POLAROGRAPHIC STUDIES OF SILVER IN SOME AQUEOUS AND NON-AQUEOUS SOLUTIONS

A thesis
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by

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A considerable amount of work has been reported on the qualitative effects of various addition agents to aqueous and non-aqueous silver electroplating solutions. This thesis reports some quantitative investigations into silver complexes in various solutions.

This work has been mainly concerned with the d.c. polarography of silver at silver and platinum electrodes in aqueous and non-aqueous systems.

In aqueous systems it was found that silver could be determined quantitatively at a stationary platinum microelectrode over the range 2.5 x 10^{-4} M to 2.0 x 10^{-3} M, the current-voltage readings were recorded manually. A wave at about -0.55V (versus the molybdenum electrode) in the current-voltage curve of aqueous solutions containing silver nitrate and sulphosalicylic acid using silver and molybdenum electrodes has been shown to be due to complex molybdenum ions produced by a first order exchange reaction at the molybdenum electrode and not to silver ions as reported by previous workers. This wave could be used for the determination of molybdenum and the specific rate constant of the exchange reaction was directly proportional to the area of the molybdenum electrode.

Silver reduction was carried out in propylene carbonate, pyridine and N,N-dimethylformamide at a stationary platinum microelectrode, some quantitative work was carried out on the silver perchlorate/propylene carbonate system. The effects of the addition of small quantities of perchloric acid and water to the above systems were also noted.

Adopting a three electrode cell system good S-shaped current-voltage curves were obtained for silver in propylene carbonate and pyridine at a vibrating platinum microelectrode and analysis of these waves for a reversible reaction yielding an insoluble product, showed them to
propylene carbonate gave good linearity between the diffusion current and the silver concentration from $2.0 \times 10^{-4}$ to $7.0 \times 10^{-3}$ M.

When pyridine was added to the silver perchlorate/propylene carbonate system, the change in the half-wave potential of silver towards the negative side was almost logarithmic with respect to the pyridine concentration and thought to be due to either solvation or a change in characteristic of the electrodeposited silver crystals. Photomicrographs of silver electrodeposition on platinum from pyridine, propylene carbonate and the propylene carbonate/pyridine mixed solvent system are included in this thesis.
Silver has been determined using polarography with both stationary and vibrating solid electrodes in the solvents propylene carbonate, pyridine and N,N-dimethylformamide. Pyridine showed a marked effect when added to solutions of silver ions in propylene carbonate, the changes of half-wave potential and associated free energy have been co-related with the structures of the electrodeposits and other factors.
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INTRODUCTION TO ELECTRODEPOSITION OF SILVER FROM
AQUEOUS AND NON-AQUEOUS MEDIA

1. SILVER PLATING FROM AQUEOUS MEDIA
The first published reference to silver plating was that of Brugnatelli\(^1\) in 1800 and the first patent was that of Elkington in 1840, the latter year often being referred to as platings' Year One. It is interesting to note that the patent described a solution essentially the same as present-day silver plating baths, namely the alkali cyanide-silver cyanide electrolyte, though at various times since 1840, different addition agents have been included in the plating solutions.

Until recently, silver deposits have been used primarily because of their decorative appeal on such articles as tableware and jewellery. Industry, however, is making increasing use of silver because of its useful electrical, mechanical and chemical properties. In the electrical industry, silver deposits are widely used where high conductivity and low contact resistance are required. Mechanical applications depend on silver's high load-carrying and nonwelding characteristics. It is an excellent heavy-duty sleeve-bearing material and is used extensively for rotating parts in the aircraft power plant industry. The adhesion of the silver deposit to the steel backing is one of the most important properties of the laminated steel-silver bearing material. The chemical stability of silver has led to its use for corrosion resistant coatings.

Since electrodeposited silver is used for the production of high quality bearings, it is not surprising that electrodeposited silver alloys have also been developed as bearing materials. Lead has proved to be a useful alloying metal and high silver-lead alloys, deposited from cyanide tartrate solutions\(^2\), produced bearings which gave good performance at heavy loads. Silver-lead alloys (1.5-3\% Pb) were found to be harder than silver and bearings produced from this alloy had ten times the service life of pure silver bearings. Silver-cadmium alloys were found to be quite ductile and could be operated at higher temperatures than pure silver.
attempts have been made to deposit silver alloys of superior tarnish resis-
tance. Mathers and Johnson studied alloys of silver codeposited with
several other metals and found silver-iron alloys to be the most tarnish
resistant. Stout and Thummel also reported that, even after exposure to
hydrogen sulphide, a silver-cadmium alloy (15% Cd) had three times the
reflecting power of pure silver. They also found that a silver-cadmium
alloy (76% Cd) gave the best all-purpose reflector.

Electrodeposited silver is used extensively in applications where
special effects are required e.g. jewellery and search-light reflectors.
In 1930, however, the noble metal rhodium was found to possess superior
properties as a white finish for jewellery, and since then, this metal
has often been plated onto silver. In the aviation industry, much use has
been made of rhodium plated silver components, primarily for electrical
and electronic applications. Silver is expensive and so is rarely used
for corrosion protection alone. Usually a protective coating of copper
or nickel is electroplated onto the surface prior to the silver coating.

Titanium is much used in the aircraft industry due to its high
strength/weight ratio and good corrosion resistance. The metal, however,
has poor resistance to wear and is difficult to join to other metals, but
these factors can be overcome by electroplated metal coatings. Titanium
plated with zinc and then successive layers of silver, copper and silver
can be brazed by heating the electroplated braze-metal joint at 800°C.
for twenty minutes. Uranium also has poor welding characteristics since
it is readily oxidised in air, but by employing a silver plated uranium
filler rod, uranium can be joined to itself by open arc welding.

Although not an electrolytic process the preparation of nonconductors
for electroplating by the 'silvering' process is perhaps worthy of
inclusion, since the art of electroplating upon nonconductors is as old
duction of a smooth continuous conductive coating which will serve as a basis for the electrodeposit. The silver and reducing solutions are mixed in the correct proportions in a special gun and then sprayed onto the non-conductor, the silver film being formed in a matter of seconds.

Silver Plating Solutions.

The normal silver plating bath consists essentially of a solution of silver cyanide together with some free potassium cyanide. Depending on the type of deposit required, the actual silver and free cyanide contents are varied. Increasing use is being made of the double salt potassium silver cyanide and a suitable bath may have the following composition.

\[
\text{AgK(CN)₂} \quad \ldots \quad 45\text{g/l.}
\]

\[
\text{KCN} \quad \ldots \quad 30\text{g/l.}
\]

A bath of this nature produces a dead white matt plate, which is then subject to 'scratch brushing' and final polishing if a brilliant and highly reflecting finish is required.

Most baths, however, are still prepared with silver cyanide, and silver plating baths in common use are shown in Table 1.

Functions of Constituents

Silver cyanide is the source of silver ions, which are present as the result of dissociation of the complex cyanide \( \text{Ag(CN)}_2^- \); thus the silver ion concentration is for practical purposes independent of small changes in total silver. Throwing power, which is the ability of a bath to produce deposits of more or less uniform thickness on cathodes having macroscopic irregularities, is improved by a decrease in silver content.
<table>
<thead>
<tr>
<th></th>
<th>KCN Bath</th>
<th>NaCN Bath</th>
<th>High Speed (Bright)</th>
<th>High Speed (Bearing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver, g/l metal</td>
<td>25-33</td>
<td>25-33</td>
<td>16-18</td>
<td>30-45</td>
</tr>
<tr>
<td>Free KCN, g/l</td>
<td>30-45</td>
<td></td>
<td></td>
<td>85-115</td>
</tr>
<tr>
<td>K₂CO₃, g/l</td>
<td>30-90</td>
<td></td>
<td></td>
<td>20-90</td>
</tr>
<tr>
<td>KNO₃, g/l</td>
<td></td>
<td>115-150</td>
<td></td>
<td>15-75</td>
</tr>
<tr>
<td>Free NaCN, g/l</td>
<td>30-38</td>
<td>15-22</td>
<td></td>
<td>45-150</td>
</tr>
<tr>
<td>Na₂CO₃, g/l</td>
<td>38-45</td>
<td>22 max.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH, g/l</td>
<td></td>
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<td>4-30</td>
</tr>
</tbody>
</table>
cathode polarisation, make for good anode corrosion and increase the conductivity of the plating baths. Potassium cyanide is preferred to sodium cyanide since the former bath has greater conductivity and 'bright' plating baths perform better when this salt is used.

The presence of potassium carbonate in silver plating baths serves to increase the conductivity, increases anode and cathode polarisation and is said to improve the physical properties of the deposit.

Potassium nitrate, by providing additional potassium ions, is helpful in extending the range of bright silver baths. The presence of nitrate ions also assists anode corrosion so that a lower free cyanide concentration may be used.

The inclusion of other anions in silver plating baths is rarely used, except for hydroxide, which has been recommended for solutions for plating bearings and some bright solutions.

**Addition Agents**

Besides the above mentioned constituents in silver plating baths, the addition of small amounts of certain substances, often organic, may influence the form or structure of the electrodeposited silver. These agents enhance smoothness and brightness to the deposit by causing silver to deposit more rapidly in pits and depressions and less rapidly on peaks and ridges than on level portions of the cathode surface. The adsorption at the cathode surface of minute quantities of the addition agent may affect the deposition of a large number of silver ions, with subsequent increase in 'brightening'. The term 'brightening' implies submicroscopic smoothing resulting in a substantial increase in specular reflection. Although mirror bright deposits may not be obtained, the use of a brightener makes for greater ease in the final buffing process because the grain structure of the silver deposit is refined.
As early as 1847, the addition of carbon disulphide to a normal plating bath resulted in a deposit that was much brighter in appearance than the normal matt finish. The effect of the addition did not produce a mirror-bright deposit, but one with a slightly 'pearl' appearance which required less polishing. Furthermore, the deposit was harder and a better wearing surface was obtained.

Silver plating baths containing the thiosulphate ion as the 'brightener' have also been used for a long time, the 'brightener' having the following composition:

- Ammonium thiosulphate...500g.
- Thiourea....70g.
- Ammonium thiocyanate....70g.
- Boric acid....70g.
- Sodium sulphite....84g.
- Acetic acid (glacial)....70g.
- Water...1136cc.

8ml. of the above 'brightener' is added to 1 litre of the plating solution.

Addition agents described in the literature include gums², sugars, unsaturated alcohols⁹, and sulphonated aliphatic acids¹⁰, but most are sulphur-bearing organic compounds such as thiourea¹¹, dithiocarbamates¹², mercaptobenzothiazole¹³, thiazolidines¹⁴, an acrolein product with carbon disulphide¹⁵. Commercial fully bright silver plating became a factor in the United States with the development of a ketone-carbon disulphide reaction product¹⁶, modification of Weiner's¹⁷ selenite bath¹⁸, and the development of bismuth or antimony polyalcohol addition agents¹⁹, ²⁰. These agents produce mirror-bright silver deposits over a wide range of current densities.
better addition agents for the production of bright silver plating, many of these agents being complex organic compounds. A few examples of these experiments will now be given:

Schloetter found that bright silver coatings were obtained over a large current density range from a cyanide bath that includes as a primary brightener $\text{H}_{2}\text{NC(S)NHNC(S)SM}$ (I) or $\text{H}_{2}\text{NNHC(S)NHNC(S)SM}$ (M is a univalent metal). Thus a bath containing silver as silver cyanide (30g/l), potassium cyanide (140g/l), (I) (0.15g/l) and condensation products from naphthalene sulphonlic acids and methanal (0.8g/l), produces bright silver deposits at a current density of 0.1-4amp/dm$^2$ at 22-25°C in 10-20 seconds. Even after baking, the brilliance of the silver coating was maintained.

To produce a plating with mirror like lustre and expand the brightness range, Matulis incorporated mercaptobenzothiazole(I) in his plating solution, the latter having the following composition: metallic Ag 45-60, KCl(free) 70-80, K$_2$CO$_3$ up to 50 and (I) 0.25-0.50g/l. The temperature was 18-25°C. and current density 2-3 amp/dm$^2$.

Skolnik obtained bright silver coatings from alkali cyanide baths containing, as the organic brightening agent, one of the metals Mo, Ni, Co, Fe, Cr, Se or As combined with one of the following: saccharic acid, gluconic acid, an amino acid or EDTA. Hardness of the silver layers was also increased by the addition of aromatic aldehydes or oxyaldehydes (0.1-1 g/l).

Radio and Vallalet obtained bright silver coatings from cyanide solutions containing seleninylbis(thioacetic acid) as brightener, OSe(SCH$_2$CO$_2$H)$_2$, and Me$_2$SO (0.5-1.0g/l). Increased brightness and the absence of pores resulted from these additions to the plating solution.

In more recent research work increasing use has been made of the
Lyde and Rickhuss\textsuperscript{25} achieved bright electrodeposits of silver using an electrolyte containing a soluble silver complex and a brightening additive consisting of a solution of dithiocarbamate derived from a polyamine compound containing two or more NH\textsubscript{2} groups, primary or secondary, not bound to an aromatic nucleus. Thus an electrolyte containing AgCN (23g/l), KCl (110g/l), K\textsubscript{2}CO\textsubscript{3} (17.5g/l), the potassium salt of the reaction product of one mole of ethylenediamine H\textsubscript{2}N(CH\textsubscript{2})\textsubscript{2}NH\textsubscript{2} and two moles of carbon disulphide CS\textsubscript{2} (0.02g/l) and sodium methylene-bis-naphthalene sulphonate (0.3g/l) gave a very bright deposit at 20\textdegree C. and at a current density of 0.5 amp/dm\textsuperscript{2}. Georgievskii\textsuperscript{26} found that monoethanolamine H\textsubscript{2}H\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OH performed the same function as cyanide ions, so it was possible to decrease the free cyanide content of the electrolyte. These electrolytes contain:

- Silver nitrate... 20-25g/l.
- Potassium ferricyanide... 40-50g/l.
- Monoethanolamine... 75-80g/l.

The temperature was 18-20\textdegree C. and the cathodic current density 0.15-0.25 amp/dm\textsuperscript{2}. Using a plating bath of this nature there is no need for preliminary amalgamation or silver plating of copper and brass objects.

Schering\textsuperscript{27} obtained bright and hard coatings of silver in a cyanide bath containing a complex of SbCl\textsubscript{3} and an alkanolamine. His plating bath had the following composition: NaAg(CN)\textsubscript{2} 30, NaCN 110, Na\textsubscript{2}CO\textsubscript{3} 25, Sb (added as a complex of SbCl\textsubscript{3} in triethanolamine) 0.5g/l.

All the silver plating solutions described above have been in the presence of cyanide. An improved quality of silver plating, however, has been achieved by Krovtsov et al.\textsuperscript{28} in the absence of cyanide with a bath of the following composition:

- Silver nitrate... 15-20g/l.
- Monoethanolamine(40%) 30-35g/l.
Ammonium nitrate  15-25g/l.
(I)  0.1-0.2g/l.
(II)  0.1-0.2g/l.

(I)- N-(sulphamoylaryl) maleamino acid.
(II)- N-phenylsulphonyl-N, N'-bis(phenylsulphonyl) benzenesulphinamidine.

The temperature of the plating solution was 15-:
density of 0.2-0.8amp/dm².

**Pulse Brightening**

A bright finish may be imparted electrolytically to freshly plated silver by making it the anode in a cyanide solution and applying a pulsed current. The smoothness of the surface depends on the grain structure of the electrodeposit, the degree of smoothness of the base metal and the duration of the electrolytic brightening process.

The electrolyte is essentially an alkali cyanide one to which a small amount of potassium carbonate is added to increase the throwing power of the bath. A small amount of silver cyanide is added to reduce excessive gassing at the cathode which may cause lowered lustre.

Potassium cyanide (free)  45g/l.
Silver (as metal)  15g/l min.
Potassium carbonate (anhydrous)  60g/l.

Using pulse and open circuit times of 5 sec. and 1 sec. respectively for a total time of two minutes and with an anode current density of 4 amp/dm², this treatment produces good results on fine grained freshly plated silver. Rough or burned deposits will not become bright and silver that has been allowed to tarnish even slightly will not brighten uniformly.

**Periodic Reverse Current Silver Plating**

Periodic reverse current has been used successfully for silver plating,
Kuronova and Katyshev\textsuperscript{30} studied the electrodeposition of silver from cyanide solutions, free from additives, by reversing the current and found that bright fine crystalline deposits could be obtained from an electrolyte containing:

\begin{align*}
\text{Silver, g/l metal} & \quad 28-32. \\
\text{Potassium cyanide, g/l} & \quad 7-15.
\end{align*}

The temperature of the plating solution was 25°C. and the current density 3-4 amp/dm\textsuperscript{2}. Reversing conditions of 3 sec. cathodic to 1 sec. anodic produces silver coatings, the hardness of which is twice that of ordinary deposits.

Summary

Continued research is being conducted on aqueous silver plating baths containing addition agents, because the presence of these can influence the following characteristics of the electrodeposited silver:

\begin{enumerate}
\item better deposit distribution.
\item increased hardness and wear resistance.
\item improved corrosion resistance.
\item improved adhesion and covering power.
\item lowered finishing costs.
\end{enumerate}
SECTION 1

2. SILVER PLATING FROM NON-AQUEOUS MEDIA
from a large variety of non-aqueous based electrolytes. The earliest published reference is that of Kahlenburg\textsuperscript{31}. He electrodeposited silver from a solution of silver nitrate in pyridine as a firm white deposit. The deposit was also compact, well-adhering, susceptible to polish and not unlike that obtained from normal cyanide plating baths.

Of its many uses, one application of the electrodeposition of silver has been the accurate determination of current strength, the most successful coulometric measurements normally being carried out by the controlled electrolysis of a silver nitrate solution. Provided the current is maintained at a constant value, coulometry may also be employed in the accurate measurement of time. Recent commercial interest\textsuperscript{32, 33} has been shown in the development of an 'elapsed time indicator' device which could operate over a wide temperature range (-45\textdegree C to +125\textdegree C), hence it was necessary to use a suitable alternative solvent to water. In order to develop such a device, the latter had to satisfy the following operative conditions:

(1) - No decomposition of the electrolyte.

(2) - Capable of usage at different values of constant current.

(3) - An operating time of up to 5000 hours.

The production of this device necessitated the generation of bright, adherent and non-dendritic electrodeposits of silver. Considering the physico-chemical properties of numerous non-aqueous solvents, Kellner\textsuperscript{34} investigated the electrodeposition of silver from the following solvents, propylene carbonate, pyridine and N\textsubscript{N}-dimethylformamide. He also noted the effects of addition agents on these solvent systems. A satisfactory electrolyte was finally based on the silver perchlorate/pyridine system.

Studies relating to the electrodeposition of silver from the solvents mentioned above have been mainly of a qualitative nature and as yet, little is known about the energetics of such processes.
actions between silver ions and solvent molecules including pyridine and to determine the effect of these interactions on the nature of the silver electrodeposits.
SECTION II

SPECTROSCOPIC INVESTIGATION OF THE SILVER NITRATE/PYRIDINE SYSTEM IN A NON-AQUEOUS MEDIUM

1. INTRODUCTION, MATERIALS AND INSTRUMENTATION
Solutions of silver nitrate, silver nitrate/pyridine and pyridine alone were investigated using ultra-violet and infra-red spectroscopy in an attempt to identify any species formed from the interaction of silver nitrate and pyridine.

Materials

a) Analar silver nitrate (B.D.H.)

b) Spectrosol methanol (B.D.H.)

c) Analar pyridine (B.D.H.) was further purified by distillation over potassium hydroxide pellets under atmospheric pressure, the middle 80% fraction (B.Pt. 115°C) was retained. The freshly distilled pyridine was then distilled under reduced pressure at a column temperature of 55°C, the middle 80°C fraction was again retained. The solvent was stored over Molecular Sieve (Linde 4A).

d) Preparation of the Silver Nitrate/Pyridine Complex

Preliminary experiments indicated the formation of a complex between silver nitrate and pyridine since a white solid was obtained on mixing the two in a 1:4 mole ratio. The reaction was exothermic.

Silver nitrate crystals (5.5g) were warmed with pyridine (10ml) in a flask (1:4 mole ratio) and the crystals dissolved. Colourless crystals appeared on cooling. These were filtered, vacuum dried to remove excess pyridine, washed three times with hexane, vacuum dried again and then stored in a vacuum dessicator. Approximately 10g. of the crystals were obtained.

Instrumentation

Ultra-violet and infra-red spectra were recorded on Pye Unicam SP 800 B and SP 200 spectrophotometers respectively.
SECTION II

2. ULTRA-VIOLET STUDIES OF THE SILVER NITRATE/PYRIDINE SYSTEM IN METHANOL
spectra recorded:

a) Silver nitrate (10^{-4} M)
b) Pyridine (3 \times 10^{-4} M)
c) Silver nitrate/pyridine mixtures (mole ratios 1:2, 1:4, and 1:8)
d) Silver nitrate/pyridine complex (2 \times 10^{-4} M)

Results

a) The silver nitrate solution gave a single absorption band, 
\( \lambda_{\text{max}} = 208\text{nm} \) (Figure 1)
b) The pyridine solution gave two absorption bands, 
\( \lambda_{\text{max}} = 204 \) and 257nm respectively (Figure 2)
c) Recorded spectra of the silver nitrate/pyridine mixtures gave two absorption bands, 
\( \lambda_{\text{max}} = 206 \) and 257nm respectively (Figure 3)
d) The silver nitrate/pyridine complex solution gave two absorption bands, 
\( \lambda_{\text{max}} = 206 \) and 257nm respectively (Figure 4)

Discussion of Results

Despite the formation of the silver nitrate/pyridine complex, the ultra-violet spectra of the various silver nitrate/pyridine mixtures and also of the prepared complex in methanol did not show the existence of any interaction between silver nitrate and pyridine when compared with their individual spectra.
Figure 1. Ultra-Violet Spectrum of AsNO$_3$(10$^{-4}$M) in Methanol

![Ultra-Violet Spectrum of AsNO$_3$(10$^{-4}$M) in Methanol](image1)

Figure 2. Ultra-Violet Spectrum of Pyridine(3x 10$^{-4}$M) in Methanol

![Ultra-Violet Spectrum of Pyridine(3x 10$^{-4}$M) in Methanol](image2)
Methanol - Mole Ratios as Indicated

Figure 4. Ultra-Violet Spectrum of Silver Nitrate/Pyridine Complex

\((2 \times 10^{-4} \text{M})\) in Methanol

Absorbance

Wavelength nm
Determination of the Extinction Coefficient of Pyridine in Methanol

In order to determine the molecular weight of the complex, use was made of the extinction coefficient of pyridine in methanol, for which a value may be determined from the following equation:

\[ A = \varepsilon cd \]  

\( A \) = Absorbance
\( \varepsilon \) = Extinction coefficient
\( c \) = Concentration (moles/l)
\( d \) = Path length (1 cm)

Results

0.063g. of pyridine were made up to 100ml. solution in methanol, and then 2ml. of this solution were diluted to 50ml. with methanol, the latter solution gave \( A = 0.88 \) at \( \lambda_{\text{max}} = 257\text{nm} \).

Concentration of pyridine = \( \frac{0.63 \times 2 \text{ g/l}}{50} \)
\[ = 0.63 \times 2 \text{ mole/l} \]
\[ = 0.63 \times 2 \text{ mole/l} \text{ (molecular wt. of } 50 \times 79 \text{ pyridine = 79)} \]

By substitution in equation (I) above, the extinction coefficient of pyridine in methanol = 2,760.

Determination of the Molecular Weight of the Silver Nitrate/Pyridine Complex

A known weight of the silver nitrate/pyridine complex was dissolved in methanol and the absorbance value (A) was recorded at \( \lambda_{\text{max}} = 257\text{nm} \).

The molecular weight of the complex is given by

\[ \text{Molecular weight} = \frac{10 \varepsilon cd}{A} \text{ (wt/vol.) of complex} \]

Results

0.010g. of the silver nitrate/pyridine complex were dissolved in methanol (25ml) and then 4ml. of this solution were diluted to 25ml. with methanol, the latter solution gave \( A = 1.09 \) at \( \lambda_{\text{max}} = 257\text{nm} \) (Figure 4).

By substitution in equation (2) above, the molecular weight of the silver nitrate/pyridine complex = 162.
Discussion of Results

A formula weight of 162 for the silver nitrate/pyridine complex corresponds to a 1:1 ratio of silver nitrate : pyridine. Gravimetric results (page 23), however, suggest that the silver nitrate/pyridine ratio is of the order of 1:2, since 5.5g of silver nitrate produced approximately 10g of the complex. (Formula weight of silver nitrate = 170, Molecular weight of pyridine = 79).

On this basis, the formula weight of the complex will now be $2 \times 162 = 324$, which agrees favourably with the formula $\text{Ag(Py)}_2\text{NO}_3$, the formula weight of which is 328.

Although there is evidence for the existence of the $\text{Ag(Py)}^+$ ion\(^{35}\), the complex prepared here is probably the one of formula $\text{Ag(Py)}_2\text{NO}_3$. 
SECTION II

3. INFRA-RED STUDIES OF THE SILVER NITRATE/PYRIDINE SYSTEM
The following infra-red spectra were recorded:

(a) Silver nitrate in KBr disc (Figure 5)
(b) Silver nitrate/pyridine complex in KBr disc (Figure 6)
(c) Pyridine between NaCl discs (Figure 7)
(d) Silver nitrate/pyridine complex in Nujol (Figure 8)
(e) Nujol (Figure 9)

Discussion of Spectra

The infra-red spectrum of silver nitrate shows a strong N-O stretching band at 1385 cm\(^{-1}\) and a second band due to the nitrate ion at 820 cm\(^{-1}\) (Figure 5).

The infra-red spectrum of the silver nitrate/pyridine complex, however, was very similar to that of silver nitrate. A more critical comparison of the complex spectrum compared with that of pyridine indicated slight evidence for the presence of pyridine at 1440 and 700 cm\(^{-1}\) respectively (Figure 6). It was possible that the silver nitrate/pyridine complex was easily decomposed both by the physical process of grinding with and in the presence of potassium bromide.

Experiments in Nujol produced much more satisfactory results, a new peak was recorded at 1310 cm\(^{-1}\) (Figure 8). The absorption band was not well defined since it was on the shoulder of the larger one due to the nitrate ion or Nujol.

A comparison of the spectra of pyridine and the complex in Nujol showed slight shifts of some of the pyridine absorption bands.

<table>
<thead>
<tr>
<th>Pyridine</th>
<th>Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>1225 cm(^{-1})</td>
<td>1215 cm(^{-1})</td>
</tr>
<tr>
<td>1090 cm(^{-1})</td>
<td>1070 cm(^{-1})</td>
</tr>
<tr>
<td>1000 cm(^{-1})</td>
<td>1015 cm(^{-1})</td>
</tr>
<tr>
<td>712 cm(^{-1})</td>
<td>700 cm(^{-1})</td>
</tr>
</tbody>
</table>
Figure 6. Infra-Red Spectrum of the Silver Nitrate/Pyridine Complex in Potassium Bromide Disc.
Figure 7: Infra-Red Spectrum of Pyridine between Sodium Chloride Discs.
Figure 8. Infra-Red Spectrum of the Silver Nitrate/Pyridine Complex in Nujol.
SECTION III

POLAROGRAPHY OF SILVER AT THE DROPPING MERCURY ELECTRODE

1. IN AQUEOUS SOLUTIONS
As both IR and UV spectroscopy failed to give conclusive results with respect to the composition of the silver nitrate/pyridine complex, it was obvious that any changes in the structure of the organo/silver compounds which might occur on the addition of other organic substances would have to be followed by some other technique.

**Basic Principles of Polarography**

The polarographic method of chemical analysis is based on the interpretation of the current-voltage curves obtained when solutions of electro-reducible substances are electrolysed in an electrochemical cell in which one electrode consists of mercury falling dropwise from a glass capillary tube. Mercury pool or saturated calomel electrodes (SCE) have long been used as non-polarisable reference electrodes. Automatically recorded current-voltage curves are called polarograms.

A typical cathodic current-voltage curve (Figure 10) can be obtained by electrolysing an air free solution of 1.3mM zinc sulphate in 0.1M potassium chloride. Since oxygen is readily reduced at the dropping mercury electrode (DME) and usually interferes with the current-voltage curves of other substances, the gas is removed by bubbling an inert gas such as nitrogen through the solution before electrolysis. From the curve it is apparent that a small current called the 'residual current' flowed through the cell until the decomposition potential of zinc was reached at an applied e.m.f. of about 1.0V. At higher potentials continuous electrolysis began, consisting of the discharge of zinc ions at the dropping mercury cathode to form a zinc amalgam and the anodic dissolution of mercury to form calomel at the anode.

\[
\begin{align*}
Zn^{2+} + 2e + Hg & \rightarrow Zn(Hg) \\
2Hg + 2Cl^- & \rightarrow 2e + Hg_2Cl_2
\end{align*}
\]

It will be noted from the current-voltage curve that after the applied potential of 1.0V was exceeded, the current increased exponentially at
Figure 10. Typical Current-Voltage Curve obtained with the Dropping Mercury Electrode with an Air-Free Solution of Zinc Sulphate (1.3 x 10^{-3} M) in 0.1M Potassium Chloride
first, then gradually approached a limiting value and finally became constant and independent of further increase in the applied e.m.f. As a result of the discharge of zinc ions, the concentration of the reducible material is depleted close to the surface of the dropping electrode, and this loss is compensated by diffusion of a fresh supply of reducible material from the bulk of the solution. With an excess of some other salt present in the solution, the limiting current is determined practically entirely by the rate of this diffusion process and hence is called a 'diffusion current'. Since the rate of diffusion attains a constant value and this is directly proportional to the concentration of the reducible species in the bulk of the solution, the diffusion current is directly proportional to the concentration in the body of the solution. This is the basis of quantitative polarographic analysis.

The decomposition potential of a given solution is characteristic of the particular electroreducible species present but even more characteristic is the 'half wave potential', which is the value of the potential of the dropping electrode against an external reference electrode, at that point on the current-voltage curve where the diffusion current is equal to one-half of the limiting value. Provided the composition of the solution with respect to other ions is kept constant, the half wave potential is usually independent of the concentration of the reducible species. This fact forms the basis of qualitative polarographic analysis.

Analysis of the Polarographic Waves of Simple and Complex Metal Ions

Consider the following reaction taking place at the dropping mercury electrode:

\[ \text{M}^{n+} + ne \rightarrow \text{M(Hg)} \]  

where the reduced metal M forms an amalgam with the mercury. If the reaction is reversible, and very rapid compared to the rate of diffusion of the metal ions up to the electrode surface, the potential of the dropping electrode at every point on the polarographic wave can be
expressed by the following fundamental equation, first derived by Heyrovsky and Ilkovic in 1935:

$$E_{d.e.} = E^\circ + \frac{0.0591}{n} \log \frac{i}{i_D - i} \tag{2}$$

$$i_D = \text{diffusion current}$$

A plot of $E_{d.e.}$ versus $\log \frac{i}{i_D - i}$ should produce a straight line with a slope equal to $\frac{0.0591}{n}$ volts. The number of electrons ($n$) involved in the electrode reaction may then be evaluated.

Suppose an addition agent $X^{b-}$ is now added to a solution containing the simple electroreducible metal ion $M^{n+}$ with the subsequent formation of a complex ion

$$M^{n+} + pX^{b-} \rightarrow MX^{(n-p)b^+} \tag{3}$$

Assuming the metal forms an amalgam with mercury, the reduction of the complex ion to the metallic state may be represented by

$$MX^{(n-p)b^+} + ne + Hg \rightarrow M(Hg) + pX^{b-} \tag{4}$$

With an excess of the complexing agent present in the solution, the potential of the dropping electrode at every point on the wave can again be expressed by equation (2) above, with the resultant evaluation of the 'n' value. The half-wave potential of a complex metal ion shifts with variation in concentration of the complex forming substance and to a first approximation

$$E_\frac{1}{2} = -\frac{p \cdot 0.0591}{n} \log C_X \text{ at } 25^\circ C$$

A plot of $E_\frac{1}{2}$ versus $\log C_X$ should produce a straight line of slope $\frac{p \cdot 0.0591}{n}$, from which a value for the co-ordination number $p$ of the complex ion may be determined.
The most widely used electrode in polarography is the dropping mercury electrode and many reactions involving the reduction of metals and their resultant complex formation with added ligands have been studied. The standard potential of the silver/silver ion couple (+0.7995 V versus the normal hydrogen electrode, NHE) is not very different from that of the mercurous/mercury couple (+0.7986 V versus NHE). The reduction of silver ions from non-complexing supporting electrolytes e.g. nitric or perchloric acids, nitrate or perchlorate salts, produces direct current that starts from zero applied e.m.f. and the half-wave potential corresponds to the anodic dissolution potential of mercury rather than the true reduction potential of silver. Since silver and mercury both form complexes of similar stabilities with the same ligands, the same effect is usually observed in most supporting electrolytes. Consequently, there is little data available on silver using the dropping mercury electrode in the literature.

Kolthoff and Lingane observed a good diffusion current for the reduction of the silver thiosulphate complex from $10^{-2}$ M to M solutions of sodium thiosulphate.

Sanigar found that fairly concentrated solutions of potassium argent cyanide, without excess cyanide present, produced a wave that started at zero applied e.m.f. The wave had a maximum, but the diffusion current was well defined, a $10^{-4}$ M solution producing a wave whose half-wave potential was about -0.3 V versus the SCE. Dagnall and West obtained a true polarographic wave for silver in cyanide medium from which excess cyanide had been removed by the addition of Ni(II). Other common ions do not interfere, with the exception of lead, but the addition of excess EDTA removes the coincident wave of Pb(I) to more cathodic potentials.
Large and Przybylowicz\cite{41} determined silver in cyanide solutions by the analysis of a combined anodic and cathodic wave with an $E_0$ of $-0.18$V versus SCE, obtained with an aqueous solution of $10^{-3}$M $\text{Ag(CN)}_2^-$ phosphate buffer at a pH of 6.7 and containing no excess cyanide. The wave is the result of anodic dissolution of mercury in the presence of cyanide and the reduction of $\text{Hg(CN)}_2^-$, both species having been produced by a rapid chemical reaction between $\text{Hg}$ and $\text{Ag(CN)}_2^-$

$$\text{Hg} + 2\text{Ag(CN)}_2^- \rightarrow \text{Hg(CN)}_2^2 + 2\text{Ag} + 2\text{CN}^-$$

Since $\text{Hg(CN)}_2^-$ gives only a cathodic reduction wave, the anodic current of the wave obtained for a mixture of $\text{Hg(CN)}_2$ and $\text{Ag(CN)}_2^-$ allows estimation of the silver content, while the difference between the anodic and cathodic current values represents the mercury content.

In their polarographic determination of silver in cyanide plating baths, Kies et al.\cite{42} initially added 50ml. 2M $\text{Na}_2\text{S}_2\text{O}_3$ or 5M KSCN, and 4ml. of 0.1% gelatin to a sample containing $(5-80) \times 10^{-5}$M silver and less than $1.5 \times 10^{-2}$M gold. After diluting to 100ml. with water, the current was measured at $-0.77$V and $-0.76$V for thiosulphate and cyanate solutions respectively against a silver chloride/silver electrode. The peak height was measured with a dropping mercury electrode. Copper and greater than $4 \times 10^{-4}$M cobalt, nickel and zinc interfere in the cyanate solutions.

Murray and McNeely\cite{43} determined silver/mercury mixtures polarographically by employing the principle of electrochemical masking, with a metal complex adsorbed on the dropping mercury electrode. The analysis solutions were 0.01M in $\text{HClO}_4$ and contained M $\text{NaBr}$ electrolyte and mM $\text{Pb(II)}$ in addition to the $\text{Ag/Hg}$ mixture. The analysis was carried out at $-0.27$V versus SCE, and the use of 5mM $\text{Pb(II)}$ permitted the determination of silver at $\text{Hg/Ag}$ ratios up to 75 with less than 1% interference from mercury.
Shetty and Subbaraman also employed the principle of electrochemical masking, the diffusion current of the silver step being measured at -0.7V versus SCE from a mixed electrolyte consisting of M KI, 0.2M sodium potassium tartrate and 0.2M KOH, and containing 0.1% camphor as the masking agent. Cu, Bi, Fe, Pb, Zn, Cd, Sn and Sb did not interfere since their steps were displaced to the desorption potential (-1.2V) of camphor. Gold and thorium did interfere.
Experimental Technique

The polarograph used in these preliminary experiments was a Tinsley MK/19, and the polarographic cell was a 15ml. cell (Figure 11). Current-voltage curves were recorded using a Servoscribe pen recorder.

Solutions were deaerated by bubbling oxygen free nitrogen for about fifteen minutes. The scan speed of the instrument was 0.2V/min. and the start potential was +0.4V (versus Hg pool anode).

Polarography of Silver in 0.1M Potassium Nitrate Aqueous Solutions

Owing to similar ion transport numbers and ion sizes, potassium chloride is frequently used as the supporting electrolyte in exploratory work in polarography. However, it was not considered advisable in this experiment and potassium nitrate was used instead to avoid any precipitation of silver chloride which might occur, if the amount of silver nitrate caused the solubility of the resultant silver chloride to be exceeded. The following solutions (0.1M in KNO₃) were studied:

(a) Containing no reducible species
(b) 3.0 x 10⁻⁴M in silver nitrate
(c) 2.0 x 10⁻⁴M in the complex Ag(Fy)₂NO₃

The recorded current-voltage curves for these solutions are shown in Figures 12, 13 and 14.

Results

(a) An increase in current was recorded at the commencement of sweep (4μA), a steady current was obtained at +0.3V. Discharge of the electrolyte occurred at -2.1V (Figure 12).

(b) A large increase in current (24μA) was recorded at the commencement of the scan, and a steady current reading was not obtained until 0V. Discharge of the electrolyte occurred at -2.25V (Figure 13).

(c) A large increase in current (12μA) was recorded at the commencement
Nitrogen

Capillary
(Dropping Mercury Electrode)

Platinum Contact

Mercury Anode

**FIGURE 11.**
Arrangement of Dropping Mercury Electrode and Electrolysis Cell with Mercury Pool Anode
Figure 12. Current-Voltage Curve of 0.1M Potassium Nitrate.

Figure 15. Current-Voltage Curve of Silver Nitrate \( (3 \times 10^{-4} \text{M}) \) in Potassium Nitrate (0.1M).
of scan, and a steady current reading was obtained at 0V (Figure 14).

**Discussion**

With the base electrolyte only, oxidation of mercury began at +0.3V. Solutions containing silver nitrate or the complex salt gave large current increases in the region +0.4V to 0V, this was probably due to the discharge of the silver ion. It was not possible to make quantitative measurements due to the lack of a base line on the polarograms. Hence it was concluded that the study of simple silver salts in aqueous media was not possible using the dropping mercury electrode.
Figure 14. Current-Voltage Curve (DME) of Silver Nitrate/Pyridine Complex (2 x 10^{-4} M) in Potassium Nitrate (0.1 M).
SECTION III

2. IN NON-AQUEOUS SOLUTIONS
Non-aqueous Media

In order to investigate the electrochemical characteristics of a compound by polarography, that compound must be soluble in the solvent to such an extent that the saturated solution has a concentration of about $10^{-3} \text{M}$ with respect to the compound. It has been a long established practice that if the solubility of the compound in water is not adequate, then aqueous-non aqueous mixtures have been used e.g. ethanol-water and methanol-water systems.

In recent years, however, the interest in non-aqueous solvents has increased considerably because certain solvents significantly increase the variety of electrochemical reactions that are possible. Also some non-aqueous solvents are much more effective solvents than water, especially for organic and organometallic compounds. The use of non-aqueous solvents extends the polarographic technique particularly where the solvent is aprotic, as this increases the voltage range of the electrochemical reductions well beyond that at which the discharge of hydrogen occurs. For example, it is possible to reduce the alkali and alkaline earth metals. Using the metal perchlorates, Broadhead and Elving\textsuperscript{45} found that Na(I), K(I), Rb(I) and Cs(I) are reversibly reduced at the dropping mercury electrode from pyridine solutions.

The most frequently used solvents are methanol and ethanol and their mixtures with water. Vleck\textsuperscript{46} succeeded in obtaining anodic waves for alkali metals in absolute alcohol thus providing a proof of the reversibility of alkali metals at the DME. In this medium, the amalgams of alkali metals are relatively stable so that oxidation-reduction waves for the system ion-amalgam of the alkali metal can be obtained. Since most organic materials are soluble in mixtures of ethanol (or methanol) with benzene and water, these solvents permit the polarographic investigation of these substances and their analytical determination\textsuperscript{47}. 
The possibility of polarographic analysis in acetic acid was first mentioned by MacGillavry in 1936. Ammonium acetate is a suitable electrolyte for this solvent and inorganic ions such as Ti\(^+\), Cd\(^{2+}\), Cu\(^{2+}\), U\(^{VI}\) and Pd\(^{II}\) have been investigated.

Valuable results have been obtained in liquid ammonia at -36\(^\circ\)C. The alkali metals are reduced reversibly and their half-wave potentials follow the sequence Li > Na > K > Rb > Cs. Many other inorganic ions have been studied in liquid ammonia, amongst these being the alkaline earth metals, Pb, Cd, Ni, Zn and Co. Since mercuric ions are reversibly reduced to mercury, the mercuric/mercury electrode functions reversibly.

Acetonitrile has proved to be a very useful solvent for the polarographic determination of inorganic ions. The energies of solvation of the cations and anions are smaller than in water and most cations are reduced at more positive potentials than in water, and well defined waves for calcium and magnesium ions can be obtained with tetraethylammonium perchlorate as the supporting electrolyte. Much information is available on the reduction of metal ions in papers published by Kolthoff and Coetzee. They divided inorganic ions into two groups. The first group includes cations with similar behaviour in acetonitrile and water whilst the behaviour of the second group of cations in acetonitrile differs considerably from that in water. In contrast to their behaviour in water, the second group of cations, are mostly reversibly reduced or at least approach reversible behaviour in acetonitrile. The following reactions take place reversibly:

- Ag\(^+/Ag\(^0\)
- Cu\(^+/Cu\(^0\)
- Mn\(^{II}/Mn\(^0\)
- Ni\(^{II}/Ni\(^0\)
- Eu\(^{III}/Eu\(^{II}\)
- Yb\(^{III}/Yb\(^{II}\)
- Sm\(^{III}/Sm\(^{II}\).

Other non-aqueous solvents that have been investigated for the polarographic reduction of metal ions are ethylenediamine, dimethylformamide, dimethylsulphoxide, dioxan, formamide, pyridine and
sulpholane. Initial polarographic investigations have been conducted on the solvent propylene carbonate.

The properties of many solvents for electrochemical studies are reviewed by Mann, and a comprehensive survey of metal ions in non-aqueous media by polarography is given in a text by Mann and Barnes.
Reduction of Silver in Non-Aqueous Media

Univalent silver is reduced in non-complexing aqueous solutions at potentials more positive than the potential at which mercury is oxidised. In nitriles, however, this is not the case, and a true silver wave corresponding to the reduction of univalent silver to the amalgam can be observed in MeCN, i-PrCN, EtCN, PhCH$_2$CN, CH$_2$=CHCN and other nitriles. In ethylenediamine Gutmann and Schober found that the reduction of univalent silver occurred at a potential comparable to those required to reduce the alkaline earth metals. Of the metals these workers studied, silver had the most negative reduction potential (-1.84V) though they considered that the wave was irreversible. The reduction potentials of magnesium and calcium in ethylenediamine were -1.80V and -1.74V respectively.

In the carboxylic acids ethanoic, propanoic, isobutyric and acrylic and also in acetone, the reduction wave of univalent silver was masked by the oxidation of mercury.

Polarographic data for silver in non-aqueous solvents are given in Table 2.

Polarography of Silver in Methanol Solutions

No mention could be found in the literature of the reduction of silver in alcohol solutions using the dropping mercury electrode and since the initial spectroscopic work with silver nitrate/pyridine mixtures was carried out in methanol, this solvent was chosen for the polarographic work.

Potassium nitrate has a low solubility in methanol. However, a solution of 2.0 x 10$^{-4}$M Ag(Py)$_2$NO$_3$ in methanol saturated with potassium nitrate gave a suitable current-voltage curve. The recorded current-voltage curve is shown in Figure 15. Basically the polarogram had the
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Supporting Electrolyte</th>
<th>Compound</th>
<th>Reference Electrode</th>
<th>Half-Wave Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>0.1M NaClO$_4$</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.32</td>
</tr>
<tr>
<td>Isobutyronitrile</td>
<td>0.05M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.49</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.42</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.54</td>
</tr>
<tr>
<td>Phenyl acetonitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.52</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.49</td>
</tr>
<tr>
<td>Propionitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.45</td>
</tr>
<tr>
<td>3-Methoxy-propionitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.38</td>
</tr>
<tr>
<td>3-Ethoxy-propionitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.38</td>
</tr>
<tr>
<td>3-Isoproxy-propionitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.39</td>
</tr>
<tr>
<td>3-Butenenitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.34</td>
</tr>
<tr>
<td>3-Chloropropionitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.40</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>0.1M NaNO$_3$</td>
<td>AgNO$_3$</td>
<td>NCE</td>
<td>-1.84</td>
</tr>
</tbody>
</table>

TEAP: Tetraethylammonium Perchlorate
NCE: Normal Calomel Electrode
Figure 15. Current-Voltage Curve(DME) of Silver Nitrate/Ethylenediamine Complex (2 x 10^-4 M) in Methanol, saturated with Potassium Nitrate.
same characteristics as that of an aqueous solution, hence it was con­
cluded that the reduction wave for silver was again masked by the oxid­
ation of mercury.

Addition of concentrated hydrochloric acid solution to a methanolic solution containing the complex did not give a precipitate of silver chloride. A precipitate of silver chloride was obtained with dilute hydrochloric acid solution. Addition of the complex to saturated sol­utions of potassium chloride and lithium chloride also produce no precipitate. It was concluded that the solubility of the complex was dependent on the chloride ion concentration.

**Polarography of Silver in Methanol (0.7M in LiCl)**

The addition of 5mg of the complex in a little methanol to 25ml of methanol (0.1M in LiCl) produced a mauve coloured precipitate, which gradually redissolved on the addition of solid lithium chloride.

Further quantitative experiments showed that 2mg of the complex (3.0 x 10^{-4}M) in methanol required 0.6g LiCl (0.7M) to clear the solution. Since the silver probably existed in the solution as some complexed species, there was the possibility that the reduction wave of this species had been moved to a more negative value and did not merge with the oxidation wave of mercury. For this polarographic work, the reference electrode was a sintered glass saturated calomel electrode directly immersed in the cell solution.

**Results**

Figure 16 shows a current-voltage curve of methanol (0.7M in LiCl) and Figure 17 that of the same solution but with 2mg of the complex added. Both show a steeply rising portion from +0.5V to 0V with discharge of the supporting electrolyte at -2.0V. There was no detectable difference between the polarograms. Vloeck\textsuperscript{62} reported that a high chloride ion
Figure 16. Current-Voltage Curve (DME) of Lithium Chloride (0.7M) in Methanol.

![Current-Voltage Curve (DME) of Lithium Chloride (0.7M) in Methanol.](image)

Figure 17. Current-Voltage Curve (DME) of Silver Nitrate/Pyridine Complex (2 x 10^{-4} M) in Methanol (0.7M in Lithium Chloride).

![Current-Voltage Curve (DME) of Silver Nitrate/Pyridine Complex (2 x 10^{-4} M) in Methanol (0.7M in Lithium Chloride.).](image)
concentration produces inexplicable effects on a mercury electrode.

Discussion

Investigation of the complex in methanol, with potassium nitrate and lithium chloride as the supporting electrolytes, did not produce a silver wave using the dropping mercury electrode. As in aqueous solutions, therefore, it was concluded that silver is reduced at potentials more positive than that at which mercury oxidises.
SECTION IV

POLAROGRAPHIC AND KINETIC STUDIES OF SILVER FROM AQUEOUS SOLUTIONS UTILISING SOLID ELECTRODES

1. INTRODUCTION
Since the anodic dissolution of mercury masks the reduction wave of silver in aqueous solutions, the DME cannot be used.

Solid electrodes do not yield results with the same degree of reproducibility as the DME, since the electrochemical processes are not constantly occurring at a fresh surface and will probably be affected by the preceding polarisation. Very often, a different pretreatment is required for each type of electrode. The obvious difficulties which are encountered with solid electrodes are the formation of reduction products and the adsorption of gases on the electrode surface.

Platinum is the most frequently used solid electrode material and its chief advantage is the possibility of reaching positive potentials as high as +1.0 to +1.5V versus the SCE, depending on the pH of the solution. Because of its noble character, gold is sometimes used as an electrode material. New types of electrode material include boron carbide, glassy carbon and carbon paste.

Various mechanical techniques have been introduced to improve the reproducibility and to increase the sensitivity of solid electrode systems. Although they can be used as stationary electrodes, the more successful electrode systems include the following:

1. Rotating platinum wire electrode
2. Vibrating platinum wire electrode
3. Rotating platinum disc electrode
4. Platinum ring-disc electrode

Details of these electrode systems and their limitations are to be found in a text by Adams. Many solid electrode systems have been used in industry in the determination of silver and the following examples will serve to illustrate the applicability of such systems.

Lyalikov et al. determined silver in solid electrodes by A.C. polarography using gold and platinum electrodes. The peak potentials
versus SCE in molar solutions of electrolytes were as follows:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>HNO₃</th>
<th>NaNO₃</th>
<th>S₂O₃²⁻</th>
<th>NH₄OH</th>
<th>OAc⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Potential</td>
<td>+0.02V</td>
<td>+0.08V</td>
<td>-0.22V</td>
<td>-0.26V</td>
<td>-0.02V</td>
</tr>
</tbody>
</table>

They found the reproducibility of results to be better in ordinary than in complex forming electrolytes and the use of a rotating disc electrode increased the sensitivity of the silver determination by a factor of three to four, with an error of ±2.5%. Lead, indium and gallium in fifty fold excess did not interfere with the analysis.

Employing a rotating platinum wire electrode (600 rpm.) in 0.01M KNO₃ plus small amounts of gelatin, Kilthoff and Lingane³⁸ found that the diffusion current was proportional to concentration for 6 x 10⁻⁵ to 4 x 10⁻⁴M AgNO₃. The silver coating adhered well and had a fine crystalline structure. The diffusion current was not independent of KNO₃ concentration and they suggested that the nature of the plated silver varied, and this directly altered the effective electrode area.

Vrtilkove and Kalvoda used a vibrating platinum electrode and determined 10⁻⁸ to 10⁻²M silver in 10M HNO₃, even in the presence of excessive amounts of iron, copper, lead and zinc.

Rybakov et al. investigated the current-voltage curves for silver in ammonium hydroxide and alkaline glycerol solutions with a rotating platinum microelectrode. The waves were well developed and could be used for the qualitative and quantitative determination of silver.

Tindall et al.⁶⁹ simultaneously determined copper and silver by stripping analysis in 0.2M H₂SO₄ supporting electrolyte using the rotating platinum ring-disc electrode. The rate of increase of voltage was 2V/min. They found reproducibility to be within 5% in 10⁻⁵M solutions and within 10-15% in 10⁻⁸M solutions.
By rapid anodic polarography with a stationary platinum micro-electrode, Nucci et al. determined small concentrations of silver in HNO₃ and 2,2'-bipyridine solutions. The oxidation of Ag to Ag displayed a well defined anodic wave, the half-wave potential being +1.180V versus SCE. The diffusion current was proportional to silver concentration down to $10^{-5}$M and Cu, Mn, Cd, Co, and Hg did not interfere.

The determination of silver by anodic stripping voltammetry has been carried out at gold and platinum electrodes and at graphite electrodes. Employing a rapid differential polarographic titration technique, Nakashima et al. determined silver in copper alloys using a glassy carbon electrode.

Kolpakova et al. jointly determined nanogram amounts of silver and mercury in high purity lead alloys by an extraction-polarographic method. The analysis of silver and mercury was carried out by stripping voltammetry with a rotating graphite electrode (200 rpm).

The first paper dealing with polarography at solid electrodes in melts was published by Delimarskii in 1948 and many papers in melts since then have been published by Russian authors. Melts have a satisfactory conductivity and the current-voltage curves are not influenced by the IR drop in the solution as in non-aqueous solvents. The reduction of Ag was studied by Gaur et al. in molten MgCl₂-KCl as solvent at 475°C, using platinum and tungsten wires as polarographic cathodes and a reference electrode of 0.01M Pt²⁺/Pt in the solvent.

I. I. Naryshkin et. al. studied the oscillographic voltammetry of AgCl in fused NaCl/KCl mixture using a platinum anode and Ag/AgCl reference electrode and found the reduction of silver to be reversible.
On a theoretical note, Bachmann et al. verified a theoretical current-voltage curve for the reversible deposition of an insoluble substance, derived by Berzins and Delahay in 1953, by linear voltage sweep polarography of silver ions at a stationary polycrystalline silver electrode in M HClO₄ supporting electrolyte. Using a silver coated platinum reference electrode, they found the diffusion constant to be the same as with direct current polarography at a dropping mercury electrode.

Electrodes are now commercially available that permit voltammetry in the anodic region where dropping mercury electrodes cannot be used. One such electrode is the glassy carbon electrode and the manufacturers claim that the electrode can be used repeatedly without interruption and that consecutive current-voltage curves show excellent repeatability. In an electrolyte of M HNO₃, the peak potential for silver is quoted as +0.27V versus SCE. Ion-selective electrodes have also been designed to determine directly the concentration of ions in aqueous and non-aqueous media. A silver-selective electrode has a quoted range of 1 to 10⁻⁷M with respect to silver ions.

In this work it was necessary to find a suitable electrode system for the quantitative determination of silver in aqueous solutions and then to ascertain its applicability to non-aqueous solvents. One method was the voltammetric analysis of aqueous solutions containing silver nitrate and sulphosalicylic acid using a silver cathode and a molybdenum anode. It had been reported that a molybdenum wire electrode, which had been used as a reference electrode under diverse experimental conditions, is primarily a pH electrode, but while the pH remains constant, it functions as a reference electrode in potentiometry.
SECTION IV

2. POLAROGRAPHY OF SILVER SOLUTIONS (0.1M IN SULPHERSALICYCIC ACID)

USING SILVER AND MOLYBDENUM ELECTRODES
Current-voltage curves were obtained using a Heathkit D.C. Polarograph on solutions maintained at 20°C. A diagram of the cell is shown in Figure 18.

**Electrodes**

The electrodes were made from silver and molybdenum wires (respective diameters 0.71 and 1.05 mm).

The silver wire was sealed in an epoxy rod (Araldite, C.I.B.A. Ltd.) leaving 2 mm exposed. The metal was cleaned with 4 M nitric acid for one minute and then washed with distilled water.

The molybdenum wire was cleaned by abrasion with fine emery paper and then washed with distilled water. A 20 mm length of molybdenum wire was immersed in each experiment.

**Reagents**

(a) Analar Silver Nitrate (B.D.H.)

(b) Sulphosalicylic Acid (B.D.H.)

(c) The prepared complex Ag(Py)$_2$NO$_3$ (see Section II)

**Procedure**

Since the original experiments were performed using a Southern Differential Cathode Ray Polarograph (DCRP), it was probable that a fairly high scan speed was adopted. Therefore, a rate of increase of voltage of $2\text{Vmin}^{-1}$ was chosen.

Further experiments were also conducted on equal aliquots of the same solution, and the current was noted at each value of the applied potential, about three minutes being required for the current to reach a steady value. In order to cause the minimum of disturbance of the diffusion layer near the electrode, the applied potential was slowly increased.
Figure 18. Polarographic Cell incorporating Solid Electrodes (Silver Wire Cathode and Molybdenum Anode).
Results and Discussion

(a) Figure 19 shows the typical current-voltage curve obtained using a silver cathode and molybdenum anode in 0.1M sulphosalicylic acid solution after deaeration with nitrogen for fifteen minutes. The voltage is expressed with respect to the molybdenum electrode, hydrogen ions being discharged at about -0.65V. The cell current at 0.0V was negligible.

(b) Addition of silver nitrate (10^{-3} M) resulted in a discharge of silver ions at about +0.2V (Figure 20), but there was no indication of a peaked wave in the region -0.55V as reported by previous workers.

(c) Manual recordings of the current-voltage readings showed that the diffusion current was proportional to the silver ion concentration over the range 0.25mM to 2.0mM. These results are shown in Figures 21 and 22. Similar results were obtained by Kolthoff and Lingane using potassium nitrate as the electrolyte and a stationary platinum micro-electrode (Figure 23).
Figure 19. Current-Voltage Curve of Sulphosalicylic Acid (0.1M) with Silver Cathode and Molybdenum Anode.

![Graph of Current-Voltage Curve with Silver Cathode and Molybdenum Anode.](image)

Figure 20. Current-Voltage Curve of Silver Nitrate (10^{-3} M) in Sulphosalicylic Acid (0.1M).

![Graph of Current-Voltage Curve with Silver Nitrate and Molybdenum Anode.](image)
Sulphosalicylic Acid (0.1M) at a Stationary Silver Electrode.

Figure 22. Diffusion Current/Silver Concentration Plot - Diffusion Current Recorded at +0.05V versus Molybdenum Electrode.
Figure 23. Typical Current-Voltage Curve of an Aqueous Solution of Silver Ions ($10^{-3} M$) obtained with a Stationary Platinum Microelectrode.

Kolthoff and Lingane
SECTION IV

3. **TIME DEPENDENT EFFECTS WITH MOLYBDENUM ELECTRODES**
On leaving the silver and molybdenum electrodes immersed in the solution of 0.1M sulphosalicylic acid containing $10^{-3}$M silver, it was observed that a reduction wave appeared in the region of -0.55V after about four minutes. This reduction current increased with time as can be seen in Figure 24. Transfer of the electrodes to a fresh solution produced a 'normal' current-voltage curve again. Figure 25 shows the effect of maintaining the cell potential at -0.53V and observing the current increase with time.

After immersion in the silver solution for half an hour, a white coating was visible on the molybdenum electrode. If left for two or three days, a white crystal growth was observed on the same electrode. Electron probe micro-analysis showed the presence of silver on the molybdenum electrode surface.

Experiments were then conducted to determine what conditions were necessary for this time-dependent effect to occur. In 0.1M potassium nitrate solution black particles gradually appeared clinging to the molybdenum electrode, but on the addition of sufficient nitric acid to make the acidity the same as that of 0.1M sulphosalicylic acid (pH = 1.3) solution, the molybdenum wire gradually took on a 'bronze' appearance. Replacement of the molybdenum wire by another silver wire did not produce the time-dependent effect, neither did the absence of silver from the solution. From these experiments the conditions necessary for the time-dependent effect were:

(a) The presence of molybdenum metal in an aqueous solution containing silver ions.

(b) pH<7 for a grey-white deposit on the molybdenum wire.

(c) pH>7 for a black deposit on the molybdenum wire.
Figure 24. Salicylic Acid (0.1M) - Periodic Scans - Cell at OV between Runs.

I - After 0 min.
II - After 4 min.
III - After 25 min.

Figure 25. Silver Nitrate \(10^{-3} \text{M}\) in Sulphosalicylic Acid (0.1M) -
Increase in cell current whilst potential held at -0.55V
versus Molybdenum Electrode.
The Presence of Molybdenum in Solution

It was found that using a solution of $10^{-2}\text{M}$ silver nitrate in $10^{-1}\text{M}$ sulphosalicylic acid in the presence of molybdenum wire, the solution slowly turned yellow.

A standard qualitative test using phenyl aniline in glacial acetic acid produced a red colouration which confirmed the presence of molybdenum in the solution.

$10^{-3}\text{M}$ ammonium molybdate in $10^{-1}\text{M}$ sulphosalicylic acid also gave a yellow solution.

Spectroscopic analysis of both solutions gave a $\lambda_{\text{max}}$ at 343nm (Figures 26 and 27).

The current-voltage curve of $10^{-4}\text{M}$ ammonium molybdate in $10^{-1}\text{M}$ sulphosalicylic acid solution using a silver cathode and molybdenum anode showed the same characteristic wave in the region of $-0.55\text{V}$ with the same time-dependent effect shown by the original silver nitrate solution.

Solutions of varying concentrations of ammonium molybdate in $10^{-1}\text{M}$ sulphosalicylic acid were studied, using a silver cathode and a molybdenum anode. The results are given in Table 3 and a plot of diffusion current versus ammonium molybdate concentration is shown in Figure 28.
Figure 28. Ultra-Violet Spectrum of Solution of Silver Nitrate\( (5 \times 10^{-3} M) \) in Sulphosalicylic Acid\( (0.1M) \) after being in Contact with Molybdenum Metal for 12 Hours.

Figure 27. Ultra-Violet Spectrum of Ammonium Molybdate\( (4 \times 10^{-5} M) \) in Sulphosalicylic Acid\( (0.1M) \).
TABLE 3

Polarographic Results of Ammonium Molybdate Solutions in Sulphosalicylic Acid (0.1M) between Silver and Molybdenum Electrodes at 20°C.

<table>
<thead>
<tr>
<th>Ammonium Molybdate Conc. (moles/l)</th>
<th>Half-Wave Potential versus Mo Electrode</th>
<th>Diffusion Current (μA)</th>
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</thead>
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<tr>
<td>$10^{-4}$</td>
<td>-0.56</td>
<td>5.2</td>
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<td>$5 	imes 10^{-5}$</td>
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<td>-0.49</td>
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<td>$2.5 	imes 10^{-6}$</td>
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<tr>
<td>$10^{-6}$</td>
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</tr>
<tr>
<td>$5 	imes 10^{-7}$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 28. Plot of Diffusion Current versus Ammonium Molybdate Concentration (Values from Table 3 above).

![Plot of Diffusion Current versus Ammonium Molybdate Concentration](image-url)
Electrochemical Displacement Experiments

Results so far indicate the possibility of electrolytic displacement between molybdenum metal and aqueous silver. To investigate the nature of the deposit on the molybdenum wire, the following solutions were prepared and left in contact with the cleaned molybdenum wire as shown in Figure 29:

(a) $10^{-2} \text{M}$ Silver nitrate in $10^{-1} \text{M}$ sulphosalicylic acid.
(b) $10^{-2} \text{M}$ Silver nitrate in $10^{-1} \text{M}$ nitric acid.

Results

(a) With this concentration of silver nitrate, a white coating was visible on the molybdenum wire after five minutes.

On standing overnight, the solution had turned yellow and an off-white deposit was observed on the wire. The coating strongly adhered to the wire, but when carefully scraped off, revealed a shiny black surface underneath. X-ray crystallography showed that the off-white deposit was silver and the black under layer was molybdenum.

In a duplicate experiment, the colour of the solution remained yellow for ten weeks and then gradually changed through green to a very dark greenish-blue.

(b) Within one minute dendritic grey crystals were observed on the molybdenum wire.

On standing overnight a tree-like growth appeared. In Figure 30, a series of photographs shows the exchange reaction taking place between silver ions and molybdenum metal at given time intervals. In this latter experiment the silver concentration was increased to $10^{-1} \text{M}$.

Over a period of ten weeks the solution changed colour as follows:-- colourless, blue, colourless, blue, yellow-brown, dark blue, yellow-brown.

X-Ray Crystallography showed the tree-like crystals to be silver metal.
Figure 29. Diagram of Cell for Electrochemical Displacement Experiments.
Figure 30  Exchange Reaction between Silver Ions (10^{-1} \text{M} \text{AgNO}_3) and Molybdenum Metal in Nitric Acid (10^{-1} \text{M})
SECTION IV

4. SPECTROSCOPIC DETERMINATION OF EXCHANGE KINETICS BETWEEN SILVER AND MOLYBDENUM
Introduction

When molybdenum wire is immersed in a solution of silver nitrate in $10^{-1}\text{M}$ sulphosalicylic acid, electrolytic displacement between the silver ions and metallic molybdenum occurs. Further evidence that the molybdenum goes into solution is obtained from the spectrophotometric analysis of the resulting yellow solution. $\lambda_{\text{max}}$ occurs at 343nm, and the following experiment was performed to follow the dissolution of molybdenum into the solution.

Experimental

(a) Cell. A two compartment cell was used. Side and plan views of the cell are shown in Figure 31.

The smaller of the two compartments contained a length of molybdenum wire in a diagonal position and nitrogen gas was bubbled through the solution in this compartment using Teflon tubing, thus keeping the whole solution deaerated and circulating.

No bubbles of gas were allowed in the large compartment, through which the light beam passed. Though smaller than the normal cell (6mm instead of 10mm) the larger cell compartment did not appear to affect the passage of the light beam. The reference cell was a standard 10mm silica cell containing a solution of $10^{-1}\text{M}$ sulphosalicylic acid.

(b) Apparatus. A Pye Unicam SP 800B Spectrometer was used, the cell compartments were thermostatted at $17{}^\circ\text{C} \pm 0.1{}^\circ\text{C}$.

(c) Procedure. Using an automatic scan the change in absorbance at 343nm was continuously monitored. Solutions of varying silver concentrations were investigated, as was the effect of varying the length of the molybdenum wire.
Figure 31. Two Compartment Cell for Exchange Kinetics Experiment

- **Nitrogen Entrance**
- **Nitrogen Exit**
- **Dividing Wall**
- **Direction of Flow of Solution**
- **Molybdenum Wire**

**Side View**

**Plan View**

**Light Beam**
Results

(a) Molybdenum wire 0.31g in weight. Silver nitrate solutions
(2.5, 5.0, 7.5 and 10.0mM) in 10⁻¹M sulphasalicylic acid

The absorbance-time changes for the above four solutions are shown in Figure 32. The absorbance increased with time. The maximum absorbance obtained was dependent upon the silver concentration.

For a reaction of the first order, the rate of the reaction is given by

\[
\frac{dx}{dt} = k(a-x) \quad (1)
\]

\(k = \) the rate constant
\(a = \) the initial concentration
\(x = \) the concentration at time \(t\)

Integration of expression (1) above produces the equation

\[
t = \frac{2.303 \log \frac{a}{(a-x)}}{k} \quad (2)
\]

A plot of log \((a-x)\) versus time should give a straight line, since \(a\) and \(k\) are constant at constant temperature. \(a\) and \(x\) can be replaced by \(A_\infty\) and \(A_t\) respectively, where \(A_\infty = \) absorbance at \(t = \infty\) and \(A_t = \) absorbance at \(t = t\), so

\[
t = \frac{2.303 \log \frac{A_\infty}{(A_\infty - A_t)}}{k} \quad (3)
\]

Values of log \((A_\infty - A_t)\) and \(t\) are given in Tables 4 and 5, and the plots of log \((A_\infty - A_t)\) against time are shown in Figures 33 and 34. Good linearity was observed showing that the exchange was a first order reaction with respect to the silver ion concentration.

(b) Determination of the specific rate constant

From (3) above, a plot of \(t\) versus log \((A_\infty - A_t)\) will give a line of gradient \(-\frac{2.303}{k}\).
Figure 32. Absorbance/Time Plots for Solutions of Silver Nitrate in Sulphosalicylic Acid (0.1M) in Contact with Molybdenum Wire of Surface Area 0.85cm²

1. AgNO₃(10⁻²M)
2. AgNO₃(7.5 x 10⁻³M)
3. AgNO₃(5.0 x 10⁻³M)
4. AgNO₃(2.5 x 10⁻³M)

Absorbance

Time in mins.
Table 4. Absorbance-Time Values for Molybdenum Electrode of Area

\( \omega = 1.49 \) \quad \quad \quad \quad \quad \quad \quad 10^{-2} M AgNO \_3

<table>
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<th>T (min)</th>
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<th>( 100(\omega - A_t) )</th>
<th>( \log 100(\omega - A_t) )</th>
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\( \omega = 1.21 \) \quad \quad \quad \quad \quad \quad \quad 7.5 \times 10^{-3} M AgNO \_3

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$A_\infty = 0.86$  \hspace{1cm} $\text{AgNO}_3 = 5 \times 10^{-3} \text{M}$

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$A_\infty = 0.48$  \hspace{1cm} $\text{AgNO}_3 = 2.5 \times 10^{-3} \text{M}$
Figure 33. Plots of $\log 100(A_0 - A_t)$ versus Time for Different Concentrations of Silver Nitrate

Silver Nitrate ($10^{-2}$M)

Silver Nitrate ($7.5 \times 10^{-3}$M)
Figure 54. Plots of \( \log 100(A_\infty - A_t) \) versus Time for Different Concentrations of Silver Nitrate

1. Silver Nitrate \( (5 \times 10^{-3} \text{M}) \)

2. Silver Nitrate \( (2.5 \times 10^{-3} \text{M}) \)
so \( k = -2.303 \frac{\text{gradient}}{} \)

From Figure 33, with a molybdenum electrode of area 0.85cm\(^2\), the specific rate constant was 8.7 x 10\(^{-4}\) sec\(^{-1}\).

(c) Effect of variation of the surface area of the molybdenum electrode. Silver nitrate solution (7.5 x 10\(^{-3}\) M) in 10\(^{-1}\) M sulphosalicylic acid. Molybdenum electrodes of areas 0.46 and 0.31cm\(^2\).

The absorbance-time changes using molybdenum electrodes of different surface areas are given in Figure 35. Values of log \((A_\infty - A_t)\) and \(t\) are given in Table 6, and the plots of log \((A_\infty - A_t)\) against time are shown in Figure 36. Good linearity was again observed showing that the exchange was a first order reaction with respect to the silver ion concentration.

Values for the specific rate constants are given in Table 7, and a plot of rate constant versus electrode area is shown in Figure 37.

The rate constant was directly proportional to the area of the molybdenum electrode.
Figure 35. Absorbance/Time Plots for Solutions of Silver Nitrate ($7.5 \times 10^{-3} \text{M}$) in Sulphosalicylic Acid (0.1M) in Contact with Molybdenum Wires of Areas 0.46(I) and 0.31cm$^2$(II) respectively.
Table 6. Absorbance-Time Values for Molybdenum Electrodes in Contact with $10^{-1}$ M Sulphosalicylic acid, $7.5 \times 10^{-3}$ M in AgNO$_3$

$A\infty = 1.12$

Area of molybdenum electrode = 0.46 cm$^2$

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<td>0.78</td>
</tr>
</tbody>
</table>

$A\infty = 1.08$

Area of molybdenum electrode = 0.31 cm$^2$

<table>
<thead>
<tr>
<th>T(min)</th>
<th>$A_t$</th>
<th>$A\infty - A_t$</th>
<th>100($A\infty - A_t$)</th>
<th>log 100($A\infty - A_t$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1.08</td>
<td>108</td>
<td>2.03</td>
</tr>
<tr>
<td>10</td>
<td>0.36</td>
<td>0.72</td>
<td>72</td>
<td>1.86</td>
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<td>20</td>
<td>0.59</td>
<td>0.49</td>
<td>49</td>
<td>1.69</td>
</tr>
<tr>
<td>30</td>
<td>0.75</td>
<td>0.33</td>
<td>33</td>
<td>1.52</td>
</tr>
<tr>
<td>40</td>
<td>0.86</td>
<td>0.22</td>
<td>22</td>
<td>1.34</td>
</tr>
<tr>
<td>50</td>
<td>0.93</td>
<td>0.15</td>
<td>15</td>
<td>1.17</td>
</tr>
<tr>
<td>60</td>
<td>0.98</td>
<td>0.10</td>
<td>10</td>
<td>1.00</td>
</tr>
<tr>
<td>70</td>
<td>1.015</td>
<td>0.065</td>
<td>6.5</td>
<td>0.81</td>
</tr>
</tbody>
</table>
Figure 36. Plots of log \(100(A_\infty - A_t)/A_\infty\) versus time for molybdenum wire in varying surface area in silver nitrate solutions (7.5 x 10^{-3} M).

Surface Area of Molybdenum
Wire is 0.51 cm^2

Surface Area of Molybdenum
Wire is 0.46 cm^2
Change of Rate Constant with Surface Area of Molybdenum Wire

<table>
<thead>
<tr>
<th>Rate Constant at 17°C in sec⁻¹</th>
<th>Surface Area of Molybdenum Wire in cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.7 \times 10^{-4}$</td>
<td>0.85</td>
</tr>
<tr>
<td>$4.8 \times 10^{-4}$</td>
<td>0.46</td>
</tr>
<tr>
<td>$3.2 \times 10^{-4}$</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Figure 57. Plot of Rate Constant versus Surface Area of Molybdenum Wire at 17°C.
SECTION IV

5. DISCUSSION AND SUMMARY
Discussion of Results

It is concluded that the wave at about -0.55V previously reported by Athavale et al. to be due to the reduction of silver ions, is in fact due to complex molybdenum ions produced by a first order exchange reaction at the molybdenum electrode. It is likely that the results obtained by the previous workers were misinterpreted by a chance correlation between the height of the wave and the silver ion concentration due to the higher detection level of the current-voltage curve made possible by the Differential Cathode Ray Polarograph. As the limit of detection of the DCRP is very low, the small amount of molybdenum displaced in the relatively short time interval between setting up the cell and recording the current-voltage curves, gave sufficient molybdenum to be detected. Since this molybdenum is a function of the silver ion concentration, it is suggested that if the time interval is reasonably constant, an apparent fortuitous linear relationship would appear to exist between the molybdenum and the added silver.

The experiment was repeated using a DCRP and the wave at about -0.55V was first noticeable within two minutes of the molybdenum being immersed in the silver (10^-3M) solution. A point of inflection was observed on the steeply rising portion of the wave and a derivative sweep confirmed the presence of two waves whose half-wave potentials were -0.52V and -0.63V respectively. The presence of molybdenum in the solution was confirmed by atomic absorption spectrometry. The deposit on the molybdenum electrode was dissolved in nitric acid and confirmed by atomic absorption spectrometry to be silver.

Using a dropping mercury cathode and a molybdenum anode (1mm diameter coiled wire) in 0.25M sulphuric acid, recent workers have also shown that depolarisers with a more negative potential than molybdenum, e.g. Ag, Fe(III), Hg(II), Au and Pt, oxidise Mo to Mo(V) in 25-30 minutes. The reaction between molybdenum and aqueous silver may be represented by
the following equation:

\[ \text{Mo} + 5\text{AgNO}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{MoO}_4 + 5\text{Ag} + 5\text{HNO}_3 \]

A solution of molybdenum in sulphosalicylic acid, however, is yellow. Cotton and Wilkinson mention that the dihydrate of molybdenum (VI) oxide, \( \text{Mo}_3 \cdot 2\text{H}_2\text{O} \), is deposited as a yellow crystalline precipitate when ammonium molybdate solutions containing nitric acid stand for long periods of time. There is the possibility that the yellow solution contained the hydrated molybdenum (VI) oxide.

The wave at about \(-0.55\text{V}\) is due to complex molybdenum ions and could be used for the determination of molybdenum, for example, \(5 \times 10^{-6}\text{M}\) ammonium molybdate in \(10^{-1}\text{M}\) sulphotosalicylic acid produces a significant wave.
SECTION V

POLAROGRAPHIC STUDIES OF SILVER IN NON-AQUEOUS MEDIA UTILISING SOLID ELECTRODES

1. INTRODUCTION
Introduction

In section III it was stated that waves corresponding to the reduction of silver (I) to the amalgam had been reported in aliphatic and aromatic nitriles and also in ethylenediamine when using the dropping mercury electrode. In carboxylic acids and acetone, however, the anodic dissolution of mercury masks the reduction of the silver ion. It was thus necessary for an electrode system without mercury to be used. According to the literature, the indicating electrode used with considerable success was the rotating platinum electrode and polarographic data for the reduction of silver in non-aqueous media are given in Table 8.

Electrochemical oxidation of silver (I) has also been reported by several workers. Barbieri produced $\text{Ag(C}_5\text{H}_5\text{N)}_4(\text{NO}_3)_2$ by electrolysing $\text{AgNO}_3$ in 40% pyridine. Noyes et al. noticed the formation of a brown colour on the oxidation of $\text{AgNO}_3$ at a platinum electrode in 8M $\text{HNO}_3$. They attributed this to the production of silver (II). Schmidt and Stange oxidised silver nitrate in acetonitrile and produced a brown solution/deposit which they attributed to the reaction between Ag(II) and $\text{N}_2\text{O}_5$. The $\text{N}_2\text{O}_5$ was thought to be the product of the oxidation of the nitrate or nitrate ion. The exact mechanism of the oxidation of the silver was not completely determined, it could occur directly at the electrode surface or by reacting with the $\text{N}_2\text{O}_5$ produced.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Supporting Electrolyte</th>
<th>Compound</th>
<th>Reference Electrode</th>
<th>Half-Wave Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>1M LiClO$_4$</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.635</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>1M LiClO$_4$</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.625</td>
</tr>
<tr>
<td>Isobutyric acid</td>
<td>1M LiClO$_4$</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.705</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>1M LiClO$_4$</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.530</td>
</tr>
<tr>
<td>Sulpholane</td>
<td>0.1M NaClO$_4$</td>
<td>AgClO$_4$</td>
<td>Ag/AgCl/TEAC(s)</td>
<td>+0.99</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.30</td>
</tr>
<tr>
<td>Propionitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.27</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>0.1M TEAP</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.36</td>
</tr>
<tr>
<td>Allyl alcohol</td>
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<td>AgClO$_4$</td>
<td>SCE</td>
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</tr>
<tr>
<td>Methanol</td>
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<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.49</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.1M LiClO$_4$</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.50</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>0.1M LiClO$_4$</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.50</td>
</tr>
<tr>
<td>Water</td>
<td>0.1M LiClO$_4$</td>
<td>AgClO$_4$</td>
<td>SCE</td>
<td>+0.49</td>
</tr>
</tbody>
</table>
SECTION V

2. MATERIALS, EXPERIMENTAL TECHNIQUE AND APPARATUS
Solvents

As mentioned in the introduction, interest in plating solutions with a wider range of useful temperatures than is available in aqueous solutions has led to the work in non-aqueous media, in particular pyridine, propylene carbonate and NN-dimethylformamide. As a non-aqueous solvent for electrochemical studies, NN-dimethylformamide has been used extensively and much literature is available. With exception of the oxidation of silver (I) to silver (II) in 40% pyridine solution, no polarographic data was available on the reduction of silver in these solvents. In considering non-aqueous solvents for electrochemical studies, the following physical properties are usually important:

(a) Liquid range
(b) Dielectric constant for electrolytic conductivity
(c) Toxicity of solvent

N,N-Dimethylformamide

This solvent, with a dielectric constant of 37 (cf water 80) is a good solvent for a wide range of polar and non-polar organic compounds, dissolving many inorganic perchlorates, especially of the alkalies and alkaline earths. N,N-Dimethylformamide has been of special interest in polarographic work because it is possible to measure half-wave potentials for a number of active metals which cannot be examined in water due to reaction and because the behaviour of the dropping mercury electrode in DMF is better at negative potentials than it is in water. It has a convenient liquid range (-61°C to +93°C). It is highly irritating to the eyes and skin.

DMF is very resistant to reduction, but is much easier to oxidise, various workers reporting that silver (I) is gradually reduced to the metal by this solvent. Since it is difficult to produce high-purity DMF, it was decided not to attempt purification of the B.D.H. reagent
until its behaviour towards silver (I) had been investigated.

**Propylene Carbonate**

Propylene carbonate, 4- methylidioxolone, $C_6H_5O_3$, CH$_2$ - CH - CH$_3$

has a high dielectric constant (69) and a convenient solvent range (-49°C to +242°C). It is an effective solvent for a wide range of organic and inorganic compounds. It is also miscible with most common organic solvents, is nontoxic, noncorrosive and chemically stable. McComsey and Spritzer reported several experiments and found no solvent deterioration even when exposed to the air for a period of eight weeks. It is a versatile solvent for electrochemical studies.

Propylene carbonate as supplied was coloured pale yellow and was purified by double vacuum distillation with a column temperature of 86°C, collecting the middle 80% fraction each time. The pure colourless solvent was stored over Molecular Sieve (Linde 4A) under an atmosphere of nitrogen.

Nelson and Adams have reported both electrochemical and electron spin resonance studies in propylene carbonate, but little polarographic work is reported in the literature. A preliminary investigation of this solvent for polarography by McComsey and Spritzer covered a variety of reference electrodes and working electrodes.

A final factor favouring propylene carbonate as a solvent for electrochemical studies is its high viscosity (2.53 cp. at 25°C). For voltammetry, mass transfer by diffusion is more easily maintained in a viscous medium.

**Pyridine**

Pyridine, $C_5H_5N$, is a complex-forming strong-base (pK = 8.8 at 25°C) which is capable of forming Lewis acid-base adducts with metallic ions. Many salts are soluble and the resulting solutions show quite low specific
resistances. Despite its rather low dielectric constant (13.24 at 20°C), it is a versatile solvent. It has a liquid range from -41°C to +115°C and its viscosity is similar to that of water.

Though the purification of pyridine has already been described in this thesis, reagent grade pyridine has been found to be suitable for electro-chemical studies, after the removal of water by shaking with Molecular Sieve (Linde 4A). Silver has been electrodeposited from pyridine.

Supporting Electrolyte

Tetraalkylammonium perchlorates are suitable as supporting electrolytes in most non-aqueous solvents and since only tetraethylammonium perchlorate (TEAP) has been mentioned as a supporting electrolyte in propylene carbonate, TEAP was chosen as the base electrolyte. It was also readily soluble in pyridine and N,N-dimethylformamide (DMF). The perchlorate ion does not appear to be electrochemically reduced in any of the common solvents over the useful range using platinum or mercury electrodes.

Tetraethylammonium perchlorate was prepared from tetraethylammonium iodide and sodium perchlorate. The crude product was recrystallised from water. In order to remove all iodide ions from the product, the recrystallisation process was repeated six times. The TEAP was dried in an oven at 80°C and kept in a vacuum desiccator over silica gel.

Silver Perchlorate

Silver perchlorate, a water soluble salt, has been used in non-aqueous media. Preliminary investigations showed the salt to be sufficiently soluble in the solvents pyridine, propylene carbonate and N,N-dimethylformamide.

To prepare silver perchlorate, Analar grade silver nitrate (B.D.H.) was heated with an excess of Analar grade 72% perchloric acid (B.D.H.). The nitric acid was distilled off and the silver perchlorate recrystallised from water. The salt is very deliquescent and forms a monohydrate.
AgClO$_4$$ \cdot $H$_2$O, which can be dehydrated by heating at 43°C. Dehydration was carried out in an oven, maintaining the temperature at 80°C. The salt was stored at 80°C. in air and darkness. After a period of two weeks, a brown colouration developed on the surface of the while salt. The salt was used before this condition developed.

It is reported in the literature that the anhydrous salt is very light sensitive but the presence of small amounts of perchloric acid had a strong stabilising effect towards light.

**Electrodes**

Since the rotating platinum electrode had been used with success in the reduction of silver (I) in many aprotic solvents, platinum was chosen as the working electrode material, though initially in the form of a stationary microelectrode. In later work the vibrating platinum electrode was used. The platinum electrode was cleaned with 4M nitric acid for one minute, washed with distilled water and dried.

Although molybdenum was found to be unsatisfactory as an electrode in aqueous solutions due to the exchange reaction with aqueous silver, this electrode was again chosen for the experimental work in non-aqueous solvents. The cleaning procedure was as before (page 66), but after washing with distilled water, the molybdenum wire was dried.

Silver wire (0.71 mm diam.) replaces molybdenum in later work as the reference electrode. This was cleaned in the same way as the platinum.

In some experiments a third or counter electrode was also introduced into the electrode system. This was platinum foil (1cm$^2$) sealed via a short length of platinum wire into a glass tube. The platinum foil was cleaned in the same way as the platinum microelectrode.

**Two Electrode Cell**

A diagram of the cell incorporating a molybdenum anode and a platinum
micro-electrode as the indicating electrode is shown in Figure 38. In this cell, the molybdenum is the reference electrode and the voltage is measured with respect to this electrode.

Current-voltage curves were obtained using a Heathkit D.C. Polaro-graph on solutions thermostatted at 25 ± 0.2°C. The rate of change of voltage was varied as indicated on the polarograms, during the experiments.
Figure 38. Polarographic Cell incorporating Solid Electrodes — Platinum

Microcathode and Molybdenum Wire Anode
SECTION V

3. INVESTIGATIONS OF ANHYDROUS SILVER PERCHLORATE IN THE SOLVENTS
   PYRIDINE, PROPYLENE CARBONATE AND N,N-DIMETHYLFORMAMIDE
Anhydrous silver perchlorate was transferred as quickly as possible from the oven to the solvent and then to a stoppered container. 5 ml. portions of solvent were used and the silver concentrations were of the order of $10^{-2}$ M.

Results

(a) Propylene carbonate

Within two minutes of the addition of silver perchlorate, a red-brown colouration developed, and after a period of one week a black deposit was observed at the bottom of the container.

The prior addition of one drop of perchloric acid to the solvent eliminated the colouration, but decomposition to the black deposit still persisted, though occurring more slowly.

Addition of one drop of 72% perchloric acid to the solvent in the absence of silver perchlorate produced a pale yellow colouration, this disappeared immediately on the addition of one drop of pyridine.

(b) Pyridine

Slight decomposition in the form of a black deposit was observed after a period of one week.

Even after eight weeks no decomposition or colouration was noticed with solutions which contained perchloric acid.

(c) N,N-Dimethylformamide

Within two minutes of the addition of N,N-dimethylformamide to silver perchlorate the solutions turned yellow and on further standing (two days), the colour changed to brown, with brown stains visible on the walls of the container. Three weeks later a characteristic 'silver mirror' effect had appeared.

55
Conclusions

In the absence of perchloric acid, decomposition of silver perchlorate takes place in all three solvents, though least rapidly in pyridine. The gradual reduction of silver (I) to metallic silver as reported by various workers\textsuperscript{55} was confirmed for solutions in DMF.

In both propylene carbonate and N,N-dimethylformamide the addition of perchloric acid slowed the rate of decomposition\textsuperscript{34}. No decomposition was apparent in the pyridine/perchloric acid/silver perchlorate system during the period of observation (ten weeks).
SECTION V

4. POLAROGRAPHY OF SILVER IN PROPYLENE CARBONATE, PYRIDINE AND N,N-DIMETHYLFORMAMIDE - TWO ELECTRODE CELL - PLATINUM AND MOLYBDENUM ELECTRODES - STATIONARY PLATINUM ELECTRODE
Polarography of Silver in Propylene Carbonate - Two Electrode Cell
(Platinum and Molybdenum) - Stationary Platinum Electrode

From the investigations of silver perchlorate in the solvents under consideration, it appeared unlikely that molybdenum would serve as a useful reference electrode since the addition of perchloric acid also necessitated the addition of a little water. In propylene carbonate, however, the decomposition of silver perchlorate is slow, and some information may be obtained if experiments were carried out quickly.

Polarography of Propylene Carbonate (0.1M in Tetraethylammonium Perchlorate)

Figure 39 shows the typical current-voltage curves obtained before and after deaeration with nitrogen. The voltage is expressed with respect to the molybdenum electrode and the rate of increase of voltage was 0.5V/min.

Before deaeration a wave of 3.5µA appeared at -0.5V, presumably due to dissolved oxygen, but this was reduced to 0.15µA after bubbling nitrogen for fifteen minutes.

It was observed that the wave height increased to 0.4µA if the platinum electrode was exposed to the air for more than about three minutes during the experiment (Figure 40). Deaeration, however, with the platinum electrode in the solution for five minutes then reduced the wave height to 0.15µA. This effect was probably due to adsorbed oxygen on the platinum surface.
Figure 39. Current-Voltage Curves of Propylene Carbonate (0.1M in TEAP) with Stationary Platinum Microelectrode (0.5V min⁻¹)

I - Before deaeration
II - After deaeration for 15 min.

Figure 40. Showing the Effect of Exposing the Platinum Microelectrode to the Air

II - From Figure 39(II) above
III - Platinum Microelectrode exposed to the air for 3 minutes

E_{w.e.} (Volts) versus Molybdenum Anode
For the preparation of a stock solution, silver perchlorate was transferred as quickly as possible from the oven (80°C) to a weighed stoppered bottle containing the electrolyte. Reweighing then gave the weight of silver perchlorate added, the resulting solution being 9.5 mM with respect to silver.

After deaeration for fifteen minutes with nitrogen, the recorded polarogram showed a wave in the region of -30 mV (Figure 41). Successive polarograms, however, did not give good reproducibility. Current-voltage values were also recorded manually from +0.33 V to -0.75 V, about three minutes being required before the current reached a steady value at each value of the applied potential.

When readings were complete, the above solution was diluted approximately twofold with the supporting electrolyte and weighed. The measurements were repeated. The dilution was carried out two times.

Results

(a) Polarograms of the three solutions are given in Figure 41, showing the increase in wave height with increasing silver concentration.

(b) Manual current-voltage plots are shown in Figure 42. Good residual current plateaus were recorded before the waves and also good current plateaus after the waves.

(c) Figure 43 shows reasonable linearity for the diffusion current versus silver perchlorate concentration plot, though the line does not pass through the origin. It must be remembered, however, that decomposition of the silver perchlorate was taking place during the experiment of duration two and a half hours.
Figure 41. Current-Voltage Curves of Silver Perchlorate in Propylene Carbonate (0.1M in TEP) - Stationary Platinum Electrode (0.5V min⁻¹)

- 9.5 x 10⁻⁵ M AgClO₄
- 5.4 x 10⁻⁵ M AgClO₄
- 3.0 x 10⁻⁵ M AgClO₄

Ew.e. (Volts) versus Molybdenum Anode
Figure 42. Current-Voltage (Anodic) plots for solutions of silver perchlorate in propylene carbonate (0.1M in TEAP) with a stationary platinum microelectrode.

Figure 43. Plot of Diffusion Current versus Silver Perchlorate Concentration from the Current-Voltage Curves in Figure 42 above.
Polarography of Silver Solutions in Propylene Carbonate (0.1 M TEAP) in the Presence of Perchloric Acid

Initial investigations on the stability of silver perchlorate in propylene carbonate showed that the addition of one drop of perchloric acid considerably reduced the rate of decomposition of silver perchlorate. Experiments were then conducted on solutions containing a small amount of perchloric acid ($10^{-3} \text{M}$) with silver perchlorate concentrations varying from 0-1.5 mM.

A stock solution of silver perchlorate (1.5 mM) in propylene carbonate was prepared and to this solution was added one drop of 72% perchloric acid. The resulting solution was added to the supporting electrolyte in varying quantities to give solutions of varying silver concentration.

After deaeration and with the cell voltage at -0.2 V (versus Mo electrode), the current was allowed to reach a steady value (after about three minutes) before a reading was taken. The cell was then reweighed, more stock silver solution added, the cell weighed again, and then the recording procedure was repeated.

Results

(a) The evaluation of the silver concentrations is given in Table 9.

(b) From the plot of diffusion current versus silver concentration (Figure 44), good linearity is observed from 0 to 1.5 mM solutions, the plot almost going through the origin.

(c) As the experiment proceeded (total time one hour), the solution gradually darkened in colour, this being due to a suspension of very fine brownish-black particles. On allowing to dry in air, it was noticed that a grey-white coating adhered to the molybdenum electrode.

(d) A duplicate experiment, in which the 10 ml. of supporting electrolyte contained one drop of 72% perchloric acid, was also performed, but it was
Table 9. Evaluation of Silver Perchlorate Concentrations in Propylene Carbonate (0.1M in TEGAP). Diffusion Currents were Recorded at -0.2V versus Mo Electrode. Stock Silver solution was 11.3mM in AgClO$_4$.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Wt. of AgClO$_4$ added</th>
<th>Total weight of AgClO$_4$ added</th>
<th>Wt. of soln.</th>
<th>AgClO$_4$ mM</th>
<th>$i_2$ (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>12.76</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.202</td>
<td>0.202</td>
<td>12.96</td>
<td>0.175</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>0.188</td>
<td>0.390</td>
<td>13.15</td>
<td>0.335</td>
<td>0.11</td>
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<td>4</td>
<td>0.202</td>
<td>0.592</td>
<td>13.35</td>
<td>0.505</td>
<td>0.17</td>
</tr>
<tr>
<td>5</td>
<td>0.193</td>
<td>0.785</td>
<td>13.54</td>
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<td>6</td>
<td>0.179</td>
<td>0.964</td>
<td>13.72</td>
<td>0.795</td>
<td>0.27</td>
</tr>
<tr>
<td>7</td>
<td>0.209</td>
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<td>13.92</td>
<td>0.950</td>
<td>0.32</td>
</tr>
<tr>
<td>8</td>
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<td>1.369</td>
<td>14.11</td>
<td>1.095</td>
<td>0.37</td>
</tr>
<tr>
<td>9</td>
<td>0.196</td>
<td>1.565</td>
<td>14.30</td>
<td>1.235</td>
<td>0.42</td>
</tr>
<tr>
<td>10</td>
<td>0.200</td>
<td>1.765</td>
<td>14.50</td>
<td>1.375</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Figure 44. Plot of Diffusion Current (Recorded at -0.2V) versus Silver Perchlorate Concentration.
observed that the darkening of the solution occurred at a much faster rate, red-brown particles appeared at the bottom of the cell on standing (within two minutes).

Discussion

The results show that silver may be determined in undisturbed solutions with a stationary platinum microelectrode, though decomposition of the silver salt does take place.

Though retarding the rate of decomposition of the silver salt, the presence of perchloric acid is probably accompanied by the reaction which was observed in aqueous solutions, namely the exchange between molybdenum and silver ions. Experiments were not conducted to ascertain the nature of the red-brown particles, but the rate of formation of these appeared to increase with increasing perchloric acid concentration, though only in the presence of molybdenum.
Polarography of Silver in N,N-Dimethylformamide and Pyridine - Two Electrode Cell (Platinum and Molybdenum) - Stationary Platinum Electrode

Though no quantitative experiments were conducted, current-voltage curves were recorded for the following solutions at a scan rate of 0.5V/min:

(a) N,N-Dimethylformamide (0.1M in TEAP), with and without deaeration.
(b) As in (a) but with anhydrous silver perchlorate added.
(c) Pyridine (0.1M in TEAP), with and without deaeration.
(d) As in (c) but with anhydrous silver perchlorate added.

The polarograms are shown in Figures 45-48.

Results

(a) and (b). After deaerating for twenty minutes, the wave of 1μA at -0.6V still persisted (Figure 45). Addition of silver perchlorate produced a wave at -40mV (Figure 46).

(c) and (d). After deaerating for twenty minutes, a wave of 1μA still persisted at -0.5V (Figure 47). Addition of silver perchlorate produced a wave at -60mV (Figure 48) but successive polarograms were not reproducible. Addition of a few drops of propylene carbonate, however, produced stability.

Although the work was not quantitative, the results indicate that silver could be determined in these solvents similar to the findings in propylene carbonate.
Figure 45. Current-Voltage Curves of N,N-Dimethylformamide (0.1M in TEAP) with Stationary Platinum Microelectrode (2V min.\(^{-1}\))

I - Before deaeration
II - After deaeration for 20 minutes

Figure 46. Current-Voltage Curve of Silver Perchlorate (5 \times 10^{-4} M) in N,N-Dimethylformamide (0.1M in TEAP) with Stationary Platinum Microelectrode (0.5V min.\(^{-1}\))
Figure 47. Current-Voltage Curves of Pyridine (0.1M in TEAP) with Stationary Platinum Microelectrode (0.5V min. $^{-1}$)

- Before deaeration
- After deaeration

Figure 48. Current-Voltage Curve of Silver Perchlorate ($2 \times 10^{-3}$M) in Pyridine (0.1M in TEAP) with Stationary Platinum Microelectrode (0.5V min. $^{-1}$)
SECTION V

5. POLAROGRAPHY OF SILVER IN PROPYLENE CARBONATE, PYRIDINE AND N,N-DIMETHYLFORMAMIDE - THREE ELECTRODE CELL WITH VIBRATING PLATINUM ELECTRODE
Although the results so far indicated that silver was being reduced in the solvents pyridine, propylene carbonate and N,N-dimethylformamide, the two electrode cell system had the following disadvantages:—

(a) In the presence of perchloric acid solution (presumably due to the added water), molybdenum was chemically reacting with silver ions. Since the silver ion was under investigation and silver wires had been used as reference electrodes, it was decided to replace the molybdenum wire with silver wire of 0.71 mm diameter. 2 cm of this wire was immersed in the solution. The silver electrode was cleaned as in the aqueous work.

(b) Satisfactory polarograms had only been achieved using a stationary platinum electrode when current readings were recorded at each value of the applied potential. The disadvantages of this method are:—

(1) Time taken to reach diffusion equilibrium.

(2) Diffusion currents were much smaller in organic solvents than in aqueous media.

Harris and Lindsay\(^2\) stated that 'The constant diffusion conditions necessary for polarographic work have hitherto been attained by use of the dropping mercury electrode, the streaming electrode, the rotating platinum microelectrode or even by a fixed microelectrode and a constant electrolyte streaming rate.

We have found that a platinum microelectrode vibrating at a constant frequency (100 Hz) with an amplitude considerably greater than its linear dimension gives constant diffusion conditions, and with such an electrode, have obtained reproducible polarograms. The electrode is free from irregularities due to its external vibration and gives smoother curves than those obtained with the dropping mercury cathode.'
The vibrating platinum electrode has been used with considerable success in amperometric titrations. The electrode gives a much greater diffusion current than a stationary electrode of the same area and the temperature control \( (+2\% \) is not as important as the stationary electrode \( (+4\% \). Adams stated that no critical treatment of mass transfer conditions at a vibrating wire electrode have been attempted, but the diffusion current is directly proportional to the concentration (bulk), where frequency and amplitude are approximately 60 Hz and 0.5mm, respectively. Lindsay investigated the relationship between diffusion current and frequency and amplitude of vibration of platinum micro-electrodes and he concluded that the average relative speed of the electrode should be about 25-30cm/sec. to maintain constant diffusion current conditions. The vibrating platinum micro-electrode was adopted, the platinum being cleaned as before.

(c) Meites stated that 'With organic solvents, the prepared solutions often have high resistances and the IR drop through the cell is considerable. To overcome this, a cell containing a second reference electrode, which is connected to one of the X-input terminals of an X-Y recorder while the indicating electrode is connected to the other, is used. Meanwhile, the IR drop derived from the passage of cell current through a standard resistor in series with the cell is applied to the Y input terminals, and the recorder then furnishes a plot of the cell current against the potential difference between the indicating electrode and the second reference electrode, through which the cell current does not flow'.

Incorporation of a second reference electrode thus overcomes the potential drop through the cell which is characteristic of a two electrode system.
A three-electrode cell system was constructed. This incorporated
a vibrating platinum micro-electrode as the indicating electrode, a
reference electrode of silver wire (0.71mm diam.) and a counter electrode
of platinum foil (1cm²). A diagram of the cell is shown in Figure 49.

Polarography of Silver in Propylene Carbonate - Three Electrode Cell
with Vibrating Platinum Electrode

Solutions of silver perchlorate in propylene carbonate (0.1M in
TEAP) were prepared as before in the presence of perchloric acid and
deaerated with nitrogen for fifteen minutes. The rate of increase of
voltage was 0.5V min⁻¹ and the voltage was expressed with respect to the
silver reference electrode. Current-voltage curves were recorded on the
following solutions:

(a) Propylene carbonate solutions (0.1M in TEAP) containing silver
perchlorate, the concentration of which ranged from 2 x 10⁻⁴M to
7 x 10⁻³M.

(b) Silver solutions as in (a) above, to which small quantities of
water, pyridine and N,N-dimethylformamide were added in separate exper­
iments to observe the effect on the recorded silver wave.

Results

(a) Figure 50 shows a typical current-voltage curve obtained using a
vibrating platinum micro-electrode.

For a reversible reaction which yields a reduction product insoluble
in mercury, e.g. metals such as molybdenum, tungsten and vanadium, the
equation for such a process at 25°C is given by:

$$E_{d.e.} = E_2 - \frac{0.059 \log i_D}{n} + \frac{0.059}{n} \left( \frac{i_D - i}{i_D} \right)$$

(1)

where $E_{d.e.}$ = the potential of the dropping mercury electrode for a
current $i$. 
Figure 49. Three Electrode Polarographic Cell incorporating Vibrating Platinum Microelectrode and Silver Reference Electrode
Figure 50: Current-Voltage Curve of Silver Perchlorate (1.85 x 10^{-5} M) in Propylene Carbonate (0.1 M in TEAP) with Vibrating Platinum Microelectrode (0.2 V min^{-1})

$E_{\text{w.e.}}$ (Volts) versus Silver Reference Electrode
$E_\frac{1}{2}$ = the half-wave potential of the species.

$n$ = the number of electrons involved in the reduction.

$i_D$ = the diffusion current.

The shape of a polarogram for this type of system is shown in Figure 51.

---

**Figure 51.** Calculated polarographic wave for the reversible two-electron reduction of a metal ion to a metal completely insoluble in mercury.

The wave is similar to that of the silver wave obtained in propylene carbonate (Figure 50) and it should be possible to apply the equation to reversible reductions of metal ions to solid metals at solid electrodes. $E_{\text{w.e.}}$ (working electrode) can replace $E_{\text{d.e.}}$, so equation (1) becomes

$$E_{\text{w.e.}} = E_\frac{1}{2} - \frac{0.059}{n} \log \frac{i_D}{2} + \frac{0.059}{n} \log (i_D - i) \quad (2)$$

or

$$E_{\text{w.e.}} = E_\frac{1}{2} - \frac{0.059}{n} \log \frac{i_D}{2(i_D - i)} \quad (3)$$

For a given polarogram $i_D$ is constant, hence a plot of $E_{\text{w.e.}}$ versus log $(i_D - i)$ should be linear and have a slope of $\frac{0.059}{n}$ at 25°C.

Convenient points are chosen on the curve (Figure 50) and values of $E_{\text{w.e.}}$ and log $(i_D - i)$ are shown in Table 10. From the plot of $E_{\text{w.e.}}$ versus log $(i_D - i)$, reasonable linearity is observed (Figure 52), the slope of this line being 0.060. Since the slope is $\frac{0.059}{n}$, this gives a value of unity for $n$, probably due to the reduction of the silver ion $Ag^+$ to metal silver.
**TABLE 10**

Analysis of Current-Voltage Curve of Silver Perchlorate \((1.85 \times 10^{-3} \text{M})\) in Propylene Carbonate \((0.1 \text{M in TEAP})\) with Vibrating Platinum Microelectrode (Figure 50)

\(i_D = \text{Diffusion Current (7.5 microamp.)}\)

<table>
<thead>
<tr>
<th>Current (i)</th>
<th>((i_D - i))</th>
<th>(\log(i_D - i))</th>
<th>(E_{\text{H.e.}} \text{ (mV)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>6.5</td>
<td>0.813</td>
<td>-7</td>
</tr>
<tr>
<td>2.0</td>
<td>5.5</td>
<td>0.740</td>
<td>-14</td>
</tr>
<tr>
<td>3.0</td>
<td>4.5</td>
<td>0.653</td>
<td>-20</td>
</tr>
<tr>
<td>4.0</td>
<td>3.5</td>
<td>0.544</td>
<td>-26</td>
</tr>
<tr>
<td>5.0</td>
<td>2.5</td>
<td>0.398</td>
<td>-35</td>
</tr>
<tr>
<td>6.0</td>
<td>1.5</td>
<td>0.176</td>
<td>-47</td>
</tr>
</tbody>
</table>

Figure 52: Plot of \(\log(i_D - i)\) versus \(E_{\text{H.e.}} \text{ (mV)}\) from Table 10 above
For a reversible wave of this type

\[ E_{1}^{0} - E_{2}^{0} = \frac{0.028V}{n} \text{ at } 25^\circ\text{C} \]

From the curve (Figure 50), \( E_{1}^{0} - E_{2}^{0} = 0.028V \), again in good agreement with the one electron change.

The evaluation of the silver concentrations is given in Table 11, and the resulting plot of diffusion current versus silver concentration (Figure 53) shows good linearity from \( 2 \times 10^{-4} \text{M} \) to \( 7 \times 10^{-3} \text{M} \) with respect to silver. The observed shifts in \( E_{1}^{0} \) are similar to those reported by Rogers et. al.

(b) The effects of water, pyridine and \( \text{N,N-dimethylformamide} \) on the half-wave potential of the silver ion are shown in Table 12. The results are not quantitative.

Discussion

The results show that the wave obtained from silver perchlorate in propylene carbonate probably corresponds to the reversible one electron reduction of silver ion to metal silver.

Silver may be determined quantitatively using a vibrating platinum micro-electrode in propylene carbonate, good linearity was observed between the diffusion current and silver concentration from \( 2 \times 10^{-4} \text{M} \) to \( 7 \times 10^{-3} \text{M} \) silver.

The addition of water, pyridine and \( \text{N,N-dimethylformamide} \) moved the half-wave potential of the silver ion to more negative values, but did not change the overall shape of the polarogram.
Table II. Evaluation of Silver Perchlorate Concentrations in Propylene Carbonate (0.1M in TEAP). $E_i$ Values are versus Silver Reference Electrode with Vibrating Platinum Electrode. Scan Speed 0.5V min$^{-1}$.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Wt. of AgClO$_4$ added</th>
<th>Total weight of AgClO$_4$ added</th>
<th>Wt. of soln. (AgClO$_4$)</th>
<th>$i_D$</th>
<th>$E_i$ $^{[\text{mV}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>11.58</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.063</td>
<td>0.063</td>
<td>11.64</td>
<td>0.216</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>0.063</td>
<td>0.126</td>
<td>11.70</td>
<td>0.432</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>0.063</td>
<td>0.189</td>
<td>11.77</td>
<td>0.644</td>
<td>2.0</td>
</tr>
<tr>
<td>5</td>
<td>0.062</td>
<td>0.251</td>
<td>11.83</td>
<td>0.848</td>
<td>2.9</td>
</tr>
<tr>
<td>6</td>
<td>0.151</td>
<td>0.402</td>
<td>11.98</td>
<td>1.344</td>
<td>5.1</td>
</tr>
<tr>
<td>7</td>
<td>0.230</td>
<td>0.632</td>
<td>12.21</td>
<td>2.07</td>
<td>6.4</td>
</tr>
<tr>
<td>8</td>
<td>0.364</td>
<td>0.996</td>
<td>12.57</td>
<td>3.17</td>
<td>13.2</td>
</tr>
<tr>
<td>9</td>
<td>0.523</td>
<td>1.519</td>
<td>13.10</td>
<td>4.64</td>
<td>19.5</td>
</tr>
<tr>
<td>10</td>
<td>0.547</td>
<td>2.066</td>
<td>13.64</td>
<td>6.06</td>
<td>26.0</td>
</tr>
<tr>
<td>11</td>
<td>0.498</td>
<td>2.564</td>
<td>14.14</td>
<td>7.26</td>
<td>32</td>
</tr>
</tbody>
</table>
Figure 55. Plot of Diffusion Current versus Silver Perchlorate (0.1M in TEAP) Concentration with Vibrating Platinum Microelectrode
Table 12. The Effect of Water, Pyridine and N,N-Dimethylformamide on the Half-Wave Potential of mM AgClO₄ in Propylene Carbonate (0.1M in TEAP)

<table>
<thead>
<tr>
<th>Solution</th>
<th>E₂ in mV versus Ag Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>mM AgClO₄ in Propylene Carbonate</td>
<td>-13</td>
</tr>
<tr>
<td>4M in Water</td>
<td>-20</td>
</tr>
<tr>
<td>0.6M in Pyridine</td>
<td>-20</td>
</tr>
<tr>
<td>1.2M in Pyridine</td>
<td>-25</td>
</tr>
<tr>
<td>0.4M in N,N-Dimethylformamide</td>
<td>-33</td>
</tr>
</tbody>
</table>
Polarography of Silver in Pyridine - Three Electrode Cell with Vibrating Platinum Electrode

Solutions of silver in pyridine were prepared in a similar manner to those in propylene carbonate. Current-voltage curves were recorded on the following solutions:

(a) Pyridine (0.1M in TEAP) solution, containing perchloric acid, and 2mM with respect to silver perchlorate.

(b) A pyridine solution as in (a) above, to which propylene carbonate has been added.

Results

(a) The current-voltage curve shown in Figure 54 is similar to that for silver in propylene carbonate, but the half-wave potential of the silver is more negative and the diffusion current greater for the same silver concentration.

The wave was analysed in a similar manner to that obtained from silver perchlorate in propylene carbonate to test for reversibility. Values of $E_{\text{w.e.}}$ and $\log (i_D - i)$ are shown in Table 13 and the subsequent plot in Figure 55. The slope was 0.062V and the $E_{\frac{1}{2}} - E_{\frac{3}{4}}$ value was 0.030V, in close agreement with a reversible one electron reduction.

(b) The addition of propylene carbonate moves the half-wave potential of silver in pyridine to a more positive potential and also reduces the diffusion current.

Discussion

A satisfactory S-shaped reduction wave was recorded for silver in pyridine and although no further quantitative experiments were conducted, the addition of silver perchlorate did increase the diffusion current.
Figure 54. Current-Voltage Curve of Silver Perchlorate ($2 \times 10^{-3}$ M) in Pyridine (0.1 M in TEMPO) with Vibrating Platinum Electrode (0.2 V min$^{-1}$)

$E_{N.S.}$ (Volts) versus Silver Reference Electrode
Analysis of Current-Voltage Curve of Silver Perchlorate (2 x 10^{-5} M) in Pyridine (0.1 M in TEAP) with Vibrating Platinum Microelectrode (Figure 54)

\[ i_D = \text{Diffusion Current (45 microamp.)} \]

<table>
<thead>
<tr>
<th>Current 1</th>
<th>( (i_D - 1) )</th>
<th>( \log(i_D - 1) )</th>
<th>( E_{\text{W.e.}} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>38</td>
<td>1.580</td>
<td>-28</td>
</tr>
<tr>
<td>14</td>
<td>31</td>
<td>1.492</td>
<td>-35</td>
</tr>
<tr>
<td>21</td>
<td>24</td>
<td>1.390</td>
<td>-45</td>
</tr>
<tr>
<td>28</td>
<td>17</td>
<td>1.230</td>
<td>-52</td>
</tr>
<tr>
<td>35</td>
<td>10</td>
<td>1.000</td>
<td>-66</td>
</tr>
<tr>
<td>40</td>
<td>5</td>
<td>0.699</td>
<td>-84</td>
</tr>
</tbody>
</table>

Figure 55. Plot of \( \log(i_D - 1) \) versus \( E_{\text{W.e.}} \) (mV) from Table 15 above
Polarography of Silver in N,N-Dimethylformamide - Three Electrode Cell
with Vibrating Platinum Electrode

Solutions of silver in N,N-dimethylformamide were prepared in a similar manner to those in the solvents pyridine and propylene carbonate. Current-voltage curves were recorded on the following solutions:

(a) N,N-Dimethylformamide (0.1M in TEA?) solution, 2mM with respect to silver perchlorate and in the absence of perchloric acid.

(b) As in (a) above but in the presence of perchloric acid.

(c) As in (b) above but with added pyridine.

Results

(a) The current-voltage curve shown in Figure 56 is typical of that obtained with the vibrating platinum electrode, the half-wave potential for silver being -83mV.

(b) This solution gave an S-shaped current-voltage curve with a half-wave potential of -45mV (Figure 56). On standing for five minutes, however, with the cell connected at the start potential of +0.25V, resulting polarograms were not reproducible, giving half-wave potentials ranging from -55mV to -70mV. Cleaning the electrodes gave reproducible polarograms with a half-wave potential of -55mV, which were unaffected by the addition of one further drop of 72% perchloric acid (volume of solution 10ml).

(c) Addition of pyridine did not change either the wave form or the half-wave potential of silver, but did reduce the diffusion current.

Discussion

A satisfactory S-shaped reduction wave was obtained for silver in N,N-dimethylformamide and although no further quantitative experiments were conducted, the addition of silver perchlorate increased the diffusion current. The half-wave potential of silver was considerably influenced by the presence of perchloric acid but no significant change was apparent on
Figure 5S. Current-Voltage Curves of Silver Perchlorate (10^-3 M) in N,N-Dimethylformamide (0.1 M in TEA) with Vibrating Platinum Microelectrode (0.5 V min^-1)

I - In the absence of perchloric acid
\[ E_{w.e.} = -35 \text{ mV} \]

II - In the presence of perchloric acid
\[ E_{w.e.} = -45 \text{ mV} \]
the addition of pyridine.

The fluctuations in the recorded half-wave potentials could have been due to the presence of perchloric acid. Thomas and Rochow\textsuperscript{96} reported that acids and bases catalyse the decomposition of \(\text{N, N-dimethylformamide}\) to give dimethylamine and carbon monoxide at room temperature.
SECTION V

6. POLAROGRAPHY OF SILVER IN THE PROPYLENE CARBONATE/PYRIDINE MIXED SOLVENT SYSTEM - THREE ELECTRODE CELL WITH VIBRATING PLATINUM ELECTRODE
From the current-voltage curves recorded for the reduction of silver in the solvents pyridine, propylene carbonate and N,N-dimethylformamide, the following points were noted:

(a) The half-wave potential of silver is least negative in propylene carbonate and this is moved to a more negative value by the addition of either pyridine or N,N-dimethylformamide (Figure 57).

(b) The rate of decomposition of silver perchlorate in propylene carbonate and pyridine is decreased by the presence of perchloric acid, but acids tend to decompose N,N-dimethylformamide.

It was decided to investigate the change in the half-wave potential of the reduction of silver in propylene carbonate by the addition of pyridine.

Procedure

A solution of propylene carbonate (0.1M in TEP) containing a small quantity (10^{-3}M) of perchloric acid and 1.5mM with respect to silver perchlorate was deaerated for fifteen minutes and a polarogram was recorded. The rate of increase of voltage was 0.2V min^{-1}. A small quantity of pyridine (0.1M in TEP) was added to the cell, care was taken to avoid disturbance of the electrode system, the solution was stirred and deaerated by bubbling nitrogen for two minutes, and then current-voltage curves were again recorded. This procedure was repeated with several separate additions of pyridine.

A solution of pyridine (0.1M in TEP) containing a small quantity of perchloric acid (10^{-3}M) and 1.5mM with respect to silver perchlorate was also prepared as above and current-voltage curves were recorded. The effects of the addition of two quantities of propylene carbonate (0.1M in TEP) were recorded.

Results

At a scan voltage of 0.2V min^{-1}, three successive polarograms on
Figure 57. Current-Voltage Curves of Silver Perchlorate ($1.85 \times 10^{-3}$ M) in
Propylene Carbonate (0.1M in TEA) with Vibrating Platinum
Microelectrode (0.2 V min$^{-1}$). Effect of Separate Additions
of Pyridine and N,N-Dimethylformamide

All solutions in the presence of perchloric acid

$E_{w, e}$ (Volts) versus Silver Reference Electrode
the same solution gave reproducibility to within 1mV (Figure 58), this compares favourably with the work of Coulter and Iwamoto who, using the rotating platinum electrode quoted reproducibility to within 3mV. Figure 58 also gives polarograms of solutions containing added pyridine. The results are given in Table 14, values of $\Delta E_{1/2}$ being corrected for dilution of the propylene carbonate solution by pyridine. A plot of the corrected half-wave potential shift $\Delta E_{1/2} \text{ (corr.)}$ versus pyridine concentration (Figure 59) is non-linear, the greatest change in $\Delta E_{1/2} \text{ (corr.)}$ occurring with the initial addition of pyridine. A plot of $\Delta E_{1/2} \text{ (corr.)}$ versus log Pyr. (Figure 60) gives a straight line.

From the experimental work, the half-wave potentials of silver from silver perchlorate/propylene carbonate and silver perchlorate/pyridine systems are $-0.024V$ and $-0.036V$ respectively. Both values are versus the silver reference electrode. In the propylene carbonate/pyridine mixed solvent systems, the change in half-wave potential was approximately logarithmic with respect to pyridine concentration.

The free energy change from the propylene carbonate system to that of the pyridine may be calculated from the following expression:

$$\Delta G = nF \Delta E \text{ n = 1 } (Ag^+ \rightarrow Ag^0)$$

$$F = \text{Faraday} = 96,500 \text{ coul. mole}^{-1}$$

$$\Delta E = -0.012V \text{ or } -0.012 \text{ joules coul}^{-1}$$

Hence $\Delta G = 1 \times 96,500 \times 0.012$

$$= -1.16 \text{ kJ mole}^{-1}$$

$$= -0.28 \text{ kcal mole}^{-1}$$
Figure 58. Current-Voltage Curve of Silver Perchlorate ($1.5 \times 10^{-5} \text{M}$) in Propylene Carbonate (0.1M in TEAP) with Vibrating Platinum Microelectrode (0.2V min.$^{-1}$). Effect of Addition of Pyridine

I - No pyridine
II - 0.5M in pyridine
III - 2.5M in pyridine

$E_{\text{w.r.e.}}$ (Volts) versus Silver Reference Electrode
Chance in the Half-Wave Potential of Silver in Propylene Carbonate on the Addition of Pyridine. Values are also given for Corrected Changes in the Half-Wave Potential due to Dilution of the Silver Solution by Pyridine.

<table>
<thead>
<tr>
<th>Pyridine Conc. (moles/l)</th>
<th>log Pyridine Conc.</th>
<th>$E_1$ (mV)</th>
<th>$\Delta E_1$ (mV)</th>
<th>$\Delta E_1$ corr. (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>25.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.159</td>
<td>-0.798</td>
<td>25.6</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>0.503</td>
<td>-0.519</td>
<td>27.0</td>
<td>3.4</td>
<td>3.5</td>
</tr>
<tr>
<td>0.67</td>
<td>-0.373</td>
<td>27.9</td>
<td>4.3</td>
<td>4.6</td>
</tr>
<tr>
<td>2.37</td>
<td>0.376</td>
<td>30.0</td>
<td>6.4</td>
<td>7.7</td>
</tr>
<tr>
<td>3.17</td>
<td>0.501</td>
<td>31.1</td>
<td>7.5</td>
<td>8.6</td>
</tr>
<tr>
<td>12.5</td>
<td>1.097</td>
<td>35.5</td>
<td>11.9</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Figure 59. Plot of $\Delta E_1$ corr. versus Pyridine Concentration.
Figure 60. Plot of $\Delta E_{corr}$ versus log Pyridine Concentration for Silver Perchlorate in Propylene Carbonate Solutions. Values from Table 14
SECTION VI

SILVER-SOLVENT-ADDITIVE INTERACTIONS

1. INTRODUCTION
The half-wave potential shift of silver in propylene carbonate to more negative values with the associated $\Delta G$ of $-0.28$ kcal mole$^{-1}$, by the addition of pyridine could be attributed to one of several factors, including the following:

(a) Adsorption
(b) Complexation
(c) Solvation
(d) Change in crystal structure of the deposited silver at the platinum electrode.

There is little data available for the system studied but some comparable results are summarised below.

**Adsorption**

Various workers have studied the effect of the adsorption of organic molecules on metal surfaces and on inorganic compounds with the resultant determination of the free energies involved.

Chu and Sukava$^{99}$ noted the effect of straight chain carboxylic acids on the cathode overpotential during the electrodeposition of copper. The addition of the organic acids did not modify the charge transfer mechanism of the copper deposition. The general behaviour was consistent with the blocking theory of additive function according to which overpotential increments were directly dependent on additive adsorbability. The fractional surface coverage from over-potential increments appeared to fit a Langmuir-type isotherm from which the free energies of adsorption of the carboxylic acids could be determined. Adsorption data for propanoic acid is given in Table 16, and the net free energies of adsorption for the carboxylic acids in Table 17.

**Table 16. Adsorption Data for Propanoic Acid**

<table>
<thead>
<tr>
<th>Conc. (mole/l)</th>
<th>$E$ (mV)</th>
<th>Conc. (mole/l)</th>
<th>$E$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.5 \times 10^{-2}$</td>
<td>18.0</td>
<td>$7.5 \times 10^{-2}$</td>
<td>37.2</td>
</tr>
<tr>
<td>$5.0 \times 10^{-2}$</td>
<td>29.4</td>
<td>$1.0 \times 10^{-1}$</td>
<td>43.0</td>
</tr>
</tbody>
</table>
Table 17. Net Free Energy of Adsorption

<table>
<thead>
<tr>
<th>Additive</th>
<th>$G^0$ (kcal mole$^{-1}$ at 25°C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propanoic acid</td>
<td>-3.81</td>
</tr>
<tr>
<td>Pentanoic acid</td>
<td>-5.60</td>
</tr>
<tr>
<td>Heptanoic acid</td>
<td>-7.35</td>
</tr>
</tbody>
</table>

The magnitude of the free energies was consistent with physical adsorption forces.

A.H. Herz et al. have studied the adsorption of cyanine dyes on silver bromide and colloidal silver and from the changes in dye spectra, have determined the standard free energies of adsorption and probable orientations of the adsorbed dyes. Adsorption data is given for cyanine dyes on silver bromide in Table 18, a solution of $7 \times 10^{-2}$ M AgBr in 0.2% gelatin being used.

Table 18. Net Free Energy of Adsorption

<table>
<thead>
<tr>
<th>Additive</th>
<th>$G^0$ (kcal mole$^{-1}$ at 25°C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudocyanine</td>
<td>-9.8</td>
</tr>
<tr>
<td>Astraphloxin</td>
<td>-8.8</td>
</tr>
</tbody>
</table>

The dyes adsorbed by colloidal silver follow Langmuir type adsorption isotherms, but no data was available on the free energy involved.

J.O.M. Bokris et al. determined the free energy of adsorption of naphthalene on various metals from M NaClO$_4$ electrolyte, their results being given in Table 19.

Table 19. Net Free Energy of Adsorption

<table>
<thead>
<tr>
<th>Metal</th>
<th>$G^0$ (kcal mole$^{-1}$ at 25°C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>-6.0</td>
</tr>
<tr>
<td>Fe</td>
<td>-7.0</td>
</tr>
<tr>
<td>Cu</td>
<td>-7.0</td>
</tr>
</tbody>
</table>
From the above examples the free energy of adsorption is in the region of \(-4\) to \(-10\) kcal mole\(^{-1}\).

**Complexation**

The addition of a complexing reagent to an electrolyte usually results in the shift of the metal half-wave potential to a more negative value. Free energy values for silver/pyridine complexes calculated from the accumulative stability constant for the following equilibrium reaction:

\[ \text{Ag}^+ + 2\text{Pyr} \rightarrow \text{Ag} \left( \text{Pyr} \right)_2^+ \]

are given in various mixed solvents in Table 20.

Table 20. Accumulative Stability Constant \(\beta_2\) of the \(\text{Ag} \left( \text{Pyr} \right)_2^+\)

<table>
<thead>
<tr>
<th>Medium</th>
<th>(\beta_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 M LiNO(_3) aq</td>
<td>4.19</td>
</tr>
<tr>
<td>&quot; 75% ethanol</td>
<td>3.88</td>
</tr>
<tr>
<td>&quot; 90% dioxan</td>
<td>4.80</td>
</tr>
<tr>
<td>&quot; 90% acetone</td>
<td>5.12</td>
</tr>
</tbody>
</table>

In the aqueous solution alone, \(\Delta H_2^0 = -6.76\) kcal mole\(^{-1}\) and \(\Delta S_2^0 = -13.8\) cal mole\(^{-1}\), so from the expression

\[
\Delta G_2^0 = \Delta H_2^0 - T \Delta S^0
\]

\[
\Delta G_2^0 = -6.76 - 298 \times (-13.8 \times 10^{-3}) \text{ kcal mole}^{-1}
\]

\[
\Delta G_2^0 = -6.4 \text{ kcal mole}^{-1}
\]

Although \(\Delta H_2^0\) and \(\Delta S_2^0\) values are not quoted for the mixed solvent systems, stability constant values indicate that free energy values will probably be of the same order as the above calculated value in aqueous solution.

By a potentiometric method Berthon investigated the complexation of thiourea with silver ions from aqueous solutions. He determined the stability constants for the four successive complexes of \(\text{Ag(Th)}_n^+\), where \(n = 1, 2, 3\) and \(4\), and hence calculated the free energy values. His results (Table 21) suggested that the complexes are bonded through S and N for \(n\) values of one and three, and two and four respectively.
Table 21. Net Free Energy of Complexation of Ag(Th)$_n^+$

<table>
<thead>
<tr>
<th>Complex ion</th>
<th>$G^\circ$ (kcal mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n = 1$</td>
<td>-9.61</td>
</tr>
<tr>
<td>$n = 2$</td>
<td>-4.87</td>
</tr>
<tr>
<td>$n = 3$</td>
<td>-2.87</td>
</tr>
<tr>
<td>$n = 4$</td>
<td>-1.06</td>
</tr>
</tbody>
</table>

Solvation

The physical and chemical properties of a solvent greatly influence the reduction potential of a metal ion. These properties are (a) the dielectric constant, (b) the acid strength, (c) the basic strength. The nature of the ion-solvent interaction or solvation of the ion is extremely difficult to interpret. Physically, solvation of an ion is the transfer of an ion from vacuum to the solvent, whilst chemically solvation describes the stoichiometric chemical reaction with the solvent.

Consider the reduction of silver in different solvents, relevant information being supplied in Table 22.

Table 22. Electrochemical Behaviour of Silver in Various Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
<th>Supporting Electrolyte</th>
<th>$E_1$ (versus SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>78.4</td>
<td>0.1M LiClO$_4$</td>
<td>+ 0.49</td>
</tr>
<tr>
<td>Glacial acetic acid</td>
<td>6.1</td>
<td>0.1M LiClO$_4$</td>
<td>+ 0.635</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>28.5</td>
<td>0.1M LiClO$_4$</td>
<td>+ 0.27</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.6</td>
<td>0.1M LiClO$_4$</td>
<td>+ 0.49</td>
</tr>
</tbody>
</table>

The half-wave potential for silver is more positive in glacial acetic acid than in water. This observation is supported by the theory that solvents with dielectric constants considerably lower than that of water favour the association of oppositely charged ions with the subsequent reduction in solvation energy of the metal ion. Being a large cation and possessing a small charge, the silver ion is not strongly solvated, so
the small change in the half-wave potential of +0.145 V from water to glacial acetic acid is probably to be expected.

Although acetonitrile has a lower dielectric constant than water, the half-wave potential of silver is considerably more negative in this solvent than in water. The strong co-ordinating ability of acetonitrile for silver, with subsequent increase in solvation energy, is thought to be due to the presence of the $- \text{C} \equiv \text{N}$ group.

Besides ion-dipole interactions which are mainly governed by the dielectric constant, the solvation of a metal ion also involves the acid-base properties of the solvent.

B. Case and R. Parsons have accumulated data for the free energies of solution of silver ions in some non-aqueous solvents (Table 23).

Table 23. Free Energies of Solution of Silver Ions in some Non-Aqueous Solvents at 25°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\alpha ^0$ kcal mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>114.4</td>
</tr>
<tr>
<td>MeOH</td>
<td>120.8</td>
</tr>
<tr>
<td>EtOH</td>
<td>120.7</td>
</tr>
<tr>
<td>HCOOH</td>
<td>121.8</td>
</tr>
<tr>
<td>MeCN</td>
<td>124.5</td>
</tr>
</tbody>
</table>

Crystallisation

In the present work silver is being electrodeposited from the solvents pyridine and propylene carbonate and according to P. R. Kellner 'the silver deposits generated from silver perchlorate/pyridine solutions are more aggregated and freer from dendritic structures than deposits generated under equivalent conditions from propylene carbonate based solutions'.

Photomicrographs of silver electrodeposition on platinum from pyridine, propylene carbonate and the propylene carbonate/pyridine mixed solvent system are included in this work (Figure 6l) to show the different natures of the deposits from these solvents. The tabulation format under which the electrolyte composition and experimental conditions of each individual test were recorded is shown in Table 24. The magnification of the deposit is shown on each photomicrograph.

The results clearly show that there is an obvious difference between the crystal forms produced from the three solvents.

To give an idea of the energy change involved in crystallisation, the interfacial free energy of linear polyethylene crystallised from toluene, xylene and octane is of the order of 3.4 kcal mol\(^{-1}\).
Figure 61  Photomicrograph of Silver Deposition on Platinum from Pyridine, Propylene Carbonate and the Propylene Carbonate/Pyridine Mixed Solvent System.
Crystal arrangement was of closely packed, indistinct, disordered forms; oval structures with some degree of angularity and of varying sizes were merged together with smaller forms.

Crystal arrangement was of definite angular forms; the crystal size tended to be somewhat larger than those obtained from pyridine.

Crystal arrangement was of definite angular forms; the crystals were of similar size to those obtained from propylene carbonate.
### TABLE 24

Tabulation Format of Results

<table>
<thead>
<tr>
<th>Salt concentration in gm. per litre</th>
<th>Salt</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Current Density employed in amps per sq.dm.</th>
<th>Time of electroplating in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Observations from magnified Stereoscan Images
SECTION VI

2. DISCUSSION
It has been mentioned previously that solvents with dielectric constants considerably lower than that of water favour the association of oppositely charged ions with the subsequent reduction in solvation energy of the metal ion. Although pyridine has a considerably lower dielectric constant (12.3) than propylene carbonate (69), experiments show that the half-wave potential of silver is more negative in pyridine than in propylene carbonate, hence the silver ion is preferentially solvated by pyridine. This effect could be due to the formation of complex ions between silver and pyridine, the complex ions $\text{Ag(C}_5\text{H}_5\text{N)}^+$ and $\text{Ag(C}_5\text{H}_5\text{H)}_2^+$ being well known. For the formation of a simple complex ion, the change in half-wave potential can be shown to be logarithmic with respect to the concentration of added ligand, an effect of this kind being shown in Figure 60 when pyridine is added to the silver perchlorate/propylene carbonate system. Popa et al. have shown that for the $\text{Ag(C}_5\text{H}_5\text{N)}_2^+$ ion, the stability constant does not change appreciably even in 90% acetone and 90% dioxan solutions and that the net free energy is still of the order of 6 kcal mole$^{-1}$. They attributed any change to an inequality between the effect of solvent on the silver activity and that on the corresponding complex ion activity.

From the available data, the net free energy of adsorption of organic compounds on metal surfaces is of the order of 4 - 10 kcal mole$^{-1}$. Also from a comparison of the study of the effect of straight chain carboxylic acids on the cathode overpotential during the electrodeposition of copper, results show that the changes in the silver perchlorate/propylene carbonate/pyridine system are much smaller than expected for pyridine adsorption. A comparison of results is given in Table 25.
Table 25. Changes in half-wave potential for copper and silver

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electrodeposited</th>
<th>Additive</th>
<th>Conc. (mole(^-1))</th>
<th>(E_2) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Propanoic acid</td>
<td>1.0 (\times) 10(^{-1})</td>
<td>-43.0</td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>Pyridine</td>
<td>1.59 (\times) 10(^{-1})</td>
<td>-2.0</td>
<td></td>
</tr>
</tbody>
</table>

The free energy change from the silver perchlorate/propylene carbonate system to the silver perchlorate/pyridine system has been calculated to be of the order of \(-0.28\) kcal mole\(^{-1}\). From the available data, the free energies of adsorption and complexation are in the region of 3 - 10 kcal mole\(^{-1}\), therefore these two effects do not appear responsible for the observed change.

Since primary and secondary amines combine chemically with propylene carbonate to form carbonates,\(^5^4\) there is the possibility that some interaction takes place between pyridine and propylene carbonate and also the silver ion, with a corresponding increase in the solvation energy.

It has also been noted that there is a difference in the nature of crystallisation of the electrodeposited silver in the two solvents propylene carbonate and pyridine, and since, from the available data, the free energy change between different crystalline states is probably of the order of 1 kcal mole\(^{-1}\) or less, this effect is another possibility.
SECTION VII

CONCLUSIONS
1. A silver nitrate/pyridine salt was prepared by direct combination of silver nitrate and pyridine, though little evidence was forthcoming for the interaction using ultra-violet and infra-red spectroscopic techniques.

2. Using the $\lambda$ max of pyridine at 257nm, the molecular weight of the salt was determined in methanol and the experimental value of 324 corresponded closely to the formula $\text{Ag(Py)}_2\text{NO}_3$.

3. Using the dropping mercury electrode, it was not possible to determine the half-wave potential of silver in aqueous solutions containing either silver nitrate or $\text{Ag(Py)}_2\text{NO}_3$ since silver is reduced at potentials more positive than that needed to oxidise mercury.

4. Using the dropping mercury electrode, it was again not possible to determine the half-wave potential of silver in methanolic solutions containing either silver nitrate or $\text{Ag(Py)}_2\text{NO}_3$ since silver is reduced at potentials more positive than that needed to oxidise mercury.

5. In methanol the salt $\text{Ag(Py)}_2\text{NO}_3$ was soluble in 0.7M LiCl, but no reduction wave due to silver was obtained using the dropping mercury electrode.

6. Using a silver cathode and molybdenum anode no reduction wave for silver was obtained at -0.55V (versus the molybdenum electrode) from aqueous solutions of silver nitrate in 0.1M sulphosalicylic acid as reported by previous workers.

7. Using a stationary silver micro-electrode and a molybdenum anode, a reduction wave for silver was obtained at +0.2V (versus the molybdenum electrode) from aqueous solutions of silver nitrate in 0.1M sulphosalicylic acid. Manual recordings of the current-voltage curves showed that the diffusion current was proportional to the silver concentration over the range $2.5 \times 10^{-4}$M to $2 \times 10^{-3}$M.
8. On leaving the silver and molybdenum electrodes in contact with an aqueous solution of silver nitrate in 0.1M sulphosalicylic acid, a wave developed at about -0.55V (versus the molybdenum electrode) and the amplitude of this wave increased with time.

9. Qualitative analysis and atomic absorption spectrometry showed that the resulting solution contained molybdenum. Electron probe micro-analysis showed the presence of silver on the molybdenum electrode.

10. The colour and nature of the silver deposit obtained on the molybdenum electrode were dependent on the electrolyte and the pH of the solution.

11. Careful removal of the silver deposit revealed a shiny black coating on the molybdenum electrode. X-Ray Crystallography showed this deposit to be some form of molybdenum.

12. A more concentrated aqueous solution of silver in 0.1M sulphosalicylic acid in contact with a molybdenum wire produced a yellow solution in time. A yellow solution was obtained when ammonium molybdate was dissolved in 0.1M sulphosalicylic acid.

13. Using a special cell containing a solution of silver nitrate in 0.1M sulphosalicylic acid in contact with molybdenum wire, the change in absorbance at 343nm was continuously monitored. The exchange reaction between the molybdenum electrode and silver ions was shown to be a first order reaction with respect to the silver ion concentration. A further experiment showed that the value of the rate constant was directly proportional to the area of the molybdenum electrode.

14. Anhydrous silver perchlorate decomposed in the solvents propylene carbonate, pyridine, and N,N-dimethylformamide, though least rapidly in pyridine, a black deposit only appearing after a few days. In propylene carbonate and N,N-dimethylformamide colouration of the solutions took place within two minutes of the addition of silver perchlorate (10^-2M).
A 'silver mirror' eventually formed from the N,N-dimethylformamide solution.

15. In solutions of propylene carbonate and N,N-dimethylformamide containing silver perchlorate, the addition of a small quantity of perchloric acid (10^{-3} M) merely served to slow down the rate of decomposition of the silver perchlorate. During the period of observation (ten weeks), no decomposition was apparent in the pyridine/silver perchlorate/perchloric acid system.

16. With a stationary platinum micro-electrode as the cathode and a molybdenum wire anode, reduction peaks were obtained for silver in pyridine, propylene carbonate and N,N-dimethylformamide. The reduction peak for silver in propylene carbonate was at a more positive potential than those in pyridine and N,N-dimethylformamide.

17. In the presence of perchloric acid (to slow down the rate of decomposition of the silver perchlorate) quantitative experiments showed that silver may be determined in quiet solutions from propylene carbonate with a stationary platinum micro-electrode, provided the determination is carried out with reasonable speed. The presence of a white coating on the molybdenum electrode, however, suggested that an exchange reaction was taking place between the molybdenum electrode and silver ions as had been observed in aqueous systems. The exchange reaction was also accompanied by the appearance of rust coloured particles in the solution.

18. By incorporating a platinum counter electrode in the polarographic cell, a three electrode cell was adopted. The molybdenum electrode was replaced by a silver wire electrode. Good S-shaped current-voltage curves were obtained for the reduction of silver in propylene carbonate, pyridine and N,N-dimethylformamide using a vibrating platinum micro-electrode. The current-voltage curves were reproducible to within one millivolt.
19. Analysis of the current-voltage curves obtained for the reduction of silver in propylene carbonate and pyridine for a reversible reaction yielding an insoluble product, namely silver metal at a platinum surface, showed them to correspond to one electron reductions.

20. The diffusion currents for the reduction of silver in pyridine and N,N-dimethylformamide were much higher than the diffusion current obtained for the reduction of silver in propylene carbonate for the same silver perchlorate concentration.

21. In propylene carbonate (10^{-3}M in perchloric acid), silver may be determined quantitatively using a vibrating platinum micro-electrode. Good linearity was observed between the diffusion current and the silver perchlorate concentration from 2.0 \times 10^{-4}M to 7.0 \times 10^{-3}M.

22. The half-wave potential for silver in propylene carbonate was dependent on the silver concentration.

23. Under identical cell conditions the diffusion current obtained with the vibrating platinum electrode was approximately ten times larger than that obtained with the stationary platinum micro-electrode of the same area.

24. The addition of water, pyridine and N,N-dimethylformamide or the absence of perchloric acid moved the half-wave potential of silver in propylene carbonate to a more negative value.

25. The addition of propylene carbonate or perchloric acid moved the half-wave potential of silver in pyridine to a more positive potential.

26. The addition of pyridine did not affect the half-wave potential of silver in N,N-dimethylformamide, but in the absence of perchloric acid this value was considerably more negative.
27. When pyridine was added to a solution of silver perchlorate in propylene carbonate in the presence of perchloric acid ($10^{-3}$ M), the change in the half-wave potential of silver towards the negative side was almost logarithmic with respect to the pyridine concentration.

28. The half-wave potentials of silver in the silver perchlorate/pyridine and silver perchlorate/propylene carbonate systems were $-0.036$ V and $-0.024$ V respectively versus the silver electrode.

29. The small change in the half-wave potentials of silver (-12 mV) in the two solvents propylene carbonate and pyridine is thought to be attributed to either solvation, or the change in characteristics of the electrodeposited silver crystals.
SECTION VIII

REFERENCES
1. L. Brugnatelli;
   Ann.Chim. (Pavia), 18 152 (1800)

2. C.L. Faust & B.Thomas;
   Trans. Electrochem. Soc., 75 185 (1939)

3. L.E.Stout & W.G.Thummel;
   Trans Electrochem. Soc., 52 337 (1931)

4. R.R.Benham;

5. D.G.Foulke & M.B.Diggin;
   Modern Electroplating, 2nd. Edt., P.A.Lowenheim Ed.,
   (Wiley, N.Y., 1963), Chapter 14

6. D.Wood;

7. M. Lyons & W. Millward;
   British Patent, 11,632 (1847)

8. M. Schlotter;
   British Patents 443,428 and 443,429 (1936)

9. A. Schwedhelm & K. Kull;
   German Patent, 921,184 (1954)

10. A. Kutzelnigg;
    German Patent, 836,721 (1952)

11. A. Gildbach & S. Korpian;
    German Patent, 959,775 (1957)

12. C. Wernlund & J. Macon;
    U.S. Patent, 2,429,970 (1947)

13. A. Kutzelnigg;
    German Patent, 848,891 (1952)
14. R. Cransberg & H. van Oosterhout;
   German Patent, 917,584 (1954)

15. J. Fischer & W. Schwarze;
   U.S. Patent, 2,800,439 (1957)

16. O. Kardos;
   U.S. Patent, 2,666,738 (1954)

17. R. Weiner;
   German Patents, 750,185 (1945) and 879,048 (1953)

18. B. Ostrow;
   U.S. Patent, 2,777,810 (1957)

19. L. Greenspan;
   U.S. Patents, 2,735,808 and 2,735,809 (1956)

20. W. Metzger;
   Metallflaeche, 13(3) 91 (1959)

21. M. Schloetter;
   British Patent 1,125,165 (28.8.1968)
   Chem. Abstr., 69 7753 (1968)

22. Y. Y. Matulis;
   Chem. Abstr., 62 15,768 (1965)

23. A. Skolnik;
   Austrian Patent 248,191 (11.7.1966)
   Chem. Abstr., 65 8356 (1966)

24. O. Radio & V. Vallalat;
   French Patent 1,533,369 (19.7.1968)
25. D. M. Lyde & K. Rickhuss;
French Patent 1,540,175 (20.9.1968)

26. B. R. Georgievskii;
Electrokhimiya 5(7) 838-40 (1969 Russ.)
Chem. Abstr., 71(18) 496 (1969)

27. A. G. Schering;
French Patent 1,429,801 (17.1.1966)
Chem. Abstr., 65, 1776 (1966)

28. E. E. Kravtsov et. al.;
U.S.S.R. Patent 295,824 (12.2.71)
Chem. Abstr., 75(6) 577 (1971)

29. S. Eaton;
U.S. Patent, 2,610,143 (1952)

30. N. V. Kuronova & A. M. Katyshev;

31. L. Kahlenberg;
J. Phys. Chem., 4 349 (1900)

32. P.R.Kellner & D.S.Allam;
revised U.K.Patent 1,033,821 (29.4.1966)

33. P.R.Kellner & D.S. Allam;

34. P. R. Kellner;

35. F. A. Cotton & G. Wilkinson;
'Advanced Inorganic Chemistry'
(Interscience Publishers, 1962)
36. I. M. Kolthoff & J. J. Lingane;
   (Interscience Publishers, N.Y., 1952) chap. I

37. J. Heyrovsky & D. Ilkovic;

38. See 36.- Vol. 2.

39. E. B. Srigar;
   Rec. trav. chim., 44, 549 (1925)

40. R. M. Dagnall & T. S. West;
   Talanta, 2, 925-929 (1962)

41. R. F. Large & E. P. Przybylowicz;
   Anal. Chem., 36(8), 1648-52 (1964)

42. H. L. Kies et al.;

43. R. W. Murray & R. L. McNeely;

44. P. S. Shetty & P. R. Subbaraman
   Indian J. Chem., 2(10), 397-8 (1964)
   Chem. Abstr., 62, 3398 (1965)

45. J. Broadhead & P. J. Elving;

46. A. A. Vloek;

47. J. Heyrovský and J. Kuta;
   'Principles of Polarography'
48. D. MacGillavry;

49. G. B. Bachman & H. J. Astle;
    J. Am. Chem. Soc., 64 1303, 2177 (1942)

50. J. Cihalik et. al.;

51. H. A. Laitinen & C. E. Shoemaker;
    J. Am. Chem. Soc., 72 663, 4975 (1950)

52. W. Hubicki & W. Dabkowska;

53. I. M. Kolthoff & J. F. Coetzee;

54. H. J. McComsey & M. S. Spritzor;
    Analytical Letters, 3(8) 427-441 (1970)

55. C. K. Mann;
    'Electroanalytical Chemistry', A Series of Advances, Vol. 3, 

56. C. K. Mann & K. K. Barnes;
    'Electrochemical Reactions in Nonaqueous Systems', 
    (Marcel Dekker, Inc., N.Y.) 1970

57. J. F. Coetzee & J. L. Hedrick;

58. R. C. Larson & R. T. Iwamoto;

59. F. Farha, Jr., & R. T. Iwamoto;
    J. Electroanal. Chem., 8 58 (1964)
60. V. Gutmann & G. Schober;
    Monatsch, Chem., 88 206 (1957)

61. J. P. Coetzee & W. S. Siao;

62. A. A. Vlcek;


64. C. L. Olson & R. N. Adams;

65. R. N. Adams;
    'Electrochemistry at Solid Electrodes' 
    (Marcel Dekker, Inc., N.Y.) 1969

66. Y. S. Lyalkov et. al.;
    Zavod. Lab., 34(I) 8-9 (1968)
    Chem. Abstr., 62(1) 1489 (1968)

67. V. Vrtlikova & R. Kalvoda;
    Chem. Zvesti, 18 410-13 (1964)
    Chem. Abstr., 61 10028 (1964)

68. B. N. Rybakov et. al.;
    Ref. Zh., Chem., Abstr. No. 19D33
    Chem. Abstr., 56 13539 (1962)

69. G. W. Tindall & S. Brockenstein;

70. L. Nucci & G. Raspi;
    J. Electroanal. Chem., 22(1) 139-146 (1969)
71. D. Sandoz et al.;

72. U. Eisner & H. B. Mark;

73. R. Nakashima et al.;
   Nagoya Kogyo Gijutsu Shikensho Hokoku, 17(9-10) 241-4 (1968) Japan

74. N. A. Kolpakova et al.;
   Chem. Abstr., 71(10) 541 (1969)

75. Yu. K. Delimarskii et al.;
   Zh. fiz. khim., 22 1108 (1948)

76. H. C. Gaur and H. L. Jindal;

77. I. I. Naryshkin et al.;

78. K. J. Bachmann & J. K. Dohrmann;

79. Chemtrix, Inc.;
   P. O. Box 725,
   Beaverton, Oregon.

80. Simac Instrumentation Ltd.;

81. M. R. Dhaneshwar;
   Ph.D. thesis,
   University of Poona, 1967
82. V. T. Athavale et. al.;
    Analyst, 94  855-859 (Oct., 1969)

83. A. I. Vogel;
    'Macro and Semimicro Qualitative Inorganic Analysis',
    (Longmans, 1962), 4th. edition

84. R. M. Novik & L. I. Dugaeva;
    Chem. Abstr., 74(26) 617 (1971)

85. P. D. T. Coulter & R. T. Iwamoto;
    J. Electroanal. Chem., 13, 21, 28  (1967)

86. G. A. Barbieri;
    Ber., 60  2424 (1927)

87. A. A. Noyes et. al.;
    J. Am. Chem. Soc., 59  1316 (1937)

88. H. Schmidt & H. Stange;

89. F. L. Lambert;
    Anal. Chem., 30  1018 (1958)

90. R. Nelson & R. N. Adams;
    J. Electroanal. Chem., 13  184 (1967)

91. J. C. Schumacher;
    'Perchlorates', A.C.S. Monograph No. 146,
    (Rheinhold, New York, 1961)

92. E. D. Harris & A. J. Lindsay;
    Nature, 162  413 (1948)

93. E. D. Harris & A. J. Lindsay;
    Analyst, 76  647 (1951)
94. A. J. Lindsay;
   J. Phys. Chem., 56 439 (1952)

95. L. Meites;
   'Polarographic Techniques', 2nd. edition,
   (Interscience, New York, 1965) p. 72

96. J. B. Headridge;
   'Electrochemical Techniques for Inorganic Chemists'

97. D. Rogers et al.;

98. A. B. Thomas and E. G. Rochow;


100. A. H. Herz et. al.;
    'Advances in Chemistry', Series 79, edited by R. F. Gould,

101. J. O. M. Bokris et. al.;
    J. Electroanal. Soc., 111 743 (1964)

102. J. G. Sillén and A. E. Martell;
    'Stability Constants Supplement', No. 1
    (Chem. Soc., 1971)

103. G. Berthon & C. Luca;
    Chem. Abstr., 71(2) 316 (1969)
104. J. F. Coetzee & C. D. Ritchie;  
'Solute-solvent Interactions'  
(Marcel Dekker, New York, 1969)

105. R. C. Larson & R. T. Iwanoto;  
J. Am. Chem. Soc., 82, 3239 (1960)

106. B. Case & R. Parsons;  
Trans. Faraday Soc., 63(2) 1224 (1967)

107. R. K. Sharma;  
Chem. Abstr., 74(26) 13 (1971)

108. G. Popa et. al.;  