I. POLAROGRAPHIC BEHAVIOR OF SIMPLE CHLORINATED ORGANOSILANES

II. POLAROGRAPHIC INVESTIGATIONS IN PYRIDINE

by

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PART I

THE POLAROGRAPHIC BEHAVIOR OF SIMPLE CHLORINATED ORGANOSILANES

Introduction

Alkylhalosilanes are particularly important today as intermediates in the field of silicone polymers. Because of their ease of polymerization, the problem of chemical analysis has been a difficult one and has usually consisted of analyzing the particular alkylhalosilane in terms of the respective elements present. Silicon has been determined by various wet oxidation procedures using sulfuric acid or nitric acid or, in the case of micro amounts, by a colorimetric procedure as the blue silicomolybdate. When the halogen present is fluorine, it may be determined following hydrolysis by the lead chlorofluoride method. Carbon and hydrogen present in the organochlorosilane have been determined by normal combustion methods with some modifications. The determination of the halogen present may be done by hydrolyzing the sample in water or aqueous alkali, neutralizing, and titrating the halide ion with a standard solution of silver nitrate using potassium chromate as an indicator. A variation of this is to hydrolyze the sample in an ice-water-ether mixture, the resulting acid being titrated with a standard base. This latter method gives very accurate results for substances such as dimethyldichlorosilane whose hydrolytic products are soluble in ether; but for substances such as silicon tetrachloride, which hydrolyze to give ether-insoluble products, the accuracy is impaired. This is due to retention of some of the hydrolyzable halogen by the precipitate causing slow attainment of the end point. In cases where the halogen does not hydrolyze readily a preliminary fusion in a Parr bomb is necessary. Gravimetric procedures, although possible, are not desirable because of the problem of removal of gelatinous hydrolysis products before precipitation of the halide ion. Molar refractions have been used to confirm the composition of organosilicon compounds (1, 2).

The mass spectrometer has been used for analysis of methylchlorosilanes by determining the relative heights of several predetermined peaks characteristic of the individual methylchlorosilanes (3). To minimize hydrolysis effects it was necessary to use 25-50 gram samples. More recently Gilman and Miller (4) have determined silanols with the Karl Fischer reagent. With some modification this reaction could be adapted to the analysis of certain organochlorosilanes by first hydrolyzing the organochlorosilane and then titrating the resulting silanol with the Karl Fischer reagent.

Since both chloroform and carbon tetrachloride are reducible at the dropping mercury electrode (5), it was thought that perhaps methyltrichlorosilane and other alkyl substituted chlorosilanes might also be reducible at the dropping mercury electrode, leading to an analytical determination of the alkylhalosilanes. However, chloroform and carbon tetrachloride both require the presence of hydrogen ions for reduction at the dropping mercury electrode and the organochlorosilanes undergo solvolysis in protonated solvents. Therefore, it was decided to carry out the investigation in non-aqueous solvents; if any reduction occurred it would have to be by a different mechanism than that proposed for chloroform and carbon tetrachloride.

The choice of a solvent involved the following considerations: 1. to choose a solvent in which the organochlorosilane was soluble without reaction, or with which the organochlorosilane reacted to give reducible products; 2. to choose a solvent in which sufficient supporting electrolyte could be dissolved to give a solution of sufficiently low resistance for polarographic work, and 3. to choose a solvent which does not itself reduce or one which reduces at such extremely negative potentials that a workable span of potential is possible. Up to the present time the only polarographic work in non-aqueous solvents has been the work of Laitinen and Nyman in liquid ammonia (6,7,8), the work of Bachman and Astle, MacGillavry and Hala in acetic acid (9,10,11,12), the work of Sartori in alcohols (13,14), the work of Zan'ko and Manuscova in formamide and alcohols (15), the work of Gentry in ethylene glycol (16), and the work of Peracchio and Meloche in alcohols (17). The organochlorosilanes would be solvolyzed by the liquid ammonia, the alcohols, or by the glycol; hence these solvents would not be suitable. Acetic acid may be a possible solvent, however there is some indication that it is not entirely satisfactory due to discontinuities that appear in many of the polarographic waves. The organochlorosilanes are soluble in ether, benzene, carbon tetrachloride, chloroform, hydrocarbons and carbon disulfide without any reaction. All these would be possibilities if sufficient supporting electrolyte could be dissolved in them. Other solvents which were deemed possible were acetone, methyl ethyl ketone, pyridine, tetrahydrofuran, acetonitrile, and formamide. Acetone and methyl ethyl ketone are fairly good solvents for some inorganic salts although some reaction might be expected with the organochlorosilane. Acetone reduces at -1.7 volts against the saturated calomel electrode (18) with hydrogen ion present, hence there should be a large operable span of potential available. Methyl ethyl ketone does not give a reduction wave. Pyridine has excellent solvent properties and, although it reduces at a potential of -1.45 volts against the saturated calomel electrode, hydrogen ions are necessary. Tetrahydrofuran has been used as a solvent for potentiometric titrations (19) and it forms conducting solutions with lithium bromide, lithium iodide and tetrabutylammonium iodide. Evidence for an addition compound of trichlorosilane and tetrahydrofuran has been found (20) which conceivably may undergo reduction. Acetonitrile is also an excellent solvent for many inorganic salts and no reduction wave for it is reported. Formamide has a high dielectric constant and is an excellent solvent for many inorganic salts and has been used as a polarographic solvent (15). It was also decided to try secondary isoamyl alcohol, the thought being that perhaps the hydrolysis might be slow enough to allow time studies to be made should either the organochlorosilane reduce or should the reaction products be reducible. Should this occur an analytical procedure might be developed based on these time studies.

Experimental Methods

For all the work a Sargent Model XXI visible recording polarograph was used. All values of potential set on the span were checked with an auxiliary potentiometric circuit. The rate of flow of mercury per second was determined with an open circuit with the mercury freely dropping in air and the drop time was determined at the half-wave potential in the respective medium. All curves were calculated by the method described in the manual of instructions for the Sargent Model XXI polarograph. A conductivity bridge Model RC-1B made by Industrial Instruments was used for all resistance measurements which were made with an open circuit through the cell and column of mercury. A Beckman Model G pH meter was used for the pH measurements on the hydrochloric acid solutions. In all measurements against the saturated calomel electrode an H-cell was used with a fritted disc to separate the solution from the saturated calomel electrode. The cell was equipped with a stopcock in one leg to allow the solution to drain after polarographic measurements. For measurements using the quiet pool of mercury as anode either a Heyrovsky Erlenmeyer-type cell was used with a cork stopper to minimize contact with the air or a two piece electrolysis cell, catalog number S-29306, made by E. H. Sargent and Company was used. The solutions were not thermostatted during a run but were brought to constant temperature in a constant temperature water bath at 25° ± 0.2° previous to the run. All solutions were bubbled with commercial nitrogen entrained over alkaline pyrogallol and magnesium perchlorate to free them from oxygen, previous to running the polarogram.

The mercury was purified by bubbling with air for 24 hours. It was allowed to spray from a funnel through 10% sodium hydroxide, then through dilute nitric acid, followed by filtering through a Bethlehem Type F mercury filter. It was finally distilled through an evacuated one piece mercury still.

All the organochlorosilanes used were products of the Anderson Laboratories, Adrian, Michigan, with the exception of the vinyltrichlorosilane which was from the Linde Air Products Company. The alkylhalosilanes were used as received because of the lack of extensive equipment to purify them by fractional distillation and because of the corrosive nature of the organochlorosilanes. In most of the cases they were from ninety to ninety-nine per cent pure. The methyl ethyl ketone was an Eastman product and was distilled, collecting that portion boiling between 79° and 80°. It was then dried over calcium chloride. The chloroform was Mallinckrodt technical grade and was twice distilled, the second time in an all-glass apparatus. The fraction boiling between 60° and 62° was collected for use. The acetone and secondary isoamyl alcohol used were Baker's

Analyzed and Merck, respectively, and were used without any further purification. The acetonitrile was a C. P. Fischer Scientific Company product and was used after drying over phosphorus pentoxide. The tetrahydrofuran was an Eastman product and was redistilled over sodium hydroxide, the portion boiling between 62° and 64° being collected and then dried over metallic sodium. The formamide was an Eastman product and was used as received for preliminary experiments. The pyridine was Baker's Analyzed and was suitable for use after being dried over potassium hydroxide for a few days, redistilled and dried over barium oxide. The pyridine was recovered from the pyridine-water-salt mixtures by distilling the pyridine-water azeotrope from the salt, removing the water from the azeotropic mixture with repeated treatments with potassium hydroxide, redistilling over barium oxide and collecting the portion from 114° to 116°. The lithium chloride, potassium chloride and zinc chloride used as supporting electrolytes were Baker's Analyzed products and were used after drying in an oven at 110° for three hours. Tetrabutylammonium iodide was recrystallized from ethyl acetate-ethanol mixtures (21), and the recrystallized product melted at 146°.

In the preliminary runs to determine whether or not reduction was possible in many of the solvents, the organochlorosilane was weighed directly into a volumetric flask containing the solvent and supporting electrolyte from a 60 ml. weighing burette tared with another 60 ml. weighing burette. Tetrabutylammonium iodide was used as supporting electrolyte in chloroform. Lithium chloride and zinc chloride were used as supporting electrolytes in methyl ethyl ketone and acetone. Lithium chloride was used as supporting electrolyte in acetonitrile, formamide, isoamyl alcohol, tetrahydrofuran and pyridine.

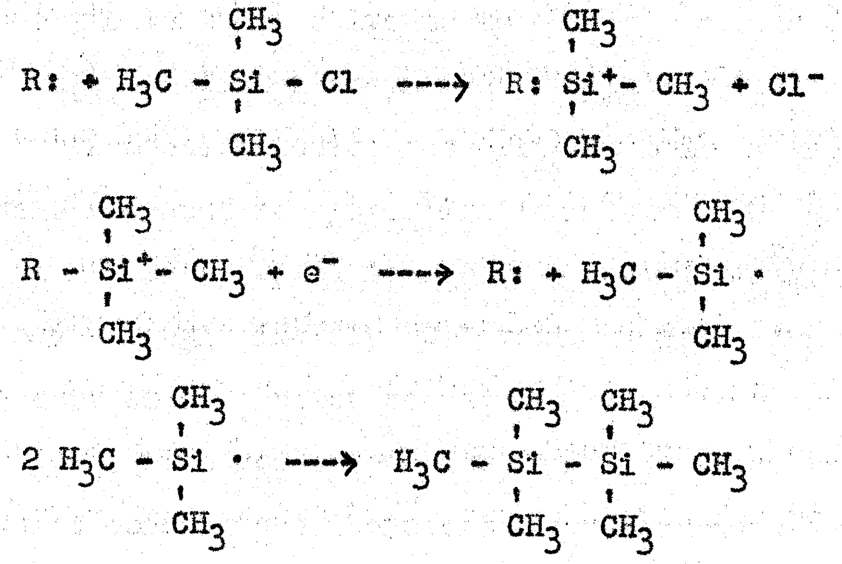
Some difficulty was encountered in the early experiments in preparing pyridine solutions of the organochlorosilanes. A compound, analogous to ammonium chloride, was formed which passed into the air as a smoke making the concentration of the solution uncertain. This problem was solved by the use of two 500 ml. Erlenmeyer flasks equipped with 24/40 female ground glass joints which could be joined by a glass joint in the shape of a V equipped with two 24/40 male ground glass joints. The organochlorosilane was weighed into one of the 500 ml. flasks and a volume of pyridine less than that required for the final solution was put in the other flask. The flasks were then joined with the V joint and the solutions mixed. After vigorous shaking the smoke dissolved in the pyridine and the mixture was transferred to the required volumetric flask and was diluted to volume with the pyridine which was used to rinse the Erlenmeyer flasks.

In the experiments involving pyridine and pyridine-water mixtures as solvents, stock solutions of the organochlorosilanes in pyridine were made up as described above. These stock solutions were usually made up in concentrations of approximately 0.08 molar. When pyridine was used as a solvent, aliquot portions of the stock solution of organochlorosilane in pyridine were added to a 50 ml. volumetric flask, weighed amounts of solid lithium chloride were added and the resulting solution diluted to 50 ml. with pyridine. Two different stock solutions of lithium chloride were prepared in water, one 6 molar and one 5 molar. When pyridine-water mixtures were used with lithium chloride as supporting electrolyte, aliquot portions of the stock solution of organochlorosilane in pyridine were added to a 50 ml. volumetric flask, pyridine added to make 37½ ml. of solution, the required amount of stock solution of lithium chloride to make the desired normality in supporting electrolyte added, and the resulting solution diluted to 50 ml. with water. In the case of pyridine-water mixtures using potassium chloride as supporting electrolyte, aliquot portions of the stock solutions of organochlorosilane in pyridine were added to a 50 ml. volumetric flask, 5 ml. of 3 M. potassium chloride in water plus 20 ml. of water were added and the resulting solution was diluted to 50 ml. with pyridine.

The hydrochloric acid solutions in pyridine-water mixtures using potassium or lithium chloride as supporting electrolyte were prepared in a similar manner. The hydrochloric acid stock solutions were standardized against sodium hydroxide previously standardized against potassium acid phthalate.

Data and Discussion

Since, in working in non-aqueous solvents hydrogen ion is not present unless the solvent itself ionizes, the question arises as to what kind of mechanism of reduction would be expected should the organochlorosilanes be found reducible. It was postulated that such a reduction might involve formation of an addition compound between the solvent and the organochlorosilane. Such an addition compound could conceivably undergo reduction by accepting an electron from the dropping mercury cathode, the addition compound then decomposing to form the solvent again and a free radical, two of which would unite immediately. This could be represented in the following manner using trimethylchlorosilane as an example and letting R: represent the solvent.



$$R{:} + H_3C - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}} - Cl \dashrightarrow R{:}\ \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si^+}} - CH_3 + Cl^-$$

$$R - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si^+}} - CH_3 + e^- \dashrightarrow R{:} + H_3C - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}\ \cdot$$

$$2\ H_3C - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}\ \cdot \dashrightarrow H_3C - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}} - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}} - CH_3$$

The chloride ion would, of course, react with the mercury to form mercurous chloride at the anode. An example of this type of reduction is known in the case of pyridinium ion (22), although this reduction does involve hydrogen ion, which takes the role of the organochlorosilane in the above representation. A reduction of this type would require a solvent such as pyridine, methyl ethyl ketone, acetone, tetrahydrofuran, formamide, or acetonitrile. The nature of this reduction should not prohibit use of other solvents for other mechanisms of reduction also may be possible.

It was found that carbon tetrachloride, benzene and dioxane, although good solvents for the organochlorosilanes, could not be used as solvents for polarographic analysis, since it was impossible to dissolve enough supporting electrolyte in these solvents to obtain a conducting solution of sufficient magnitude for polarographic analysis. Tetrabutylammonium iodide was quite soluble in chloroform. However, repeated recrystallizations from ethyl acetate-ethanol mixtures failed to remove a reduction wave which occurred at approximately -0.3 volts against the quiet pool of mercury in a solution containing only the salt and chloroform. The reduction wave failed to level off into a diffusion current and therefore any reduction of organochlorosilanes occurring beyond -0.3 volts would be obscured.

No reduction was found to occur within the useable span of 0.3 of a volt. Any rubber connections present in contact with chloroform must be eliminated for they cause the solution to be capillary active.

Many of the iodides and bromides are soluble in methyl ethyl ketone but yield solutions which are capillary active and hence are not suitable for use. Zinc chloride and lithium chloride, moderately soluble in methyl ethyl ketone, seem to have their solubility enhanced by the presence of an organochlorosilane and thus are suitable for use. A blank containing only the salt and methyl ethyl ketone did not undergo any reduction until -1.1 volts. Reduction waves were obtained using either lithium chloride or zinc chloride as supporting electrolyte. In the case of methyltrichlorosilane the half-wave potential is approximately -0.6 volts measured against the quiet pool of mercury when the solution is first prepared; but if the solution is allowed to age, the half-wave potential shifts to more positive potentials and a second wave appears with approximately the same half-wave potential as the first wave initially. The solution which is colorless when first prepared becomes yellow with standing, and eventually becomes a deep dark red. Similar results were obtained with dimethyldichlorosilane and trimethylchlorosilane, although the time for development of the red color varied in each case. The same phenomena were observed using acetone as a solvent. These results suggested that time studies be made, the thought being that each organochlorosilane might react differently and therefore offer a possibility for developing an analytical method. All attempts to obtain reproducible results failed. One of the main problems in attempting to standardize conditions was the corrosive effect of the reaction upon the capillary, causing the capillary characteristics to change before any time studies could be completed.

Obviously there is a reaction occurring between the organochlorosilane and the solvent. A reaction has been reported (2) between n-butyltrichlorosilane and acetone which results in a deep red solution, probably containing mesityl oxide and phorone, condensation products of acetone, which are produced by the hydrolytic products of the organochlorosilane. This could explain the reaction occurring between the organochlorosilane and methyl ethyl ketone as well as acetone. This condensation is acid-catalyzed, and the presence of minute amounts of water vapor would be sufficient to hydrolyze the organochlorosilane and cause the condensation. The condensation products are probably reducible due to the presence of carbonyl groups, but no data is reported in the literature for phorone or mesityl oxide.

No reduction wave was obtained using tetrahydrofuran, formamide, acetonitrile, or isoamyl alcohol as solvents. This is especially significant in the case of tetrahydrofuran since an addition compound between tetrahydrofuran and trichlorosilane is known and because tetrahydrofuran is a solvent from which all water can be removed quite readily.

A well defined reduction wave with no maximum was obtained using pyridine as a solvent and lithium chloride as supporting electrolyte. Trimethylchlorosilane gave a half-wave potential of -0.947 volts against the quiet pool of mercury and dimethyldichlorosilane gave a half-wave potential of -0.950 against the quiet pool of mercury. It was found that the diffusion current was proportional to the concentration as predicted by the Ilkovic equation.

On the assumption that the reduction followed the previous postulated mechanism and assuming that the addition compound of pyridine and the organochlorosilane would be stable towards hydrolysis, water-pyridine mixtures were tried and the resulting reduction waves obtained were even better defined than in pyridine alone. Therefore concentration studies were made in water-pyridine mixtures. The pyridine-water ratio was chosen rather arbitrarily. A 75%-25% pyridine to water ratio by volume using lithium chloride as supporting electrolyte was sufficient to bring the resistance through the polarographic cell down to 300 ohms. Similarly, since potassium chloride is less soluble in pyridine, the addition of more water is necessary to bring the resistance across the cell down to a similar value, when using potassium chloride as supporting electrolyte. Therefore a mixture of 50% water and 50% pyridine by volume was used.

The results of the concentration studies using the various organochlorosilanes are presented in tables 1 through 20. The values of i_d/c, in which i_d is the diffusion current in microamperes and c represents the concentration expressed in millimoles per liter, are constant to within 2% indicating that the diffusion current is a linear function of the concentration as predicted by the Ilkovic equation. The half-wave potentials measured against the saturated calomel electrode are constant for any one study and do not shift with concentration. The half-wave potentials for each separate organochlorosilane show remarkable similarity and indicate that the same product is being reduced in all cases. This is not in accord with the previously postulated mechanism, which predicts different reduction potentials for the different organochlorosilanes, since the ease of reduction should be influenced somewhat by the alkyl groups and by the number of chlorine atoms present on the molecule. It also might be expected that a compound such as diphenyldichlorosilane might not form an addition compound with pyridine due to steric hindrance. However, a reduction is obtained in the case of diphenyldichlorosilane.

Based on this evidence it was assumed that the polarographic wave was due to the reduction of pyridinium ion, formed by hydrolysis of the organochlorosilane in the presence of pyridine. Since pyridine is very difficult to dry and the concentration of the organochlorosilane is quite small, it is believed the wave obtained in pyridine was also due to pyridinium ion formed by sufficient water present in the pyridine to cause hydrolysis. It was calculated that 0.02 ml. of water in 50 ml. of pyridine would be more than sufficient to completely hydrolyze the largest sample of organochlorosilane used. To test this hypothesis an attempt was made to make completely anhydrous pyridine and run one of the organochlorosilanes in it. If no water were present the wave would be eliminated. The pyridine in this case was distilled from the addition compound formed with aluminum chloride, removing only the fraction boiling at 113.5°. This was then redistilled from a mixture of barium oxide and silica gel onto lithium chloride previously dried in an oven at 110° for twelve hours. The solutions of the organochlorosilane were made up with a minimum contact with air. The solutions were run polarographically and, contrary to expectations, a reduction wave was obtained that checked the other values previously run. Since the organochlorosilanes are so easily hydrolyzed by moist air, it was thought that they might contain a certain amount of hydrochloric acid. The presence of any hydrochloric acid in the organochlorosilane itself would lead to formation of pyridinium ion when dissolved in pyridine, and would account for the wave obtained.

The possibility of pyridinium ion being reduced was further tested by preparing similar pyridine-water mixtures with various concentrations of hydrochloric acid and using both lithium chloride and potassium chloride as supporting electrolytes. The results of these concentration studies are presented in tables 21 and 22. Again the diffusion current is found to be proportional to the concentration within 2% average deviation. The half-wave potentials measured against the saturated calomel electrode are constant during a series of runs and agree quite well with those of the organochlorosilanes. A summary of the half-wave potentials of the organochlorosilanes together with those obtained for hydrochloric acid is given in table 23. The agreement is better using potassium chloride as supporting electrolyte than using lithium chloride. This can be explained if a variation of the half-wave potential of the system as a function of the ionic strength of the solution is considered (18). Since three different concentrations of lithium chloride were used as supporting electrolyte the ionic strength of the solution was not constant. In the case of the potassium chloride solutions the concentration was maintained at 0.3 molar. Therefore greater accuracy is to be expected in averaging the half-wave potentials of the mixtures using potassium chloride as supporting electrolyte.

Some of the discrepancies are a little larger than can be explained on the basis of ionic strength alone. It was believed that a part of these variations could be due to the effect of the pyridine on the agar plug and subsequently upon the saturated calomel electrode, since the agar plug breaks down upon contact with the pyridine-water solutions after a few days of use and has to be remade. To test this effect three methylchlorosilanes in 75%-25% pyridine-water mixtures using 0.6 molar lithium chloride as supporting electrolyte were run against the quiet pool of mercury as anode and the following results were obtained.

Methyltrichlorosilane	-1.178 v.
Dimethyldichlorosilane	-1.180 v.
Trimethylchlorosilane	<u>-1.188 v.</u>
Avg.	-1.182 ± .004 v.

These results indicate that the effect is small if present at all.

One other factor may be considered in regard to the discrepancies in the half-wave potentials. It is known that the half-wave potential shifts with the pyridine-water ratio.

If the original pyridine from which the stock solutions were prepared were not completely dried but contained varying amounts of water, it would cause some shift in half-wave potential from one stock solution to another. Since pyridine is difficult to dry this factor should be considered as contributing a small part to the discrepancies. The further discussion of the effects of the pyridine-water ratio upon the half-wave potential is reserved for the second part of this thesis.

It is to be noted in table 23 that the half-wave potential is more negative in 50%-50% pyridine-water mixtures than in 75%-25% mixtures. This is merely an effect due to the difference in water content. The value of -1.419 volts for 50%-50% mixtures is in fair agreement with the value of -1.429 volts reported by Tompkins and Schmidt (23) for pyridinium ion in 0.001 M. HCl, 0.1 M. KCl and 0.0125 M. pyridine.

Further evidence for the reduction of pyridinium ion may be obtained by consideration of the diffusion constants. On the basis of the Ilkovic equation

$$id = kncm^{2/3}t^{1/6}$$

the quantity $id/cm^{2/3}t^{1/6}$, known as the diffusion constant, should be constant for any one substance regardless of the capillary used. According to the following equations

1. $R_3SiCl + H_2O \longrightarrow R_3SiOH + HCl$

2. $R_2SiCl_2 + 2H_2O \dashrightarrow R_2Si(OH)_2 + 2HCl$
   $x[R_2Si(OH)_2] \dashrightarrow [R_2SiO]_x + xH_2O$
3. $RSiCl_3 + 3H_2O \dashrightarrow RSi(OH)_3 + 3HCl$
   $x[RSi(OH)_3] \dashrightarrow [RSiO_{1.5}]_x + 1.5xH_2O$

one mole of hydrochloric acid would be expected from hydrolysis of a monochlorosilane, two moles from a dichlorosilane and three moles from a trichlorosilane. If these reactions are quantitative and a diffusion constant is calculated using the concentration of hydrochloric acid formed instead of the concentration of organochlorosilane, a constant value for the diffusion constant should be obtained for all the organochlorosilanes and for hydrochloric acid. The fact that a linear relationship exists between diffusion current and concentration for any one organochlorosilane over its respective concentration range indicates that the hydrolysis is quantitative. The results of calculating the diffusion constant on the basis of hydrochloric acid concentration are presented in tables 24 and 25. The agreement in the case of the 75%-25% mixtures is good to approximately 6% if the two values marked b in the table are excluded from the average. These values are obviously in error, probably because of faulty measurements of the capillary characteristics. The values in 75%-25% mixtures are good to approximately 2.5%. A possible reason for this is that the diffusion constant changes more rapidly with small variations in water

Table 1

Studies of trimethylchlorosilane in 75%-25% pyridine-water mixtures with 0.125 M. LiCl as supporting electrolyte.

m = 1.969 mg./sec.; t = 3.2 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μamps.	i_d/c
0.9600	-	1.86	1.94
0.9600	-	1.95	2.04
4.800	-1.375	9.30	1.94
9.600	-1.380	19.2	2.00
14.30	-1.375	28.0	1.95
23.90	-1.378	49.5	2.07
28.70	-1.385	56.8	1.98
38.20	-1.375	74.7	1.98
47.80	-1.385	94.4	1.98
Avg.	-1.379 ± .004		1.99
% Avg. Dev.	0.29		1.73

Table 2

Studies of trimethylchlorosilane in 75%-25% pyridine-water mixtures with 0.6 M. LiCl as supporting electrolyte.

m = 1.656 mg./sec.; t = 3.3 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
10.85	-1.340	15.0	1.38
21.70	-1.337	29.4	1.36
32.50	-1.338	45.7	1.40
43.40	-1.350	62.0	1.43
43.40	-1.338	60.0	1.38
Avg.	-1.340 ± .003		1.39
% Avg. Dev.	0.22		1.43

Table 3

Studies of trimethylchlorosilane in 75%-25% pyridine-water mixtures with 0.6 M. LiCl as supporting electrolyte.

m = 1.094 mg./sec.; t = 3.7 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
7.317	-1.340	-	-
10.98	-1.345	-	-
14.63	-1.350	16.2	1.11
21.95	-1.350	24.8	1.13
29.26	-1.350	33.4	1.14
36.59	-1.344	40.8	1.12
Avg.	-1.347 ± .003		1.13
% Avg. Dev.	0.22		0.88

Table 4

Studies of dimethyldichlorosilane in 75%-25% pyridine-water mixtures with 0.6 M. LiCl as supporting electrolyte.

m = 1.094 mg./sec.; t = 3.7 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
7.875	-1.327	18.6	2.36
11.81	-1.332	27.7	2.43
15.75	-1.335	37.5	2.38
23.62	-1.340	57.2	2.42
31.50	-1.344	77.2	2.45
39.37	-1.344	95.1	2.41
Avg.	-1.337 ± .006		2.41
% Avg. Dev.	0.45		1.03

Table 5

Studies of dimethyldichlorosilane in 75%-25% pyridine-water mixtures with 0.6 M. LiCl as supporting electrolyte.

m = 1.656 mg./sec.; t = 3.3 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
9.350	-1.344	31.0	3.32
18.70	-1.352	62.4	3.34
28.04	-1.357	92.4	3.29
37.39	-1.366	127.6	3.41
46.74	-1.372	156.0	3.34
Avg.	-1.358 ± .009		3.34
% Avg. Dev.	0.66		0.59

Table 6

Studies of methyltrichlorosilane in 75%-25% pyridine-water mixtures with 0.6 M. LiCl as supporting electrolyte.

m = 1.650 mg./sec.; t = 3.3 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μamps.	i_d/c
4.836	-1.345	22.6	4.67
9.672	-1.342	46.0	4.75
14.51	-1.345	70.4	4.85
19.34	-1.355	90.0	4.65
24.18	-1.362	116.8	4.83
Avg.	-1.350 ± .007		4.75
% Avg. Dev.	0.52		1.52

Table 7

Studies of triethylchlorosilane in 75%-25% pyridine-water mixtures with 1.25 M. LiCl as supporting electrolyte.

m = 1.094 mg./sec.; t=3.7 sec

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μamps.	i_d/c
7.850	-1.340	9.4	1.19
10.46	-1.350	13.0	1.24
15.69	-1.350	19.1	1.22
20.92	-1.340	26.2	1.25
26.15	-1.340	31.5	1.20
Avg.	-1.344 ± .005		1.22
% Avg. Dev.	0.37		1.64

Table 8

Studies of diethyldichlorosilane in 75%-25% pyridine-water mixtures with 0.6 M. LiCl as supporting electrolyte.

m = 1.288mg./sec.; t = 3.7 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
3.400	-1.361	11.3	3.32
6.800	-1.366	22.3	3.28
10.20	-1.360	33.2	3.25
13.60	-1.365	43.4	3.19
17.00	-1.342	53.4	3.14
Avg.	-1.359 ± .007		3.24
% Avg. Dev.	0.52		1.73

Table 9

Studies of ethyltrichlorosilane in 75%-25% pyridine-water mixtures with 1.25 M. LiCl as supporting electrolyte.

m = 1.969 mg./sec.; t = 3.2 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
2.850	-1.355	13.6	4.77
5.690	-1.342	25.6	4.50
8.550	-1.342	40.1	4.69
11.40	-1.348	54.2	4.76
14.20	-1.344	66.6	4.66
17.10	-1.346	77.6	4.54
22.70	-1.345	103.0	4.54
Avg.	-1.346 ± .003		4.64
% Avg. Dev.	0.22		2.03

Table 10

Studies of diphenyldichlorosilane in 75%-25% pyridine-water mixtures with 1.25 M. LiCl as supporting electrolyte.

$m = 1.969$ mg./sec.; $t = 3.2$ sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
3.264	-1.331	9.95	3.05
4.896	-1.328	14.7	2.99
6.528	-1.318	19.0	2.90
8.160	-1.316	24.8	3.04
9.792	-1.320	30.0	3.06
13.06	-1.322	40.8	3.12
16.32	-1.320	50.4	3.08
Avg.	-1.322 ± .004		3.03
% Avg. Dev.	0.30		1.74

Table 11

Studies of phenyltrichlorosilane in 75%-25% pyridine-water mixtures with 1.25 M. LiCl as supporting electrolyte.

$m = 1.656$ mg./sec.; $t = 3.3$ sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
3.400	-1.325	10.3	3.03
13.40	-1.328	40.2	3.00
20.10	-1.328	60.0	2.99
26.80	-1.330	79.2	2.96
33.50	-1.335	96.8	2.89
Avg.	-1.329 ± .003		2.97
% Avg. Dev.	0.23		1.35

Table 12

Studies of vinyltrichlorosilane in 75%-25% pyridine-water mixtures with 0.6 M. LiCl as supporting electrolyte.

m = 1.094 mg./sec.; t = 3.7 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	id μ amps.	i_d/c
4.800	-1.329	17.5	3.65
9.600	-1.327	34.4	3.58
14.40	-1.330	50.1	3.48
19.20	-1.335	67.2	3.50
24.00	-1.334	85.6	3.56
Avg.	-1.331 ± .003		3.55
% Avg. Dev.	0.23		1.46

Table 13

Studies of trimethylchlorosilane in 50%-50% pyridine-water mixtures with 0.3 M. KCl as supporting electrolyte.

m = 1.656 mg./sec.; t = 3.8 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	id μ amps.	i_d/c
10.85	-1.405	19.6	1.81
21.70	-1.403	39.6	1.82
32.55	-1.406	60.8	1.87
43.40	-1.405	82.2	1.89
54.25	-1.410	98.4	1.81
Avg.	-1.406 ± .002		1.84
% Avg. Dev.	0.14		1.74

Table 14

Studies of dimethyldichlorosilane in 50%-50% pyridine-water mixtures with 0.3 M. KCl as supporting electrolyte.

m = 1.094 mg./sec.; t = 4.3 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
7.875	-1.395	25.4	3.22
15.75	-1.393	49.8	3.16
23.62	-1.395	77.4	3.28
31.50	-1.405	103.2	3.27
39.37	-1.405	127.2	3.22
Avg.	-1.398 ± .005		3.23
% Avg. Dev.	0.36		1.11

Table 15

Studies of methyltrichlorosilane in 50%-50% pyridine-water mixtures with 0.3 M. KCl as supporting electrolyte.

m = 1.656 mg./sec.; t = 3.8

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
4.836	-1.406	28.8	5.96
9.672	-1.406	59.2	6.12
14.51	-1.410	91.2	6.28
19.34	-1.409	117.6	6.08
24.18	-1.420	151.2	6.25
Avg.	-1.410 ± .004		6.14
% Avg. Dev.	0.28		1.66

Table 16

Studies of triethylchlorosilane in 50%-50% pyridine-water mixtures with 0.3 M. KCl as supporting electrolyte.

m = 1.656 mg./sec.; t = 3.8 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
5.230	-1.410	9.9	1.89
7.850	-1.408	15.6	1.99
10.46	-1.407	21.1	2.01
20.92	-1.408	42.0	2.01
26.15	-1.408	53.3	2.04
Avg.	-1.408 ± .001		1.99
% Avg. Dev.	0.07		1.91

Table 17

Studies of diethyldichlorosilane in 50%-50% pyridine-water mixtures with 0.3 M. KCl as supporting electrolyte.

m = 1.656 mg./sec.; t = 3.8 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
6.800	-1.393	28.5	4.19
10.20	-1.398	44.1	4.32
13.60	-1.405	59.2	4.35
17.00	-1.402	71.4	4.20
Avg.	-1.400 ± .004		4.27
% Avg. Dev.	0.29		1.64

Table 18

Studies of ethyltrichlorosilane in 50%-50% pyridine-water mixtures with 0.3 M. KCl as supporting electrolyte.

$m = 1.094$ mg./sec.; $t = 4.3$ sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
4.720	-1.425	22.5	4.77
9.440	-1.428	46.2	4.89
14.16	-1.425	68.0	4.80
18.88	-1.428	90.6	4.79
28.32	-1.440	140.0	4.94
Avg.	-1.429 ± .005		4.84
% Avg. Dev.	0.35		1.60

Table 19

Studies of phenyltrichlorosilane in 50%-50% pyridine-water mixtures with 0.3 M KCl as supporting electrolyte.

$m = 1.094$ mg./sec.; $t = 4.3$ sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
3.400	-1.408	15.8	4.63
6.700	-1.408	30.9	4.61
13.40	-1.408	62.7	4.68
20.10	-1.415	95.4	4.78
26.80	-1.423	129.0	4.81
Avg.	-1.412 ± .005		4.70
% Avg. Dev.	0.35		1.57

Table 20

Studies of vinyltrichlorosilane in 50%-50% pyridine-water mixtures with 0.3 M. KCl as supporting electrolyte.

m = 1.094 mg./sec.; t = 4.3 sec.

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
4.800	-1.398	21.7	4.52
9.600	-1.395	45.2	4.71
14.40	-1.395	68.4	4.89
19.20	-1.398	90.6	4.72
24.00	-1.405	112.0	4.70
Avg.	-1.398 ± .003		4.70
% Avg. Dev.	0.21		1.83

Table 21

Studies of hydrochloric acid in 75%-25% pyridine-water mixtures with 0.6 M. LiCl as supporting electrolyte.

m = 1.161 mg./sec.; t = 3.8

millimolar conc.	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
6.680	-1.364	8.92	1.33
9.970	-1.372	13.7	1.37
20.89	-1.366	27.6	1.32
56.82	-1.359	77.6	1.35
78.65	-1.348	110.4	1.41
97.86	-1.363	132.0	1.35
Avg.	-1.362 ± .006		1.36
% Avg. Dev.	0.44		1.83

Table 22

Studies of hydrochloric acid in 50%-50% pyridine-water mixtures with 0.3 M. KCl as supporting electrolyte.

$m = 1.161$ mg./sec.; $t = 4.5$ sec.

millimolar conc.	pH	$E_{\frac{1}{2}}$ volts	i_d μ amps.	i_d/c
5.980	7.7	-1.423	10.32	1.73
6.680	7.7	-1.426	11.84	1.77
7.976	7.5	-1.421	14.10	1.78
9.970	-	-1.421	17.25	1.73
20.89	-	-1.420	37.20	1.78
33.44	6.9	-1.414	61.84	1.85
45.44	6.8	-1.418	84.30	1.86
56.80	-	-1.412	105.0	1.85
68.16	6.6	-1.414	125.0	1.85
78.65	6.6	-1.413	145.0	1.85
90.88	6.4	-1.412	179.0	1.79
117.4	6.4	-1.426	209.0	1.78
125.8	6.4	-1.419	227.3	1.81
137.0	6.4	-1.432	246.8	1.80
Avg.		-1.419 ± .005		1.80
% Avg. Dev.		0.35		2.02

Table 23

Summary of $E_{\frac{1}{2}}$'s for organochlorosilanes

Organochlorosilane	$E_{\frac{1}{2}}$ in 75%-25% pyridine-water	$E_{\frac{1}{2}}$ in 50%-50% pyridine-water
Trimethylchlorosilane	-1.379	-1.406
	-1.340	-1.415
	-1.347	-
Dimethyldichlorosilane	-1.337	-1.398
	-1.358	-1.420
Methyltrichlorosilane	-1.350	-1.410
Triethylchlorosilane	-1.344	-1.408
Diethyldichlorosilane	-1.359	-1.400
Ethyltrichlorosilane	-1.346	-1.429
Diphenyldichlorosilane	-1.322	-
Phenyltrichlorosilane	-1.329	-1.412
Vinyltrichlorosilane	-1.331	-1.398
Avg.	-1.346 ± .012	-1.410 ± .008
Hydrochloric acid	-1.362 ± .006	-1.419 ± .005

Table 24

Summary of diffusion constants for organochlorosilanes in 75%-25% pyridine-water mixtures with LiCl as S. E.

Organochlorosilane	$m^{2/3}t^{1/6}$ $mg.^{2/3}sec.^{-\frac{1}{2}}$	$\frac{i_d}{cm^{2/3}t^{1/6}}$	$\frac{i_d}{ncm^{2/3}t^{1/6}}$[a]
Trimethylchlorosilane	1.907	1.04	1.04[b]
	1.708	0.81	0.81
	1.321	0.86	0.86
Dimethyldichlorosilane	1.321	1.82	0.91
	1.708	1.96	0.98
Methyltrichlorosilane	1.708	2.78	0.93
Triethylchlorosilane	1.321	0.92	0.92
Diethyldichlorosilane	1.472	2.20	1.10[b]
Ethyltrichlorosilane	1.907	2.43	0.81
Diphenyldichlorosilane	1.708	1.71	0.86
Phenyltrichlorosilane	1.321	2.25	0.75
Vinyltrichlorosilane	1.321	2.69	0.89
Avg.			0.87
% Avg. Dev.			5.7
Hydrochloric acid	1.380	0.99	0.99
	1.813	0.98	0.98[c]

a. Product nc is equal to millimolar concentration of hydrochloric acid formed on the basis of complete hydrolysis.

b. These values excluded in calculating average.

c. These values abstracted from Part II of this thesis.

Table 25

Summary of diffusion constants for organochlorosilanes in 50%-50% pyridine-water mixtures with KCl as S. E.

Organochlorosilane	$m^{2/3}t^{1/6}$ $mg.^{2/3}sec.^{-\frac{1}{2}}$	$\frac{i_d}{cm^{2/3}t^{1/6}}$	$\frac{i_d}{ncm^{2/3}t^{1/6}}$ [a]
Trimethylchlorosilane	1.749	1.05	1.05
Dimethyldichlorosilane	1.354	2.39	1.19
Methyltrichlorosilane	1.749	3.51	1.17
Triethylchlorosilane	1.749	1.14	1.14
Diethyldichlorosilane	1.749	2.44	1.22
Ethyltrichlorosilane	1.354	3.57	1.19
Phenyltrichlorosilane	1.354	3.47	1.16
Vinyltrichlorosilane	1.354	3.47	1.16
Avg.			1.16
% Avg. Dev.			2.48
Hydrochloric acid	1.419	1.27	1.27
	1.815	1.13	1.13[c]

a. Product nc is equal to millimolar concentration of hydrochloric acid formed on the basis of complete hydrolysis.

c. These values abstracted from Part II of this thesis.

content in the region of 25% water by volume than in the region of 50% water by volume, as will be shown in part II of this thesis. Another reason for error is the lack of temperature control during the actual polarographic measurement. Although temperature changes have a negligible effect on half-wave potentials, they do have a large effect on the diffusion current, approximately 1.5% to 2% increase per degree increase of temperature.

The agreement is especially good when the impurity of the organochlorosilanes is considered. The purity of the organochlorosilanes ranges from 90% to 99% and the impurities in many cases consist of other chlorosilanes. For example, a trichlorosilane containing some monochlorosilane as impurity would tend to give low results. Low results are experienced with all the trichlorosilanes using lithium chloride as supporting electrolyte. A dichlorosilane would give high or low results depending on whether or not the impurity was a trichlorosilane or a monochlorosilane. Similar arguments could be made for the monochlorosilanes. Therefore considering all the errors it is thought that the agreement is remarkably good and that the evidence is overwhelmingly in favor of a reduction of pyridinium ion.

Plots of log $i/(i_d - i)$ versus E were made for waves of hydrochloric acid using potassium chloride as supporting electrolyte, and a straight line resulted with a slope of

-0.055 indicating a reversible reduction involving one electron. Similar plots for the organochlorosilanes also indicated a reversible reduction involving one electron. Using 75%-25% pyridine-water mixtures the reduction is not as reversible, but indications are that it is also a one electron reduction.

This reduction now can be simply adapted for analysis of the organochlorosilanes in terms of chloride content, since the diffusion current is proportional to concentration within 2%. All that is necessary is to make a calibration curve for known solutions of hydrochloric acid in some definite pyridine-water mixture, plotting diffusion current versus concentration of chloride. Then by running an unknown organochlorosilane under the same conditions and comparing its diffusion current with the calibration curve, the percentage of chloride can be obtained. The concentration of the organochlorosilane must fall in the range of 0.15 molar to 6×10^{-3} molar. It may be possible to analyze smaller concentrations of the organochlorosilanes by increasing the proportion of water in the pyridine-water mixtures since the diffusion current is greater in solutions of increased water content. This method will not permit the determination of one organochlorosilane in the presence of others. However, in a mixture of two known organochlorosilanes it is possible to determine the percentage of each constituent, but a mixture of any more than two is impossible to analyze in this way.

Summary

Studies have been made in acetone, methyl ethyl ketone, tetrahydrofuran, formamide, acetonitrile, isoamyl alcohol, pyridine and pyridine-water mixtures in an attempt to find a polarographic method of analysis for organochlorosilanes. It was definitely established that the organochlorosilanes are not reducible at the dropping mercury electrode in any of the solvents examined. However, they could be hydrolyzed in pyridine-water mixtures and the resulting pyridinium ion could be polarographically reduced. This reduction was found to give a diffusion current proportional to the concentration of the organochlorosilane.

A method is described for the determination of organochlorosilane in terms of chloride content, covering a concentration range of 0.15 molar to 6 x 10^{-3} molar. This method fails in analyzing for the presence of one organochlorosilane in a mixture of several.

PART II

POLAROGRAPHIC INVESTIGATIONS IN PYRIDINE

Introduction

In the work reported in Part I it was found that pyridine-water mixtures and pyridine itself could be used as solvents for polarographic investigations. Two different ratios of pyridine to water by volume were used in the previous investigation and some differences were noted in the half-wave potentials and in the diffusion constants. This was to be expected. It was thought that a knowledge of the variation of these properties as a function of the water to pyridine ratio over a wide range in ratios would be of value in interpreting some of the discrepancies that were noted in Part I and also be of some theoretical interest. The effects of varying the proportions of alcohol and water upon the half-wave potentials and diffusion constants of strontium and barium have been studied by Zlotowski and Kolthoff (24) and some interesting results obtained. It would be of interest to determine whether these results are characteristic of alcohol-water mixtures or whether a parallelism exists in pyridine-water mixtures.

Due to the current interest in non-aqueous solvents in various fields of analytical chemistry and to the relatively small number of references to the use of non-aqueous solvents as media for polarographic investigations (6,7,8,9,10,11,12,13,14,15,16,17,24,25,26,), it was thought that a study of the reduction of some inorganic cations in pyridine might be of some practical as well as theoretical interest.

In aqueous media it is impossible to obtain two separate waves for two cations whose half-wave potentials are not more than 200 millivolts apart. A separation is usually accomplished by forming complexes with the cations which differ in their comparative ease of reduction as compared to the simple hydrated cations. Since pyridine is known to form complexes with many of the heavy metals in aqueous solution, use of it as a solvent in polarographic reductions might be effective in analytical separations impossible in water. It might also be of practical interest to use pyridine in mixtures with water for reductions of organic substances which are difficultly soluble in water alone.

It was thought that the effect of pyridine on half-wave potentials and diffusion constants would be of some theoretical interest. Although some attempt has been made to compare potentials obtained in non-aqueous media with potentials obtained in water through the use of the chloranil electrode in the case of acetic acid (9) and by direct use of the saturated calomel electrode connected to the quiet pool of mercury by a salt bridge in the case of fused salts (26), it is believed that it is unsatisfactory to attempt to make this correlation. A more satisfactory method is to consider the solvent as an entirely independent medium and obtain a table of half-wave potentials for the specific medium. If this were done for each medium the ease of reduction in each medium could then be compared, thus furnishing the basis for a qualitative comparison from one solvent to another. In order to compare half-wave potentials in one solvent it is necessary that an anode be used which will retain a constant potential such that the differences in half-wave potentials which are obtained are due only to the cation reduction involved and not to the anodic process taking place. Such an electrode is the quiet pool of mercury which remains depolarized and retains a constant potential, provided that its area is at least one square centimeter and provided that the solution contains halide ions or other ions that form insoluble salts or complex ions with mercury (27). Since half-wave potentials are also functions of ionic strength and affected somewhat by the type of supporting electrolyte, it is necessary for means of comparison to use the same supporting electrolyte and to keep its concentration constant. Because lithium chloride is quite soluble in pyridine and because it satisfies the requirement for an anode with constant potential, it was chosen as supporting electrolyte. Lithium nitrate was used in some cases when lithium chloride was not feasible because of maxima which could not be suppressed. Half-wave potentials obtained and tabulated for aqueous media are usually in varied supporting electrolytes and very few have been listed using lithium chloride as supporting electrolyte. The concentration of supporting electrolyte generally used is either 1 molar or 0.1 molar. To facilitate a comparison of ease of reduction in the two solvents, many of the cations were run with identical concentrations and identical supporting electrolyte in water against the quiet pool of mercury as anode. In water in the presence of large amounts of chloride ion the quiet pool of mercury functions as a calomel electrode.

In general diffusion constants have been found to be smaller in non-aqueous solvents and, in the case of some solvents, the diffusion current has been found to be inversely proportional to the square root of the viscosity (16). Any change in the diffusion current constant in going from one solvent to another will be due primarily to a change in the diffusion coefficient. Since the diffusion coefficients are affected slightly by the supporting electrolyte, a comparison of diffusion constants between water and pyridine would also require that the type and concentration of supporting electrolyte be maintained constant, and thus any difference in diffusion constant is due to the effect of the solvent alone.

It is to be expected that pyridine would offer some possibilities as a solvent for polarographic investigations. It has a dielectric constant of approximately 12.5 which indicates that it should have fairly good solvent properties. Many salts are known to be quite soluble in pyridine. Although pyridine is polarographically reducible, giving two waves in unbuffered media at about -1.5 volts and -1.7 volts against the saturated calomel electrode (23), the reductions are both dependent upon hydrogen ion. Theoretically if no hydrogen ion were present no wave would be observed. Because these reductions occur at very negative potentials and since they are hydrogen-ion dependent, it was expected that pyridine would not undergo any reduction over a wide potential span and thus be suitable as a polarographic solvent. Probably the chief disadvantage in the use of pyridine as a solvent is the difficulty in making it anhydrous. Although it is not claimed that the pyridine is anhydrous in the following investigation, it is believed that the pyridine does not contain more than 1% water by volume.

Experimental

The equipment used for this investigation was identical with that described in Part I of this thesis, with the exception of the polarographic cell used for all measurements against the quiet pool of mercury as anode. This cell, made in this laboratory, was cylindrically shaped, four centimeters in diameter, six centimeters high, with a stopcock sealed into the bottom of the cell to permit drainage of the cell. A tube was sealed into the side of the vessel for the purpose of bubbling nitrogen through the solution and a platinum wire was sealed into the bottom of the cell making contact with the quiet pool of mercury and a tube of mercury sealed to the outside of the vessel. Two female joints, a 12/20 and a 7/25, were sealed to the top of the cylinder for the purpose of introduction of the capillary into the cell and for the purpose of bubbling nitrogen over the solution during the course of a run. For the few runs made against the saturated calomel electrode the H-cell previously described was used. The capillaries were 6 to 10 inch lengths of Corning Glass Works marine barometer tubing and the characteristics were determined as described in Part I. The solutions were brought to equilibrium in a constant temperature water bath held constant at $25^\circ \pm .02^\circ$ and were thermostatted in a second bath at the same temperature during the polarographic determination.

The solutions were bubbled with nitrogen which had previously been bubbled through alkaline pyrogallol, sulfuric acid, and pyridine, for ten minutes to rid them of oxygen previous to the run, and nitrogen was bubbled over the solution during the run. The nitrogen was obtained from the Ohio Chemical and Surgical Equipment Company. The curves were calculated as described in Part I of this thesis unless otherwise stated. The mercury was purified as previously described.

The lead chloride, lithium chloride, zinc chloride, antimony trichloride, lithium nitrate, bismuth trichloride, ferric chloride hexahydrate, chromic chloride hexahydrate, uranyl nitrate hexahydrate, nickel chloride hexahydrate, cobalt nitrate hexahydrate, mercurous chloride and chromium nitrate nonahydrate were all Baker's Analyzed C. P. chemicals. The cupric chloride and cobaltous chloride hexahydrate were Baker and Adamson reagents. The cadmium chloride, silver nitrate, and stannous chloride dihydrate were Mallinckrodt analytical reagents. The ferrous chloride tetrahydrate was a Merck product. The above hydrated salts were all used as received but those that were not hydrated were dried in an oven at 110 degrees for from one to six hours depending upon the hygroscopicity of the salt. Lithium chloride, for example, was dried for six hours. In some cases the hydrated salts were dehydrated when this was possible without decomposition. The nickel chloride hexahydrate was dehydrated by drying for six hours in an oven at 110° and the resulting salt was yellow in color and crystalline. An attempt was made to dehydrate the cobaltous chloride hexahydrate. If it was dried for three hours at 110° in an oven, the resulting blue crystals were obtained with some decomposition. If the salt was dried for six hours a dark blue tarry mass resulted.

Stock solutions of approximately 2 molar lithium chloride in pyridine and approximately 1.7 molar in lithium nitrate were prepared as needed by weighing the dried salt in a beaker on a platform balance, transferring it to a volumetric flask and adding the pyridine. In the case of the lithium chloride it was usually necessary to allow the solution to stand for two or three days before it would completely dissolve. Stock solutions of the various metal salts were prepared by weighing out the salt by difference on an analytical balance into a volumetric flask and dissolving in pyridine. Solutions were heated when necessary to hasten the solution. Solutions for polarographic analysis were made up by pipetting the required amounts of stock solution of the cation for analysis into a 50 ml. volumetric flask. The resulting solution was then diluted to 25 ml. with pyridine by the use of pipettes. The pipettes were of 10 ml., 5 ml., 2 ml., and 1 ml. volumes and were calibrated by the National Bureau of Standards. All the solutions were made up using these four pipettes. The hydrochloric acid solutions were prepared from Baker and Adamson hydrochloric acid and were standardized against sodium carbonate using methyl orange as an indicator.

All the gums that were used in the search for maximum suppressors were made up in pyridine as saturated solutions, since they were all difficultly soluble with the exception of gum gambogi, which seemed to be a little more soluble than the rest. A great many surface active agents were obtained from the Atlas Powder Company and tried as maximum suppressors. Many of the more common dyes which are quite soluble in pyridine were also tried as maximum suppressors. The gum tragacanth and gum gambogi were products of the J. L. Hopkins Company. The titan yellow was obtained from the Eastman Kodak Chemical Company. The Triton W-30 was a Rohm and Haas product. When a maximum suppressor was found that was effective it was usually found that, contrary to experiences in aqueous media, quite a large concentration of the suppressant was necessary. Therefore, the following procedure was usually adopted. The stock solution of supporting electrolyte to be used was saturated with the maximum suppressor to be used and 10 ml. of this stock solution was added to a 50 ml. volumetric flask. Aliquot portions of the stock solution of the salt to be analyzed were added and the resulting solution was diluted to 25 ml. with the pipettes previously mentioned.

Data and Discussion

Pyridinium Ion in Pyridine-Water Mixtures

Studies were made on the effect of water on the reduction of pyridinium ion in pyridine using lithium chloride as supporting electrolyte. The concentration of the hydrochloric acid was kept constant at 4.408 millimolar in all the solutions and the concentration of the lithium chloride was 0.8 molar in all the runs. The concentration of the supporting electrolyte was therefore approximately 200 times greater than that of the reducible ion. This is more than sufficient to make the diffusion current completely diffusion controlled.

The effects of the variation of the pyridine to water ratio upon the half-wave potential of pyridinium ion are presented in tables 26 and 27 and are graphically presented in figures 1 and 2. All the half-wave potentials have been corrected for resistance by using the minimum resistance obtained with the conductivity bridge. This minimal resistance was multiplied by the current at the half-wave potential and the result subtracted from the value of the half-wave potential obtained from the wave. The use of the minimal resistance is not altogether correct, since an average resistance should be used which, according to an equation derived by Ilkovic (28) is equal to 4/3 the minimal resistance. However, if the value of 4/3 the minimal

Table 26

Effect of pyridine-water ratio on half-wave potential measured against the quiet pool of mercury.

% water by volume	R ohms	uncorrected $E_{\frac{1}{2}}$, volts	corrected $E_{\frac{1}{2}}$, volts
4	1250	-0.965	-0.960
6	850	-0.983	-0.980
8	700	-1.007	-1.004
10	600	-1.023	-1.021
20	400	-1.123	-1.121
30	300	-1.208	-1.207
40	200	-1.265	-1.264
50	170	-1.313	-1.312

Table 27

Effect of pyridine-water ratio on half-wave potential measured against the saturated calomel electrode.

% water by volume	R ohms	uncorrected $E_{\frac{1}{2}}$, volts	corrected $E_{\frac{1}{2}}$, volts
4	3000	-1.317	-1.309
6	1850	-1.314	-1.309
8	1400	-1.317	-1.313
10	1200	-1.323	-1.320
20	780	-1.361	-1.359
30	475	-1.388	-1.386
40	375	-1.416	-1.414
50	225	-1.433	-1.432

Fig. 1

Effect of pyridine-water ratio on $E_{1/2}$

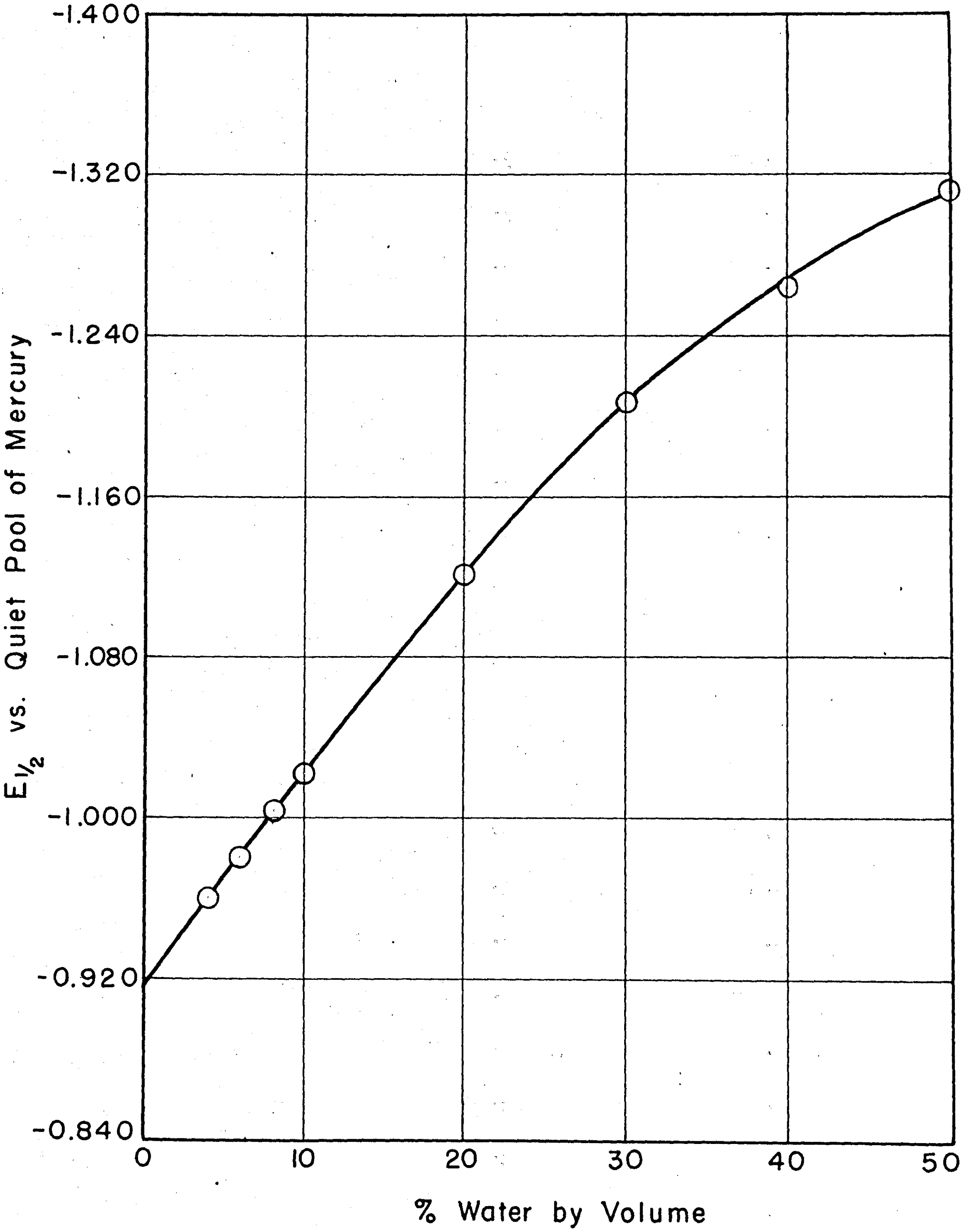
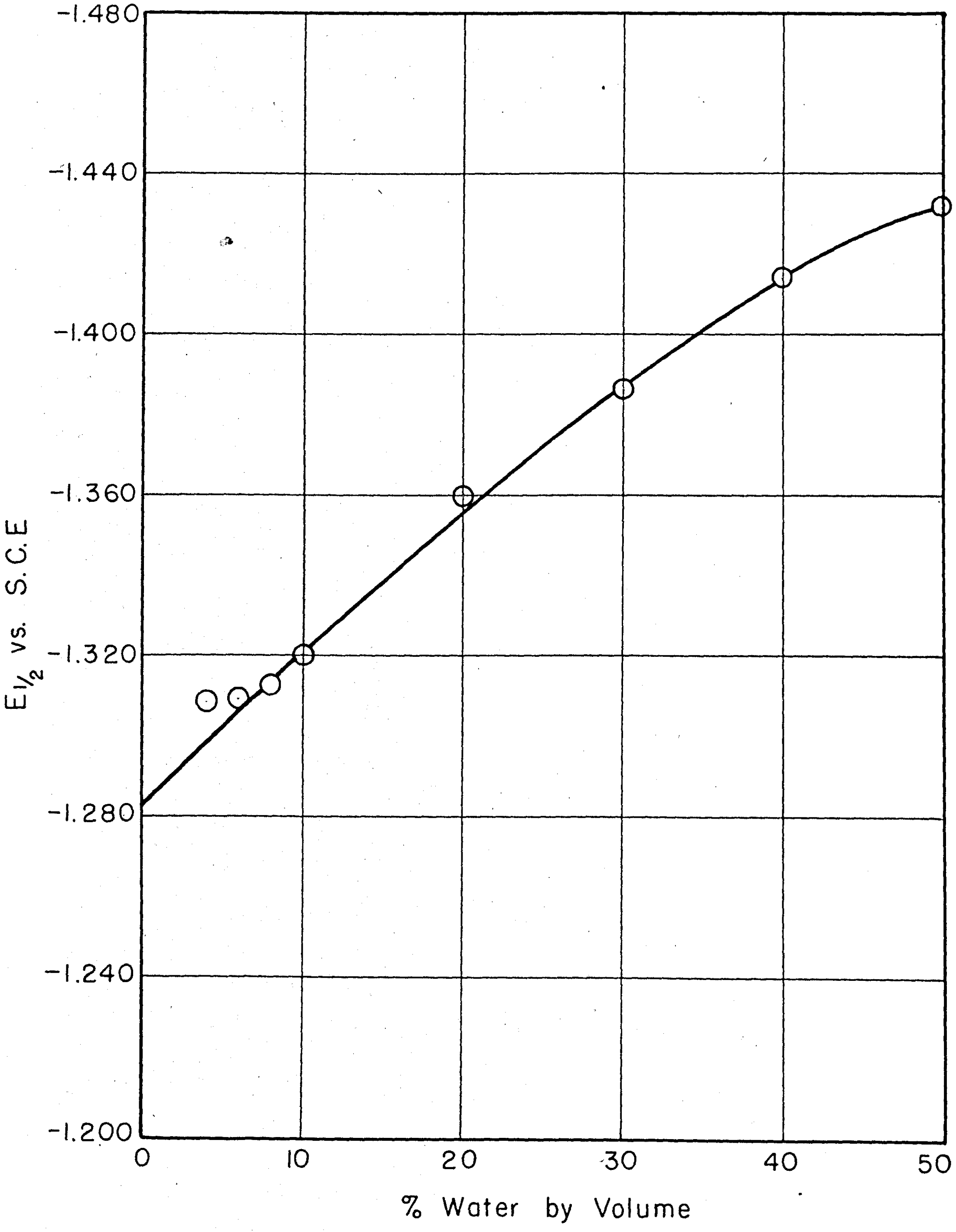


Fig. 2

Effect of pyridine-water ratio on $E_{1/2}$



resistance is set on the conductivity bridge, no fluctuation on the cathode ray visual null indicator is shown. For this reason the minimal value of the resistance was used. From the tables and graphs mentioned previously, it is observed that the half-wave potential shifts to more positive potentials with increasing pyridine concentrations. The relationship is linear up to approximately 20% water concentration but beyond this the rate of change of potential with increasing water concentration is not nearly as rapid. Although the curves are of much the same shape using either the quiet pool of mercury or the saturated calomel electrode as anode, the change of potential with increasing water concentration is greater using the quiet pool of mercury as anode. This is very likely due to a variation in the inconsistency of constant potential of the two anodes and shows immediately why it is impossible to compare half-wave potentials obtained in two different solvents. It also illustrates that any values of potentials obtained in solutions containing a large proportion of non-aqueous solvent, measured against the saturated calomel electrode, are very likely in error due to an unknown liquid junction potential. It is also noted that a deviation occurs from the curve at low concentrations of water, in the case of values measured against the saturated calomel electrode. This also indicates the unsatisfactory use of a saturated calomel electrode in high concentrations of non-aqueous solvents in water. The fact that there is not a linear relationship between potential and volume concentration of water is not in complete agreement with the data obtained by Zlotowski and Kolthoff (24) who found a linear relationship over the whole concentration range, in the case of reduction of strontium and barium in alcohol and water mixtures. This is not serious since alcohol and water are very similar solvents whereas water and pyridine are quite dissimilar. The extrapolated value of the half-wave potential of pyridinium ion against the quiet pool of mercury is -0.918 volts and -1.283 volts versus the saturated calomel electrode.

In table 28 the effect of the pyridine-water ratio upon the diffusion current is presented. The same data are presented graphically in figures 3 and 4. It is known that any changes in diffusion current resulting from a change in solvent are due to changes in the diffusion coefficient of the ion and changes in the drop time. However, since the drop time appears in the Ilkovic equation only to the one sixth power, changes in it can usually be neglected. That this effect can usually be neglected is illustrated by the values of $m^{2/3}t^{1/6}$ listed in the table. The average deviation of all the values amounts to less than 0.2%. It is noted from the figures that the diffusion current and the diffusion current constant attain a minimum value in

Table 28

Effect of pyridine-water ratio on diffusion current

% water by volume	$m^{2/3}t^{1/6}$ mg.$^{2/3}$sec.$^{-\frac{1}{2}}$	t sec.	i_d μ amps.	$\frac{i_d}{cm^{2/3}t^{1/6}}$
4	1.820	4.37	7.85	0.98
6	1.819	4.35	7.50	0.94
8	1.816	4.32	7.23	0.90
10	1.820	4.37	6.84	0.85
20	1.813	4.27	7.80	0.98
30	1.809	4.22	8.58	1.08
40	1.816	4.32	9.15	1.14
50	1.815	4.30	9.06	1.13

Fig. 3

Effect of pyridine-water ratio on diffusion current

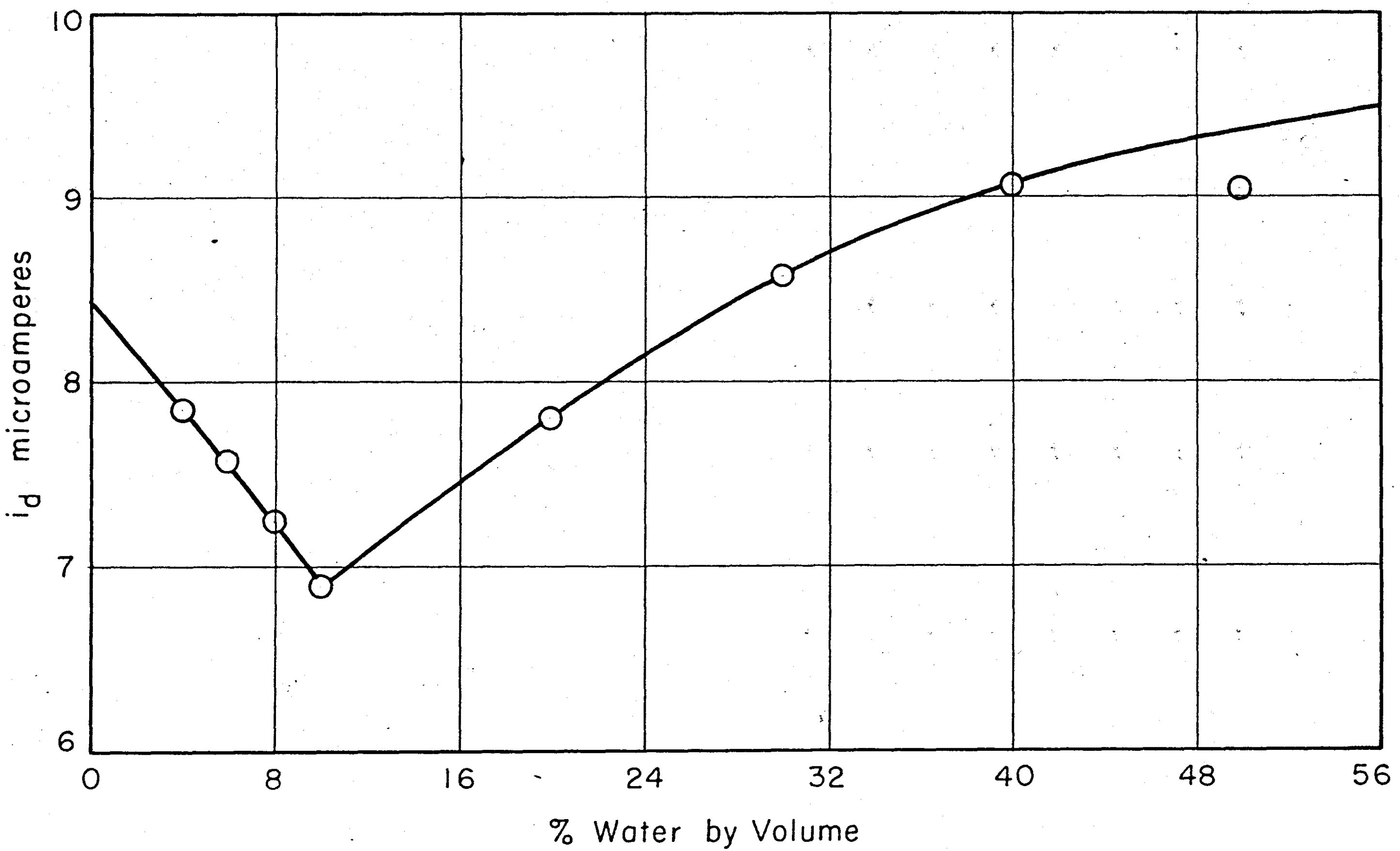
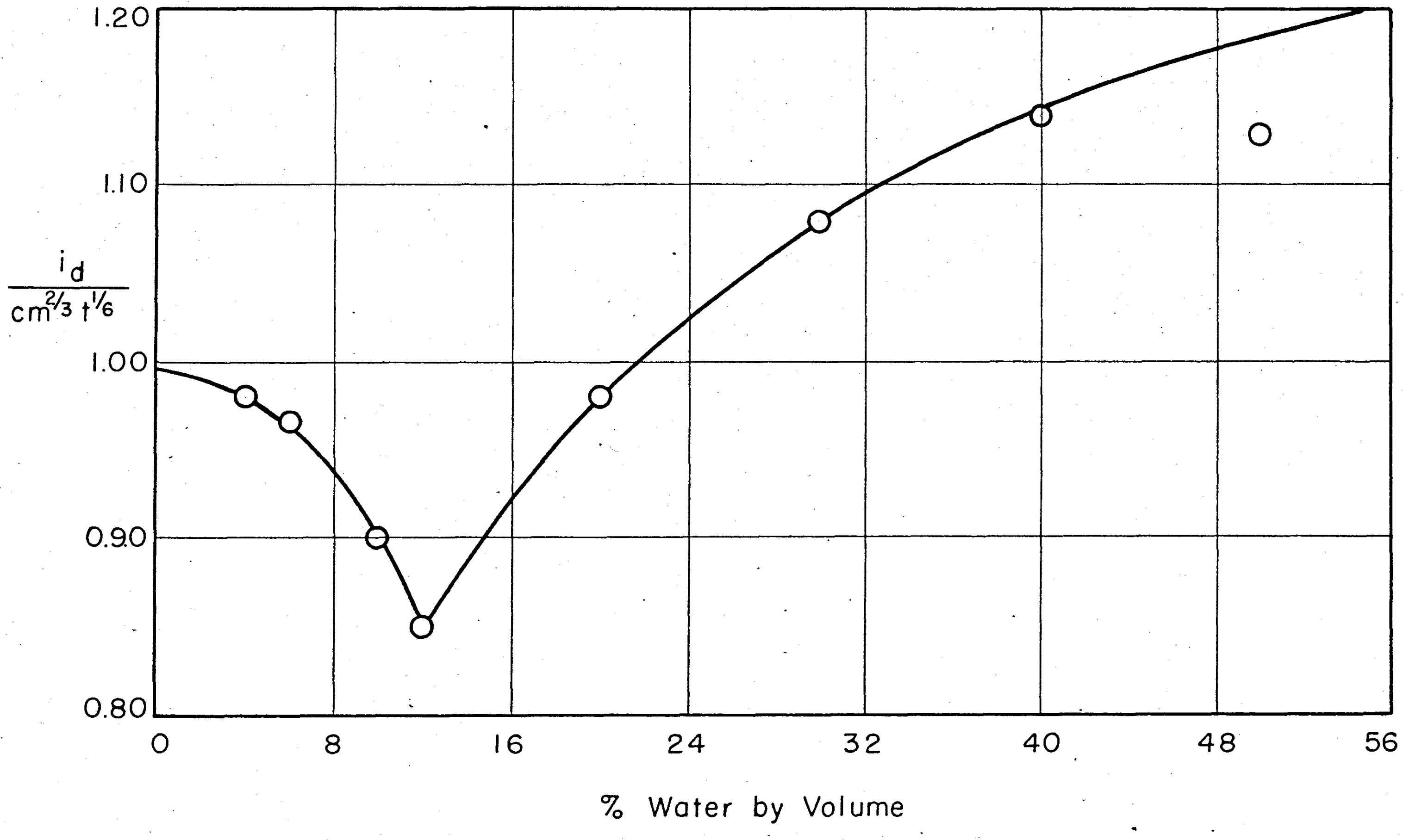


Fig. 4

Effect of pyridine-water ratio on diffusion current constant



about 90% pyridine. The curves and the points of minimum bear a remarkable resemblence to those obtained by Zlotowski and Kolthoff (24) who found a minimum at 80% ethanol for ethanol-water mixtures. Extrapolation to 100% pyridine gives a value of 0.99 for the diffusion current constant. The values obtained at 50% are very likely in error since it is to be expected that the curves will continue to increase up to 100% water.

An analysis of the plots of log $i/(i_d - i)$ against applied potential show that the values of the slopes range from -0.050 at 4% water to -0.042 at 50% water. In these plots the applied potential was corrected for resistance. The values indicate that the reduction is irreversible in all cases but approaches the theoretical value of -0.059 more closely with increased concentrations of pyridine. Zlotowski and Kolthoff found that the waves of strontium and barium were most reversible in 50% ethanol solutions (24). The lack of agreement between the values of pyridine-water mixtures and ethanol-water mixtures is not surprising since the reversibility is dependent also upon the cation being reduced and not only upon the solvent medium.

Qualitative Survey

Polarograms run on pyridine and lithium chloride, but containing no solute salts, showed a small residual current which increased rapidly with applied potential above -1.6 volts against the quiet pool of mercury. In some cases a small wave was obtained at about -1.3 volts which was attributed to an impurity present in the barium oxide which was used to dry the pryidine. If this wave occurred coincidentally with reduction of some cation, a correction could be applied since the wave is small. If lithium nitrate is used as supporting electrolyte, the small background current begins to increase rapidly at potentials above -1.55 volts against the quiet pool of mercury.

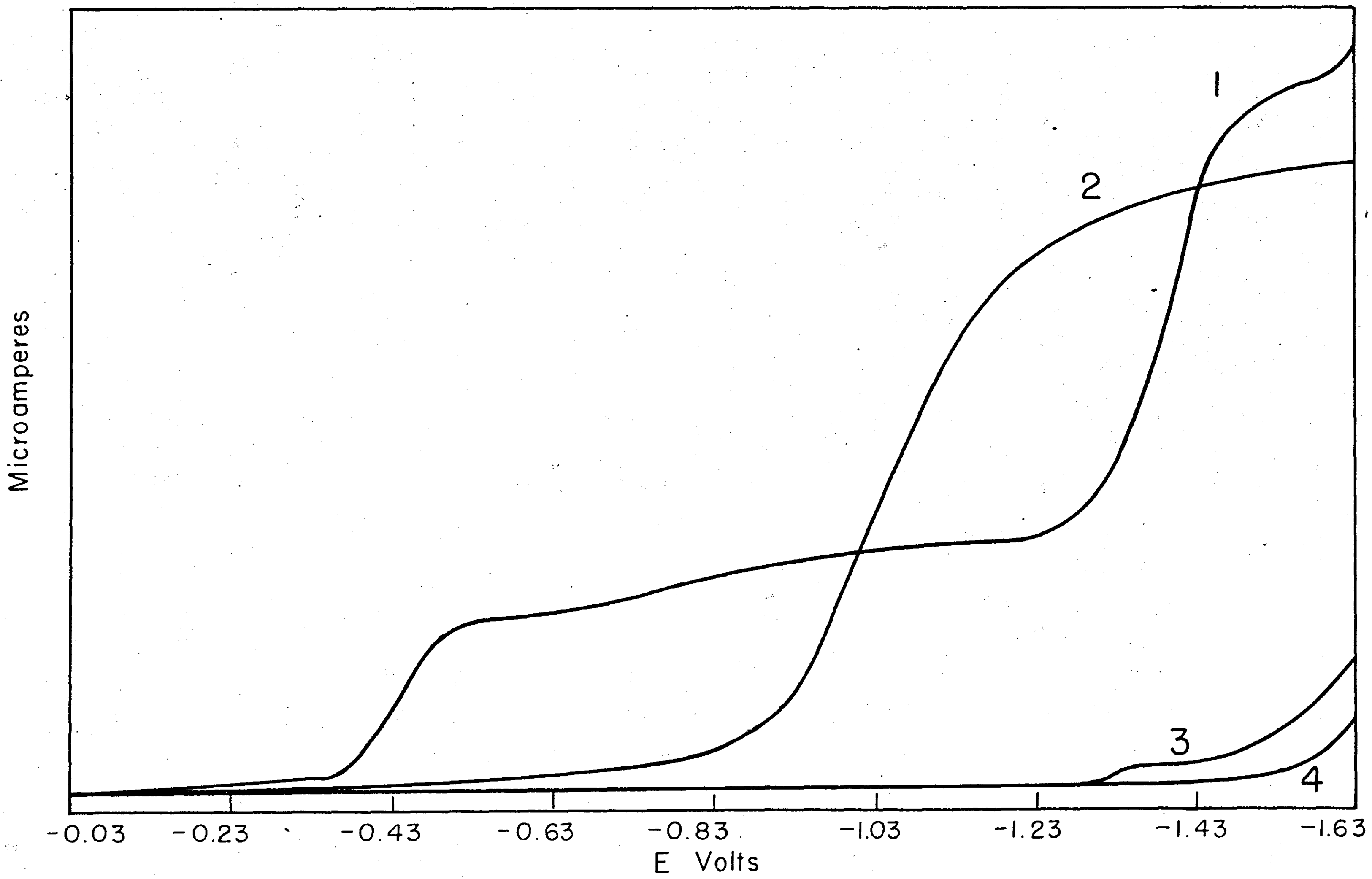
Many cations were investigated in an attempt to find those which would give polarographic waves in the operable range. Salts of chromium were the only ones tested which gave well defined waves with no semblance of a maximum. Chromium chloride hexahydrate in the presence of lithium chloride as supporting electrolyte gave two well defined waves which are shown graphically in figure 5, curve number 1. Curve 3 is the blank of lithium chloride in pyridine for comparison. The second wave is in many cases twice the height of the first if calculated by the method previously described. This is consistent with the mechanism of reduction of Cr(III) to Cr(II) and a subsequent reduction of Cr(II) to Cr.

According to the Ilkovic equation (18) this interpretation would require a wave height ratio of 2 since n would have values of 1 and 2. If chromium nitrate nonahydrate is run in pyridine using lithium chloride as a supporting electrolyte only one wave is obtained within the operable range. Since it has a maximum no further work was done on this reduction. With lithium nitrate, however, chromium nitrate nonahydrate gives one well defined wave, the second reduction presumably occurring coincidentally with the current rise of the blank. This curve is represented by curve 2 in figure 5 whereas curve 4 represents the blank using lithium nitrate as supporting electrolyte. Since the figures containing example curves are presented only to show the character of the reduction waves the scale of the ordinate is arbitrary and is the same only for a reduction wave and its respective blank. If two reduction waves are represented on the same graph, the relative magnitudes of each should not be compared since the scale of the ordinate is not necessarily the same for each. Anhydrous chromic chloride did not give a reduction wave in pyridine since no appreciable solution resulted after standing for a week.

Cobaltous chloride hexahydrate, lead chloride, zinc chloride and ferrous chloride tetrahydrate gave waves with smooth residuals, smooth current increases, but slightly

Fig. 5

Reduction Waves of Cr^{+++} in Pyridine



erratic behavior in the region of the diffusion current. In all cases it was found possible to smooth out this erratic behavior by using gum tragacanth as previously described. Although this behavior is very likely similar to maxima in aqueous solutions, it resembles a minimum in some cases more than it does a maximum. The usual maximum suppressors used in aqueous solution as gelatin and methyl cellulose are ineffective in pyridine due to their small solubility. A search was conducted for a maximum suppressor which would prove effective in pyridine, using cobaltous chloride hexahydrate as the test ion. The following substances were tried as maximum suppressors and found to be ineffective: indian gum, gum copal, gum damar, gum arabic, gum guiaiac, gum elemi, agar, egg albumen, camphor, methyl red, phenol red, titan yellow, acid yellow, naphthalene and twenty five surface active agents from the Atlas Powder Company. Gum tragacanth and gum gambogi were found to be effective in suppressing the maximum of cobaltous ion. Gum gambogi yields an increased background current and a couple of small reduction waves. Therefore when it is used as a maximum suppressor it is necessary to apply a correction for the blank. Two ml. of a gum gambogi solution containing 0.5 gram in a 100 ml. of pyridine in 25 ml. of solution was sufficient to suppress the maximum of cobaltous ion in solutions up to 5 millimolar. An example of a polarographic wave due to cobaltous ion in the presence of gum gambogi is given in figure 6, curve 1. Curve 2 represents a blank containing gum gambogi. A well defined wave was also obtained for cobaltous ion using lithium nitrate as supporting electrolyte in the presence of gum tragacanth as maximum suppressor. Lead chloride gave a well defined S shaped wave in the presence of lithium chloride, as well as lithium nitrate, as supporting electrolyte in the presence of gum tragacanth. Gum gambogi, gum damar, nacconol, methyl red and fuchsine were ineffective in suppressing the lead maximum. An example of a reduction wave of zinc ion in the presence of gum tragacanth is given in figure 7, curve 2. Curve 1 represents the wave before addition of gum tragacanth and curve 3 is the blank containing gum tragacanth. In figure 8, curve 1, an example of a reduction wave of ferrous chloride tetrahydrate is given, with curve 2, the blank, for comparison. The reduction of ferrous ion occurs at such negative potentials that some interference is obtained with the blank and the necessary correction must be applied in calculating the diffusion current.

Nickel chloride hexahydrate gave a well defined wave in lithium nitrate as supporting electrolyte but if lithium chloride was used as supporting electrolyte a drawn out wave was obtained giving a semblance of two waves, the second one containing a maximum. If the nickel chloride hexahydrate

Fig. 6

Reduction Wave of Co^{++} in Pyridine

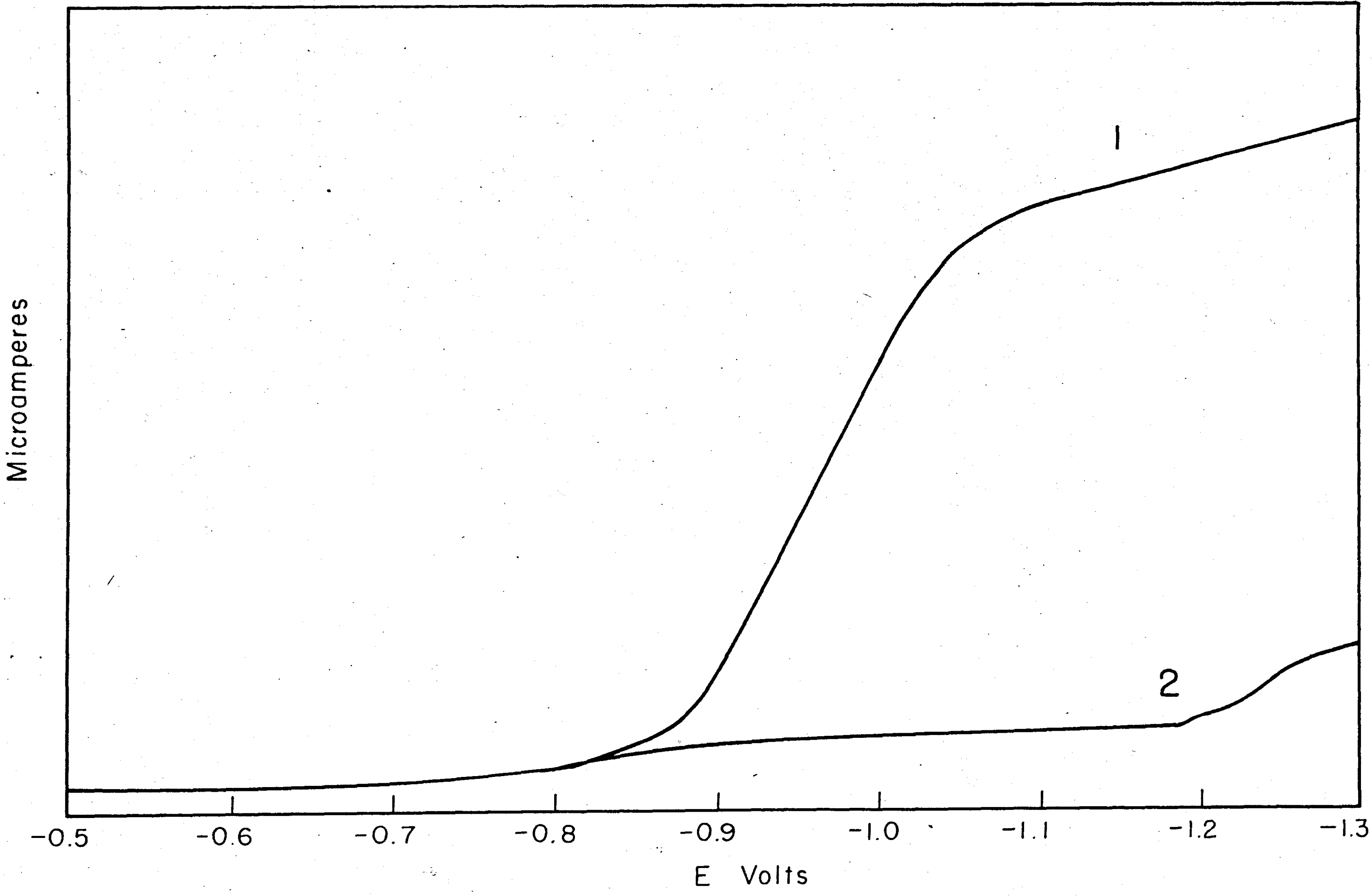


Fig. 7

Reduction Wave of Zn^{++} in Pyridine

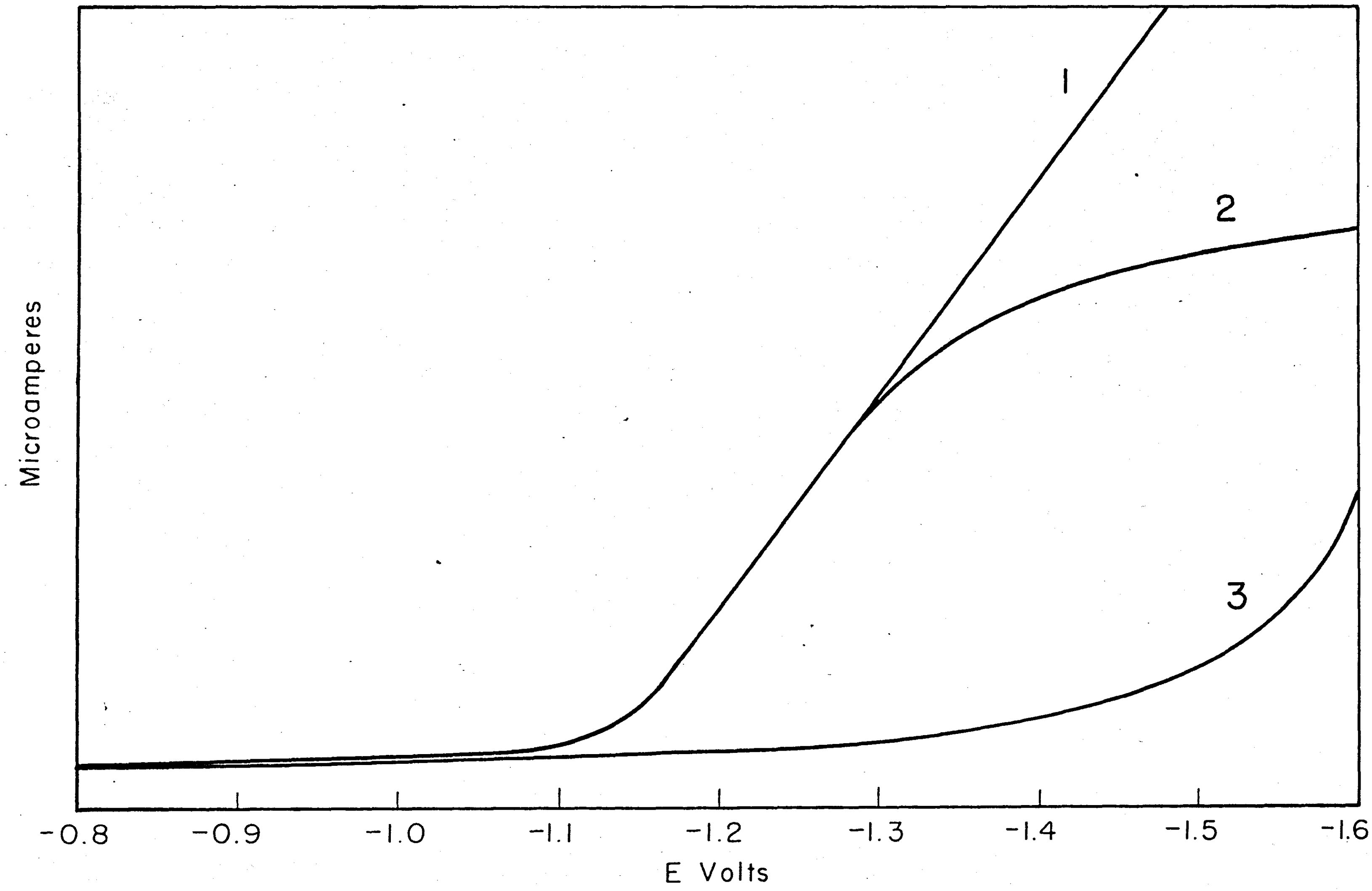
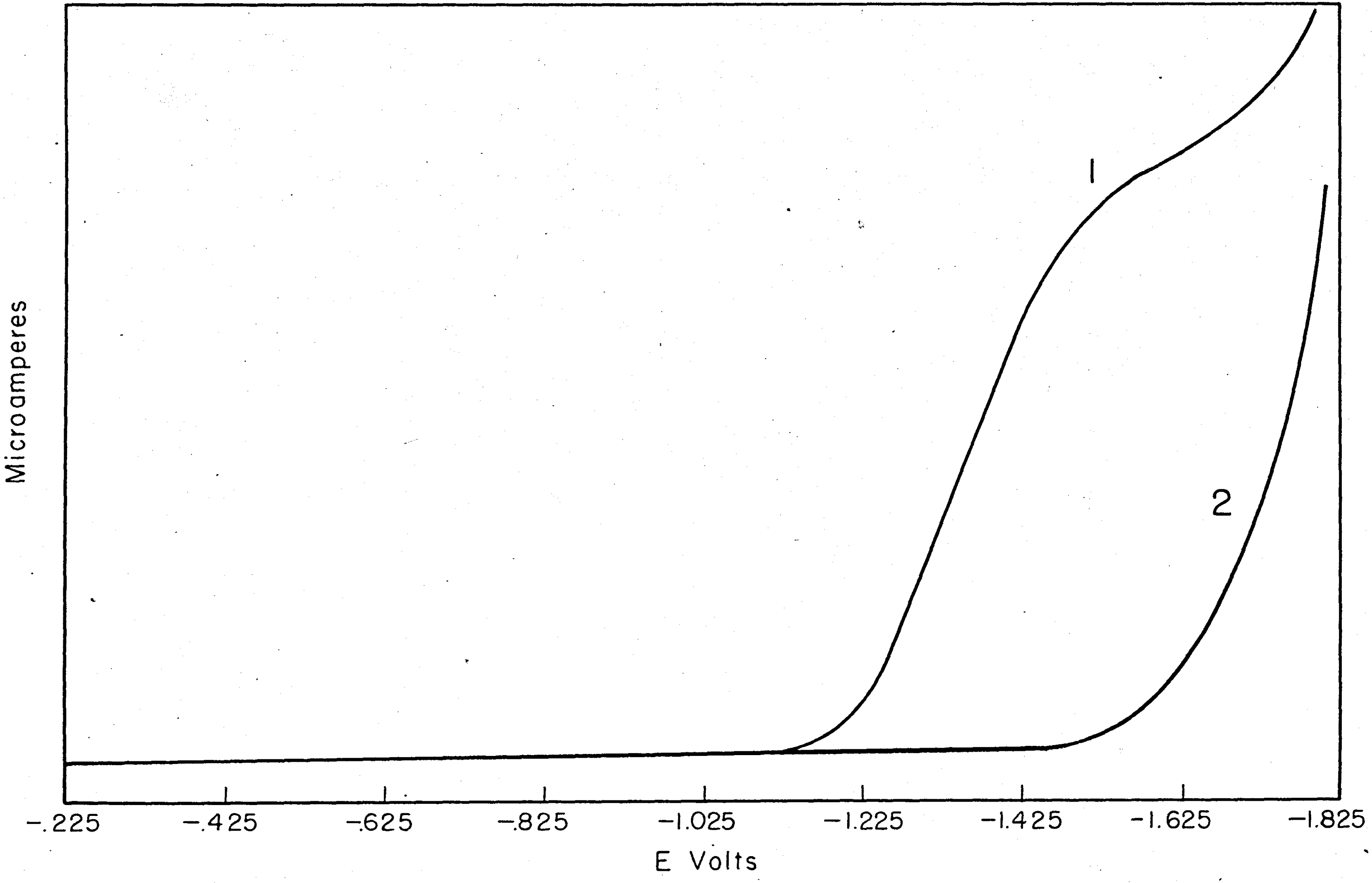


Fig. 8

Reduction Wave of Fe^{++} in Pyridine



was dehydrated similar results were obtained. These curves are presented in figure 9, curves 1 and 2, and in this particular case the same concentration of anhydrous nickel chloride was used in both cases so that the relative heights of the two curves could be compared. Curve 3 represents the blank containing lithium nitrate. All attempts to suppress the maximum in the case of the reduction wave in the presence of lithium chloride failed but the presence of large amounts of Triton W-30, which gave partial suppression seemed to indicate that only one wave was present. Similar results were obtained in the presence of lithium chloride if methyl cellulose, dissolved in water, was added to the solution. Figure 10 shows the effect of adding successive increments of 10 drops of a 1% solution of methyl cellulose, dissolved in water, to the nickel chloride solution using lithium chloride as supporting electrolyte, curve 1 representing the initial wave. It is possible that the appearance of two possible waves is due to the presence of both a nickel pyridine complex and a nickel chloride complex in equilibrium with each other in solution, each of which reduce at different potentials. Nickel chloride complexes are known to form in the presence of concentrations of dehydrating chlorides of about 6 molar in aqueous solution (29). It is significant also, that in the presence of lithium nitrate only one wave is obtained, the height of which is

Fig. 9

Reduction Wave of Ni^{++} in Pyridine

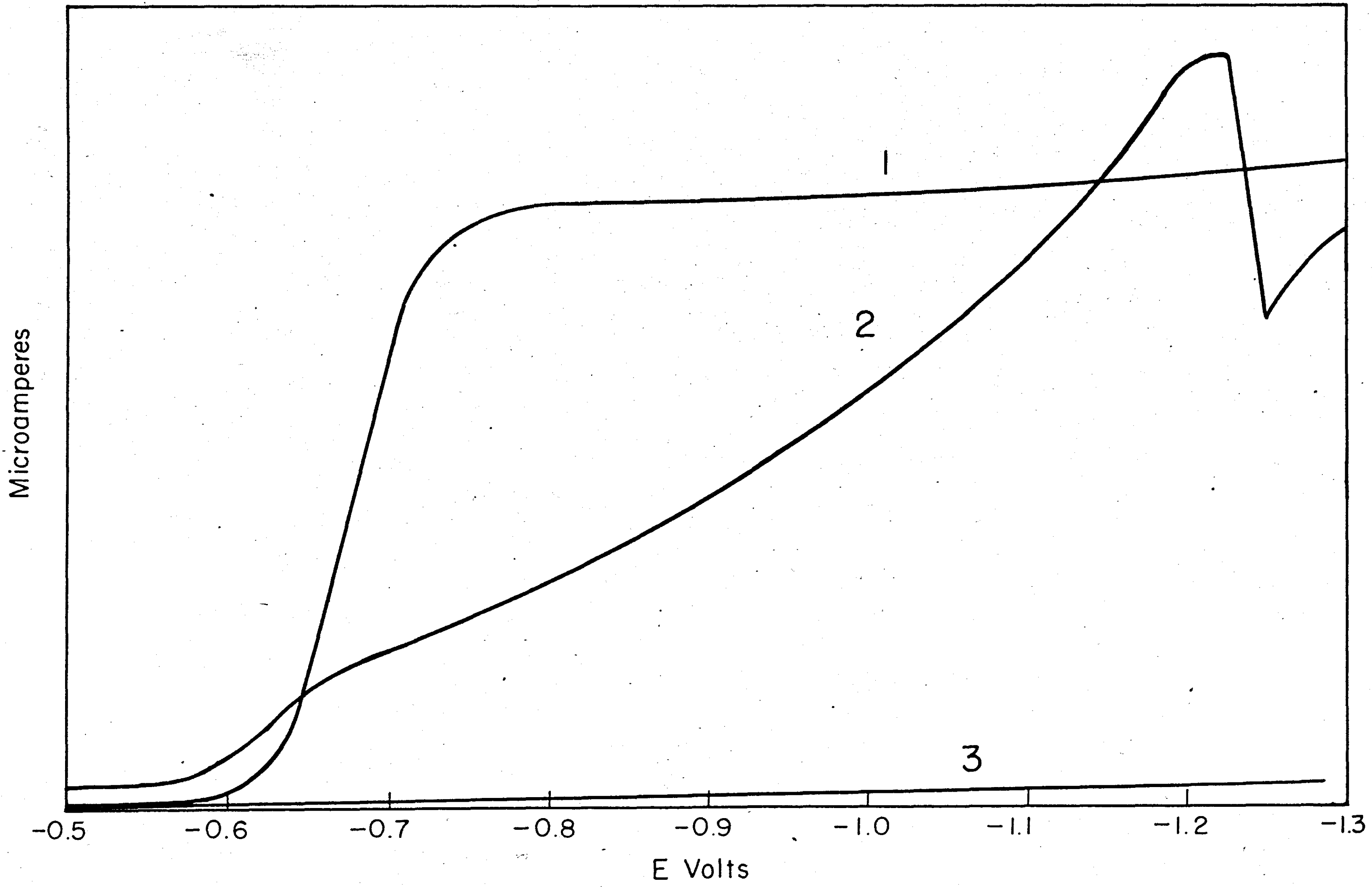
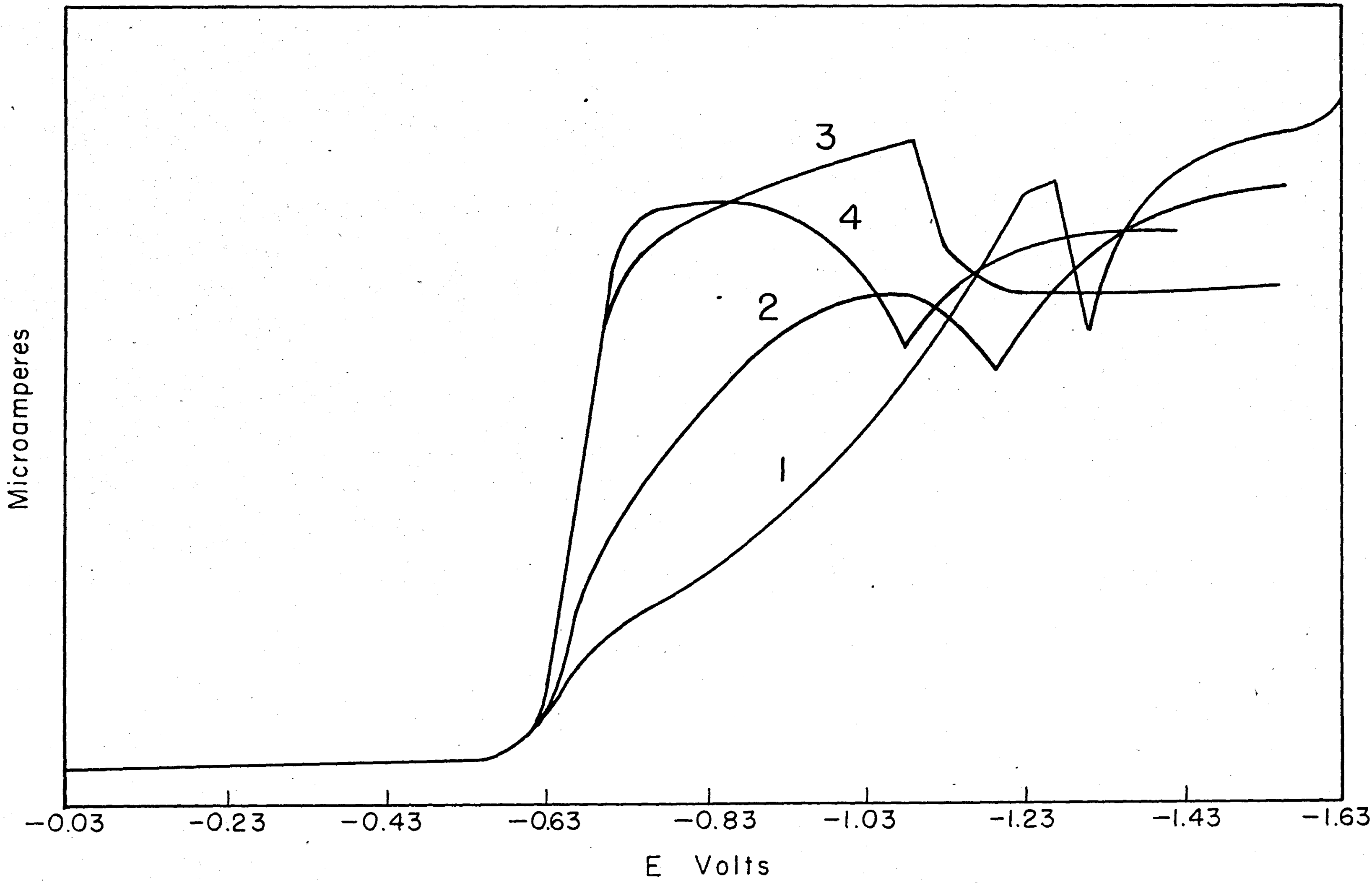


Fig. 10

Effect of Methyl Cellulose on Reduction Wave of Ni^{++}



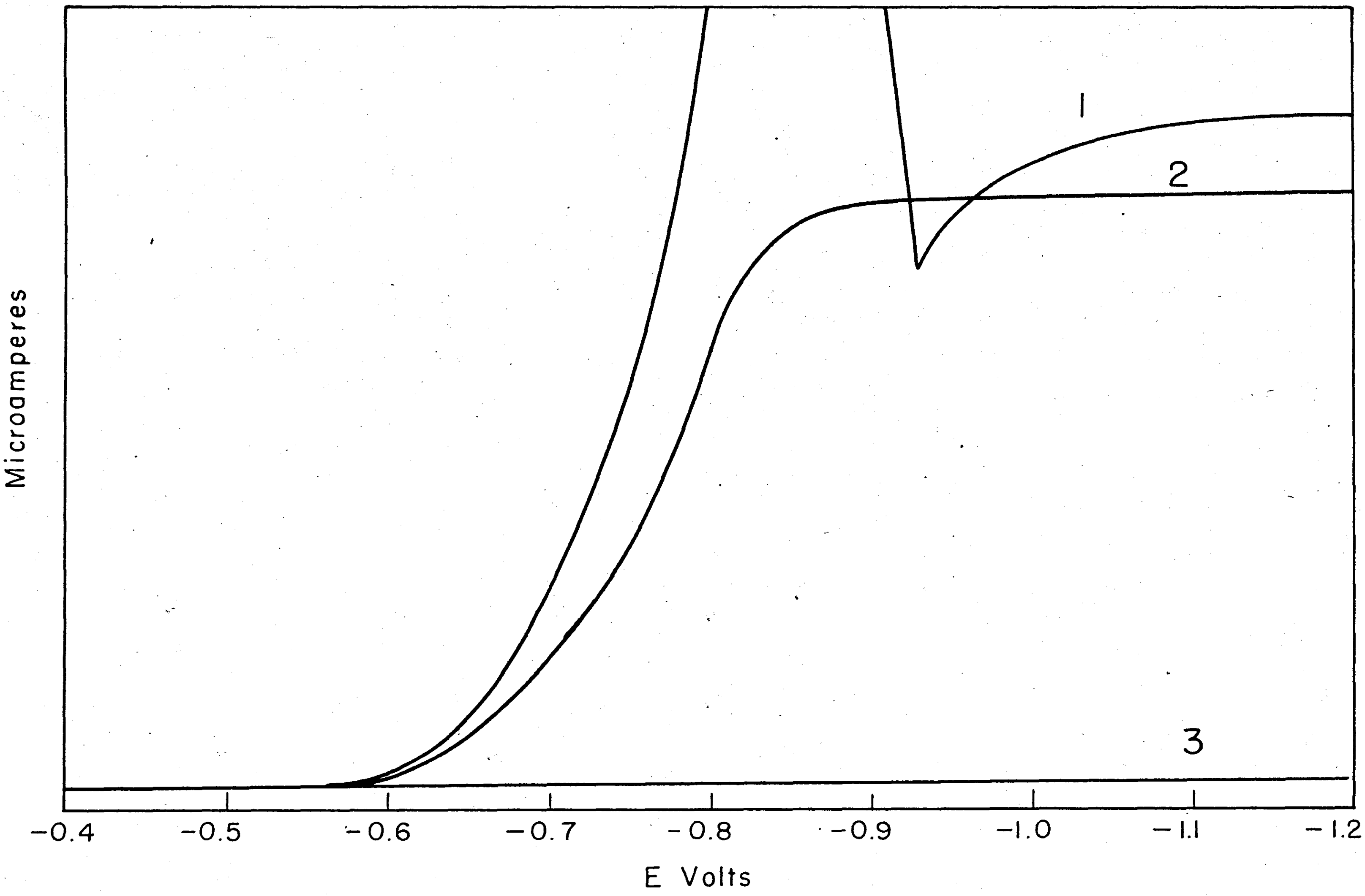
approximately equal to that obtained following the maximum when lithium chloride is used as supporting electrolyte. It is thought that the addition of methyl cellulose dissolved in water or Triton W-30 shift the equilibrium between the two complexes in favor of the pyridine complex and hence in their presence only one wave is indicated.

A well defined wave is obtained with cadmium chloride using lithium nitrate as supporting electrolyte if gum tragacanth is present as a maximum suppressor. However, the current rise seems to undergo a change of slope before the diffusion current is reached as is shown by curve 2, figure 11. Curve 1 represents the same solution with no gum tragacanth present and curve 3 is the blank. No explanation is offered for the two slopes during the current rise. Using lithium chloride as supporting electrolyte and in the presence of gum tragacanth, cadmium ion exhibits a wave which is much more drawn out and which is not too reproducible.

Uranyl nitrate hexahydrate, which seems to be quite soluble in pyridine, in the presence of lithium chloride as supporting electrolyte gives a wave containing a maximum which is neither suppressed by the maximum suppressors previously mentioned nor by caffeine, meta cresol purple, thymol blue, bromthymol blue or thymolphthalein. Using lithium nitrate as supporting electrolyte and gum tragacanth as maximum suppressor, three waves are obtained which vary

Fig. 11

Reduction Wave of Cd^{++} in Pyridine

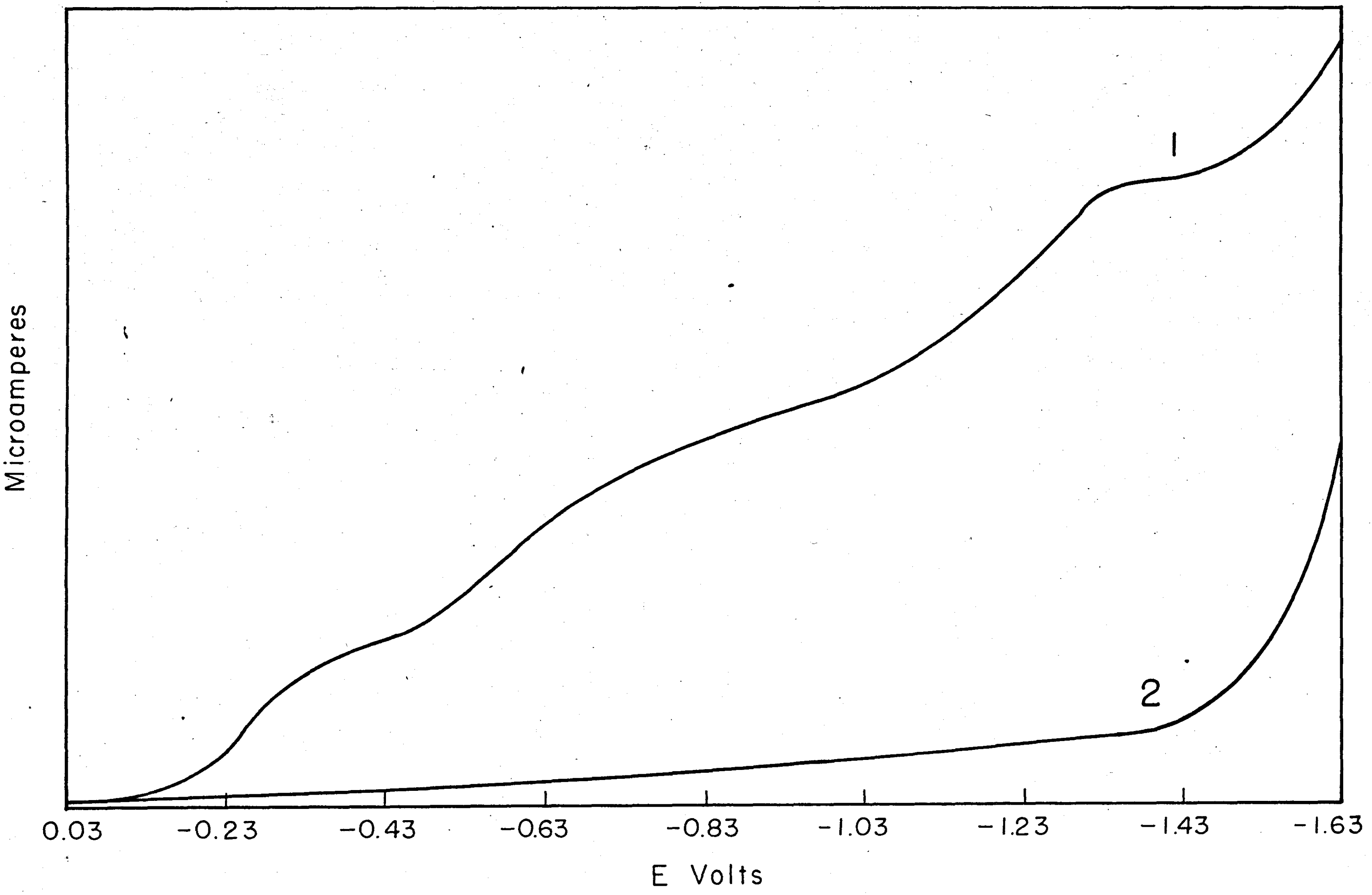


in their degree of definition depending upon the concentration of the uranyl ion. At concentrations below 0.9 millimolar the second wave is well defined. At the same concentration the first wave begins to fade out since the instrument is not sensitive enough to give a wave large enough to be measured easily. Curve 1, figure 12, is an example of the wave obtained with uranyl ion in the presence of lithium nitrate and curve 2 is the reference blank.

Cupric chloride, ferric chloride hexahydrate, bismuth trichloride, silver nitrate and mercurous chloride all yield waves with very pronounced maxima which begin at applied zero voltages. The maxima are straight lines of rapid current increase which decrease rapidly and discontinuously after the maximum. These ions are all similar in that in aqueous media they all begin to reduce in the region of zero applied potential if an internal mercury anode is used. It was found that by using titan yellow as a maximum suppressor, the maxima could be completely suppressed in all cases except in that of silver nitrate. Titan yellow was effective in the case of silver nitrate when the concentration of silver nitrate was less than 3 millimolar. All attempts to begin these curves at positive potentials in order to obtain a residual curve failed so the standard procedure for calculating diffusion currents and half-wave potentials had to be modified. Since a blank gives a residual current which

Fig 12

Reduction Wave of UO_2^{++} in Pyridine



increases very slowly, a line was drawn parallel to the base line at the point of zero potential and the standard procedure was then used. Cupric ion gives two waves in the presence of titan yellow and using lithium chloride as supporting electrolyte. Curve 2, figure 13, is an example of the copper wave in the presence of titan yellow whereas curve 1 is the same curve in the absence of titan yellow. Curve 3 is a blank of titan yellow and lithium chloride. The ratio of the height of the first wave to the height of the second wave is one which is consistent with a reduction of Cu(II) to Cu(I) and a subsequent reduction of Cu(I) to Cu. Ferric chloride hexahydrate yields two waves in the presence of lithium chloride as supporting electrolyte and titan yellow as maximum suppressor. However, the second wave cannot be calculated because of interference with the blank containing titan yellow. These two curves are represented by figure 14. Mercurous ion and silver ion each give one wave which is similar to the first waves of copper and iron and hence are not illustrated graphically. Although bismuth trichloride is not very soluble in pyridine, a saturated solution was prepared. In the presence of titan yellow and lithium chloride as supporting electrolyte, bismuth trichloride gave one well defined wave followed by a second wave with a maximum present. If tragacanth is also added to the solution the maximum disappears and a third

Fig. 13

Reduction Wave of Cu^{++} in Pyridine

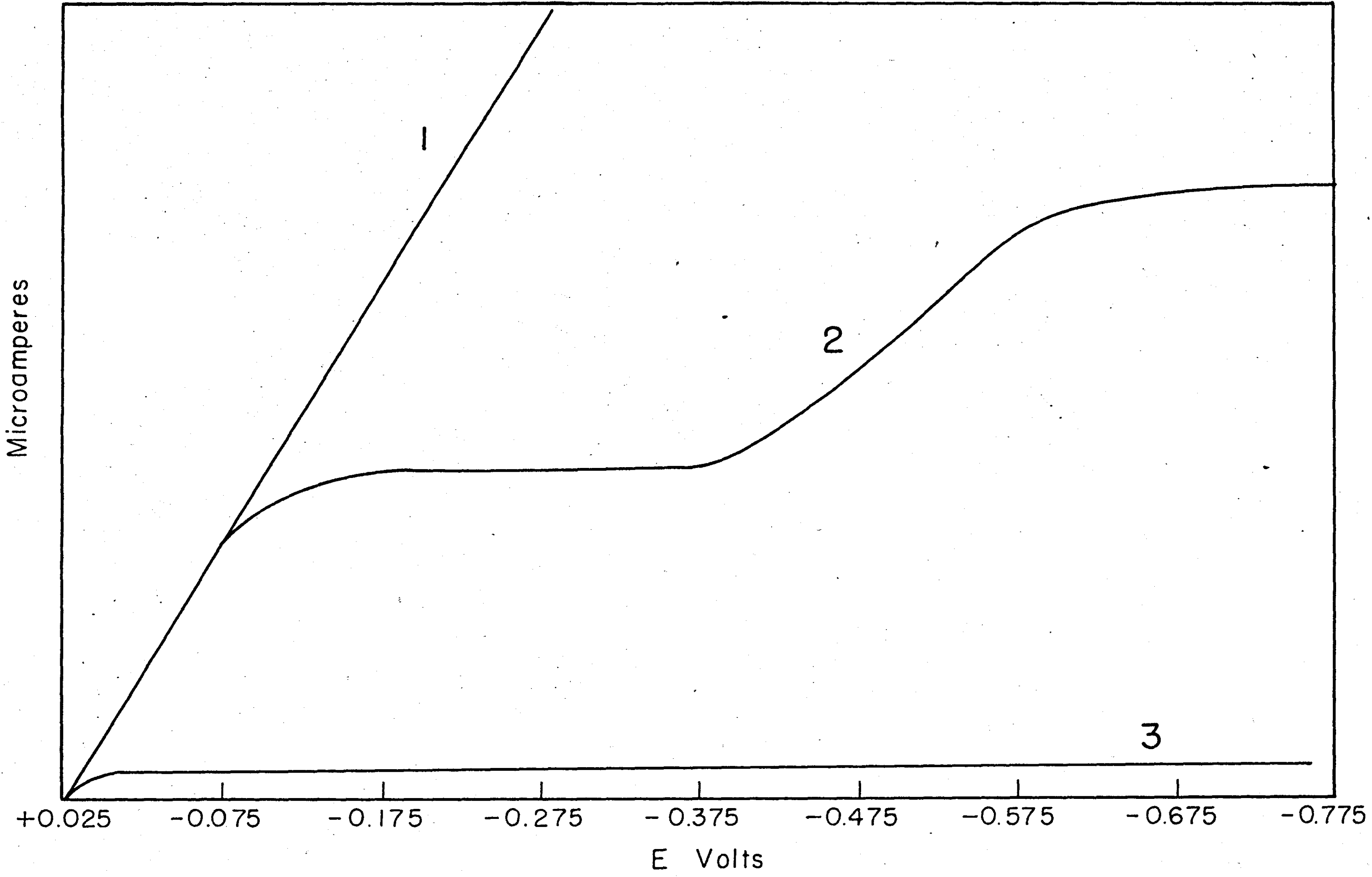
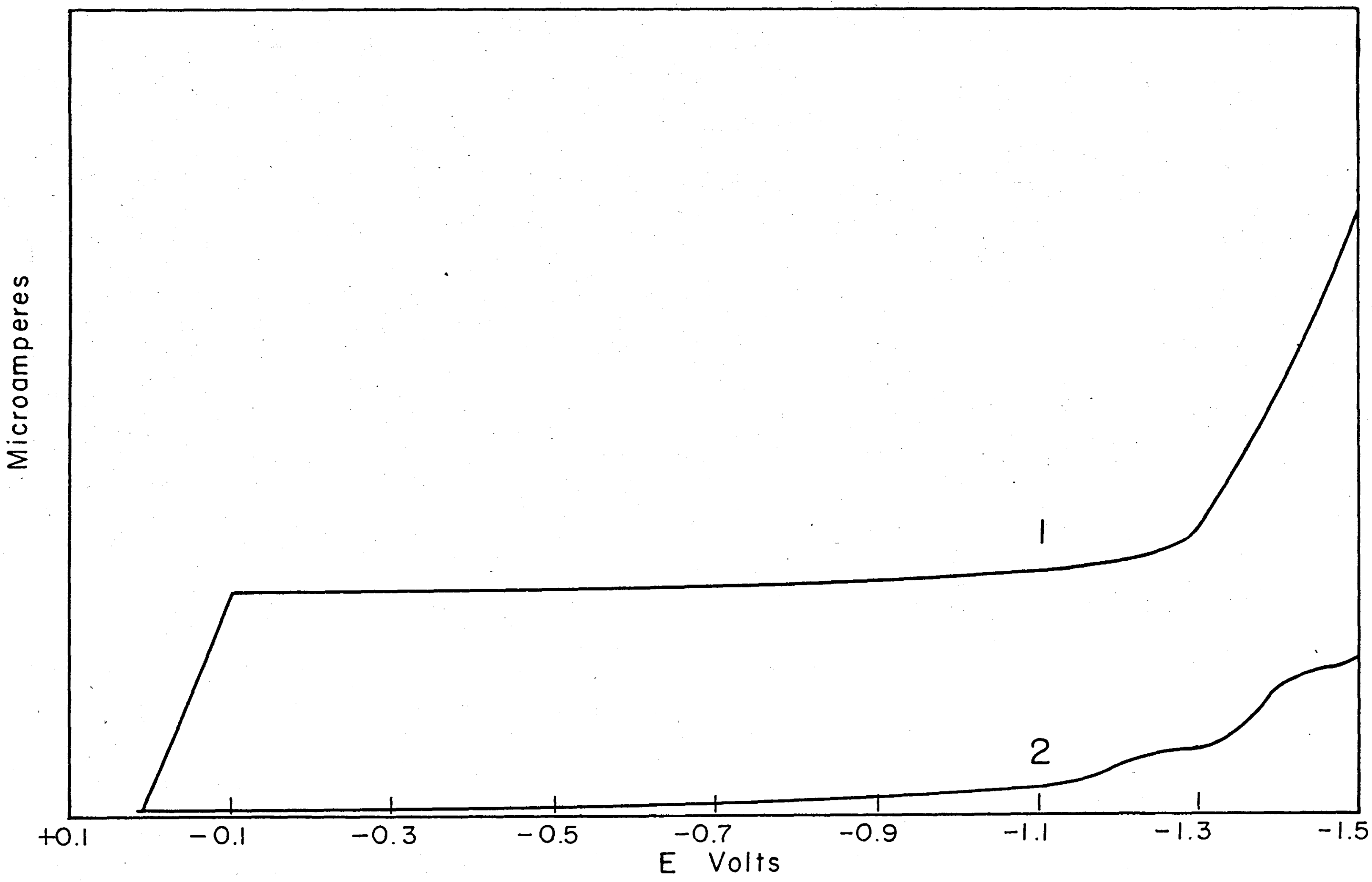


Fig. 14

Reduction Wave of Fe^{+++} in Pyridine



wave also appears. This is shown diagrammatically in figure 15, curve 1, and the blank containing titan yellow and tragacanth is shown in curve 2. It is possible that the third wave is due to pyridinium ion which results from hydrolysis due to the presence of some water in the salt. The first and second waves may be due to a reduction of tripositive bismuth to unipositive bismuth with subsequent reduction to bismuth. Evidence for such a reduction has been obtained in alkaline citrate media (30).

In an effort to find out by what mechanism the titan yellow suppresses the maximum, electrocapillary curves of lithium chloride in pyridine were run with and without titan yellow. In figure 16, curve 1 is the curve obtained without titan yellow and curve 2 is the curve obtained with titan yellow. It is to be noted that the electrocapillary maximum occurs at -0.125 volts measured against the quiet pool of mercury. The curve is considerably flatter than a similar curve in water. The titan yellow shifts the electrocapillary maximum to more negative values. The maxima of the previously discussed cations all occur on the positive side of the electrocapillary maximum. The suppression of the maxima cannot be explained on the basis of shifting the electrocapillary zero to coincide with the maximum since the electrocapillary zero is shifted in the opposite direction. However, it can be explained on the basis of

Fig. 15

Reduction Wave of Bi^{+++} in Pyridine

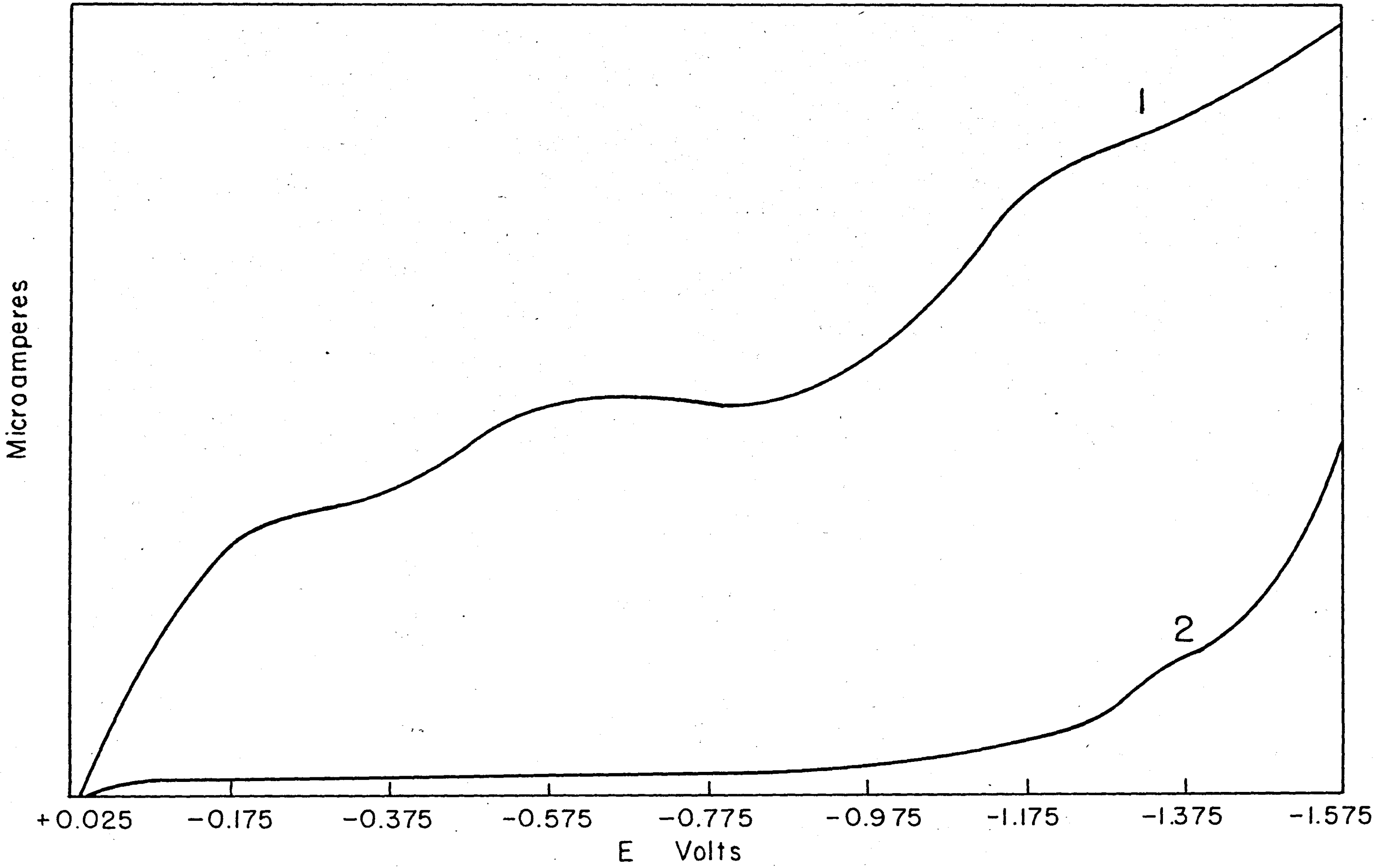
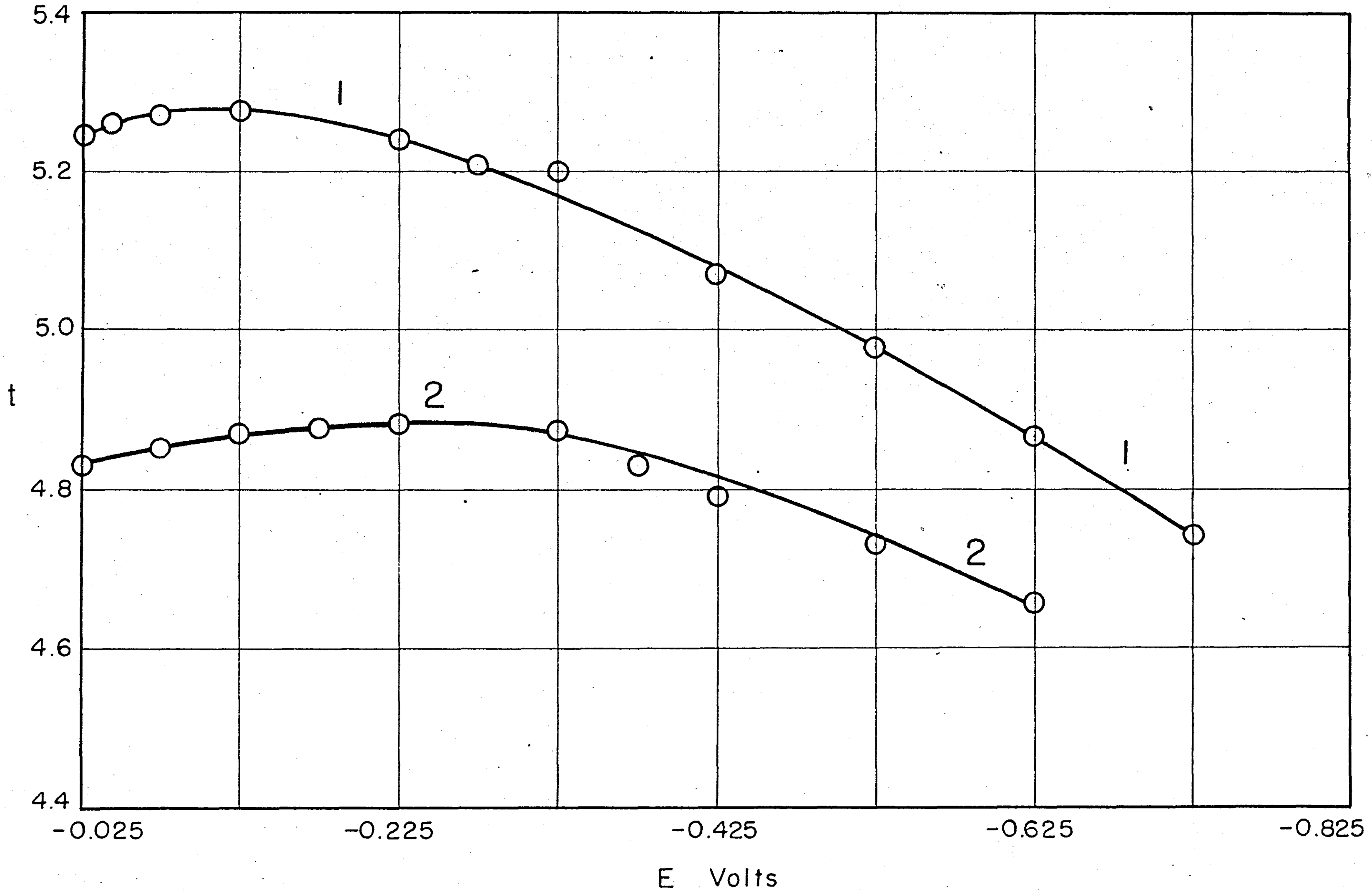


Fig. 16

Electrocapillary Curves

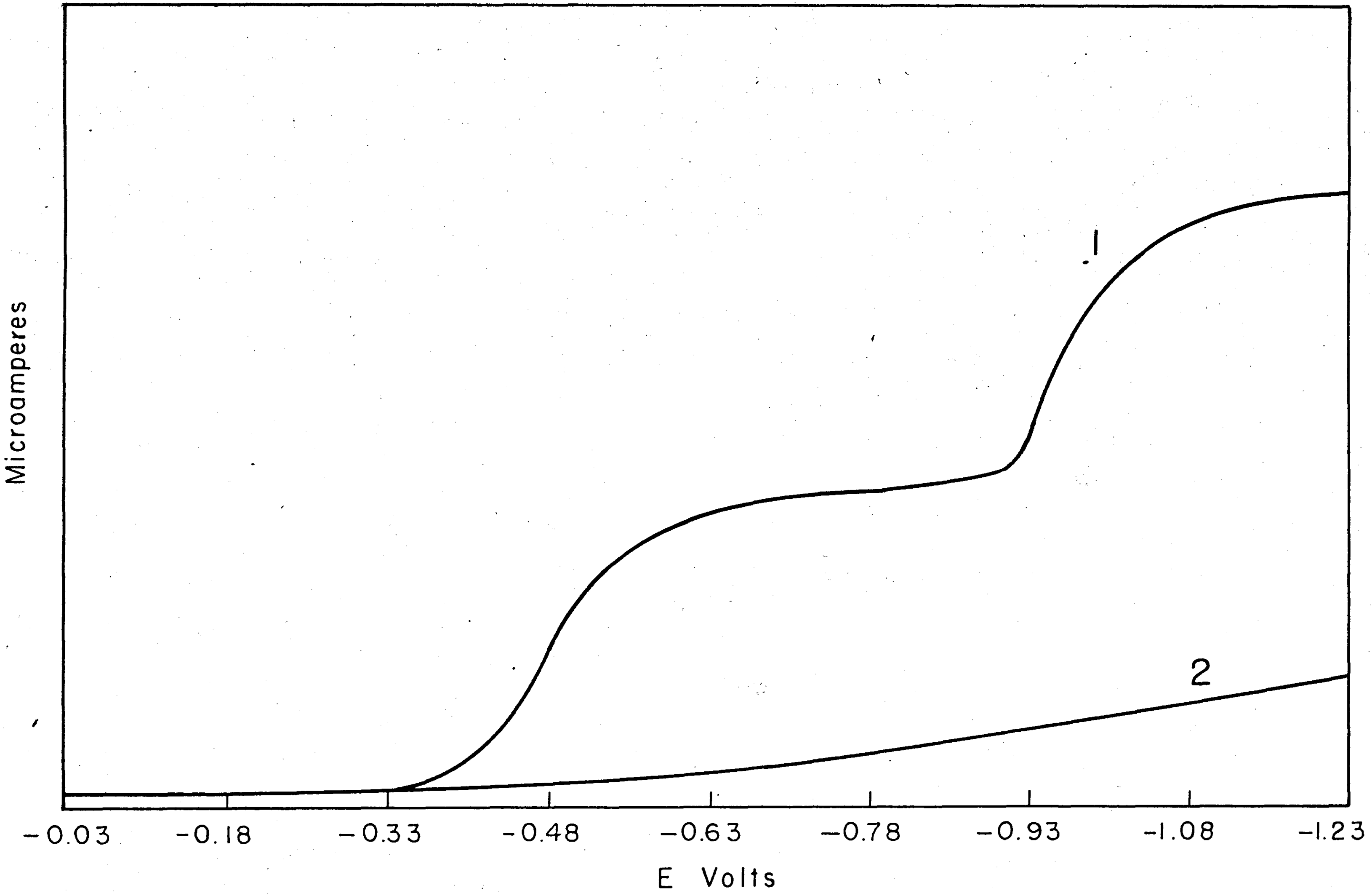


complex formation between the cations and the titan yellow which shifts the discharge potentials of the cations involved, such that they practically coincide with the electrocapillary maximum. The electrocapillary maximum in pyridine is rather flat instead of being a sharply defined point and therefore the above explanation seems plausible. Attempts to obtain an electrocapillary curve in the presence of gum tragacanth failed since the results were not reproducible. It is a common occurrence in the presence of gum tragacanth for a drop of mercury to dislodge prematurely. This did not prevent proper calculation of curves but did affect the reproducibility of taking electrocapillary measurements.

In the presence of lithium chloride as supporting electrolyte, stannous chloride dihydrate yields a curve containing a maximum. This maximum, although in evidence in solutions immediately after preparation, disappears as the solution ages and a second wave appears. If the solutions were prepared with one half a ml. of Triton W-30 present for every 25 ml. of solution, the maximum was suppressed. Curve 1, figure 17, represents a polarographic wave of stannous chloride dihydrate in the presence of Triton W-30 obtained after the solution had stood 22 hours. Curve 2 represents a blank containing Triton W-30. The second wave which occurs is due to pyridinium ion which results from the hydrolysis of the stannous chloride. Studies made against time show

Fig. 17

Reduction Wave of Sn^{++} in Pyridine



that the height of the first wave decreases whereas the second wave increases in support of the reduction of pyridinium ion. Similar results were found with antimony trichloride, although in this case the waves contained maxima which did not disappear with time nor were they capable of suppression with gum tragacanth or Triton W-30.

Magnesium perchlorate and manganese chloride tetrahydrate did not yield a reduction wave within the operable span. Nickel cyanide seemed to be practically insoluble in pyridine and a saturated solution did not exhibit any wave within the workable range of potential. Anhydrous aluminum chloride dissolved in pyridine was hydrolyzed by the presence of water in the pyridine and gave a wave due to the pyridinium ion formed.

Test of the Ilkovic Equation

The Ilkovic equation, derived for the diffusion current obtained with a dropping electrode can be written in the following manner

$$\frac{i_d}{cm^{2/3}t^{1/6}} = 605nD^{\frac{1}{2}}$$

in which i_d is the diffusion current of an ion in microamperes, n is the number of faradays of electricity required per mole of electrode reaction, D is the ionic diffusion coefficient, c is the concentration of reducible ion in millimoles per liter and m(mg./sec.) and t(sec.) are the capillary characteristics. The quantity on the left hand side of the equation which can be referred to as I, the diffusion current constant, can be determined from experimental data and should be a constant for a given ion at a given temperature if the Ilkovic equation is obeyed. Concentration studies were run on the various ions mentioned in the qualitative survey under the conditions which produced well defined waves. Either 0.8 molar lithium chloride or 0.7 molar lithium nitrate was used as supporting electrolyte. The range of concentrations used for each salt depended upon the solubility of the particular salt in pyridine. Data for these concentration studies are presented in tables 29 through 53 and the results indicate that the Ilkovic equation is obeyed to within an average deviation of 2% for the salts,

Table 29

Studies of first wave of $CrCl_3 \cdot 6H_2O$ with LiCl as S. E.

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I	$m^{2/3}t^{1/6}$ $mg.^{2/3}sec.^{-\frac{1}{2}}$
2.447	6500	-0.439	4.00	0.91	1.800
2.430	5600	-0.430	3.39	0.79	1.779
2.187	6100	-0.436	3.36	0.87	1.779
2.121	6900	-0.436	3.46	0.91	1.800
1.842	6600	-0.436	2.85	0.86	1.793
1.631	7000	-0.442	2.54	0.87	1.800
1.578	6100	-0.433	2.23	0.79	1.793
1.468	6200	-0.443	2.26	0.87	1.800
1.458	6300	-0.430	2.16	0.84	1.789
1.314	5800	-0.439	2.09	0.89	1.789
1.134	6200	-0.439	1.80	0.88	1.800
1.105	6400	-0.447	1.68	0.86	1.779
1.053	6500	-0.445	1.53	0.85	1.793
0.9787	6700	-0.437	1.40	0.79	1.800
0.8156	7000	-0.443	1.21	0.82	1.800
0.7891	6500	-0.436	1.18	0.84	1.789
0.6576	6800	-0.442	1.01	0.87	1.793
Avg.		-0.438 ± .004		0.85	
% Avg. Dev.		0.91		3.53	

Table 30

Studies of second wave of $CrCl_3 \cdot 6H_2O$ with LiCl as S. E.

$m^{2/3}t^{1/6} = 1.698$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps	I
2.427	6500	-1.387	10.28	2.47
2.121	6600	-1.384	9.06	2.52
1.631	6700	-1.370	6.84	2.47
1.468	6200	-1.360	6.35	2.55
1.305	6500	-1.351	5.58	2.52
1.134	6500	-1.368	4.93	2.56
0.9787	6700	-1.342	4.29	2.58
0.8156	6400	-1.359	3.51	2.53
0.6525	6500	-1.367	2.72	2.45
0.3262	6600	-1.368	1.44	2.59
Avg.		-1.366 ± .010		2.52
% Avg. Dev.		0.73		1.50

Table 31

Studies of $CoCl_2 \cdot 6H_2O$ with LiCl as S. E. in the presence of gum gambogi. $m^{2/3}t^{1/6} = 1.769$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d µamps.	I
2.214	6100	-0.921	9.14	2.33
2.013	6400	-0.930	8.51	2.39
1.611	6400	-0.926	6.74	2.36
1.208	6400	-0.919	5.32	2.40
1.007	6800	-0.920	4.32	2.42
0.805	6800	-0.917	3.26	2.29
0.604	6800	-0.931	2.57	2.40
Avg.		-0.923 ± .005		2.37
% Avg. Dev.		0.54		1.56

Table 32

Studies of $CoCl_2 \cdot 6H_2O$ with LiCl as S. E. in the presence of gum tragacanth. $m^{2/3}t^{1/6} = 1.876$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d µamps.	I
3.180	5200	-0.961	12.30	2.06
2.953	5600	-0.942	12.00	2.16
2.498	5300	-0.949	9.96	2.13
2.044	5400	-0.941	8.46	2.21
1.590	6000	-0.937	6.56	2.20
1.136	5900	-0.931	4.35	2.04
0.6818	6000	-0.960	2.87	2.24
Avg.		-0.945 ± .009		2.15
% Avg. Dev.		0.95		2.80

Table 33

Studies of $CoCl_2 \cdot 6H_2O$ with LiCl as S. E. $m^{2/3}t^{1/6}$ = 1.876

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μ amps.	I
3.407	5600	-0.932	14.55	2.31
2.953	6200	-0.928	13.00	2.35
2.725	6000	-0.929	12.32	2.41
2.498	5500	-0.922	11.00	2.35
2.271	5500	-0.925	9.87	2.32
2.044	6600	-0.919	9.12	2.38
1.817	6200	-0.922	7.98	2.34
1.590	6200	-0.928	7.08	2.37
1.362	6200	-0.918	6.12	2.39
1.136	6000	-0.914	5.02	2.36
0.9085	5400	-0.914	4.17	2.45
0.4542	6200	-0.929	2.04	2.39
Avg.		-0.923 ± .005		2.37
% Avg. Dev.		0.54		1.43

Table 34

Studies of $CoCl_2 \cdot 6H_2O$ with $LiNO_3$ as S. E. in the presence of gum tragacanth. $m^{2/3}t^{1/6} = 1.636$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d µamps.	I
2.239	2000	-0.942	8.00	2.18
1.866	2000	-0.928	6.62	2.17
1.493	2000	-0.929	5.24	2.15
1.120	2000	-0.928	3.88	2.12
0.7464	2000	-0.925	2.61	2.14
0.3732	2000	-0.925	1.26	2.06
Avg.		-0.930 ± .005		2.12
% Avg. Dev.		0.54		1.72

Table 35

Studies of $PbCl_2$ with $LiNO_3$ as S. E. in the presence of gum tragacanth. $m^{2/3}t^{1/6} = 1.635$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d µamps.	I
1.063	2000	-0.398	4.95	2.85
0.8501	2000	-0.398	3.82	2.75
0.7084	2000	-0.399	3.26	2.81
0.5667	2000	-0.397	2.60	2.80
0.4250	2000	-0.396	1.96	2.82
0.2833	2000	-0.389	1.35	2.91
Avg.		-0.396 ± .003		2.82
% Avg. Dev.		0.76		1.66

Table 36

Studies of $PbCl_2$ with LiCl as S. E. in the presence of gum tragacanth.

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps	I	$m^{2/3}t^{1/6}$ $mg.^{2/3}sec.^{-\frac{1}{2}}$
1.683	6900	-0.321	7.88	2.61	1.819
1.063	6800	-0.322	4.50	2.60	1.629
0.8976	6050	-0.313	4.36	2.67	1.819
0.8501	6400	-0.324	3.74	2.70	1.629
0.7084	6400	-0.323	3.21	2.78	1.629
0.6732	6500	-0.314	3.23	2.63	1.819
0.5667	6400	-0.322	2.52	2.73	1.629
0.5610	6300	-0.319	2.70	2.65	1.819
0.4250	6600	-0.324	1.91	2.76	1.629
0.2833	6700	-0.321	1.29	2.79	1.629
0.1417	6500	-0.323	0.636	2.75	1.629
Avg.		-0.321 ± .004		2.66	
% Avg. Dev.		1.25		2.23	

Table 37

Studies of $ZnCl_2$ with LiCl as S. E. in the presence of gum tragacanth.

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μ amps.	I	$m^{2/3}t^{1/6}$ mg.$^{2/3}$sec.$^{-\frac{1}{2}}$
10.20	3800	-1.222	33.20	1.95	1.668
8.504	4300	-1.210	27.80	1.96	1.668
7.342	4300	-1.222	23.60	1.97	1.635
5.530	4800	-1.221	17.25	1.91	1.635
5.102	4400	-1.222	16.28	1.91	1.668
3.402	4500	-1.224	10.75	1.89	1.668
3.318	4500	-1.209	10.80	1.99	1.635
1.701	4900	-1.217	5.52	1.95	1.668
Avg.		-1.218 ± .005		1.94	
% Avg. Dev.		0.41		1.49	

Table 38

Studies of $CdCl_2$ with LiCl as S. E. in the presence of gum tragacanth.

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μ amps.	I	$m^{2/3}t^{1/6}$ mg.$^{2/3}$sec.$^{-\frac{1}{2}}$
1.496	5600	-0.829	5.76	2.05	1.871
0.9972	5800	-0.828	4.04	2.17	1.871
0.7978	5300	-0.825	3.54	2.37	1.871
0.4157	6500	-0.783	1.36	2.05	1.603
0.3326	6600	-0.794	1.15	2.16	1.603
0.2772	6600	-0.789	1.03	2.32	1.603
0.2217	6000	-0.807	0.834	2.35	1.603
Avg.		-0.808 ± .017		2.21	
% Avg. Dev.		2.10		5.29	

Table 39

Studies of $CdCl_2$ with $LiNO_3$ as S. E. in the presence of gum tragacanth.

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I	$m^{2/3}t^{1/6}$ mg.$^{2/3}$sec.$^{-\frac{1}{2}}$
2.020	2000	-0.765	8.12	2.36	1.702
1.748	2000	-0.762	7.06	2.37	1.702
1.326	2000	-0.762	5.55	2.41	1.702
1.077	2000	-0.756	4.54	2.48	1.702
0.8078	2000	-0.749	3.41	2.48	1.702
0.3326	2000	-0.723	1.24	2.32	1.623
0.2217	2000	-0.719	0.849	2.36	1.623
0.1109	2000	-0.705	0.411	2.28	1.623
Avg.		-0.743 ± .020		2.38	
% Avg. Dev.		2.69		2.33	

Table 40

Studies of first wave of $FeCl_3 \cdot 6H$ O with LiCl as S. E. in the presence of titan yellow. $m^{2/3}t^{1/6} = 1.901$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I
2.031	6100	-0.019	5.28	1.37
1.624	6300	-0.018	4.32	1.40
1.354	6300	-0.016	3.60	1.40
1.083	6200	-0.017	2.90	1.41
0.8124	6600	-0.016	2.12	1.37
0.5415	6600	-0.014	1.46	1.41
0.2708	6600	-0.015	0.23	1.39
Avg.		-0.016 ± .001		1.39
% Avg. Dev.		6.25		1.00

Table 41

Studies of $FeCl_2 \cdot 4H_2O$ with LiCl as S. E. in the presence of gum tragacanth. $m^{2/3}t^{1/6} = 1.736$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I
3.407	6700	-1.316	12.10	2.04
2.726	6700	-1.301	10.10	2.11
2.272	6700	-1.298	8.28	2.10
1.577	6700	-1.296	6.48	2.06
1.363	6200	-1.308	4.92	2.08
0.9086	7000	-1.298	3.36	2.13
Avg.		-1.303 ± .006		2.09
% Avg. Dev.		0.46		1.27

Table 42

Studies of $NiCl_2$ with $LiNO_3$ as S. E. in the presence of gum tragacanth. $m^{2/3}t^{1/6} = 1.640$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μ amps.	I
5.153	2000	-0.679	15.20	1.80
4.122	2000	-0.689	12.90	1.90
3.602	2000	-0.685	11.00	1.86
3.435	2000	-0.684	10.32	1.83
2.881	2000	-0.689	9.03	1.91
2.401	2000	-0.688	7.58	1.93
1.921	2000	-0.680	6.09	1.93
1.201	2000	-0.681	3.78	1.92
0.9605	2000	-0.675	2.98	1.89
Avg.		-0.683 ± .004		1.89
% Avg. Dev.		0.59		1.85

Table 43

Studies of $NiCl_2$ with LiCl as S. E. $m^{2/3}t^{1/6} = 1.797$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I
3.416	6700	-0.626	2.93	0.48
2.928	6200	-0.625	2.64	0.50
2.440	6200	-0.621	2.18	0.50
1.952	7100	-0.630	1.88	0.54
1.464	6600	-0.628	1.46	0.55
1.220	7000	-0.630	1.04	0.47
0.732	6300	-0.604	0.54	0.44
Avg.		-0.623 ± .006		0.50
% Avg. Dev.		0.96		5.20

Table 44

Studies of first wave of $CuCl_2$ with LiCl as S. E. in the presence of titan yellow. $m^{2/3}t^{1/6} = 1.912$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I
5.175	6100	-0.027	12.90	1.30
4.140	5600	-0.024	10.70	1.37
3.450	5900	-0.022	9.00	1.37
3.421	5900	-0.020	8.70	1.33
2.070	6600	-0.016	5.40	1.37
1.380	6600	-0.016	3.63	1.38
Avg.		-0.021 ± .004		1.35
% Avg. Dev.		19.0		1.97

Table 45

Studies of second wave of $CuCl_2$ with LiCl as S. E. in the presence of titan yellow.

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I	$m^{2/3}t^{1/6}$ mg.$^{2/3}$sec.$^{-\frac{1}{2}}$
5.559	5800	-0.420	14.64	1.44	1.825
5.175	6000	-0.410	14.03	1.42	1.911
4.485	5300	-0.412	11.90	1.45	1.825
4.140	5600	-0.403	11.30	1.43	1.911
3.795	6700	-0.415	10.30	1.49	1.825
3.450	6000	-0.400	9.45	1.46	1.911
3.421	6200	-0.398	9.36	1.43	1.911
3.105	6300	-0.404	8.16	1.44	1.825
2.415	6200	-0.395	6.24	1.41	1.825
2.070	6300	-0.397	5.58	1.41	1.911
1.380	6400	-0.415	3.82	1.45	1.911
1.033	6400	-0.405	2.18	1.42	1.825
0.6900	6400	-0.403	1.88	1.42	1.911
Avg.		-0.406 ± .007		1.44	
% Avg. Dev.		1.72		1.16	

Table 46

Studies of $AgNO_3$ with LiCl as S. E. in the presence of titan yellow. $m^{2/3}t^{1/6} = 1.692$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I
9.726	4600	-0.028	20.00	1.23
7.781	4200	-0.024	16.20	1.24
6.484	5100	-0.023	13.80	1.27
5.187	5200	-0.020	11.76	1.34
3.242	5200	-0.018	7.68	1.40
1.945	6500	-0.014	4.96	1.51
0.6484	6500	-0.013	1.74	1.59
Avg.		-0.020 ± .004		1.37
% Avg. Dev.		20.0		8.25

Table 47

Studies of HgCl with LiCl as S. E. in the presence of titan yellow. $m^{2/3}t^{1/6} = 1.702$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I
1.255	5300	-0.012	2.94	1.37
1.004	5200	-0.012	2.38	1.39
0.8369	5200	-0.011	1.97	1.38
0.6697	5600	-0.011	1.57	1.37
0.4184	5500	-0.011	1.08	1.51
0.3347	5400	-0.011	0.898	1.57
Avg.		-0.011 ± .0003		1.43
% Avg. Dev.		2.72		5.00

Table 48

Studies of $BiCl_3$ with LiCl as S. E. in the presence of titan yellow.

C ml./25ml.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μ amps.	$\frac{i_d}{ml.}$ x 10
15	8000	-0.049	3.00	2.00
12	6600	-0.062	2.68	2.23
10	6500	-0.063	2.20	2.20
8	6300	-0.061	1.46	1.83
6	6300	-0.060	1.50	2.50
4	6400	-0.056	1.04	2.60
2	6600	-0.053	0.625	3.12
Avg.		-0.057 ± .004		2.35
% Avg. Dev.		7.02		14.04

Table 49

Studies of first wave of $UO_2(NO_3)_2$ with $LiNO_3$ as S. E. in the presence of gum tragacanth. $m^{2/3}t^{1/6} = 1.655$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μ amps.	I
3.576	2000	-0.299	3.84	0.65
2.384	2000	-0.297	2.42	0.61
1.907	2000	-0.280	1.76	0.56
1.765	2000	-0.277	1.27	0.44
1.412	2000	-0.273	0.735	0.31
0.9536	2000	-0.265	0.484	0.31
0.4706	2000	-0.262	0.150	0.19
Avg.		-0.279 ± .011		
% Avg. Dev.		3.94		

Table 50

Studies of second wave of $UO_2(NO_3)_2$ with $LiNO_3$ as S. E. in the presence of gum tragacanth. $m^{2/3}t^{1/6} = 1.648$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I
2.861	2000	-0.789	3.74	0.65
2.384	2000	-0.755	2.97	0.34
1.765	2000	-0.604	1.26	0.43
1.430	2000	-0.603	0.90	0.38
1.412	2000	-0.602	0.78	0.34
1.176	2000	-0.610	0.88	0.45
0.9536	2000	-0.591	0.76	0.48
0.9411	2000	-0.573	0.58	0.37
0.7058	2000	-0.570	0.79	0.68
0.4768	2000	-0.585	0.61	0.76
0.4706	2000	-0.565	0.64	0.85
0.2384	2000	-0.589	0.48	1.22
0.2353	2000	-0.545	0.60	1.54

Table 51

Studies of third wave of $UO_2(NO_3)_2$ with $LiNO_3$ as S.E. in the presence of gum tragacanth. $m^{2/3}t^{1/6} = 1.630$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I
3.576	2000	-1.301	3.69	0.23
2.861	2000	-1.306	1.08	0.23
1.765	2000	-1.254	1.12	0.39
1.430	2000	-1.216	1.04	0.45
1.412	2000	-1.221	1.10	0.47
1.176	2000	-1.206	1.28	0.67
0.9536	2000	-1.193	1.04	0.67
0.9411	2000	-1.184	1.10	0.72
0.7058	2000	-1.175	0.99	0.85
0.4768	2000	-1.143	0.69	0.89
0.4706	2000	-1.139	0.90	1.17

Table 52

Studies of first wave of $SnCl_2$ with LiCl as S. E. in the presence of Triton W-30. $m^{2/3}t^{1/6} = 1.622$

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	I	t min.
2.419	3000	-0.471	9.48	2.42	30
1.935	3000	-0.478	7.38	2.35	50
1.827	3025	-0.474	6.12	2.06	70
1.462	3200	-0.472	4.83	2.03	90
1.097	3200	-0.474	3.40	1.91	110
0.731	3700	-0.479	1.98	1.67	140
3.148	2500	-0.470	5.04	0.99	22 hrs.
Avg.		-0.474 ± .003			
% Avg. Dev.		0.63			

Table 53

Studies of second wave of $SnCl_2$ with LiCl as S. E. in the presence of Triton W-30.

C mm./l.	R ohms	Corr. $E_{\frac{1}{2}}$ volts	i_d μamps.	i_d/c	t min.
2.419	3000	-0.963	0.278	0.12	30
1.935	3000	-0.954	1.02	0.54	50
1.827	3025	-0.961	1.05	0.57	90
1.462	3200	-0.962	0.816	0.56	110
3.148	2500	-0.956	5.04	1.60	22 hrs.
Avg.		-0.959 ± .003			
% Avg. Dev.		0.31			

chromium chloride hexahydrate, cobaltous chloride hexahydrate, lead chloride, zinc chloride, ferric chloride hexahydrate, ferrous chloride tetrahydrate, nickel chloride and cupric chloride under certain conditions of maximum suppression and type of supporting electrolyte. Cadmium chloride obeys the Ilkovic equation with slightly more than 2% average deviation using lithium nitrate as supporting electrolyte.

From tables 29 and 30 it is obvious that the second wave of chromium obeys the Ilkovic equation more accurately than the first wave. The values of I for the second wave are greater than twice the values of I for the first wave in contrast with what was stated previously. This is because the diffusion current of the second wave was calculated by drawing a line through the diffusion current parallel to the residual current instead of using the normal procedure. This was done because it gave a more linear relationship between i_d and concentration. If the standard prodecure was used the second wave was usually twice the first. A linear relationship between i_d and concentration was also obtained for the salt, chromium nitrate nonahydrate, when lithium nitrate was used as supporting electrolyte, although I, in this case, was found to be 2.63. This is considerably higher than the value 0.85 obtained for chromium chloride hexahydrate in the presence of lithium chloride as supporting electrolyte. This indicates that a different species was reduced in the two cases. It is known that when chromium chloride hexahydrate is treated with pyridine two chlorine atoms are replaced by pyridine and two water molecules by hydroxyl groups (31). This is not known to occur with the nitrate. Although the composition of each complex being reduced cannot be determined, there is obviously more pyridine coordinated with the chloride than with the nitrate.

It is apparent from the tables that gum gambogi and gum tragacanth have a slightly different effect on the cobalt wave, I being smaller in the case of gum tragacanth. Table 33 represents calculations in which the maxima were ignored, if present. This could be done since the maximum was small and not present in some cases. The results agree with those using gum gambogi as maximum suppressor, even though a different capillary was used. Indications are that gum gambogi is preferable as a maximum suppressor although a correction must be made for the blank. Using anhydrous cobaltous chloride and lithium nitrate as supporting electrolyte, a value of I is obtained which, although slightly smaller than when using lithium chloride as supporting electrolyte, is in sufficient agreement to indicate the same species is being reduced. However, in this latter case the color of the solution is pink whereas in solution using the hydrated cobaltous chloride the solution becomes blue upon addition of lithium chloride. If cobaltous chloride is dehydrated for six hours and dissolved in pyridine, the solution is blue. The value of I in this case is much smaller, having a value of 0.40 with a corresponding shift of half-wave potential indicating a different species is being reduced. Again the forms of the complex being reduced cannot be determined from the evidence presented.

Although lead chloride gives a percentage average deviation of more than 2% using two capillaries, a value of less than 2% is obtained for each capillary singly. Good agreement is obtained for the values of I for lead chloride and cadmium chloride using either lithium nitrate or lithium chloride as supporting electrolyte indicating the same species is reduced in both cases. Lithium nitrate is preferable as supporting electrolyte in the case of cadmium chloride.

According to the Ilkovic equation the value of I for the ferrous wave should be twice the value of I for the ferric wave since the ratio of the values of n is 2. This assumes that the two ions are coordinated with the same number of complexing groups, so that their diffusion coefficient is the same in the two cases. Since titan yellow is used as a maximum suppressor for ferric ion and gum tragacanth is used as a maximum suppressor for ferrous ion, it is not surprising that the values of I are not in the ratio of 2 to 1.

As in the case of cadmium chloride, lithium nitrate is preferable as supporting electrolyte for nickel chloride. Values of I indicate that a different species is being reduced in the presence of lithium chloride as supporting electrolyte than in the presence of lithium nitrate as supporting electrolyte, lending support to the possibility of competition between pyridine and chloride ion to complex with the nickel ion. The two waves of copper give approximately equal values of I indicating that both are one electron reductions. Whether the reduction is one of a copper pyridine complex or whether it is that of a complex between titān yellow and copper can not be determined from the data available.

It is not possible to evaluate the right hand side of the Ilkovic equation as a check since independent diffusion data for the ions in pyridine do not exist. However, in view of the success of the Ilkovic equation in other solvents there is little reason to doubt its validity in the present case.

The Ilkovic equation was not obeyed by silver nitrate, mercurous chloride, bismuth trichloride, stannous chloride dihydrate and uranyl nitrate hexahydrate. In the case of silver nitrate and mercurous nitrate, the Ilkovic equation seems to be obeyed over a very limited concentration range. In both cases the value of I begins to increase with decreasing concentration. It is believed the error lies in the method of calculating the diffusion current. Since it was impossible to obtain a residual current by beginning the curve at positive potentials due to anodic oxidation of mercury, the curves were calculated by drawing an arbitrary residual current at zero applied potential and the standard procedure employed.

The failure of the Ilkovic equation in the case of stannous and bismuth ions is attributed to hydrolysis. This is definitely established in the case of stannous ion by time studies shown in tables 52 and 53. The diffusion current of the first wave decreases with time and the diffusion current of the second wave increases with time. The half-wave potential of the second wave is also in agreement with that of pyridinium ion previously reported. The third wave of bismuth is also very likely that of pyridinium ion. The lack of linear relationship between diffusion current and concentration for the first and second wave of bismuth cannot be explained on this basis and at the present remains unexplained.

No reason is known for the failure of the Ilkovic equation in the case of uranyl nitrate hexahydrate. The values of I for the first wave decrease with decreasing concentration, values of I for the third wave increase with decreasing concentration and the values of I for the second wave seem to pass through a minimum with concentration. Three waves have been reported in aqueous solution, but the evidence for the reduction of the +5, +4, and +3 states, respectively, is rather meager (18). Only two waves are reported for uranyl ion in aqueous solution using a pyridine buffer (32). It is also known that in the presence of nitrate ion, uranyl ion causes a catalytic nitrate wave (33). This might explain the third wave.

Table 54 represents a comparison of diffusion current constants in water and pyridine. It is noted that in practically all cases the ratio of I for aqueous solutions to that of I for pyridine solutions varies from about 1.4 to 1.75. The values of this ratio for copper and mercury are a little low probably due to the presence of titan yellow in the solutions. The value of I for stannous ion used for comparison was one for which the solution had been standing only thirty minutes and a minimum of hydrolysis had taken place. A value of 1.55 was used for comparison in the case of silver ion since the maximum present did not disappear until concentrations below 3 millimolar were reached. The value of 1.4 - 1.75 may be compared to values of 1.5 - 1.6 for acetic acid (9), 1.29 for ethanol (24), 2.18 for fused salt media (26) and approximately .65 for liquid ammonia (6).

Table 54

Comparison of I in pyridine and water

Cation	$I(H_2O)$	S.E.(H_2O)	I(py.)	S.E.(py.)	$\frac{I(H_2O)}{I(py.)}$
Cd^{++}	3.58^a	1MHCl	2.21	0.8MLiCl	1.62
	3.54^b	0.7MLiNO$_3$	2.38	0.7MLiNO$_3$	1.49
Pb^{++}	3.86^a	1MHCl	2.66	0.8MLiCl	1.45
	3.76^b	0.8MLiCl	2.66	0.8MLiCl	1.41
Zn^{++}	3.24^c	-	1.94	0.8MLiCl	1.67
	3.35^b	0.8MLiCl	1.94	0.8MLiCl	1.73
Ni^{++}	3.18^c	-	1.89	0.7MLiNO$_3$	1.68
Co^{++}	3.15^b	0.8MLiCl	2.15	0.8MLiCl	1.47
Fe^{++}	3.24^b	0.8MLiCl	2.09	0.8MLiCl	1.55
Sn^{++}	4.07^a	1MHCl	2.42	0.8MLiCl	1.68
Cr^{+++}	1.31^b	0.8MLiCl	0.86	0.8MLiCl	1.52
(two waves)	3.28^b	0.8MLiCl	2.09	0.8MLiCl	1.57
Ag^{+}	2.49^c	-	1.55	0.8MLiCl	1.61
Hg^{+}	1.83^c	-	1.38	0.8MLiCl	1.32
Cu^{++}	1.70^d	1MHCl	1.35	0.8MLiCl	1.26
(two waves)	1.70^d	1MHCl	1.44	0.8MLiCl	1.19

a These values taken from the literature (34).

b Values determined in this laboratory.

c Values calculated from diffusion coefficients (18).

d Value of two electron reduction divided by two (34).

Reversibility Considerations

Perhaps the most useful criterion of reversibility of an electrode reaction in polarographic work is to plot the applied potential against the quantity log $i/(i_d - i)$ (18). If the electrode reaction is reversible the plot should give a straight line with a slope of -RT/nF in which R is the molar gas constant, T the temperature, F the value of the faraday and n the number of equivalents involved in the electrode reaction. For a one electron reduction the theoretical value at 25°C. would be -0.059 whereas -0.030 would be the theoretical value for a two electron reduction. To test the reversibility of the reduction of the cations previously mentioned these plots were made, in all cases correcting the values of applied potential for the iR drop.

In accord with results observed for cobaltous chloride hexahydrate in water (18) it was found that the reduction of cobaltous ion became more reversible with increased concentrations of chloride ion. Using 0.8 molar lithium chloride a slope of -0.072 was obtained whereas with 1 M lithium chloride a slope of -0.058 was obtained. Although a slope of -0.058 indicates a one electron reduction, and a one electron reduction of Co(II) to Co(I) has been reported in fused salt media (26) and in aqueous cyanide media (35), it is thought that in this case the reduction is merely an irreversible two electron reduction. In support of this the value of -0.044 was obtained using lithium nitrate as supporting electrolyte. This value, although indicating irreversibility, is closer to the theoretical value for a two electron reduction. It has also been reported that cobaltous ion yields a reversible two electron reduction in aqueous media with pyridine buffer (36).

Plots of log $i/(i_d - i)$ versus applied potential for chromic chloride hexahydrate gave values for the slopes of -0.066 and -0.076 for the first and second wave, respectively. The value of -0.066 is in sufficient agreement with the theoretical value of -0.059 to indicate a one electron reduction. The value of -0.076 for the second wave denotes irreversibility. This is in agreement with reduction in aqueous solutions as reported by Hamm and Shull (37).

Lead chloride was found to give a reversible two electron reduction in pyridine using lithium chloride as supporting electrolyte, giving a value for the slope of -0.033, in fair agreement with the theoretical value of -0.029. Using lithium nitrate as supporting electrolyte a slope of -0.041 was obtained indicating less reversibility.

The polarographic waves of cadmium chloride, zinc chloride, ferrous chloride and nickel chloride were found to be irreversible. Using lithium nitrate as supporting electrolyte, reversibility plots for cadmium chloride gave two straight lines of slopes of -0.143 and -0.071 indicating the possibility of two species being reduced whose half-wave potentials are too close together to permit complete separation. This may be due to an equilibrium between two pyridine complexes, one containing six moles of pyridine and one containing two moles of pyridine, both of which are known (38), or due to an equilibrium between a pyridine complex and a complex between the gum tragacanth and cadmium ion. Values of -0.078 and -0.068 were obtained from similar plots for the waves of zinc chloride and ferrous chloride, respectively. No attempts were made to make slope calculations for nickel chloride when lithium chloride was used as supporting electrolyte since it was obviously irreversible. When lithium nitrate was used as supporting electrolyte a value of the slope of -0.041 was obtained. Nickel is known to reduce reversibly in aqueous solutions using pyridine buffer (36) or in the presence of high concentrations of dehydrating chlorides (18).

For all the ions which required titan yellow as a maximum suppressor, slope plots yielded some rather peculiar results. The slopes for the cations involved are as follows: mercurous ion -0.015, ferric ion -0.008, silver ion -0.025, and for the two waves of copper -0.025 and -0.061. The values are all abnormally small except the second wave of copper which checks the theoretical value for a one electron reduction. Although the values of -0.025 are in fair agreement with the theoretical value for a two electron reduction, there is no mechanism of reduction that would be consistent with these values. The relative wave heights of the two waves for copper indicate that both are one electron reductions. Therefore, it must be concluded that all are irreversible except the second wave of copper.

Plots were not made for uranyl nitrate hexahydrate, stannous chloride or bismuth trichloride since the waves were obviously irreversible.

Considerations of Half-Wave Potential

As was stated previously, the only satisfactory procedure for comparing half-wave potentials in one solvent with those of another is to set up a table of half-wave potentials in each solvent and compare the order of ease of reduction in each solvent. Table 55 and 56 contain a summary of half-wave potentials in pyridine and in water in the order of ease of reduction in water. All the values in pyridine were run using 0.8 molar lithium chloride as supporting electrolyte. In setting up a table in water, values were selected in which the supporting electrolyte was a chloride salt of comparable concentration in so far as this was possible. In cases where values were given for 0.1 molar chloride, values were run in this laboratory against the quiet pool of mercury using 0.8 molar lithium chloride as supporting electrolyte.

The first significant thing about the table is that the ions mercurous, ferric, silver, and cupric have definite values, whereas in water they all reduce at zero applied potentials. Actually the reduction begins at zero applied potential in pyridine also, but the slopes are such that a value for the half-wave potential can be assigned. The order of ease of reduction is considerably different in pyridine than it is in water. Lead and copper (I) have changed places in pyridine, the lead reducing more easily. Nickel

Table 55

Summary of Half-Wave Potentials

Cation	$E_{\frac{1}{2}}(H_2O)$ S.C.E.	S.E.	$E_{\frac{1}{2}}(H_2O)$ Q.P.M.[e]	$E_{\frac{1}{2}}$(py.) Q.P.M.[e]	S.E.
Hg_2^{++}	zero[a]	KCl	-	-0.011±.001	0.8MLiCl
Fe^{+++}	zero[a]	KNO_3	-	-0.016±.001	0.8MLiCl
Ag^{+}	zero[a]	KCl	-	-0.020±.004	0.8MLiCl
Cu^{++}	zero[d]	0.8MLiCl	-	-0.021±.004	0.8MLiCl
Bi^{+++}	-0.08[a]	1MHCl	-	-0.057±.004	0.8MLiCl
Cu^{+}	-0.166[d]	0.8MLiCl	-0.222[d]	-0.406±.007	0.8MLiCl
Pb^{++}	-0.435[a]	1MKCl	-0.432[b]	-0.321±.004	0.8MLiCl
Sn^{++}	-0.47[c]	1MHCl	-	-0.474±.003	0.8MLiCl
Cd^{++}	-0.642[a]	1MKCl	-	-0.808±.017	0.8MLiCl
Cr^{+++}	-0.88[a]	0.1MKCl	-0.904[b]	-0.430±.004	0.8MLiCl
Zn^{++}	-1.022[a]	1MKCl	-1.044[b]	-1.218±.005	0.8MLiCl
Ni^{++}	-1.1[a]	1MKCl	-	-0.623±.006	0.8MLiCl
Co^{++}	-1.2[a]	0.1MKCl	-1.221[b]	-0.923±.005	0.8MLiCl
Fe^{++}	-1.30[a]	0.1MKCl	-1.400[b]	-1.303±.006	0.8MLiCl
Cr^{++}	-1.53[a]	0.1MKCl	-1.525[b]	-1.366±.010	0.8MLiCl

a. Values taken from the literature (18)

b. Values determined in this laboratory.

c. Value taken from the literature (34).

d. Value determined in this laboratory using titan yellow as maximum suppressor.

e. Q.P.M. represents quiet pool of mercury

Table 56

Summary of Half-Wave Potentials

Cation	$E_{\frac{1}{2}}(H_2O)$ S.C.E.	S.E.	$E_{\frac{1}{2}}(H_2O)$ Q.P.M.[d]	$E_{\frac{1}{2}}$(py.) Q.P.M.[d]	S.E.
UO_2^{++}	-0.190[b]	0.7M$LiNO_3$	-0.502[b]	-0.279±.011	0.7M$LiNO_3$
Pb^{++}	-0.405[a]	1MKNO_3	-	-0.396±.003	0.7M$LiNO_3$
Sn^{++}	-0.44[c]	1MKNO_3	-	-0.380	0.7M$LiNO_3$
Cd^{++}	-0.586[a]	1MKNO_3	-0.762[b]	-0.743±.020	0.7M$LiNO_3$
Cr^{+++}	-0.88[a]	0.1MKCl	-	-0.995±.004	0.7M$LiNO_3$
Ni^{++}	-1.044[b]	0.7M$LiNO_3$	-1.225[b]	-0.683±.004	0.7M$LiNO_3$
Co^{++}	-1.20[a]	1MKCl	-	-0.930±.005	0.7M$LiNO_3$

a. These values were taken from the literature (18).

b. These values were determined in this laboratory.

c. This value was taken from the literature (34).

d. Q.P.M. represents quiet pool of mercury.

and cobalt have changed places in the two tables. This is to be expected since it is known that pyridine is used in aqueous solutions to shift the potentials of nickel and cobalt such that they can be determined. The relative difference in their potentials in aqueous pyridine buffered solutions and in pyridine as a solvent is of the same magnitude. The first step in the reduction of chromium chloride hexahydrate undergoes a shift to a position of greater ease of reduction in pyridine as a solvent as compared to its position in water as a solvent. This shift is attributed to the complex of chromium and pyridine previously mentioned. If chromium nitrate nonahydrate is run in the presence of lithium chloride only one wave is obtained, which reduces at -1.300 volts against the quiet pool of mercury, whereas if it is run using lithium nitrate as supporting electrolyte only one wave is obtained which reduces at -0.995 volts against the quiet pool of mercury. This is added evidence that only the chloride forms the complex with pyridine as previously described. Zinc is the only ion which is shifted to a position of more difficult reducibility in the table. This can only be attributed to a more stable complex of zinc and pyridine relative to the other pyridinated ions.

In the presence of lithium nitrate as supporting electrolyte, there are also some changes in the order of reduction as seen in table 56. Lead and stannous ion interchange places in pyridine as do nickel and cobalt. The relative difference between the potentials of cobalt and nickel is smaller when lithium nitrate is used as supporting electrolyte.

It was found that it was possible to prepare both blue and pink solutions of cobalt in pyridine by different degrees of dehydration of the hydrated cobalt chloride. By dehydrating for three hours a blue salt was obtained which gave a pink solution when dissolved in pyridine. By dehydrating for six hours a blue tarry mass was obtained which gave a blue solution in pyridine. These two solutions gave different half-wave potentials. The blue solution gave a half-wave potential of -1.000 volts versus the quiet pool of mercury, whereas the pink solution gave a half-wave potential of -0.927 volts versus the quiet pool of mercury. This shift of half-wave potential is in the opposite direction to that in which the shift of half-wave potential occurs in aqueous solutions from the blue to the pink state.

Cadmium chloride and uranyl nitrate hexahydrate are the only cations in which the half-wave potential is not constant with changes in concentration of the reducible ion. In the case of the cadmium chloride, the half-wave potential shifts to more positive values with decreasing concentration using either lithium chloride or lithium nitrate as supporting electrolyte. This might also be explained on the basis of an equilibrium between two different complexes with pyridine as mentioned before or an equilibrium between a pyridine complex and a complex between cadmium ion and gum tragacanth. The half-wave potentials of the first, second and third waves of uranium shift to more positive values with decreasing concentration of uranyl ion. The only explanation that can be offered for this non-constancy of half-wave potentials is the irreversibility of the reaction.

In considering water as a solvent for analytical applications, it is usually stated that if one cation is to be analyzed for in the presence of another, their half-wave potentials should differ by 200 millivolts. Since many of the waves are less reversible in pyridine and have a greater slope due to the resistance of the solution a separation of 200 millivolts is not always sufficient, but the slope of the wave in question must be considered. It would be impossible to determine nickel and cobalt in the presence of each other using lithium chloride as supporting electrolyte, since the wave for nickel requires such a large span for development. However, using lithium nitrate as maximum suppressor it becomes possible. The following cations give waves which might be used for analysis: lead, chromium, zinc, ferrous, cobalt, nickel and copper.

Summary

It was found that the half-wave potential of pyridinium ion was shifted to more positive potentials by increasing the percentage of pyridine by volume in the solution. Extrapolation gives a value of -0.918 volts against the quiet pool of mercury and -1.283 volts against the saturated calomel electrode for the half-wave potential of pyridinium ion. The diffusion current of pyridinium ion decreases with the water-pyridine ratio, passing through a minimum at 10% water, and then increasing with increasing values of the water-pyridine ratio.

A survey was made of the ions which could be reduced in pyridine. The salts chromium chloride hexahydrate, cobaltous chloride hexahydrate, lead chloride, zinc chloride, ferric chloride hexahydrate, ferrous chloride tetrahydrate, nickel chloride, cupric chloride and cadmium chloride were found to give well defined waves which obeyed the Ilkovic equation. Silver nitrate, mercurous chloride, bismuth trichloride, stannous chloride dihydrate and uranyl nitrate hexahydrate all yield polarographic waves but do not obey the Ilkovic equation. For those ions that obey the Ilkovic equation it was found that the diffusion current constant was smaller in pyridine than in water and that the ratio of diffusion current constant in water to the diffusion current constant in pyridine varied from 1.4 to 1.75.

Reversibility plots of the salts tested indicate that only the first wave of chromic chloride hexahydrate, the second wave of cupric chloride, and the wave of lead chloride are reversible in pyridine.

A table of half-wave potentials against the quiet pool of mercury as reference electrode in pyridine is presented. The changes in ease of reduction as compared to water are discussed.

Possibilities For Future Work

In so far as a polarographic determination of organochlorosilanes through use of non-aqueous media is concerned, there is one solvent that might bear further investigation. Since it is believed that hydrogen ion is a necessity if any polarographic separation of one organochlorosilane in the presence of another is to be obtained, anhydrous acetic acid might be a possibility. It has one difficulty in that it has a very limited operable span of potential. It would seem that a better form of analysis would result by trying other methods than the polarograph. An analysis of organochlorosilanes by use of infrared spectrophotometry seems very possible and should be worthy of investigation. A review of the literature indicates that infrared spectrophotometry has been applied to only trichlorosilane (39).

The success of the polarographic investigation of cation reduction in pyridine leads to three possibilities for future work. First, it would be of interest to investigate reductions of organic compounds in pyridine as a solvent. Presumably, many organic compounds which are insoluble in water and hence cannot be tested polarographically in that medium could be treated in pyridine, provided they did not react with the pyridine. Secondly, it would be of interest to investigate the effect of water on many of the cation reductions tested in pyridine. Although the effect of pyridine-water ratios was tested on pyridinium ion, this does not necessarily mean similar effects would be observed for other cations. Chromium chloride hexahydrate should be of special interest in this respect since it seems to undergo the greatest change of half-wave potential in the presence of pyridine. Thirdly, it would be of interest to investigate the reduction of cations in other organic solvents more thoroughly. Some work has been done in formamide (15), but only in water mixtures. Formamide has a very high dielectric constant, higher than that of water, and for this reason should have excellent solvent properties. Acetamide would be of similar interest, but it has the added inconvenience of the necessity for working at elevated temperatures since it is a solid at room temperature. Acetonitrile is another solvent that should be worthy of investigation since it has a relatively high dielectric constant and is not known to reduce polarographically.

Further work should also be done on electrocapillary curves in pyridine in an effort to determine the reason for maxima in pyridine. This might also be of value in determining the mechanism of maxima suppression in pyridine through analogy with aqueous solutions.

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