

ELECTROCHEMICAL STUDIES

IN

ANHYDROUS FORMIC ACID.

A THESIS

Presented to the University of Cape Town

for the Degree of

Doctor of Philosophy

by

T. A. PINFOLD, B.Sc.(Hons).

Department of Chemistry,
University of Cape Town,
March, 1956.

The copyright of this thesis vests in the author. No quotation from it or information derived from it is to be published without full acknowledgement of the source. The thesis is to be used for private study or non-commercial research purposes only.

Published by the University of Cape Town (UCT) in terms of the non-exclusive license granted to UCT by the author.

TO

MOTHER AND OUPA

"Alles zal recht komen,

Als iedereen zyn plicht doet."

ACKNOWLEDGMENTS.

The author wishes to express his sincere appreciation and indebtedness to

- (1) Dr. F. Sebba for his unfailing interest and his ever-ready guidance and advice throughout the course of this research.
- (2) Professor F. Holliman and Dr. A.H. Spong for their interest generally.
- (3) Mr. J.H. Sutton for being the most helpful and obliging Storeman with whom it has been his pleasure to work.
- (4) Mr. W.C. Lewis for his excellent work in the construction of numerous pieces of apparatus that were required.
- (5) Mr. M.C.B. Hotz, B.Sc., for the measurements of the conductance of formic acid and his assistance in the use of the Karl Fischer titration apparatus.
- (6) All the members of the Department of Chemistry of the University of Cape Town for their kind co-operation.
- (7) The Council for Scientific and Industrial Research for a Research Scholarship (1955-56).

C O N T E N T S.

| | Page |
|---|------|
| Introduction | 1 |
| Section A - General | 4 |
| Section B - Experimental | 10 |
| Section C - The Quinhydrone-in-Formic Acid Electrode | 31 |
| Section D - Inorganic Polarography | |
| (I) Bismuth | 43 |
| (II) Antimony | 48 |
| (III) Lead | 53 |
| (IV) Tin | 59 |
| (V) Thallium | 64 |
| (VI) Cadmium | 70 |
| (VII) Indium | 77 |
| (VIII) Nickel | 93 |
| (IX) Zinc | 96 |
| Section E - Electrocapillary Curves | 102 |
| Section F - Polarographic Overcurrents | 114 |
| Section G - Organic Polarography | 139 |
| Discussion | 147 |
| Bibliography | 153 |

INTRODUCTION

INTRODUCTION.

Although anhydrous formic acid exhibits all the properties required by a solvent for ideal polarographic characteristics, no study of the dropping mercury electrode in this medium has hitherto been described. Formic acid besides having a high dielectric constant (56.1 at 25°C (1)) and considerable ionizing properties, also exhibits a strong solvent action upon many organic compounds. Furthermore, it has been shown by Pleskov (2) to be a solvent with small complexing power, a feature which enhances its value for the examination of ions which are normally hydrated in aqueous solution. The above author also showed that the standard electrode potentials in formic acid, of the elements he studied, differed little from the values found in aqueous solution. Exceptional behaviour was shown by zinc and cadmium the potentials of which were displaced to more positive values. This shift was attributed to hydration of ions in aqueous solution as opposed to the absence of solvation in formic acid.

The remaining electrochemical investigations in anhydrous formic acid have been confined to conductance measurements, the measurement of transport numbers and potentiometric titrations.

The conductance measurements were made almost entirely

by Schlesinger and his co-workers. The conductivities of ammonium (3) alkali (4) and alkaline earth (5) formates as well as hydrogen chloride (6) solutions in anhydrous formic acid were measured together with the behaviour of mixtures of two salts containing a common ion (7). More recently Lange (8) has measured the conductance of potassium chloride in this solvent. Schlesinger and Bunting (9) obtained values for the transference numbers of the formates of sodium potassium and calcium in formic acid.

The outcome of these experiments was that anhydrous formic acid should be considered to be a highly acidic solvent; hydrogen chloride was, for example, found to be incompletely ionised, while salts such as the alkali and alkaline earth formates, which are bases in anhydrous formic acid, were highly ionized.

A number of workers (10-15) have employed anhydrous formic acid as the medium for potentiometric titrations and conclude that "formic acid is more like water, than is such a solvent as acetic acid, in that solutions of salts give cryoscopic and conductivity values which correspond to extensive dissociation. With respect to acidity and basicity, however, formic acid differs greatly from water, and solutions in it are even more deserving of the term superacid than those acetic acid solutions in which the pioneer work on the potentiometric investigation of strongly acid solvents was done".

In view of the interesting properties shown by anhydrous formic acid, it was decided to investigate the electrochemical properties of this solvent, paying particular attention to its suitability for the reduction of electroreducible ions at a dropping mercury cathode.

SECTION A.

GENERAL.

GENERAL.

It is desirable before discussing the polarographic investigation of anhydrous formic acid solutions, to give a resume of the equations used for the calculation of appropriate quantities.

The fundamental equation on which all quantitative polarographic calculations are based is that due to Ilkovic (16, 17)

$$i_d = 607 n D^{1/2} C_m^{2/3} t^{1/6} \dots\dots\dots (1)$$

where i_d is the average current in microamperes during the life of a drop, n is the number of Faradays of electricity required per mole of the electrode reaction, D is the diffusion coefficient of the reducible substance in the units $\text{cms.}^2/\text{sec.}$, C is its concentration in millimoles/litre, m is the rate of flow of mercury from the dropping electrode capillary expressed in the units mgs./sec. and t is the drop time in seconds.

The diffusion current constant, the value of which has been measured for each inorganic cation in anhydrous formic acid is

$$I = \frac{i_d}{C_m^{2/3} t^{1/6}} = 607 n D^{1/2} \dots\dots\dots (2)$$

This quantity should be independent of the character-

istics of the capillary tube used for the dropping electrode and thus characteristic of each ionic species. Because it neglects the curvature of the electrode surface, however, the Ilkovic equation is not strictly valid and, in consequence, the diffusion current 'constant' does show a small variation from one capillary tube to the next. In this investigation however, only approximate values were required, in order to compare with those in aqueous solution. For this purpose Eqn. 2 was quite adequate.

In order to offer some information on the size of the ion under investigation the diffusion coefficient of each has been calculated from Eqn. 2. These results, although obtained from careful measurements, must be regarded as no more than approximations.

Most of the inorganic cations investigated were found to undergo complex formation in the presence of various supporting electrolytes. The structure of some of these complex ions was achieved by measurement of the half-wave potential at two different concentrations of the complex ion.

$$\frac{E_{1/2}}{\log C} = -p \times \frac{0.0591}{n} \dots\dots\dots (3)$$

The above formula gives an approximate value of p, the co-ordination number of the metal ion. The concentration of the complexing supporting electrolyte is denoted by C

while n has the same value as in Eqn. 1.

The structure of only a few complex ions could be attempted because of a lack of knowledge of the liquid-junction potential between anode and cathode compartments, and consequently an uncertainty in the actual value of the change in the half-wave potential. On the occasions when values of the ionic conductance in formic acid of the ions considered, were available, the liquid junction potential was calculated using the Hendersen Equation)18)

$$E_d = - \frac{RT}{F} \frac{D'' - D'}{S'' - S'} \ln \frac{S''}{S'} \dots\dots\dots (4)$$

where $D = (\sum C_i l_i)$ cations - $(\sum C_i l_i)$ anions

$S = (\sum C_i Z_i l_i)$ cations + $(\sum C_i Z_i l_i)$ anions

where l is the ionic conductance at infinite dilution of the ion considered, Z its valence and C its concentration.

Employing this equation it was calculated that the half-wave potentials of the ions should shift by 20 millivolts to more negative potentials on increasing the concentration of sodium formate, used as supporting electrolyte, from 0.5 M to 2.0 M. The observed shifts were found to be close to this value.

In order to determine whether a given element was reversibly or irreversibly reduced, a plot was made from each polarogram of E vs $\log \frac{1}{i_d - i}$ where i_d is the value of

the diffusion current and i the value of the current at an applied potential of E . The theoretical values of the slope of this plot for reversible one-, two- and three electron reductions are 0.020, 0.030 and 0.059. This slope has been labelled ' $\tan \alpha$ ' for brevity, a value being quoted for each reduction.

It has been decided in this dissertation to discard the usual practice of referring to peaks on the diffusion current as "polarographic maxima" and hence forth to name them "polarographic overcurrents". The reason for this change is two-fold. Firstly, as the height of these overcurrents will be shown to vary, passing through maximum values, the confusion of referring to maximal maxima is avoided. Secondly, the term is believed to be a better description of the phenomenon than the non-committal term of "maximum".

Two actual polarograms have been included, one for lead and the other for thallium. The polarogram for lead is so typical of those measured for all the elements that it is included as a general photograph. The picture for thallium is included to show the way in which all the waves measured were spread out as much as was practically possible, by decreasing the voltage scan, to increase the accuracy in measuring the half-wave potential.

Several of the supporting electrolytes such as potassium sulphate, sodium citrate, etc. had added to them certain amounts of sodium formate. In the cases of bismuth, antimony, lead and tin, this was done mainly to ensure complete suppression of the overcurrent (See Section E). With other elements the addition of sodium formate was found to greatly improve the shape of the wave. This addition lowered the resistance of the polarographic cell appreciably, thus rendering the voltage drop correction of much less consequence and ensuring that the movement of the ions to the mercury-solution interface was completely diffusion controlled.

In order to obtain a value of the diffusion current constant, the diffusion currents at known electro-reducible ion concentrations have been measured for each of the elements. Although the figures are quoted in each case, the curve has only been plotted in the case of bismuth and indium. With the exception of indium, which shows unusual behaviour, all the curves were similar to that for bismuth differing only in slope. It was thus felt that nothing would be achieved by including curves for all the elements and in these cases only the results are included.

It was decided to precede the polarographic investigation of each inorganic cation with an examination of the effect of an added quantity of distilled water on the half-

wave potential. The addition of 2% (v/v) of water was thus made in the case of each element.

Whenever complex formation has been shown to occur in formic acid solutions, an attempt has been made to give the structure of the complex ion by quoting the corresponding complex species formed in aqueous solution.

The range of measurable potentials in formic acid using the quinhydrone-in-formic acid electrode was between +0.2 volts and -0.8 volts vs S.C.F.A.E. Potentials more positive than +0.2 volts were excluded due to the presence of anodic waves, while at potentials more negative than -0.8 volts, the wave due to the discharge of hydrogen interferes.

SECTION B.

EXPERIMENTAL.

EXPERIMENTAL.

Apparatus:

The instrument used for this investigation was a Heyrovsky polarograph Model V301, the polarograms being photographically recorded. The galvanometer used (W.G. Pye and Co. Ltd., Cambridge, England) had the following characteristics - Period 9.8 secs, Resistance 1890 ohms, Critical damping resistance 24,000 ohms, the reflector being a plane mirror with a front lens focus of 100 cms.

The resistance of the polarographic cell was measured using an A.C. Nivoc Wheatstone Bridge as supplied by George and Baker Ltd., London, at 115 volts and 50 cycles/sec. The null point of the bridge was determined using a magic-eye valve bridge balance detector.

The thermostatic bath which was used had a capacity of 90 litres and was heated by a rectangular coil, resistance 165 ohms, the temperature being maintained by a spiral toluene - mercury thermo-regulator. The liquid was stirred by a propeller-type stirrer of diameter 12 cms. set at an angle to the vertical. A temperature of $25.00 \pm 0.01^{\circ}\text{C}$ was readily maintained.

The mercury used throughout was purified by allowing it to run through a tube one metre long containing 5% nitric acid, filtering and then distilling twice, in an atmosphere of dry nitrogen, under reduced pressure. All contact between the

mercury used and the wires of the apparatus were made by platinum-glass seals to prevent any amalgamation.

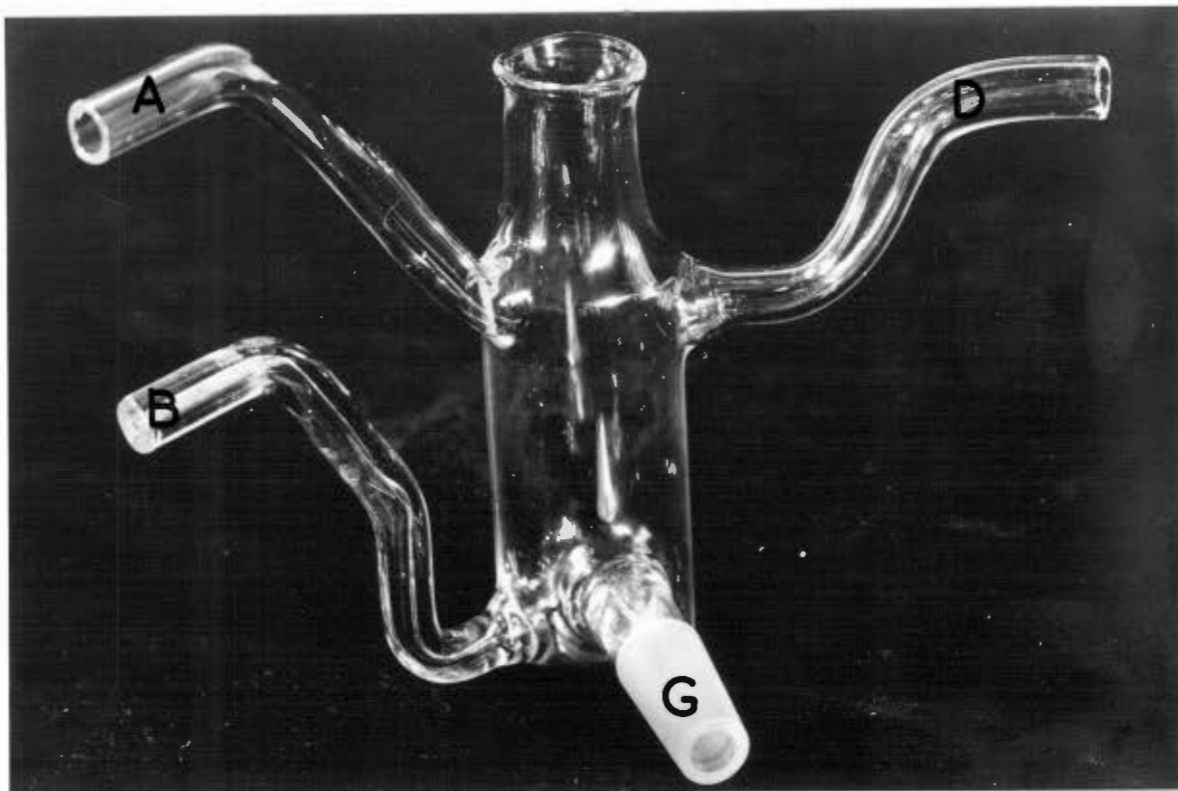
The potentials recorded were measured using a Cambridge Slide Wire Potentiometer and a recently standardised Weston Cell, the E.M.F. of which was 1.01835 volts at 25°C. The difference of potential applied to the polarographic cell was supplied by a DFG Constant Voltage Exide 2 volt accumulator which was found to maintain a constant voltage to 0.2 millivolts.

The head of mercury, (h), that is the height of the mercury column between the level in the reservoir and the tip of the dropping electrode was measured with a cathetometer. In order to facilitate the adjustment and accurate measurement of h, use was made of the arrangement described by Lingane and Laitinen (19) shown in Plate 1.

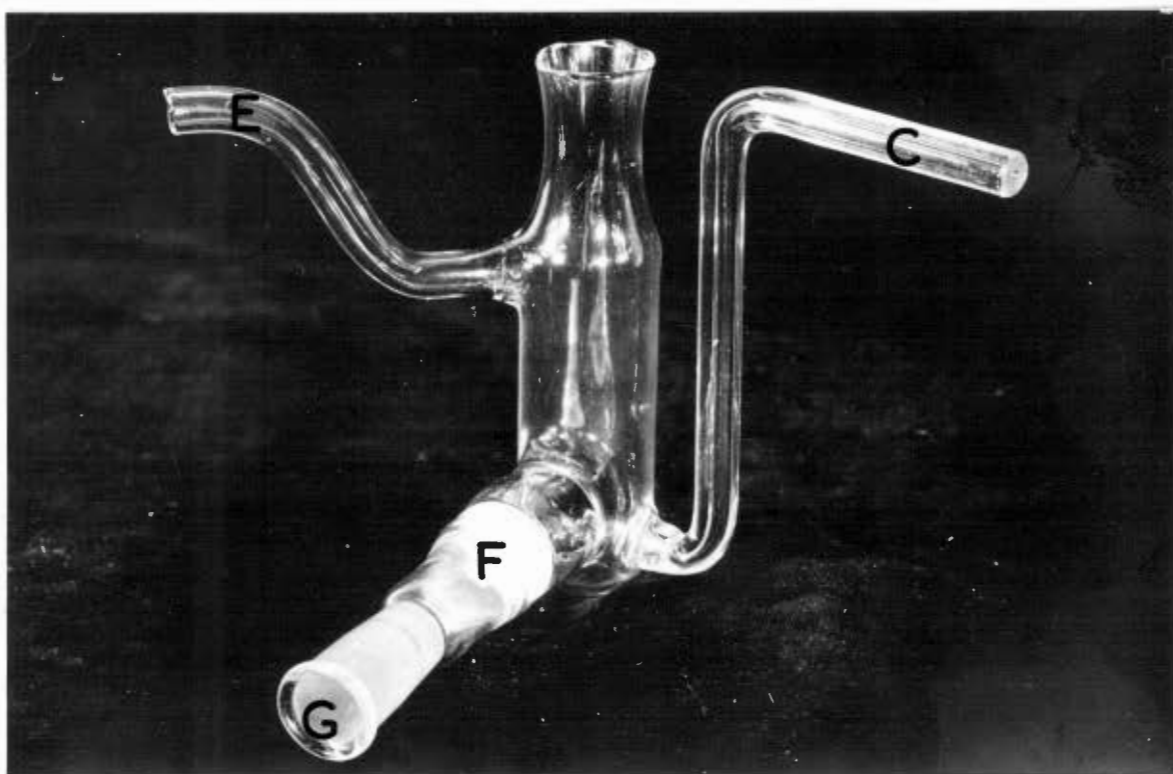
The Polarographic Cell:

The polarographic cell used in this research is exhibited overleaf in photographs 1 - 4. Photographs 1 and 2 show the cathode and anode compartments respectively, separated, and in 3, the cell is shown complete. The fourth view taken from above, is included to clarify the positions of the nitrogen inlet and outlet tubes with respect to one another.

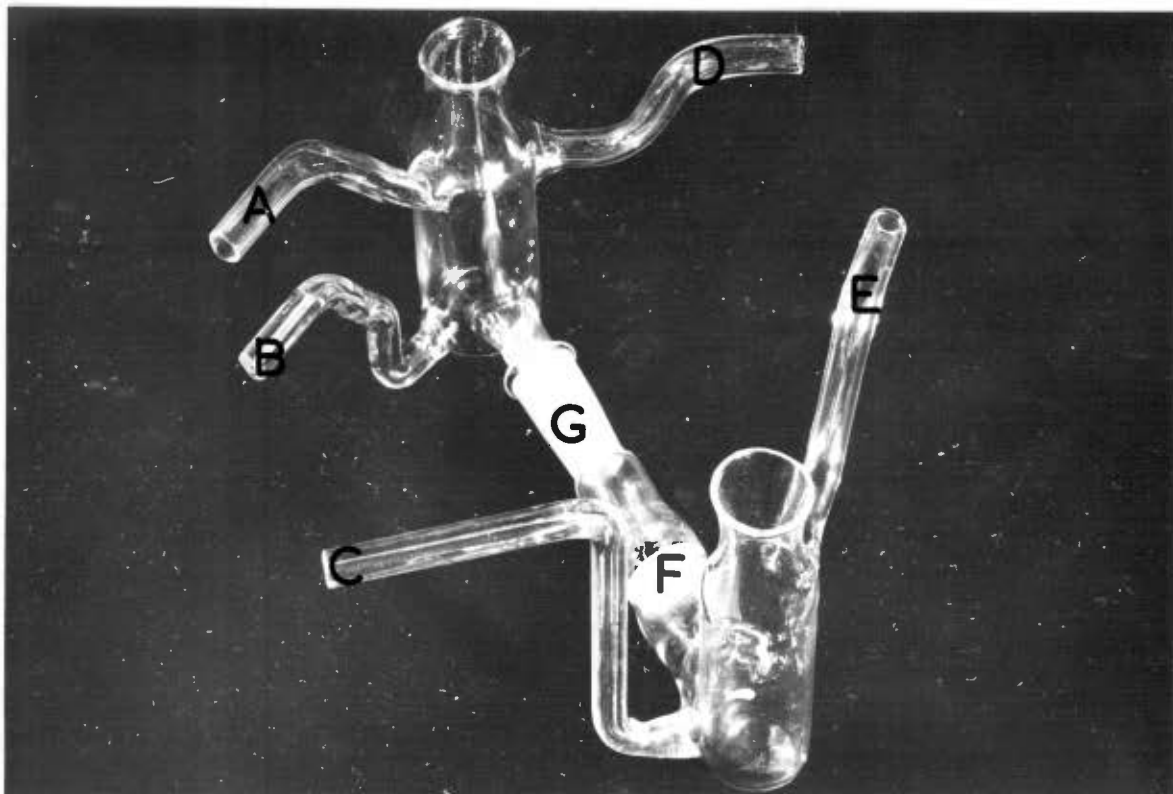
Tubes A, B and C are joined by a Y-joint to the nitrogen source, while the outlet tubes D and E are connected by a second Y-joint to a drying tube of calcium chloride, open to the air. Capillary tubes of 1 mm. bore at B and C ensure a



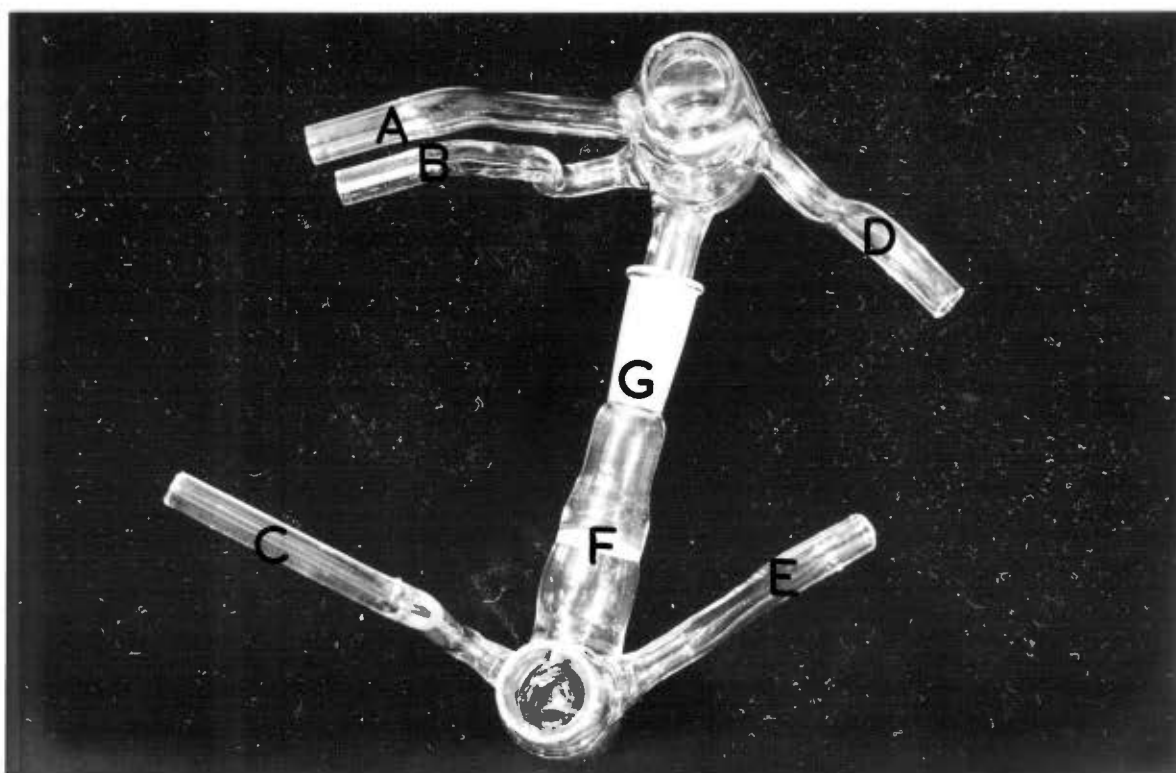
1



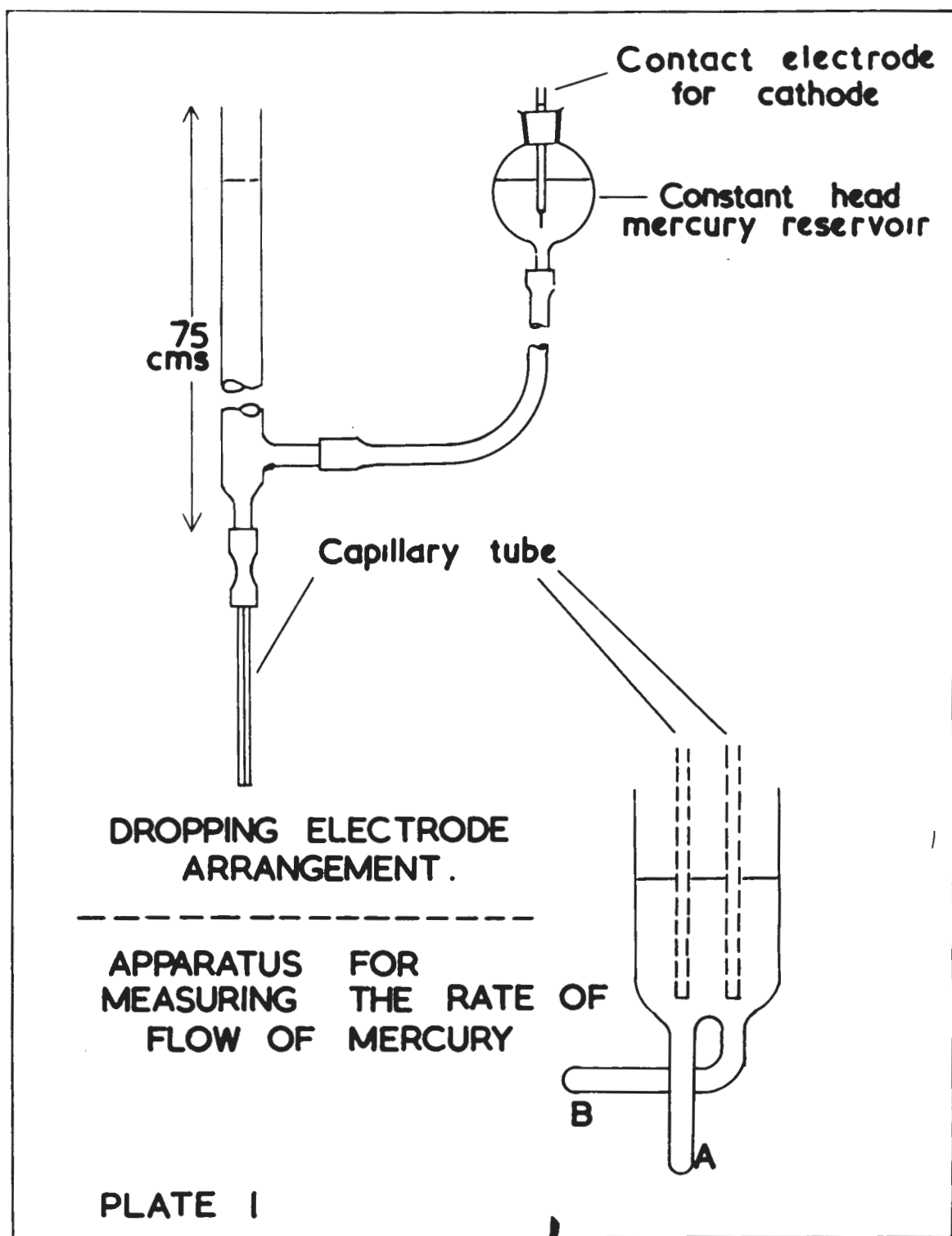
2



3



4



steady stream of nitrogen in each compartment. A two-way tap links A and B such that, when the removal of the dissolved gases in the cathodic electrolyte is complete, the stream of nitrogen is maintained through tube A, over the surface of the liquid, thus eliminating any possible ingress of oxygen through tube D (20). The compartments are joined by a Bl2 ground-glass joint G, maintained completely watertight by application of Dow Corning High Vacuum Silicone grease which is insoluble in formic acid. The cathodic and anodic electrolytes are separated by a sintered glass disc F, the pore size of which was 5 - 10 microns; this was found to be most satisfactory, in that, while maintaining a sharp solution interface, the electrical resistance of the cell was not greatly increased.

The nitrogen used was first bubbled through alkaline pyrogallol to remove any oxygen present and then thoroughly dried by passing over phosphorus pentoxide. In quantitative determinations, the dried nitrogen was initially saturated with formic acid by bubbling the gas through a tube of the anhydrous solvent, thus ensuring that there was no increase in the concentration of the solution caused by loss of the solvent due to vaporisation.

The Calibration of Polarograms:

In order to measure the absolute value of the diffusion current, a knowledge of which is of fundamental interest, it was necessary to calibrate the polarograms. The polarographic

circuit was modified by inclusion of a double-pole double-throw switch such that the cell could be replaced by a standard 10,000 ohm resistance. By application of a suitable voltage, the light spot from the galvanometer was made to deflect about one quarter of the way across the drum of the polarograph. The shutter was then opened for two seconds, thus recording its position on the photograph by a black dot: the fall of potential measured across the standard resistance enabled the current flowing to be readily calculated by Ohms Law. The voltage was then increased so that the light spot was deflected half way across the drum and the above procedure repeated. Finally a third measurement was made with the spot three quarters of the distance across the drum.

The outcome of these measurements was that the polarogram was labelled with three dots at which the current was accurately known and by comparison with which, the diffusion current could readily be computed.

The Capillary for the Dropping Mercury Electrode.

(1) Measurement of the capillary radius:

The usual method for this operation was employed, viz. an unbroken thread of electrolytically purified mercury was introduced into the capillary tube and its length was measured with a travelling microscope. The density of mercury at the temperature of the experiment was known from tables and thus the tube radius was readily computed. The results obtained

are tabulated below:

TABLE 1.

| No. | Length of thread (cms) | Temp. t°C (°C) | Density of mercury at t°C (gms/cc) | Wt. of mercury (gms.) | Radius of tube (mm.) |
|-----|------------------------------|----------------------|---|-----------------------------|----------------------------|
| 1 | 11.065 | 18.1 | 13.551 | 0.00778 | 0.0406(4) |
| 2 | 10.225 | 18.5 | 13.550 | 0.00726 | 0.0408(4) |
| 3 | 10.809 | 18.4 | 13.550 | 0.00780 | 0.0411(7) |
| 4 | 10.440 | 18.1 | 13.551 | 0.00742 | 0.0408(6) |

Mean radius = 0.0409 mm.

Variation of above results 1%

Length of capillary tube = 12.495 cms.

The uniformity of bore of the capillary tube was tested by introducing a thread of mercury about 2 cms. long and measuring its length in various parts of the tube. Allowing for slight temperature variations, this length remained constant, showing the tube to be suitable for use as a dropping electrode.

(2) Care of the Capillary Tube:

After use the capillary tube was washed with distilled water, then absolute alcohol and was finally immersed in a pool of mercury. It was occasionally found necessary to clean the capillary, which was achieved by first drawing aqua regia, then water and finally acetone through the tube with a

vacuum pump. One cleaned, the tube was not allowed to remain immersed in solution without continually discharging mercury.

(3) Determination of Drop Time:

The times of mercury discharge were recorded using a Cyma Stop-watch which had been standardised over 120.0 secs. against a standard chronometer (Spindler and Hoyer, Gottingen). A consistent error of +0.2 secs (< 0.2%) was found, which could be ignored considering that only $t^{1/3}$ or $t^{2/3}$ was required. In these determinations the time of dropping of a recorded number of drops was always as close to 120 secs as possible, the time for one drop thus being known with accuracy.

(4) Comparison of the Observed and Calculated Values of the Rate of Flow of Mercury from the Dropping Electrode Capillary:

In order to avoid continual measurement of the rate of flow of mercury from the capillary (m), it was decided to compare a series of measured and calculated values of this rate and, if the agreement justified it, to obtain the value of (m), in future, by calculation.

The equation used to compute the rate of flow of mercury (21) was:

$$m = \frac{\pi r^2 d}{8 l \eta} \left[h d g - 4.31 \frac{\sigma d^{1/2}}{(m t)^{1/2}} \right] \dots (5)$$

where r is the radius of the capillary tube used
 l is the length of the capillary tube used
 d is the density of mercury
 η is the viscosity of mercury
 h is the height of the mercury column between the level of mercury in the reservoir and the tip of the dropping electrode.
 σ is the interfacial tension at the mercury-formic acid solution interface.
 t is the drop time and therefore mt , the drop weight.

The second term in (5) represents a correction for the back pressure, due to the interfacial tension at the surface of the growing drops which opposes the applied pressure. Due to the relatively low value of this correction term, it would be sufficiently accurate to assume $\sigma = 400$ dynes/cm. for use in calculating (m) , (22). It was, nevertheless, decided, for completeness, to measure (σ) with accuracy.

The measurements were carried out on pure formic acid and a 0.5M ammonium formate-formic acid solution. Besides the primary objective of accumulating more evidence for the comparison of the observed and calculated values of (m) , the ammonium formate solution was chosen to observe the effect on (σ) of the addition of an hygroscopic salt to the pure solvent. The ammonium formate used, B.D.H. grade, was further purified by recrystallisation from absolute alcohol and was stored in a desiccator over concentrated sulphuric acid in vacuo. The

melting point of this product was 117.0°C, in good agreement with the value of $117.3 \pm 0.2^\circ\text{C}$ found by Kendall and Adler (23).

The equation used to derive (σ) was

$$m_t = \frac{2\pi r\sigma}{g} \quad \dots\dots (6)$$

This arises from the fact that when a mercury drop forms at the capillary it is influenced by a gravitational force ($m_t g$) and a restraining force ($2 r$). The drop continues to grow until ($m_t g$) becomes equal to ($2 r$), at which point it falls. Thus the drop weight (m_t) should be directly proportional to (σ) and further for a given capillary, in a given supporting electrolyte, the drop weight should be constant and independent of the rate of flow of mercury.

A difficulty is that the mercury surface absorbs very readily any water which the formic acid may take up, and this may possibly change the interfacial tension appreciably. The effect on the surface tension of small additions of water to anhydrous formic acid have, however, been shown to be particularly small for this solvent (24). As the duration of each measurement occupied a maximum time of 40 minutes, it was decided to note the amount of water absorbed by the formic acid (by lowering of its freezing point) under the same conditions over this period. Thus about 15 ml of pure anhydrous formic acid at 25°C were placed in the vessel depicted in Plate 1 which stood in a thermostatic bath at

25.00 \pm 0.01°C. The capillary was then introduced and the height of the mercury reservoir, adjusted to give a drop time of approximately 2.5 secs.

This drop time was determined on seven occasions during the chosen interval of 40 minutes, but no measurable variation in this value was found. Assuming, with justification, that (m) remained invariant over this period, the drop time would be directly proportional to the interfacial tension. In view of the above, the variation of (σ) must be at most less than 0.5%. The freezing point of this formic acid was then found to be 8.34°C which represents an absorption of moisture to a content of 0.04% (25).

The measurements were now accomplished by placing 15 ml of ammonium formate-formic acid solution (or pure formic acid in the second determination) in the vessel as before, in the thermostat. The capillary was then introduced and allowed to discharge into limb A at which stage the mercury head (h) was measured with a cathetometer, and the drop time determined until agreement was obtained. The capillary was then moved into limb B and allowed to discharge for a known time, after which it was removed from the vessel. The shape of this container facilitates the retention of the mercury in B during the washing out, with distilled water, of the formic acid solution and mercury in A. The mercury in B was then dried and weighed.

The results obtained are quoted in the following tables.

TABLE 2.

For 0.5M Ammonium formate-formic acid solution.

| Wt. of mercury discharge (gms) | Duration of discharge (secs) | Ht. of mercury column (cms) | Drop Time (secs) | Drop Wt. (mgms) | Interfacial Tension (dynes/cm) | Calc. Value $\frac{m}{n}$ (mg/sec) | Observed Value $\frac{m}{n}$ (mg/sec) | Diff. % | (mc) % |
|--------------------------------|------------------------------|-----------------------------|------------------|-----------------|--------------------------------|------------------------------------|---------------------------------------|---------|--------|
| 9.2903 | 1920.0 | 48.266 | 1.92(0) | 9.29(1) | 354.4 | 4.863 | 4.839 | +0.5 | 2.102 |
| 5.2447 | 1803.9 | 43.725 | 2.14(0) | 9.32(2) | 355.6 | 4.383 | 4.366 | +0.8 | 2.105 |
| 4.6438 | 1182.0 | 38.765 | 2.42(4) | 9.31(8) | 356.4 | 3.879 | 3.844 | +0.9 | 2.104 |
| 4.8639 | 1377.5 | 35.530 | 2.62(8) | 9.28(0) | 354.0 | 3.546 | 3.531 | +0.3 | 2.101 |
| 4.5833 | 1537.0 | 30.260 | 3.11(9) | 9.30(1) | 354.8 | 2.998 | 2.982 | +0.5 | 2.103 |
| 4.8572 | 1795.0 | 27.690 | 3.44(6) | 9.32(5) | 355.7 | 2.732 | 2.706 | +1.0 | 2.106 |

Mean values: $\sigma = 355.0 \pm 0.3$ dynes/cm.

$$\frac{(mc)}{\%} = 2.103 \text{ (mg)} \%$$

Variation in mt is approx. 0.2%.

TABLE 3.

For Anhydrous Formic Acid.

| Wt. of Mercury discharge (gms) | Duration of discharge (secs) | Ht. of mercury column (cms) | Drop time t (secs) | Drop Wt. (mt) (mgs) | Interfacial Tension (dynes/cm) | Calc. value m mgs/sec | Obs. value m (mgs/sec) | Diff. % | (mt) ^{1/2} (mgs) ^{1/2} |
|---|---------------------------------------|--------------------------------------|-----------------------------|---------------------------|--------------------------------------|--------------------------------|---------------------------------|------------|---|
| 5.9864 | 1218.9 | 49.040 | 1.96(1) | 9.632 | 367.4 | 4.940 | 4.911 | +0.6 | 2.128 |
| 5.1760 | 1124.5 | 46.210 | 2.07(5) | 9.551 | 364.3 | 4.647 | 4.603 | +1.0 | 2.122 |
| 5.4248 | 1192.1 | 45.525 | 2.11(1) | 9.607 | 366.4 | 4.576 | 4.551 | +0.6 | 2.126 |
| 4.6280 | 1075.6 | 43.095 | 2.23(9) | 9.634 | 367.4 | 4.325 | 4.303 | +0.6 | 2.128 |
| 4.2166 | 1013.7 | 41.705 | 2.29(0) | 9.526 | 363.3 | 4.181 | 4.160 | +0.5 | 2.120 |
| 4.3849 | 1210.8 | 36.560 | 2.65(0) | 9.596 | 366.0 | 3.648 | 3.621 | +0.7 | 2.125 |
| 4.1021 | 1441.9 | 29.080 | 3.35(2) | 9.536 | 363.7 | 2.873 | 2.845 | +1.0 | 2.121 |
| 3.9652 | 1494.0 | 27.165 | 3.62(1) | 9.610 | 366.5 | 2.675 | 2.654 | +0.8 | 2.126 |

Mean values: $\sigma = 365 \pm 0.5$ dynes/cm.

(mt)^{1/2} = 2.125 (mgs)^{1/2}

Variation in mt is approximately 1%.

The durations of mercury discharge in these results were measured with a stop-watch and checked against a standard chronometer. A range of values of t from 2 to 4 secs. was chosen as these represent the drop times to be used in the polarographic determinations.

In calculating (m) by equation A the following numerical values were used:

$$\begin{aligned}r &= 0.0409 \text{ mm.} \\ \ell &= 12.495 \text{ cms.} \\ g &= 979.6(6) \text{ cms/sec.} \\ d &= 13.53(4) \text{ gms/sec.} \\ \eta &= 0.0152(1) \text{ poise.}\end{aligned}$$

The drop weight is thus shown to be constant to 1%. The difference in calculating and measuring (m) is thus seen to be less than 1.2% which justified calculation as opposed to measurements of this quantity in future work.

Thus values of the interfacial tension between mercury and 0.5M ammonium formate-formic acid solution was 355.0 ± 0.3 dynes/cm. and between mercury and pure anhydrous formic acid, 365.6 ± 0.5 dynes/cm.

ANHYDROUS FORMIC ACID.

(1) PURIFICATION:

Even at room temperature formic acid slowly decomposes to water and carbon dioxide (10) in addition to which

it is hygroscopic; water is thus by far, the major impurity. Due to a difference in boiling point of only 0.7°C between these two liquids, purification by distillation alone is impossible. It is therefore necessary to dry the formic acid before distillation. Of the usual dessicants phosphorus pentoxide, acid sodium sulphate and sodium all react with formic acid while magnesium perchlorate trihydrate absorbs it copiously (26); boric anhydride and copper sulphate anhydrous (27) are, however, suitable.

The starting material was 98 - 100% BDH formic acid which was dried over anhydrous copper sulphate for 2 days with continuous agitation. It was then fractionally distilled at 25°C under a pressure of 25 mm. of mercury in an atmosphere of dry nitrogen. The fractionating column used was of 50 cms. length packed with glass rings (diam. 0.7 cms.) and was water cooled to 15°C ; the condenser unit was cooled by circulating water at 4°C . The first fraction, of about 10% of the original volume, was discarded with about 15% remaining undistilled. The formic acid so obtained usually froze at about 8.2°C , pure formic acid freezing at 8.40°C ; it was, therefore, further purified by fractionally freezing once. The pure formic acid was stored in sealed glass stoppered 125 ml bottles at -10°C . Thus stored, no deterioration was observed over one month.

(2) CRITERIA OF PURITY OF THE FINAL PRODUCT.

The quality of formic acid may be assessed by examination under five criteria of purity:

- (a) an upper consolute temperature with benzene at 73.2°C and 48% formic acid (25).
- (b) a boiling point of 100.70°C (28) (although there is a possibility of very slight decomposition during boiling (26)).
- (c) a freezing point of 8.40°C (1).
- (d) a value of the specific conductivity not in excess of 7.5×10^{-8} mhos/sq. cm.
- (e) a refractive index of n_D^{20} 1.3714 (29).

As the freezing point has been shown to be very sensitive to the adsorption of small amounts of water (25), measurement of this quantity was selected as being both highly satisfactory and convenient. The influence of water on the freezing point of formic acid is given below (25).

TABLE 4.

| % Water | Depression of Freezing point °C |
|---------|---------------------------------------|
| 0 | 0 |
| 0.053 | 0.07 |
| 0.099 | 0.16 |
| 0.244 | 0.305 |
| 0.502 | 0.70 |
| 0.984 | 1.35 |
| 2.04 | 2.67 |

From these results it follows that the effect of water on the freezing point of the acid, is additive.

The freezing points were measured using about 4 ml. of the acid in a stoppered Dewar tube, the temperature being measured by a standard thermometer -10°C to $+50^{\circ}\text{C}$ graduated in tenths of a degree inserted through the stopper. Only samples of acid melting above 8.36°C (corresponding to a maximum water content of 0.03%) were used.

The refractive index was found to be insufficiently sensitive to traces of water in the acid; although, at first, it was measured frequently, this physical property was discarded as a criterion of purity. The measurements were made using an Abbe refractometer with water at 20.0°C circulating in the outer metal jacket. All the samples of acid measured gave a value of 1.3714.

The best value of the conductivity of anhydrous formic acid is claimed by Pleskov (2) as $5.8 - 6.0 \times 10^{-8}$ mhos/cm. while Schlesinger and Calvert using the acid for conductivity measurements obtained a value of 6.35×10^{-8} mhos/sq. cm. (3).

In measuring the conductivity of the formic acid used in this research, use was made of the cell shown in Plate 2 . The constant of this cell was determined by measuring the resistance of a 0.01 M potassium chloride solution at known temperatures. The potassium chloride used was recrystallised

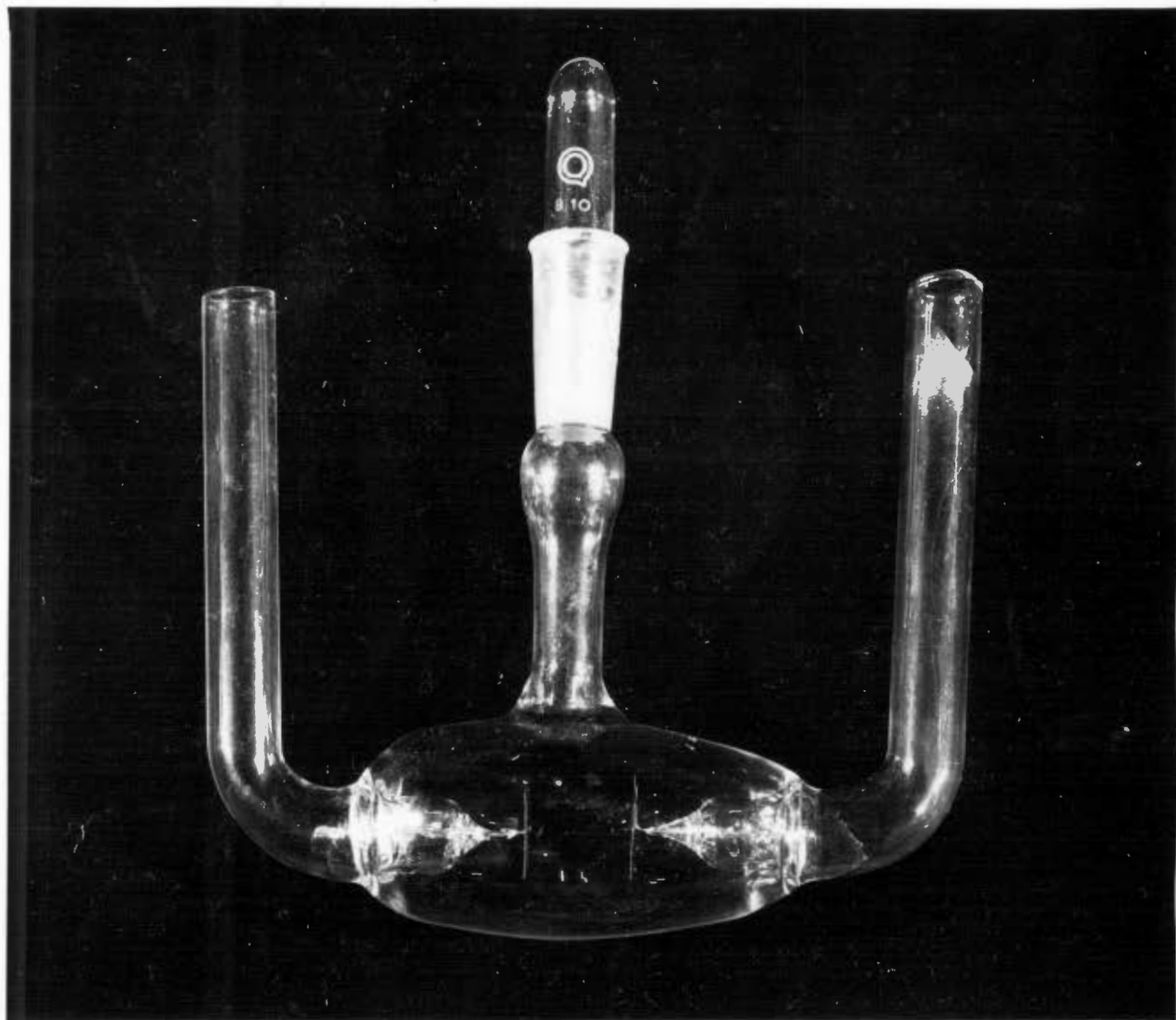


PLATE 2

three times from water, three times from 'conductivity water' and dried by heating at 450°C for 48 hours; it was cooled and stored in a desiccator over calcium chloride. The values of the specific conductivity of this potassium chloride solution at these respective temperatures is accurately known; the values used here were taken from the results of Jones and Prendergast (30). The temperature of the liquid in the cell was measured by the immersion of a thermistor which had been sealed into the B10 stopper (replaced in Plate 2 by an ordinary stopper). The cell was then immersed in a thermostatically controlled oil bath at $25.00 \pm 0.01^\circ\text{C}$ the whole being contained in an air thermostat maintained at $24.2 \pm 0.1^\circ\text{C}$. (This temperature was found to be most suitable for the maintenance of a temperature of 25.00°C in the oil bath).

The cell was then washed out and dried in an oven at 120°C for 1 hour, cooled in a desiccator and filled with formic acid, the resistance of which was then measured. The best value of the specific conductivity obtained was 6.734×10^{-5} mhos/sq. cm. As the formic acid was not being used for conductivity purposes and could thus afford to have a slightly higher conductance, an upper limit of 7.5×10^{-5} mhos/sq. cm. was imposed on the acid used, provided it conformed to the limits imposed by the freezing point determinations.

The results of the above measurements are quoted below.

TABLE 5.

For 0.01 M potassium chloride solution.

| Thermistor reading ohms | Temperature from thermistor t°C | Sp. cond. of KCl at t°C mhos/sq. cm. x 10 ⁻⁶ | Resistance of cell ohms | Cell constant |
|----------------------------|---------------------------------------|--|-------------------------------|------------------|
| 2528 | 24.82 | 1406.56 | 285.7(7) | 0.4019(7) |
| 2517 | 24.94 | 1409.81 | 284.6(2) | 0.4012(6) |
| 2512 | 24.99 | 1411.18 | 284.5(4) | 0.4015(4) |
| 2511 | 25.00 | 1411.45 | 284.4(2) | 0.4014(6) |

Mean value of the cell constant = 0.4015(6).

For anhydrous formic acid.

| Thermistor reading ohms | Temperature from thermistor t°C | Resistance of cell ohms | Sp. cond. of HCOOH at t°C mhos/sq. cm. x 10 ⁻⁵ |
|----------------------------|------------------------------------|-------------------------------|---|
| 2534 | 24.75 | 5998.0 | 6.694(8) |
| 2533 | 24.76 | 5997.9 | 6.698(0) |
| 2526 | 24.84 | 5985.5 | 6.709(0) |
| 2518 | 24.93 | 5973.1 | 6.722(7) |
| 2511 | 25.00 | 5963.4 | 6.733(8) |

Each batch of anhydrous formic acid prepared was shown to be polarographically pure by observing the polarogram obtained using a 0.5 M sodium formate indifferent electrolyte, without any electro-reducible ion present, and noting the absence of any spurious waves. When the highest galvanometer sensitivities practical were used, the residual current was always found to be very small, showing the absence of electro-reducible impurities.

ESTIMATION OF THE WATER ABSORBED BY ANHYDROUS FORMIC ACID.

(a) During a Polarographic Run:

From the depression of the freezing point the amount of moisture taken up by the anhydrous acid during a polarographic run could be determined. It was decided, however, to certify the validity of the results obtained by the above method, by titration of the formic acid with Karl Fischer reagent.

A volume of 20 ml. of anhydrous formic acid mp = 8.40°C was found to require no Karl Fischer reagent at all for titration showing it to be uncontaminated with water. A volume of 55 ml. of this acid was now subjected to the same treatment as that undergone in a polarographic determination. This involved both exposure to the air while making up solutions and the passing of dried nitrogen through the cell to remove dissolved oxygen. The melting point of the acid was measured and 50 ml. were used for titration with the Karl Fischer reagent. The results tabulated below show close agreement between the value of the water absorbed as measured by titration and that obtained by measurement of the freezing point.

The apparatus used for the Karl Fischer titrations is shown in Plate 3.

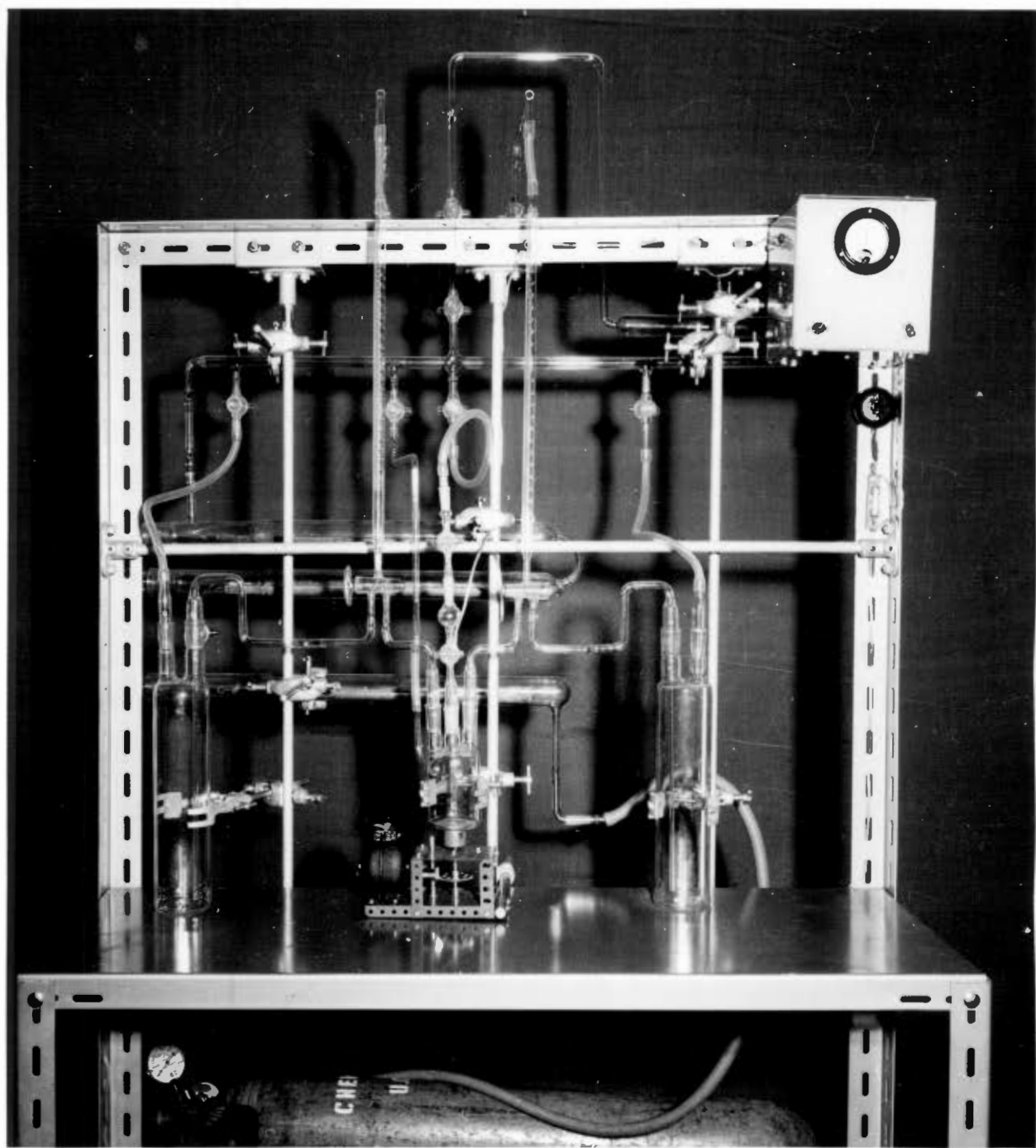


PLATE 3

TABLE 6.

| Sample No. | Freezing point of Acid °C | % Water Content | |
|------------|---------------------------|-------------------|-----------------|
| | | By Freezing Point | By Karl Fischer |
| 1 | 8.34 | 0.05 | x |
| 2 | 8.32 | 0.06 | 0.07 |
| 3 | 8.34 | 0.05 | 0.06 |

x Result was discarded.

Maximum water content of acid = 0.07%.

(b) When exposed to atmospheric moisture.

Four samples of anhydrous formic acid, freezing point 8.40°C, were exposed to the atmosphere for known lengths of time, after which their melting points were determined. Each was contained in a tube of 2.0 cms. internal diameter, giving a surface of exposure of the acid of 3.1 sq. cms. The acid surface lay at a depth of 12 cms. in the tube. The relative humidity was 59% and the temperature 20.8°C at the time of the experiment.

The results recorded are tabulated below.

TABLE 7.

| Time of exposure | Freezing Pt. of sample | Water content % (w/w) |
|------------------|------------------------|-----------------------|
| 0 | 8.40 | 0 |
| 30 mins. | 8.37 | 0.02 |
| 60 mins. | 8.34 | 0.04 |
| 90 mins. | 8.30 | 0.07 |
| 4.5 hrs. | 8.15 | 0.22 |

The above experiments demonstrate clearly that although anhydrous formic acid is hygroscopic it can be exposed to the atmosphere for short periods without deteriorating in purity due to the absorption of moisture. The quantity of water absorbed during the time taken for, and under the conditions prevailing in, a polarographic run, had been shown to be very small. Further it has been demonstrated that the addition of quantities of water, of the order of 30 times the amounts absorbed by the acid, have only a small effect polarographically. Thus, although it had had brief contact with atmospheric moisture during the making up of the solutions, in view of the above observations, it was felt justifiable to describe the formic acid used in this research as anhydrous.

Dehydration of Supporting Electrolytes.

The following reagents were dried by heating in an oven at 130°C for 5 hours and cooled over anhydrous calcium chloride:- potassium chloride as supplied by Merck Co.; sodium tartrate and sodium formate by British Drug Houses and sodium bromide by May and Baker Ltd. British Drug Houses Analar grade sodium citrate was dried at 180°C for 3 hours and May and Baker oxalic acid at 90°C for 2 hours, all being cooled over anhydrous calcium chloride. British Drug Houses ammonium formate was recrystallised from absolute alcohol and then desiccated over concentrated

sulphuric acid in vacuo. British Drug Houses potassium sulphate, Merck sodium fluoride and Analar sodium acetate were dried in a desiccator over anhydrous calcium chloride for 5 days.

SECTION C.

THE QUINHYDRONE-IN-FORMIC

ACID ELECTORDE.

THE QUINHYDRONE-IN-FORMIC ACID ELECTRODE.

In view of the necessity of employing as anode in the polarographic cell, an electrode of constant potential to which the measured half-wave potentials of the electro-reducible species could be compared, it was decided to examine the properties of the quinhydrone electrode with this end in view.

On consideration of the minute currents involved in polarographic electrolyses (e.g. 20 microamps) it is to be expected that a quinhydrone electrode would remain unpolarised and of constant potential during the passage of such currents; could it be shown that this is actually the case, the electrode would be admirably suited for use as anode in a polarographic circuit.

A quinhydrone electrode has only once previously been reported as a polarographic anode (31). This was in aqueous solution, and was found to undergo polarisation, which was somewhat reduced by bubbling nitrogen through the solution. Because of it the electrode was discarded as unsatisfactory. Whether this rejection was justifiable

on the limited nature of the investigation was left undecided, effort being concentrated on examination of the electrode in formic acid. Thus the saturated calomel electrode, itself the reference standard for half-wave potentials in aqueous solution, is unchallenged in its superiority in aqueous media.

In anhydrous formic acid, however, where slow adsorption of moisture is operative, an electrode is required which is capable of rapid preparation, one which will attain a reproducible potential instantaneously and, further maintain this value for a period of at least half an hour. It is also desirable that the electrode should not be significantly affected by traces of moisture and small concentrations of salts; further it must be such that liquid junction potentials are minimised without the institution of gel-salt bridges.

In each of these considerations the quinhydrone-in-formic acid electrode was found to exhibit marked superiority over the formic acid analogue of the saturated calomel electrode. The

only adverse possibility was that formic acid exhibiting reducing properties as it does, may have partially reduced the quinone to hydroquinone, thereby altering the potential and so vitiating its use as reproducible electrode. Had this reduction been operative, the potential of the quinhydrone electrode would have depended markedly on the concentration of quinhydrone present - an effect which was not observed on any occasion. The quinhydrone electrode has been used in formic acid on two occasions in potentiometric studies of acid-base titrations ^(10,11); it is quoted in ⁽¹⁰⁾ that in the sodium formate solutions used, there was no evidence of any reaction between the formic acid and the quinhydrone.

These authors ⁽¹⁰⁾ maintain, however, that platinum electrodes are unsatisfactory, often showing differences in the same solution of several millivolts and submit that gold electrodes be used in preference. The platinum electrodes employed in this research and described below were found to be entirely satisfactory; in a wide range of solutions of the most divergent concentrations of quinhydrone and salts chosen as supporting electrolytes the maximum difference of potential observed between any two electrodes was 0.0002 volts. With electrodes cleaned overnight in chromic acid, the difference was often undetectable.

It remained at this stage to examine the performance of the quinhydrone electrode quantitatively under the conditions existing in polarographic electrolysis.

PREPARATION OF THE QUINHYDRONE HALF CELL.

Two platinum electrodes were prepared as described (32). The platinum used was in the form of bright unused foil and measured 10 mm. x 15 mm.; it was sealed into soft glass tubing and carefully annealed. The perfection of the seals was tested by suspending the electrodes in distilled water, which was then heated to boiling point and finally allowed to cool to room temperature. Careful examination of the seals under a magnifying glass showed no imperfections. This care was necessitated due to imperfections in the metal-glass seals being one of the reasons for non-reproducible potentials. The electrodes were cleaned by immersion in cold chromic acid cleaning mixture (prepared from chemically pure constituents) which was heated to 125°C and allowed to cool overnight. After rinsing well with distilled water and absolute alcohol, the electrodes were placed in a stream of dry air for 20 minutes; when not in use they were stored in a desiccator over anhydrous calcium chloride.

The electrode has been shown in aqueous solution, to be independent of the quality of quinhydrone used (32-35). This conclusion was verified in formic acid by comparison of the electrode potentials developed using B.D.H. Analar reagent and quinhydrone that was further purified by recrystallising twice from distilled water and then dried for several days over calcium chloride. The potential difference of two such electrodes was on no occasion more than 0.0001 volts; it was

therefore decided to use B.D.H. Analar quinhydrone, without further purification, throughout this research.

In view of the necessity of maintaining the resistance of the polarographic cell at as low a value as possible and further to minimise the liquid junction potential between the anode and cathode compartments, a concentration of 0.25 M sodium formate was maintained in the quinhydrone compartment. It is desirable, in the choice of this added substance, to select a salt, the anion of which would not, in any way, interfere with the electro-reducible ions under investigation at the dropping mercury electrode, should a small amount of this salt diffuse across the sintered glass boundary. In solutions of lead and alkaline earth salts, the presence of the sulphate ion would cause precipitation, while in chloride medium, lead, cadmium, and zinc form monovalent chloride complexes. Although these effects would, in all probability, be negligible, the choice of a formate is free of any complication: sodium formate was preferred to the ammonium salt because the latter is very hygroscopic. Although it has been shown that the potential of the quinhydrone-in-formic acid electrode is independent of the concentration of quinhydrone and small quantities of added salts, it was decided to always maintain a concentration of 0.25 sodium formate and 0.05 M quinhydrone in the anode compartment.

EXAMINATION OF THE SALT EFFECT ON THE ELECTRODE POTENTIAL

The possibility of a small amount of diffusion of the supporting electrolyte across the sintered glass disc, into the anode compartment, cannot be ignored and it was therefore necessary to investigate the effect of added salt concentrations on the quinhydrone electrode. This effect has been shown (36) in aqueous solution to be extremely small for the salt concentrations under consideration in this work. In view of the small amount of diffusion across the boundary that would occur, in formic acid the effect would supposedly have to be considerable to exert any influence on the electrode potential. It was decided to use salt concentrations far in excess of those likely to occur, in order to verify this supposition.

A cell of two identical quinhydrone-in-formic acid electrodes containing 0.25 M sodium formate and 0.05 M quinhydrone, was prepared, the solutions being separated as usual by a No. 4 sintered glass disc. Nitrogen was bubbled through both compartments and the potential difference of the electrodes, measured. The concentration of sodium formate at one electrode was then increased to 0.35 M; on solution of the added solid, the potential difference between the electrodes was again measured. The concentration was then increased to 0.45 M and finally to 0.55 M as against the original molarity of 0.25 M in the other electrode. The above procedure was repeated using potassium chloride in place of the sodium formate as the salt added to one electrode. In calculating the

diffusion potentials, the ionic conductances at infinite dilution of the sodium and formate ions in anhydrous formic acid were taken as 14.6 and 51.5 mhos/sq. cm. (9). The equivalent conductance at infinite dilution of potassium chloride is 35.8 mhos/sq. cm. (8) the ionic conductance of the potassium ion at infinite dilution is 17.5 mhos/sq. cm. (9) from which the corresponding value for the chloride ion is computed as 18.3 mhos/sq. cm. As shown in the table below, the potential differences were adequately accounted for as liquid junction potentials, showing the salt effect to be negligible. On the several occasions on which these measurements were recorded, the results proved satisfactorily reproducible. Further the potential differences, once established, decreased very slowly with time, showing the diffusion across the sintered glass boundary to be small.

All calculated values of the diffusion potentials were obtained using Henderson's Approximate Equation ((4).- Sect. A).

TABLE 8.

| Difference of salt concentration between electrodes | Potential Diff. of Electrodes | | | |
|---|-------------------------------|-------|--------------------|-------|
| | Sodium formate | | Potassium chloride | |
| | Obs. | Calc. | Obs. | Calc. |
| 0 | 0.0 | 0.0 | 0.1 | 0.0 |
| 0.1 M | 4.4 | 4.8 | 0.4 | 0.2 |
| 0.2 M | 7.8 | 8.4 | 0.5 | 0.3 |
| 0.3 M | 10.6 | 11.3 | 0.5 | 0.5 |

The above measurements were repeated using the three other salts likely to be employed as supporting electrolytes. It is unfortunately not possible to compare these data with calculated values of the liquid junction potentials, due to lack of information regarding the ionic conductance of the ions concerned. The values measured for these salts have, however, been recorded below.

TABLE 9.

| Diff. of salt conc. between electrodes | Potential Difference of Electrodes | | |
|--|------------------------------------|-------------------|--------------------|
| | Pot. sulphate mv. | Sod. tartrate mv. | Sodium citrate mv. |
| 0 | 0.1 | 0.1 | 0.2 |
| 0.1 M | 3.6 | 8.2 | 11.0 |
| 0.2 M | 6.6 | 13.5 | 17.6 |
| 0.3 M | 9.8 | 18.1 | 23.0 |

The potential of the quinhydrone electrode has been shown, in aqueous solution, to be considerably influenced by the presence of proteins (37). Although gelatin has been used, where necessary, for the suppression of polarographic overcurrents throughout this research, it is necessarily used in this capacity in very small concentrations. Two electrodes were compared, however, as just described, one of which contained 0.01% gelatin, a quantity greatly in excess of the amount that could diffuse into the anode compartment. No potential difference was recorded between the electrodes.

POLARISATION OF THE QUINHYDRONE ELECTRODE.

In order to test the non-polarisability of the electrode, a prime consideration in its role as polarographic anode, a cell was formed of two identical electrodes of composition as quoted above and again separated by a sintered glass disc. With nitrogen bubbling through each compartment the difference of potential was found to be 0.0001 volts. A current of 40 microamperes was then passed through the cell for 1 hour, after which no measurable difference was noticed, the value remaining 0.0001 volts. The above operation was then repeated without passing nitrogen through either compartment and the potential difference again measured. The value had risen from 0.0001 v to 0.0015 volts but immediately dropped to 0.0001 v on agitating the solutions with nitrogen. This experiment was repeated on five occasions and the above results reproduced. Further the relationship between current flowing and voltage applied to the cell, was found to be a straight line function over a range of 0 to 1.4 volts both with and without the passage of nitrogen through the solution.

It was concluded that the electrode was reversible, reproducible and non-polarisable whether or not nitrogen was employed to agitate the solution. During all polarographic measurements throughout this research, however, a stream of nitrogen was kept flowing through the anode compartment.

MEASUREMENT OF THE POTENTIAL OF THE QUINHYDRONE-IN-FORMIC ACID ELECTRODE VS SATURATED CALOMEL-IN-FORMIC ACID ELECTRODE.

In order to conform with the standard practice of quoting polarographic half-wave potentials against the saturated calomel electrode, it was decided to prepare the formic acid analogue of this electrode and measure its potential with respect to the quinhydrone electrode as prepared above. The saturated calomel-in-formic acid electrode was prepared similarly to the aqueous counterpart. Analar grade potassium chloride was used, after further purification by recrystallizing once from distilled water and drying at 180°C for 5 hours; the mercury employed was of the same purity as that used for the dropping mercury electrode. The calomel paste was prepared by rubbing together in a mortar, Analar grade calomel and mercury with some formic acid previously saturated with potassium chloride and calomel. The paste was then washed with a quantity of this solution, the mixture being allowed each time to stand until the calomel had settled and the solution then decanted off.

With the electrode thus prepared its potential was measured against the quinhydrone-in-formic acid electrode at $25.00 \pm 0.01^\circ\text{C}$ the surface of separation between the electrodes being, as before, a No. 4 sintered glass disc. The result of the ten determinations made are tabulated below:

TABLE 10.

| No. of determination | Measured potential | Mean value |
|----------------------|--------------------|--------------|
| 1 | 0.5382 | |
| 2 | 0.5384 | |
| 3 | 0.5376 | |
| 4 | 0.5386 | |
| 5 | 0.5380 | |
| 6 | 0.5387 | 0.5384 |
| 7 | 0.5384 | |
| 8 | 0.5379 | ± 0.0005 |
| 9 | 0.5374 | |
| 10 | 0.5389 | volts |

x Value ignored in the mean.

The value of the potential of the Quinhydrone-in-Formic Acid Electrode (QFAE) against the Saturated Calomel-in-Formic Acid Electrode (SCFAE) is taken as $+0.5384 \pm 0.0005$ volts at $25.00 \pm 0.01^\circ\text{C}$.

As found previously, the effect of bubbling nitrogen over the quinhydrone electrode was immeasurably small.

As the effect of small quantities of water on the potential of the quinhydrone electrode may be important, it was studied by the addition of 0.5% (v/v) of distilled water to the anodic electrolyte, all other variables remaining unchanged as in the preceding determinations. The potential of the quinhydrone-calomel cell was found to drop by about 0.4 mv. The dependence of the potential of the quinhydrone electrode on such quantities of water is thus shown to be insignificant.

The polarographic investigation of anhydrous formic acid

solutions has been so greatly facilitated by the institution of the quinhydrone-in-formic acid electrode that should similar quinhydrone electrodes be found to be suitable in other non-aqueous solvents, their utility would be very considerable.

SECTION D.

INORGANIC POLAROGRAPHY.

(I) BISMUTH.

As in aqueous solution the waves for the reduction of trivalent bismuth ions to the metallic state, gave rise to well developed waves. With each of the supporting electrolytes used the value of $\tan \alpha$ was close to the theoretical value of 0.020 for a reversible three electron reduction.

As the half-wave potentials of bismuth, in the variety of media studied, are all appreciably more positive than the potential of the electro capillary maximum, the appearance of overcurrents was expected. These were observed at low salt concentrations but were suppressed by increasing the concentration of the supporting electrolyte. The discussion of this phenomenon is included in Section F.

Basic bismuth carbonate was found to be moderately soluble in formic acid and was used in this investigation. May and Baker grade $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ was dried over anhydrous calcium chloride for several days and used without further purification.

The presence of small quantities of water was found to exert very little influence on the half-wave potentials. The addition of 2% (v/v) of water shifted the half-wave potential of bismuth in a 0.5 M sodium formate medium by 0.003 volts, to more negative values, showing the effect over this range to be small.

The value of the diffusion coefficient of bismuth ions in a 0.5 M sodium formate medium was determined by the measurement of the diffusion current at various concentrations of the bismuth salt. Calculation by means of the Ilkovic equation ((1) Section A) established this value as 0.23×10^{-5} cms.²/sec. Use of Lingane's (38) measured value of the diffusion current constant of bismuth in 1 M nitric acid, in which this element is uncomplexed, led to a diffusion coefficient of 0.65×10^{-5} cms.²/sec. for the bismuth ion in aqueous solution.

TABLE 11.

| Concentration of Bismuth $\times 10^4$ gm. ions/litre | Diffusion Current (microamps) |
|--|----------------------------------|
| 2.536 | 2.22 |
| 3.804 | 3.26 |
| 5.072 | 4.42 |
| 6.340 | 5.56 |

These results are plotted in Plate 4.

$$h = 43.26 \text{ cms.}$$

$$t = 2.40 \text{ secs.}$$

$$m = 4.474 \text{ mgs./sec.} \quad m^{2/3} t^{1/6} = 3.142 \text{ mgs.}^{2/3} \text{ secs.}^{-1/6}$$

$$i_d/c = 8.70 \text{ microamps/mgm. ion/litre.}$$

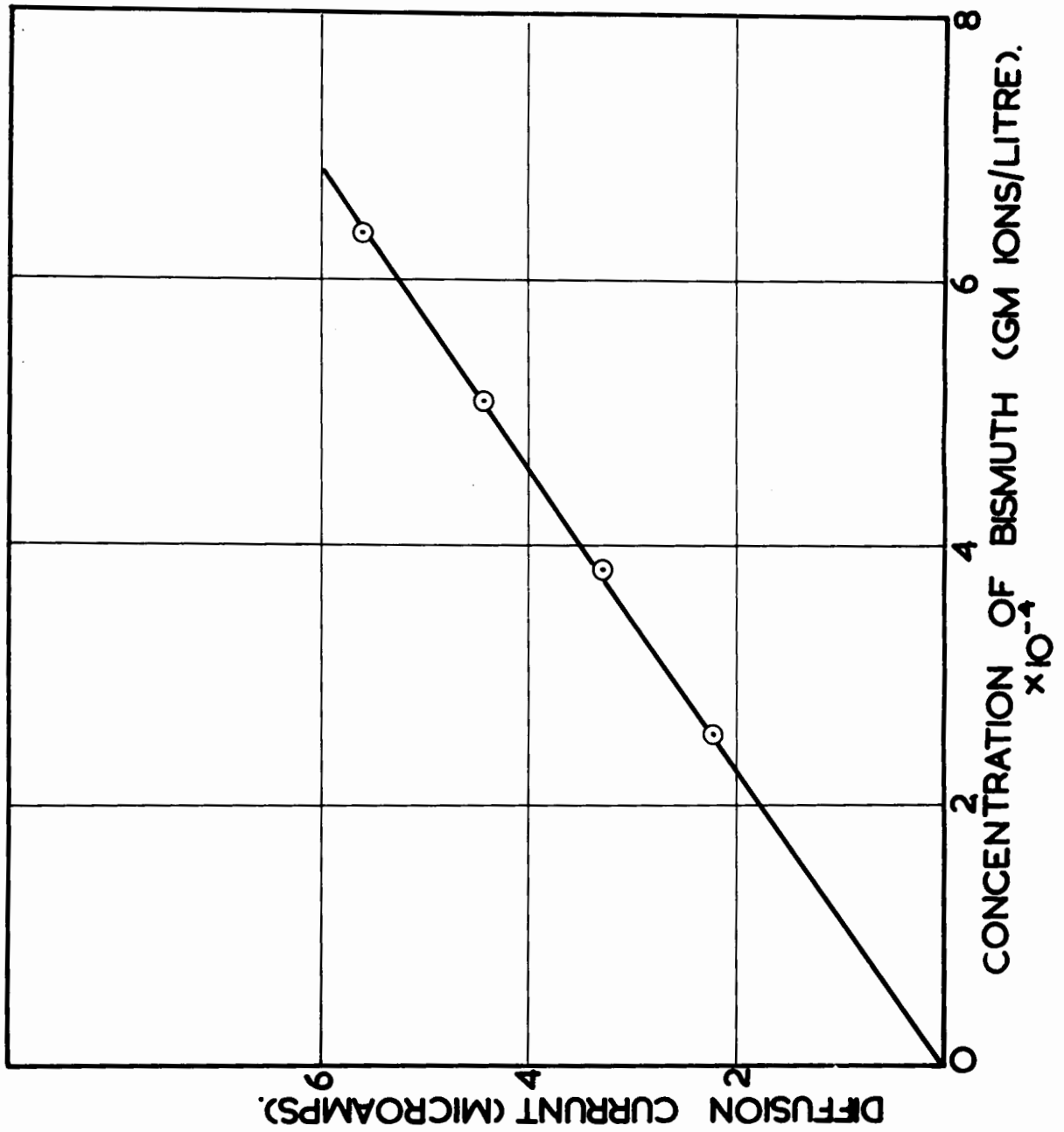
Diffusion current constants:

$$I_{\text{HCOOH}} = 2.8$$

$$I_{\text{H}_2\text{O}} = 4.64$$

The half wave potential of bismuth when using a 0.5 M sodium formate supporting electrolyte was $+0.136 \pm 3$ volts

PLATE 4



vs S.C.F.A.E. (-0.402 volts vs Q.F.A.E.). On increasing the formate concentration the value was found to be -0.114 ± 3 volts vs S.C.F.A.E. (-0.424 volts vs Q.F.A.E.) The shift of 22 millivolts is almost exactly that expected on consideration of the increase in the liquid junction potential arising from the increment in the sodium formate concentration. The value of $\tan \alpha$ for both media was 0.021.

The half wave potential when using a supporting electrolyte of 0.2 M sodium fluoride and 0.5 M sodium formate was $+0.132 \pm 3$ volts vs S.C.F.A.E. (-0.406 volts vs Q.F.A.E.) which on increasing the sodium fluoride concentration to 0.4 M while maintaining that of the sodium formate constant, changed to $+0.117 \pm 3$ volts vs S.C.F.A.E. (-0.421 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.022. In aqueous solution it has been shown (39) that the complex ion $[\text{BiF}_4]^-$ is formed but is unstable. As shown above, there is little evidence of complex formation in formic acid.

When using 0.5 M potassium chloride and 0.5 M sodium formate as the carrier electrolyte, the half wave potential is -0.016 ± 5 volts vs S.C.F.A.E. (-0.554 volts vs Q.F.A.E.) and this increases to -0.050 ± 5 volts vs S.C.F.A.E. (-0.588 volts vs Q.F.A.E.) when the composition of the electrolyte is changed to 1.0 M potassium chloride and 0.5 M sodium formate. The value of $\tan \alpha$ was 0.024. The chloro-bismuth complex ions formed are probably $[\text{BiCl}_4]^-$ and $[\text{BiCl}_5]^{2-}$ (40). The

sodium formate was added in this instance to suppress the overcurrent, as the concentrations of potassium chloride used were not quite sufficient. The sodium formate was successful in achieving this suppression. The wave was found, however, to be slightly irregular at the beginning of the diffusion current plateau and this was overcome by the addition of 0.05% gelatin. The initial part of the curve, before the onset of the wave for the reduction of bismuth was much restricted in length and in consequence the limits of accuracy of the measurements of the potentials are larger than usual. This restriction is caused by a shift of the anodic wave of mercury to more negative values due to the formation of insoluble mercurous chloride with the chloride ions present.

The determination of bismuth in a bromide medium was found to be impossible because the anodic wave for mercury, in a bromide medium, completely obscured the lower portion of the bismuth wave, thus excluding any possibility of measurement.

Complex formation was observed when using a supporting electrolyte of 0.25 M oxalic acid and 0.5 M sodium formate, the half-wave potential in this medium being $+0.067 \pm 3$ volts vs S.C.F.A.E. (-0.471 volts vs Q.F.A.E.) This potential changed to $+0.059 \pm 3$ volts vs S.C.F.A.E. (-0.479 volts vs Q.F.A.E.) on increasing the oxalic acid concentration to 0.5 M, the sodium formate content remaining

unaltered. The oxalato-complex ion formed is probably $[Bi(C_2O_4)_2]^-$ (41). The value of $\tan \alpha$ was 0.018.

A weak sulphato-bismuth complex is probably formed in formic acid. The half wave potential in a 0.5 M potassium sulphate - 0.5 M sodium formate is $+0.113 \pm 3$ volts vs S.C.F.A.E. (-0.425 volts vs Q.F.A.E.) which on changing the constitution of the supporting electrolyte to 1.0 M potassium sulphate - 0.5 M sodium formate, shifts to a value of $+0.102 \pm 3$ volts vs S.C.F.A.E. (-0.436 volts vs Q.F.A.E.). The complex ion formed is probably $[Bi(SO_4)_2]^-$ (41). The value of $\tan \alpha$ was 0.024.

SUMMARY.

| Supporting Electrolyte | vs S.C.F.A.E. (volts) | vs Q.F.A.E. (volts) | Limits (volts) | $\tan \alpha$ |
|---|-----------------------------|---------------------------|-------------------|---------------|
| 0.5 M sodium formate | +0.136 | -0.402 | ± 0.003 | 0.021 |
| 0.5 M sodium formate + 2% water | +0.133 | -0.405 | ± 0.003 | 0.021 |
| 2.0 M sodium formate | +0.144 | -0.424 | ± 0.003 | 0.021 |
| 0.2 M sod. fluoride + 0.5 M sod. formate | +0.132 | -0.406 | ± 0.003 | 0.022 |
| 0.4 M sod. fluoride + 0.5 M sod. formate | 0.117 | -0.421 | ± 0.003 | 0.022 |
| 0.5 M pot. chloride + 0.5 M sod. formate | -0.016 | -0.554 | ± 0.005 | 0.024 |
| 1.0 M pot. chloride + 0.5 M sod. formate | -0.050 | -0.588 | ± 0.005 | 0.024 |
| 0.5 M pot. sulphate + 0.5 M sod. formate | +0.113 | -0.425 | ± 0.003 | 0.024 |
| 1.0 M pot. sulphate + 0.5 M sod. formate | +0.102 | -0.436 | ± 0.003 | 0.024 |
| 0.25 M oxalic acid + 0.5 M sod. formate | +0.067 | -0.471 | ± 0.003 | 0.018 |
| 0.50 M oxalic acid + 0.5 M sod. formate | +0.059 | -0.479 | ± 0.003 | 0.018 |

(II) ANTIMONY.

The polarographic reduction of trivalent antimony in formic acid was found to produce well developed waves with several supporting electrolytes. Some media, however, showed limited suitability, the reduction being either irreversible or producing an immeasurable wave. In most of the media, the reductions involved three electrons and were reversible. Very pronounced overcurrents were observed with this element. This was to be expected in view of a disparity of 0.5 volts between the electrocapillary maximum and the half-wave potentials. These overcurrents were, however, totally suppressible by increase of the supporting electrolyte concentration.

Tartar emetic was found to be highly soluble in formic acid and thus eminently suitable. The [$\frac{1}{2}\text{H}_2\text{O}$] water crystallisation was removed by heating the salt, as supplied by May and Baker Ltd., in an oven at 130°C for 5 hours after which it was cooled in a desiccator over anhydrous calcium chloride.

The presence of small quantities of water was found to exert very little influence on the half-wave potentials. The addition of 2% (v/v) of water shifted the half-wave potential of antimony in a 0.5 M sodium formate medium by 0.003 volts, to more negative potentials.

The value of the diffusion coefficient of antimony ions in a 0.5 M sodium formate medium was determined by the measurement of the diffusion current at various concentrations of the antimony salt. Calculation by means of the Ilkovic equation ((1) Section A) suggested this value to be 0.46×10^{-5} cms.²/sec. Use of Lingane's (38) measured value of the diffusion current constant of antimony in 1 M HNO₃ in which this element is uncomplexed led to a diffusion coefficient value of 0.78×10^{-5} cms.²/sec. in aqueous solution.

TABLE 12.

| Concentration of Antimony x 10 ³ (gm. ions/litre) | Diffusion Current (microamperes) |
|---|-------------------------------------|
| 1.022 | 12.23 |
| 1.471 | 18.08 |
| 1.885 | 22.78 |

$$h = 41.16 \text{ cms.}$$

$$m = 4.254 \text{ mgs./sec.}$$

$$t = 2.65 \text{ secs.}$$

$$m^{2/3} t^{1/6} = 3.087 \text{ mgs.}^{2/3} \text{ secs.}^{-1/6}$$

$$id/C = 12.0 \text{ microamps/mgm. ion/litre.}$$

$$I_{\text{HCOOH}} = 3.89$$

$$I_{\text{H}_2\text{O}} = 5.10.$$

The half-wave potential of antimony in a 0.5 M sodium formate solution was
 0.000 ± 3 volts vs S.C.F.A.E. (-0.538 volts vs Q.F.A.E.)
 which changed to a value of

-0.023 ± 3 volts vs S.C.F.A.E. (-0.561 volts vs Q.F.A.E.) when the sodium formate concentration was increased to 2.0 M, showing an absence of complex formation in this medium. The value of $\tan \alpha$ was 0.022 .

The characteristic potential of antimony in a 0.5 M potassium sulphate medium was $+0.004 \pm 3$ volts vs S.C.F.A.E. (-0.534 volts vs Q.F.A.E.) showing no complex formation. The value of $\tan \alpha$ was 0.023 .

The polarogram of antimony in a 0.2 M sodium fluoride 0.5 M sodium formate medium was found to be most unsatisfactory. The wave was extended, poorly developed and generally immeasurable. As this behaviour was observed on two occasions no further attempts were made to investigate antimony in the presence of fluoride ions. No comparable measurements of this element in aqueous fluoride media have been made.

The wave in a medium of 0.5 M potassium chloride - 0.5 M sodium formate was well formed the half wave potential being -0.073 ± 4 volts vs S.C.F.A.E. (-0.611 volts vs Q.F.A.E.). This value changed to -0.093 ± 4 volts vs S.C.F.A.E. (-0.631 volts vs Q.F.A.E.) on increasing the supporting electrolyte concentration to 1.0 M potassium chloride - 0.5 M sodium formate. This is due to complex formation probably with the formation of the ion $[\text{SbCl}_4]^-$ (42). The value of $\tan \alpha$ was 0.023 .

The polarogram obtained when using a supporting electro-

lyte of 0.2 M sodium bromide - 0.5 M sodium formate was quite immeasurable. Because of a large anodic wave due to the presence of the bromide ions the lower portion of the wave was completely obscured.

The half wave potential when using 0.25 M oxalic acid - 0.5 M sodium formate as background electrolyte was -0.069 ± 4 volts vs S.C.F.A.E. (-0.607 volts vs Q.F.A.E.) which on increasing the supporting electrolyte concentration to 0.5 M oxalic acid - 0.5 M sodium formate, changed to -0.081 ± 4 volts vs S.C.F.A.E. (-0.619 volts vs Q.F.A.E.). The complex ion formed is probably $[\text{Sb}(\text{OX})_3]^-$ (43). The electroreduction of this complex however, was not reversible, the value of $\tan \alpha$ being 0.033. It is supposed that the disintegration of the complex at the dropping electrode is a slow process leading to irreversible conditions.

SUMMARY.

| Supporting Electrolyte | Half-wave potentials | | Limits | tan α |
|---|----------------------|-------------|-------------|--------------|
| | vs S.C.F.A.E. | vs Q.F.A.E. | | |
| 0.5 M sodium formate | 0.000 | -0.538 | ± 0.003 | 0.022 |
| 0.5 M sod. formate + 2% water | -0.003 | -0.541 | ± 0.003 | 0.022 |
| 2.0 M sod. formate | -0.023 | -0.561 | ± 0.003 | 0.022 |
| 0.5 M pot. sulphate + 0.5 M sod. formate | +0.004 | -0.534 | ± 0.003 | 0.023 |
| 0.5 M pot. chloride + 0.5 M sod. formate | -0.073 | -0.611 | ± 0.004 | 0.023 |
| 1.0 M pot. chloride + 0.5 M sod. formate | -0.093 | -0.631 | ± 0.004 | 0.023 |
| 0.25 M oxalic acid + 0.5 M sod. formate | -0.069 | -0.607 | ± 0.004 | 0.033 |
| 0.5 M oxalic acid + 0.5 M sod. formate | -0.081 | -0.619 | ± 0.004 | 0.033 |

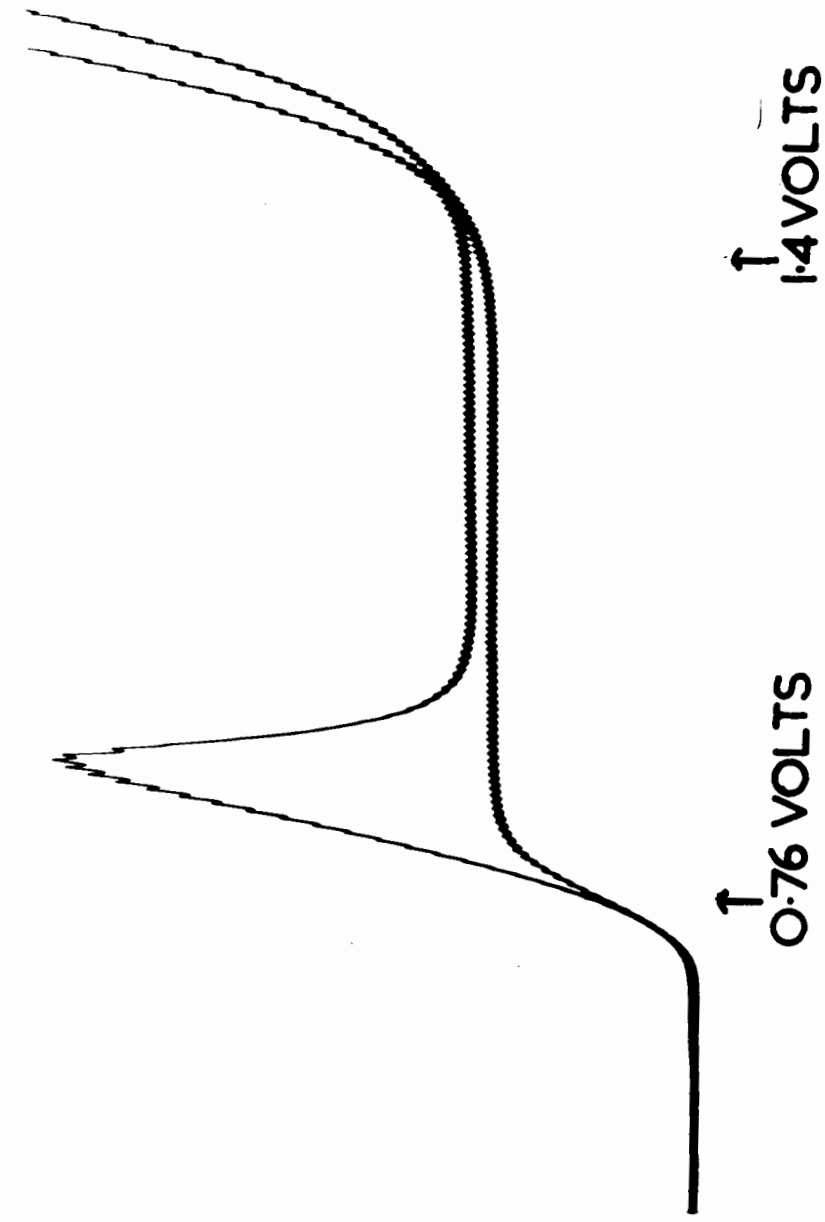
(III) LEAD.

The polarographic characteristics of lead in formic acid were found to be most favourable, very well developed waves being formed from a variety of supporting electrolytes. The polarogram shown above, using 0.25 M sodium formate as indifferent electrolyte is typical of lead, showing also the pronounced overcurrent observed with this element (Plate 5). In all the supporting electrolytes studied the slopes of the waves corresponded closely to a reversible two-electron reduction, the values of $\tan \alpha$ being in good agreement with the theoretical value of 0.030.

The addition of 2% (v/v) of water to the cathode electrolyte was found to shift the half-wave potential of lead to more negative values. In the three determinations made, this shift was found to be 0.003, 0.003 and 0.004 volts respectively, which shows the effect of added quantities of water, over this range to be small.

None of the lead salts tried was found to be more than sparingly soluble in formic acid, the most suitable being lead acetate. The lead acetate trihydrate used as supplied by May and Baker, was heated in an oven at 100°C for 3 hours; the anhydrous salt so formed was cooled and stored in a desiccator over anhydrous calcium chloride.

LEAD



Supporting electrolyte for upper curve 0.25M HCOONa
for lower curve 0.50M HCOONa

The half-wave potential of lead in a 0.5 M sodium formate medium was found to be -0.224 ± 3 volts vs S.C.F.A.E. (-0.762 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.032. On increasing the concentration of sodium formate to 2.0 M the half wave potential was found to shift to -0.242 ± 3 volts vs S.C.F.A.E. (-0.780 volts vs Q.F.A.E.). This change in reduction potential is readily accounted for as a liquid junction potential showing the lead to undergo no complex formation.

The diffusion coefficient of lead in formic acid was estimated by measurements of the diffusion current produced by known concentrations of the lead salt. Calculation by means of the Ilkovic equation ((1) - Section A) established this value as 0.25×10^{-5} cms.²/sec. The corresponding value as calculated by Lingane (38) from measurements of the diffusion current constant of lead in an aqueous non-complexing medium (1 M nitric acid) was 0.91×10^{-5} cms.²/sec.

TABLE 13.

| Concentration of Lead $\times 10^3$ gm. ions/litre | Diffusion Current (microamperes) |
|---|-------------------------------------|
| 0.332 | 2.02 |
| 0.498 | 3.03 |
| 0.664 | 3.87 |

$$\begin{aligned}
 h &= 42.25 \text{ cms.} & m &= 4.368 \text{ mgs./sec.} \\
 t &= 2.57 \text{ secs.} & m^{2/3} t^{1/3} &= 3.127 \text{ mgs.}^{2/3} \text{ secs.}^{-1/3} \\
 i_d/C &= 5.98 \text{ microamperes/mgm. ion/litre} \\
 I_{\text{HCOOH}} &= 1.9 & I_{\text{H}_2\text{O}} &= 3.67
 \end{aligned}$$

It was noticed during these measurements that lead acetate was very insoluble in formic acid but that the solubility was markedly increased by the addition of sodium formate. A similar observation was made by Davidson and Holm (44) who reported on the increased solubility of cupric formate in formic acid on the addition of ammonium formate.

Ammonium and potassium formates must be regarded as bases in formic acid. The above authors explain this enhanced solubility of cupric formate in the presence of ammonium and potassium formates by drawing an analogy with the appreciable solvent action of strong bases on cupric hydroxide in aqueous solution. The increased solubility of lead formate in the presence of sodium formate is thus not unexpected.

This enhanced solubility in the presence of sodium formate, although noticed first for lead acetate, was found to extend to the salts of all the other ions studied.

When a supporting electrolyte consisting of 0.25 M sodium citrate - 0.5 M sodium formate was used, the half wave potential of lead was found to be -0.238 ± 3 volts vs

S.C.F.A.E.

(-0.776 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.032.

The tendency of lead ions to form complexes in an aqueous acetate medium has been shown to be small (45), what complex formation there is, leading predominantly to $[\text{PbAc}_2]^-$ (46,47) and in smaller measure to $[\text{PbAc}]^+$ (48). The half-wave potential with an indifferent electrolyte of 0.25 M sodium acetate - 0.5 M sodium formate was found to be -0.232 ± 3 volts vs S.C.F.A.E. (-0.770 volts vs Q.F.A.E.) clearly showing the absence of complex formation in formic acid. The value of $\tan \alpha$ was 0.033.

Examination of the half wave potential of lead with a supporting electrolyte of 0.25 M sodium tartrate - 0.5 M sodium formate gave a value of -0.230 ± 4 volts vs S.C.F.A.E. (-0.768 volts vs Q.F.A.E.) showing little tendency to complex formation. This tendency is also small in aqueous solution where the complex formed contains one tartrate ion per lead ion (49-52). The value of $\tan \alpha$ was 0.029.

In an indifferent electrolyte of 0.25 M oxalic acid and 0.5 M sodium formate, the half-wave potential was found to be -0.273 ± 4 volts vs S.C.F.A.E. (-0.811 volts vs Q.F.A.E.) which, when the oxalic acid concentration was increased to 2.0 M, was found to shift to -0.310 ± 4 volts vs S.C.F.A.E. (-0.848 volts vs Q.F.A.E.). This is distinct evidence of complex formation the oxalato-

complex of lead being generally accepted as $[\text{Pb}(\text{C}_2\text{O}_4)_2]^{2-}$ (51-55). The value of $\tan \alpha$ was 0.032.

All attempts to obtain a measurable polarographic wave for lead in chloride medium failed due probably to a very low solubility of lead chloride in formic acid. The three indifferent electrolytes in which the measurement was attempted were 0.5 M potassium chloride, 0.25 M sodium formate - 0.5 M potassium chloride and finally 0.5 M ammonium chloride. Apart from a slight indentation in the polarogram at an applied potential of -0.24 volts vs S.C.F.A.E. using the highest galvanometer sensitivities reasonably possible, no measurable wave was obtained from any of these media.

In a medium of 0.5 M potassium sulphate not even the suggestion of a wave was noticed almost certainly due again to a very low solubility of the lead sulphate in formic acid. Both the chloride and sulphate media are thus quite unsuitable for the determination of lead in formic acid.

SUMMARY.

| Supporting Electrolyte | Half-wave Potentials | | Limits | tan α |
|--|----------------------|----------------|-------------|--------------|
| | vs S.C.F.A.E. | vs Q.F.A.E. | | |
| 0.5 M sod. formate | -0.224 | -0.762 | ± 0.003 | 0.032 |
| 0.5 M sod. formate + 2% (v/v) water | -0.227 | -0.765 | ± 0.003 | 0.032 |
| 2.0 M sod. formate | -0.242 | -0.780 | ± 0.003 | 0.032 |
| 0.5 M sod. formate + 0.25 M sod. citrate | -0.238 | -0.776 | ± 0.003 | 0.032 |
| 0.5 M sod. formate + 0.25 M sod. acetate | -0.232 | -0.770 | ± 0.003 | 0.033 |
| 0.5 M sod. formate + 0.25 M sod. tartrate | -0.230 | -0.768 | ± 0.003 | 0.029 |
| 0.5 M sod. formate + 0.25 M oxalic acid | -0.272 | -0.811 | ± 0.004 | 0.032 |
| 0.5 M sod. formate + 2.0 M oxalic acid | -0.310 | -0.848 | ± 0.004 | 0.032 |

(IV) TIN.

The reduction of stannous tin to the metal produced excellently defined waves in formic acid from most of the supporting electrolytes used. The reductions were found in all cases, to be reversible and to involve two electrons, giving values of $\tan \alpha$ close to the theoretical value of 0.030. Polarographic overcurrents were observed with this element, as is to be expected when considering the disparity between the half-wave potentials and the potential of the electrocapillary maximum. The overcurrents were suppressed by use of the optimum concentration of supporting electrolyte.

The effect of water on the characteristic potentials of tin was shown to be inappreciable. The addition of 2% (v/v) of water caused these potentials to shift by 0.003 volts to more negative potentials.

Stannous chloride, which is moderately soluble in formic acid, was found to be suitable. The anhydrous salt, as supplied by British Drug Houses, was dried by heating in an oven at 130°C for 5 hours and then allowed to cool over anhydrous calcium chloride.

By determination of the diffusion current at various concentrations of stannous chloride, a value of the diffusion

coefficient of the stannous ion in a 0.5 M sodium formate medium was obtained. Calculation by means of the Ilkovic equation ((1) Section A) established this value as 0.21×10^{-5} cms.²/sec. The corresponding value in aqueous solution as calculated from Lingane's (38) polarographic measurements on tin solutions in 1 M nitric acid was 1.1×10^{-5} cms.²/sec. The much larger value in aqueous solution is attributed to the existence in formic acid of a formate stannous complex ion as opposed to the presence of a much smaller uncomplexed species in aqueous solution.

TABLE 14.

| Concentration of Tin gm. ions/litre $\times 10^3$ | Diffusion Current (microamperes) |
|--|-------------------------------------|
| 0.510 | 2.77 |
| 0.941 | 5.38 |
| 1.223 | 6.86 |

$$h = 43.43 \text{ cms.}$$

$$t = 2.47 \text{ secs.}$$

$$m = 4.492 \text{ mgs./sec.} \quad m^{2/3} t^{1/6} = 3.165 \text{ mgs.}^{2/3} \text{ secs.}^{-1/6}$$

$$id/C = 5.62 \text{ microamps/mgm. ions/litre}$$

$$\text{Diffusion current constant } I_{\text{HCOOH}} = 1.8$$

$$I_{\text{H}_2\text{O}} = 4.02$$

The half-wave potential of stannous tin in a 0.5 M sodium formate medium was -0.281 ± 3 volts vs S.C.F.A.E. (-0.819 volts vs Q.F.A.E.) which on increasing the sodium

formate concentration to 2.0 M changed by -0.026 volts to a value of -0.307 ± 3 volts vs S.C.F.A.E. (-0.845 volts vs Q.F.A.E.). This change of the half-wave potential is slightly in excess of that attributable to liquid junction potential. It is believed to arise from the formation of weak formate-stannous complex $[\text{Sn}(\text{OOCH})_4]^{2-}$ as in aqueous solution (56). The value of $\tan \alpha$ was 0.034.

No evidence of complex formation was found when using a 0.5 M potassium sulphate supporting electrolyte, the characteristic potential being -0.282 ± 3 volts vs S.C.F.A.E. (-0.820 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.034.

The appreciable displacement of the half-wave potential when using oxalic acid as the background electrolyte indicated the formation of a complex. This may be of the form $[\text{Sn}_2(\text{C}_2\text{O}_4)_4]^{4-}$ as in aqueous solution (57). The half-wave potential in a 0.25 M oxalic acid - 0.5 M sodium formate medium was -0.346 ± 3 volts vs S.C.F.A.E. (-0.884 volts vs Q.F.A.E.), and with a supporting electrolyte of 0.5 M oxalic acid - 0.5 M sodium formate was -0.359 ± 3 volts vs S.C.F.A.E. (-0.897 volts vs Q.F.A.E.). The value of $\tan \alpha$ for both reductions was 0.033.

Stannous ions have been shown to undergo complex formation in a fluoride medium giving rise to the ion $[\text{SnF}_3]^-$ (58). It is probably the formation of this complex which causes an appreciable shift of potential in a fluoride-formic acid

medium. The half-wave potential when using a carrier electrolyte of 0.2 M sodium fluoride - 0.5 M sodium formate was -0.333 ± 3 volts vs S.C.F.A.E. (-0.871 volts vs Q.F.A.E.) In a medium of 0.4 M sodium fluoride - 0.5 M sodium formate this potential was $-0.355 \pm$ volts vs S.C.F.A.E. (-0.893 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.033 in each case.

The polarographic examination of tin in chloride and bromide media proved most disappointing. Without the addition of gelatin the waves were poorly defined. The addition of 0.01% of gelatin improved the wave when using a chloride supporting electrolyte but that in a bromide medium was so irregular as to warrant no further investigation. An estimation of the half-wave potentials was, however, attempted. When using an indifferent electrolyte of 0.5 M potassium chloride - 1.0 M sodium formate this potential was -0.38 ± 1 volts vs S.C.F.A.E. (-0.92 volts vs Q.F.A.E.). With an electrolyte composition of 1.0 M potassium chloride - 1.0 M sodium formate the half-wave potential was -0.40 ± 1 volts vs S.C.F.A.E. (-0.94 volts vs Q.F.A.E.). The shift of potential may be due to the complex species $[\text{SnCl}]^+$, SnCl_2 and $[\text{SnCl}_3]^-$ formed in aqueous solution (58). No attempt was made to measure $\tan \alpha$.

A half-wave potential of -0.39 ± 0.015 volts vs S.C.F.A.E. (-0.93 volts vs Q.F.A.E.) was found when the indifferent electrolyte was 0.2 M sodium bromide - 0.5 M sodium formate.

The bromo-stannous complex ion probably formed is $[SnBr_3]^-$ as in aqueous solution (58). The difficulty in measuring the half-wave potential was added to by the close proximity of the anodic wave of the bromide ions. This limited the length of the base of the wave making accurate measurement impossible.

SUMMARY.

| Supporting Electrolyte | Half-wave potentials | | Limits | tan α |
|---|----------------------|----------------|-------------|--------------|
| | VS S.C.F.A.E. | VS Q.F.A.E. | | |
| 0.5 M sodium formate | -0.281 | -0.819 | ± 0.003 | 0.034 |
| 0.5 M sodium formate + 2% water | -0.284 | -0.822 | ± 0.003 | 0.034 |
| 2.0 M sodium formate | -0.307 | -0.845 | ± 0.003 | 0.034 |
| 0.5 M potassium sulphate | -0.282 | -0.820 | ± 0.003 | 0.034 |
| 0.25 M oxalic acid + 0.5 M sod. formate | -0.346 | -0.884 | ± 0.003 | 0.033 |
| 0.5 M oxalic acid + 0.5 M sod. formate | -0.359 | -0.897 | ± 0.003 | 0.033 |
| 0.2 M sod. fluoride + 0.5 M sod. formate | -0.333 | -0.871 | ± 0.003 | 0.033 |
| 0.4 M sod. fluoride + 0.5 M sod. formate | -0.355 | -0.893 | ± 0.003 | 0.033 |
| 0.5 M pot. chloride + 1.0 M sod. formate | -0.38 | -0.92 | ± 0.01 | - |
| 1.0 M pot. chloride + 1.0 M sod. formate | -0.40 | -0.94 | ± 0.01 | - |
| 0.2 M sod. bromide + 0.5 M sod. formate | -0.39 | -0.93 | ± 0.015 | - |

(V) THALLIUM.

The most suitable thallium salt for the investigation of the behaviour of thalious ions was found to be the carbonate which was moderately soluble in formic acid. Thalious carbonate as supplied by British Drug Houses was allowed to stand over anhydrous calcium chloride for 5 days after which it was used without further purification.

The half-wave potential of thallium in a 0.5 M sodium formate supporting electrolyte was found to be -0.386 ± 3 volts vs S.C.F.A.E. (-0.924 volts vs Q.F.A.E.). The reduction was, however, found to proceed somewhat irreversibly, the value of $\tan \alpha$ being 0.073. The addition of 2% (v/v) of water was found to shift the potential by about 0.003 volts to more positive values; a shift in the positive direction was in complete contrast to all other cations examined in formic acid. On increasing the sodium formate concentration to 2.0 M, the half-wave potential was -0.312 ± 3 volts vs S.C.F.A.E. (-0.850 volts vs Q.F.A.E.), a distinct shift towards more positive values. The value of $\tan \alpha$ was found to be 0.062.

In view of the unique behaviour of thallium it was decided to measure the half-wave potential and value of $\tan \alpha$ at even higher sodium formate concentrations. The results are tabulated in Table 15, and plotted in Plate 7. The plot was initially curved after which a linear relationship developed. The increase of the liquid junction potential between the anode

and cathode compartments has, in this investigation, always caused the half-wave potential to change to more negative values.

TABLE 15.

| Conc. of sod. formate | Half-wave Potential vs S.C.F.A.E. (volts) |
|--------------------------|---|
| 0.5 M | -0.382 |
| 1.0 M | -0.366 |
| 1.5 M | -0.354 |
| 2.0 M | -0.343 |
| 2.5 M | -0.333 |
| 3.0 M | -0.326 |
| 3.5 M | -0.318 |
| 4.0 M | -0.308 |
| 4.5 M | -0.300 |
| 5.0 M | -0.294 |

It was decided to completely eliminate this junction potential, however, by making the sodium formate concentrations in the anode and cathode equal. In view of the investigation of the salt effect of the quinhydrone-in-formic acid electrode described in Section C, the increase of sodium formate in the anode compartment should be little effect on the electrode potential. The result of increasing the sodium formate concentrations in the two compartments on the half-wave potential of thallium is plotted in Table 16 and shown in Plate 7. As anticipated this shows the value of the half-wave potential in Graph I to be a combination of a positive shift and a change, due to junction potential,

THALLIUM



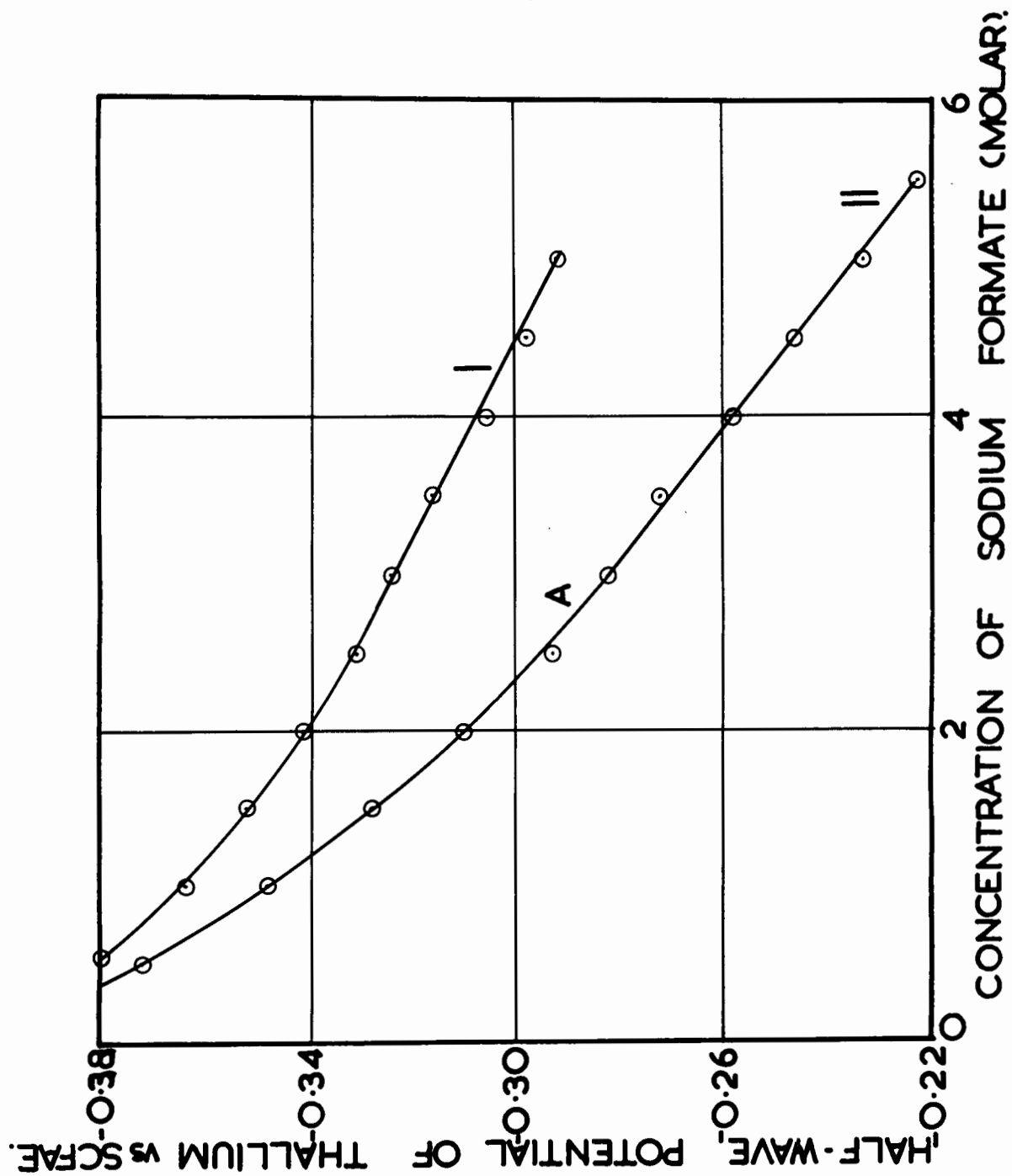
Potential of line
vs Q.F.A.E.

| | | |
|---|---|--------|
| 1 | — | 0.865 |
| 2 | — | 0.8947 |
| 3 | — | 0.9250 |
| 4 | — | 0.9552 |
| 5 | — | 0.986 |

↑ 1
↑ 2
↑ 3
↑ 4
↑ 5

supporting electrolyte
0.50M HCOONa.

PLATE 7



to more negative values. With the latter effect eliminated the positive shift was even more marked. The potential at which the reduction first becomes reversible is about -0.29 volts vs S.C.F.A.E. (-0.83 volts vs Q.F.A.E.).

TABLE 16.

| Conc. of sod. form. | Half-wave potential vs S.C.F.A.E. (volts) | $\tan \alpha$ |
|------------------------|---|---------------|
| 0.5 M | -0.374 | 0.073 |
| 1.0 M | -0.350 | 0.068 |
| 1.5 M | -0.330 | 0.065 |
| 2.0 M | -0.312 | 0.062 |
| 2.5 M | -0.295 | 0.059 |
| 3.0 M | -0.284 | 0.059 |
| 3.5 M | -0.274 | 0.060 |
| 4.0 M | -0.260 | 0.059 |
| 4.5 M | -0.248 | 0.058 |
| 5.0 M | -0.235 | 0.059 |
| 5.5 M | -0.224 | 0.060 |

It was also at this potential that the plot ended the curved portion and began the linear relationship. It was thus taken as the half-wave potential of thallium.

It has been found, although not examined in such detail, that increase of concentration of other electrolytes also caused a shift in the half-wave potential. The values, as found at the usual concentrations of these supporting electrolytes are quoted.

The half-wave potential in a 0.2 M sodium fluoride -

0.5 M sodium formate medium was -0.382 ± 3 volts vs S.C.F.A.E. (-0.920 volts vs Q.F.A.E.) the value of $\tan \alpha$ being 0.069.

No waves were obtained in the presence of chloride or bromide supporting electrolytes, due to the high insolubility of these salts in formic acid.

In a medium of 0.25 M oxalic acid and 0.5 M sodium formate the wave although not well defined, was measurable giving a value of the half-wave potential of -0.411 ± 5 volts vs S.C.F.A.E. (-0.949 volts vs Q.F.A.E.). In a medium of 0.5 M potassium sulphate the wave was also not well defined, the value of the half wave potential being taken as -0.408 ± 5 volts vs S.C.F.A.E. (-0.946 volts vs Q.F.A.E.). Due to the slightly irregular shape of these curves, no measurement of $\tan \alpha$ could be made. The reduction appeared, nevertheless, to be irreversible.

The wave in a medium of 0.25 M sodium acetate - 0.5 M sodium formate was well developed the half-wave potential being -0.374 ± 3 volts vs S.C.F.A.E. (-0.912 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.068.

The polarogram for thallium using a supporting electrolyte of 0.5 M sodium formate is shown in Plate 6.

No explanation of the anomalous behaviour of thallium has been found. The diffusion coefficient of thallium in aqueous solution is abnormally high being attributed to the

completely unhydrated state of the thalious ion (59). The diffusion coefficient in formic acid, although smaller than in water, is not as greatly reduced as the other ion by change of medium from water to formic acid. Not much importance is attached, however, to this observation. The anomalous behaviour is believed to be due to some circumstance operative in formic acid but entirely absent in aqueous solution. That the thalious ion migrates at a rate somewhat in excess of that expected is a matter of degree rather than kind. The solution to the problem is not to be found in the high solubility of thallium in mercury as this factor is the same in both solvents.

The change in the half-wave potential to more positive values is not explained on the grounds of increased ionic strength of the medium. The half-wave potential for the thallium in aqueous solution has been shown to shift to more negative potentials on increase of the ionic strength (60).

The phenomenon can not be due to complex formation of any kind as this would result in a negative shift of the half-wave potential. A shift to more positive values is expected if the reduction is becoming more reversible but once reversibility is attained the potential would be expected to remain constant and then gradually to move back towards more negative values under the influence of the liquid junction potential. This was not the case.

The only possible difference between formic acid and water that could have an influence was that the former solvent is a powerful reducing agent while the other is not and furthermore that formic acid molecules are capillary active. It is difficult, however, to see how either effect can cause the observed anomalies. Under the circumstances, therefore, it is not possible to suggest an explanation of the phenomenon.

The value of the diffusion coefficient of thallous ions in a 0.5 M sodium formate medium was determined by the measurement of the diffusion current at various concentrations of thallous salt. Calculation by means of the Ilkovic equation ((1) - Section A) established this value as 0.96×10^{-5} cms.²/sec. The value derived by Lingane (61) from conductance measurements was 1.08×10^{-5} cms.²/sec.

TABLE 17.

| Concentration of Thallium x 10 gm. ions/litre | Diffusion Current (microamps) |
|--|----------------------------------|
| 1.60 | 9.11 |
| 2.32 | 13.34 |
| 2.96 | 17.00 |

$$h = 41.52 \text{ cms.}$$

$$t = 2.59 \text{ secs.}$$

$$m = 4.293 \text{ mgs./sec.} \quad m^{2/3} t^{1/6} = 3.096 \text{ mgs.}^{2/3} \text{ secs.}^{-1/6}$$

$$i_d/c = 5.81 \text{ microamps/mgm ion/litre}$$

Diffusion current constants

$$I_{H_2O} = 2.00$$

$$I_{HCOOH} = 1.90$$

(VI) CADMIUM.

The very favourable polarographic characteristics of cadmium in formic acid enabled the determination of this element to be made in a variety of supporting electrolytes. The waves were well defined, showing a reversible two electron reduction of the bivalent ions to metallic cadmium. With all the supporting electrolytes studied, the value of $\tan \alpha$ was always in close agreement with the theoretical value of 0.030.

In view of the relatively small differences between the half-wave potentials of cadmium and the potential of the electro-capillary maximum it was not thought likely that polarographic overcurrents would be encountered in the investigation of this element. No such overcurrents were observed even at such low supporting electrolyte concentrations as 0.1 M (Section F).

Of the cadmium salts tried, the chloride was found to be most suitable. Cadmium chloride as supplied by May and Baker Ltd., was heated in an oven for 5 hours at 130°C after which the anhydrous salt was cooled and stored in a desiccator over anhydrous calcium chloride.

The effect of added small quantities of water on the half-wave potential of cadmium in a sodium formate medium

was shown to be small. The shift to more negative potentials caused by the addition of 2% (v/v) of distilled water was 0.005 volts, on both occasions that the measurement was made.

The value of the diffusion coefficient of cadmium ions in a 0.5 M sodium formate medium was determined by the measurement of the diffusion current at various concentrations of cadmium chloride. Calculation by means of the Ilkovic equation ((1) - Section A) gave this value as 0.32×10^{-5} cms.²/sec. The corresponding value in aqueous solution as derived from the measurements of Lingane (38) was 0.64×10^{-5} cms.²/sec.

TABLE 18.

| Concentration of Cadmium x 10 ³ gm. ions/litre | Diffusion Current (microamps) |
|--|----------------------------------|
| 1.18 | 7.6 |
| 1.78 | 12.4 |
| 2.38 | 16.1 |

$$h = 42.45 \text{ cms.}$$

$$t = 2.51 \text{ secs.}$$

$$m = 4.391 \text{ mgs./sec.} \quad m^{3/2} t^{1/2} = 3.126 \text{ mgs.}^{3/2} \text{ secs.}^{-1/2}$$

$$id/C = 6.80 \text{ microamps/mgm. ion/litre.}$$

Diffusion current constants:-

$$I_{\text{HCOOH}} = 2.2$$

$$I_{\text{H}_2\text{O}} = 3.06.$$

In a 0.5 M sodium formate medium, the half-wave potential of the cadmium wave was shown to be -0.337 ± 3 volts vs

S.C.F.A.E. (-0.875 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.030. The half-wave potential was found on increasing the formate ion concentration to 2.0 M, to change to -0.356 \pm 3 volts vs S.C.F.A.E. (-0.894 volts vs Q.F.A.E.).

Unlike zinc, cadmium is reduced at a potential appreciably more positive than that for the discharge of hydrogen ions and is thus considerably more suitable for the study of the complexes formed by both these elements, with the halogens. As is to be expected, from observations in aqueous solution, no complex was formed by cadmium with fluoride ions with an indifferent electrolyte of 0.5 M sodium formate - 0.2 M sodium fluoride, the half-wave potential was -0.344 \pm 3 volts vs S.C.F.A.E. (-0.882 volts vs Q.F.A.E.). On increasing the sodium fluoride concentration to 0.4 M the half-wave potential remained almost unchanged at -0.349 \pm 3 volts vs S.C.F.A.E. (-0.887 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.032.

In a medium of 0.5 M sodium formate - 0.2 M potassium chloride, however, there is very considerable complex formation. The half-wave potential was -0.489 \pm 3 volts vs S.C.F.A.E. (-1.027 volts vs Q.F.A.E.) which on increasing the concentration of potassium chloride to 0.4 M shifted by 0.033 volts to a value of -0.522 \pm 3 volts vs S.C.F.A.E. (-1.060 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.032.

In order to gain some idea of the nature of the complex present, the above results were substituted in ((3) - Section

A). In this case, although the liquid junction potential is not known, it has been shown in Section C that the addition of potassium chloride to one compartment of the cell gives rise to an inappreciable diffusion potential.

The shift ΔE of -0.033 volts was caused by an increase in the complexing reagent concentration from 0.2 M to 0.4 M. On making this substitution, the co-ordination number of the metal ion in the complex was 3.7 which suggested the complex species to be mainly $[\text{CdCl}_3]^-$. All the intermediate complexes $[\text{CdCl}]^+$, CdCl_2 , $[\text{CdCl}_2]^-$, $[\text{CdCl}_3]^-$ and $[\text{CdCl}_4]^{2-}$ will almost certainly also be present and thus the above result may be to some extent fortuitous. On the other hand, the data for aqueous solution (62-69) suggest that the tetra-halogenated bivalent form greatly predominates at the concentrations of chloride ion employed in these measurements.

In an indifferent electrolyte of 0.5 M sodium formate - 0.2 M sodium bromide the half-wave potential was -0.585 \pm 4 volts vs S.C.F.A.E. (-1.123 volts vs Q.F.A.E.) which was displaced by 0.036 volts to a value of -0.621 \pm 4 volts vs S.C.F.A.E. (-1.159 volts vs Q.F.A.E.) on increasing the concentration of sodium bromide to 0.4 M. The value of $\tan \alpha$ was 0.032. On substitution of these data in Equation (3) the co-ordination number, p , was found to be 4.1 which suggests the complex to be $[\text{CdBr}_4]^{2-}$. As for the chloro complexes intermediate species such as $[\text{CdBr}]^+$, CdBr_2

[CdBr_2] are also formed (66-68). Here, however, an increase in the atomic number of the halogen causes an increase in the stability of the complexes of higher co-ordination number increasing the probability of the tetra-brominated divalent ion being the predominant complex.

In view of the slight decomposition of bromides in formic acid, it was thought possible that this would initiate the measurement of reliable half-wave potentials in this medium. The solution, employing as supporting electrolyte 0.5 M sodium formate - 0.4 M sodium bromide was left standing in an atmosphere of nitrogen, for 60 minutes, after which time the half-wave potential was re-determined. The value was found to be -0.623 volts vs S.C.F.A.E., a variation well within the limits of accuracy of the measurements. Further, the waves in this medium were well developed giving no indication of the small decomposition. The solutions were, however, very slightly brown in colour.

Due to the appreciable decomposition suffered by iodides in formic acid, this medium was quite unsuitable for polarographic determinations. From the appearance of the polarogram it seems likely that the wave for cadmium had been shifted beyond the decomposition potential of the hydrogen ions and was totally obscured. In view of the existing decomposition, however, this could not be regarded as certain.

The half-wave potential of cadmium in a 0.5 M potassium sulphate was -0.356 ± 3 volts vs S.C.F.A.E. (-0.894 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.031.

With a supporting electrolyte of 0.5 M sodium formate - 0.1 M sodium tartrate the half-wave potential was -0.347 ± 4 volts vs S.C.F.A.E. (-0.885 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.031.

Finally use was made of a mixture of 0.5 M sodium formate and 0.1 M oxalic acid as indifferent electrolyte, the value of the half-wave potential being -0.350 ± 3 volts vs S.C.F.A.E. (-0.888 volts vs Q.F.A.E.). The values of $\tan \alpha$ was 0.032.

SUMMARY.

| Supporting Electrolyte | Half-wave potential | | Limits | tan α |
|---|---------------------|----------------|-------------|--------------|
| | vs S.C.F.A.E. | vs Q.F.A.E. | | |
| 0.5 M sod. formate | -0.337 | -0.875 | ± 0.003 | 0.030 |
| 0.5 M sod. formate + 2% (v/v) water | -0.342 | -0.880 | ± 0.003 | 0.031 |
| 2.0 M sod. formate | -0.356 | -0.894 | ± 0.003 | 0.030 |
| 0.5 M sod. formate + 0.2 M sod. fluoride | -0.344 | -0.882 | ± 0.003 | 0.032 |
| 0.5 M sod. formate + 0.4 M sod. fluoride | -0.349 | -0.887 | ± 0.003 | 0.032 |
| 0.5 M sod. formate + 0.2 M pot. chloride | -0.489 | -1.027 | ± 0.003 | 0.032 |
| 0.5 M sod. formate + 0.4 M pot. chloride | -0.522 | -1.060 | ± 0.003 | 0.032 |
| 0.5 M sod. formate + 0.2 M sod. bromide | -0.585 | -1.123 | ± 0.004 | 0.033 |
| 0.5 M sod. formate + 0.4 M sod. bromide | -0.621 | -1.159 | ± 0.004 | 0.032 |
| 0.5 M pot. sulphate | -0.356 | -0.894 | ± 0.003 | 0.031 |
| 0.5 M sod. formate + 0.1 M sod. tartrate | -0.347 | -0.885 | ± 0.004 | 0.031 |
| 0.5 M sod. formate + 0.1 M oxalic acid | -0.350 | -0.888 | ± 0.003 | 0.032 |

(VII) INDIUM.

In aqueous solution, indium present as the aquo-indic ion, is irreversibly reduced to produce an extended wave (70). The polarogram of indium in a formate-formic acid medium, however, showed that provided the indium concentration was kept low a reversible three-electron reduction was operative. The waves obtained from all the supporting electrolytes were well defined. No polarographic overcurrents were encountered, their absence being due to the close proximity of the half-wave and electrocapillary maximum potentials.

Indic chloride was found to be readily soluble in formic acid and was employed throughout the investigation. It had been made by dissolving B.D.H. grade metallic indium in aqua regia and evaporating the solution to dryness. The evaporation was repeated three times with the addition of more hydrochloric acid each time, so as to remove all nitric acid. The solid was purified by sublimation and dried at 120°C for 5 hours.

Unlike the other inorganic cations investigated in this research, with the exception of tin, indium undergoes complex formation in a formate medium. In consequence of this, indium was examined more closely, in an endeavour to elucidate the structure of the complex ion, and, in passing, was found to behave in an unusual manner. The odd behaviour

of indium in formate medium was closely paralleled by that of the same element in a sulphate medium where the effects were larger and even more obvious. It is thus proposed to describe the examination of indium using potassium sulphate as the supporting electrolyte and then to compare the behaviour when using sodium formate.

It was observed that, with the concentration of potassium sulphate maintained constant at 0.5 M, increase in the indic ion concentration caused a slight shift of the half-wave potential to more negative values. The value of $\tan \alpha$ also increased showing that the reduction was becoming less reversible. If, however, the indic ion concentration was kept constant and the concentration of potassium sulphate increased, the value of $\tan \alpha$ tended to decrease and return to the theoretical value of 0.020. The plot of $\tan \alpha$ against the ratio of indic to sulphate ion concentrations, $[\text{In}]/[\text{SO}_4]$, was found to be linear for both sets of results. Extrapolation of these curves to zero indium concentration gave values of $\tan \alpha$ of 0.020 and 0.021.

TABLE 19.

| Conc. of Indium $\times 10^3$ M | Half-wave potential (volts) | $\tan \alpha$ | $[\text{In}]/[\text{SO}_4]$ $\times 10^4$ |
|------------------------------------|--------------------------------|---------------|--|
| 0.344 | -0.871 | 0.023 | 6.9 |
| 0.662 | -0.875 | 0.026 | 13.2 |
| 0.956 | -0.878 | 0.029 | 19.1 |
| 1.230 | -0.882 | 0.032 | 24.6 |

Conc. of potassium sulphate = 0.50 M.

These results are plotted in 2 Plate 8.

TABLE 20.

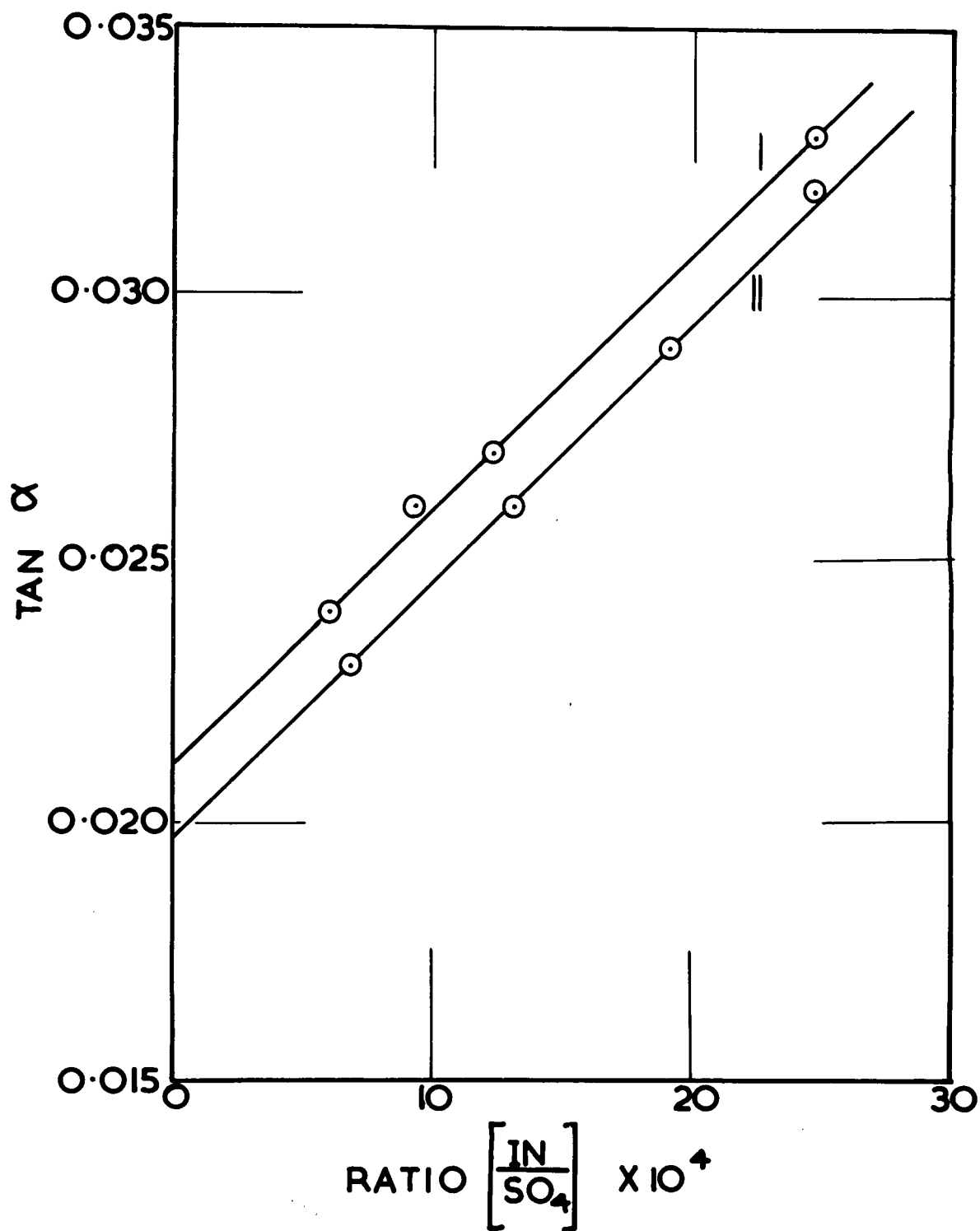
| Conc. of potassium sulphate | Half-wave potential (volts) | $\tan \alpha$ | $[\text{In}]/[\text{SO}_4]$ $\times 10^4$ |
|-----------------------------|--------------------------------|---------------|--|
| 0.5 M | -0.882 | 0.033 | 24.6 |
| 1.0 M | -0.905 | 0.027 | 12.3 |
| 1.5 M | -0.922 | 0.026 | 9.22 |
| 2.0 M | -0.942 | 0.024 | 6.15 |

Conc. of indium = 1.23×10^{-3} gm. ions/litre.

These results are plotted in 1 Plate 8.

The results in Table 20 show the half-wave potential to shift appreciably to more negative values on increasing the potassium sulphate concentration. Although this shift is indicative of complex formation, a lack of knowledge of the liquid junction potential introduces a measure of uncertainty.

PLATE 8



With the potassium sulphate concentration maintained at 0.5 M, the diffusion currents i_d produced by known concentrations of indium, C , were measured. The plot of i_d against C was linear but on extrapolation did not pass through the origin, as expected. From the data tabulated below it was possible to calculate the diffusion coefficient for indium under these conditions.

TABLE 21.

| Concentration of Indium $\times 10^3$ gm. ions/litre | Diffusion Current (microamps) |
|---|----------------------------------|
| 0.602 | 3.19 |
| 1.075 | 7.48 |
| 1.377 | 10.36 |
| 1.654 | 12.55 |
| 1.910 | 14.96 |
| 2.151 | 17.13 |
| 2.374 | 19.30 |
| 2.580 | 21.00 |

The concentration of potassium sulphate was 0.5 M.

The capillary details were:

$$h = 41.71 \text{ cms.}$$

$$m = 4.313 \text{ mgs./sec.}$$

$$t = 2.58 \text{ secs.}$$

$$m^{2/3} t^{1/3} = 3.10(3) \text{ mgs.}^{2/3} \text{secs.}^{1/3}$$

From Plate 9 $i_d/C = 9.15$ microamps/mgm. ions/litre

and by using the Ilkovic equation ((1) - Section A) the diffusion current of indium in this environment was

$0.25 \times 10^{-5} \text{ cms.}^2/\text{sec.}$ The above results are plotted in

Plate 9.

With the potassium sulphate concentration maintained at 0.75 M, however, the plot of id against C was shown clearly to be composed of two separate straight lines. Assuming each curve to be due to an ionic species, the slopes of the lines were used to furnish values of the corresponding diffusion coefficients.

TABLE 22.

| Concentration of Indium $\times 10^3$ gm. ions/ litre | Diffusion Current (microamps) |
|---|----------------------------------|
| 0.191 | 1.22 |
| 0.374 | 2.52 |
| 0.550 | 3.90 |
| 0.717 | 4.93 |
| 0.878 | 6.12 |
| 1.03 | 7.90 |
| 1.32 | 10.22 |
| 1.60 | 12.99 |

These results are plotted in Plate 10.

The concentration of potassium sulphate was 0.75 M.

Also $h = 42.68$ cms.

$m = 4.415$ mgs./sec.

$t = 2.55$ secs.

$m^{2/3} t^{1/3} = 3.14(6)$ mgs.^{2/3} secs.^{-1/3}.

For curve X $id/C = 6.90$ microamps/mgm. ions/litre and thus the diffusion coefficient was 0.15×10^{-5} cms.²/sec.

$I_{\text{HCOOH}} = 2.2$

For curve Y $id/C = 9.11$ microamps/mgm. ions/litre and thus

PLATE 9

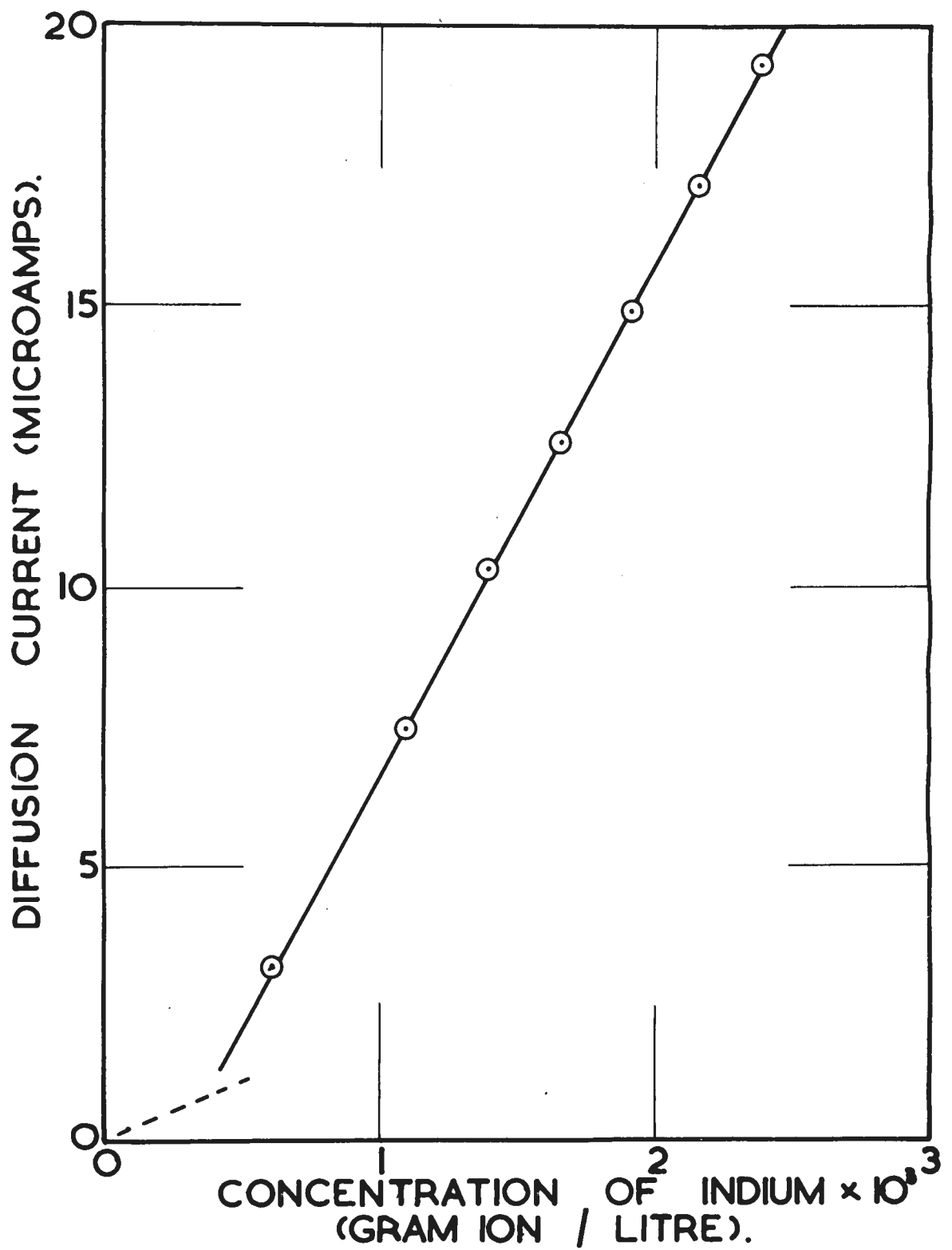
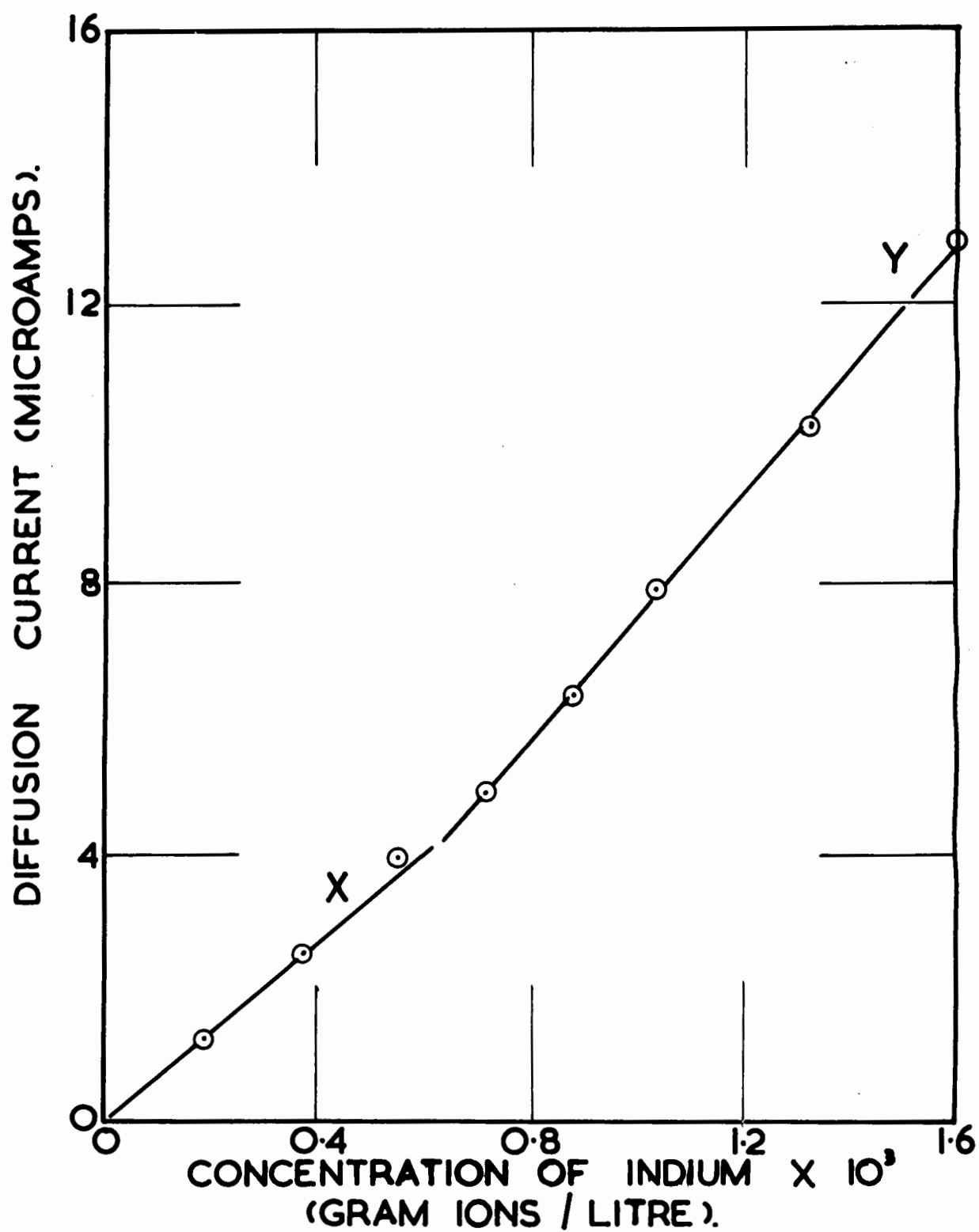


PLATE 10



the diffusion coefficient was 0.25×10^{-5} cms.²/sec.

$$I_{\text{HCOOH}} = 2.9.$$

This immediately suggested that the indium was present in two different species and that this cation formed two sulphato complexes depending on the relative values of the indium and sulphate ion concentrations. The increase in $\tan \alpha$ on increasing the value of $[\text{In}]/[\text{SO}_4]$ could readily be explained if it was supposed that the one sulphato-indic complex was reversibly reduced and the other irreversibly reduced.

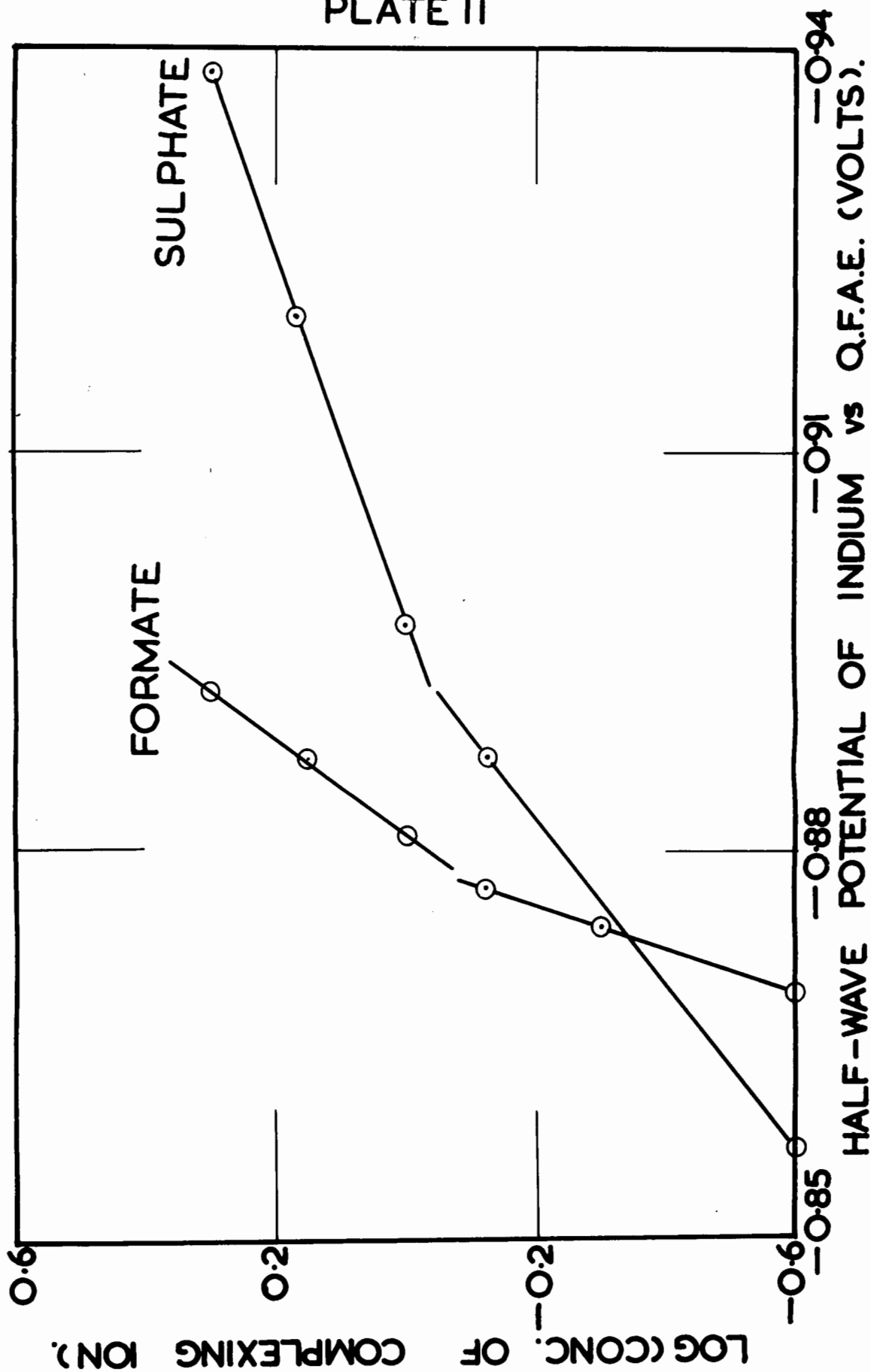
A final test of the existence of two such complexes would be furnished by measuring the half-wave potentials at various concentrations of potassium sulphate. Two intersecting straight lines would be expected, the slopes of which would indicate the structures of each of the complexes.

TABLE 23.

| Conc. of pot. sulphate C | log C | Half-wave potentials (volts) |
|-----------------------------|--------|---------------------------------|
| 0.25 M | -0.602 | -0.857 |
| 0.50 M | -0.301 | -0.874 |
| 0.75 M | -0.125 | -0.887 |
| 1.0 M | 0 | -0.897 |
| 1.5 M | +0.176 | -0.920 |
| 2.0 M | +0.301 | -0.938 |

The results quoted above are plotted in Plate 11.

PLATE II



As can be seen from the plot, this was found to be the case. The structures of each complex cannot be known with certainty due to a lack of knowledge of the liquid junction potential at the sintered glass boundary. The slope of the one line is, however, almost exactly twice that of the other, showing the number of sulphate ligands in the one complex to be twice that in the other. It would thus appear very likely that at low indium concentrations a complex $[\text{In}(\text{SO}_4)_2]^-$ which is reversibly reduced is formed but on increasing the cation content, the indium is in the form of the complex $[\text{In}(\text{SO}_4)]^+$, the reduction of which tends to be somewhat irreversible.

The restricted length of the first line in Plate 9 as compared with that in Plate 10 is due to the smaller proportion of $[\text{In}(\text{SO}_4)_2]^-$. This arises from the smaller value of 0.5 M, (in Plate 9) for the sulphate ion concentration, a consequently higher value for the $[\text{In}]/[\text{SO}_4]$ ratio and therefore a predominance of the $[\text{In}(\text{SO}_4)]^+$ complex. For this reason, with the sulphate ion concentration of 0.75 M, more of the higher complex $[\text{In}(\text{SO}_4)_2]^-$ is present and its corresponding line more in evidence. Both sets of results give the value of the diffusion coefficient of the $[\text{In}(\text{SO}_4)]^+$ complex as 0.25×10^{-5} cms.²/sec. A third determination at a sulphate concentration of 0.5 M gave a value of 0.26×10^{-5} cms.²/sec.

The determinations quoted in Table 23 were done at as low an indium concentration as possible so that the reductions were completely reversible. Thus no error was incurred because of a negative shift in the half-wave potentials due to the reduction being irreversible.

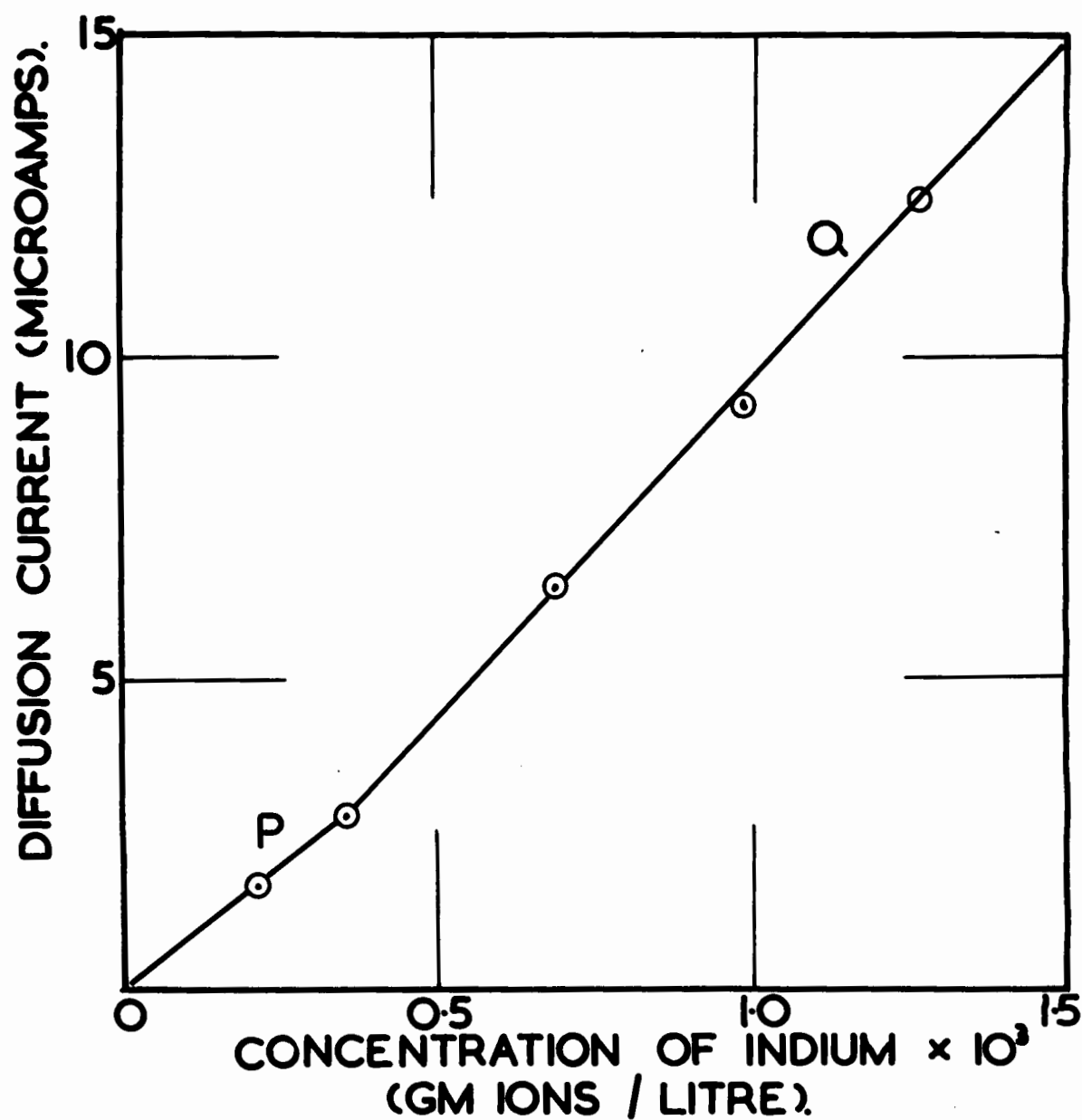
The addition of 2% (v/v) of water was found to have an inappreciable effect on the above results.

Whereas the behaviour of indium in formate medium has been shown to be very similar to that described above, it is likely that the one formate complex is not reduced as irreversibly as its sulphato counterpart. The increase in $\tan \alpha$ on increasing the indium concentration was not as marked as in sulphate medium. A plot of the diffusion current against indium concentration showed two separate curves (Plate 12).

It was possible, by using the Hendersen equation ((4) - Section A) to calculate the liquid junction potential set up when the formate ion concentration was increased. Thus by plotting the corrected values of $E_{1/2}$ against $\log C$, as before, indium was shown to form two complexes $[\text{In}(\text{OOCH})]^{++}$ and $[\text{In}(\text{OOCH})_2]^+$, the reduction of the former being somewhat irreversible, the reduction of the latter being completely reversible.

The structures of these complex ions were determined by

PLATE 12



examination of Plate 11 and substitution in the equation ((3) - Section A). From these considerations the values of p were 0.84 and 1.86, leading to the suggested complex structures.

TABLE 24.

| Concentration of $\text{In}^{+++} \times 10^3$ gm. ions/litre | Diffusion Current (microamps) |
|---|----------------------------------|
| 0.22 | 1.71 |
| 0.36 | 2.81 |
| 0.69 | 6.44 |
| 0.99 | 9.22 |
| 1.27 | 12.42 |

Also $h = 42.28$ cms.

$m = 4.372$ mgs./sec.

$t = 2.53$ secs. $m^{2/3} t^{1/3} = 3.12(1)$ mgs.^{2/3}secs.^{1/3}.

For curve P $i_d/c = 7.90$ microamps/mgm. ions/litre giving a value of the diffusion coefficient of 0.19×10^{-5} cms.²/sec.

$$I_{\text{HCOOH}} = 2.5$$

For curve Q $i_d/c = 11.98$ microamps/mgm. ions/litre giving a value of the diffusion coefficient of 0.44×10^{-5} cms.²/sec.

$$I_{\text{HCOOH}} = 3.8.$$

TABLE 25.

| Conc. of sod. formate C | log C | Observ. Half-wave Potential (volts) | Liquid Junction Potential (volts) | Corrected Half-wave Potential (volts) |
|----------------------------------|--------|--|--|--|
| 0.25 M | -0.602 | -0.869 | 0 | -0.869 |
| 0.50 M | -0.301 | -0.884 | 0.010 | -0.874 |
| 0.75 M | -0.125 | -0.894 | 0.016 | -0.878 |
| 1.0 M | 0 | -0.901 | 0.020 | -0.881 |
| 1.5 M | 0.176 | -0.914 | 0.027 | -0.887 |
| 2.0 M | 0.301 | -0.922 | 0.030 | -0.892 |

Indium in aqueous solution tends to be irreversibly reduced when feebly complexed, e.g. indic aquo ion, but reversibly reduced when strongly complexed as in the chloro-indic ion. Thus it may be expected that the mono-ligated complexes, $[\text{In}(\text{OOCH})]^{++}$ and $[\text{In}(\text{SO}_4)]^+$, which, as shown by their potentials, are weaker than their disubstituted counterparts, should be reduced less reversibly.

It was noticed by Kolthoffe Lingane (71) that "large concentrations of sulphate ion greatly suppress the diffusion current" of indium. Unfortunately no figures are available in support of this observation. Similar behaviour was noticed in formic acid on increasing the sulphate concentration from 0.5 M to 2.0 M. As the solubility of potassium sulphate in formic acid is not much in excess of 2.0 M, however, the solution at this concentration had a high viscosity. The reduction of the wave height in formic acid

was attributed to this cause. To ensure that it was not due in the main to the formation of the complex sulphate ion which would have a lower diffusion coefficient and consequently give a lower wave height, the depression of the wave was examined in the presence of potassium chloride. The wave height was measured in a 0.5 M potassium chloride - 0.5 M potassium sulphate solution and compared with that in a 0.5 M potassium chloride - 2.0 M potassium sulphate solution. In the presence of the chloride ion it is most likely that all the indium is in the form of the stronger chloro-indic complex and addition of sulphate ions will result in no formation of a sulphate-indic complex. Thus any reduction in the wave height on adding the potassium sulphate would be due to increase in the viscosity of the solution.

TABLE 26.

| Concentration of Indium $\times 10^3$ moles | Height of Wave | | Ratio of Wave Heights |
|--|--|--|-----------------------|
| | In 0.5 M pot. sulphate (microamps) | In 2.0 M pot. sulphate (microamps) | |
| 0.75 | 6.08 | 2.25 | 2.70 |
| 1.23 | 9.61 | 3.74 | 2.57 |
| 2.26 | 16.07 | 6.14 | 2.62 |
| | In 0.5 M pot. chloride + 0.5 M pot. sulphate (microamps) | In 0.5 M pot. chloride + 2.0 M pot. sulphate (microamps) | |
| | 9.93 | 4.21 | 2.36 |
| | 12.09 | 4.99 | 2.42 |

The values quoted in Table 26 show that approximately 10% of the reduction in wave-height can be ascribed to the formation of a sulphato complex with about 90% probably due to increase in the viscosity of the solution.

Further Lingane (70) noticed that in a 1 M aqueous potassium chloride solution the diffusion current was well defined for about 0.3 volts beyond the half-wave potential but then decreased markedly, reached a minimum and finally rose to its initial value. When methyl red was added to the solution, the minimum first decreased, but, with larger amounts of the dye, it developed into a maximum. This peculiar behaviour has not been explained.

The polarogram for indium in 1 M potassium chloride in formic acid showed no such depression. The discharge of the hydrogen ion in formic acid is, however, only 0.36 volts more negative than the half-wave potential of indium and the non-appearance of the depression is most probably due to obstruction by the hydrogen wave.

The investigation made by Lingane in aqueous solution was repeated and his results substantiated. Instead of adding methyl red, however, formic acid was added in increasing quantities, to the aqueous solution. Precisely the same behaviour was observed. The minimum in the curve decreased until at a formic acid concentration of 3 M, no indentation was visible in the curve. At a formic acid

content of 5 M, a small but distinct hump was observed. The wave due to the discharge of hydrogen ions, although in close proximity did not restrict the above observations.

Examination of the polarographic characteristics of indium in other supporting electrolytes showed no unusual behaviour. In these media the indium was strongly complexed and reversibly reduced. The effect of water on the half-wave potentials was found to be small, an addition of 2% (v/v) of water causing a negative shift of about 0.005 volts.

As in aqueous solution, indium was found to form fluoro, chloro and bromo complexes, the stability of which decreased in the order bromo chloro fluoro.

In a medium of 0.2 M sodium fluoride and 0.5 M sodium formate the half-wave potential was found to be -0.364 ± 3 volts vs S.C.A.F.E. (-0.902 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.025. If, without varying the quantity of sodium formate the sodium fluoride concentration was increased to 0.4 M, the characteristic potential was -0.379 ± 3 volts vs S.C.F.A.E. (-0.917 volts vs Q.F.A.E.) This shift was due to the formation of the complex ions $[\text{InF}]^{++}$ and InF_2^+ (72).

Using 0.5 M potassium chloride as background electrolyte, the half-wave potential was -0.467 ± 3 volts vs S.C.F.A.E. (-1.005 volts vs Q.F.A.E.). The value of $\tan \alpha$

was 0.023. Increasing the potassium chloride concentration to 1.0 M caused the half-wave potential to shift to -0.494 ± 3 volts vs S.C.F.A.E. (-1.032 volts vs Q.F.A.E.). The marked change in the half-wave potentials of indium in chloride medium is due to the formation of the complex ions $[\text{InCl}_4]^-$ and $[\text{InCl}_5]^{2-}$ (73).

It will be shown (see Summary) that for cations unaffected by complex formation, e.g. Bi^{+++} , Sn^{++} , Pb^{++} , there exists an almost constant difference between the half-wave potentials in aqueous and anhydrous formic acid solutions. The half-wave potential of indium in formate medium, cannot be used to substantiate this constant difference, in view of the fact that it is complexed in this medium and hydrated in water, thus leading to the formation of two quite different ionic species. Furthermore, it has been shown that the one reduction proceeds reversibly, the other irreversibly and on this account alone the half-wave potentials must differ markedly. In a 1.0 M potassium chloride medium, however, both reductions are reversible and the ionic species are very likely to be the same in both solvents. Under these conditions the difference in the half-wave potentials in each solvent showed good agreement with the value found for Bi^{+++} , Sn^{++} and Pb^{++} .

If the background electrolyte consists of 0.2 M sodium bromide and 0.5 M sodium formate the half-wave potential was found to be -0.464 ± 3 volts vs S.C.F.A.E. (-1.002 volts vs Q.F.A.E.). The value of $\tan \alpha$ is 0.023. When the concentration of sodium formate was maintained constant and that of sodium bromide increased to 0.4 M, the half-wave potential changed to a value of -0.485 ± 3 volts vs S.C.F.A.E. (-1.023 volts vs Q.F.A.E.). The complex ion probably formed which is responsible for this behaviour is $[\text{InBr}_2]^+$ (74).

The half-wave potential of indium in a 0.25 M oxalic acid - 0.5 M sodium formate medium was found to be -0.416 ± 3 volts vs S.C.F.A.E. (-0.954 volts vs Q.F.A.E.); the value of $\tan \alpha$ was 0.025. In a 0.50 M oxalic acid - 0.5 M sodium formate medium this potential shifted to a value of $-0.425 \pm$ volts vs S.C.F.A.E. (-0.963 volts vs Q.F.A.E.). The oxalato-indic ion responsible for this behaviour is very likely $[\text{In}(\text{C}_2\text{O}_4)]^+$ (75).

SUMMARY OF MEASUREMENTS.

| Supporting Electrolyte | vs S.C.F.A.E. (volts) | vs Q.F.A.E. (volts) | Limits (volts) | tan α |
|---|-----------------------------|---------------------------|-------------------|--------------|
| 0.5 M potassium chloride | -0.467 | -1.005 | ± 0.003 | 0.023 |
| 1.0 M potassium chloride | -0.494 | -1.032 | ± 0.003 | 0.023 |
| 0.2 M sod. bromide + 0.5 M sod. formate | -0.464 | -1.002 | ± 0.003 | 0.023 |
| 0.4 M sod. bromide + 0.5 M sod. formate | -0.485 | -1.023 | ± 0.003 | 0.023 |
| 0.2 M sod. fluoride + 0.5 M sod. formate | -0.364 | -0.902 | ± 0.003 | 0.025 |
| 0.4 M sod. fluoride + 0.5 M sod. formate | -0.379 | -0.917 | ± 0.003 | 0.025 |
| 0.25 M oxalic acid + 0.5 M sod. formate | -0.416 | -0.954 | ± 0.003 | 0.025 |
| 0.50 M oxalic acid + 0.5 M sod. formate | -0.425 | -0.963 | ± 0.003 | 0.025 |

(VIII) NICKEL.

The polarographic reduction of nickel was found to proceed irreversibly and, as in aqueous solution, the slope of the wave was abnormally small, extending over 0.2 volts. The wave was not particularly well formed, especially when employing small quantities of nickel and large voltage scans, necessary for the precise estimation of the half-wave potential. The accuracy of measurement of this quantity was thus limited. It was for this reason that the measurement of the diffusion current constant for nickelous ions in a 0.5 M sodium formate medium, although attempted, was abandoned.

Polarographic overcurrents were not encountered during the investigation of this element. This was to be expected, in view of the half-wave potential of nickel being almost co-incident with that of the electro-capillary maximum.

The half-wave potential of nickel was found to be greatly influenced by the addition of small quantities of water. The addition of 1% (v/v) of water shifts this characteristic potential by about 0.02 volts, 2% (v/v) of water causing a shift of 0.05 volts. This is about ten times as much as was noticed for most other elements examined and is explained by the great ease of formation of the hexaquaonickel ion. The divalent nickel ion, uncomplexed in anhydrous formic acid,

immediately combines with the water to give an ion reduced irreversibly at a more negative potential; the shift in the negative direction is due to complex formation with the water molecules. It was also noticed that, on the addition of the water, the height of the wave was reduced. Addition of water, which has a lower viscosity than formic acid should, if anything, increase the wave height. This decrease is explained by the appreciable increase in the size of the nickel ion on hydration, a reduction in its diffusion coefficient and a corresponding decrease in the diffusion current.

Nickelous chloride hexahydrate, as supplied by Merck Co., was found most suitable and was dehydrated by heating in an oven at 130°C for 5 hours. It was stored in a well stoppered weighing bottle in a desiccator over anhydrous calcium chloride.

The half-wave potential in a 0.5 M sodium formate medium was found to be -0.61 ± 1 volts vs S.C.F.A.E. (-1.15 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.068 as opposed to the theoretical value of 0.030, showing the reduction to be irreversible. The above values were found to be exactly the same in a 0.5 M potassium sulphate medium.

As in aqueous solution, it was shown that the addition of large concentrations of chloride to a nickel salt solution, shifted the reduction potential markedly to a more positive value. In the presence of a high concentration of chloride, the wave also had a more normal slope. These effects appear

to be due to the formation of complexes between the chloride and nickelous ions which are reduced more reversibly than the uncomplexed nickel ion.

The half-wave potential in a 1.0 M potassium chloride medium was -0.344 ± 3 volts vs S.C.F.A.E. (-0.882 volts vs Q.F.A.E.) the value of $\tan \alpha$ being 0.041. The wave extended over 0.12 volts. On increasing the chloride concentration to 2.0 M the half-wave potential changed to -0.352 ± 3 volts vs S.C.F.A.E. (-0.890 volts vs Q.F.A.E.); the value of $\tan \alpha$ also underwent little change giving a value of 0.040. The effect of added quantities of water were shown to be considerably less 2% (v/v) of water causing a shift of 0.021 volts in a negative direction. This was to be expected as the nickel ion, now complexed with chloride ions, gave much less opportunity of formation of the hexaquo-complex and consequently less shift of the half-wave potential to negative values.

In aqueous solution the thiocyanate complex of nickel is also reduced more reversibly and at more positive potentials. An attempt was made to observe this phenomenon by using 0.5 M potassium thiocyanate - 0.25 M sodium formate as supporting electrolyte. No wave was found, however, due probably to the high insolubility of the brown nickelous thiocyanate in formic acid, rendering this medium unsuitable.

(IX) ZINC.

Despite the fact that the half-wave potential of zinc in non-complexing media is only 0.14 volts more positive than the decomposition potential of the hydrogen ions, it was found to produce well-developed and easily measurable polarographic waves. With all the supporting electrolytes used, zinc was found to undergo a reversible two-electron reduction with values of $\tan \alpha$ close to the theoretical value of 0.030. Examination of zinc in complex forming supporting electrolytes was mostly not possible as any shift of the wave to more negative potentials caused it to be obscured by that due to the discharge of hydrogen ions. Measurements were attempted, however, using chloride and oxalate supporting electrolytes, in both of which zinc undergoes appreciable complex formation.

The half-wave potentials of zinc have been shown to be close to the potential of the electro-capillary maximum. Actually the potentials of zinc are about as much to the negative side of this maximum as those of cadmium are to the positive side. It is for this reason that, like cadmium, no polarographic overcurrents were observed even at low supporting electrolyte concentrations.

Of the zinc salts tried, the chloride, due to its appreciable solubility in formic acid, was found to be most suitable. Zinc chloride, as supplied by Merck and Co., was

heated for 5 hours at 120°C, the anhydrous salt so formed being stored in a stoppered weighing bottle and dried in a desiccator over phosphorus pentoxide.

The addition of water was found to exert little influence on the half-wave potential of zinc. For the two measurements made with a 0.5 M sodium formate supporting electrolyte, this potential was found to shift to more negative values by 0.006 and 0.005 volts respectively on the addition of 2% (v/v) of distilled water.

The diffusion coefficient of zinc in a 0.5 M sodium formate medium was investigated by measurement of the slope of the linear plot of the zinc salt concentration against the resulting diffusion current. The diffusion coefficient was found to be 0.36×10^{-5} cms.²/sec. The value of this coefficient in aqueous solution at infinite dilution as calculated from conductance measurements (61) was 0.72×10^{-5} cms.²/sec.

TABLE 27.

| Concentration of Zinc $\times 10^3$ gm. ions/litre | Diffusion Current (microamps) |
|---|----------------------------------|
| 1.64 | 11.9 |
| 3.28 | 23.7 |
| 4.09 | 29.1 |

$$h = 42.52 \text{ cms.}$$

$$m = 4.397 \text{ mgs./sec.}$$

$$t = 2.45 \text{ secs.} \quad m^{3/2} t^{1/2} = 3.117 \text{ mgs.}^{3/2} \text{secs.}^{-1/2}$$

$$i_d/c = 7.1(3) \text{ microamps/mgm. ion/litre.}$$

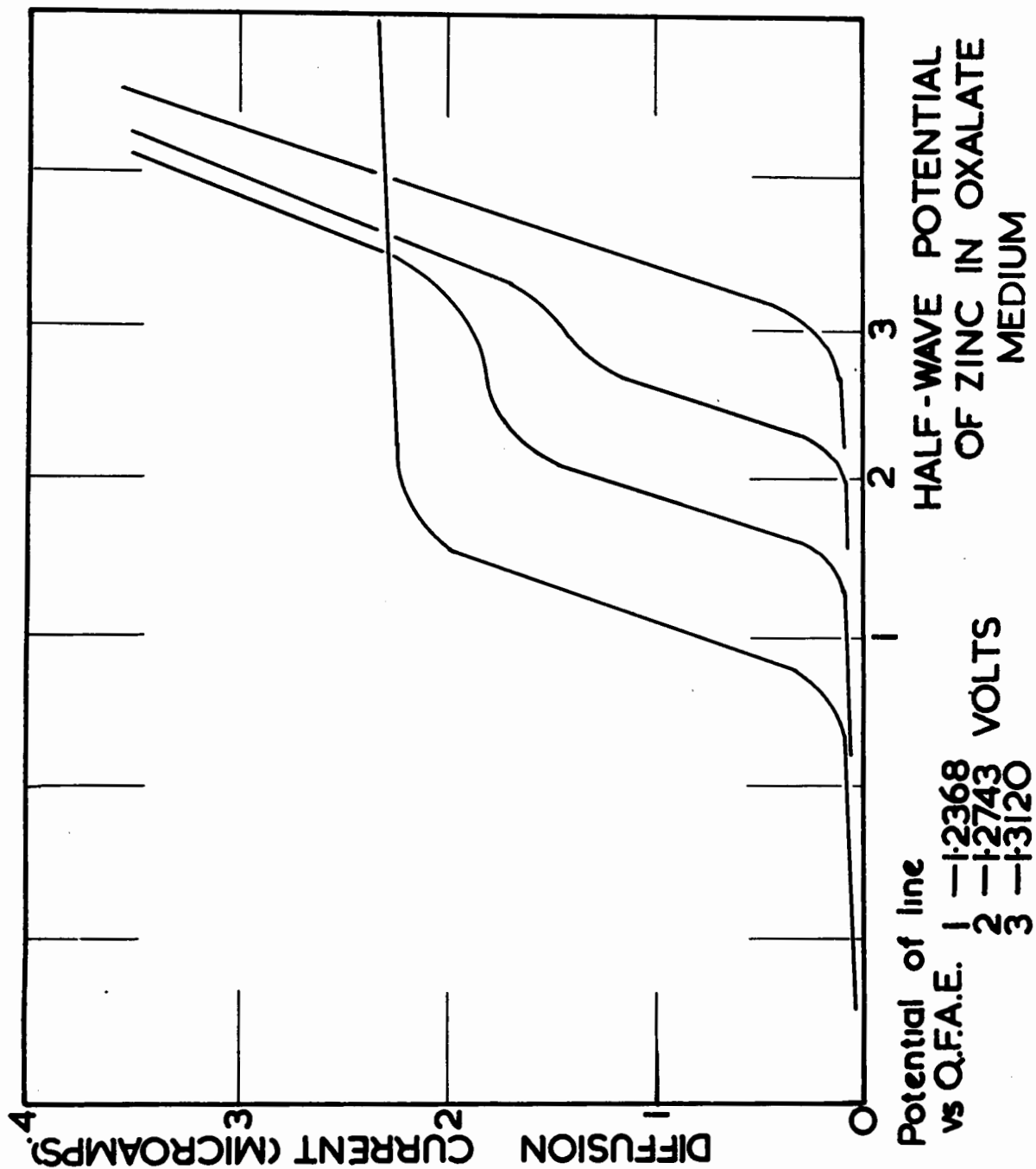
$$I_{\text{HCOOH}} = 2.3.$$

The half-wave potential in a 0.5 M sodium formate medium was found to be -0.706 ± 3 volts vs S.C.F.A.E. (-1.244 volts vs Q.F.A.E.) and, on increasing the sodium formate concentration to 2.0 M, it shifted to -0.733 ± 3 volts vs S.C.F.A.E. (-1.271 volts vs Q.F.A.E.). These results were closely paralleled using a 0.5 M ammonium formate medium in which the half-wave potential was -0.708 ± 3 volts vs S.C.F.A.E. (-1.246 volts vs Q.F.A.E.) shifting to -0.735 ± 3 volts vs S.C.F.A.E. (-1.273 volts vs Q.F.A.E.) for a similar increase in the supporting electrolyte concentration. The value of $\tan \alpha$ in both media was 0.033.

On replacement of sodium formate by potassium sulphate as indifferent electrolyte no change was noted in the half-wave potential showing that as in aqueous solution, zinc does not tend to complex in sulphate medium. The measured potentials were -0.706 ± 3 volts vs S.C.F.A.E. (-1.244 ± 3 volts vs Q.F.A.E.) in 0.5 M potassium sulphate which shifted to -0.729 ± 4 volts vs S.C.F.A.E. (-1.267 volts vs Q.F.A.E.) on increasing the potassium sulphate concentration to 2.0 M. The value of $\tan \alpha$ was 0.034.

As in aqueous solution, use of a fluoride medium does not induce any complex formation with zinc ions. A supporting

PLATE 13



electrolyte of 0.1 M sodium fluoride and 0.5 M sodium formate gave a value of -0.707 ± 3 volts vs S.C.F.A.E. (-1.245 volts vs Q.F.A.E.) for the characteristic potential. On increasing the fluoride concentration to 0.2 M, the value changed to -0.710 ± 3 volts vs S.C.F.A.E. (-1.248 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.032.

In a 0.5 M potassium chloride medium, however, no wave was obtained for zinc ions before the discharge of hydrogen. Use of a 0.25 M potassium chloride solution also failed to produce a wave which was finally obtained using a 0.1 M potassium chloride - 0.5 M sodium formate supporting electrolyte. In this medium the half-wave potential was -0.826 ± 4 volts vs S.C.F.A.E. (-1.364 volts vs Q.F.A.E.). The first two media had, of course, failed to produce waves because, due to complexing, the electroreduction had occurred at a potential more negative than that of the discharge of hydrogen, consequently obscuring the waves. At the prevailing chloride ion concentration it is probable that the complex species present is $[\text{ZnCl}]^+$ with a small proportion of undissociated ZnCl_2 (76-78). The value for $\tan \alpha$ was 0.034.

An interesting example of the effect on the polarographic wave of the addition of a complex forming indifferent electrolyte arose with zinc on the addition of small quantities of oxalic acid. The first wave A, (Plate 13), shows zinc in a 0.5 M sodium formate supporting electrolyte, curve B on the

addition of 0.01 M oxalic acid, curve C with an oxalic ion concentration of 0.02 M and curve D with a total oxalic acid content of 0.04 M. In curve B the wave is almost obscured by that of the hydrogen discharge, shifted to more positive potentials by the addition of oxalic acid. The height of the wave for zinc is reduced for two reasons: firstly, the zinc oxalato complex ion being appreciably larger than the uncomplexed zinc ion has a lower diffusion coefficient resulting in a smaller diffusion current. In addition, as zinc oxalate has a low solubility in formic acid, some precipitation probably occurred decreasing the concentration of zinc in solution and further lowering the diffusion current. The half-wave potential can be seen to have shifted to more negative potentials as a result of this complex formation. In curve C with an increased oxalic acid concentration, the effect is seen to be more pronounced while in curve D the wave for zinc, shifted to still greater negative potentials, is totally obscured by the hydrogen discharge wave. It is generally agreed that the oxalato-zinc complex is $[\text{Zn}(\text{C}_2\text{O}_4)_2]^{4-}$ (79-81) with the additional probability of $[\text{Zn}(\text{C}_2\text{O}_4)_3]^{4-}$, above an oxalate ion concentration of 0.15 M.

SUMMARY.

| Supporting Electrolyte | Half-wave potentials | | Limits | tan α |
|---|----------------------|------------|--------|--------------|
| | vs S.C.F.A.E. | S.C.F.A.E. | | |
| 0.5 M sod. formate | -0.706 | -1.244 | *0.003 | 0.033 |
| 0.5 M sod. formate + + 2% (v/v) water | -0.711 | -1.249 | ±0.003 | 0.033 |
| 2.0 M sod. formate | -0.733 | -1.271 | ±0.003 | 0.033 |
| 0.5 M amm. formate | -0.708 | -1.246 | ±0.003 | 0.033 |
| 2.0 M amm. formate | -0.735 | -1.273 | ±0.003 | 0.033 |
| 0.5 M sod. formate + 0.1 M pot. chloride | -0.826 | -1.364 | ±0.004 | 0.034 |
| 0.5 M pot. sulphate | -0.706 | -1.244 | ±0.003 | 0.034 |
| 2.0 M pot. sulphate | -0.729 | -1.267 | ±0.004 | 0.034 |
| 0.1 M sod. fluoride + 0.5 M sod. formate | -0.707 | -1.245 | ±0.003 | 0.032 |
| 0.2 M sod. fluoride + 0.5 M sod. formate | -0.710 | -1.248 | ±0.003 | 0.033 |
| 0.01 oxalic acid | | | | |
| 0.5 sod. 0.02 oxalic formate acid | -0.7 | -1.2(6) | - | - |
| 0.04 oxalic acid | | | | |

SECTION E.

ELECTROCAPILLARY CURVES.

THE ELECTROCAPILLARY CURVE OF MERCURY IN ANHYDROUS FORMIC
ACID.

No information on the electrocapillary curve of mercury in anhydrous formic acid has yet been published. In view of its relationship to the fact that the polarographic over-current occurs with some elements and does not occur with others, the measurement of this curve was undertaken at six different concentrations of sodium formate.

The curves were obtained by plotting the drop time of mercury (t) instead of the surface tension γ against the potential applied to the dropping electrode. As the value of (t) is directly proportional to the surface tension, the resulting plot is almost identical to the electrocapillary curve. The same arrangement was used as in the polarographic determination of current-voltage curves.

The curves were measured at sodium formate concentrations of 0.05 M, 0.1 M, 0.25 M, 2.0 M, 4.0 M and 5.5 M. The results are recorded in Table 28 and the curve at 2.0 M sodium formate, taken as representative of the six, is plotted in Plate 14. The curve is seen to be slightly flattened near the maximum value of the surface tension. This phenomenon has been observed in aqueous solution and is attributed to the adsorption of neutral capillary-active molecules at the

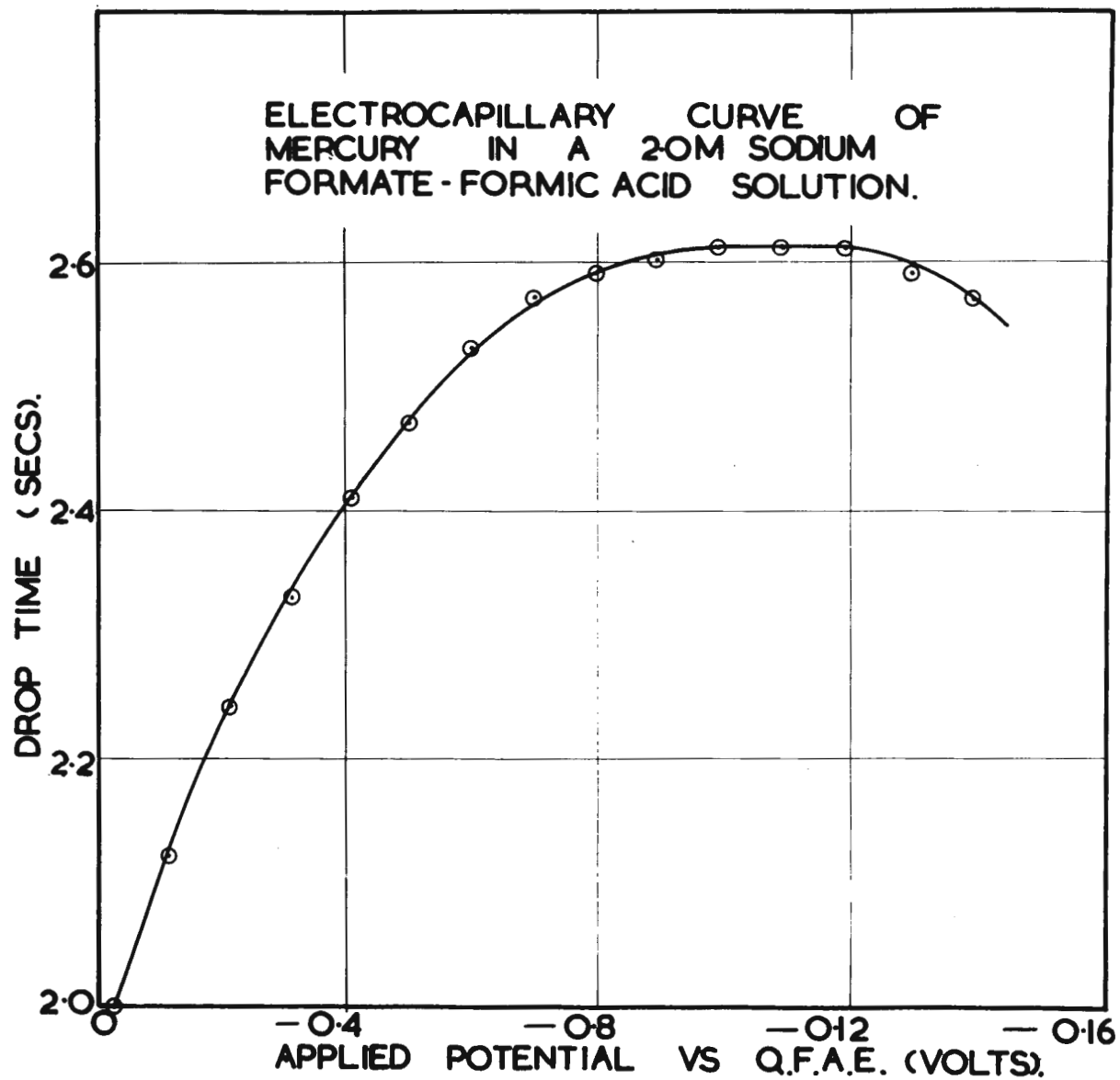


TABLE 28

vs Q.F.A.E.

| Concentration of Sodium Formate | | | | | | | | | | | |
|---------------------------------|-----------------------|---------------|-----------------------|---------------|-----------------------|---------------|-----------------------|---------------|-----------------------|---------------|-----------------------|
| 0.05 M | | 0.1 M | | 0.25 M | | 2.0 M | | 4.0 M | | 5.5 M | |
| Potential volts | Drop Time secs. | Pot. volts | Drop Time secs. | Pot. volts | Drop Time secs. | Pot. volts | Drop Time secs. | Pot. volts | Drop Time secs. | Pot. volts | Drop Time secs. |
| -0.016 | 2.00 | -0.016 | 2.00 | -0.018 | 2.00 | -0.019 | 2.00 | -0.017 | 2.00 | -0.017 | 2.00 |
| -0.113 | 2.14 | -0.111 | 2.13 | -0.112 | 2.13 | -0.113 | 2.12 | -0.114 | 2.13 | -0.114 | 2.08 |
| -0.210 | 2.24 | -0.208 | 2.23 | -0.211 | 2.23 | -0.211 | 2.24 | -0.210 | 2.23 | -0.211 | 2.19 |
| -0.308 | 2.31 | -0.304 | 2.33 | -0.307 | 2.33 | -0.308 | 2.33 | -0.309 | 2.31 | -0.309 | 2.27 |
| -0.406 | 2.38 | -0.402 | 2.41 | -0.403 | 2.41 | -0.405 | 2.41 | -0.406 | 2.38 | -0.406 | 2.34 |
| -0.504 | 2.45 | -0.501 | 2.47 | -0.506 | 2.47 | -0.504 | 2.47 | -0.504 | 2.43 | -0.504 | 2.39 |
| -0.602 | 2.49 | -0.603 | 2.52 | -0.602 | 2.53 | -0.605 | 2.53 | -0.603 | 2.47 | -0.603 | 2.44 |
| -0.698 | 2.53 | -0.696 | 2.55 | -0.699 | 2.57 | -0.699 | 2.57 | -0.699 | 2.50 | -0.698 | 2.47 |
| -0.797 | 2.55 | -0.796 | 2.58 | -0.797 | 2.59 | -0.798 | 2.59 | -0.796 | 2.52 | -0.796 | 2.49 |
| -0.895 | 2.57 | -0.896 | 2.60 | -0.893 | 2.61 | -0.898 | 2.60 | -0.896 | 2.53 | -0.896 | 2.50 |
| -0.993 | 2.58 | -0.993 | 2.61 | -0.991 | 2.62 | -0.993 | 2.61 | -0.993 | 2.53 | -0.993 | 2.50 |
| -1.093 | 2.58 | -1.090 | 2.61 | -1.092 | 2.62 | -1.091 | 2.61 | -1.093 | 2.53 | -1.093 | 2.50 |
| -1.191 | 2.58 | -1.186 | 2.61 | -1.188 | 2.62 | -1.189 | 2.61 | -1.192 | 2.52 | -1.190 | 2.49 |
| -1.290 | 2.57 | -1.286 | 2.60 | -1.291 | 2.60 | -1.288 | 2.59 | -1.291 | 2.50 | -1.291 | 2.48 |
| -1.389 | 2.55 | -1.383 | 2.58 | -1.386 | 2.58 | -1.387 | 2.57 | -1.387 | 2.46 | -1.387 | 2.46 |

mercury-solution interface.

From several observations made in this research, monomeric formic acid molecules are believed to be capillary active and responsible for the flattening of the electrocapillary curves. Formic acid molecules have a dipole moment of 1.98 D (82), the -OH group being the positive pole. As the remainder of this homologous series of carboxylic acids are capillary active (83) and adsorb at interfaces by attachment of the -OH group, formic acid is believed to act similarly.

It was shown in Section D-VII, during the investigation of the polarographic curve of indic ions in a 1 M aqueous potassium chloride medium, that the addition of formic acid had precisely the same effect, although to a lesser extent, as did methyl red, a substance known to be very capillary active. Further it has been found that formic acid is capable of suppressing polarographic overcurrents obtained in aqueous solution.

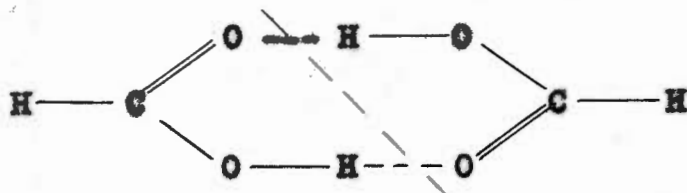
Although anhydrous formic acid exists largely as dimeric molecules these are in equilibrium with some monomeric molecules which in turn ionize to give formate ions. It may thus be argued that the capillary-activity attributable to formic acid may arise from the presence of formate ions on dimeric formic acid molecules. The latter

TABLE 22.

| Conc. of Sodium Formate | Electrocapillary Maximum Potential (volts vs Q.F.A.E.) | |
|-------------------------|--|-----------|
| | Measured | Corrected |
| 0.05 M | -1.09 | -1.12 |
| 0.10 M | -1.09 | -1.10 |
| 0.25 M | -1.09 | -1.09 |
| 2.0 M | -1.07 | -1.04 |
| 4.0 M | -0.99 | -0.95 |
| 5.5 M | -0.99 | -0.94 |

In view of the uncertainty in the calculations of liquid junction potential and the difficulty of estimating the actual electrocapillary maximum from the curves, these values must be regarded only as approximations. They do, however, show that the maximum is shifted in a positive direction.

Anhydrous formic acid exists very largely as dimeric molecules. Although there is at present no experimental proof, it is suggested that the addition of foreign salts to anhydrous formic acid tends to lessen the strength of the hydrogen bonds in the dimeric molecule.



and give rise to more monomeric molecules. It appears very probable that this disintegration of dimeric molecules will be directly proportional to the ionic strength which varies

directly as the salt concentration. Thus it is postulated that the increase in the concentration of the monomer is a linear function of the added salt concentration. This conclusion is to be utilised later in an interpretation of some of the results involving overcurrents.

THE ELECTROCAPILLARY CURVE IN THE PRESENCE OF ELECTRO-
REDUCIBLE IONS.

The suppression of the maxima on the current-voltage curves of bismuth, antimony, lead and tin was initially thought to be due to a shift of the electrocapillary curve under the influence of increased quantities of sodium formate. When, however, it was shown that sodium formate had very little effect on the position of this curve it was decided, nevertheless, to measure the electrocapillary curve in the presence of a known concentration of these ions. The data for the curves at different concentrations of antimony ions are quoted in Table 30 and plotted on Plate 15.

It can be seen that the curves rise normally as the applied voltage is increased but at approximately the value of the half-wave potential of antimony -0.54 volts vs Q.F.A.E., the surface tension does not continue to increase but remains constant. After the plateau is past, the curve regains its normal appearance although the potential of the maximum has been shifted to more negative values.

It has been shown that the increase of the applied potential over the length of the plateau is the same as the voltage (iR) drop in the solution. It is thus impossible for the potential of the dropping electrode to vary and it remains constant from the beginning of the discharge until the greatest value of the overcurrent is reached at which stage there is a considerable drop in (i) from the maximal value to the normal diffusion current. The applied potential is now in excess of the voltage drop and the potential of the dropping electrode can increase normally. The potential of the electrocapillary maximum is shifted in a negative direction by the amount of the new voltage drop i.e. (diffusion current \times cell resistance). In order, however, that a measurable arrest in the electrocapillary curve be obtained, the concentration of the electro-reducible ion had to be relatively high. At such concentrations of the electro-reducible ion, it will be shown that the value of the overcurrent is not greatly in excess of the diffusion current and thus the shift of the electrocapillary maximum is not much less than the original voltage drop which caused the plateau on the electrocapillary curve. Further, the change in the voltage drop for these curves being relatively small, the electrocapillary curve does not increase exceptionally steeply, after the plateau, as it would have done had the ratio of the overcurrent to diffusion current been of the order of 4 say, as opposed to about 1.5.

TABLE 30.

| CURVE A | | CURVE B | | CURVE C | |
|-----------------------------|-----------------------|-----------------------------|-----------------------|-----------------------------|-----------------------|
| Potential vs Q.F.A.E. | Drop Time secs. | Potential vs Q.F.A.E. | Drop Time secs. | Potential vs Q.F.A.E. | Drop Time secs. |
| -0.016 | 1.90 | -0.013 | 2.00 | -0.019 | 1.77 |
| -0.114 | 2.06 | -0.107 | 2.17 | -0.113 | 1.93 |
| -0.210 | 2.21 | -0.205 | 2.31 | -0.211 | 2.06 |
| -0.306 | 2.31 | -0.302 | 2.44 | -0.308 | 2.19 |
| -0.403 | 2.40 | -0.399 | 2.53 | -0.405 | 2.28 |
| -0.499 | 2.47 | -0.498 | 2.60 | -0.504 | 2.37 |
| -0.545 | 2.49 | -0.549 | 2.62 | -0.564 | 2.41 |
| -0.565 | 2.49 | -0.569 | 2.62 | -0.605 | 2.41 |
| -0.584 | 2.49 | -0.597 | 2.62 | -0.699 | 2.41 |
| -0.606 | 2.49 | -0.628 | 2.62 | -0.798 | 2.41 |
| -0.631 | 2.49 | -0.649 | 2.62 | -0.895 | 2.41 |
| -0.641 | 2.49 | -0.670 | 2.62 | -0.993 | 2.41 |
| -0.650 | 2.50 | -0.694 | 2.63 | -1.041 | 2.42 |
| -0.693 | 2.53 | -0.794 | 2.68 | -1.091 | 2.44 |
| -0.791 | 2.58 | -0.893 | 2.72 | -1.189 | 2.52 |
| -0.891 | 2.61 | -0.991 | 2.74 | -1.288 | 2.58 |
| -0.990 | 2.62 | -1.000 | 2.76 | -1.389 | 2.63 |
| 1.089 | 2.63 | -1.190 | 2.76 | -1.485 | 2.65 |
| 1.189 | 2.63 | -1.289 | 2.76 | -1.585 | 2.65 |
| 1.287 | 2.62 | -1.388 | 2.74 | | |
| 1.387 | 2.60 | -1.488 | 2.72 | -1.684 | 2.63 |

$[Sb^{+++}] = 0.49 \times 10^{-2} M$
 $[NaOOCH] = 0.2 M$
 $I = 53.66 \text{ ua}$
 $R = 1498 \text{ ohms}$
 $IR = 0.080 \text{ volts}$
 Plateau on curve
 $= 0.09 \text{ volts}$

$[Sb^{+++}] = 1.23 \times 10^{-2} M$
 $[NaOOCH] = 0.2 M$
 $I = 81.52 \text{ ua}$
 $R = 1412 \text{ ohms}$
 $IR = 0.115 \text{ volts}$
 Plateau on curve
 $= 0.12 \text{ volts}$

$[Sb^{+++}] = 2.03 \times 10^{-2} M$
 $[NaOOCH] = 0.05 M$
 $I = 103.6 \text{ ua}$
 $R = 4592 \text{ ohms}$
 $IR = 0.476 \text{ volts}$
 Plateau on curve
 $= 0.48 \text{ volts}$

This same effect has been noticed before. Heyrovsky and Dillinger (84) describe the electrocapillary curve for thallous sulphate while Herasymenko, Heyrovsky and Tancakivsky (85) examined the curve for an acid mercuric

nitrate solution. They did not quantitatively compare the measured values of the voltage drop in the solution with the length of the plateau on the electrocapillary curve. They do, however, explain the plateau as being due to a state of non-polarisation of the electrode and its maintenance of a constant potential due to the IR drop in the solution. In both papers, however, they maintain that once the plateau is passed, the electrocapillary curve follows the original parabola; this is not in agreement with the results obtained in this investigation in which it has been shown that if ANY current flows the whole curve must be displaced in a negative direction.

Bachman and Astle (86) describing a similar plateau found on the electrocapillary curve in the electrolyte ammonium acetate-copper acetate-acetic acid, maintain that "in this region there is no change in the degree of polarisation and hence no change in the surface potential of the electrode. This is a result of the fact that the electrons flowing into the drop from the external source are being neutralised by the reduction process". In the light of the explanation just given this conclusion must be regarded as invalid.

One electrocapillary curve for each of the other three electroreducible ions has been measured and plotted in Plate 16, the relevant data being tabulated in Table 31. The

ELECTROCAPILLARY CURVE IN THE PRESENCE OF BISMUTH, LEAD AND TIN.

DROP TIME (SECS.)

2.4
2.2
2.0
2.5
2.3
2.1
2.5
2.3
2.1

BISMUTH

LEAD

Diagram of the polarogram for tin.

TIN

APPLIED POTENTIAL vs Q.F.A.E. (VOLTS).

0 0.4 0.8 1.2 1.6

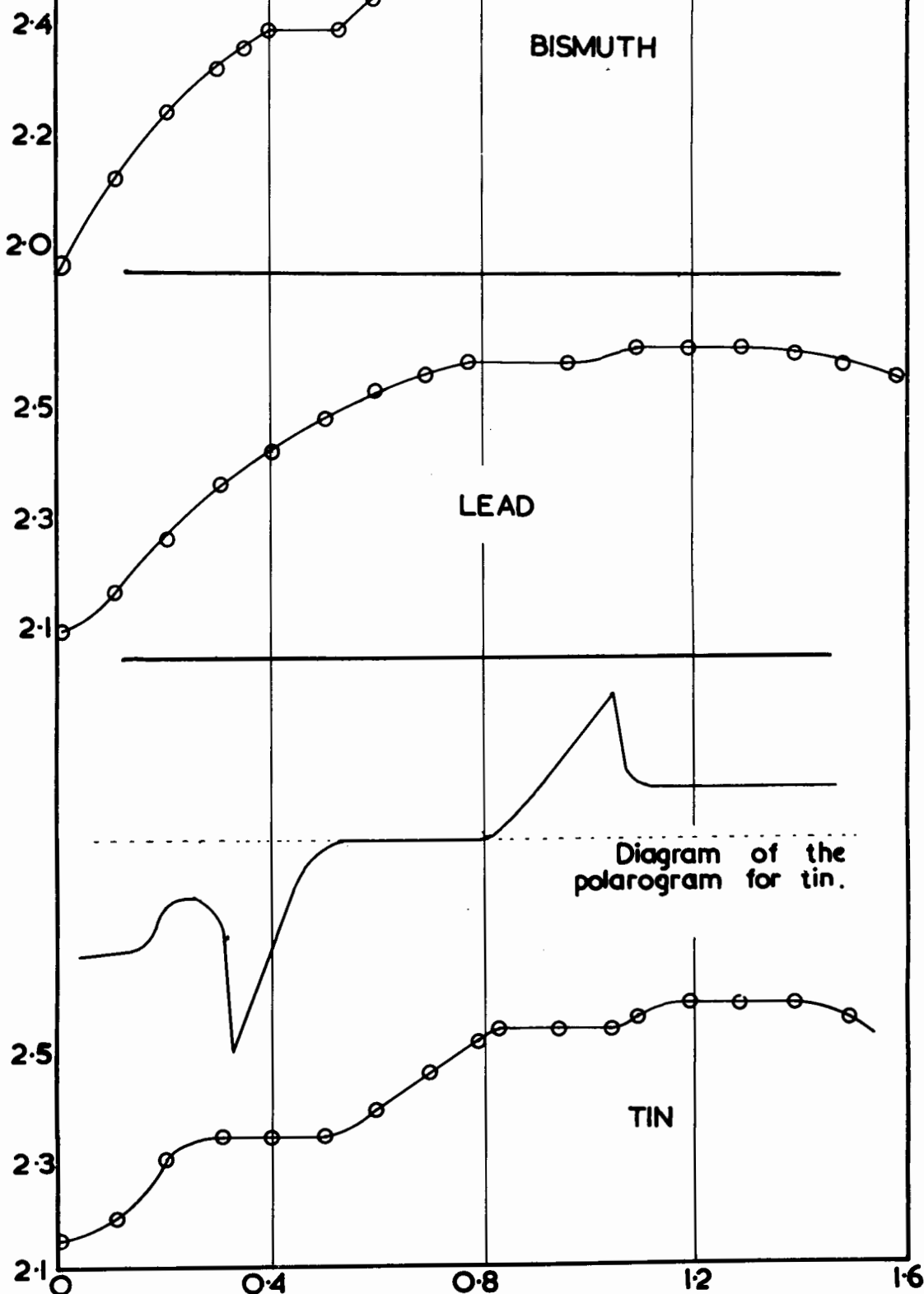


TABLE 31.

| BISMUTH | | TIN | | LEAD | |
|-----------------------------|-----------------------|-----------------------------|-----------------------|-----------------------------|-----------------------|
| Potential vs Q.F.A.E. | Drop Time secs. | Potential vs Q.F.A.E. | Drop Time secs. | Potential vs Q.F.A.E. | Drop Time secs. |
| -0.012 | 1.96 | -0.013 | 2.15 | -0.013 | 2.09 |
| -0.110 | 2.12 | -0.110 | 2.19 | -0.110 | 2.16 |
| -0.206 | 2.24 | -0.206 | 2.30 | -0.205 | 2.26 |
| -0.304 | 2.32 | -0.304 | 2.34 | -0.303 | 2.36 |
| -0.350 | 2.36 | -0.405 | 2.34 | -0.405 | 2.42 |
| -0.405 | 2.39 | -0.500 | 2.34 | -0.501 | 2.48 |
| -0.451 | 2.39 | -0.596 | 2.39 | -0.597 | 2.53 |
| -0.500 | 2.39 | -0.696 | 2.46 | -0.696 | 2.56 |
| -0.530 | 2.39 | -0.795 | 2.52 | -0.748 | 2.58 |
| -0.555 | 2.42 | -0.828 | 2.54 | -0.775 | 2.59 |
| -0.595 | 2.45 | -0.846 | 2.54 | -0.795 | 2.59 |
| -0.696 | 2.50 | -0.893 | 2.54 | -0.893 | 2.59 |
| -0.795 | 2.53 | -0.990 | 2.54 | -0.961 | 2.59 |
| -0.893 | 2.55 | -1.044 | 2.54 | -0.991 | 2.60 |
| -0.991 | 2.56 | -1.090 | 2.56 | -1.090 | 2.61 |
| -1.090 | 2.56 | -1.188 | 2.59 | -1.188 | 2.61 |
| -1.188 | 2.56 | -1.287 | 2.59 | -1.286 | 2.61 |
| -1.287 | 2.56 | -1.385 | 2.59 | -1.385 | 2.60 |
| -1.385 | 2.55 | -1.485 | 2.56 | -1.484 | 2.58 |
| -1.485 | 2.52 | -1.584 | 2.52 | -1.584 | 2.56 |
| -1.585 | 2.47 | -1.682 | 2.46 | | |

$[Bi^{+++}] = 2.7 \times 10^{-3}$ gm. ions/l.
 $[NaOOCH] = 0.2$ M
 $I = 107.7$ ua
 $R = 1420$ ohms
 $IR = 0.153$ volts
 Curve plateau
 $= 0.13$ volts

$[Sn^{++}] = 4.2 \times 10^{-3}$ gm. ions/l.
 $[NaOOCH] = 0.02$ M
 $I = 131.1$ ua
 $R = 1620$ ohms
 $IR = 0.212$ volts
 Curve plateau
 $= 0.22$ volts

$[Pb^{++}] = 7.7 \times 10^{-3}$ gm. ions/l.
 $[NaOOCH] = 0.2$ M
 $I = 111.8$ ua
 $R = 1630$ ohms
 $IR = 0.182$ volts
 Curve plateau
 $= 0.19$ volts

wave, the second, to that on the wave for the cathodic reduction of stannous ions. From the electrocapillary curve it was to be expected that no current flowed between the applied potentials of -0.5 and -0.8 volts vs Q.F.A.E. and this was found to be the case. It would appear likely

that if the plateau on the electrocapillary curve in the presence of lead can only be measured with reduced accuracy because of the close proximity of the electrocapillary maximum, this should be even more so in the case of tin, which has a more negative half-wave potential. That this does not occur is, however, explained by the greater value of the diffusion current for tin than for lead. This has no effect on the plateau length but shifts the electrocapillary maximum for tin to more negative values than for lead.

SECTION F.

POLAROGRAPHIC OVERCURRENTS.

POLAROGRAPHIC OVERCURRENTS.

Of the nine inorganic cations studied polarographically in anhydrous formic acid only four, tin, lead, antimony and bismuth were found to produce polarographic overcurrents. Even in these cases the appearance of an overcurrent was seldom observed and their suppression, for want of a better reason, was attributed to some unknown impurity in the formic acid used. A number of samples of acid was tried purified in various ways, by redistillation, by fractional recrystallization or a combination of both methods. The irregular appearance of the overcurrents, however, persisted. It was then discovered that the appearance of an overcurrent depended on the relative concentrations of supporting electrolyte and electro-reducible ion. If the concentration of the latter was maintained constant, it was found that on increasing the supporting electrolyte concentration from zero, the height of the overcurrent at first increased, then decreased and was finally suppressed completely at relatively low concentrations of the supporting electrolyte. The higher the concentration of the electro-reducible ion, the higher the concentration of indifferent electrolyte required to suppress its overcurrent.

In examining this effect quantitatively it was decided to measure the ratio (β) of the overcurrent to that of the diffusion current. This had the marked advantage over simple

measurement of the overcurrent in being relatively independent, of the time of dropping of mercury from the capillary. Both the overcurrent and the diffusion currents depend on this drop time, their ratio, however, being much less effected.

The measurements were made by mounting a scale securely in front of the polarograph and noting the deflections visually. A known amount of the electroreducible ion was dissolved in pure formic acid and weighed quantities of sodium formate were added; at each concentration of indifferent electrolyte the positions on the scale of the light spot corresponding to the zero, overcurrent and diffusion current was noted. With the exception of the measurements on stannous tin solutions, the results were found to be well reproducible. Further, the addition of 2% (v/v) of water to the solutions had a completely negligible effect on the results. The curves obtained are shown in Plates 17 - 20 and the data tabulated in Tables 32 - 45. The measurements quoted in these tables were done with solutions, in the anodic compartment, that were 0.1 M with respect to sodium formate. Although diffusion of salts across the sintered glass disc has been shown to be small, it was thought best to minimise this possibility by decreasing the sodium formate concentration at the anode. All measurements were made with the light spot initially at the zero mark on the scale. The measurements were not all done at one shunt setting, the sensitivity being varied to suit each deflection. No

PLATE 17

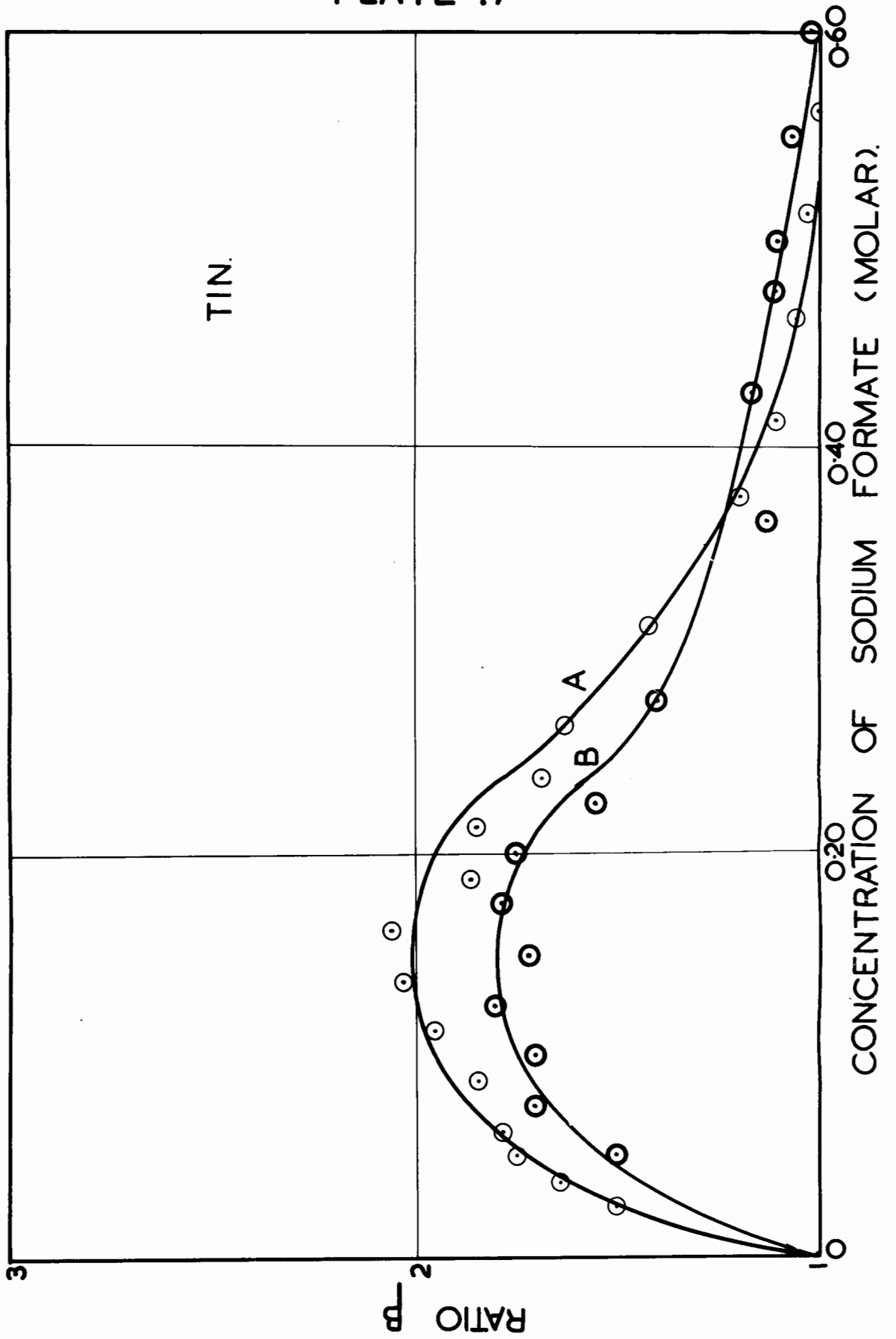


PLATE 18

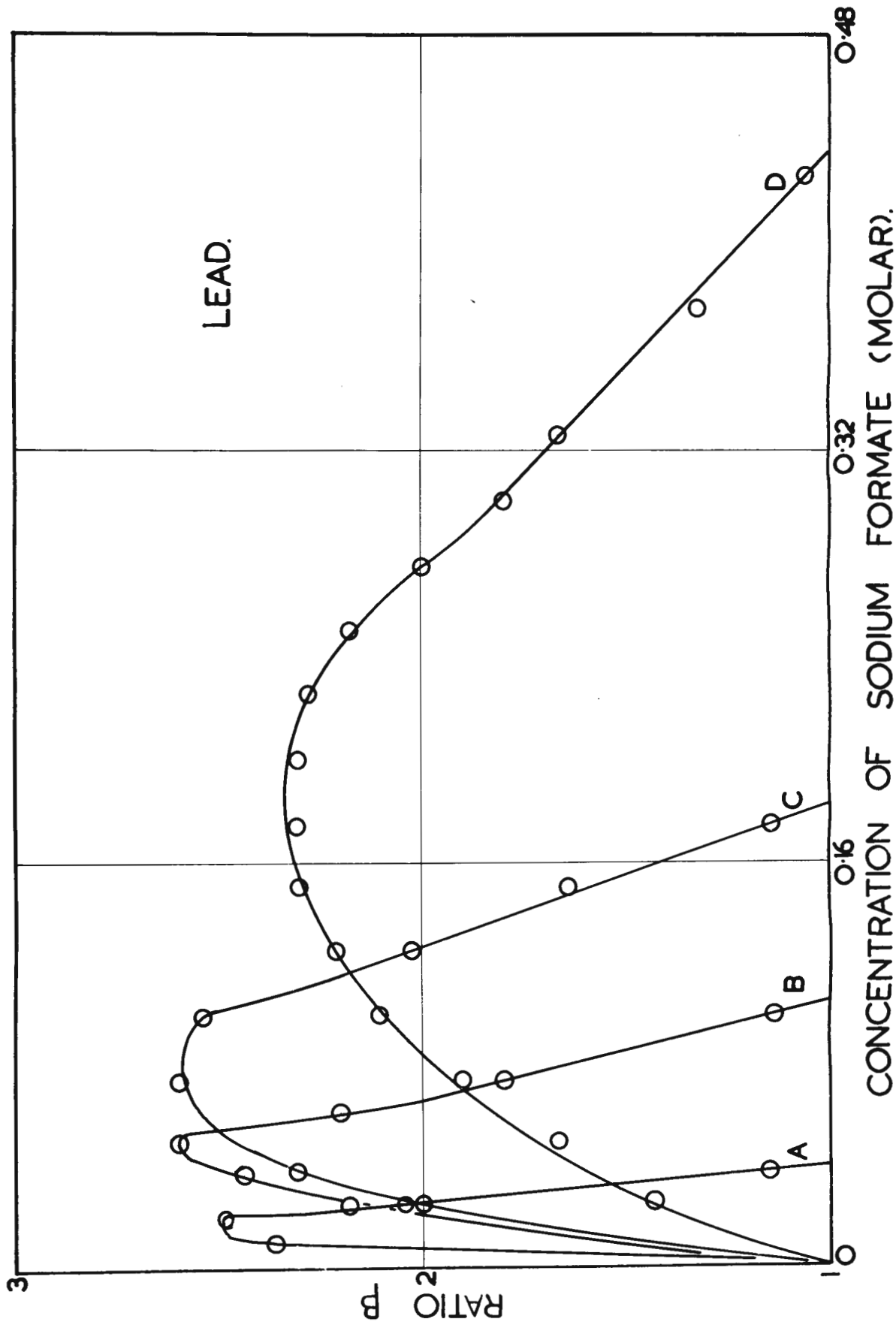


PLATE 19

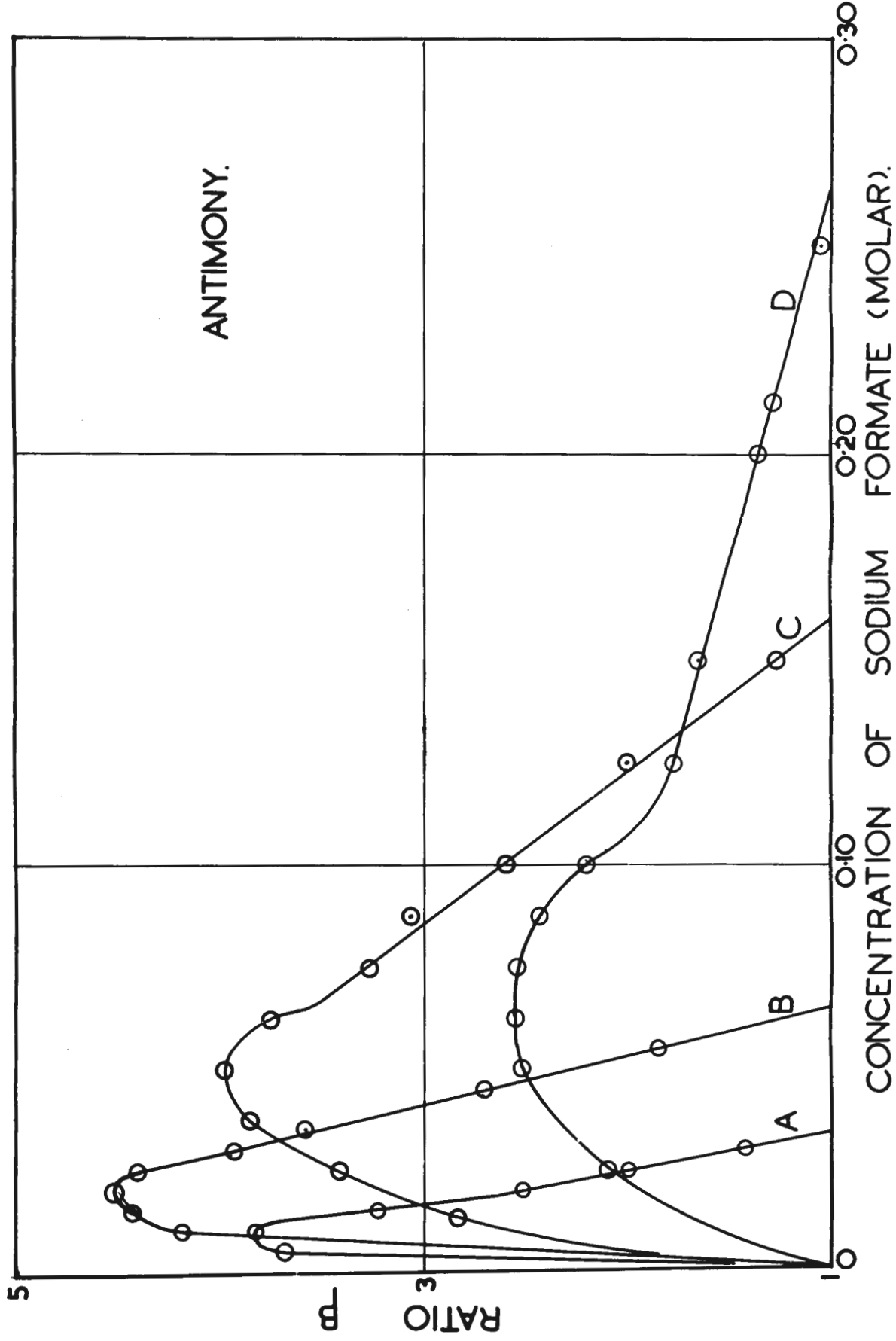
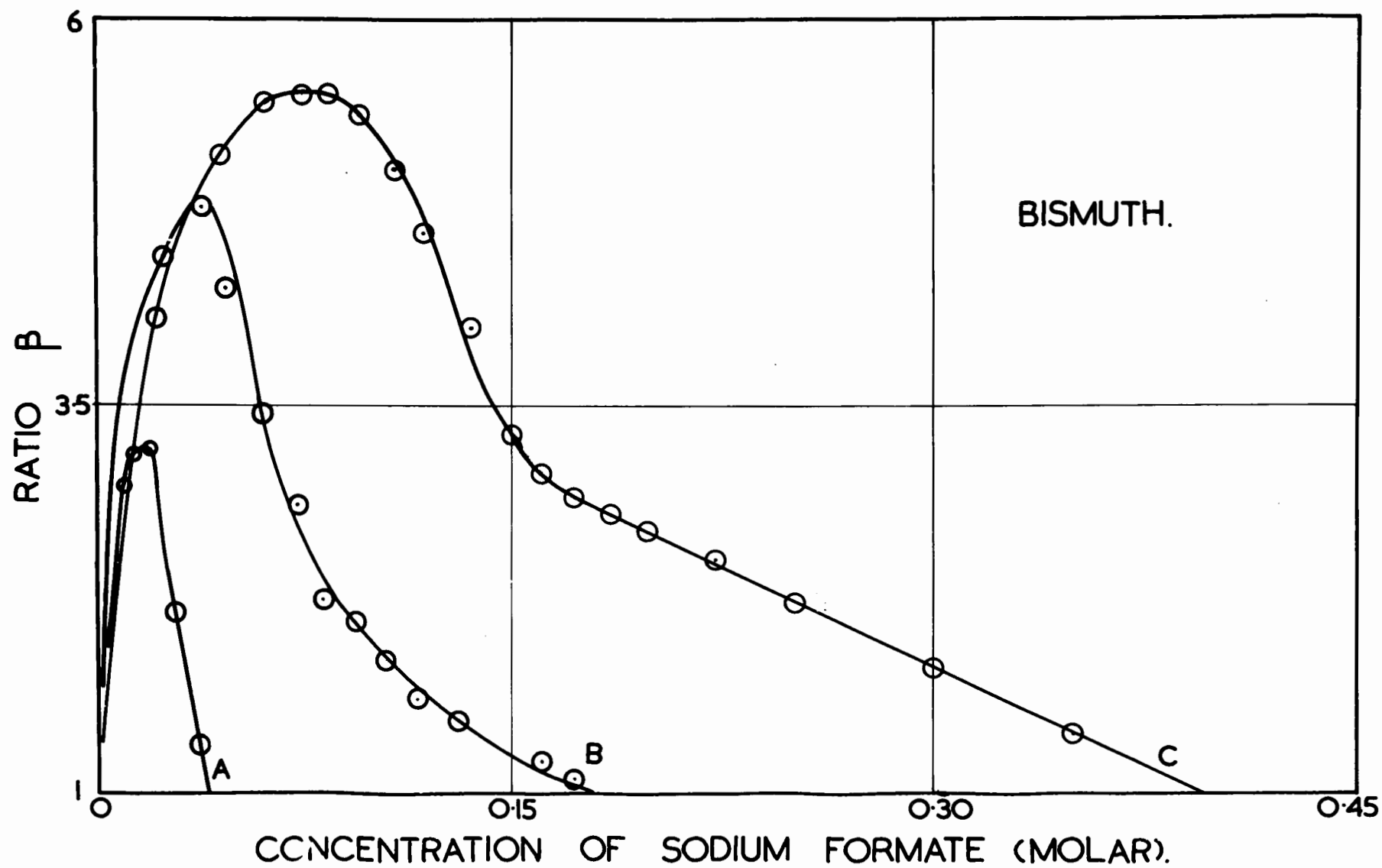


PLATE 20



difference in the ratio β was found at different shunt settings.

It will be noted that with the exception of tin, the curves are parabolic until at some stage on the downward branch, the plot changes to a straight line, this linear variation being maintained to the point of extinction of the overcurrent. Further, as the concentration of the electro-reducible ion is increased the maximal ratio increases, itself passes through a minimum and at very large concentrations almost disappears. The concentration of sodium formate corresponding to the maximal overcurrent is directly proportional to the electro-reducible ion concentration. Consideration of the curves for antimony in Plate 19 give the values quoted in Table 42 from which the proportionality is obvious. In the case of lead the linear portion of the curve is seen to exist for about $\frac{1}{2}$ of the span of the whole curve, for antimony $\frac{1}{2}$ and for bismuth about $\frac{2}{3}$ (see Plate 22). Finally the values of the ratio (β) for bismuth are greater than for antimony, than for lead, with tin showing the smallest values of the four cations.

Previously reported observations, regarding the dependence of the overcurrent on supporting electrolyte concentration, were done in the case of the overcurrents existing on the waves for the electro-reduction of the non-electrolytes, oxygen and mercuric cyanide and for uranyl salt solutions as described below.

TABLE 32.

$[\text{Sn}^{++}] = 2.45 \times 10^{-3}$ gm. ions/litre

Plotted in A Plate 17

| Concentration molar | Readings | | Ratio β |
|------------------------|----------------------|-------------------------|---------------|
| | Peak (scale divs) | Plateau (scale divs) | |
| 0.025 | 18.4 | 12.(3) | 1.5(0) |
| 0.038 | 17.5 | 10.(7) | 1.6(4) |
| 0.050 | 16.2 | 9.(3) | 1.7(4) |
| 0.0625 | 14.4 | 8.1 | 1.78 |
| 0.0875 | 10.1 | 5.5 | 1.84 |
| 0.1125 | 11.7 | 6.0 | 1.95 |
| 0.1375 | 12.2 | 6.0 | 2.03 |
| 0.1625 | 9.7 | 4.8 | 2.06 |
| 0.1875 | 7.8 | 4.2 | 1.86 |
| 0.2125 | 6.4 | 3.5 | 1.84 |
| 0.2375 | 4.0 | 3.0 | 1.68 |
| 0.2625 | 4.2 | 2.6 | 1.62 |
| 0.3125 | 7.5 | 5.3 | 1.42 |
| 0.3625 | 5.7 | 5.1 | 1.12 |
| 0.4125 | 4.4 | 3.9 | 1.10 |
| 0.4625 | 4.2 | 4.0 | 1.05 |
| 0.5125 | 3.9 | 3.8 | 1.02 |
| 0.5625 | 3.6 | 3.6 | 1.00 |

[The galvanometer sensitivity was changed for the last six readings].

TABLE 33.

$[\text{Sn}^{++}] = 1.25 \times 10^{-3}$ gm. ions/litre

Plotted in B Plate 17

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|----------------------|-------------------------|---------------|
| | Peak (scale divs) | Plateau (scale divs) | |
| 0.050 | 33.0 | 22 | 1.5 |
| 0.075 | 30.7 | 18 | 1.7 |
| 0.100 | 24.5 | 14 | 1.7 |
| 0.125 | 20.3 | 11.3 | 1.80 |
| 0.150 | 17.0 | 9.9 | 1.72 |
| 0.175 | 14.8 | 8.3 | 1.78 |
| 0.200 | 13.2 | 7.5 | 1.75 |
| 0.225 | 10.4 | 6.7 | 1.55 |
| 0.275 | 8.5 | 5.9 | 1.40 |
| 0.325 | 7.1 | 5.4 | 1.35 |
| 0.375 | 6.1 | 5.1 | 1.19 |
| 0.425 | 5.6 | 4.8 | 1.17 |
| 0.475 | 5.1 | 4.6 | 1.11 |
| 0.500 | 5.0 | 4.5 | 1.10 |
| 0.550 | 4.6 | 4.3 | 1.07 |
| 0.600 | 4.4 | 4.2 | 1.04 |
| 0.650 | 4.1 | 4.1 | 1.00 |

TABLE 34.

$[Pb^{++}] = 0.13 \times 10^{-2}$ gm. ions/litre

Plotted in A Plate 18

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.013 | 18.1 | 7.6 | 2.36 |
| 0.020 | 18.6 | 7.5 | 2.48 |
| 0.025 | 15.3 | 7.5 | 2.04 |
| 0.038 | 8.5 | 7.4 | 1.15 |
| 0.050 | 7.4 | 7.4 | 1.00 |

TABLE 35.

$[Pb^{++}] = 0.24 \times 10^{-2}$ gm. ions/litre.

Plotted in B Plate 18

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.025 | 31.4 | 14.4 | 2.18 |
| 0.038 | 34.2 | 14.0 | 2.44 |
| 0.050 | 35.9 | 13.8 | 2.60 |
| 0.063 | 30.1 | 13.7 | 2.20 |
| 0.075 | 24.6 | 13.7 | 1.80 |
| 0.083 | 20.3 | 13.7 | 1.48 |
| 0.100 | 15.4 | 13.6 | 1.13 |
| 0.113 | 13.6 | 13.6 | 1.00 |

TABLE 36

$[\text{Pb}^{++}] = 0.39 \times 10^{-2}$ gm. ions/litre

Plotted in C Plate 18

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.025 | 24.8 | 12.4 | 2.00 |
| 0.050 | 27.9 | 12.1 | 2.31 |
| 0.075 | 30.2 | 11.6 | 2.60 |
| 0.100 | 29.2 | 11.5 | 2.54 |
| 0.125 | 23.2 | 11.4 | 2.03 |
| 0.150 | 18.5 | 11.3 | 1.64 |
| 0.175 | 13.0 | 11.3 | 1.14 |
| 0.200 | 11.2 | 11.2 | 1.00 |

TABLE 37.

$[Pb^{++}] = 0.87 \times 10^{-2}$ gm. ions/litre

Plotted in D Plate 18

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.025 | 13.1 | 9.5 | 1.38 |
| 0.050 | 15.7 | 9.4 | 1.67 |
| 0.075 | 17.3 | 9.1 | 1.90 |
| 0.100 | 19.2 | 9.1 | 2.11 |
| 0.125 | 20.2 | 9.1 | 2.22 |
| 0.150 | 20.7 | 9.0 | 2.30 |
| 0.175 | 20.9 | 9.0 | 2.32 |
| 0.200 | 20.8 | 9.0 | 2.31 |
| 0.225 | 20.3 | 8.9 | 2.28 |
| 0.250 | 19.2 | 8.8 | 2.18 |
| 0.275 | 17.6 | 8.8 | 2.00 |
| 0.300 | 16.0 | 8.8 | 1.82 |
| 0.325 | 14.7 | 8.8 | 1.67 |
| 0.375 | 12.0 | 8.7 | 1.32 |
| 0.425 | 9.2 | 8.7 | 1.06 |
| 0.450 | 8.7 | 8.7 | 1.00 |

TABLE 38.

$[\text{Sb}^{+++}] = 0.25 \times 10^{-3}$ gm. ions/litre.

Plotted in A Plate 19

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.005 | 12.5 | 3.4 | 3.68 |
| 0.010 | 13.0 | 3.4 | 3.82 |
| 0.015 | 10.6 | 3.3 | 3.23 |
| 0.020 | 8.3 | 3.3 | 2.51 |
| 0.025 | 6.4 | 3.2 | 2.00 |
| 0.030 | 4.4 | 3.1 | 1.42 |
| 0.035 | 3.0 | 3.0 | 1.00 |

TABLE 39.

$[\text{Sb}^{+++}] = 0.49 \times 10^{-3}$ gm. ions/litre

Plotted in B Plate 19

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.010 | 24.3 | 5.8 | 4.19 |
| 0.015 | 25.2 | 5.7 | 4.42 |
| 0.020 | 25.7 | 5.7 | 4.51 |
| 0.025 | 25.1 | 5.7 | 4.40 |
| 0.030 | 22.5 | 5.7 | 3.93 |
| 0.035 | 20.1 | 5.6 | 3.59 |
| 0.045 | 14.6 | 5.4 | 2.70 |
| 0.055 | 10.0 | 5.4 | 1.85 |
| 0.065 | 5.4 | 5.4 | 1.00 |

TABLE 40.

$[Sb^{+++}] = 1.23 \times 10^{-3}$ gm. ions/litre

Plotted in C Plate 19

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.013 | 19.6 | 6.9 | 2.84 |
| 0.025 | 23.2 | 6.8 | 3.41 |
| 0.038 | 25.0 | 6.5 | 3.85 |
| 0.050 | 25.8 | 6.5 | 3.97 |
| 0.063 | 24.0 | 6.4 | 3.75 |
| 0.075 | 20.3 | 6.2 | 3.27 |
| 0.088 | 19.0 | 6.2 | 3.06 |
| 0.100 | 15.7 | 6.0 | 2.61 |
| 0.125 | 11.8 | 5.8 | 2.00 |
| 0.150 | 7.2 | 5.7 | 1.26 |
| 0.163 | 5.6 | 5.6 | 1.00 |

TABLE 41.

$[Sb^{+++}] = 1.96 \times 10^{-3}$ gm. ions/litre

Plotted in D Plate 19

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.025 | 21.0 | 10.0 | 2.10 |
| 0.050 | 24.2 | 9.6 | 2.52 |
| 0.063 | 24.2 | 9.6 | 2.55 |
| 0.075 | 24.1 | 9.5 | 2.54 |
| 0.088 | 22.4 | 9.2 | 2.43 |
| 0.100 | 20.2 | 9.2 | 2.20 |
| 0.125 | 16.3 | 9.2 | 1.77 |
| 0.150 | 15.2 | 9.2 | 1.66 |
| 0.200 | 12.4 | 9.2 | 1.35 |
| 0.213 | 11.9 | 9.2 | 1.29 |
| 0.250 | 9.7 | 9.2 | 1.05 |
| 0.263 | 9.2 | 9.2 | 1.00 |

TABLE 42.

| Curves | Concentration of Antimony $\times 10^3$ gm. ions/ litre | Concentration of Sod. formate $\times 10$ (molar) | Ratio |
|--------|---|--|-------|
| A | 0.25 | 0.010 | 0.25 |
| B | 0.49 | 0.020 | 0.25 |
| C | 1.23 | 0.050 | 0.25 |
| D | 1.96 | 0.068 | 0.29 |

TABLE 43.

$[Bi^{+++}] = 0.32 \times 10^{-3}$ gm. ions/litre

Plotted in A Plate 20

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.010 | 11.8 | 4.0 | 2.95 |
| 0.020 | 9.3 | 2.9 | 3.20 |
| 0.030 | 6.0 | 2.8 | 2.14 |
| 0.040 | 3.5 | 2.7 | 1.30 |
| 0.050 | 2.6 | 2.6 | 1.00 |

TABLE 44.

$$[Bi^{+++}] = 0.7 \times 10^{-3} \text{ gm. ions/litre}$$

Plotted in B Plate 20

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.013 | 27.8 | 6.9 | 4.03 |
| 0.025 | 30.2 | 6.8 | 4.44 |
| 0.038 | 31.5 | 6.6 | 4.77 |
| 0.050 | 27.3 | 6.4 | 4.27 |
| 0.063 | 21.1 | 6.2 | 3.40 |
| 0.075 | 17.3 | 6.1 | 2.84 |
| 0.088 | 14.5 | 6.1 | 2.38 |
| 0.100 | 12.4 | 5.9 | 2.10 |
| 0.113 | 10.9 | 5.9 | 1.85 |
| 0.125 | 9.4 | 5.9 | 1.60 |
| 0.138 | 8.7 | 5.9 | 1.47 |
| 0.163 | 7.0 | 5.8 | 1.20 |
| 0.175 | 6.3 | 5.8 | 1.09 |
| 0.188 | 5.8 | 5.8 | 1.00 |

TABLE 45.

$[Bi^{+++}] = 1.5 \times 10^{-3}$ gm. ions/litre

Plotted in C Plate 20

| Concentration (molar) | Readings | | Ratio β |
|--------------------------|---------------------|------------------------|---------------|
| | Peak scale divs. | Plateau scale divs. | |
| 0.013 | 20.9 | 6.6 | 3.17 |
| 0.025 | 26.5 | 6.5 | 4.08 |
| 0.038 | 30.2 | 6.4 | 4.72 |
| 0.050 | 31.7 | 6.2 | 5.11 |
| 0.063 | 33.7 | 6.2 | 5.44 |
| 0.075 | 34.0 | 6.2 | 5.49 |
| 0.088 | 34.1 | 6.2 | 5.50 |
| 0.100 | 32.9 | 6.2 | 5.30 |
| 0.113 | 28.2 | 6.2 | 5.00 |
| 0.125 | 26.0 | 6.1 | 4.60 |
| 0.138 | 24.4 | 6.1 | 4.00 |
| 0.150 | 18.9 | 6.0 | 3.30 |
| 0.163 | 18.2 | 6.0 | 3.03 |
| 0.175 | 17.3 | 6.0 | 2.87 |
| 0.188 | 16.8 | 6.0 | 2.80 |
| 0.200 | 16.1 | 6.0 | 2.68 |
| 0.225 | 14.7 | 5.9 | 2.49 |
| 0.250 | 13.3 | 5.9 | 2.25 |
| 0.300 | 10.3 | 5.7 | 1.80 |
| 0.350 | 7.6 | 5.5 | 1.39 |
| 0.400 | 5.4 | 5.4 | 1.00 |

Varasova (87) studied the behaviour of the overcurrent of oxygen. He showed that on increasing the supporting electrolyte concentration this overcurrent increased, passed through a maxima value and then decreased. No mention was made in this paper, however, of the complete suppression of the overcurrent by the addition of salts and it must be assumed that the investigation was not extended that far. Varasova noticed too that the concentration of the electrolyte solution, at which the overcurrent reached its maximum value, was directly proportional to the concentration of oxygen.

To quote his explanation ... "We may imagine that oxygen molecules are associated with ions of the electrolyte, become thus polar and are then more quickly attracted to the interface where, no doubt, electric forces are displayed. At the maximal maximum all oxygen molecules are supposed to be saturated with ions; any excess addition of electrolytes above this causes an increase of the adsorption velocity of the electrolyte above that of oxygen; consequently the electrolyte will penetrate more into the interface than oxygen, accumulate there and drive out oxygen from the interface, i.e. lessen the adsorption current.

The greater the concentration of oxygen the more ions are necessary to render all the molecules adsorptive, i.e. to reach the maximal maximum and the more ions will be necessary to suppress the maximum".

Part of this explanation is probably of value. It is not believed, however, that increase of the ions of the electrolyte increase the adsorption velocity of the inorganic cations, as postulated for oxygen, Varasova is probably correct in the idea, however, that the ions of the supporting electrolyte block out those of the electro-reducible species, as will be discussed later.

Rasch (83) examined the influence of fatty acids on the overcurrent of the oxygen wave and estimated their relative absorbability by determining their suppressive effects on this overcurrent. He correctly explains this suppression "by preferential adsorption of the added substance which pushes out the reducible matter from the mercury-solution interface". He concludes that the anions of the acid are inactive and that the suppression of the overcurrent is due entirely to undissociated molecules. Rasch maintains, however, that "for the development or suppression of the maximum, the undissociated molecules of formic acid are quite indifferent". In the light of several observations, however, this latter conclusion cannot be accepted.

Dillinger (88) undertook a study of the overcurrent occurring in the electrolysis of mercuric cyanide solutions. The outcome was found to be similar to that observed for oxygen. He, too, does not mention the complete suppression

of the overcurrent by the addition of supporting electrolyte but is also of the opinion "that a maximum of the current, observable with the dropping mercury cathode arrangement, requires a certain concentration of indifferent electrolytes to reach the highest dimension".

Herasymenko (89) noticed the same effect when examining the overcurrents on the curves of uranyl salt solutions. After passing through their greatest values, these overcurrents were completely suppressed at concentrations of 0.5 M. This concentration is exceptionally low for the suppression of overcurrents in aqueous solution by salt concentration alone. Herasymenko admits that this "case is complicated by the presence of products of reduction of uranyl salts i.e. of the pentavalent uranium, which accumulates in the interfacial layer. Owing to the presence of this probably strongly adsorbed matter the specific adsorptive influences of other ions present in solution are greatly inhibited".

That large concentrations of supporting electrolyte are required before the overcurrents are suppressed is recognised by Heyrovsky and Simunek (90) who maintain that "the maxima of the current are suppressed by surface active matter, active anions or great concentrations of electrolytes".

In order to explain the curves obtained for overcurrents in formic acid, at various sodium formate concentrations, it

is necessary to consider first a similar curve in aqueous solution, in the absence of any capillary-active substance. According to the authors quoted the overcurrent or likewise the current ratio β should increase on increasing the supporting electrolyte concentration pass through a maximum and fall away gradually as shown in Plate 21 (the complete curve, i.e. both full and dotted lines). An attempt can be made to explain this curve on the grounds of either of the existing theories used to account for the occurrence of the polarographic overcurrent. The explanation on the Heyrovsky-Ilkovic adsorption theory has been quoted above in the extract from the paper by Varasova (87).

A more plausible explanation is based on the "streaming theory" of Antweiler and von Strackelberg. At all potentials more positive than the electrocapillary maximum, the mercury drop is positively charged. The curvature of the mercury surface at the bottom of the drop is much less than at the mouth of the capillary and consequently the charge density will be appreciably more at the top than at the bottom. To quote from Kolthoff and Lingane's (91) treatise on the subject "the top of the drop behaves as if it has a more positive potential than the bottom although it is more exact to say that the solution i.e. the adsorption layer is more negative at the top of the drop than at other parts of the surface. If the drop behaves as if it has a more positive potential at the top than at the bottom, the

surface tension at the top is smaller than at the bottom when dealing with positive maxima. The interface therefore is pulled from top to bottom which is in the direction of streaming observed by Antweiler. Near the isoelectric point the electrocapillary curve is very flat and a slight difference in potential between the top and the bottom does not cause any movement of the streaming layers*.

According to this view, the mechanism in formic acid would be that the formate ions are attracted to the positively charged drop and adsorbing with different intensity at the top and the bottom, produce streaming of the electrolyte round the drop. This flow of liquid sweeps to the interface many electro-reducible ions giving rise to a current much in excess of the normal diffusion current. Increase of the sodium formate concentration, rapidly increases the rate of streaming; this rate must itself reach a maximum as the viscosity of the solution increases but this fact will be considered later. As the concentration of the supporting electrolyte increases, the cations of the indifferent salt, sodium in this case, tend more and more to block out the electro-reducible ions at the mercury-solution interface. Although the streaming may still be increasing, the sodium ions swept to the interface with the electro-reducible species, begin to exert a pronounced effect and the value of the overcurrent begins to decrease. It is for this reason that the concentration of the supporting electrolyte

at the maximum value of ratio β is directly proportional to the concentration of the electro-reducible ion.

Ions reduced at potentials appreciably more positive than the electrocapillary maximum are found to give rise to greater overcurrents, the value decreasing from element to element as the isoelectric point is approached. At this potential, overcurrents are non-existent. This phenomenon is readily explained by considering the change of slope of the electrocapillary curve in moving from positive values towards the isoelectric point. For an equal difference in potential, the difference in surface tension is greatest at more positive values and decreases as the curve approaches its maximum. As the curve is flat at this point the surface tension difference is zero and no streaming can occur. It is thus explained why the elements bismuth, antimony, lead and tin have overcurrents, the value of which decrease in the same order as do their half-wave potentials in approaching the electrocapillary maximum. The curves of the above elements as they would appear in aqueous solution are depicted in Plate 21 (the complete curve i.e. both full and dotted lines).

It has been postulated in Section E that monomeric formic acid molecules are capillary active, their concentration increasing linearly with increase of supporting electrolyte concentration. It would thus be necessary to superimpose on the curves in Plate 21, a linear function,

the effect of which would be to suppress the overcurrent. If an arbitrary choice of some linear function which would suppress the overcurrent is made, and plotted on the same graph (Plate 21) and the resultant of the two curves drawn, the curves obtained are identical in form to those plotted in Plates 17 - 20.

It is thus believed that the adsorption of monomeric formic acid molecules at the mercury-solution interface increases as the supporting electrolyte concentration is built up. These monomeric molecules greatly assist the sodium ions in blocking out the electro-reducible species, the two effects operating together.

The influence of the monomeric formic acid molecules is thus a matter of degree rather than kind. Both the cations of the supporting electrolyte and the formic acid molecules suppress maxima by blocking out the electro-reducible ions; the absorbability of the formic acid is, however, much greater.

Consideration of Plate 21 will explain why the linear portion of the curve is so much more pronounced in bismuth than for antimony and in turn, greater than for lead. The curve for bismuth, for example, rising higher than that for lead meets the straight line at a higher sodium formate concentration than does the lead curve. As the bismuth curve extends further over to the right of the graph, there

PLATE 2I

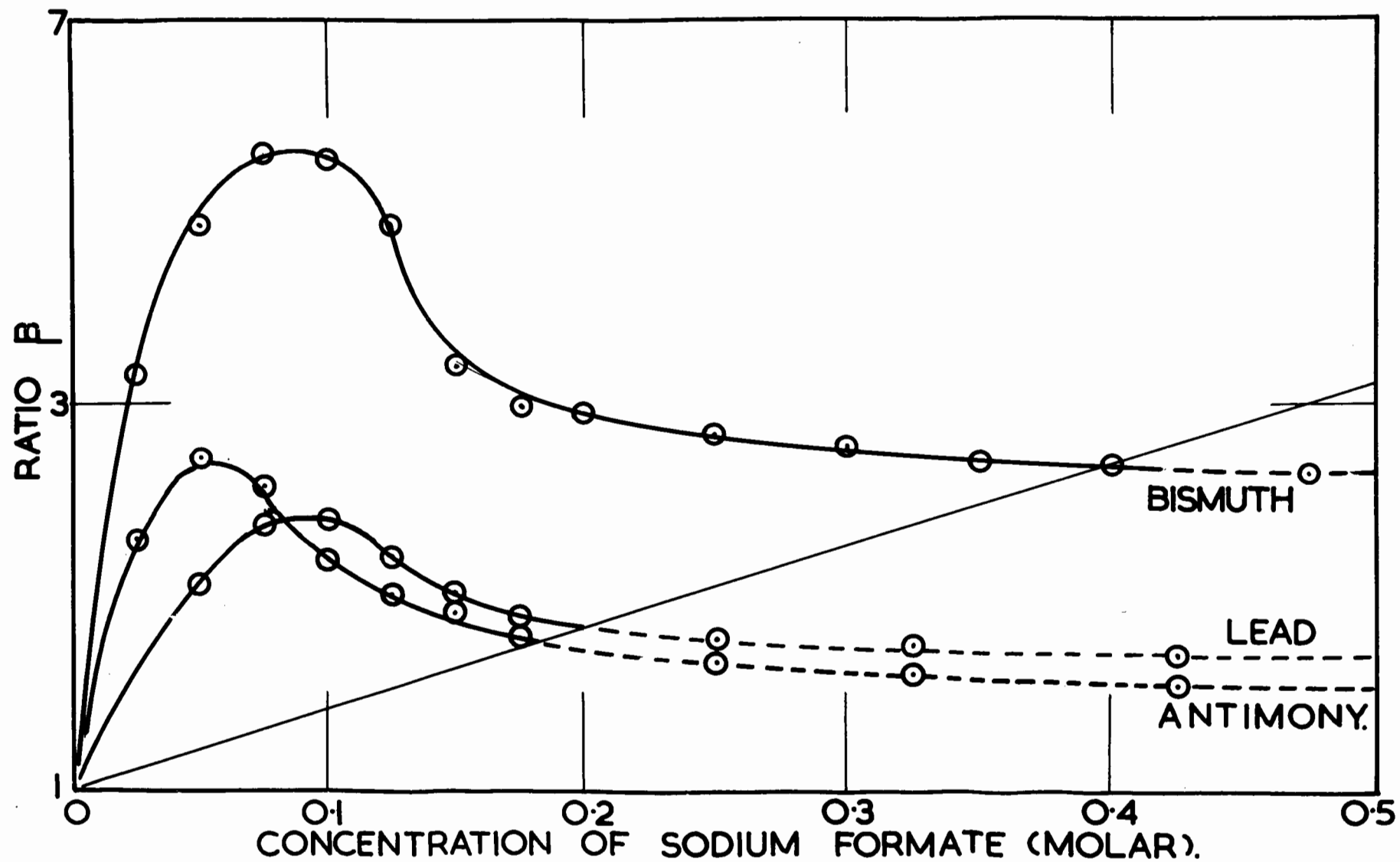


PLATE 22

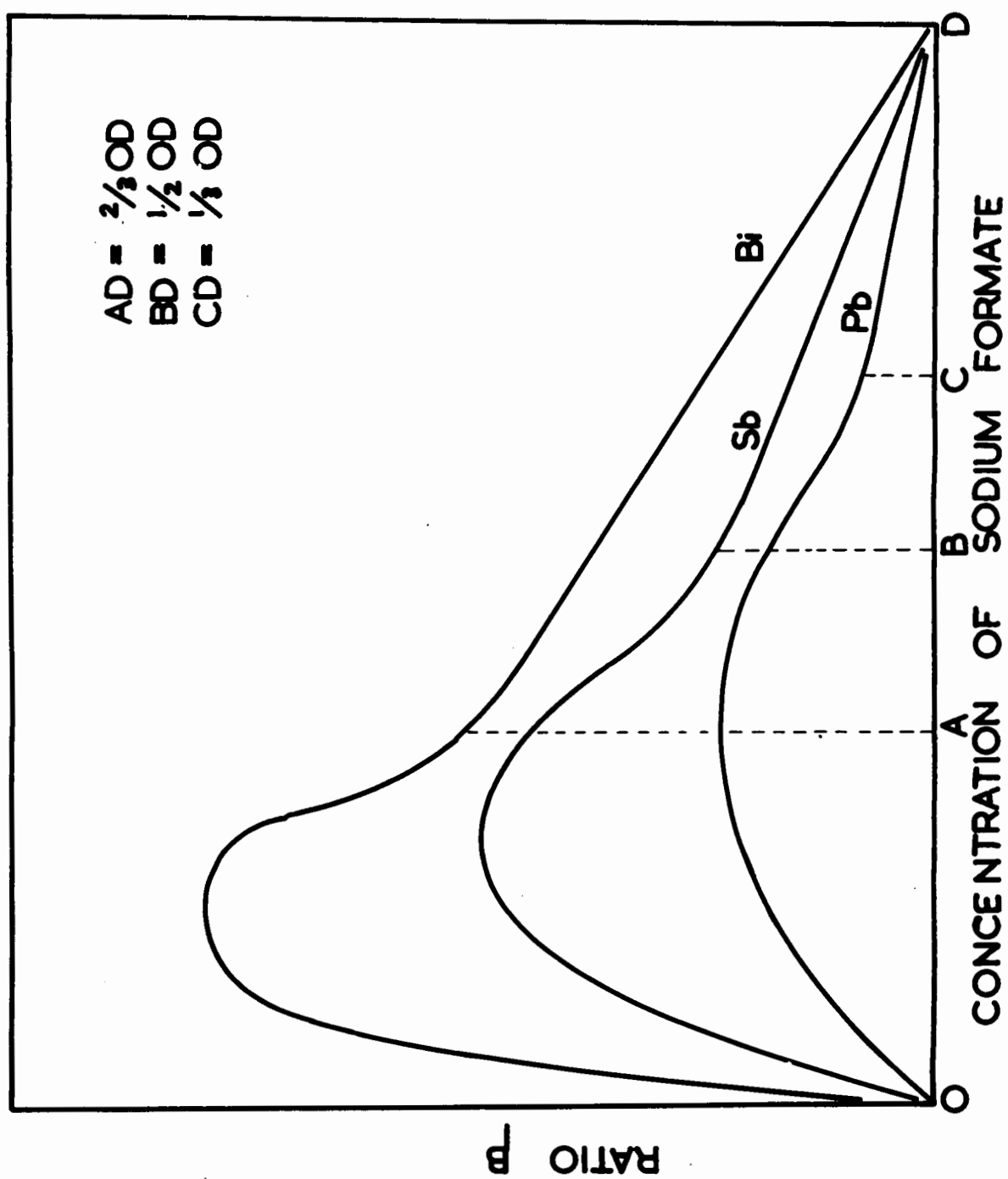
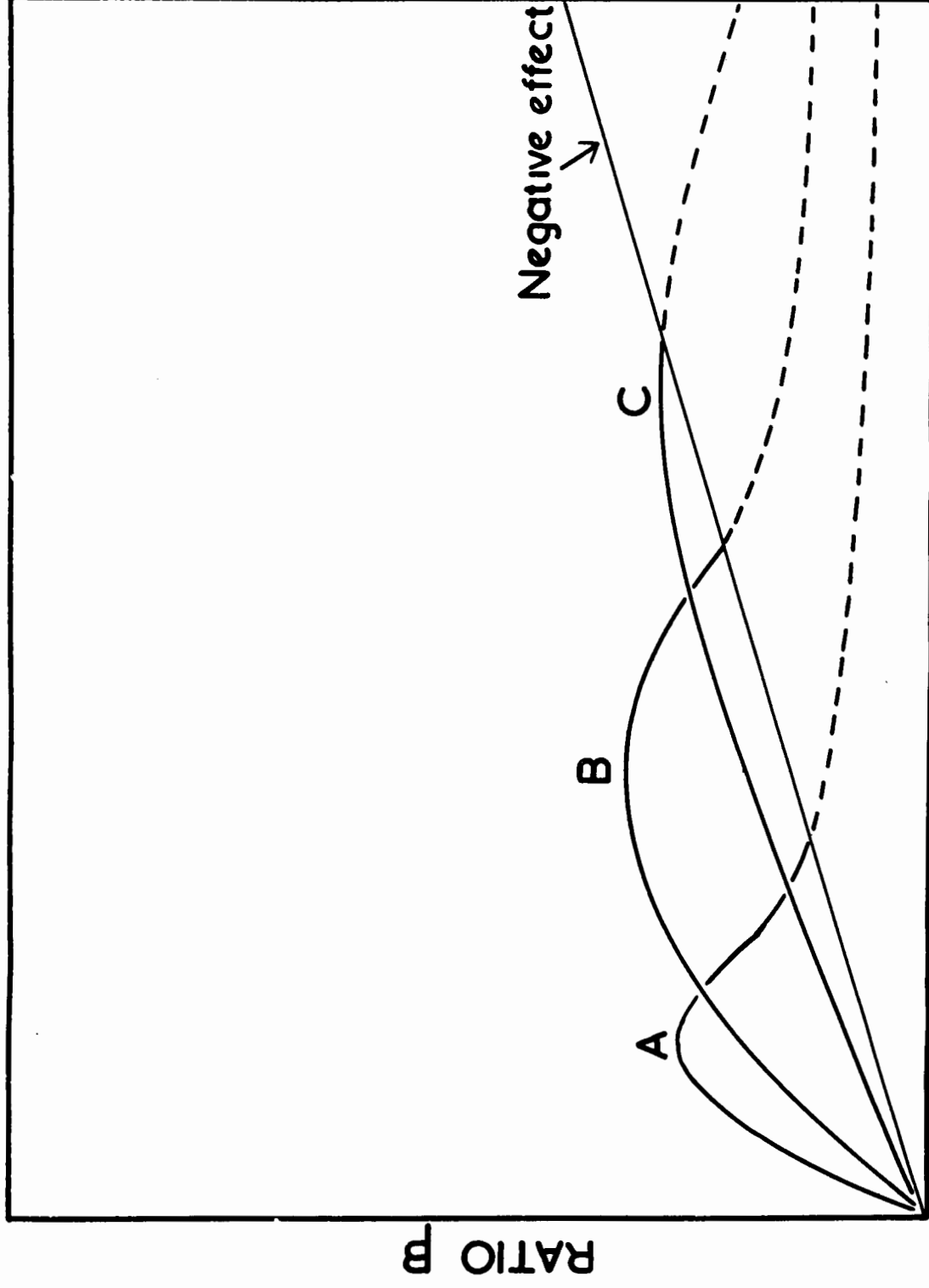


PLATE 23



CONCENTRATION OF SODIUM FORMATE

there is more of the linear portion than for the curve of lead.

Consideration of Plate 23, a series of curves at various concentrations of antimony shows why the height of the maximum overcurrent for the elements increases at first, itself passes through a maximum and then begins to decrease being almost non-existent at very high concentrations of electro-reducible ion. The concentration of indifferent electrolyte at the maximum overcurrent increases on increasing the concentration of the electro-reducible ion. The maximum overcurrent consequently moves more towards the depreciating straight line giving rise to resultant curves with lesser values for the maximum overcurrent. To this must be added the fact that the rate of streaming must itself pass through a maximum, beginning to decrease as the viscosity of the solution increases. [The viscosity of a 0.5 M sodium formate-formic acid solution is 22.1 millipoise (6) as compared with a value of 10.9 millipoise (92) for a 0.5 M aqueous sodium formate solution] .

Thus in Plate 23, the maximal overcurrent value increases because of a greater rate of streaming due to increase in the sodium formate concentration (curve B is higher than curve A). At curve B, however, the rate of streaming has reached its maximum value and on further increase of the supporting electrolyte concentration to curve C a slight decrease in the streaming rate and consequently a decrease in the maximal

overcurrent, is observed due to the greater viscosity of the solution. A combination of the two effects leads first to an increase, then to a decrease and then to a complete suppression of the overcurrent at very high values of the electro-reducible ion.

The reason for the strict proportionality of the electro-reducible ion concentration and the supporting electrolyte concentration at the maximum overcurrent as shown in Table 42 is to be expected. The more electro-reducible ions present, the more indifferent electrolyte will be required before the blocking out of the electro-reducible species causes a decrease in the overcurrent or ratio β .

It only remains at this stage to explain the behaviour of the overcurrents in the case of stannous ions. The plot of the current ratio β against the supporting electrolyte concentration is seen to be poorly defined and was not reproducible.

This is due to the fact that tin is the only element of the four under consideration that undergoes complex formation in formic acid. The weak formate stannous complex is believed to be $[\text{Sn}(\text{OOCH})_4]^{2-}$ (See Section D-IV).

The diffusion coefficient of the complex ion, because of its size, must be lower than that of an uncomplexed

stannous ion, leading to a lower diffusion current. Thus as every addition of sodium formate causes more complex formation it is to be expected that the diffusion current would decrease at each addition. The results quoted in Tables 32 and 33 show this to be the case. This decreasing value of the diffusion current decreases the accuracy and reproducibility of the current ratio β leading to poorly defined curves. One thing is, however, immediately evident from these curves: the maxima are not sharply suppressed as for the other elements but gradually decrease over a relatively large concentration range.

It is believed that the complex at the interface being much larger than the uncomplexed ions of antimony, bismuth and lead are able to hold the formic acid molecules at a greater distance from the interface. The electrometric potential falling off exponentially as it does, with distance from the interfacial double layer, exerts much less effect on the formic acid molecules which are held some distance away. It is thus more difficult for the formic acid to adsorb and the complete blocking out of the stannous ions requires a higher concentration of monomeric formic acid.

The curves obtained using potassium sulphate as the supporting electrolyte showed much the same form as those in a sodium formate medium. The height of the maximum overcurrent was close to the corresponding value for sodium

formate. This maximal value occurred, however, at slightly lower concentrations of potassium sulphate than sodium formate. This is to be expected as the sulphate ion, being divalent can give rise to a greater streaming rate than can sodium formate, for equal concentrations. The maximum streaming rate is thus reached at lower concentrations of added salt, giving rise to an earlier maximum. This in turn should give rise to a curve, the linear portion of which should represent a greater fraction of the whole curve than was found in the presence of sodium formate. The linear portion of the curve for antimony in the presence of potassium sulphate was about $\frac{2}{3}$ as opposed to $\frac{1}{2}$ for sodium formate.

There was, unfortunately, no way of testing the all important assumption that increase of the supporting electrolyte concentration led to a weakening of the hydrogen bond in dimeric formic acid, with the production of monomeric molecules. The only method available was the examination of the infra-red adsorption spectrum of formic acid. A peak in the plot of the molal absorption coefficient against the wave number in the region of 7000 cm^{-1} would be found due to the presence of the hydrogen bonds. If the above supposition was true, a lowering of this peak would be found on the addition of electrolytes, due to a decrease in the amount of hydrogen bonding.

As an infra-red spectrometer was not available in this Department, the assistance of the Council for Scientific and Industrial Research in Pretoria, was sought, they being the only people in a position to assist. They maintained, however, that the formic acid solutions would conceivably damage the windows of their cells and they were thus not prepared to make the required measurements. It was thus felt that the investigation had been carried as far as was possible.

SECTION G.

ORGANIC POLAROGRAPHY.

ORGANIC POLAROGRAPHY.

To conclude the investigation of the polarographic characteristics of anhydrous formic acid solutions , it was decided to make a study of a few organic compounds. This was not intended to be a detailed survey but only to gain a general impression from the few compounds investigated of the possibilities of organic polarography in formic acid.

The half-wave potential of each compound investigated was measured using a supporting electrolyte concentration of 0.5 M sodium formate. The value of $\tan \alpha$ was measured for each reduction.

From the outset it appeared likely that the number of compounds, which would produce polarographic waves from a formic acid medium would be limited. This conclusion was reached because the investigation of the inorganic cations showed that electro-reducible species with half-wave potentials in water more negative than -0.7 volts vs S.C.E. would be reduced in formic acid at a potential too negative to be observed. This was found to be the case and showed formic acid to be a solvent, unsuitable for the examination of organic compounds. The measurements carried out on organic compounds were, however, useful in substantiating an observation made during the investigation of the inorganic cations. It was found that the potentials in formic acid

and water showed a constant difference and the investigation of the organic compounds provided further proof of this relationship. It was thought at first that the potentials of organic compounds would not be of much value in establishing this constant difference because their half-wave potentials in aqueous media are dependent on the pH of the solutions. This leaves some doubt as to the actual value to be taken for the half-wave potential in aqueous medium. If, however, the potential in the solution of lowest pH was selected, the comparison with the potentials in formic acid proved of interest. This comparison will be given further consideration in the final section head 'Discussion'.

One compound, typical of the group, was selected from each series of organic substances. Naphthalene was investigated polarographically as being typical of the aromatic polynuclear hydrocarbons but, as expected, was reduced at too negative a potential to give a wave. This was found to be the case with compounds such as oxalic acid among the simple polybasic acids, and benzoic acid amongst the aromatic acids. Of the aliphatic aldehydes, acetaldehyde failed to give a wave although cinnamaldehyde, being the aromatic aldehyde with the most positive half-wave potential, gave a well formed wave just before the discharge potential of hydrogen ions. Acetone of the aliphatic ketones and benzophenone of the aromatic ketones failed to give waves being reduced at potentials too negative.

The organic nitro compounds were found to be suitable for investigation in formic acid, the first to be examined being nitrobenzene.

Nitrobenzene.

The half-wave potential of nitrobenzene in water has been shown to be greatly influenced by the pH of the solution. The polarogram in acid solution was made up of two waves involving 4 and 2 electrons, the half-wave potentials of which in a solution of pH 1 were -0.22 volts and -0.675 volts vs S.C.E. The reductions involved are from nitrobenzene to phenylhydroxylamine, the second wave being due to further reduction to aniline. The value of $\tan \alpha$ was 0.075 at pH of 2.5 and 0.088 at pH of 9.2 (93).

Nitrobenzene as supplied by May and Baker Ltd. was used. The polarogram in formic acid showed a clearly defined wave, the half-wave potential of which was -0.06 volts vs S.C.F.A.E. (-0.60 volts vs Q.F.A.E.); the value of $\tan \alpha$ was 0.071. At a potential of about -0.30 volts vs S.C.F.A.E. the polarogram ceased to be horizontal and began to increase gradually until the discharge potential of the hydrogen ion was reached. The solution was degassed with nitrogen for 2 hours to determine whether this would influence the gradual increase of the diffusion current but no change was observed. Thus only one measurable wave was observed for nitrobenzene.

Nitromethane.

It was decided to select nitromethane as typical of the polarographically reversible aliphatic nitro-compounds. These compounds showed two waves in aqueous solutions of pH greater than 4.5. In acid medium, however, only one wave was obtained, the half-wave potential of which did not vary greatly with pH. The half-wave potential of nitromethane at a pH of 1.8 was -0.75 volts vs S.C.E. The reduction was irreversible involved four electrons and produced hydroxylamine (94).

For the investigation in formic acid nitromethane as supplied by Eastman Kodak Co. was used. One wave was found which extended over as much as 0.5 volts and showed the reduction to be irreversible. The value of $\tan \alpha$ was 0.137. The half-wave potential was -0.63 volts vs S.C.F.A.E. (-1.17 volts vs Q.F.A.E.) in a 0.5 M sodium formate medium.

Nitrotoluene.

m-Nitrotoluene was chosen from the nitroalkylbenzenes which have been investigated polarographically. In aqueous solution this substance has been shown to give rise to two waves, the half-wave potentials of which at pH 1 are -0.22 and -0.71 volts vs S.C.E. (95).

m-Nitrotoluene as supplied by Eastman Kodak Co. was examined in formic acid and found to give rise to only one wave, the half-wave potential of which was -0.04 volts vs

S.C.F.A.E. (-0.58 volts vs Q.F.A.E.). This wave was well defined, the value of $\tan \alpha$ being 0.068. No second wave was encountered.

p-Nitrobenzoic Acid.

Of the nitrobenzoic acids, the above compound was representative of the group. The reduction of this compound in water gives rise to two waves, the half-wave potentials of which are -0.11 and -0.645 volts vs S.C.E. (93).

p-Nitrobenzoic acid as supplied by Judex Chemicals was used. Only one wave was found in formic acid, the half-wave potential of which was -0.05 volts vs S.C.F.A.E. (-0.49 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.052. After the completion of this wave the polarogram was found to gradually slope upwards being somewhat irregular, until the discharge potential of hydrogen was reached. Continued degassing failed to alter the shape of the polarogram.

m-Nitrobenzaldehyde.

The above compound typified the behaviour of the nitro substituted aromatic aldehydes. This compound gave rise to two waves in a dilute alcohol solution, the half-wave potentials of which were -0.21 and 1.01 volts vs S.C.E. (96). The first wave represents the reduction of the nitro group to the hydroxylamine, the second wave representing a combination of the reduction of the phenylhydroxylamine to the amine and the reduction of the aldehyde group apparently

to the carbinol since a total of 4 electrons is involved in each case.

m-Nitrobenzaldehyde as supplied by the Merck Co. was used in formic acid and was found to give one wave, the half-potential of which was -0.02 volts vs S.C.F.A.E. (-0.56 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.029. The potential of the second wave in aqueous solution was too negative to expect this wave to become evident in formic acid.

m-Nitrophenol.

This compound was selected from the polarographically reducible nitrophenols. Its reduction in aqueous solution gives rise to one wave, the half-wave potential of which is -0.25 volts vs S.C.E. (95) in an 8% ethanol solution. The reduction is believed to proceed to the amine but even then there appears to be some phase intermediate between the reduction to the hydroxylamine and that to the amine.

m-Nitrophenol as supplied by Hopkins and Williams Ltd. was used and found to produce a fairly well shaped wave, the half-wave potential of which was -0.06 volts vs S.C.F.A.E. (-0.60 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.051.

Azobenzene.

This compound has an half-wave potential of -0.04 volts vs S.C.E. in aqueous solution. As anticipated, this

potential was too positive for observation from formic acid solutions and no measurable wave was obtained.

α -Nitroso β -Naphthol.

This compound also has a half-wave potential which is too positive to give a well shaped wave in formic acid. An approximation of this potential was made and it is believed to be +0.21 volts vs S.C.F.A.E., although no certainty can be attached to this value.

Azoxybenzene.

No data are available for the half-wave potential of this compound in aqueous solution at low values of the pH. The wave in formic acid was poorly developed, the half-wave potential being +0.05 volts vs S.C.F.A.E. (-0.49 volts vs Q.F.A.E.).

Iodoform.

Iodoform shows three distinct waves in aqueous solution, the half-wave potentials of which are -0.49, -1.09 and -1.50 volts vs S.C.E. Only the first of these waves could possibly be found when using a formic acid medium, the potentials of the others being too negative.

Iodoform as supplied by May and Baker was used, the half-wave potential being -0.28 volts vs S.C.F.A.E. (-0.82 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.053.

Cinnamaldehyde.

The half-wave potential of this compound in aqueous solution was -0.78 volts vs S.C.E.; it was examined in formic acid as an example of the aromatic aldehydes.

Cinnamaldehyde, as supplied by British Drug Houses, was used. A well defined wave was obtained, the half-wave potential of which was -0.58 volts vs S.C.F.A.E. (-1.11 volts vs Q.F.A.E.). The value of $\tan \alpha$ was 0.066.

DISCUSSION.

DISCUSSION.

In conclusion, it would be of advantage to make a final assesment of anhydrous formic acid as a medium for polarographic investigation. It is intended first, however, to demonstrate that the series of half-wave potentials measured in aqueous solution, differ little from those measured in anhydrous formic acid.

In order to make this comparison the half-wave potentials have been tabulated in Tables 46, 47. The inorganic cations are compared first in Table 46; the potentials in water are quoted with reference to the saturated calomel electrode, the supporting electrolyte being 1 M nitric acid. The half-wave potential of indium in both solvents was obtained with a 1 M potassium chloride supporting electrolyte. The potentials in formic acid are quoted with reference to the saturated calomel-in-formic acid electrode; from each of these potentials the arbitrary value of 0.17 volts has been subtracted. In Table 47 the half-wave potentials of the organic compounds are compared in the same manner. As the half-wave potentials of organic compounds in aqueous solution are so dependent on the pH of the solution, it was necessary to select the potential most suitable for comparison with anhydrous formic acid i.e. at the lowest pH value. Further it will be seen that some of the half-wave

potentials were measured in aqueous solution to which small quantities of ethanol were added. These potentials were used in the absence of measurements in pure water, and were found to agree well with those in formic acid.

TABLE 46.

| Cation | Half-wave Potential | | |
|----------|--|---------------------------------------|-------------------------|
| | <u>Formic Acid</u> vs (S.C.F.A.E. - 0.17) volts | <u>Water</u> vs S.C.E. volts | Difference volts |
| Bismuth | -0.04 | -0.03 | -0.01 |
| Antimony | -0.17 | -0.17 | 0.00 |
| Lead | -0.39 | -0.41 | +0.01 |
| Tin | -0.45 | -0.44 | -0.01 |
| Thallium | -0.46 | -0.47 | +0.01 |
| Indium | -0.66 | -0.60 | -0.06 |
| Cadmium | -0.51 | -0.59 | +0.08 |
| Zinc | -0.88 | -1.0 | +0.1 |
| Nickel | -0.78 | -1.1 | +0.3 |

TABLE 47.

| Compound | Half-wave Potential | | | pH of aqueous medium |
|---------------------|---|-----------------------|------------------|------------------------|
| | Formic Acid vs S.C.F.A.E. (-0.17) volts | Water vs S.C.E. volts | Difference volts | |
| Nitrobenzene | -0.23 | -0.22 | -0.01 | 1.0 |
| Nitromethane | -0.80 | -0.75 | -0.05 | 1.8 |
| m-Nitrotoluene | -0.21 | -0.22 | +0.01 | 1.0 |
| p-Nitrobenzoic Acid | -0.12 | -0.11 | -0.01 | 1.0 + (10% ethanol) |
| m-Nitrobenzaldehyde | -0.19 | -0.21 | +0.02 | 1.0 + (Dilute ethanol) |
| m-Nitrophenol | -0.23 | -0.25 | +0.02 | 2.0 + (8% ethanol) |
| Iodoform | -0.45 | -0.49 | +0.04 | Independent of pH |
| Cinnamaldehyde | -0.74 | -0.78 | +0.04 | 1.5 |

The organic compounds show good agreement. With the exception of cadmium, zinc and nickel the agreement of the potentials of the inorganic cations is even more striking. That these three elements have potentials in formic acid which are more positive than those in water is readily explained on the basis of hydration of the ions in aqueous solution and a lack of solvolysis in formic acid. The effect can be seen to be greatest for nickel and least for cadmium which is the same order as the affinity for combination with water to form hydrates. The close agreement of the series of potentials in the two solvents is thus established.

In keeping with the observations made for other non-aqueous media, the diffusion current constants of the ions in formic acid are lower than the corresponding values in aqueous solution. This is to be expected in view of the higher viscosity of formic acid.

The disadvantages of anhydrous formic acid as solvent for polarographic investigation are due largely to its acidic nature. The use of supporting electrolytes such as cyanides, hydroxides or ammonia is therefore excluded; due to its reducing properties, formic acid solutions of iodides and nitrates are also unsuitable. Further, the range of measurable potentials is restricted to values between +0.2 and -0.8 volts vs S.C.F.A.E. It is this fact which shows formic acid to be of restricted use in the polarographic study of organic compounds.

Anhydrous formic acid does, however, show some very useful advantages. Besides being a solvent with small solvating power the addition of as much as 2% (v/v) of water, its main impurity, has been shown to exert little effect. Dissolved oxygen the presence of which is so undesirable, is more readily removed than from aqueous solution by bubbling nitrogen through the solvent; ten minutes degassing is usually sufficient. The solubility of inorganic salts is relatively high for an organic solvent; it was noticed throughout, that salts which are readily soluble in aqueous

solution e.g. potassium chloride, showed appreciable solubility in formic acid, while salts sparingly soluble in water e.g. lead sulphate, thallous chloride etc., showed a correspondingly low solubility in formic acid. Finally the necessity of having to suppress polarographic overcurrents as in aqueous solution, was absent.

REFERENCES.

REFERENCES.

- (1) Johnson and Cole, J.A.C.S., 73, 4536, (1951).
- (2) Pleskev, Acta Physicochimica U.R.S.S., 21, 41 (1946).
- (3) Schlesinger and Calvert, J.A.C.S., 36, 1589, (1914).
- (4) Schlesinger and Coleman, Ibid. 38, 271, (1916).
- (5) Schlesinger and Mullinix, Ibid. 41, 72, (1919).
- (6) Schlesinger and Martin, Ibid, 36, 1586, (1914).
- (7) Schlesinger and Reed, Ibid. 41, 1921, (1919).
- (8) Lange, Z. Physik. Chem. A187, 27, 1940.
- (9) Schlesinger and Bunting, J.A.C.S., 41, 1934, (1919).
- (10) Hammett and Diets, Ibid. 52, 4795, (1930).
- (11) Tomicek and Vidner, Chem. Listy. 47, 516, (1953).
- (12) Shkodin, Ismailov and Dzyuba, Zhur. Obshchei. Khim. 23, 27, (1953).
- (13) Shkodin, Ismailov and Dzyuba, J. Gen. Chem. USSR. 20, 2071, (1950).
- (14) Shkodin, Ismailov and Dayuba, Zhur. Obshchei. Khim. 20, 1999, (1950).
- (15) Shkodin, Ismailov and Dzyuba, Zhur. Anal. Khim. 6, 273, (1951).
- (16) Ilkovic, J. Chim. Phys. 35, 129, (1938).
- (17) Ilkovic, Collec. Czech. Chem. Commun. 6, 498, (1934).
- (18) Sillen, Lange and Gabrielson, "Problems in Physical Chemistry" - p. 250.
- (19) Lingane and Laitenen, Ind. Eng. Chem. Anal. Ed. 11, 504, (1939).
- (20) Kolthoff and Lingane, 'Polarography' - 1952 edn., p. 383.
- (21) Kolthoff and Lingane, Ibid. - p. 80.
- (22) Kolthoff and Lingane, Ibid. p. 81

- (23) Kendall and Adler, J.A.C.S., 43, 1470, (1921).
- (24) Livingston, Morgan, and Neidle, Ibid. 35, 1856, (1913).
- (25) Ewins, J.C.S., 105, 358, (1914).
- (26) Coolidge, J.A.C.S. 50, 2166, (1928).
- (27) Garner, Saxton, and Parker, Amer. Chem. Journal, 46, 236, (1911).
- (28) Timmermans and Mnd. Hennault-Roland, J. Chim. Phys. 27, 401, (1930).
- (29) Meissner and Michaels, Ind. Eng. Chem. 41, 2782, (1949).
- (30) Jones and Prendergast, J.A.C.S. 59, 731, (1937).
- (31) Baumberger and Bardwell, Ind. Eng. Chem. Anal. Ed. 15, 639, (1943).
- (32) Livingston, Morgan, Lammett and Campbell, J.A.C.S. 53, 454, (1931).
- (33) Billman and Jensen, Bull. Soc. Chem. 41, 151, (1927).
- (34) Bayer, J. Amer. Soc. Agron 20, 1125, (1928).
- (35) Morgan, Lammett and Campbell, Trans. Amer. Chem. Soc. 61, 405, (1932).
- (36) Hovorka and Dearing, J.A.C.S. 57, 446, (1935).
- (37) Kolthoff, Z. Physiol. Chem. 144, 259, (1925).
- (38) Lingane, Ind. Eng. Chem. Anal. Ed. 15, 583, (1943).
- (39) Gutbier and Muller, Z. Anorg. Chem. 128, 137, (1923).
- (40) Ephraim and Mosimann, Ber. 54, 396, (1921).
- (41) Skramovsky, Collec. Czech. Chem. Commun. 2, 292, (1930).
- (42) Haight, J.A.C.S. 75, 3848, (1953).
- (43) Sidgwick, 'Chemical Elements and Their Compounds', 1951 edn., p.799.
- (44) Davidson and Holm, J.A.C.S. 53, 1350, (1931).
- (45) Desesa and Hume, Anal. Chem. 25, 983, (1953).

- (46) Blomberg, Chem. Weekblad 11, 1030, (1914).
- (47) Jacques, Trans. Farad. Soc. 5, 225, (1909).
- (48) Chatterji, J. Ind. Chem. Soc. 27, 551, (1950).
- (49) Anokhin, Acta Univ. Voronegientis USSR, 11, 2, 35, (1939).
- (50) Jellinek and Gordon, J. Phys. Chem. 112, 207, (1924).
- (51) Meites, J.A.C.S. 73, 1161, (1951).
- (52) J.-L. Delsal, J. Chim. Phys. 35, 314 (1938).
- (53) Scholder, Gadenne and Niemann, Ber. 60B, 1489, (1927).
- (54) Kolthoff, Perlich, and Weiblen, J. Phys. Chem. 46, 561, (1942).
- (55) Scholder and Linstrom, Ber. 63B, 2831, (1930).
- (56) Elod and Kolbach, Z. Anorg. Chem. 164, 297, (1927).
- (57) Willard and Toribara, J.A.C.S. 64, 1759, (1942).
- (58) Vanderzee and Rhodes, Ibid. 76, 5226, (1954).
- (59) Kolthoff and Lingane, "Polarography" - 1952 Edn., p.520.
- (60) Kolthoff and Lingane, Ibid. p.198.
- (61) Kolthoff and Lingane, Ibid. p.52.
- (62) Strocchi, Gazz. Chim. Ital 79, 270, (1948).
- (63) Strocchi, Ibid. 80, 234, (1950).
- (64) Bourion and Hunn, Compt. Rend. 191, 97, (1930).
- (65) Bourion and Reuyer, Ibid. 184, 598, (1927).
- (66) Spacu and Pepper, Bul. Soc. Stiinte Chij. 7, 400, (1934).
- (67) Vasiliev and Preukhina, Zhur. Anal. Khim 6, 218, (1951).
- (68) Leden, Z. Physik. Chem. A188, 160, (1941).
- (69) Dergunen, Doklady. Akad. Nauk USSR 64, 517 (1949).
- (70) Lingane, Ph.D. Thesis, Univ. of Minnesota (1938).
- (71) Kolthoff and Lingane, "Polarography" - 1952 Edn., p.520.

- (72) Hepler, Kury, and Hugus, *J. Phys. Chem.* 58, 26, (1954).
- (73) Schufle, Stubbs and Witman, *J.A.C.S.*
- (74) Schufle and Morris-Eiland, *Ibid.* 76, 960, (1954).
- (75) Moeller, *Ibid.* 62, 2444, (1940).
- (76) Sillen and Andersson, *Svensk. Kem.Tid.* 55, 13, (1943).
- (77) Sillen and Liljeqvist, *Ibid.* 56, 85, (1944).
- (78) Gunther and Schultze, *Z. Elektrochem* 28, 387, (1922).
- (79) Kunshert, *Z. Anorg. Chemie* 41, 337, (1904).
- (80) Scholder, Gadenne and Niemann, *Ber.* 60B, 1510, (1927).
- (81) Scholder, *Ber.* 60B, 1525, (1927).
- (82) Potapenko and Wheeler, *Revs. Modern Phys.* 20, 143, (1948).
- (83) Rasch, *Collec. Czech. Chem. Commun.* 1, 560, (1929).
- (84) Heyrovsky and Dillinger, *Ibid.* 2, 626, (1930).
- (85) Herasymenko, Heyrovsky and Tancakivsky, *Trans. Farad. Soc.* 25, 152, (1929).
- (86) Bachman and Astle, *J.A.C.S.* 64, 2177, (1942).
- (87) Varasova, *Collec. Czech. Chem. Commun.* 2, 8, (1930).
- (88) Dillinger, *Ibid.* 1, 638, (1929).
- (89) Herasymenko, *Trans. Farad. Soc.* 24, 267, (1928).
- (90) Heyrovsky and Simunek, *Phil. Mag.* 7, 951, (1929).
- (91) Kolthoff and Lingane, *"Polarography"*, 1952 Edn., p. 177.
- (92) Simon, *Compt. Rend.* 181, 862, (1915).
- (93) Page, Smith and Waller, *J. Phys. and Colloid Chem.* 53, 545, (1949).
- (94) Petru, *Collec. Czech. Chem. Commun.* 12, 620, (1947).
- (95) Pearson, *Trans. Farad. Soc.* 44, 683, (1948).
- (96) Korshunov and Sazanova, *Zhur. Fiz. Khim* 23, 1299, (1949).

SUMMARY OF THE DISSERTATION

ELECTROCHEMICAL STUDIES IN ANHYDROUS FORMIC ACID

by T.A. PINFOLD.



Before beginning the actual polarographic investigation of anhydrous formic acid solutions, it was necessary to develop a reference electrode in that solvent to which the measured half-wave potentials could be referred. It was essential that the electrode be non-polarisable, reversible and reproducible, that it be capable of rapid preparation and, if possible, insensitive to small amounts of water. The quinhydrone-in-formic acid electrode was found to satisfy all these requirements admirably, besides which it had a very small salt effect and did not depreciate over a period of several hours. It was thus well suited to the role of polarographic anode. As this electrode had only been used in this capacity once previously, in aqueous solution where it was found to undergo polarisation and be unsatisfactory, it is hoped that its usefulness will be extended to other non-aqueous solvents.

In order to conform with polarographic practice in aqueous solution it was decided to prepare a formic acid analogue of the saturated calomel electrode and measure its potential with respect to the quinhydrone-in-formic acid electrode. This potential was found to be -0.5384 ± 0.0005 volts vs Q.F.A.E., the mean of ten determinations. The half-wave potentials were thus measured against the quin-

hydrone electrode and quoted as against the calomel electrode.

The measurable range of potentials using the quin-hydrone-in-formic acid electrode was +0.2 to -0.8 volts vs S.C.F.A.E. Nine inorganic cations were found to have their half-wave potentials within this range and these potentials were measured in about seven different supporting electrolytes. Formic acid was found to be a good solvent for many salts, the solubility relationships being similar to those in aqueous solution. The incidence of complex formation in formic acid was also shown to be very similar to that in water.

For all the inorganic and organic electro-reducible species investigated, a constant difference of -0.17 volts was found between the potentials in formic acid against the saturated calomel-in-formic acid electrode and those in aqueous solution against the saturated calomel electrode. The elements, cadmium, zinc and nickel, however, showed exceptional behaviour in having more positive half-wave potentials in formic acid than in aqueous solution. It has been shown that formic acid must be regarded as a solvent with low solvating power and it is postulated that these elements show this anomalous behaviour because of appreciable hydration in water but lack of solvolytic effects in formic acid. It is for this reason too that indium was found to be reversibly reduced in formic acid and irreversibly reduced in aqueous solution. The half-wave potential of thallium

exhibited the most unusual characteristic of shifting appreciably to more positive potentials on increase of the supporting electrolyte concentration.

It was found that the appearance of polarographic overcurrent in anhydrous formic acid were most irregular; in most cases being altogether absent. After showing conclusively that this phenomenon was not attributable to the presence of impurities in the solvent, it was discovered to be dependent on the concentration of supporting electrolyte, small concentrations of which were sufficient to suppress the overcurrent completely. As this feature is quite unique it was further investigated by plotting the ratio of the overcurrent to diffusion current against supporting electrolyte for the elements bismuth, antimony, lead and tin, the only elements whose curves exhibited overcurrents. The plots were found to be initially parabolic, changing to a linear relationship until final suppression of the overcurrent. The curves were explained as being the composite effect of the normal curve in aqueous solution and a reducing linear effect which was found to be due to capillary-activity of monomeric formic acid molecules. It is postulated that under the influence of increased ionic strength, the hydrogen bonding of the dimeric molecule is reduced giving rise to increased concentrations of the monomer which is responsible for the suppression of the overcurrent.

The theory was supported by examination of the electrocapillary curves of mercury in formic acid. Further investigation of these curves in the presence of the electroreducible ions showed regular plateaus and electrocapillary maxima shifts all of which were explained.

The research was completed by a polarographic examination of some organic compounds in anhydrous formic acid, to ascertain the possibilities of further work in this field. It was found, however, that due to the acidity of the solvent, and consequently the early appearance of the wave due to the discharge of hydrogen ions, few organic compounds could be examined. Formic acid is thus unsuitable from this aspect, but exhibits some most favourable characteristics as a medium for polarographic investigation.