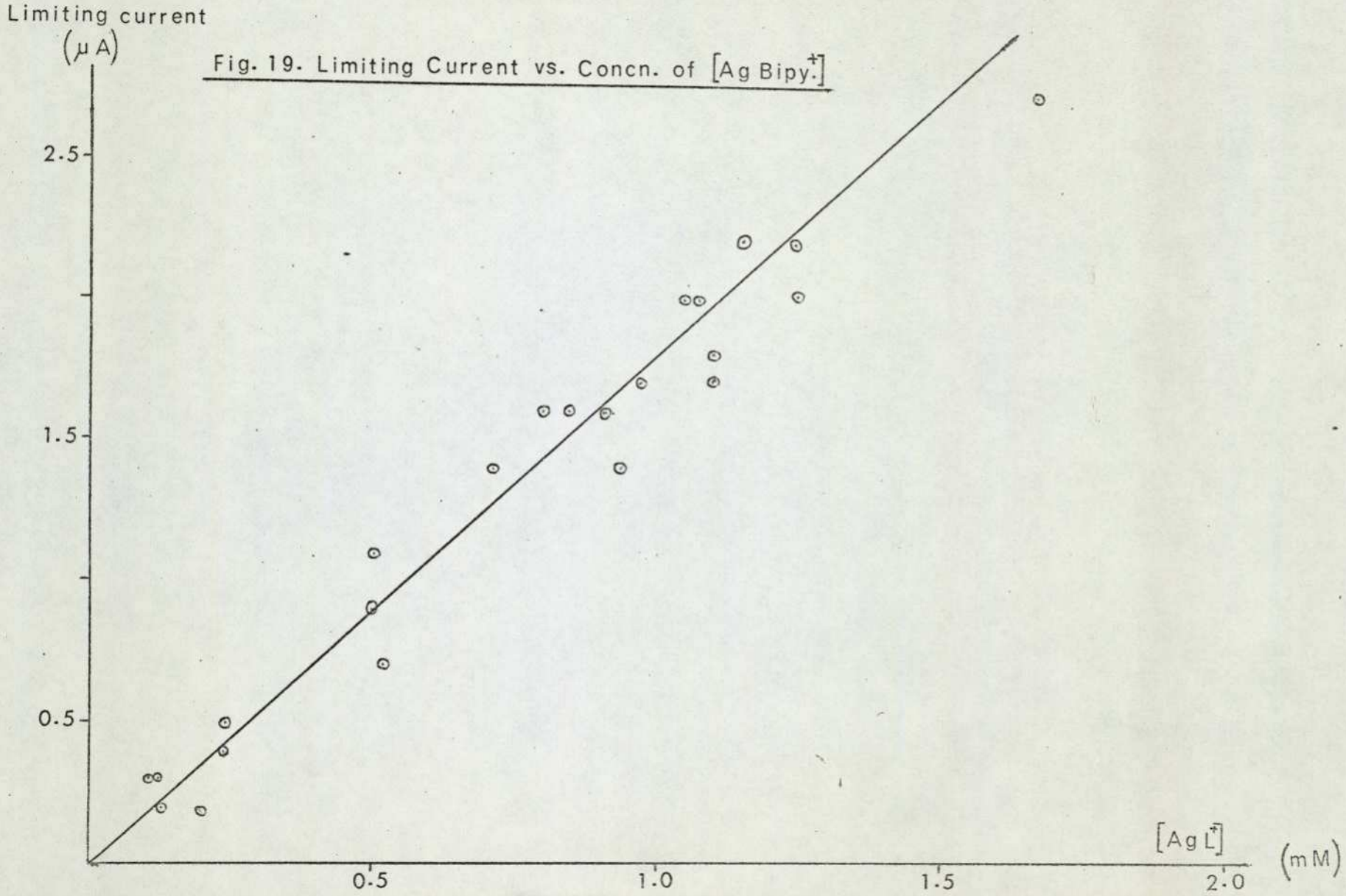
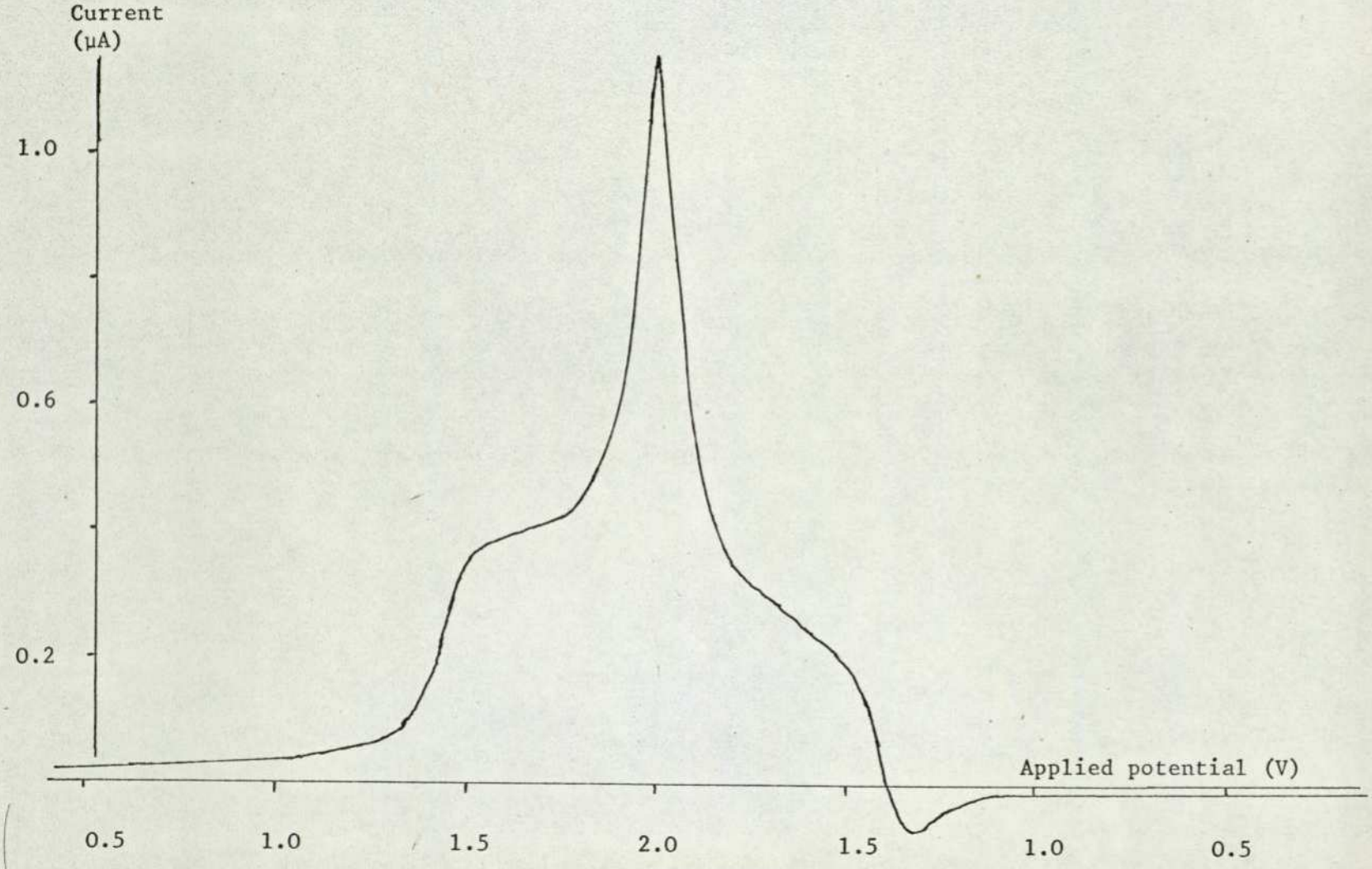


Fig. 19. Limiting Current vs. Concn. of [Ag Bipy.$^{+}$]

Fig.20 Oscilloscopic polarography of $AgNO_3$ with Bipy



4.4. Electrochemical Oxidation of Silver(I) Nitrate and Silver(I) Perchlorate in the Presence of 4,4'-Dimethyl 2,2'-Bipyridyl, 2,2',2''-Terpyridyl, 5,5'-Dibutyl 2,2'-Bipyridyl and 2,2'-Biquinolyl.

The electrochemical oxidation of silver(I) nitrate and silver(I) perchlorate in the presence of various polypyridyls was studied using the techniques of anodic polarography and controlled potential electrolysis described for the silver(I)/bipy system. Polarographic studies were largely restricted to the determination of the half-wave potential of the silver(I)/silver(II) process in the presence of the various polypyridyls; controlled potential electrolysis could then be carried out at the appropriate fixed potential for each system. In all cases, controlled potential electrolyses were conducted on a preparative scale, and coulometric determination (c.f. section 3.3.4., p. 51) were made simultaneously.

4.4.1. Anodic polarography of polypyridyls.

The anodic polarography of the polypyridyls was first studied to ascertain whether or not the ligands themselves underwent electro-oxidation in the absence of metal salts and, if so, to determine the extent of the interference which might be expected.

Fig. 21, p. 136 gives a representative polarogram for a 2.0 mM solution of 4,4'-dimethyl 2,2'-bipyridyl (4,4'-dimebipy) in 0.1 M tetra-n-butylammonium perchlorate at a scan rate of 0.4 V min^{-1}. A small wave was observed at a half-wave potential of 2.04 V, the limiting current being about 0.3 μA. Several polarograms were obtained at

different concentrations of the ligand (up to 10 mM) and it was found that the limiting current was independent of concentration for the particular R.P.E. used. This effect, which has already been noted in the case of 2,2'-bipyridyl (c.f. section 4.3.1., p. 84) was also found for other polypyridyls.

The anodic polarography of 5,5'-dibutyl 2,2'-bipyridyl (5,5'-dibut.bipy) and 2,2',2"-terpyridyl gave somewhat smaller limiting currents (about 0.2 μA) compared to 2,2'-bipyridyl and 4,4'-dimethyl 2,2'-bipyridyl, the half-wave potentials for 5,5'-dibutyl 2,2'-bipyridyl and 2,2'2"-terpyridyl being 2.0 V and 1.9 V respectively. Representative polarograms for these ligands are shown in Fig. 23, p.138 , and Fig. 22, p.137 . Again the limiting currents were found to be independent of concentration which was varied in each case over the range 1 mM to 10 mM.

The anodic polarography of 2,2'-biquinolyl was limited to solutions having concentrations in the range 1 mM to 2 mM due to the low solubility of this ligand in acetonitrile. The current versus potential plots for such solutions gave a constant limiting current of the order of about 0.1 μA, the half-wave potential being about 1.9 V, a value similar to that of 2,2'2"-terpyridyl.

The observation of small limiting currents which remain constant over a wide range of concentration does not appear to have been reported in the literature and an explanation for the effect is not obvious. A possible basis for the phenomenon is that it is associated with a surface effect at the electrode involving the oxidation of platinum atoms in the vicinity of adsorbed ligand molecules to give a platinum complex molecules

which then leave the surface; in such a case, the limiting current would be proportional to the surface area of the electrode. This might be checked using platinum electrodes of different surface areas and by the use of electrode materials which do not interact with the ligand (e.g. graphite). In the present work it will be shown that the first oxidation waves of silver(I) salts in the presence of the polypyridyls listed above occur (as in the case of 2,2'-bipyridyl) at half-wave potentials more negative than those observed for the ligands only (i.e. in the absence of metal ions.) Fixed potential electrolyses in the region of the first waves could therefore be carried out without interference from this effect.

4.4.2. Polarography of solutions of silver(I) nitrate and silver(I) perchlorate in the presence of polypryidyls.

The main purpose of the polarographic study was to determine the anodic potentials required for the electro-oxidation of silver(I) complexes as a preliminary to preparative scale electrolyses using the three-compartment cell (section 3.2.1.).

Figures 24, 25, 26 and 27, pages 139, 140, 141, and 142, show representative polarograms for solution of silver(I) nitrate and silver(I) perchlorate in the presence of various polypyridyl ligands using 0.1 M tetra-n-butylammonium perchlorate as the supporting electrolyte. In all cases the rate of voltage scan was 0.4 V min^{-1}. Tables X, XI, XII and XIII give details of the variation of limiting current with the concentration of silver(I) salt and ligand and also include values of the half-wave potentials of the waves observed.

Table X Anodic Polarography of Silver Perchlorate/4,4'-dimebipy solutions

C_M mM	C_L mM	$i_L(I)$ μA	$E_{\frac{1}{2}}(I)$ V	$E_{\frac{1}{2}}(II)$ V
2.85	6.09	0.9	1.40	2.0
3.69	6.09	0.6	1.40	2.0
3.69	10.04	1.7	1.38	1.9
2.85	14.38	0.3	1.41	1.9

Table XI Anodic Polarography of Silver(I)terpy solutions

	C_M mM	C_L mM	$i_L(I)$ μA	$E_{\frac{1}{2}}(I)$ V	$i_L(II)$ μA	$E_{\frac{1}{2}}(II)$ V
Silver nitrate	1.62	1.70	0.4	1.31	4.0	1.91
	4.00	1.70	0.7	1.29	7.5	1.95
	1.11	20.20	<0.1	-	4.3	1.93
Silver perchlorate	0.92	1.74	0.2	1.30	-	2.0
	0.92	15.33	0.0	-	-	1.9
	1.60	6.12	0.1	1.25	-	1.9
	3.56	6.12	0.4	1.30	-	1.9

Table XII Anodic Polarography of Silver Perchlorate/5,5¹ dibut bipy solutions

C_M mM	C_L mM	i_L(ii) μA	$E_{\frac{1}{2}}$(I) V	$E_{\frac{1}{2}}$(II) V
3.00	10.04	0.2	1.42	2.05
3.00	19.87	0.4	1.41	2.03
3.00	47.35	0.1	1.43	2.08

Table XIII Anodic Polarography of Silver Nitrate/biquinolyl solutions

C_M mM	C_L mM	i_L(I) μA	$E_{\frac{1}{2}}$(I) V	i_L(II) μA	$E_{\frac{1}{2}}$(II) V
0.52	2.01	0.3	1.76	0.3	2.15
0.80	1.72	0.5	1.70	0.7	2.20
1.50	3.00	0.6	1.73	0.4	2.06
2.02	4.00	0.7	1.75	0.5	2.17
2.50	5.10	0.8	1.75	0.6	2.05
2.81	5.90	0.9	1.74	0.7	2.15
3.01	3.00	1.2	1.76	0.8	2.02

The polarograms exhibit characteristics similar to those found for solutions of silver(I) nitrate and silver(I) perchlorate in the presence of 2,2'-bipyridyl (section 4.3, p.84). Two well defined waves are observed in the case of silver(I) nitrate/polypyridyl systems; for the silver(I) perchlorate systems, the second wave is usually complicated by a maximum which is followed by a marked drop in current as in the case of the silver(I) perchlorate/bipy system. (Because of this effect, values of the limiting current for the second wave of silver(I) perchlorate systems are not quoted in Tables X, XI and XII and half-wave potentials corresponding to these waves are only approximate). For each polypyridyl, where the complete data are available, the half-wave potentials of the first wave for both silver(I) nitrate and silver(I) perchlorate systems are found to be the same.

Values for the limiting currents of the first wave for these systems are again small compared to the values expected for a one-electron change based on the total metal present. In the case of the silver(I) nitrate/bipy system, this effect was explained in terms of the involvement of the intermediate species, $Ag(bipy)^+$. Unfortunately, stability constant data are not available to enable similar calculations to be made of the concentrations of the intermediate complexes associated with the silver(I) polypyridyl systems studied here. However, it is found, in all cases, that the limiting current is reduced to low values when the ligand is in excess, in qualitative agreement with the dependence of $i_L(I)$ on the concentration of an intermediate species. The values of the limiting currents of the second wave for silver(I) nitrate systems again occur at about 2.0 V. In the case of the 2,2'-biquinolyl system

the values of the limiting current appear to be much smaller than the corresponding values for the 2,2'-bipyridyl system; this may be due to a higher ratio of the successive stability constants (K_2/K_1) for the 2,2'-biquinolyl system which would lead to a reduction in the concentration of the intermediate species.

The variation of the half-wave potential of the first wave with the nature of the ligand is given in Table XVII which includes the value of $E_{\frac{1}{2}}(I)$ determined earlier for the 2,2'-bipyridyl system.

Table XVII $E_{\frac{1}{2}}(I)$ for Silver(I) polypyridyls

Ligand	$E_{\frac{1}{2}}(I)$ V
2,2'-biquinolyl	1.74
2,2'-bipyridyl	1.44
5,5'-dibutyl 2,2'-bipyridyl	1.42
4,4'-dimethyl 2,2'-bipyridyl	1.40
2,2',2''-terpyridyl	1.30

A decrease in the value of half-wave potential for first wave should reflect an increase in the stabilisation of the silver(II) state compared to the corresponding silver(I) state. However, the non-availability of stability constant data, particulary for silver(II) complex systems in acetonitrile, prevents a correlation between $E_{\frac{1}{2}}$ being made. In the present work, Table XVII has been used to indicate the fixed potentials required for the electro-oxidation of silver(I) salts in the presence of the polypyridyls listed.

4.4.3. Controlled potential electrolysis of solutions of silver(I) nitrate and silver(I) perchlorate in the presence of 4,4'-dimethyl 2,2'-bipyridyl.

Preparative scale electrolyses at a fixed potential (in the range 1.35 - 1.50 V) corresponding to the first polarographic wave were carried out using solutions of silver(I) nitrate and silver(I) perchlorate in the presence of 4,4'-dimethyl 2,2'-bipyridyl with 0.1 M tetra-n-butylammonium perchlorate as supporting electrolyte. Coulometric determinations were obtained simultaneously. The ratio of ligand to metal salt concentration in these experiments was about 2 : 1 and under these conditions the product was not deposited on the electrode surface during electrolysis, permitting accurate coulometric determinations to be made. (In the case of silver(I)/bipy system it was necessary to maintain a much higher ligand to metal ratio in order to keep the silver(II) complex in solution (cf. section 4.3). Table XIV gives details of the experiments and includes calculations of the number of electrons involved per molecule in the electrode reaction. In all cases, a one-electron oxidation was indicated confirming that the first polarographic wave corresponds to the oxidation of silver(I) to silver(II).

After each electrolysis, the anolyte was transferred to a round-bottomed flask and the solvent was removed under vacuum. The residue consisted of dark-red crystals mixed with white crystals of supporting electrolyte and excess ligand. The silver(II) complex was isolated by washing the residue several times with dry ethyl acetate in which the supporting electrolyte and the ligand were appreciably soluble but in which the silver(II) complex did not dissolve. The removal of the

Table XIV Coulometry of silver(I)/4,4'Dim.bipy solutions

Silver nitrate

(A) Weight of silver nitrate electrolysed	= 0.0368 g.
Bu_4NClO_4 concentration	= 0.1M
Anodic applied potential	= 1.46V
Initial current	= 80 mA
Electrolysis time	= 20 min.
Total quantity of electricity for electrolysis	= 19.568 coulombs
Molecular ratio of L : $AgNO_3$	= 2 : 1

$$n = \frac{Q.M}{F.W} = 0.94 \text{ electron/mole}$$

(B) Weight of silver nitrate electrolysed	= 0.0365 g.
Bu_4NClO_4 concentration	= 0.1M
Anodic applied potential	= 1.50V
Initial current	= 90 mA
Electrolysis time	= 15 min.
Total quantity of electricity for electrolysis	= 19.780 coulombs
Molecular ratio of L : $AgNO_3$	= 2 : 1

$$n = 0.95 \text{ electron/mole}$$

Silver perchlorate

(C) Weight of silver perchlorate electrolysed = 0.0253 g.

Bu_4NClO_4 concentration = 0.1 M

Anodic applied potential = 1.38 V

Initial current = 2.97 mA

Electrolysis time = 92 min.

Total quantity of electricity for electrolysis = 12.140 coulombs

Molecular ratio of L : $AgClO_4$ = 2 : 1

N = 1.03 electron/mole

(D) Weight of silver perchlorate electrolysed = 0.0507 g.

Bu_4NClO_4 concentration = 0.1 M

Anodic applied potential = 1.35 V

Initial current = 40 mA

Electrolysis time = 28 min.

Total quantity of electricity for electrolysis = 22.930 coulombs

Molecular ratio of L : $AgClO_4$ = 2 : 1

n = 0.97 electron/mole

L = 4,4'-Dimethyl 2,2'bipyridyl

impurities was accomplished after about seven washings, the solvent being removed by centrifugation after each washing; the purification process was considered to be complete when evaporation of the centrifugate gave no residue. After purification , the product was dried in vacuum for two hours at 30°C and stored in a desiccator over phosphorous pentoxide.

The technique used for the isolation of silver(II) bipy complexes, by the addition of silver(I) salt to remove excess ligand, was also found to be applicable in the present case. However, the evaporation method was preferred since higher yields were obtained.

Analysis of the product obtained from silver(I) nitrate/4,4'-dime-bipy solutions.

The C, H, N and Ag(II) analysis data for the dark red crystals (which decomposed at about 200°C) obtained from silver(I) nitrate are given below:

	C%	H%	N%	Ag(II)%
Found	45.18	3.77	9.88	16.6

As in the silver(I) nitrate/bipy system, the analysis of the product corresponds to the formation of a mixed nitrate-perchlorate complex, the theoretical percentage composition of $[Ag(4,4'\text{-dime-bipy})_2]NO_3.ClO_4$ being

	C%	H%	N%	Ag(II)%
Theoretical	45.19	3.79	10.98	16.91

which is in close agreement with the above data. The infra-red spectrum of this product showed an ionic nitrate band at 1387 cm^{-1} and a strong, broad band at 1092 cm^{-1} corresponding to ionic perchlorate. This supports the formulation of a mixed anion complex. A single absorption band at

19,417 cm^{-1} was observed in the diffuse reflectance spectrum which is probably associated with a d-d transition of the d^9 configuration.

The mass spectrum of the silver(II) complex gave a maximum mass number of 184.1002 corresponding to the mass of the 4,4'-dimethyl 2,2'-bipyridyl molecule. As in the case of $[Ag(bipy)_2](ClO_4)_2$ it appears that the complex is decomposed under the conditions used to obtain the mass spectrum (ion source temperature 220°C, electron energy 70 eV). However, the result is useful in confirming that the ligand is not involved in the oxidation process occurring at the potential corresponding to the first wave and remains unoxidised.

Analysis of the product obtained from silver(I) perchlorate/4,4'-dime bipy solutions

Analytical data for the red crystals (m.pt. 158-162°C) obtained from silver (I) perchlorate are given below:

	C%	H%	N%	Ag(II)%
Found	42.29	3.59	8.19	15.6

This composition corresponds to the formulation $[Ag(4,4'\text{-dime bipy})_2](ClO_4)_2$ for which the theoretical percentages are:

	C%	H%	N%	Ag(II)%
Theoretical	42.69	3.58	8.30	15.97

The infra-red spectrum showed the presence of a strong, broad band at 1090 cm^{-1} confirming the presence of an ionic perchlorate group. The single absorption band of the diffuse reflectance spectrum was at a somewhat higher frequency (20,576 cm^{-1}) compared to the mixed nitrate-perchlorate complex; this effect was also observed in the case of silver(II)-bipy complexes.

4.4.4. Controlled potential electrolysis of solutions of silver(I) nitrate and silver(I) perchlorate in the presence of 2,2',2''-terpyridyl.

Preparative scale electrolyses at fixed potentials (in the range 1.2 - 1.3 V), corresponding to the first polarographic wave were carried out using solution of silver(I) nitrate and silver(I) perchlorate in the presence of 2,2',2''-terpyridyl with 0.1 M tetra-n-butylammonium perchlorate as supporting electrolyte. Coulometric determinations were obtained simultaneously. A ratio of ligand to metal ion concentration of about 2 : 1 was again sufficient to prevent deposition of the products on the electrode during electrolysis. For each metal salt, two sets of coulometric determinations were obtained and the results are given in Table XV. In each case, a one-electron oxidation process was indicated confirming that at the fixed potential used, silver(I) was oxidised to silver(II).

The product was isolated by the same method as used for the silver(II)-4,4'-dime bipy complex (p.122) but using chloroform instead of ethyl acetate as the solvent.

The method of isolating silver(II)-bipy complexes, also found applicable to the silver(II)-4,4'-dime bipy complexes, by the addition of silver(I) salt to remove excess ligand, was not successful in the case of the silver(II)-terpy complex. On addition of silver(I) nitrate to the oxidised solution, the colour remained unchanged and no precipitation occurred. This indicates that the silver(II)-terpy complex is quite soluble in acetonitrile. However, when almost half of the acetonitrile was removed under vacuum, dark-red crystals began to separate.

Analysis of the product obtained from silver(I) nitrate/terpy solutions

The combined products obtained from electrolyses (A) and (B) of

Table XV Coulometry of silver(I)/terpyridyl solutions

Silver nitrate

(A) Weight of silver nitrate electrolysed	= 0.0330 g.
Bu_4NClO_4 concentration	= 0.1 M
Anodic applied potential	= 1.3 V
Initial current	= 18.5 mA
Electrolysis time	= 25 min.
Total quantity of electricity for electrolysis	= 17.650 coulombs
Molecular ratio of terpy:$AgNO_3$	= 2 : 1

$$n = \frac{Q.M}{F.W.} = 0.94 \text{ electron/mole}$$

(B) Weight of silver nitrate electrolysed	= 0.0322 g.
Bu_4NClO_4 concentration	= 0.1 M
Anodic applied potential	= 1.35 V
Initial current	= 22 mA
Electrolysis time	= 21 min
Total quantity of electricity for electrolysis	= 19.496 coulombs
Molecular ratio of terpy:$AgNO_3$	= 2 : 1

$$n = 1.06 \text{ electron/mole}$$

Silver perchlorate

(C) Weight of silver perchlorate electrolysed = 0.0104 g.

Bu_4NClO_4 concentration = 0.1 M

Anodic applied potential = 1.2 V

Initial current = 2.25 mA

Electrolysis time = 60 min.

Total quantity of electricity for electrolysis = 4.830 coulombs

Molecular ratio of terpy:$AgClO_4$ = 2 : 1

n = 1.00 electron/mole

(D) Weight of silver perchlorate electrolysed = 0.0452 g.

Bu_4NClO_4 concentration = 0.1M

Anodic applied potential = 1.25 V

Initial current = 22 mA

Electrolysis time = 40 min.

Total quantity of electricity for electrolysis = 21.729 coulombs

Molecular ratio of terpy:$AgClO_4$ = 2 : 1

n = 1.03 electron/mole

Table XV gave the following analysis:

	C%	H%	N%	Ag(II)%
Found	46.6	3.3	10.8	13.5

It was anticipated that this complex would have a terpy:silver(II) ratio of 1 : 1 as reported by Morgan and Burstall[60] who claim to have isolated $[Ag(terpy)NO_3]NO_3$ from the electrochemical oxidation of $[Ag(terpy)NO_3]$. Further, by comparison with the product obtained from the oxidation of silver(I) nitrate in the presence of 2,2'-bipyridyl and 4,4'-dimethyl 2,2'-bipyridyl, a mixed anion complex was expected. However, the analytical data are consistent with the formulation $[Ag(terpy)_2](ClO_4)_2$ for which the theoretical percentage composition is

	C%	H%	N%	Ag(II)%
Theoretical	46.59	2.87	10.87	13.95

The percentage composition of other possible products are listed below for comparison.

	C%	H%	N%	Ag(II)%
$[Ag(terpy)_2]NO_3.ClO_4$	48.96	3.01	13.32	14.66
$[Ag(terpy)NO_3]ClO_4$	35.84	2.21	11.15	21.46
$[Ag(terpy)ClO_4]ClO_4$	33,36	2.05	7.78	19.97

The analysis obtained for this product clearly provides strong evidence that it is $[Ag(terpy)_2](ClO_4)_2$. Further evidence for this product was obtained from infra-red data. Firstly, the silver(II) complex gave neither an ionic nitrate band in the region of 1380 cm^{-1}, expected for a mixed anion complex, nor a covalent nitrate band in the region of 1250 cm^{-1} which would be expected for the 1 : 1 complex $[Ag(terpy)NO_3]ClO_4$

as found by Morgan and Burstall.[60] Secondly, the 1:1 complex $[Ag(terpy)ClO_4]ClO_4$ containing a coordinated perchlorate ion would be expected to give strong bands in the region of 1000 - 1200 cm^{-1} and a strong band at 920 cm^{-1} as described by Wickenden et al;[116] in fact, only a broad ionic perchlorate band was observed in the region of 1090 cm^{-1}.

Analysis of the product obtained from silver(I) perchlorate/terpy solutions

The combined products obtained from electrolyses (C) and (D) of Table XV gave the following analysis:

	C%	H%	N%	Ag(II)%
Found	45.84	2.88	10.84	13.7

This analysis is very close to that of the product obtained from silver(I) nitrate/terpy solutions and corresponds, therefore, to $[Ag(terpy)_2](ClO_4)_2$. Again, the product gave an ionic perchlorate band in the region of 1090 cm^{-1}, covalent perchlorate bands being absent. Disappointingly, mass spectrum data did not confirm the above formulation. The mass spectrum gave a maximum mass of 233.0953 corresponding to the mass of the terpyridyl molecule. It appears, therefore, that under the conditions used to determine the mass spectrum (ion source temperature 240°C, electron energy 70 eV), the complex underwent decomposition as did the bis(bipy)silver(II) complex. However, the mass spectrum does provide useful evidence that the ligand remains unchanged during electrochemical oxidation of the silver(I)terpy solution.

Although the products obtained from silver(I) nitrate and silver(I) perchlorate gave the same analysis, there were differences in the physical properties of the two complexes. For example, the product obtained from silver(I) nitrate/terpy solutions consisted of dark-red plate shaped crystals melting over the range 216 - 220°C, while silver(I)perchlorate/terpy

solutions gave dark-red needle shaped crystals melting over the range 208 - 215°C. The diffuse reflectance spectra showed a single absorption band at about 19,000 cm^{-1} for the product prepared from silver(I) nitrate compared to a band at 18,200 cm^{-1} for the complex prepared from silver(I) perchlorate. These data indicate the possible existence of different isomers.

The formulation $[Ag(terpy)_2](ClO_4)_2$ suggests the possibility of a six-coordinated complex if the terpyridyl molecules act as tridentate ligands. Although structural data would be required to resolve this problem, it is noted that an example of a six-coordinated silver(II) complex (silver(II) bis(pyridine-2,6-dicarboxylate monohydrate) has been reported[71] and its structure confirmed.

4.4.5. Controlled potential electrolysis of solutions of silver(I) perchlorate in the presence of 5,5'-dibutyl 2,2'-bipyridyl

Preparative scale electrolyses were carried out at a fixed potential (in the range 1.4 - 1.5 V) corresponding to the first wave of the silver(I) perchlorate/5,5'-dibutyl bipy system with 0.1 M tetra-n-butylammonium perchlorate as supporting electrolyte. Table XVI gives details of the electrolyses and gives the calculated number of electrons involved per molecule in the electrode reaction. As in all other silver(I) polypyridyl systems, the results confirmed that a one-electron oxidation process occurred at potentials corresponding to the first polarographic wave.

Repreated attempts to isolate the product obtained from these electrolyses were unsuccessful. The oxidised solution was dark red-brown in colour, characteristic of silver(II)-polypyridyl complexes. A portion of this solution was treated with silver(I) salt but no silver(II) complex

Table XVI Coulometry of silver(I)ClO_4/5,5'-Dibut.bipy solutions

(A) Weight of silver perchlorate electrolysed	= 0.0311 g.
Bu_4NClO_4 concentration	= 0.1 M
Anodic applied potential	= 1.4 V
Initial current	= 8.3 mA
Electrolysis time	= 96
Total quantity of electricity for electrolysis	= 16.500 coulombs
Molecular ratio of L : $AgClO_4$	= 3 : 1

$$n = \frac{Q.M}{F.W.} = 1.14 \text{ electron/mole}$$

(B) Weight of silver perchlorate electrolysed	= 0.0598 g.
Bu_4NClO_4 concentration	= 0.1 M
Anodic applied potential	= 1.5 V
Initial current	= 40 mA
Electrolysis time	= 32
Total quantity of electricity for electrolysis	= 27.340 coulombs
Molecular ratio of L : $AgClO_4$	= 3 : 1

n = 0.98 electron/mole

was precipitated, the colour of anolyte remaining unaltered. Next, the solvent was removed under vacuum from the remainder of the solution until a viscous reddish brown residue containing an excess of supporting electrolyte and excess 5,5'-dibutyl 2,2'-bipyridyl remained. The reddish brown residue gave iodine with aqueous potassium iodide solution indicating the presence of silver(II). A variety of solvents was used in an attempt to isolate the product from the residue but without success. Table XVIII gives a summary of the techniques used.

4.4.6. Controlled potential electrolysis of solutions of silver(I) nitrate in the presence of 2,2'-biquinolyl

Contolled potential electrolysis of silver(I) nitrate solutions in the presence of 2,2'-biquinolyl using 0.1 M tetra-n-butylammonium perchlorate as the supporting electrolyte was attempted. The potential used was 1.74 V which corresponded to the half-wave potential of the first anodic wave. However, it was found that, for this system, the initial current rapidly fell to very low levels apparently due to a deposit which formed on the electrode surface. Previous difficulties of this nature were overcome by the addition of an excess of ligand which prevented the deposition of the product on to the electrode surface. Unfortunately, for the present system, the low solubility of the ligand in acetonitrile did not permit this technique to be applied and coulometric determination were not possible.

TABLE XVIII

Solvent	Observation
Acetone	Completely soluble
Ethyl acetate	Completely soluble
Chloraform	Immediately dissolved
Ether	Colour of the product fades gradually
Carbon tetrachloride	Decolourised
Nitromethane	Immediately decolourised
Methanol	Immedi-ately decolourised
Ethanol	Immediately decolourised
Benzene	Reddish brown viscous liquid settled down at the bottom of the test tube, stirred and decanted benzene. Repeated this treatment four times. Reddish brown liquid obtained which decolourised on drying under vacuum.

Fig. 21. Anodic Polarography of 4,4'-Dimethyl-2,2'-Bipyridyl

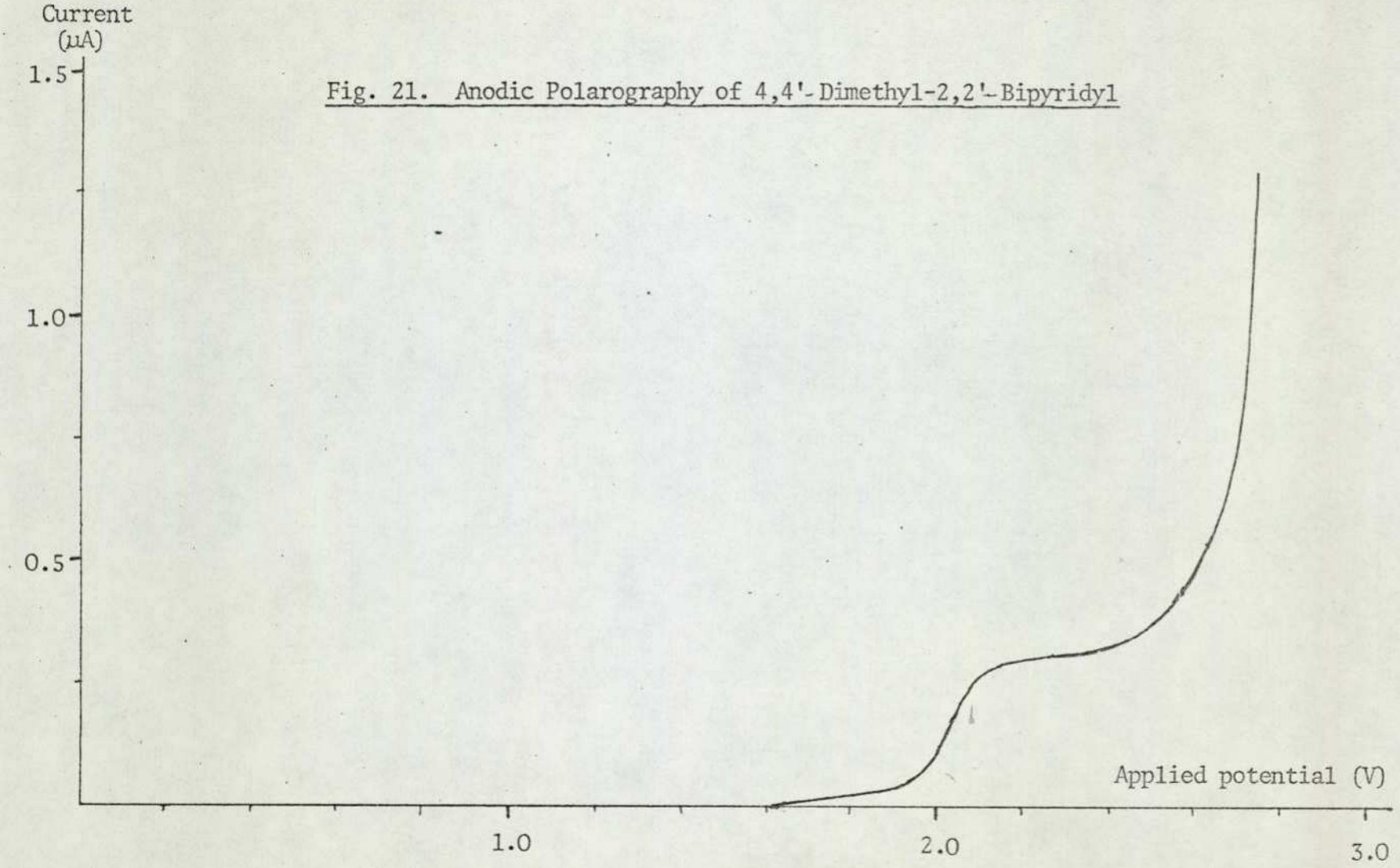


Fig. 22. Anodic Polarography of 2,2'2''-Terpyridyl

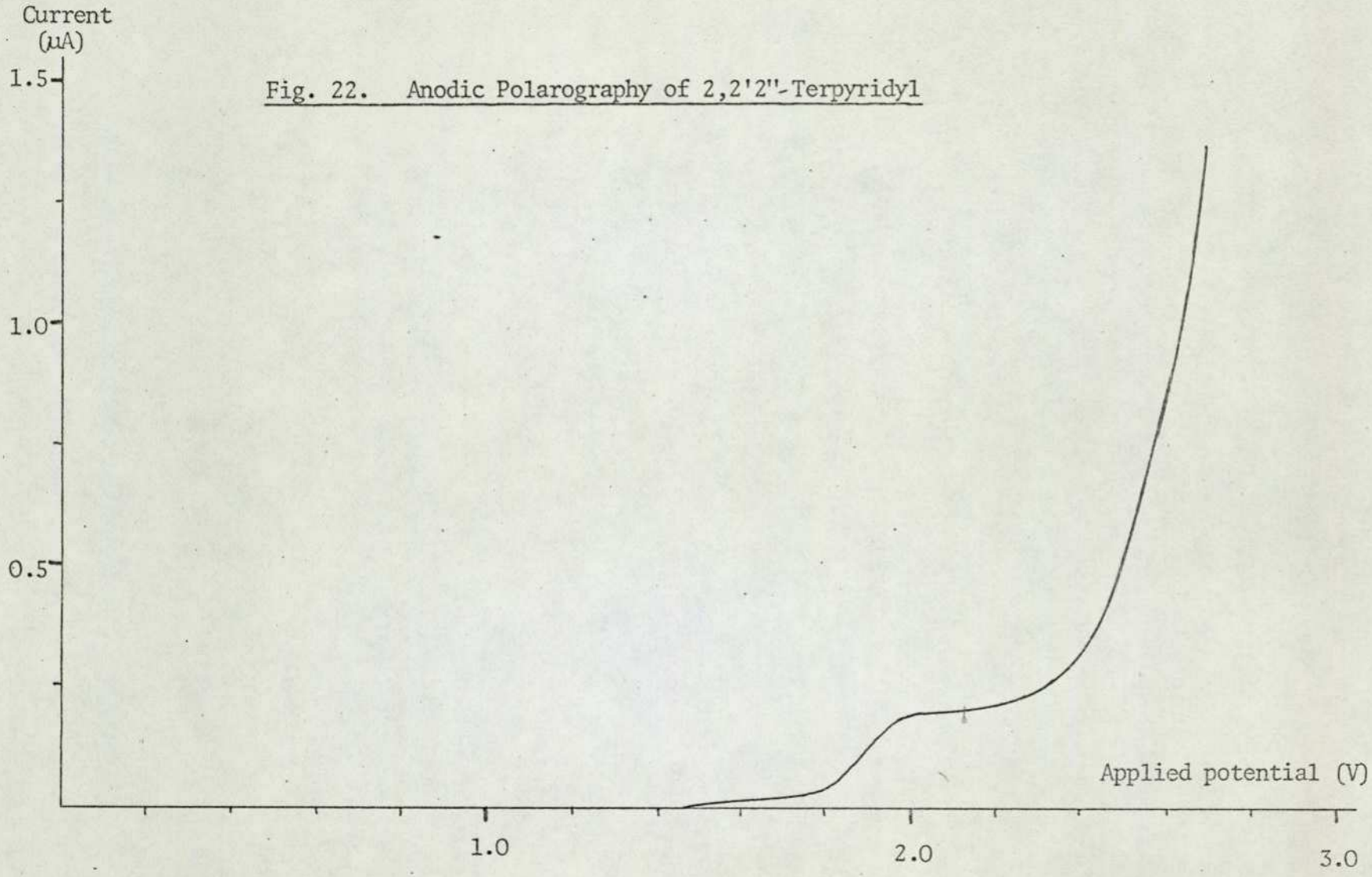
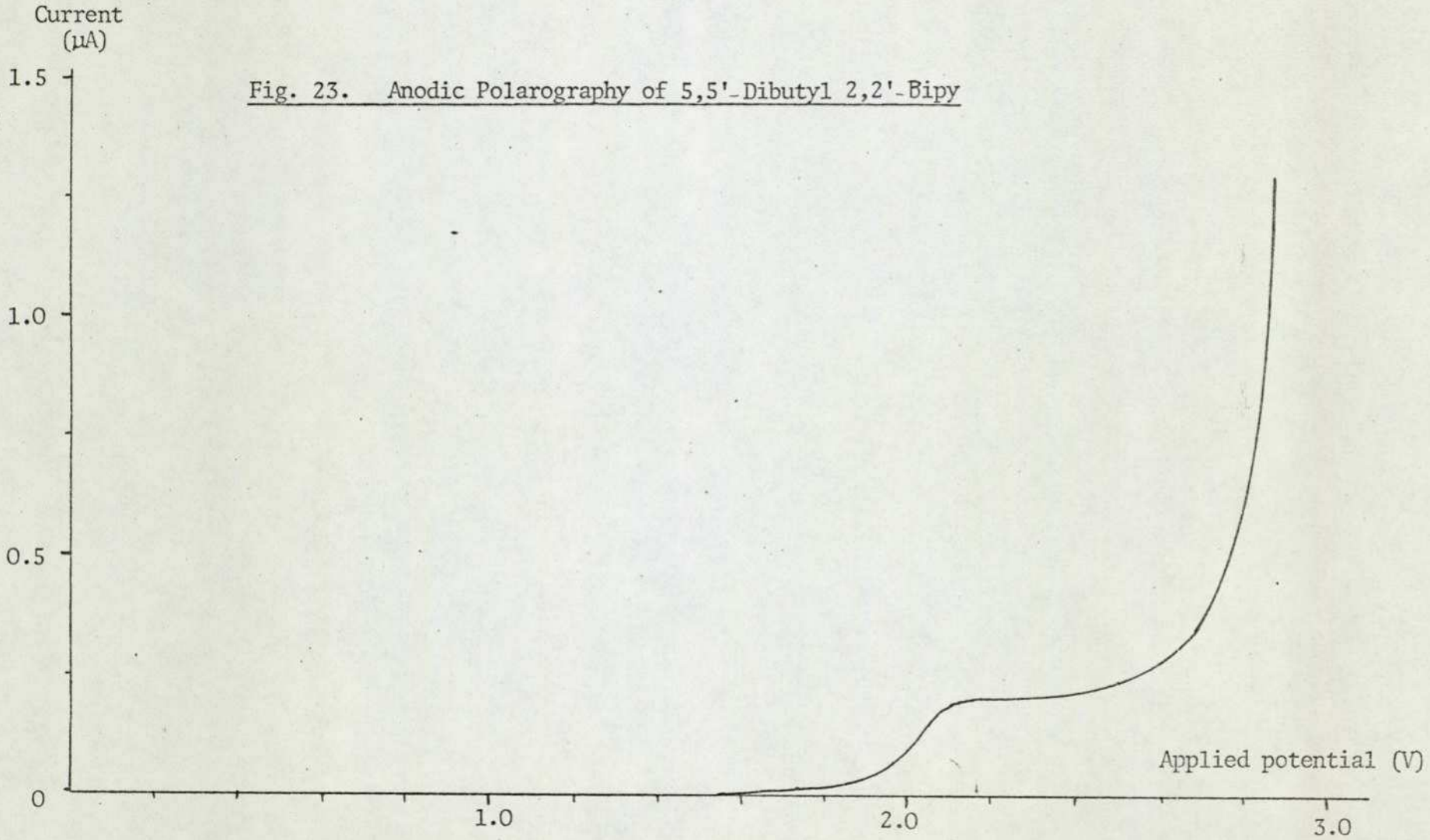


Fig. 23. Anodic Polarography of 5,5'-Dibutyl 2,2'-Bipy



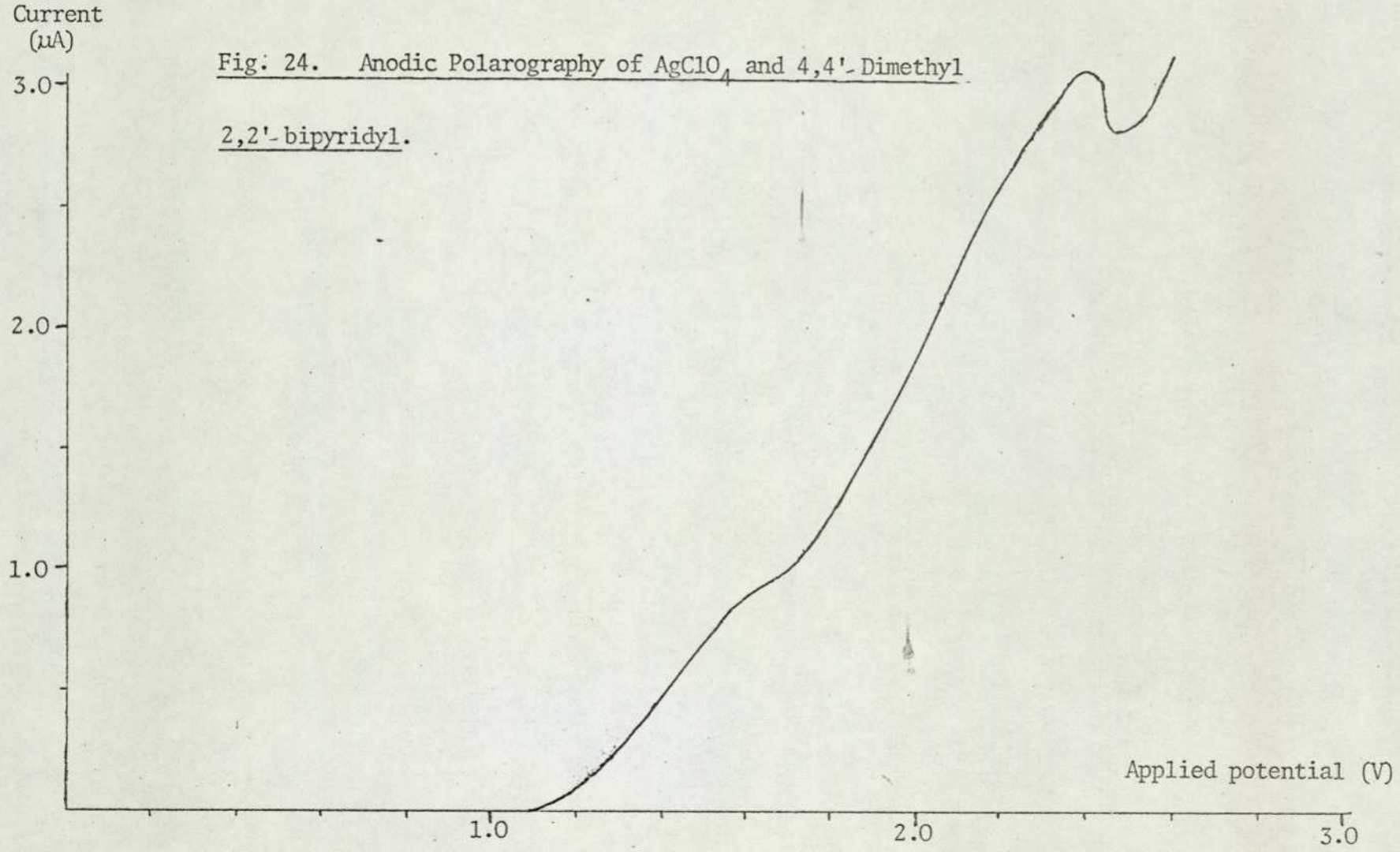


Fig. 24. Anodic Polarography of $AgClO_4$ and 4,4'-Dimethyl 2,2'-bipyridyl.

Fig. 25. Anodic Polarography of $AgNO_3$ with 2,2',2''-Terpyridyl

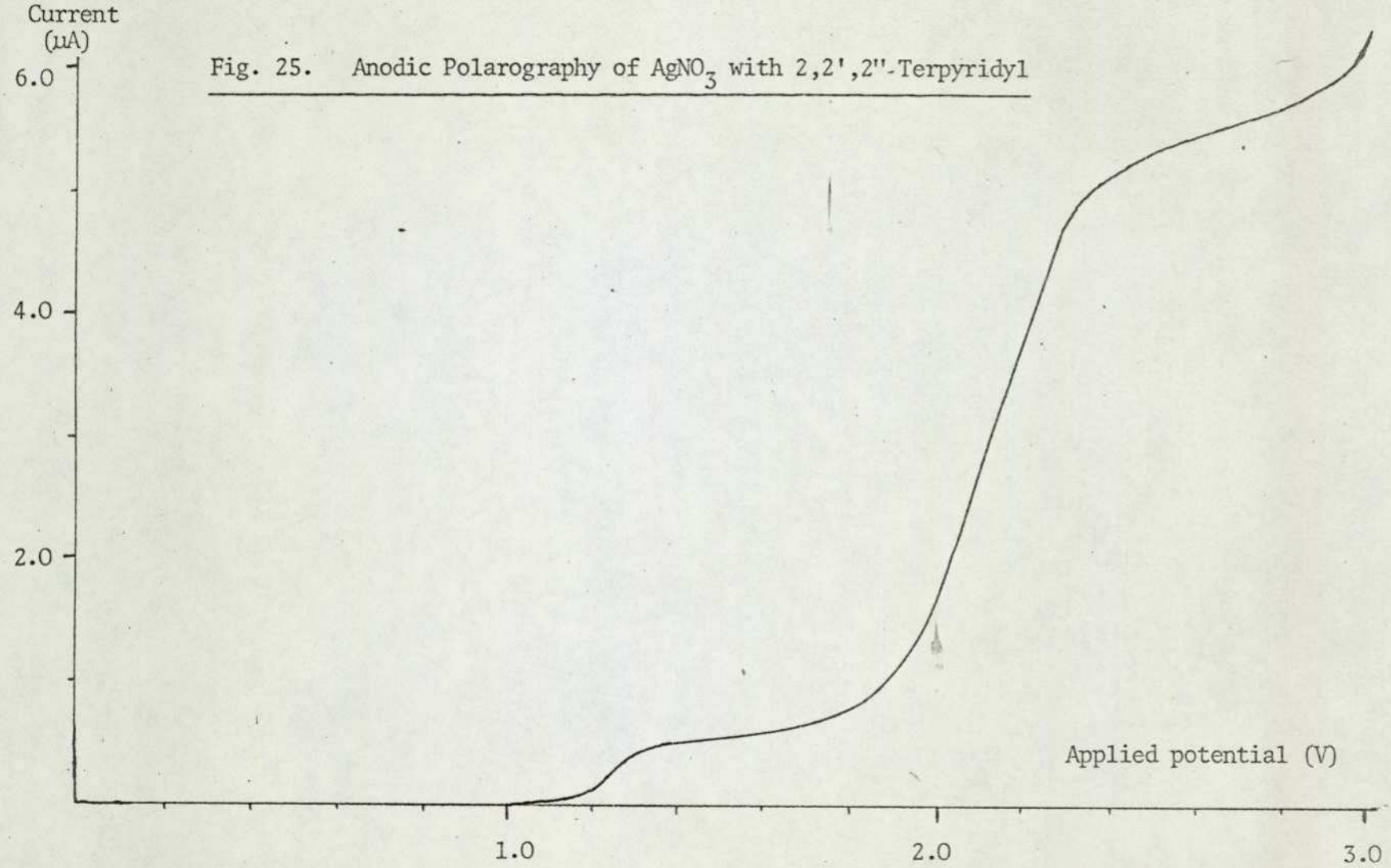


Fig. 26 Anodic Polarography of $AgClO_4$ with Terpy

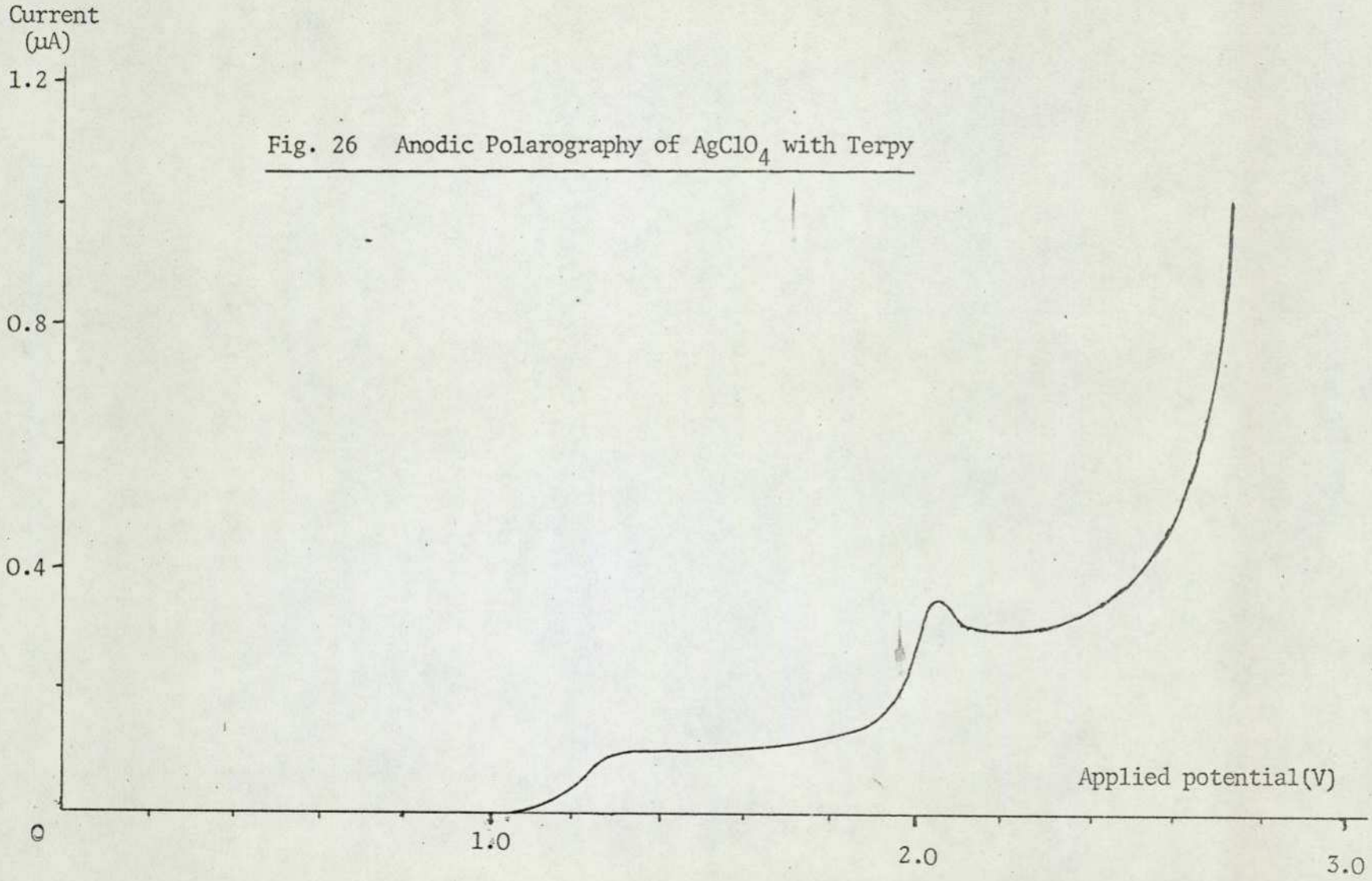
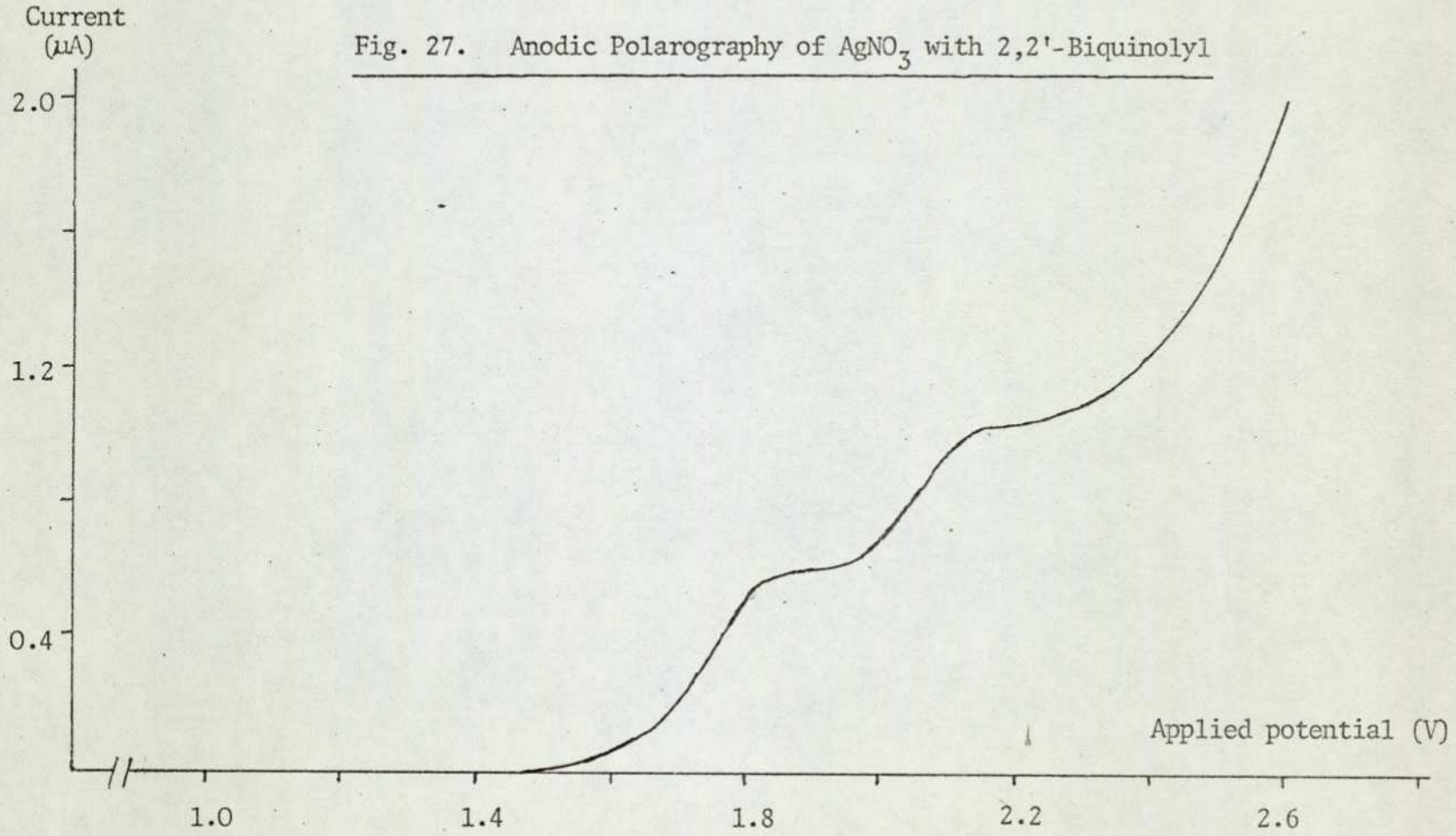


Fig. 27. Anodic Polarography of $AgNO_3$ with 2,2'-Biquinolyl



4.5 Preliminary Study of the Electrochemical Oxidation of Nickel(II) Perchlorate and Copper(II) Nitrate in the Presence of 2,2'-bipyridyl.

Electrochemical preparations of complexes of nickle(III) and copper(III) with the cyclic amine ligands, trans-tetramine and trans-diene, in acetonitrile have recently been reported,[117, 118] the one-electron oxidation of nickel(II) and copper(II) being confirmed by cyclic voltammetry. Copper(III) complexes with tellurate and periodate are also known.[119] The techniques used in the present work for the electro-oxidation of silver(I) complexes were applied to the nickel(II)/bipy and copper(II)/bipy systems in an attempt to prepare Ni(III) and Cu(III) complexes of 2,2'-bipyridyl.

Polarographic data for $Ni(ClO_4)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$ were obtained with 0.1M tetra-n-butylammonium perchlorate as supporting electrolyte. Nickel(II) perchlorate did not give an oxidation wave and in the case of copper(II) nitrate only one wave at about 2.1V, thought to be due to nitrate ion oxidation, was observed. Table XIX gives details of polarograms obtained for different concentrations of metal salt. The plot of i_L vs $[NO_3^-]$ is given in Fig. 28, p.151 from which the slope was determined as 1.2 $\mu A\ mM^{-1}$. Although this value is appreciably lower than the value of 1.8 $\mu A\ mM^{-1}$ determined for the iodide ion (section 4.1.3) it is considered to be associated with the one-electron oxidation of the nitrate. The discrepency might be due to the incomplete dissociation of copper(II) nitrate in acetonitrile.

Table XIX Anodic polarography of copper(II) nitrate solutions

C_M mM	i_L μA	$E_{\frac{1}{2}}$ V
0.93	2.5	2.09
1.00	2.7	2.14
1.55	3.5	2.05
1.42	3.5	2.12
2.00	4.8	2.15
2.63	6.0	2.09
2.93	7.6	2.15
5.43	15.2	2.20

Solutions of copper(II) nitrate in the presence of 2,2'-bipyridyl give a single wave having a half-wave potential identical to that obtained in the absence of the ligand. Values of the limiting current, however, are much larger than those given in the absence of ligand, Table XX giving details of the complete set of polarographic experiments. It is thought that this wave corresponds to the catalytic oxidation of the ligand, an explanation put forward to account for the second wave of the silver(I) nitrate/bipy system (section 4.3).

In the presence of 2,2'-bipyridyl, the nickel(II) perchlorate system gave a single oxidation wave having a half-wave potential of 1.85 V. Fig. 29, p. 152 shows a representative polarogram for a 2.68 mM nickel(II) solution containing 4.1 mM bipyridyl; details of other polarograms are given in Table XXI. The polarograms obtained were much less reproducible than those for the corresponding silver(I) system although the maximum current effect of the silver(I) perchlorate systems was absent. The values of limiting current are much smaller than expected for one-electron oxidation of nickel(II) based on the total concentration of nickel(II) present, and it seems likely that a similar explanation in terms of an electroactive intermediate complex species might be found.

The preliminary polarographic study indicated that controlled potential electrolysis of nickel(II) perchlorate/bipy solutions at 1.85 V might yield a nickel(III) complex. Table XXII gives details of controlled potential electrolyses for this system

Table XX Anodic polarography of copper(II) nitrate/bipy solutions

C_M mM	C_L mM	i_L μA	$E_{\frac{1}{2}}$ V
0.96	1.85	3.8	2.05
0.96	5.13	9.1	2.06
0.96	6.62	9.7	2.08
1.00	1.59	3.8	2.05
1.00	3.89	8.1	2.04
1.42	3.85	6.3	2.03
1.42	7.85	10.0	2.07
1.42	13.18	12.0	2.06
1.42	17.59	12.6	2.06
2.00	6.00	11.0	2.05
2.93	6.41	11.2	2.10
2.93	9.74	16.9	2.12

Table XXI Anodic polarography of nickel(II)/bipy solutions

C_M mM	C_L mM	i_L μA	$E_{\frac{1}{2}}$ V
2.22	7.49	0.3	1.90
2.68	4.10	0.7	1.85
4.84	0.67	0.2	1.86
4.84	2.62	0.6	1.85
4.84	5.85	1.2	1.83
4.84	11.85	2.4	1.80
5.02	12.06	2.2	1.82
5.10	11.13	1.1	1.84
5.10	14.00	2.6	1.90
5.33	11.90	2.1	1.85
5.33	14.46	3.0	1.90

Table XXII Coulometry of nickel(II)/bipy solutions

(A)	Weight of nickel(II) perchlorate hexahydrate electrolysed	= 0.0355 g
	Bu_4NClO_4 concentration	= 0.1 M
	Anodic applied potential	= 1.9 V
	Initial current	= 3.1 mA
	Electrolysis time	= 125 min.
	Total quantity of electricity for electrolysis	= 15.10 coulombs
	Molecular ratio of Bipy : $Ni(ClO_4)_2.6H_2O$	= 3.9 : 1
	$n = \frac{Q.M}{F.W}$ = 1.61 electron/mole	
(B)	Weight of nickel(II) perchlorate hexahydrate electrolysed	= 0.0313 g.
	Bu_4NClO_4 concentration	= 0.1 M
	Anodic applied potential	= 1.9 V
	Initial current	= 2.3 mA
	Electrolysis time	= 108
	Total quantity of electricity for electrolysis	= 5.70 coulombs
	Molecular ratio of Bipy : $Ni(ClO_4)_2.6H_2O$	= 3 : 1
	n = 0.69 electron/mole	
(C)	Weight of nickel(II) perchlorate hexahydrate electrolysed	= 0.0364 g.
	Bu_4NClO_4 concentration	= 0.1 M
	Anodic applied potential	= 1.9 V
	Initial current	= 3.1 mA
	Electrolysis time	= 143 min
	Total quantity of electricity for electrolysis	= 12.23 coulombs
	Molecular ratio of Bipy : $Ni(ClO_4)_2.6H_2O$	= 9.2 : 1
	n = 1.27 electron/mole	

(D)	Weight of nickel(II) perchlorate hexahydrate	= 0.0370 g.
	Bu_4NClO_4 concentration	= 0.1 M
	Anodic applied potential	= 1.9 V
	Initial current	= 3.1 mA
	Electrolysis time	= 110 min
	Total quantity of electricity for electrolysis	= 11.19 coulombs
	Molecular ratio of Bipy : $Ni(ClO_4)_2.6H_2O$	= 9.9 : 1

n = 1.15 electron/mole.

and includes calculations of the number of electrons involved per molecule in the electrode reaction. Although a one electron oxidation is indicated, further evidence would be required for confirmation of the Ni(II) to Ni(III) oxidation due to the lack of reproducibility of the coulometric data. During electrolysis, the anode solution changed from the light pink colour to a very dark green. Removal of the acetonitrile from the oxidised solution gave a dark-green viscous liquid which on exposure to the atmosphere quickly reverted to the light pink colour of the original unoxidised solution. Unfortunately, attempts to isolate the oxidation product from the dark green viscous liquid were unsuccessful; even with careful handling the green colour gradually disappeared.

This preliminary study, while indicating that oxidation of nickel(II)/bipy solutions occurred, was not successful in isolating a nickel(III) complex. However, the study was of use in giving direction to future investigations. Since it appears that the product of the oxidation of nickel(II)/bipy solutions is sensitive to small amounts of water then, clearly, it would be advantageous to use anhydrous nickel perchlorate instead of the hydrate. Further, due to the interference of the nitrate oxidation wave, the use of anhydrous copper(II) perchlorate would be preferred for the study of the copper(II)/bipy system.

In this connection, however, the anodic polarogram of bis(2,2'-biquinolyl) copper(II) perchlorate showed the complete absence of an oxidation wave.

Fig. 28. i_L vs $[NO_3^-]$

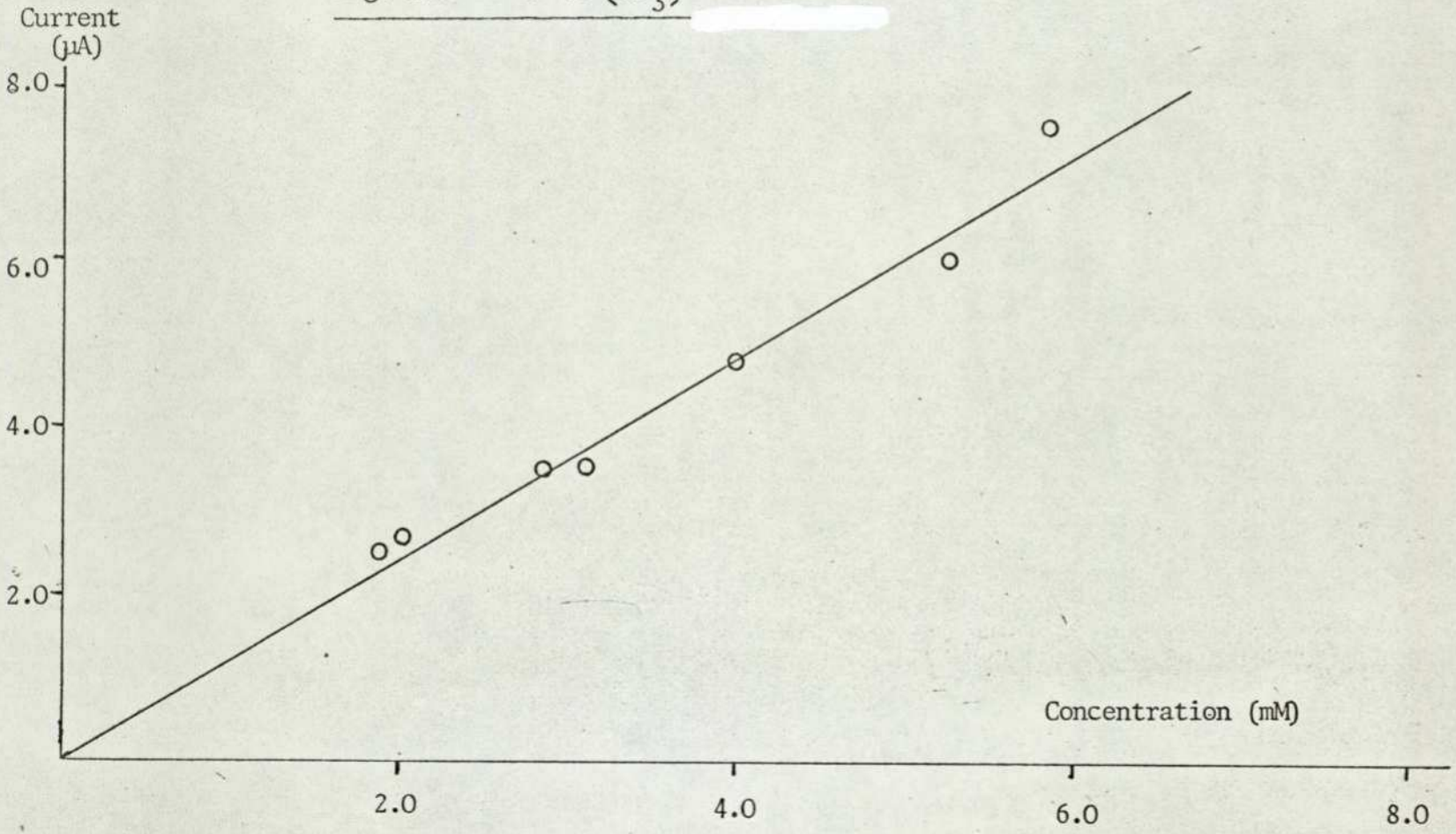
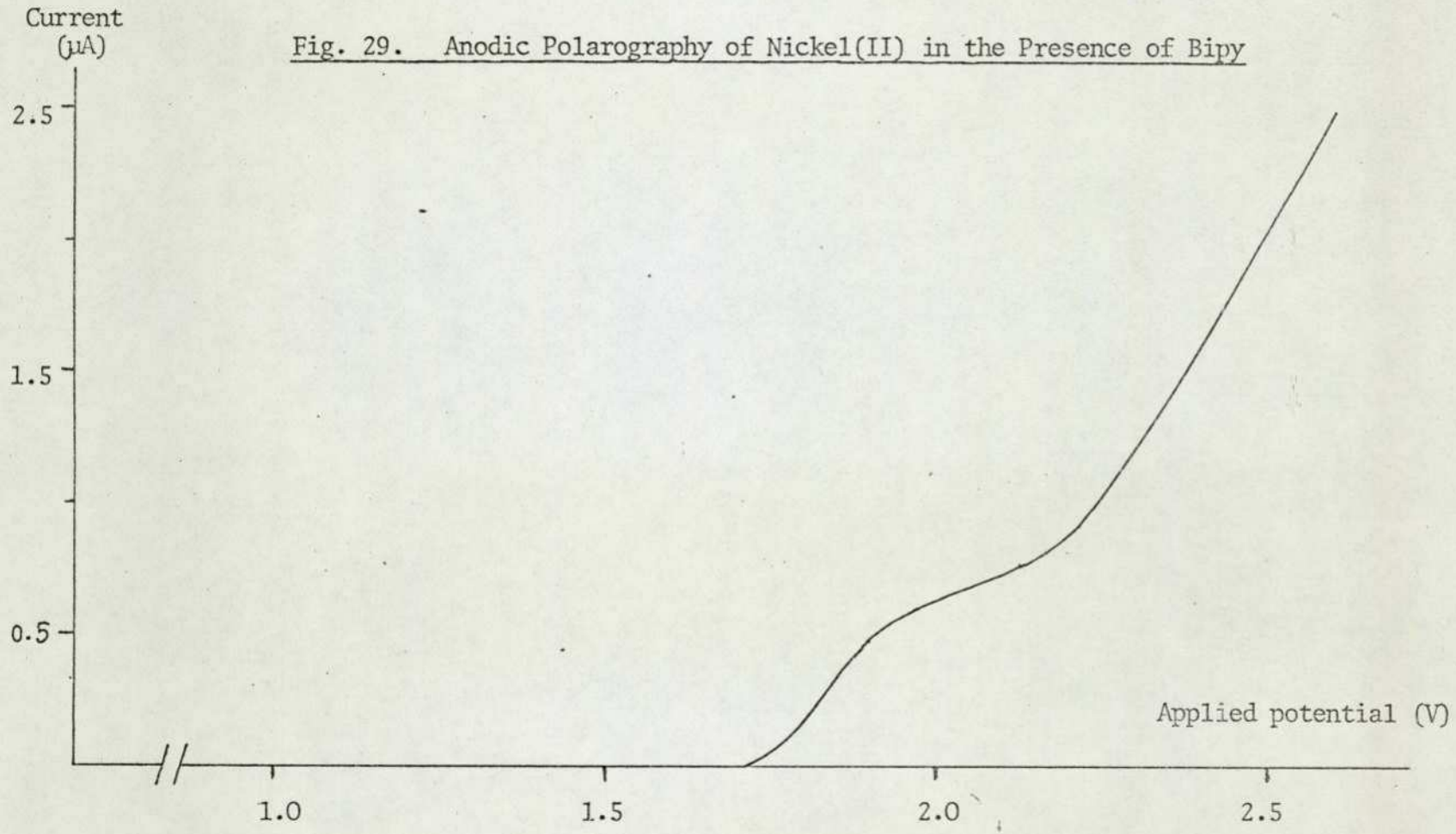


Fig. 29. Anodic Polarography of Nickel(II) in the Presence of Bipy



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