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DETERMINATION OF HEXAFLUOROPHOSPHATE AND TETRAFLUOROBORATE ANIONS WITH TETRAARYLARSONIUM SALTS.

The University of Oklahoma, Ph.D., 1964
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

DETERMINATION OF HEXAFLUOROPHOSPHATE AND TETRAFLUOROBORATE ANIONS WITH TETRAARYLARSONIUM SALTS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

VERNON SHELBY ARCHER

Norman, Oklahoma

1964

DETERMINATION OF HEXAFLUOROPHOSPHATE AND

TETRAFLUOROBORATE ANIONS WITH

TETRAARYLARSONIUM SALTS

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ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. Harold E. Affsprung for suggesting the problem and for his patience, guidance, and encouragement during the course of this research.

In addition the author wishes to thank all of the faculty for their guidance and assistance.

He would also like to express his appreciation to Dr. W. E. White of the Ozark-Mahoning Company of Tulsa, Oklahoma, for donating various fluoride compounds used in this research.

Finally, the author wishes to express his gratitude to his wife for typing the dissertation and for her assistance during the course of his graduate program.

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DETERMINATION OF HEXAFLUOROPHOSPHATE AND TETRAFLUOROBORATE ANIONS WITH TETRAARYLARSONIUM SALTS

CHAPTER I

INTRODUCTION

The fluorophosphoric acids and their salts were first prepared by Lange (25) in the late 1920's. Small amounts of hexafluorophosphoric acid, as well as difluorophosphoric acid, were formed by dissolving phosphorus pentoxide in a concentrated hydrofluoric acid solution. It was found that the difluorophosphoric acid hydrolyzed faster than hexafluorophosphoric acid, which made it possible to hydrolyze the HPO_2F_2 and afterwards precipitate the HPF_6 with Nitron (1:4-Diphenyl-3:5-endanilo-4:5-dihydro-1:2:4-triazole) acetate reagent. The potassium salt could then be prepared by a metathesis reaction of Nitron hexafluorophosphate with potassium nitrate, since the highly insoluble Nitron nitrate would precipitate out of solution leaving relatively pure KPF_6 in the supernatent liquid. This original preparative method of Lange gave only 0.4% yields.

A method of preparation originating with Lange and

Krueger (27) involves heating phosphorus pentachloride with an alkali metal fluoride at 80°-110°C.:

$$PCl_5 + 6MF = MPF_6 + 5MCl.$$

If "M" is potassium, an 80% yield is obtained, whereas a 67% yield is obtained if "M" represents the ammonium radical. In this procedure the hexafluorophosphate is precipitated with Nitron after dissolving the reaction products in water.

Another method (61) for preparing ammonium and alkali metal salts of hexafluorophosphoric acid involves reacting phosphorus pentachloride with the chloride of the cation in anhydrous liquid hydrogen fluoride:

$$MCl + PCl_5 + 6HF = MPF_6 + 6HCl.$$

In this procedure the metal chloride is dissolved in anhydrous hydrogen fluoride in a monel, stainless steel, or nickel vessel which is cooled in an ice-salt bath. The PCl_5 is very slowly added with stirring to the solution. The hexafluorophosphate salt precipitates immediately. The excess hydrogen fluoride is removed by heating the reaction mixture on an oil bath at 150°C. Since the ammonium and sodium salts are very soluble in water, they are usually recrystallized from methanol under reduced pressure after first making the solution basic with the appropriate hydroxide in order to precipitate iron impurities.

Hexafluorophosphoric acid (57) may be prepared by reacting phosphorus pentoxide with anhydrous hydrogen fluoride in a closed silver or aluminum container with cooling. It is

not possible to reach the theoretical composition of 76.5 weight percent HPF_6 due to hydrolysis of the hexafluorophosphate anion in the strongly acid medium.

$$12HF + P_2O_5 = 2HPF_6 + 5H_2O$$

A recent method (20) for preparation of hexafluorophosphate involves the use of sulfur tetrafluoride as a fluorinating agent. A mixture of molar ratio $2NaF:1P_2S_5$ is fluorinated with excess SF_4 in a stainless steel bomb under pressure. The bomb is rocked and heated overnight, and the gaseous products are removed. The following equation has been found to hold for this reaction:

$$2NaF + P_2S_5 + 3SF_4 = 2NaPF_6 + 6S + S_2F_2.$$

Lange (25) determined that the hexafluorophosphate anion was extremely stable in basic solution, whereas it was hydrolyzed slowly in acidic solutions. Indeed it was found that molten alkali is required in order to decompose the ion in basic media. The following equilibria (26) have been found to hold in acid solution:

$$H_3PO_4 \underset{-H_2O}{\overset{HF}{=}} H_2PO_3F \underset{-H_2O}{\overset{HF}{=}} HPO_2F_2 \underset{-2H_2O}{\overset{4HF}{=}} HPF_6.$$

Pure Hexafluorophosphoric acid cannot be prepared; however, $HPF_6 \cdot 6H_2O$ (26) crystallizes from solution when concentrations of water and the acid are carefully adjusted to the stoichiometric amounts, and the solution is cooled immediately to low temperatures to "freeze" the equilibrium. This hexahydrate melts at 31.5°C. and immediately upon melting,

begins to reestablish equilibrium conditions so that the melt will soon contain equilibrium concentrations of the other fluorophosphoric acids, H_3PO_4 and HF.

Commercial samples of concentrated hexafluorophosphoric acid (57) will have an approximate concentration as follows: 65% HPF_6, 6% HF, 21% H_2O, and 8% of a mixture of HPO_2F_2, H_2PO_3F, and H_3PO_4.

Johnson and Bands (19) found that HPF_6 titrates as a strong acid and that its conductivity corresponds to that of a strong electrolyte.

Potassium hexafluorophosphate (47) has been one of the easiest salts to purify due to its large positive heat of solution in water. Aqueous solutions of this salt are neutral and quite stable. From apparent molecular weight determinations by measurements of vapor pressures and electrical conductivities (43) it appears that KPF_6 is associated to a considerable extent as ion pairs and higher aggregates in aqueous solutions.

The sodium salt can be crystallized from aqueous methanol solution as the monohydrate. This hydrate (61) can be dehydrated over sulfuric acid.

The double salt $NH_4PF_6 \cdot NH_4F$ (26) crystallizes from solutions of ammonium hexafluorophosphate which contain fluoride. The crystalline compound (55) is unreactive toward glass, but the salt sublimes at 140°C. and its vapor does attack glass. This would seem to indicate partial dissociation

to give HF.

It has been found that many slightly soluble hexafluorophosphates (28) correspond to slightly soluble perchlorates. This correspondence is helpful in finding suitable analytical reagents for hexafluorophosphate analysis.

The only method, reported prior to 1963, for the specific analysis of hexafluorophosphates involves a gravimetric precipitation of HPF_6 with Nitron reagent according to the method of Lange and Muller (28):

$$C_{20}H_{12}N_4HAc + HPF_6 = C_{20}H_{12}N_4HPF_6 + HAc.$$

At this time two articles (1,2) were published on the determination of hexafluorophosphate with tetraphenylarsonium chloride. These papers reported upon a portion of the material presented in this dissertation.

According to Booth and Martin (13), Gay-Lussac and Thenard first produced a fluoroboric acid in 1809. The acid was obtained by passing excess BF_3 gas into water. The resulting solution was a clear syrupy liquid which was much denser than water. The acid thus obtained was probably HBF_3OH rather than HBF_4.

Another early method (13) for the preparation of tetrafluoroboric acid involved the addition of boric acid to a solution of concentrated hydrofluoric acid at 0°C. Wamser (56) has shown that the following reactions occur when boric acid is added to concentrated hydrofluoric acid:

$$H_3BO_3 + 3HF = HBF_3OH + 2H_2O$$

$$HBF_3OH + HF = HBF_4 + H_2O.$$

The first reaction occurs very rapidly, but the second is sufficiently slow to allow a study of its kinetics. Both HBF_4 and HBF_3OH are strong acids, but conductance measurements indicate that the former is somewhat stronger than the latter in aqueous solution.

Tetrafluoroboric acid solutions hydrolyze slowly to give HBF_3OH and HF. Wamser (56) found that a 0.01018 molar solution was 35.5% hydrolyzed at equilibrium. The hydrolysis constant at 25°C. was found to be 2.3×10^{-3} moles per liter. Ryss (44) reported this constant to be 2.8×10^{-3} moles per liter at 25°C.

The various salts of tetrafluoroboric acid may be prepared from solutions of the acid mixed with the appropriate base, and by methods analogous to the preparation methods utilized for hexafluorophosphates.

It was shown earlier (58) that the tetrafluoroborate ion and the perchlorate ion show some similarities in their properties. Klinkenberg (21) determined by means of an x-ray crystallographic analysis that sodium, cesium, and lithium tetrafluoroborates are isomorphous with the corresponding perchlorates. In addition the sodium and ammonium salts are quite soluble, but the potassium salt has a low solubility in water, as is also the case for the corresponding perchlorates.

At present two methods for the direct determination

of tetrafluoroborate are described in the literature: the method of Lange (24) which involves the precipitation of Nitron tetrafluoroborate and the method of Schaak and Wagner (48) which utilizes cetyltrimethylammonium chloride as a precipitating reagent.

In the gravimetric Nitron procedure (24), approximately 20 milliliters of 5% acetic acid containing 1.3 grams of Nitron reagent is added slowly with stirring to 100 milliliters of dilute acetic acid solution containing approximately 200 milligrams of the tetrafluoroborate. The mixture is then cooled in an ice bath for two hours, filtered and washed with a small amount of dilute acetic acid. Unfortunately, the Nitron tetrafluoroborate is too soluble for a simple gravimetric procedure and it is necessary to apply an empirical correction factor in this determination.

The second method (48) involves a rather complicated indirect titration procedure. Cetyltrimethylammonium tetrafluoroborate is one-tenth as soluble as Nitron tetrafluoroborate; however, the precipitate sinters when heated at 105°C., and the gravimetric procedure does not give reproducible results. In the titrimetric procedure an excess of a standard solution of the reagent is added to an HBF_4 solution. The solution is neutralized with sodium hydroxide, filtered, and excess standard $K_4Fe(CN)_6$ is added to the filtrate. The excess $K_4Fe(CN)_6$ is then titrated with standard $KMnO_4$ in dilute sulfuric acid medium. The following series of equations represent

the reactions that occur:

$$C_{19}H_{42}NCl + HBF_4 = C_{19}H_{42}NBF_4 + HCl$$

$$4C_{19}H_{42}NCl + K_4Fe(CN)_6 = (C_{19}H_{42}N)_4Fe(CN)_6 + 4KCl$$

$$4H_2SO_4 + 5K_4Fe(CN)_6 + KMnO_4 = MnSO_4 + 5K_3Fe(CN)_6 + 4H_2O + 3K_2SO_4.$$

Other methods for the determination of tetrafluoroborate ion depend upon the hydrolysis of the anion and subsequent determination of the amount of fluoride or borate produced. A recent method (17) for the analysis of borates involves the conversion of the borate to tetrafluoroborate, extraction of tetraphenylarsonium tetrafluoroborate into chloroform, and subsequent determination of the boron colorimetrically with curcumin (turmeric) by the method of Philipson (42).

Typical of one type of fluoride analysis used for tetrafluoroborate solutions is the following procedure due to Ryss (45). An aqueous solution of tetrafluoroborate is boiled with excess calcium chloride:

$$BF_4^- + 2Ca^{+2} + 3H_2O = 2CaF_2 + H_3BO_3 + 3H^+.$$

The reaction is quantitative if some base is added to take up the hydrogen ion. Sodium acetate serves this purpose very well. The precipitate is filtered, dried, and weighed.

Another scheme for fluorine analysis in tetrafluoroborate solutions is that of Maksimycheva, Talipov, and Koginova (31). They utilize acid hydrolysis of the tetrafluoroborate anion and subsequent titration of the fluoride with 0.1 normal $Th(NO_3)_4$ using sodium alizarin sulphonate as indicator.

Of the many metal-organic "onium" compounds synthesized during the last thirty years, tetraphenylarsonium chloride has been most utilized as an analytical reagent. The first preparation of tetraarylarsonium salts was reported in a short communication by Blicke and Marzano (9). Later Blicke and Monroe (10) reported on the synthesis of tetraphenylarsonium chloride. They prepared tetraphenylarsonium salts by addition of phenylmagnesium bromide to the arsenic-oxygen double bond in triphenylarsine oxide.

Chatt and Mann (16) later synthesized tetraphenylarsonium halides by reacting anhydrous aluminum chloride, triphenylarsine and bromobenzene at high temperatures. This method was also used to prepare tetraphenylphosphonium and tetraphenylstibonium salts. Lyon and Mann (29) investigated the mechanism of the reaction and determined the best experimental conditions, in addition to synthesizing some new tetraarylonium compounds.

Lamprey (23) in 1935 utilized tetraphenylarsonium chloride as a gravimetric reagent for perchlorate, periodate, and for gold and platinum chloride complexes. One of the earliest analytical procedures (60) utilizing tetraphenylarsonium chloride involved the addition of an excess of a standard solution of tetraphenylarsonium chloride to precipitate an anionic complex followed by a subsequent potentiometric titration with potassium triiodide. This method was used to determine mercury, cadmium, and zinc as the chloride complexes.

Affsprung, Barnes, and Potratz (3) developed a spectrophotometric method for determination of cobalt by extraction of the tetraphenylarsonium salt of a cobalt thiocyanate complex into chloroform. This method was later adapted to the determination of cobalt in stainless steels, inconels, nickel, and chromium by Pepkowitz and Marley (41).

Tribalet (54) developed a colorimetric method for rhenium based in part on the extraction of tetraphenylarsonium perrhenate. Beeston and Lewis (8) determined rhenium spectrophotometrically by extraction of tetraphenylarsonium perrhenate into chloroform solution. Andrew and Gentry (6) have utilized tetraphenylarsonium chloride to determine rhenium in tungsten-rhenium and molybdenum-rhenium alloys spectrophotometrically. Magee and Al-Kayssi (30) have reported an infrared method for determination of small quantities of perrhenate and pertechnetate. These ions are coprecipitated with perchlorate as the tetraphenylarsonium salts. A weighed amount of the precipitate is pressed into a KBr disc and the absorbance is measured in the infrared.

An amperometric titration method utilizing tetraphenylarsonium chloride as titrant for stannic and mercuric chloride complexes has been reported by Kolthoff and Johnson (22). Menis, Ball, and Manning (33) have developed an amperometric titration method which involves the precipitation of $(C_6H_5)_4AsHgCl_2NO_3$.

A gravimetric procedure for tellurium has been

developed by Bode (12). This method depends upon the precipitation of $(C_6H_5)_4AsTeCl_6$. The same author (11) has determined platinum as the bromide complex gravimetrically with tetraphenylarsonium chloride.

Murphy and Affsprung (35) have reported a spectrophotometric method for gold based upon the extraction of tetraphenylarsonium tetrachloroaurate (III) into chloroform.

Shinagawa, Matsuo, and Nakashima (50) studied the polarographic behavior of tetraphenylarsonium chloride in the concentration range 10^{-2} to 10^{-4} molar using 0.1 molar KCl as supporting electrolyte. The half-wave potential was -1.42 volts versus SCE and the limiting diffusion current was found to be proportional to the concentration in this concentration range. They used tetraphenylarsonium chloride for amperometric titrations of iodide, thiocyanate, and the cyanide complexes of bismuth, cadmium, and mercury.

Neeb (36, 37, 38, 39, 40) has utilized tetraphenylarsonium and tetraphenylphosphonium chlorides for the determination of iridium, platinum, and osmium by gravimetric and spectrophotometric techniques.

Willard and Perkins (59) have determined tin (IV), cadmium, and mercury as the chloride complexes using tetraphenylphosphonium chloride. In addition they determined permanganate and perchlorate using both tetraphenylphosphonium chloride and tetraphenylstibonium chloride.

Bismuth (32) has been determined spectrophotometri-

cally by extraction of $(C_6H_5)_4PBiI_4$ into chloroform.

Shinagawa, Matsuo, and Nezu (49) have investigated the polarographic behavior of tetraphenylphosphonium chloride using 0.1 molar KCl as supporting electrolyte. A maximum occurred at -1.85 volts versus SCE, and the limiting diffusion current was found to be proportional to the concentration of tetraphenylphosphonium chloride in the range 10^{-2} to 5×10^{-5} molar.

Affsprung and May (5) have utilized tetraphenylstibonium sulfate to form derivatives of organic acids for qualitative analysis purposes. Affsprung and Gainer (4,18) found that tetratolylstibonium sulfate formed better organic acid derivatives than did tetraphenylstibonium sulfate. They have tabulated melting point data for a great number of these salts.

Shinagawa, Matsuo, and Okashita (51) studied the polarographic behavior of tetraphenylstibonium chloride and found that the onium ion was reduced in two steps. The two half-wave potentials were found to be -0.74 volts and -1.13 volts versus SCE. They found that the diffusion current of the first wave was proportional to the concentration of tetraphenylstibonium ion for concentrations less than 6×10^{-3} molar.

Lyon and Mann (29) first prepared tetra-p-tolylarsonium iodide using the aluminum chloride reaction with tri-p-tolylarsine and p-bromotoluene. The melting point was found to be 253-255°C. Gainer (18) later prepared tetra-p-

tolylarsonium chloride by reacting tri-p-tolylarsine oxide with p-tolylmagnesium bromide. The hydrochloride of tetra-p-tolylarsonium chloride came down as an oil and he did not succeed in crystallizing the chloride salt.

Michaelis (34) has prepared tri-p-tolylarsine by reacting p-bromotoluene and arsenic trichloride with sodium in ether. Sachs and Kantorowicz (46) have described the preparation of tri-p-tolylarsine by reacting p-tolylmagnesium bromide with arsenious acid. Tri-p-tolylarsine (53) has also been prepared by reacting arsenic trichloride with p-tolylmagnesium bromide in ether. The yield was 46% of product which melted at 147°-148°C.

Tri-p-tolylarsine oxide has been reported by Carson and Wong (15). The oxide, which melted at 130°-133°C., was found to take up water rapidly and to form tri-p-tolylarsine dihydroxide (M. P. 92°-93°C.).

CHAPTER II

OBJECTIVES

The objectives of this research were:

1. To develop new analytical methods for the hexafluorophosphate and tetrafluoroborate anions;
2. To study analytically useful properties of tetraphenylarsonium chloride and apply these to the determination of the above fluoride complexes; and
3. To prepare tetra-p-tolylarsonium salts and study some of their physical properties.

CHAPTER III

EXPERIMENTAL

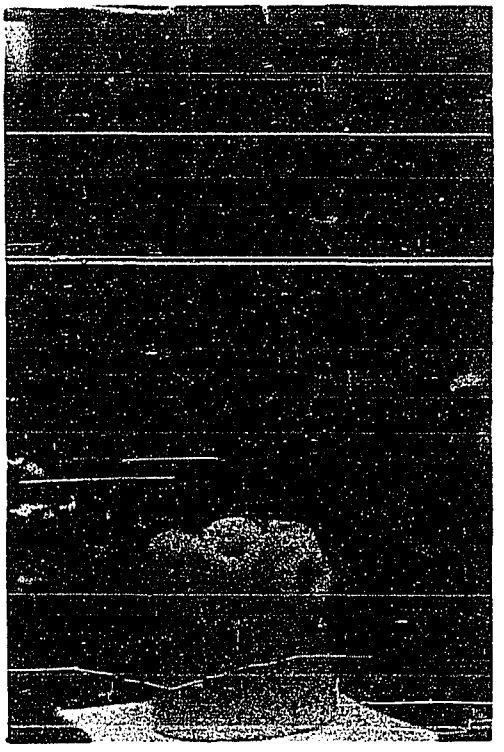
Apparatus

The following instruments and special apparatus were used in the course of this investigation:

1. Sargent Model XXI recording polarograph.
2. Beckman Zeromatic pH Meter.
3. Beckman DK-1, DB, and DU spectrophotometers.
4. A large circulating water bath utilizing a Sargent Thermonitor temperature regulator with an accuracy of $\pm 0.01^{\circ}C$.
5. A Manostat microburet capable of measurements in the range 0 to 10 ml. with a precision of ± 0.002 ml.
6. An H-type polarograph cell with a sintered glass disc and agar-agar saturated KCl bridge separating the sample half-cell from the saturated calomel reference (SCE).
7. A special cell, shown in Figure 1, designed for amperometric titrations. A cut-off 250 ml. polyethylene bottle was used as the titration vessel. The bottom half of a 500 ml. polyethylene bottle was used as a cover. Holes were cut in the cover to admit the dropping mercury elec-

FIGURE 1

AMPEROMETRIC TITRATION APPARATUS



trode, the reference half cell, a nitrogen tube, a thermometer, and the buret. A saturated calomel dip cell was used as the reference electrode. Contact was made with the solution by means of an asbestos fiber acting as a KCl salt bridge.

Reagents

Tetraphenylarsonium chloride (TPAC) was obtained from K and K Laboratories and G. F. Smith Chemical Company.

Potassium hexafluorophosphate, ammonium tetrafluoroborate, sodium monofluorophosphate and difluorophosphoric acid were donated by the Ozark-Mahoning Company. The KPF_6 was recrystallized by dissolving in hot water, adding sufficient potassium hydroxide to make the solution strongly basic, filtering out any metallic hydroxides which precipitate and allowing the filtrate to cool until the salt crystallized out. The white salt was then washed with cold water and ethanol, and dried in a vacuum desiccator.

Nitron (1:4 Diphenyl-3:5-endanilo-4:5-dihydro-1:2:4-triazole) reagent was obtained from Eastman Organic Chemicals.

Para-bromotoluene was purchased from Columbia Organic Chemicals and purified by crystallization until the bulk melting point was 26.8°C.

All additional chemicals were either reagent grade or analytical reagent grade materials.

Study of Analytically Useful Properties of Tetraphenylarsonium Chloride

Preparation and Standardization of a Tetraphenylarsonium Chloride Solution

A solution was prepared containing 11.3838 g. of tetraphenylarsonium chloride (TPAC) in 360 ml. of water containing sufficient sodium hydroxide to give a final pH of 7. This solution was then standardized against a triiodide solution according to the method of Willard and Smith (60).

An iodine solution containing approximately 40 g. of potassium iodide and 13 g. of iodine diluted to one liter was prepared. This solution was standardized titrimetrically against arsenious oxide using starch indicator. Table I (a) gives the results of this standardization.

Two milliliter aliquots of the tetraphenylarsonium chloride solution were taken using the Manostat microburet. One hundred milliliters of 3 M. sodium chloride was added to each aliquot and the solutions were titrated to a potentiometric end-point using a Beckman Zeromatic pH meter equipped with a SCE reference electrode and a shiny platinum wire indicator electrode. Just before the end-point was reached the solution was saturated with sodium chloride. Table I (b) contains these data.

Polarographic Investigation of Tetraphenylarsonium Chloride in Basic Media

Five milliliters of 0.06593 M. tetraphenylarsonium chloride was diluted to 100 ml. to give a solution of concen-

TABLE I

STANDARDIZATION DATA

(a) Standardization of a Triiodide Solution against Primary Standard Arsenious Oxide

Wt. As_2O_3	Vol. I_3^-	Normality I_3^-	Molarity I_3^-
0.2354	36.10	0.1318	0.06590
0.3412	52.30	0.1319	0.06590

(b) Standardization of a Tetraphenylarsonium Chloride Solution with a 0.01054 molar Triiodide Solution

Vol. TPAC	Vol. I_3^-	Molarity TPAC
2.000	12.51	0.06593
2.000	12.51	0.06593

tration 3.297×10^{-3} M. A series of solutions in the concentration range 10^{-5} to 10^{-4} M. was prepared from this solution using 30 ml. aliquots of an ammonium chloride-ammonium hydroxide buffer in each 100 ml. as the supporting electrolyte. The buffer used contained 13.40 g. of NH_4Cl and 10 ml. of 15 M. NH_4OH in 250 ml. Various amounts of 0.2% gelatin were added to the solutions as a maximum suppressor. It was found that 0.004% gelatin was sufficient to suppress the maximum in most cases.

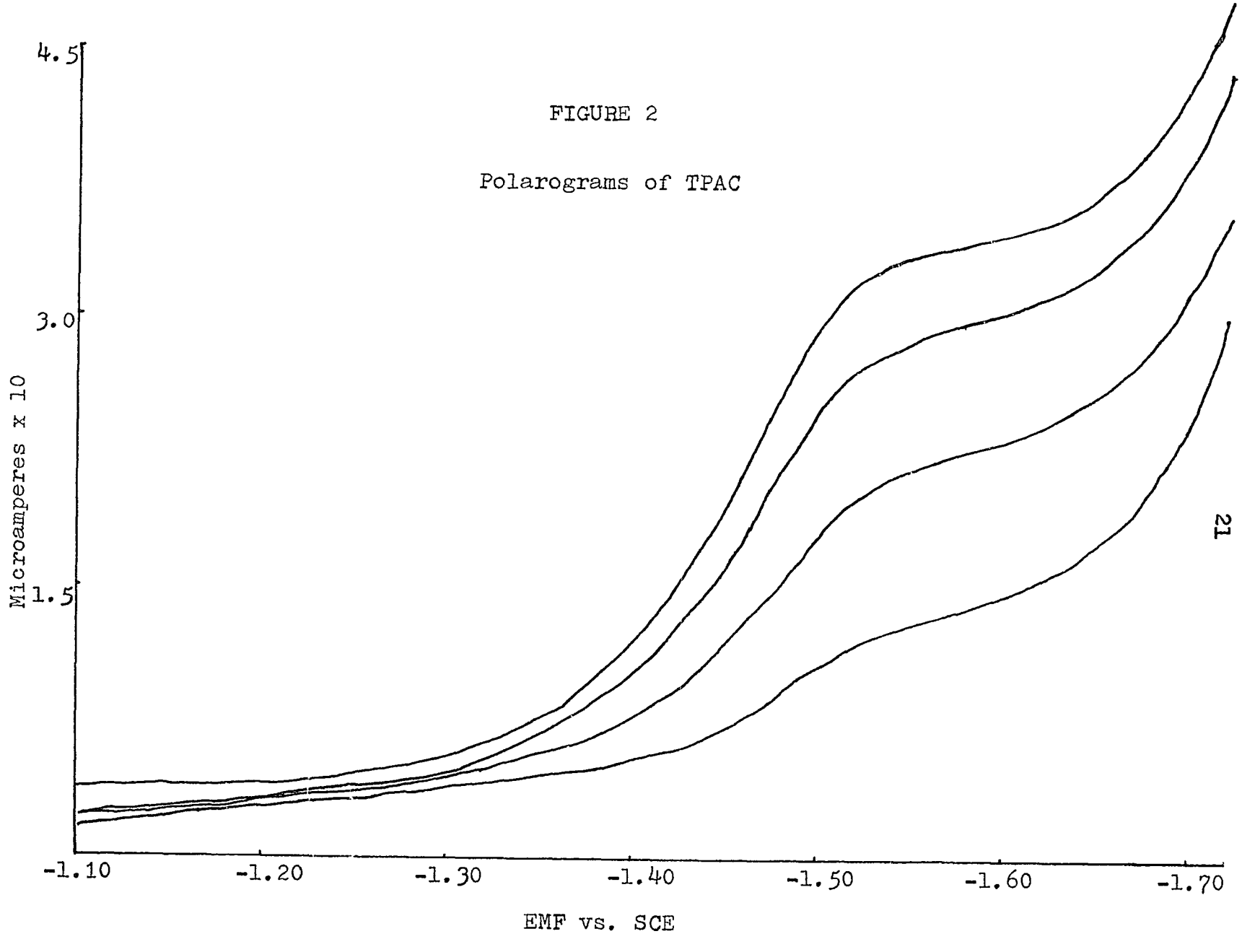
Polarograms of these solutions were taken on a Sargent Model XXI recording polarograph using an H-type cell with a Saturated Calomel Electrode (SCE) reference. The cell was kept in a water bath at $20.0^{\circ} \pm 0.1^{\circ}C.$ and nitrogen was bubbled through the solutions for thirty minutes before running each polarogram.

A one-step wave was obtained indicating a single reduction process was occurring. The half-wave potential varied between -1.50 volts and -1.43 volts due to the irreversible character of the wave. Figure 2 shows a series of typical polarographic waves obtained for the reduction of tetraphenylarsonium ion.

After the wave was developed the current showed a continuous increase, and it was necessary to make wave height measurements at a particular potential in order to get consistent results. The limiting diffusion current was obtained by extrapolating the residual current and measuring the difference

FIGURE 2

Polarograms of TPAC



between this line and the wave height at -1.56 volts. These diffusion current data are tabulated in Table II. These data were taken at a current sensitivity of either 0.003 or 0.004 microamperes per millimeter. The points thereon were fitted to a straight line by a least squares analysis and the following equation was found for the line of regression:

$$I = 3436M + 15 \times 10^{-3}.$$

"M" is the molarity of TPAC and "I" is the limiting diffusion current. The slope is 3436 liters microamperes per mole.

For a reversible polarographic process the following expression should hold:

$$E = E_{\frac{1}{2}} + 0.059/n \log(I-i/i),$$

where "i" is the current after the decomposition potential has been passed and $E_{\frac{1}{2}}$ is the half-wave potential. A plot of applied potential "E" versus log(I-i/i) is shown in Figure 3. The intercept of this line "$E_{\frac{1}{2}}$" was found to be -1.434 volts versus SCE. The slope was found to be 0.09756 volts, which corresponds to an electron change of 0.61 for the reduction process. This value for "n" cannot be interpreted but does indicate that the wave is irreversible.

Spectrophotometric Investigation of Tetraphenylarsonium Chloride

A small quantity of tetraphenylarsonium hexafluorophosphate was placed in distilled water and heated to 50°C. The solution was cooled to room temperature and an absorption spectrum was obtained from 350 to 200 millimicrons on the

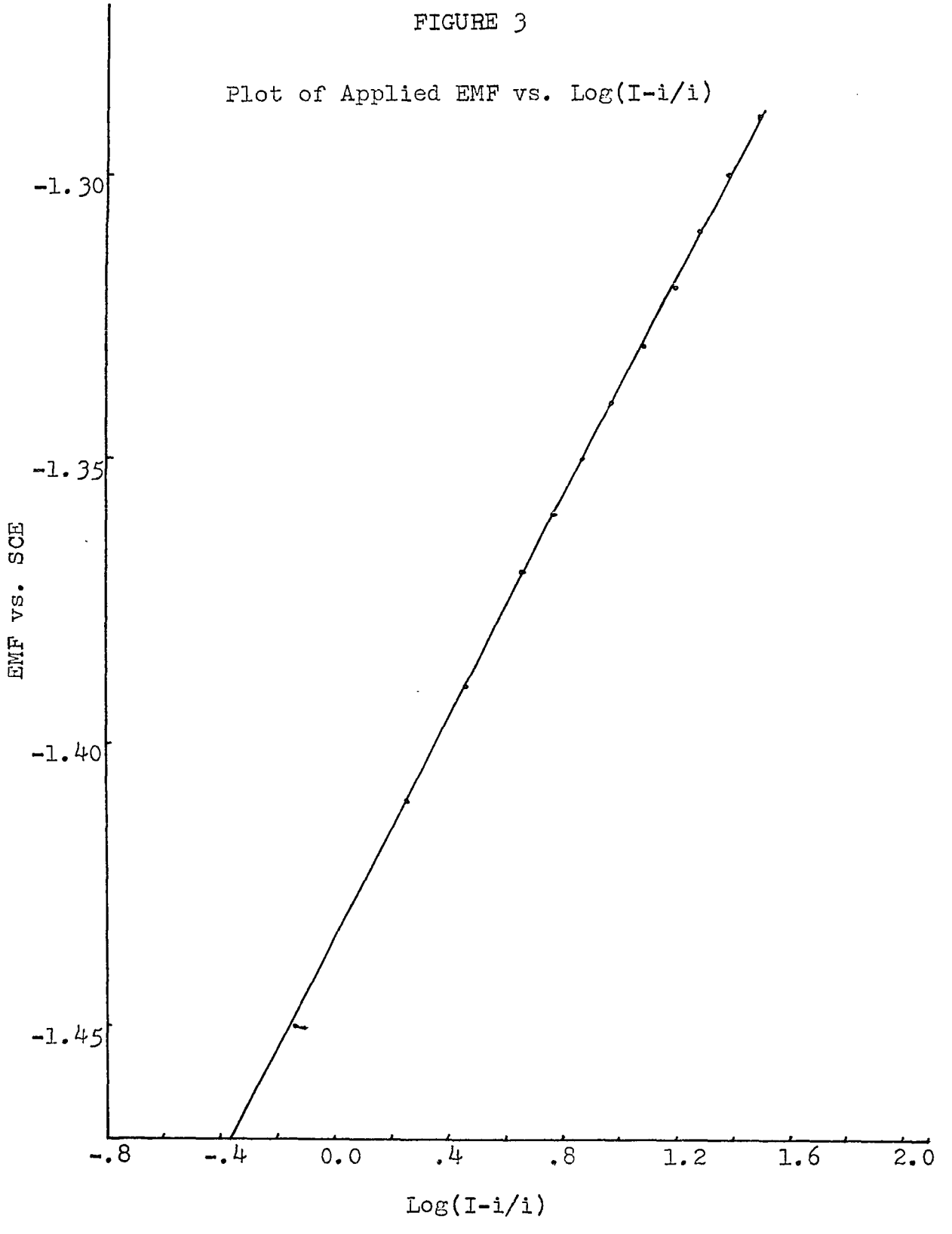
TABLE II

LIMITING DIFFUSION CURRENT OF TETRAPHENYLARSONIUM CHLORIDE SOLUTIONS USING AN AMMONIUM CHLORIDE-AMMONIUM HYDROXIDE BUFFER OF pH 9 AS SUPPORTING ELECTROLYTE

Molarity TPAC x 10^5	% Gelatin	Diffusion Current (μ Amperes) x 10^3
0.9891	0.010	50.1
1.649	0.010	65.1
3.297	0.010	133.2
3.297	0.004	130.5
3.956	0.010	151.5
4.946	0.010	193.5
4.946	0.004	187.5
5.605	0.010	219.0
6.594	0.010	231.6
6.594	0.004	236.1
7.253	0.010	255.3
8.243	0.010	294.3
8.902	0.010	298.8
9.891	0.010	362.1
9.891	0.004	356.4
10.55	0.010	376.5
10.55	0.004	394.8

FIGURE 3

Plot of Applied EMF vs. Log(I-i/i)



Beckman DK-1 recording spectrophotometer. A solution approximately 2 x 10^{-5} molar in TPAC was treated similarly. The two spectra were identical and the transmittances were quite close, which indicated that only the tetraphenylarsonium ion was absorbing in this spectral range and that the solubility of tetraphenylarsonium hexafluorophosphate was of the order of 10^{-5} molar. Figure 4 is the curve of percent transmittance versus wavelength for the 2 x 10^{-5} M. solution of TPAC. The curve has minima at 269, 263, and 257 millimicrons and has a large shoulder at 220 millimicrons. It was decided that the shoulder at 220 millimicrons was the most feasible wavelength for measurements in the concentration range of interest.

A 1.055 x 10^{-4} M. solution of TPAC was prepared by volumetric dilution of a 0.06593 M. TPAC solution. This solution was used to prepare a series of standards in the concentration range 10^{-6} to 10^{-4} M. for a spectrophotometric investigation. The absorbance of each of these reference solutions was then measured at 220 millimicrons with a slit width of 0.1 millimeter on a Beckman DU spectrophotometer.

A second set of reference solutions was prepared, and the absorbance of each was measured in a similar manner. Table III contains the absorbance data from these standard solutions. These data were fitted to an equation of the form $A = aM$ by the method of least squares. The least squares absorptivity "a" was found to be 35,700 liters per mole centimeter with a standard deviation of 220 liters per mole cm.

FIGURE 4

Absorption Spectrum of $(C_6H_5)_4AsCl$

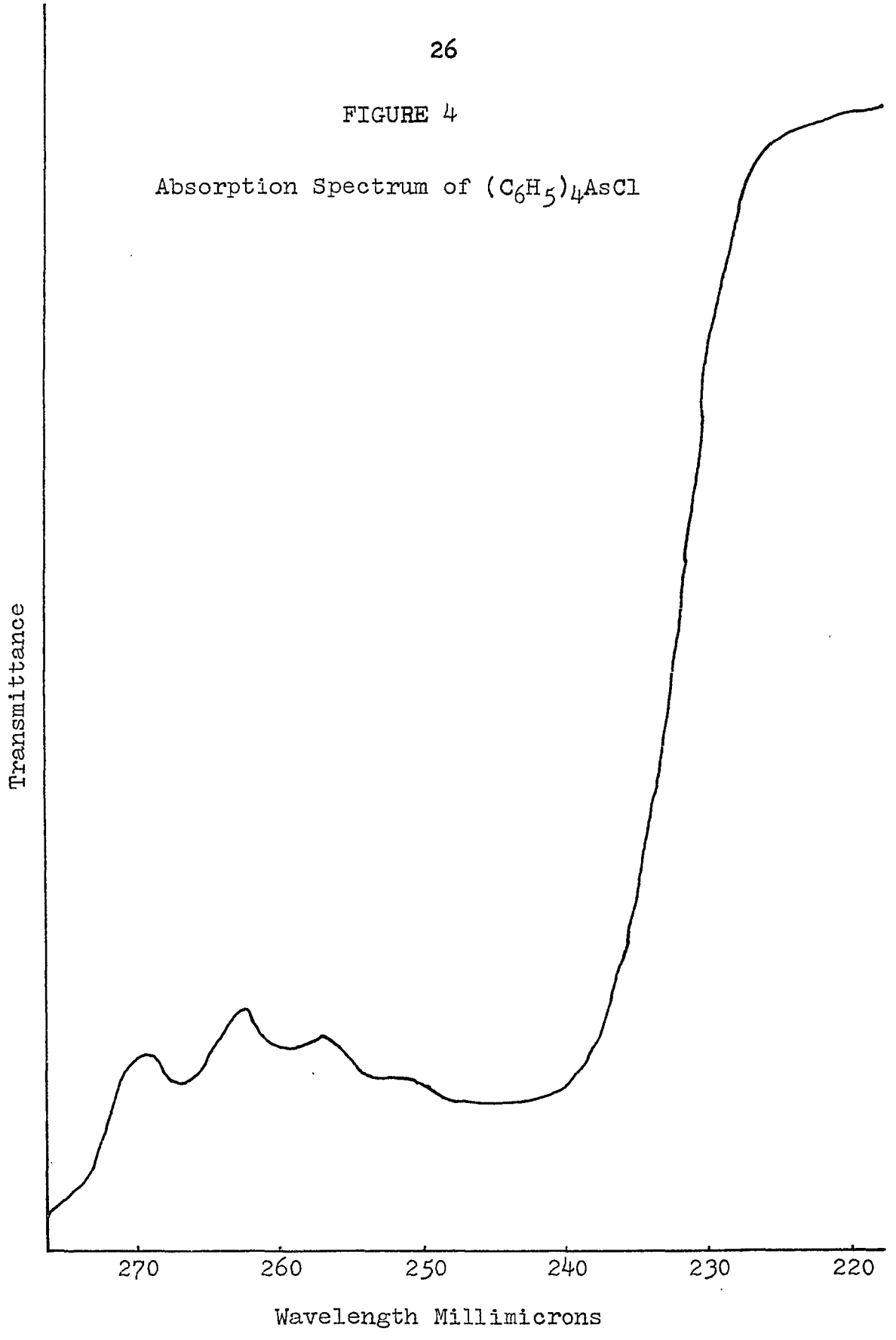


TABLE III

ABSORBANCE DATA ON STANDARD TPAC SOLUTIONS AT 220 MILLIMICRONS

Molarity TPAC x 10^5	Absorbance
0.2110	0.061
0.2637	0.087
0.5274	0.170
0.7912	0.278
1.055	0.383
1.319	0.477
1.582	0.551
1.846	0.658
2.110	0.748
2.397	0.821
2.637	0.963
5.274	1.89

Determination of the Solubility and Purity of the Tetraphenylarsonium Hexafluorophosphate Precipitate

Solid tetraphenylarsonium hexafluorophosphate (TPAP) was prepared by slow addition of an excess of TPAC to an ammoniacal solution of potassium hexafluorophosphate. The precipitate was filtered onto a sintered glass crucible, washed with about 50 ml. of dilute ammonia and dried to constant weight at 105°C.

A small amount of this solid tetraphenylarsonium hexafluorophosphate was placed in several flasks and a hot solution of TPAP, saturated at the boiling point, was added. The solutions were shaken and allowed to equilibrate in a water bath at 20°C. After several hours of equilibration, the solutions were removed from the bath and filtered quickly through a good grade of filter paper. The absorbance of each of these solutions was then measured on the Beckman DU spectrophotometer at 220 millimicrons. The solubility was determined by dividing the absorbances by the least squares absorptivity and assuming the formula $(C_6H_5)_4AsPF_6$. Table IV contains the data obtained in this way.

Verification of the formula of the TPAP was accomplished by an elemental analysis. The results of the elemental analyses are compared with the theoretical percentages in Table V.

TABLE IV

DETERMINATION OF THE SOLUBILITY OF TETRAPHENYL-ARSONIUM HEXAFLUOROPHOSPHATE AT 20°C.

Absorbance	Molar Solubility x 10^5
0.437	1.22
0.426	1.19
0.399	1.12
0.482	1.35

Average = 1.22×10^{-5} moles/liter

Standard Deviation = 0.10×10^{-5} moles/liter

TABLE V

PERCENTAGE COMPOSITION OF TPAP PRECIPITATE

Elements	*Experimental	Theoretical
Carbon	54.37	54.56
Hydrogen	3.89	3.82
Phosphorus	6.01	5.86
Arsenic	13.95	14.18
Fluorine	21.80	21.58

*The TPAP precipitate was analyzed by Galbraith Microanalytical Laboratories of Knoxville, Tennessee.

Determination of the Solubility of Tetraphenylarsonium Tetrafluoroborate

A small amount of tetrafluoroborate was precipitated with tetraphenylarsonium chloride from a dilute ammonia solution and dried to constant weight at 105°-110°C. Some of this dried salt was added to approximately 200 ml. of water, and this mixture was stirred with a magnetic stirrer for three hours. The mixture was placed in a water bath at 25°C. and shaken periodically. Five millliliter aliquots of this solution were taken and diluted to 250 ml. at various time intervals. The absorbances of these solutions were measured at 220 millimicrons on a Beckman DU spectrophotometer. It was found that equilibrium was reached after about one day. The absorbance of the final solution was 0.333, which indicated that the solubility of tetraphenylarsonium tetrafluoroborate (TPAB) was 4.66×10^{-4} M. at 25°C.

Determination of Hexafluorophosphate

Preparation and Standardization of Solutions

Three stock solutions of KPF_6 were prepared for analysis. Solutions number one and two were made up from the same batch of reprecipitated KPF_6 and contained respectively 1.0525 g. of the salt in 500 ml. and 1.3602 g. in 250 ml. Solution number three was prepared from a different batch of KPF_6 and contained 9.2060 g. in 250 ml. of solution.

Solution number three was analyzed by the Nitron gravimetric method. The procedure used was essentially that

of Lange and Muller (28) except that the washing procedure was altered. Nitron acetate is adsorbed on the precipitate under the conditions of precipitation, and it is found that this salt decomposes leaving a yellow to black decomposition product upon heating to 105°C. This decomposition product is soluble in benzene, whereas Nitron acetate and Nitron hexafluorophosphate are insoluble in this solvent. Therefore, the precipitate was put through a series of heating and washing cycles, utilizing a saturated benzene solution of Nitron hexafluorophosphate. This procedure was continued until the precipitate no longer darkened upon heating and constant weight was obtained. Table VI contains the data from this determination.

The standard 0.06593 M. TPAC solution was used for the amperometric titrations. A solution which was approximately 0.07 M. in TPAC was used as a stock solution for the gravimetric determinations. This solution was used to prepare the 0.015 M. solutions used directly in the gravimetric procedure.

Gravimetric Determination of Hexafluorophosphate with TPAC

Aliquots of KPF_6 solution containing 36 to 55 mg. of the salt were taken, and sufficient water and aqueous ammonia were added to give an ammonia concentration of 5 to 11 M. with a total solution volume of 50 ml. The solution was warmed to about 50°C. and approximately twice the equi-

TABLE VI

GRAVIMETRIC DETERMINATION OF KPF_6
(SOLUTION NUMBER 3)
WITH NITRON

Wt. KPF_6 grams	Wt. Nitron HPF_6 grams	Wt. PF_6^- grams	% PF_6 in KPF_6
0.3682	0.9252	0.2926	79.48
0.3682	0.9242	0.2923	79.39
0.3682	0.9237	0.2922	79.35
0.3682	0.9210	0.2913	79.12

Mean % PF_6^- = 79.34

Standard Deviation = 0.15

valent amount of 0.015 M. TPAC was added slowly with stirring. The precipitate was allowed to digest for about thirty minutes, filtered on a sintered glass crucible of medium porosity, and washed with 50 ml. of dilute ammonium hydroxide in small portions. The precipitate was dried to constant weight at 105°C. and weighed as $(C_6H_5)_4AsPF_6$.

Data on the determination of relatively pure KPF_6 samples are given in Table VII (a).

Interference studies were made with phosphate, monofluorophosphate, difluorophosphate, and fluoride ions. The only anion of this group which gave a precipitate with tetraphenylarsonium chloride was difluorophosphate. A series of determinations was performed on KPF_6 solutions containing various amounts of salts of the above anions with the exception of difluorophosphate. Aliquots of solution number three were used for these analyses. These data are summarized in Table VII (b). None of these anions interfered.

Amperometric Titration of Hexafluorophosphate with TPAC

A 25 ml. aliquot of KPF_6 solution number three was diluted to 250 ml. This solution was then used for amperometric titrations. A ten ml. aliquot of this solution, ten to twenty ml. of the NH_4Cl-NH_4OH buffer and sufficient water to give a total volume of 55 ml. were combined in a polyethylene beaker. Nitrogen was bubbled through the solution for about thirty minutes, while the solution was stirred with a magnetic

TABLE VII

GRAVIMETRIC DETERMINATION OF HEXAFLUOROPHOSPHATE AS $(C_6H_5)_4AsPF_6$

(a) Analysis of Pure Samples of KPF_6

Solution	Weight KPF_6 (grams)	Number of Determinations	Average Percent PF_6^- Found in KPF_6	Standard Deviation
1	0.05263	6	78.93	0.18
2	0.05441	5	78.82	0.07
3	0.03682	8	79.66	0.32

(b) Determination of Hexafluorophosphate in the Presence of Possible Interferences. Each sample contained 0.03682 grams of KPF_6.

Weight KF (g.)	Weight Na_2PO_3F (grams)	Weight Na_3PO_4 (grams)	Number of Determinations	Avg. Percent PF_6^- in KPF_6	Standard Deviation
0.1507	-------	-------	4	79.29	0.06
1.3218	-------	-------	4	79.44	0.18
0.2644	0.3732	0.66	6	79.57	0.21

stirrer. The solution was then titrated amperometrically with 0.06593 M. TPAC utilizing the Sargent Model XXI recording polarograph at a constant applied potential of -1.7 volts versus the saturated calomel electrode. Current readings were taken at 0.500 ml. intervals before the end-point and at 0.100 ml. intervals after the end-point. After addition of each increment, nitrogen was bubbled through and the solution was stirred for about five minutes to assure attainment of equilibrium before a current reading was made. One ml. of 0.2% gelatin was added to each sample just before the end-point. All current readings were corrected for dilution effects. Figure 5 shows a typical amperometric titration curve obtained in this way. The results of the amperometric titrations are summarized in Table VIII. The last three titrations of this group were performed with 0.171 g. of KF added to each sample to test for fluoride interference. No interference occurred at this concentration level.

The Preparation of Tetra-p-tolylarsonium Chloride and Study of Some of Its Physical Properties

Preparation of Tetra-p-tolylarsonium Salts

Preparation of arsenic triiodide

The procedure used for preparation of AsI_3 was essentially that of Bailar (7) with some modifications. A solution of 49 g. of As_2O_3 in 700 ml. of concentrated HCl was mixed with a solution of 245 g. of KI in 245 ml. of water.

FIGURE 5

Amperometric Titration Curve of KPF_6 with TPAC

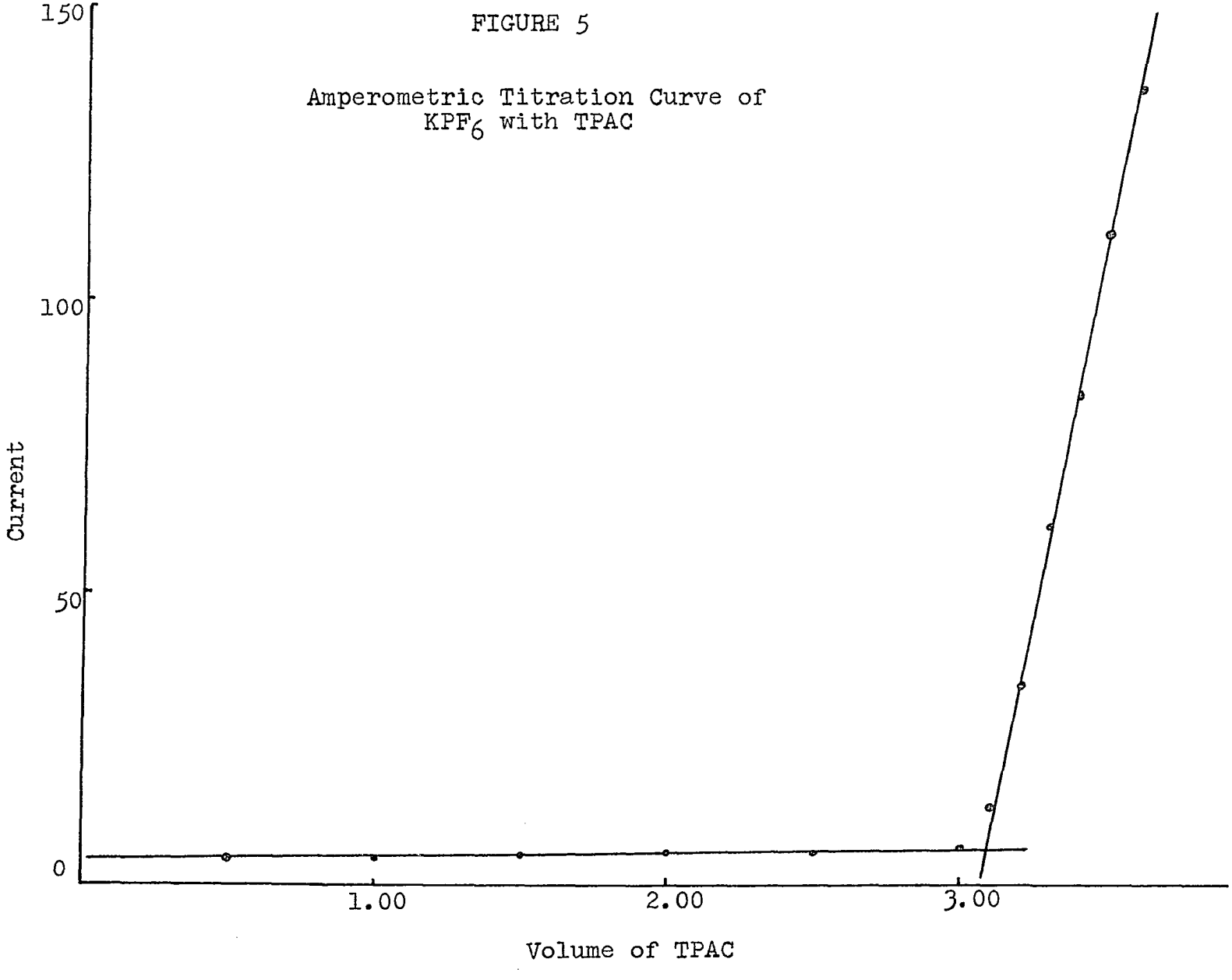


TABLE VIII

AMPEROMETRIC TITRATIONS OF HEXAFLUOROPHOSPHATE WITH TPAC

Sample Number*	Vol. $(C_6H_5)_4AsPF_6$ 0.06593 M.	Wt. of PF_6^- Found (grams)	% PF_6^- in KPF_6
1	3.055	0.02920	79.31
2	3.040	0.02906	78.92
3	3.080	0.02944	79.96
4	3.100	0.02963	80.47
5	3.040	0.02906	78.92
6	3.100	0.02963	80.47
7	3.090	0.02954	80.22
8	3.060	0.02925	79.44
9**	3.065	0.02930	79.57
10**	3.075	0.02939	79.83
11**	3.060	0.02925	79.44

* Each solution contained 0.03682 g. of KPF_6.

** Each solution contained 0.171 g. of KF.

Average % PF_6 = 79.69%.

Standard Deviation = 0.55.

The precipitate was filtered on sintered glass and placed in a beaker. Sufficient CCl_4 was poured over the material to completely cover it. The mixture was stirred for ten to fifteen minutes until most of the aqueous HCl came to the top. The aqueous layer was poured off and the precipitate was then filtered onto a sintered glass funnel. The precipitate was then repeatedly extracted with CS_2. The carbon disulfide was then removed by vacuum distillation leaving red-orange crystals of AsI_3. The yield was 177.7 g. The above procedure was repeated once and an additional 175.2 g. was obtained. The crystals were dried in vacuum.

Preparation of tri-p-tolylarsine

The first procedure used for the preparation of tri-p-tolylarsine was essentially the same as that used by Burrows and Turner (14) for preparation of tri-o-tolylarsine.

A Grignard reagent was prepared from 390 g. of p-bromotoluene, 59.6 g. of magnesium turnings, and 1200 ml. of dry ether. Solid arsenic triiodide (342 g.) was added slowly with rapid stirring. After the initial vigorous reaction had abated, the mixture was refluxed for four hours. The reaction mixture was decomposed by adding ice and dilute hydrochloric acid. The ethereal layer was separated and dried over anhydrous magnesium sulfate. The ether was then removed by vacuum distillation and the solid product dissolved in CCl_4, which was extracted with small quantities of 5% sodium hydroxide. The CCl_4 was distilled off under a vacuum, and

the resultant crystals were washed with a small amount of ethanol and air dried. The yield of off-white crystals melting at 135°-140°C. was 117 g.

Another batch of tri-p-tolylarsine was prepared at a later date utilizing the reaction of $AsCl_3$ with p-tolylmagnesium bromide in tetrahydrofuran as solvent. The following procedure was used.

Tetrahydrofuran was first dried over sodium wire for several days, distilled off, and dried again by distilling from lithium aluminum hydride.

A Grignard reagent was prepared from 60 g. (2.4 moles) of magnesium, 390 g. (2.28 moles) of p-bromotoluene, and 1200 ml. of dry tetrahydrofuran (THF). After all of the p-bromotoluene had been added, the mixture was refluxed gently for three hours. Arsenic trichloride (137 g.) was then added dropwise with stirring over a five-hour period. The mixture was refluxed for two hours and allowed to sit overnight. The next morning a huge batch of white crystals were visible in the solvent. The solvent was poured off and the crystals were washed with additional THF. The crystals were then dissolved in hot benzene, which was mixed with 250 ml. of 2 M. HCl and 500 ml. of crushed ice. The mixture was stirred for thirty minutes and the layers separated. The organic layer was filtered, and the solvent was distilled off under vacuum leaving pale brown crystals behind. The crystals were washed with 1200 ml. of water containing 200 ml. of concentrated ammonium

hydroxide and air dried for one hour. They were subsequently washed with 500 ml. of cold denatured ethanol and air dried. The yield of white crystals melting at 144°-147°C. was 228 g.

Preparation of tri-p-tolylarsine oxide

The procedure used for preparation of tri-p-tolylarsine oxide was that used by Shriner and Wolf (52) for the synthesis of triphenylarsine oxide. Tri-p-tolylarsine (TPTAs) (118.5 g.) was added to 600 ml. of acetone. Most of the TPTAs remained undissolved. To this mixture 61 g. of 30% H_2O_2 was added with vigorous stirring. The temperature was kept between 25° and 30°C. with an ice-water bath. After all of the H_2O_2 was added, the solution was stirred until all of the solid had been dissolved for one hour. The acetone was distilled off under a vacuum and 500 ml. of benzene was added, and the water was removed by azeotropic distillation. The residual oil was cooled yielding a slightly yellow solid. This residue was washed with two 25 ml. portions of cold benzene and filtered on sintered glass. The air dried material weighed 123 g., and after drying in a vacuum for a few hours the melting range was 95°-96°C. which corresponds to the melting point of tri-p-tolylarsine oxide hydrate (the dihydroxide). The hydrate was dried in a vacuum desiccator over P_2O_5 for two weeks. The white solid was then recrystallized from dry benzene and again dried over P_2O_5 in a vacuum desiccator for two days. The melting point was now found to be 125°-128°C. Carson and Wong (15) reported a melting point of 130°-

133°C. for tri-p-tolylarsine oxide.

Preparation of tetra-p-tolylarsonium compounds

The first method used for preparation of tetra-p-tolylarsonium salts was essentially that used by Shriner and Wolf (52) for the preparation of tetraphenylarsonium chloride-hydrochloride.

A Grignard reagent was prepared containing 56.55 g. of p-bromotoluene, 300 ml. of dry ether, and 9.0 g. of magnesium. This Grignard reagent was added dropwise with stirring to 67.5 g. of tri-p-tolylarsine oxide in 1500 ml. of hot, dry benzene. After the addition of the Grignard was complete, the mixture was stirred and heated under reflux for thirty minutes on a steam bath. The solvent was removed by decantation and the viscous addition product was washed with 500 ml. of benzene. The addition product was then hydrolyzed with 150 ml. of water containing 10 ml. of concentrated hydrochloric acid. Seven-hundred and fifty ml. of concentrated HCl was added, and the mixture was heated on a steam bath for 1½ to 2 hours. The benzene and ether remaining were distilled off and the mixture placed in a dry ice-acetone bath. A viscous yellow oil separated. The oil was extracted with 5 M. NH_4OH and the extracts were made about 15 M. in HCl by bubbling HCl gas through the solution. The oil was again dissolved in 5 M. NH_4OH and KI was added to precipitate the iodide salt. The yield of 55 g. of crude, yellow product was filtered on sintered glass. Attempts were made to purify the

iodide and convert it to a more soluble salt. The salt was converted to the sulfate by stirring with excess silver sulfate in 300 ml. of water for three hours. After filtering the AgI precipitate, the filtrate was again made strongly acid with concentrated HCl, which caused a yellow oil to precipitate. The oil was again dissolved in dilute ammonia and tetra-p-tolylarsonium iodide (TPTAsI) was precipitated with potassium iodide. The melting range of the TPTAsI was found to be 248°-252°C. Lyon and Mann (29) report a melting point of 253°-255°C. for this salt. The TPTAsI was dissolved in acetone, and several grams of Norit was added. After standing thirty minutes the Norit was removed by filtration. Most of the yellow color remained in the acetone solution. The acetone was removed by vacuum distillation leaving the yellow solid. In the process of these attempts at purification, a large amount of the salt had been lost, and it was decided to synthesize another batch.

A Grignard reagent was prepared from 76 g. of p-bromotoluene, 15.0 g. of magnesium and 400 ml. of dry THF as solvent. The p-bromotoluene was added over a two-hour period, and the solution was refluxed for two additional hours. This Grignard reagent was added dropwise with stirring to a solution of 73.7 g. of tri-p-tolylarsine oxide in one liter of hot benzene over a period of seven hours. The mixture was allowed to cool for four hours, after which the solvent was decanted from the dark viscous oil which sepa-

rated. The oil was decomposed with 200 ml. of water and 10 ml. of concentrated HCl. The hydrolysis mixture was heated on the steam bath for two hours after the addition of 600 ml. of concentrated HCl. The mixture was cooled and the aqueous layer was decanted from the oil which precipitated. Benzene was then added to the oil, and the water was azeotropically distilled. The remnants of the solvent were removed by vacuum distillation. The oil was exhaustively extracted with water, and the extracts were filtered twice through filter paper. The water was distilled leaving behind a yellow oil. The oil was dissolved in acetone and the acetone removed by evaporating on a steam bath. The residual oil was cooled in an ice bath and stirred for several minutes until it became very viscous. One hundred ml. of benzene were then poured over the solid and the mixture stirred for several minutes. The oil crystallized into a yellow solid. The crude tetra-p-tolylarsonium chloride (TPTAC) weighed 57 g.

Several attempts were made to recrystallize the material from benzene-acetone, benzene-ethanol, and hexane-ethanol mixtures, but either a yellow oil or impure crystals were produced. The TPTAC was reprecipitated by dissolving in a minimum quantity of hot acetone, allowing to cool slowly to room temperature, and cooling in an ice bath. The precipitate was filtered out, and the filtrate concentrated and more TPTAC recovered. This product was relatively pure, but it still gave a yellow color in solution. The TPTAC was dissolv-

ed in hot water and run through an alumina column, which removed part of the yellow color, but a large part of the TPTAC was adsorbed on the column and lost. The water was distilled off under vacuum, and a pale yellow residue was left.

The $AlCl_3$ method was used next to synthesize tetra-p-tolylarsonium bromide (TPTABr). A mixture composed of 51 g. of purified p-bromotoluene, 13.2 g. of aluminum chloride, and 33 g. of tri-p-tolylarsine (TPTAs) was heated with stirring for 1½ hours at 180°-200°C. before being allowed to cool slowly to room temperature. The solution was extracted exhaustively with hot water, and the water extracts were filtered. Potassium bromide was added slowly to the water extracts until precipitation was complete. The crude brown product was filtered on sintered glass and air dried. The yield of impure product was approximately 24 g. A small amount of acetone was added to the TPTABr, and the mixture was heated with stirring for thirty minutes. The mixture was cooled, and the solid was filtered and washed with small amounts of cold acetone. The yield was 19 g. of fairly white product. The TPTABr was further purified by dissolving in a minimum amount of hot dioxane and adding water until the solution became cloudy. A little ethanol was added to clarify the solution and KBr solution was added slowly until the first permanent cloudiness appeared. The solution was filtered at this point, and the remainder of the TPTABr was precipitated by adding excess KBr to the filtrate. The first precipitate fraction

which came down was much more impure than the second fraction. The purer fraction was reprecipitated several times by dissolving in ethanol, adding about five times as much water as ethanol, and adding KBr solution until precipitation was complete. The final purification consisted of dissolving the TPTABr in minimum ethanol, adding water until the solution had clouded, heating on a steam bath until the solution had clarified, and adding a spatula tip of Norit. The solution was stirred and heated for thirty minutes and filtered hot. When the filtrate was cooled slowly to room temperature, beautiful white crystals precipitated. The crystals were filtered on sintered glass, washed with water and dried in a desiccator over Drierite.

An attempt was made to obtain tetra-p-tolylarsonium chloride-hydrochloride by heating the TPTABr with concentrated HCl, but an oil was obtained.

The TPTABr was converted to the chloride by a metathesis reaction with excess silver chloride. Eleven g. of TPTABr was heated with approximately 300 ml. of water and excess silver chloride for one hour. About 10 to 15 ml. of concentrated HCl was added and the AgBr was removed by filtration. The tetra-p-tolylarsonium chloride (TPTAC) was extracted into chloroform in order to get rid of any residual silver salts. The chloroform extracts were back extracted with a small amount of dilute HCl (0.5 M.), and subsequently the solvent was removed by vacuum distillation. Approximately

400 ml. of water was added to the residue and distilled off under vacuum to remove the remaining chloroform. The residue was dissolved in 250 ml. of water and heated with a small amount of Norit for thirty minutes. The solution was filtered hot and diluted to approximately 250 ml.

Standardization of the Tetra-p-tolyl-arsonium Chloride Solution

The TPTAC solution was analyzed gravimetrically by precipitating the hexafluorophosphate salt. A solution of 0.025 M. in KPF_6 was prepared. Three milliliter aliquots of the TPTAC solution were added to 25 ml. of water and 25 ml. of concentrated ammonium hydroxide. The solution was warmed on the steam bath while 40 ml. of 0.025 M. KPF_6 was added slowly with stirring. After sitting for a few minutes, the precipitate was filtered on a weighed sintered glass crucible and washed with 50 ml. of 0.3 M. NH_4OH. The results of this determination are summarized in Table IX.

The TPTAC solution was subsequently analyzed by potentiometric titration with potassium triiodide (60). A solution was prepared containing 40 g. of KI and 12.9 g. of I_2 diluted to one liter. The solution was standardized against primary standard arsenious oxide using starch as indicator. The results are given in Table X (a). A 50 ml. aliquot of the 0.0580 M. KI_3 solution was diluted to 250 ml. giving a solution 0.0116 M. in triiodide. This dilute solution was used to titrate the TPTAC solution to a potentiometric end-point.

TABLE IX

GRAVIMETRIC DETERMINATION OF TETRA-P-TOLYLARSONIUM CHLORIDE AS TETRA-P-TOLYLARSONIUM HEXAFLUOROPHOSPHATE

Vol. TPTAC (ml.)	Wt. TPTAP (g.)	Molarity TPTAC
3.000	0.1157	0.0660
3.000	0.1153	0.0658
3.000	0.1172	0.0668
		Average = 0.0662
		Standard Deviation = 0.0005

TABLE X

DETERMINATION OF TETRA-P-TOLYLARSONIUM CHLORIDE BY POTENTIOMETRIC TITRATION WITH POTASSIUM TRIIODIDE

(a) Standardization of Triiodide Solution with Arsenious Oxide

Wt. As_2O_3 (grams)	Vol. I_3^- (ml.)	Normality I_3^-	Molarity I_3^-
0.2292	39.96	0.1160	0.0580
0.2552	44.50	0.1160	0.0580
0.2440	42.54	0.1160	0.0580

(b) Titration of Tetra-p-tolylarsonium Chloride with 0.0116 M. KI_3

Vol. TPTAC	Vol. KI_3	Molarity TPTAC
3.000	16.61	0.0642
3.000	16.63	0.0643
3.000	16.63	0.0643

Three milliliter aliquots of the TPTAC solution were taken using the microburet. Fifty to seventy-five ml. of water and 50 ml. of 3 M. NaCl were added to each sample. Each solution was titrated using a Beckman Zeromatic pH Meter with a saturated calomel reference and a platinum indicator electrode. Just before the end-point the solution was saturated with sodium chloride. The curves were qualitatively the same as those obtained for similar titrations of TPAC but the potential change at the end-point was not as great. The results of these titrations are summarized in Table X (b).

The difference between the concentrations of TPTAC as found by the two methods was almost 3%. Since normally a gravimetric procedure is more reliable, it was assumed for subsequent work that the solution was 0.0662 M. in TPTAC.

Polarographic Investigations of TPTAC

Preliminary polarographic investigations indicated that the tetra-p-tolylarsonium ion had a reduction wave very close to that for tetraphenylarsonium chloride. The wave was found to have a very large maximum, but this was easily suppressed in ammoniacal media with 0.01% gelatin.

A series of solutions of TPTAC were prepared in the concentration range 10^{-5} to 10^{-4} M. Each solution was 0.25 M. in NH_3, 0.25 M. in NH_4Cl, and 0.01% in gelatin. Polarograms of these solutions were taken on a Sargent Model XXI recording polarograph using an H-type cell with a saturated calomel reference electrode. The solutions were placed in the sample

half-cell in a bath at 25.0° ± 0.1°C., and nitrogen was bubbled through for thirty minutes. Scans were run between -1.00 and -2.00 volts versus SCE.

Figure 6 shows a series of the polarographic curves obtained for these solutions. The half-wave potential varied between -1.52 and -1.45 volts indicating that the reduction was irreversible. Limiting diffusion current values were obtained by extrapolating the residual current line and measuring the difference between this line and the wave height at -1.60 volts. These diffusion current data are tabulated in Table XI. The data were all taken at a current sensitivity of 0.003 microamperes per millimeter. The data were fitted to a straight line by the method of least squares, and the following equation was found for the line of regression:

$$I = 2842M + 23.2 \times 10^{-3}.$$

"M" is the molarity of TPTAC and "I" is the limiting diffusion current in microamperes. The diffusion current constant is 2842 liters microamperes per mole. The standard deviation of this constant was found to be 16.1 microamperes liters per mole.

Spectrophotometric Investigation of TPTAC

A 1.3×10^{-5} M. solution of TPTAC was prepared, and its spectrum was taken between 340 and 200 millimicrons on the Beckman DB recording spectrophotometer. Figure 7 shows a plot of transmittance versus wavelength obtained in this way. There are three small absorption peaks at 271,261 and

FIGURE 6

Polarograms of TPTAC

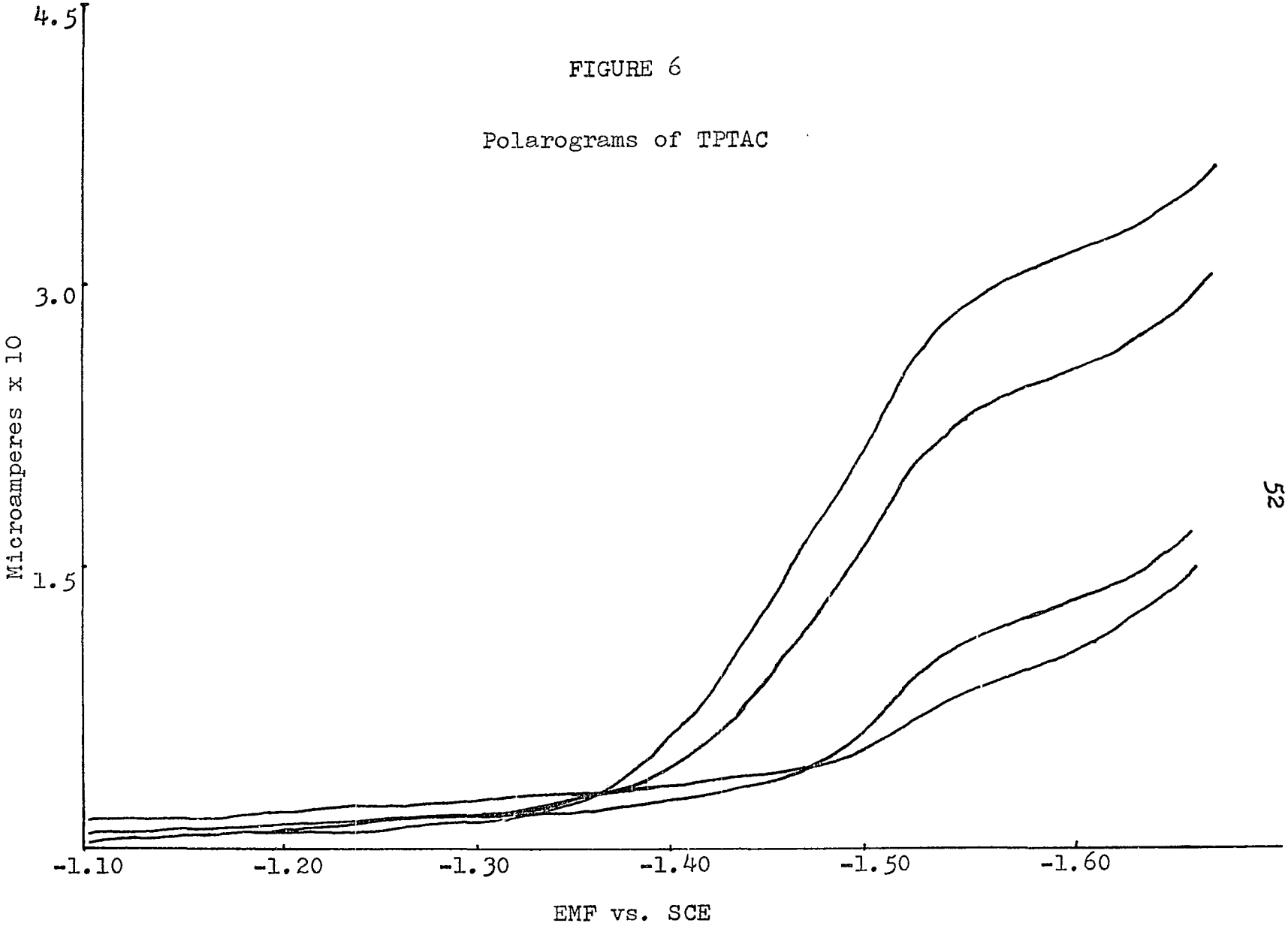


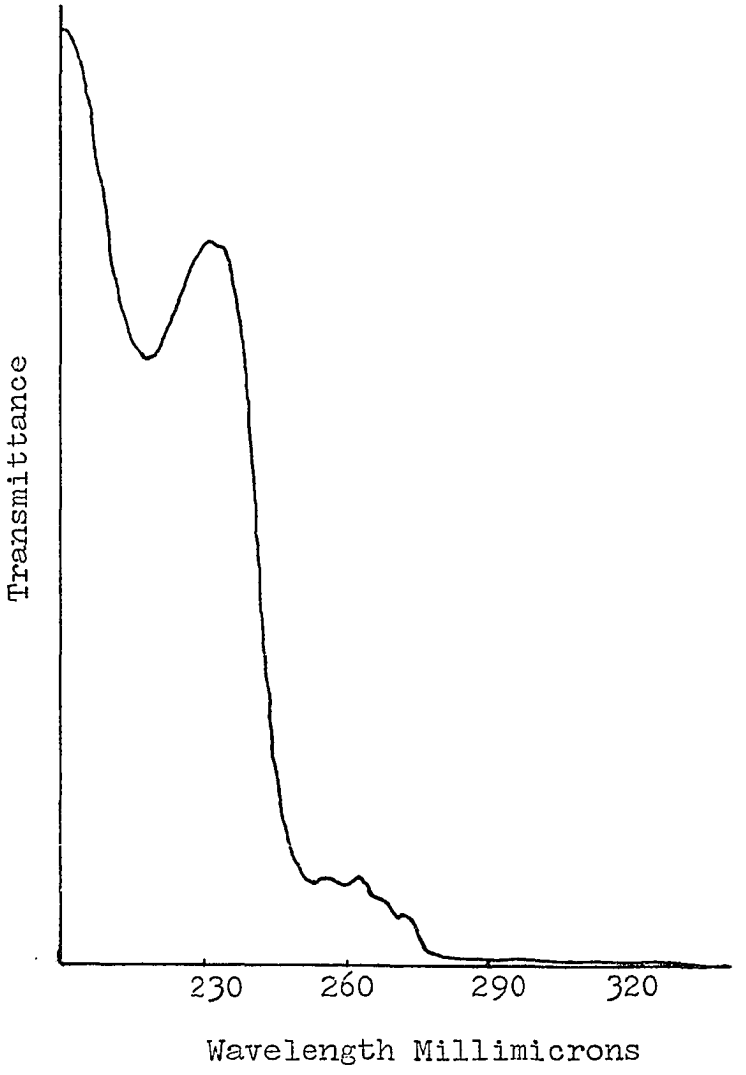
TABLE XI

LIMITING DIFFUSION CURRENT DATA ON TPTAC SOLUTIONS AT 25°C.

Molarity TPTAC x 10^5	Diffusion Current, (microamperes x 10^3)
1.324	59.1
2.649	94.2
6.62	216
7.95	252
9.27	286
13.24	399
16.56	491
19.87	594
26.49	772

FIGURE 7

Absorption Spectrum of TPTAC



255 millimicrons and a large peak at 230 millimicrons. It was decided that the peak at 230 millimicrons would be the most suitable wavelength for analytical use.

A series of solutions in the concentration range 3×10^{-6} to 1.5×10^{-5} M. was prepared. The absorbances of these solutions were measured at 230 millimicrons on a Beckman DU spectrophotometer. The data obtained in this manner are tabulated in Table XII. The data in Table XII were fitted to a straight line of the form A = aM by the method of least squares. The least squares absorptivity "a" was found to be 51,900 liters per mole centimeter with a standard deviation of 270 liters per mole centimeter.

Estimation of the Solubility of Tetra-p-tolylarsonium Hexafluorophosphate and Tetra-p-tolylarsonium Tetrafluoroborate

Samples of tetra-p-tolylarsonium hexafluorophosphate (TPTAP) and tetra-p-tolylarsonium tetrafluoroborate (TPTAB) were obtained by precipitation from ammoniacal media. These samples were dried to constant weight at 105°C. Small amounts of these salts were placed in flasks of distilled water and heated with shaking for about an hour. The mixtures were then allowed to sit in a bath at 25°C. for several days with occasional shaking. The absorptivity of each of these solutions was measured at 230 millimicrons over a period of several days. When the absorbance no longer increased with time, it was assumed that equilibrium conditions prevailed. The final ab-

TABLE XII

ABSORBANCE DATA ON STANDARD TPTAC SOLUTIONS AT 230 MILLIMICRONS

Molarity TPTAC (x 10^6)	Absorbance
3.311	0.198
6.62	0.350
7.95	0.394
9.93	0.505
11.25	0.612
13.24	0.682
15.89	0.807
16.56	0.850
18.54	0.940
19.87	1.024
23.18	1.234
26.49	1.394
29.79	1.51
33.11	1.71
39.73	2.09

sorbance of the TPTAP solution was .903, which corresponded to a solubility of 1.74×10^{-5}. The absorbance of a saturated solution of TPTAB diluted by a factor of 25 was found to be 1.32, which corresponded to a solubility of 6.35×10^{-4}.

Determination of Tetrafluoroborate

Gravimetric Determination of Tetrafluoroborate with Nitron

The NH_4BF_4 used for the determinations was dried in a desiccator over anhydrous magnesium perchlorate. It was found that stock solutions could not be used for more than one day due to slow hydrolysis of the tetrafluoroborate anion.

The NH_4BF_4 was analyzed with Nitron reagent by the procedure of Lange (24). In this procedure it is necessary to add an empirical correction factor to the weight of the precipitate due to the unfavorable solubility of Nitron tetrafluoroborate.

Two-hundred to four-hundred milligrams of NH_4BF_4 were dissolved in about 80 ml. of 5% acetic acid. To this was added 20 ml. of a solution containing 3.9 g. of Nitron in 60 ml. of 5% acetic acid. The solution was cooled in an ice bath for two hours, filtered on a sintered glass crucible of medium porosity, and washed with 20 ml. of ice-cold 5% acetic acid in small portions. The precipitate was dried to constant weight at 105°C. and the empirical correction factor of 18.9 milligrams was added to the weight of each sample. Table VIII contains the results of this determination.

TABLE XIII

GRAVIMETRIC DETERMINATION OF TETRAFLUOROBORATE WITH NITRON

Weight NH_4BF_4	Weight of Precipitate	Corrected Weight of Precipitate	Percent BF_4^- in NH_4BF_4
0.3670	1.3770	1.3959	82.51
0.3670	1.3785	1.3974	82.60
0.3670	1.3774	1.3963	82.54

Average Percent BF_4^- = 82.55

Standard Deviation = 0.05

Gravimetric Determination of Tetrafluoroborate as Tetraphenylarsonium Tetrafluoroborate

At first it was attempted to determine tetrafluoroborate gravimetrically with TPAC without utilizing a special washing procedure and it was found that the results had poor reproducibility and were quite low. Therefore a new procedure was devised which involved washing the precipitate with a saturated solution of tetraphenylarsonium tetrafluoroborate. The procedure finally used is given below.

A ten ml. aliquot of a freshly prepared solution containing about 0.03 g. of NH_4BF_4 was taken. To this was added 5 ml. of NH_4OH and 5 ml. of water just before adding the TPAC. A volume of 0.07 M. TPAC sufficient to give a final concentration of 0.018 M. was added slowly with stirring. The solution was allowed to stand in an ice bath for one hour and filtered on a sintered glass crucible of medium porosity. The precipitate was first washed with 3 ml. of ice cold dilute ammonium hydroxide and then with about 30 to 40 ml. of a solution prepared by combining 250 ml. of a saturated solution of tetraphenylarsonium tetrafluoroborate with ten ml. of concentrated NH_4OH. After transfer of the precipitate to the crucible was complete, the precipitate was washed with 5 ml. of ice-cold dilute NH_4OH. Table XIV gives the results of these determinations.

TABLE XIV

GRAVIMETRIC DETERMINATION OF TETRAFLUOROBORATE AS $(C_6H_5)_4AsBF_4$.

Solution	Wt. NH_4BF_4	Number of Determinations	Average Weight $(C_6H_5)_4AsBF_4$	Percent BF_4^- in NH_4BF_4	Standard Deviation
1	0.02691	3	0.1187	81.46	0.14
2	0.02965	1	0.1309	81.53	----
3	0.02488	3	0.1097	81.42	0.07
4	0.02830	3	0.1244	81.17	0.07
5*	0.02685	3	0.1178	81.02	0.14

*Each aliquot of solution Number 5 contained 0.2644 grams of KF.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

The principal objective of this research was the development of better analytical procedures for hexafluorophosphate ion. This has been accomplished. Table XV compares the results obtained by analyzing KPF_6 (solution number 3) gravimetrically with Nitron and TPAC, and amperometrically with TPAC. The results are in substantial agreement with one another, but it should be pointed out that the apparent greater precision of the Nitron method is due to the fact that samples ten times as large were used for that determination, so that the relative precision of weighing the Nitron hexafluorophosphate precipitate was much greater. It should also be mentioned that twenty-two samples were determined by the gravimetric procedure utilizing TPAC, whereas only four samples were determined by the gravimetric Nitron procedure. This means that the standard deviations of the means would be 0.055 for the TPAC and 0.075 for the Nitron method. Therefore the mean percentage found by the gravimetric TPAC determinations is known with greater certainty.

The gravimetric method utilizing TPAC is the best of the three methods for determining relatively small amounts

TABLE XV

DETERMINATION OF HEXAFLUOROPHOSPHATE:

COMPARISON OF RESULTS FOR THREE DIFFERENT METHODS

Method	Average Percent PF_6^- Found in KPF_6	Number of Determinations	Standard Deviation
Gravimetric Nitron	79.34	4	0.15
TPAC Amperometric	79.69	11	0.55
TPAC Gravimetric	79.53	22	0.26
Theoretical	78.76		

of hexafluorophosphate because of its simplicity, speed, and good precision. A sample of KPF_6 weighing as little as 0.035 g. will give a precipitate weighing approximately 0.1 g., which can be weighed to within 0.2% on an ordinary analytical balance. The amperometric method offers the advantage of analyzing much smaller samples of KPF_6 than the gravimetric method if desired. Both of the methods using TPAC offer the advantage of utilizing a stable reagent whose solutions can be kept for long periods of time, whereas Nitron solutions are unstable. The decomposition products of Nitron also contaminate the hexafluorophosphate precipitate, which necessitates a careful washing procedure.

The washing procedure devised for the Nitron determination results in a much purer precipitate than the original method of Lange (24). However, the results obtained by the Nitron method without this innovation were closer to those obtained by the gravimetric TPAC procedure. This could indicate that the adsorbed impurity compensates for losses due to the solubility of the precipitate, since Nitron hexafluorophosphate is more soluble than TPAP.

Early in these studies it was found that TPAC formed a very insoluble precipitate with hexafluorophosphate, which indicated that this "onium" compound might be a good analytical reagent for this fluorophosphate ion. In previous studies (60) it had been found that a high ionic strength was necessary in order to quantitatively precipitate tetraphenylarsonium

salts. For this reason a method was sought where contamination of the precipitate with coprecipitated salts would not cause error in the determination. It was decided that an amperometric titration method might work very well, because this type of method uses high concentrations of an inert salt as supporting electrolyte. Therefore, a polarographic investigation of TPAC was undertaken as the first step in the study of the proposed amperometric titration procedure.

The polarographic wave of TPAC was found to be irreversible, and the half-wave potential varied from -1.50 volts to -1.43 volts versus SCE. There appear to be two inflection points on the wave of TPAC, which could indicate that two reduction processes are occurring at two very close potentials rather than a single process. This would seem plausible since both tetraphenylstibonium ion (51) and tetra-p-tolylstibonium ion (4,18) exhibit a double reduction wave.

Although the waves obtained for TPAC were irreversible, there is still a linear relation between the limiting diffusion current and the concentration. Theoretically the plot of diffusion current versus concentration should have an intercept at the origin, but the extrapolation procedure used for measuring the wave height introduced a constant positive error, which resulted in an intercept of 0.015 microamperes. This constant factor was probably due to the beginning of the reduction wave of the supporting electrolyte. This translation of the line along the vertical axis does not af-

fect the results in polarographic analyses so long as the same supporting electrolyte and the same extrapolation procedure are used.

The first amperometric titrations were performed on solutions of NH_4PF_6 and $NH_4PF_6 \cdot NH_4F$ using KCl as supporting electrolyte. These salts were rather impure, but the form observed for the amperometric titration curves was quite encouraging. It was then decided to titrate solutions of KPF_6, because this salt could be obtained in a much purer form than the other salts. Large, spurious diffusion currents were observed before the end-point when titrations of KPF_6 solutions, using KCl as supporting electrolyte, were attempted. It was decided that the impurities present in the other salts were responsible for the better titration curves obtained in those cases. Experiments were run on partially titrated KPF_6 solutions by adding small amounts of KF, NH_4Cl, NH_4HF_2 and KOH, and observing the effect of the addition of each material on the diffusion current. It was found that addition of the fluoride salts and KOH appreciably lowered the diffusion current. In addition it was observed that these reagents flocculated the TPAP precipitate. For this reason it was decided that the diffusion current observed before the end-point was due to reduction of colloidally dispersed precipitate at the mercury drop.

A new series of amperometric titrations was undertaken using an NH_4Cl-NH_4OH buffer of pH 9 as supporting elec-

trolyte. This procedure was successful and was used in all successive titrations.

As a result of the success with the amperometric titrations, it was decided to attempt the development of a gravimetric procedure for hexafluorophosphate using TPAC. In previous attempts, the precipitate often passed through the filter. Since it was assumed that this phenomenon was due to a colloidal dispersion of the precipitate, the precipitations were attempted in the presence of high concentrations of NH_4OH. This base flocculated the precipitate quite well, and any of it adsorbed on the precipitate volatilized upon drying at 105°C. In the quantitative gravimetric work concentrations of NH_4OH in the range 5-11 M. were used to flocculate the precipitate; however qualitative tests indicate that concentrations as low as 1 M. could be adequate.

The only ion, commonly contaminating hexafluorophosphate salts, which interferes with these methods is the difluorophosphate ion. According to White (57) this ion may be quantitatively removed by basic hydrolysis.

Whenever a new gravimetric procedure, using a new type of reagent, is studied it is necessary to know the solubility of the precipitate. Since one could expect the tetraphenylarsonium ion to have a large absorptivity in the near ultraviolet because of the attached benzene rings, a spectrophotometric investigation was undertaken to develop an analytical technique suitable for the needed solubility

determinations. It was found that the spectra of TPAC and TPAP were identical between 350 and 200 millimicrons, which indicated that the tetraphenylarsonium ion was the absorbing species. The large absorption shoulder at 220 millimicrons was chosen for measurements of absorption in the concentration range 10^{-6} to 10^{-5} M., and this allowed a simple determination of the solubility of tetraphenylarsonium salts.

Since TPAC was found to give a precipitate with tetrafluoroborate ion, an attempt was made to develop a gravimetric method with this reagent. Unfortunately, the method which was developed was not as good as that for hexafluorophosphate. The tetraphenylarsonium tetrafluoroborate (TPAB) precipitate was somewhat more soluble than the Nitron tetrafluoroborate, which made necessary the special washing procedure described previously. The results obtained with TPAC as precipitant using this procedure were essentially the same as those obtained with Nitron before the empirical correction factor, suggested by Lange (24), was added to the weight of the Nitron tetrafluoroborate. TPAC does offer the advantage over Nitron that it is a stable reagent.

It was predicted that the tetrafluoroborate salts of higher molecular weight tetraarylarsonium ions should be more insoluble than TPAB. Therefore tetra-p-tolylarsonium chloride (TPTAC) was synthesized with the expectation that this "onium" compound would prove to be a suitable analytical reagent for tetrafluoroborate ion.

Many difficulties were encountered in synthesizing TPTAC. The first procedure tried, which involved the addition of a molecule of Grignard reagent to the arsenic-oxygen double bond of tri-p-tolylarsine oxide, resulted in a very impure product, apparently due to a large number of side reactions. A yellow organic impurity of highly polar character seemed to have almost the same solubility behavior as the TPTAC. This difficulty was compounded by the fact that tetra-p-tolylarsonium chloride-hydrochloride came down as an oil even when quite pure, which eliminated the possibility of using the method used by Shriner and Wolf (52) for the purification of TPAC. In a second procedure which involved the reaction of $AlCl_3$ with tri-p-tolylarsine and p-bromotoluene at circa 200°C., similar purification problems were encountered. The purification method used with most success was the repeated precipitation of the bromide salt of tetra-p-tolylarsonium with KBr from alcohol-water or dioxane-water mixtures, followed by a final recrystallization from an ethanol-water mixture. The bromide salt was then converted to the chloride by a metathesis reaction with freshly prepared AgCl.

The better synthesis method was the $AlCl_3$ procedure. One synthesis step was eliminated; and, in addition, the one step conversion of tri-p-tolylarsine to tetra-p-tolylarsonium ion was much faster than either of the two steps which it replaced.

A polarographic investigation of TPTAC was under-

taken to facilitate use of this reagent for amperometric titrations. The curves obtained were quite similar to those obtained with TPAC. The half-wave potential decreased with increase in concentration from about -1.52 volts to -1.45 volts versus SCE. Also the same form of curve as TPAC with two inflection points was observed. The fact that the diffusion current constant was 20% smaller than that for TPAC can be explained in terms of the greater size and weight of the tetra-p-tolylarsonium ion.

A spectrophotometric investigation of TPTAC was undertaken in order to develop an easy method for determination of the solubility of the various salts of this "onium" ion. The spectrum in the range 340-200 millimicrons was qualitatively very similar to that of TPAC with a broad peak at 230 millimicrons replacing the shoulder at 220 millimicrons. However, the molar absorptivity of this peak was considerably greater than that of the TPAC shoulder.

Unfortunately, the solubility of tetra-p-tolylarsonium tetrafluoroborate was of the same order of magnitude as TPAB, so that TPTAC offers no advantage over TPAC for determination of tetrafluoroborate.

Finally it should be mentioned that the work in this dissertation suggests some further avenues for investigation. An extensive study of the solubilities of tetra-p-tolylarsonium salts could indicate other analytical applications for this reagent. Also investigations of other "onium"

compounds might yield a better analytical reagent for tetrafluoroborate and other fluoride complexes. In particular a combination of various organic arsonium and stibonium salts, using both gravimetric and extraction techniques, should provide a powerful method of attack upon the general problem of the analysis of fluoride complexes.

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