PHOTOMETRIC STUDIES OF NON-AQUEOUS ACID-BASE REACTIONS

by

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Submitted to the Department of Chemistry on May 28, 1959 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Abstract

The photometric titration technique was applied to the determination of acids and bases in non-aqueous solvents. Isopropanol was found to be a good solvent for photometric titration of acids as weak as phenol [$pK_a(H_2O) = 9.9$] using tetra-n-butylammonium hydroxide in isopropanol as titrant. Bases as weak as 4-methyl-2-nitroaniline [$pK_b(H_2O) = 13.5$] were successfully titrated in glacial acetic acid with a perchloric acid titrant made up in the same solvent.

As expected from theory, the photometric method was found particularly useful for differentiating titrations of acids or bases of similar strength. It was demonstrated that mixtures containing up to four components can be resolved by a single photometric titration, provided that a suitable change in wavelength setting is made during the titration. Acids or bases whose aqueous pK values differed by 1.5 units or more were quantitatively resolved and analytically useful differentiation was sometimes achieved when the difference was as small as 0.8 units. Differentiating titrations of base mixtures containing strong components are best performed in a non-leveling solvent, such as acetonitrile.

Comparison with potentiometric titrations demonstrated that useful photometric breaks can be obtained in many cases where a potentiometric curve shows no inflection whatsoever.

The photometric technique is directly applicable to large groups of organic compounds, such as phenols, aromatic amines and heterocyclic aromatic nitrogen bases, which absorb in the visible or ultraviolet wavelength region. In addition, any sufficiently strong non-absorbing acid or base can be titrated photometrically by adding an indicator compound.

The Beckman spectrophotometer models B and DU were adapted for titrations in a very simple manner. Beakers of glass or Vycor were used as titration cells and efficient mixing was provided by an ordinary magnetic stirring motor. This simple and inexpensive system compares favorably with arrangements reported in the literature, many of which are of the circulation type.

While most compounds were found to give photometric titration curves in close agreement with the expected linear shape, exceptions were found, particularly among the phenols. The deviations from linearity for these compounds are apparently due to the formation of strongly hydrogen-bonded phenol-phenolate complexes during the titration. Previous investigators have reported potentiometric and conductometric evidence for such complexes in solvents without hydrogen-bonding capability while the photometric evidence obtained in the present study indicates that some complexation occurs even in pure isopropanol. Photometric titration in benzene gave an increase in curvature while linear curves were obtained in ethanol. In connection with these studies it was demonstrated that nonlinear photometric curves may also result from spectral shifts due to a change in solvent composition during the titration if titrant and sample solvent differ.

Some anomalous photometric curves were also obtained in titrating aromatic amines in glacial acetic acid and it is suggested that these are caused by the formation of hydrogen-bonded complexes between the amine and its conjugate acid.

A spectrophotometric indicator method developed by Kolthoff and Bruckenstein for the study of acid-base equilibria in glacial acetic acid was critically examined. Successful repetition of one of the experiments reported by Kolthoff and Bruckenstein demonstrated the reliability of the method in glacial acetic acid but attempts to apply it to acid-base systems in non-acidic solvents of low dielectric constants failed. The failure was apparently caused by extensive formation of higher ionic aggregates in these solvents. Application of the Kolthoff-Bruckenstein method may be possible in solvents such as o-dichlorobenzene, provided that a strongly basic indicator with high molar absorptivity is found so that weak acids can be studied at very low concentration.

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I. GENERAL INTRODUCTION AND STATEMENT OF THE PROBLEM

The practical value of non-aqueous solvents in chemical analysis has long been realized and their popularity grows as a greater number of solvents become commercially available at reasonable cost. Organic solvents are particularly useful in acid - base titrimetry where they make possible the determination of many acids and bases which are too weak to be titrated in aqueous media.

In non-aqueous acid - base titrations the end-point is usually detected either potentiometrically, or visually using as indicator. There are, however, many cases in which both these methods are unsatisfactory. Examples are titrations of very weak acids and bases, or differentiating titrations of mixtures where the components are similar in acidic or basic strength. In such cases it may be difficult or impossible to locate the inflection point in a potentiometric curve or the color change in a visual titration. It has been shown, in particular by Goddu and Hume (27, 28), that the photometric titration technique offers very definite advantages in aqueous media in such situations and it is somewhat surprising that this method has not yet been extensively used in non-aqueous solvents. One of the main objectives of this thesis is to study the utility of the photometric titration technique in non-aqueous acid - base titrations in the hope of facilitating the analysis of systems which are inaccessible to other titration methods.

While extensive practical use has been made of non-aqueous solvents, the theory of acid - base reactions in these media has been largely neglected. In general, the analyst has tried to extrapolate his knowledge of aqueous chemistry to non-aqueous media, thereby often encountering puzzling anomalies. The recent work of Kolthoff and Bruckenstein (46, 47, 8, 9, 10) on acid - base equilibria in glacial acetic acid is one of the outstanding achievements in developing the theory of non-aqueous acid - base reactions. These investigators developed a spectrophotometric method whereby they were able to study the reaction between a relatively weak acid and an indicator base, obtaining such information as the dissociation constant of the acid, the formation constant of the ion-pair form of the indicator salt, and the dissociation constant of this ion-pair. The often peculiar behavior of solutions in low dielectric solvents, such as glacial acetic acid, depends largely on the extensive ion association and a theory that takes this into account is therefore imperative. It appears that the approach of Kolthoff and Bruckenstein may be useful also in non-acidic solvents of low dielectric constant and the latter part of this thesis is devoted to the exploration of this possibility. A number of acid - base systems in benzene, chlorobenzene, o-dichlorobenzene, o-dichlorobenzene-acetonitrile, and glacial acetic acid are studied.

II. PHOTOMETRIC ACID-BASE TITRATIONS

A. INTRODUCTION AND LITERATURE SURVEY

1. Comparison of the Photometric Technique with Other Methods

In a potentiometric titration the measured quantity is a logarithmic function of some concentration or concentration ratio. Hence, there is a gradual and relatively small change in potential up to the equivalence point where a sudden potential jump occurs as a result of the dramatic decrease in the concentration of the titrated species. If the reaction is incomplete at the stoichiometric end-point, the concentration of the reactant changes less sharply and the resulting potential break is smaller. In many cases the potential changes so gradually that the inflection point is difficult to locate. In such situations it is advantageous to measure some quantity which is directly proportional to the concentration of one of the reactants or products rather than being a logarithmic function thereof (28). This results in a titration curve with linear portions which can be located by relatively few measurements. A particularly attractive feature of such a titration is that the location of the end-point does not depend on measurements taken in the immediate vicinity of the stoichiometric equivalence point where the reation may be incomplete. The extrapolated linear portions of the curve intersect at the end-point which therefore can be determined with good accuracy even in cases where the titration curve shows a rounded break due to incomplete or slow reaction.

There are three types of titration techniques which give such linear plots, namely the amperometric, conductometric, and photometric methods. In an amperometric titration the diffusion current of a reducible or oxidizable species is measured as a function of the volume of titrant added. This method is relatively slow and can be applied only when an electroactive substance is consumed or formed in the reaction. The concentration of the electroactive species must be low, usually 10^{-3}-10^{-4} M, and a supporting electrolyte is needed to ensure proportionality between limiting current and concentration. The polarographic characteristics of purely non-aqueous solutions are relatively unexplored. Thus the amperometric technique can hardly be expected to become important in non-aqueous acid - base titrations.

The conductometric method, on the other hand, has found rather extensive application in non-aqueous acid - base titrations (11, 31, 55, 56, 48). Good results have been obtained in many cases and the conductometric method is definitely of practical value in titrating weak acids or bases. In low-dielectric media, non-linear conductometric titration curves have been encountered (11) due to various association phenomena which will be discussed in a later section.

However, the experimental measurement of conductance is quite complicated in solvents of low dielectric constant where the resistance is very high. In such media it is also generally difficult to obtain stable potentiometric readings. These difficulties are avoided by use of the photometric titration technique, in which the absorbance of the solution, at a selected wavelength, is measured as a function of the volume of titrant added. The absorbance $\underline{A}$ is related to the transmittance $\underline{T}$, the concentration $\underline{c}$ and molar absorptivity $\underline{a}$ of the absorbing species, and the length of the light path $\underline{b}$, through the Bouguer-Lambert-Beer law:

$$A = - \log T = abc$$

In this expression $\underline{a}$ signifies the molar absorptivity at the particular wavelength used. A photometric titration can often be made quite selective by changing the wavelength setting and its sensitivity can be varied in the same way. In the absence of complicating side reactions $\underline{A}$ is a linear function of $\underline{c}$ and the end-point can be located by extrapolation. The precision of photometric measurements is not very high but the uncertainty in the curve is smaller than that of a single measurement since the curve is determined by several readings. Hence the titration technique compares favorably in accuracy and precision with direct photometric determination. No calibration curve is needed and the presence of non-reactive absorbing materials does not interfere, provided that the solution has a sufficiently high transmittance at the desired wavelength.

There are, of course, serious limitations to the photometric titration technique. Direct titration obviously requires a change in absorbance and the solvent must be sufficiently transparent at the selected wavelength. However, a non-absorbing acid or base may be titrated if a more weakly acidic or basic substance is added whose reaction with the titrant involves a change in absorption characteristics. In this connection one has to distinguish between photometric detection of ordinary indicator end-points and differentiating photometric titrations. In the latter enough indicator substance is present to give a titration curve with two breaks, the first for the non-absorbing substance and the second for the indicator. On the other hand, in an ordinary indicator titration only a very small amount of absorbing material is present, and no titration curve for this component but merely a sudden color change is obtained. Such an end-point can often be detected equally well visually and full advantage is not taken of the photometric method. The optimum strength of the indicator depends on the method chosen since an ordinary indicator should have its maximum color change at the equivalence point while a photometric indicator should react mainly after the end-point (27, 28).

2. Literature Survey of Photometric Acid-Base Titrations in Non-Aqueous Solvents

In view of the many attractive features of the photometric technique it is rather surprising that it has not yet found many practical applications in the non-aqueous field. The exhaustive literature search by Goddu and Hume (28) revealed only one application to photometric detection of indicator end-points in alcohol-acetone media. Goddu and Hume (27) reported the use of 1-butanol as solvent in the photometric titration of p-toluidine. This titration was performed at 289mμ using the Beckman DU spectrophotometer and the standard 1-cm. Beckman cell. Reilley and Schweizer (63) titrated quinoline, m-chloroaniline, o-chloroaniline, and a mixture of o-chloroaniline and sodium acetate in glacial acetic acid using an acetic acid solution of perchloric acid as titrant. They too employed the Beckman DU spectrophotometer. Aronoff (1) titrated porphyrins in nitrobenzene using perchloric acid in dioxane as titrant. He recorded the complete spectrum after each addition of titrant to elucidate the step-wise neutralization of porphyrins. Higuchi et al. (41, 62) have developed special plotting techniques for indicator titrations with photometric end-point detection and applied them to titrations in glacial acetic acid. Other investigators have developed generally useful apparatus (44, 61, 66, 67) without reporting any applications to non-aqueous acid-base titrations. Grunwald (29) has discussed an objective method of end-point calculation for conductometric and photometric titrations which exhibit no sharp break.

3. Present Study

In this thesis a survey is presented of photometric titrations of both acids and bases in several non-aqueous media. The study is restricted to true photometric titrations, i.e., it does not include photometric detection of ordinary indicator end-points. For the purpose of comparison a number of potentiometric titrations have also been performed.

B. APPARATUS AND MATERIALS

1. Spectrophotometers and Titration Assemblies

Many of the titrations in the visible wavelength region were performed using the Beckman Model B spectrophotometer with the simple titration assembly developed by Goddu and Hume (28). The cell carriage and the cover and floor of the cell compartment are removed and a magnetic stirrer covered with a wooden beaker support is inserted in their place. Special covers are made from wood. Since the stirring is magnetic only one small hole for the buret has to be drilled in the top cover. This simple arrangement compares favorably with more elaborate titration assemblies described in the literature. Many of these (61, 66) are of the circulation type in which the titration is performed outside the cell compartment and a stream of sample solution is continuously passed through the spectrophotometer. This system makes it difficult to obtain rapid mixing. In other arrangements (63) an overhead stirrer is used which makes it more difficult to prevent light leakage. Also, the conventional 150-ml. beaker used in the system of Goddu and Hume is far less expensive and much more convenient in use than more elaborate titration cells.

For titrations in the ultraviolet region the Beckman DU spectrophotometer was adapted. In this case the only modification needed was the replacement of the metal cover of a standard 10-cm. cell compartment with a cover made from wood through which a hole for the buret was drilled. The cell carriage was removed from the cell compartment so that the titration beaker could be placed directly on the floor. The spectrophotometer was placed on wooden blocks to provide space for a conventional magnetic stirring motor directly underneath the cell compartment. A similar but more elaborate arrangement has been described by Klingman et al. (44).

The titration cell used in the ultraviolet region was a 150-ml. beaker made of Vycor grade 7910 which transmits light down to about 241 mμ . The beaker was manufactured on special order at the Corning Glass Works, Corning, N.Y.

Since run-to-run reproducibility of the light path is not needed in photometric titrations, very simple clamping devices can be used to keep the titration beaker in place during a titration. In the present study, pads of sponge rubber were preferred.

During titrations of acids a stream of prepurified nitrogen was passed over the sample solution in order to minimize the interference from atmospheric carbon dioxide. The nitrogen was introduced into the cell compartment through a syringe needle which was inserted through a small hole in the cover.

Absorption spectra of compounds to be titrated were measured using the Beckman spectrophotometers B, DU, and DK-2 or the Cary recording spectrophotometer Model 11MS.

2. Burets and Titrant Dispensing Systems

For titrations using perchloric acid titrant a 5-ml. "Exax" microburet was used. Basic titrants were delivered from a closed system consisting of a 5-ml. Fisher and Porter "Lab-Crest" microburet equipped with a 3-way Teflon stopcock for filling from a polyethylene storage bottle connected to the buret with polyethylene tubing. The reagent was protected from the atmosphere with an Ascarite tube. A similar tube was attached to the top of the buret.

The burets were painted black or wound with black tape below the graduation in order to avoid conducting light into the cell compartment.

3. Equipment for Potentiometric Titrations

The potentiometric titrations were performed with a Leeds and Northrup pH meter using a Leeds and Northrup glass electrode (std. 1199-30) and a sleeve-type calomel electrode. In titrating acids the sample solution was protected with a blanket of prepurified nitrogen.

4. Solvents and Chemicals

Commercially available materials were used without purification when possible. Reagent grade acetic acid, benzene, chloroform and absolute ethanol were ordinarily used without purification. Dry acetic acid was prepared by adding the calculated amount of acetic anhydride (as determined by Karl Fischer titration) and some sulfuric acid catalyst, and distilling using the method and apparatus of Keily (43). Commercial isopropanal (99%) was found quite satisfactory for titration purposes, but the technical grade acetonitrile appeared to be of varying quality. The latter solvent sometimes showed an abnormally high absorption below 290 mμ and developed a red color upon acidification. The impurity could be removed satisfactorily by distillation from phosphorous pentoxide and most of the acetonitrile used was purified in this manner. The more expensive Fisher Reagent grade acetonitrile can be used without purification.

Most chemicals were of Eastman White Label grade and they were used without further purification when possible. All the nitroanilines and N,N-dimethyl substituted nitroanilines were purified by recrystallization from water or water-ethanol mixtures. The purification of diphenyl phosphate is described in section IIIC. In the preparation of titrants reagent or polarographic grade materials were used.

C. PHOTOMETRIC TITRATION OF ACIDS

1. Solvents

The first problem in attempting non-aqueous titration of acids was the selection of a generally useful solvent. The solvent should be as weakly acidic as possible in order not to interfere with the titration of very weak acids. It should also be sufficiently transparent to allow photometric titration of substances, such as phenol, which absorb at short wavelengths. The transparency requirement excluded the general use of ketones such as acetone and methyl isobutyl ketone which have been extensively used in potentiometric titrations of acids (26, 12). These solvents could, however, be used in the visible region. Dimethyl formamide has been shown to be unsuitable for titrations involving a strongly basic titrant because of rapid hydrolysis (16). An attempt to use acetonitrile resulted in rapid color formation. Pyridine is a good solvent for titration of acidic substances (15) but its strong absorption in the ultraviolet restricts its use as a solvent for photometric titrations. It also has a very unpleasant odor, a characteristic which it has in common with ethylenediamine and n-butylamine, the most strongly basic solvents which have found extensive use in acid-base titrations (57, 23). Low dielectric solvents such as benzene, toluene or dioxane may be useful in many cases but they often present solubility problems which prevent general use in photometric titrations.

Such a survey revealed that only the alcohols showed promise as generally useful solvents for the photometric titration of acids. Their chief disadvantage is their weakly acidic character but this becomes less pronounced in going to the higher members of the series (35). Isopropanol was selected as solvent because it is less acidic than methanol or ethanol, has good solvent properties and is readily available in sufficient purity at low cost. It is also relatively nontoxic.

For comparison purposes a number of titrations were also performed in benzene or absolute ethanol or mixtures of these solvents with isopropanol.

2. Titrants

a. Advantages of Tetraalkylammonium Bases:

One of the most significant advances in non-aqueous acid-base titrimetry during recent years is the introduction of anhydrous tetraalkylammonium base titrants (15, 34). These are very strongly basic and their salts are, as a rule, soluble even in low-dielectric media, in contrast to the salts of alkali hydroxides or alkoxides. The solubility is particularly important in photometric titrations. In potentiometric titrations tetraalkylammonium base titrants have been found to give much more stable readings with the glass electrode than the corresponding alkali bases, presumably due to absence of alkali errors.

Most of the titrations reported in the literature have been performed using tetra-n-butylammonium hydroxide in methanol, isopropanol or methanol-benzene. Since this base appears to be very satisfactory it was selected for use in the present study.

b. Effect of Solvent on Titrant Properties:

Harlow and Wyld (35) have compared the potentiometric inflections in titrations of phenols in acetone or pyridine using tetrabutylammonium hydroxide made up in water, methanol, ethanol or isopropanol. The sharpest inflection was obtained using isopropanol as solvent for the titrant and a still less acidic solvent would presumably be even better from this viewpoint. However, Harlow and Wyld claim that quaternary ammonium titrants prepared in less acidic solvents tend to be more unstable and isopropanol therefore appears to be a good compromise.

c. Preparation of Tetrabutylammonium Hydroxide in Isopropanol:

The first successful preparations of anhydrous tetrabutylammonium hydroxide titrants were reported in 1956 by Harlow, Noble and Wyld (34) and Cundiff and Markunas (15). The former investigators passed a saturated solution of tetrabutylammonium iodide in isopropanol through an anion exchange resin (Amberlite IRA-400) in its hydroxide form. In this way they obtained a 0.2 N titrant containing about 0.5% water. An attempt to prepare tetrabutylammonium hydroxide in pyridine using the same method was unsuccessful. At this time Harlow and his co-workers also attempted to prepare a titrant by reacting a quaternary ammonium halide with finely powdered silver oxide, a method which has been extensively used in aqueous media. While Harlow et al. failed in this attempt Cundiff and Markunas (15) succeeded in preparing tetrabutylammonium hydroxide in methanol using the silver oxide method. They diluted the methanol solution with ten volumes of benzene to obtain the final titrant. Recently Harlow and Bruss (33) have reported the successful preparation of 1.5 N tetrabutylammonium base in isopropanol using the silver oxide method.

In a photometric titration it is advantageous to use a relatively concentrated titrant in order to avoid excessive dilution during the titration. Since it appeared impossible to prepare a stronger titrant than about 0.2 molar using the ion-exchange method the silver oxide method was chosen in the first attempt to prepare a tetrabutylammonium base titrant in isopropanol. However, the reaction of tetrabutylammonium iodide with silver oxide in isopropanol was found exceedingly slow. Prolonged shaking (about 30 hours) on a mechanical shaker resulted in formation of a semicolloidal suspension which continued to settle over a long period of time despite repeated filtrations. Apparently the rate of the heterogeneous reaction between suspended silver oxide and partially dissolved tetrabutylammonium iodide depends very strongly on the surface condition of the reactants since a relatively fast reaction (within one hour) has been reported in the literature (15, 33). The initial failure of Harlow et al. (34) with the silver oxide method tends to support the view that the success of this method in non-aqueous media depends strongly on factors which are difficult to control.

Rather than continuing the costly and time-consuming experiments with the silver oxide method it was decided to use the 1.0 M methanolic tetrabutylammonium hydroxide of Southwestern Analytical Chemicals, Austin, Texas, as starting material. This solution could have been used as such but it was felt desirable to reduce the methanol content of the titrant as far as possible (35). For this purpose the methanolic solution was concentrated in a rotating flask evaporator at room temperature to about half of its original volume. The resulting roughly two-molar solution was diluted with four volumes of isopropanol (Merck Reagent grade), giving a 0.4 M tetrabutylammonium hydroxide solution containing no more than 10 - 15% methanol.

d. Composition of Tetraalkylammonium Base Titrants:

In the previous discussion no distinction has been made between titrants prepared using different methods. When the titrant is prepared from a quaternary ammonium halide by anion exchange in an anhydrous solvent, pure tetraalkylammonium hydroxide is obtained. If the solvent is an alcohol one might expect the reaction $ROH + OH^- \rightarrow RO^- + H_2O$ to produce some alkoxide ion. However, water is also acidic and an equilibrium is therefore set up.

When the titrant is prepared by reacting the quaternary ammonium halide with silver oxide in an anhydrous medium it must necessarily contain a mixture of alkoxide and hydroxide (13, 33), though it is usually referred to as hydroxide for the purpose of simplicity. Cluett (13) has very recently reported a determination of the actual composition of a methanolic titrant which had been prepared using the silver oxide method. In order to establish the hydroxide content he added an aliquot of the tetrabutylammonium titrant to a methanol solution containing a fifteenfold excess of glacial acetic acid and determined the water formed by Karl Fischer titration. Comparison of the result with the total base content indicated that the titrant consisted of a 1:1 mixture of hydroxide and methoxide, as would be expected from the stoichiometry of the reaction

$$2BU_4N^+I^- + \underline{Ag_2O} + CH_3OH \rightarrow Bu_4N^+OH^- + Bu_4N^+OCH_3^- + 2\underline{AgI}.$$

The presence of some moisture in the solvent tended to make the hydroxide content slightly greater than the methoxide concentration.

In actual titrations there appears to be little difference between mixed base titrants and those containing pure hydroxide. The reason is probably that the hydroxyl and alkoxide ions are quite similar in basic strength. However, the alkoxide ion would be expected to be somewhat more basic than the hydroxyl ion and mixed titrants (prepared by the silver oxide method in anhydrous solution) are therefore probably to be preferred for titration of extremely weak acids.

The titrant used in the present investigation is assumed to be pure hydroxide since it was prepared from methanolic tetrabutylammonium hydroxide.

e. Effect of Carbonate in Titrant:

Potentiometric titrations of portions of the tetrabutylammonium hydroxide titrant, diluted with distilled water, revealed the presence of a weakly basic impurity as shown in Figure 1 (circles). By a similar titration of a portion of the original one-molar methanolic solution it was shown that this did not contain any significant amount of impurity, since only one inflection was obtained. Hence, it appeared that the impurity had been formed or introduced during the evaporation of the methanol or during the subsequent dilution with isopropanol. While the possibility of chemical decomposition of the hydroxide could not be excluded it seemed more probable that the impurity was carbon

Figure 1

Potentiometric Titrations of 4.00 ml. Portions of Tetrabutylammonium Hydroxide Titrant in Water with 0.09691 M Aqueous Perchloric Acid

—○—○— Before Treatment with Carbon Dioxide
—△—△— After " " " "

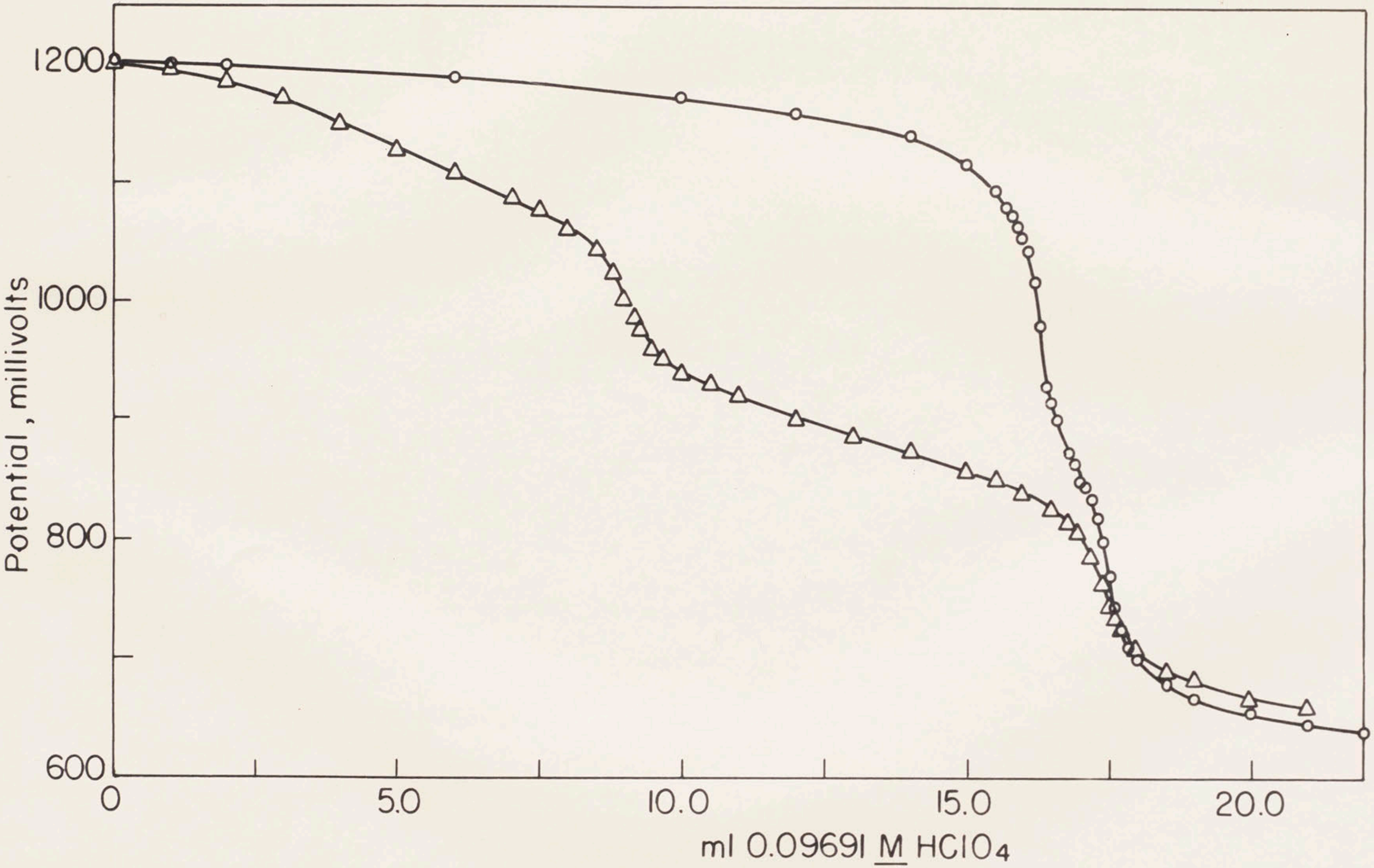

1200
1000
800
600
Potential, millivolts
0
5.0
10.0
15.0
20.0
ml 0.09691 M HClO4

TABLE I

REACTION OF CO_2-TREATED TETRABUTYLAMMONIUM HYDROXIDE WITH PHENOLS OF DIFFERENT ACIDIC STRENGTH

Compound	$pK_a(H_2O)$	Milliequivalents Taken	Milliliters of Titrant Consumed	Apparent Molarity of Titrant*
Phenol	9.89	0.2024	0.930	0.2176
2,4,6-Trichlorophenol	6.0	0.2325	0.616	0.3774
Pentachlorophenol	4.0	0.2189	0.527	0.4154

* Assuming the phenols to be 100% pure

dioxide which had leaked in from the atmosphere, probably during the vacuum evaporation.

In order to study the behavior of carbonate a small piece of dry ice was added to 10.0 ml. of the tetrabutylammonium hydroxide in isopropanol. No precipitate was formed. A 4.00 ml. portion of the CO_2 - treated titrant was immediately pipetted into 70 ml. distilled water and titrated potentiometrically using 0.09691 M aqueous perchloric acid. The titration curve, indicated by triangles in Figure 1, shows that the titrant had been almost completely converted into carbonate. The first inflection occurs at 9.05 ml., and the second at 17.45 ml., indicating a hydroxide content corresponding to 9.05 - 8.40 = 0.65 ml.

The remainder of the CO_2-treated titrant was transferred to a 5-ml. microburet and immediately used for photometric titration of phenol, 2,4,6-trichlorophenol, and pentachlorophenol. The results are summarized in Table I, which shows a striking variation in apparent titrant molarity depending on the acidic strength of the titrated phenol. The molarity obtained against pentachlorophenol is practically identical with the average molarity, 0.4223, of the titrant before addition of CO_2, as calculated from the <u>second</u> inflection in the potentiometric titrations with aqueous perchloric acid. It also agrees with the molarity 0.4228 calculated from the <u>second</u> inflection in the titration curve for the CO_2-treated titrant (Figure 1). 2,4,6-Trichlorophenol gives a slightly lower apparent titrant molarity while phenol gives the much lower value 0.2176. This figure is in excellent agreement with the molarity 0.2193 calculated from the first inflection in the potentiometric curve for the CO_2-treated titrant. Since this first inflection corresponds to titration of all hydroxide and conversion of the carbonate to bicarbonate it is apparent that phenol is a strong enough acid in isopropanol to react with carbonate to form bicarbonate. Further reaction of the bicarbonate to CO_2 does not occur with phenol while both 2,4,6-trichlorophenol and pentachlorophenol are strong enough acids to react with the bicarbonate ion.

From these results it is obvious that presence of carbonate in the titrant leads to a titer which varies with the strength of the acid titrated. Cundiff and Markunas (17) have recently reported that tetrabutylammonium hydroxide prepared by the silver oxide method contains a basic impurity which causes errors in potentiometric titrations of acid mixtures containing a strong component. For example, the titration of sulfuric acid in pyridine gave a correct value for the total acidity but unequal results for the two equivalents, the second being consistently higher than the first. The amount by which the second equivalent was high corresponded very closely to the value by which the first equivalent was low. Other acid mixtures containing a strong component gave similar results, the error being generally 1-3% but occasionally as high as 6-7%.

Cundiff and Markunas were unable to identify the impurity but found that it could be removed by passing the titrant through a short anion exchange column with the resin in its hydroxide form. They considered the possibility that the impurity might have been carried over from the tetrabutylammonium halide used in preparing the titrant but the use of more highly purified starting material did not lead to a significant improvement. Addition of tributylamine to strong acid solutions in pyridine did not affect the titration results showing that the basic impurity could not be tributylamine. Cundiff and Markunas suggested that the impurity was some mysterious by-product of the reaction of the quaternary ammonium halide with silver oxide. They based this suggestion on the fact that preparation of tetrabutylammonium hydroxide in a flask held in an ice bath seemed to yield a titrant containing less impurity than one prepared at room temperature.

The results obtained in the present study seem to indicate that the observations of Cundiff and Markunas could well be explained on the assumption that the unknown impurity was carbonate. It is, in fact, quite surprising that the above mentioned investigators do not even mention this possibility in spite of the fact that their titrant preparation procedure seems to provide ample opportunity for absorption of carbon dioxide from the atmosphere. For instance, the silver iodide is apparently removed by filtration through an open sintered-glass funnel. Carbonate present in the titrant would probably react with phenols and other weak acids in pyridine to form bicarbonate, which would not react further. A strong acid, on the other hand, would convert the bicarbonate into carbon dioxide, which would be back titrated as a weak acid. This would lead to a correct value for the total acidity while the results for strong acids would be low and those for weak acids correspondingly high, as observed by Cundiff and Markunas. This explanation becomes particularly plausible in view of the finding that the basic impurity was easily removable by anion exchange, which would be expected for the divalent carbonate ion.

Cundiff and Markunas standardized their titrant against benzoic acid in pyridine. Apparently the benzoic acid was not strong enough in this solvent to react with bicarbonate. In isopropanol, the solvent used in the present study, benzoic acid was found to be intermediate to pentachlorophenol and 2,4,6-trichlorophenol in strength, and hence it would be expected to convert bicarbonate into carbon dioxide (Table I). However, the interaction of benzoic acid with the basic solvent pyridine probably decreases its acidic strength to the point where it no longer reacts with the bicarbonate ion. This is not too surprising, since benzoic acid, being only slightly stronger than 2,4,6-trichlorophenol, is a borderline case even in isopropanol.

It is conceivable that Cundiff and Markunas excluded carbonate as a possible impurity on the assumption that tetrabutylammonium carbonate would be insoluble in their titrant medium, which was a 10:1 mixture of benzene and methanol. In order to test this possibility the last milliliter of the CO_2-treated titrant in isopropanol was successively diluted with benzene. No precipitate was observed and it is concluded that tetrabutylammonium carbonate is quite soluble in low-dielectric media in contrast to alkali metal carbonates and bicarbonates.

The only factor which seems contradictory to the assumption of carbonate as the unknown titrant impurity of Cundiff and Markunas is their statement that better results could be obtained by reacting tetrabutylammonium iodide and silver oxide in methanol at decreased temperature. The solubility of a gas normally increases with decreasing temperature and hence no improvement would be expected. However, the viscosity of the solvent also increases with decreasing temperature, thereby decreasing the rate of diffusion. This may well explain the observation of Cundiff and Markunas. It is also possible that the improvement in titrant quality upon lowering the preparation temperature was purely incidental, being due to uncontrolled variations in exposure to the atmosphere.

f. Standardization of Titrant:

In the previous section it was pointed out that the tetrabutylammonium hydroxide titrant was found to contain a basic impurity, apparently carbonate. It was also shown that the presence of carbonate causes variations in apparent titrant molarity depending on the strength of the acid titrated. The carbonate could be removed by anion exchange, and such a procedure is to be recommended for careful work (17). However, the conversion of the anion exchange resin into its hydroxide form and the subsequent washing and removal of the water with organic solvents is a lengthy procedure which did not seem warranted in the present study which is a general survey of the applicability of the photometric titration technique rather than a rigorous test of its accuracy and precision. It was therefore decided to use the impure tetrabutylammonium hydroxide as such. Variations in titrant consumption can be taken as a rough measure of the degree to which the particular acids react with bicarbonate since it has been shown that even the weakest acids, such as phenol, are strong enough to convert carbonate into bicarbonate.

Two potentiometric titrations of portions of the titrant with perchloric acid in aqueous solution gave the average molarities 0.3947 and 0.4223, as shown in Table II, depending on whether the first or the second inflection was used for the calculation. In addition, a total of ten photometric titrations of pentachlorophenol were performed in two different batches of commercial isopropanol in order to establish the magnitude of the solvent blank and also to obtain a measure of the precision of the method. The results of these photometric titrations (Table III) can be compared with the potentiometric standardization (Table II). The purity of the pentachlorophenol (Eastman White Label) was determined by potentiometric titrations with 0.09818 $\underline{M}$ NaOH in water-ethanol solutions, which gave an average of 100.69%. This result indicates the presence of some tetrachlorophenol, which is so similar to pentachlorophenol in acidic strength that they undoubtedly react

TABLE II

POTENTIOMETRIC STANDARDIZATION OF TETRABUTYLAMMONIUM HYDROXIDE TITRANT (CONTAINING CARBONATE) AGAINST 0.09691 M AQUEOUS PERCHLORIC ACID

	Titrant Molarity	
	a	b
Titration 1	0.3944	0.4206
Titration 2	0.3949	0.4240
Average	0.3947	0.4223

a: Calculation based on first inflection
b: Calculation based on second inflection

TABLE III

PHOTOMETRIC STANDARDIZATION OF TETRABUTYLAMMONIUM HYDROXIDE TITRANT AGAINST PENTACHLOROPHENOL IN ISOPROPANOL

Solvent Batch	Blank/ 110 ml Solvent	Titrant Molarity*		
		a	b	c
1	0.045 ml.	0.4172	0.4201	0.4207
2	0.025 ml.	0.4184	0.4213	

* Based on five titrations per solvent batch
a:Assuming pure pentachlorophenol
b:Corrected for tetrachlorophenol content
c:Average of corrected molarities

simultaneously during the photometric titrations. Table III shows that the photometric titrations give an average molarity of 0.4178 for the titrant if the pentachlorophenol is assumed to be pure. Correction for the observed purity of 100.69% gives a titrant molarity of 0.4207, which agrees well with the value 0.4223 calculated from the second inflections in the potentiometric standardizations. This is the inflection which should be used in calculating the titrant strength versus pentachlorophenol since it has been shown that this compound reacts quantitatively with bicarbonate (Table I).

On the basis of these titrations the tetrabutylammonium hydroxide titrant in isopropanol can be expected to show a maximum molarity of about 0.421 against acids comparable in strength to pentachlorophenol, and a minimum molarity of about 0.395 against very weak acids, such as phenol. Acids of intermediate strength probably react with the bicarbonate ion to some extent and the apparent titrant molarity will then fall somewhere between the two limiting values.

3. Titrations

a. Titration Technique:

All acid titrations were performed using a Beckman DU spectrophotometer, adapted for titrations as described in section B1. The sample volume was 110 ml. and the titrant consumption before the end-point was usually 1-3 ml. Hence, the effect of dilution on the absorbance readings was small and no dilution corrections were made in plotting the titration curves. Absorption of atmospheric carbon dioxide was minimized by passing a stream of prepurified nitrogen over the solution surface.

b. Single Acids in Isopropanol:

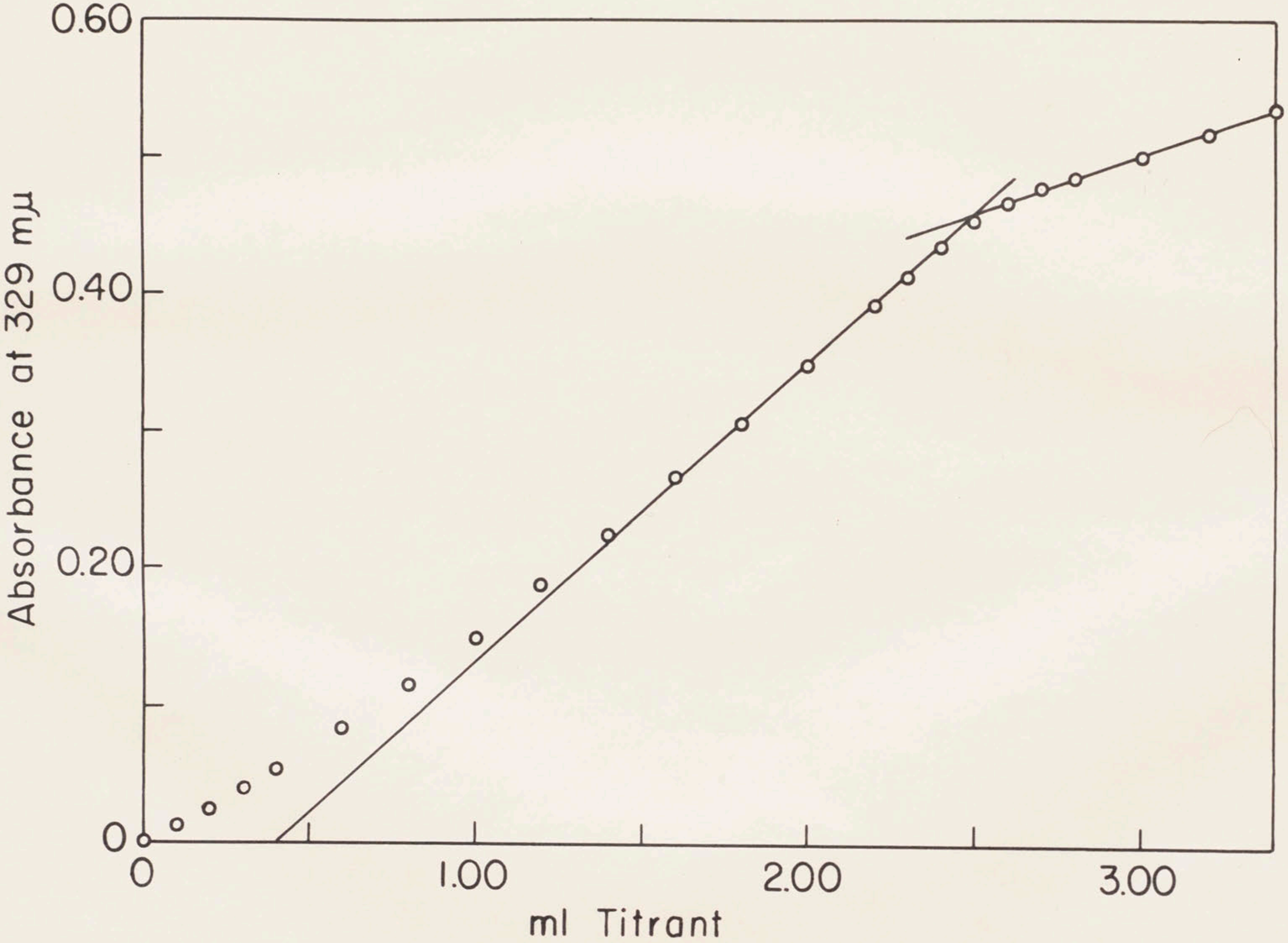
Most of the acids titrated in the present study are phenols since this important group of compounds has members which cover a wide range of acidic strength and also have suitable absorption characteristics. They include some of the weakest acids normally encountered in analytical work, thereby providing a good test of the photometric titration method.

Some representative absorption spectra of phenolic compounds in their acidic and basic forms are shown in the Appendix (Figures 36 and 37). It is seen that the phenolate ions absorb at longer wavelengths than the free phenols. Photometric titration at a wavelength close to the long-wavelength edge of a phenolate absorption band would therefore be expected to give a linear increase in absorbance up to the end-point, where the readings should level off at a constant absorbance value, provided that the titrant does not absorb significantly. The titration curve for phenol (Figure 2) shows two deviations from this expected shape. First, the titration curve is not completely linear before the end-point, and second, it shows a positive slope rather than a constant absorbance after the end point.

The non-linear curve shape was found to be a common characteristic for most phenols and an explanation for this phenomenon will be

Figure 2

Photometric Titration of Phenol (1.012 meq.) in Isopropanol with 0.395 M Tetrabutylammonium Hydroxide


0.60
0.40
0.20
0
Absorbance at 329 mμ
0
1.00
2.00
3.00
ml Titrant

given in a later section. The observed curvature in isopropanol was not large enough to prevent a reliable location of the end-point, provided that the latter rather than the initial part of the curve was used for extrapolation.

The slope of the titration curve after the end-point is due to titrant absorption of unknown origin. This absorption reduces the sharpness of the break and is therefore somewhat detrimental. Fortunately, the titrant absorption decreased with increasing wavelength so that phenols titrated at longer wavelengths (about 400 mμ) gave curves with a practically constant absorbance reading after the end-point. It seems likely that a more highly purified titrant would show less absorption at short wavelengths.

In spite of its weak acidic strength $\left[pK_a(H_2O) = 9.89\right]$ phenol gives a distinct photometric break with little rounding in isopropanol, while strongly basic solvents such as ethylenediamine (57) or pyridine (15) have been recommended for potentiometric or visual titrations of such compounds. Recently, weak phenols have been titrated potentiometrically in acetone (26) and methyl isobutyl ketone (12) but the inflections are quite small and difficult to locate exactly. It is therefore apparent that the photometric technique compares favorably with other methods for titration of very weak acids. In particular, it is advantageous to be able to use a non-basic solvent such as isopropanol instead of ethylenediamine, n-butylamine or pyridine which absorb atmospheric carbon dioxide quite strongly and also have very unpleasant odors.

Table IV shows the results of the photometric titrations of a number of phenols. All compounds were Eastman White Label products with the exception of phenol, which was Merck Reagent grade. The results are calculated for the limiting titrant molarities 0.421 and 0.395 and compared with the first column, which gives the number of milliequivalents taken, assuming the phenol to be 100% pure. Using the higher molarity, results are obtained which are too high except for the relatively strong acid 2,4-dinitrophenol, where a reasonable agreement is found. The lower titrant molarity, 0.395, gives results which are in fair agreement with expectation, considering that commercial materials were used. It should be borne in mind that most phenols are hygroscopic and most of the impurity is therefore probably water.

In connection with the standardization of the titrant, it was mentioned that solvent blanks were estimated from a series of pentachlorophenol titrations in two different isopropanol batches. The blanks were estimated by titrating weighed pentachlorophenol samples of varying size and plotting the titrant consumption versus the amount of pentachlorophenol taken. Extrapolation to zero pentachlorophenol addition gave a titrant consumption of 0.045 and 0.025 ml., respectively, for the two batches of 99% isopropanol. These blanks refer to the titrant consumption for about 110 ml. solvent. The blank is a complication

TABLE IV

PHOTOMETRIC TITRATIONS OF SINGLE ACIDS IN ISOPROPANOL

Compound	Milliequivalents Taken	Milliliters Titrant Consumed	Milliequivalents Found		%Purity
			a	b	
Phenol	1.012	2.480	1.044	0.9796	98.6
o-Chlorophenol	1.042	2.595	1.092	1.025	98.4
m-Chlorophenol	1.045	2.638	1.109	1.041	99.6
o-Bromophenol	1.052	2.615	1.101	1.033	98.2
p-Bromophenol	1.003	2.465	1.038	0.9737	97.1
2,4-Dichlorophenol	0.9683	2.310	0.9725	0.9125	94.2
2,4-Dibromophenol	1.016	2.525	1.063	0.9974	98.2
2,4,6-Trichlorophenol	0.8718	2.155	0.9073	0.8512	97.6
2-Naphthol	1.007	2.525*	1.063	0.9974	99.0
o-Nitrophenol	1.010	2.450*	1.031	0.9678	95.8
p-Nitrophenol	1.018	2.510*	1.057	0.9915	97.4
m-Nitrophenol	1.005	2.510*	1.057	0.9915	98.7
2,4-Dinitrophenol	1.004	2.410*	1.015	0.9520	101.1

a: Calculated from maximum titrant molarity (0.421)

b: Calculated from minimum titrant molarity (0.395)

c: Based on minimum titrant molarity except in the case of 2,4-dinitrophenol

* No blank subtracted (0.025 ml. from all other results)

normally encountered in titrating weak acids and it is apparently due to dissolved CO_2 and traces of stronger acids. Most authors state that the solvent blank should be determined and subtracted from the amount of titrant consumed in a titration. The majority of the titrations summarized in Table IV were performed using the isopropanol batch with a blank of 0.025 ml. per 110 ml. solvent, and this quantity was then subtracted from the actual titrant consumption. The last five titrations were performed in another batch of solvent, for which the blank had not been determined. In these cases, marked with an asterisk, the titrant volumes consumed are uncorrected for solvent blank.

Considering the uncertainties arising from the aforementioned sources, the average purity of 97.9% obtained for the phenols must be considered satisfactory, and there is little doubt that the photometric titration method gives accurate results when proper precautions are taken. A measure of the precision of the method is given by the pooled standard deviation for the ten titrations of pentachlorophenol, which was 1.15%.

c. Differentiating Titrations:

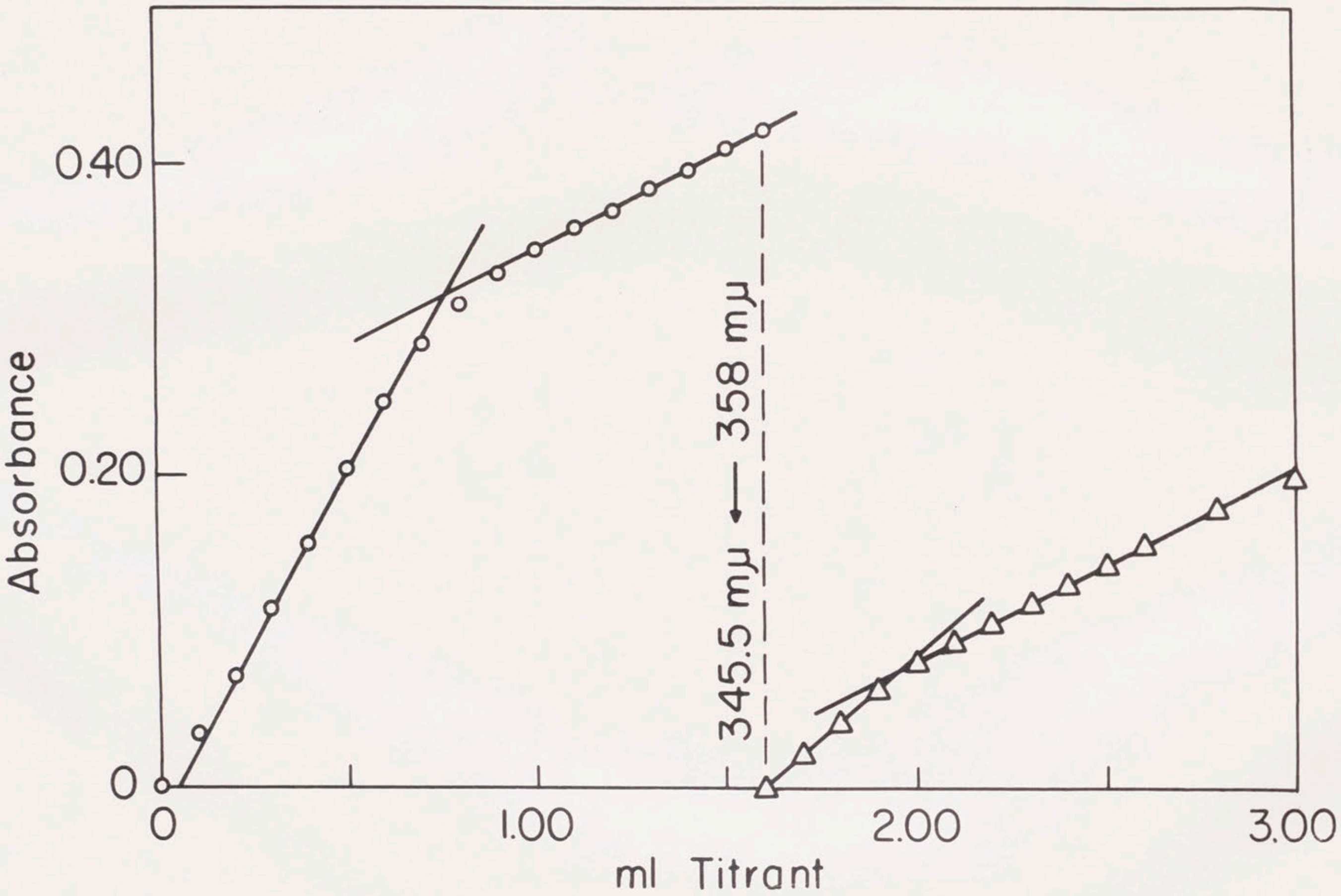
The photometric technique should be particularly well suited for differentiating titrations of mixtures containing acids of similar strength. Unfortunately the spectral characteristics of substituted phenols are, in general, not very favorable for differentiating titrations. The reason is that the stronger acids usually absorb at longer wavelengths than the weaker ones, and the same is true for the corresponding phenolate ions. Since the stronger acid titrates first it tends to obscure the absorption of the next component. This difficulty can often be overcome by changing the wavelength and opening the slit after obtaining the first break, as shown in Figure 3, which gives the titration curve for a mixture of 2,4,6-trichlorophenol and 2,4-dichlorophenol. The first break is obtained at 358mμ, where only the 2,4,6-trichlorophenolate ion absorbs. In order to measure the increase in absorption due to formation of 2,4-dichlorophenolate one has to shift to a shorter wavelength, where the 2,4,6-trichlorophenolate ion shows a still stronger absorption. It is therefore necessary to open the slit in order to obtain a sufficient light intensity. This results in a broader band-width which normally gives lower sensitivity to the absorption change due to the titration of the second component. Hence the slope of the titration curve before the second break cannot be made very steep. In the present example the sharpness of the breaks is further reduced by the fact that the titrant absorbs at the wavelengths used. However, this titration still represents a differentiation which can hardly be accomplished using the potentiometric method as shown by Figure 8. A comparison of Figures 3 and 8 suggests that a combination of the photometric and potentiometric techniques may be fruitful in cases where the absorption characteristics of the system make it difficult to obtain a good photometric break for the second component while this still is strong enough to give

Figure 3

Photometric Titration of a Mixture of 2,4,6-Trichlorophenol (0.291 meq.) and 2,4-Dichlorophenol (0.484 meq.) in Isopropanol with 0.395 M Tetrabutylammonium Hydroxide

—○—○— Titrated at 358 mμ

—△—△— " " 345.5 mμ


Absorbance
0.40
0.20
0
0
1.00
2.00
3.00
ml Titrant
345.5 mμ ⟵ 358 mμ

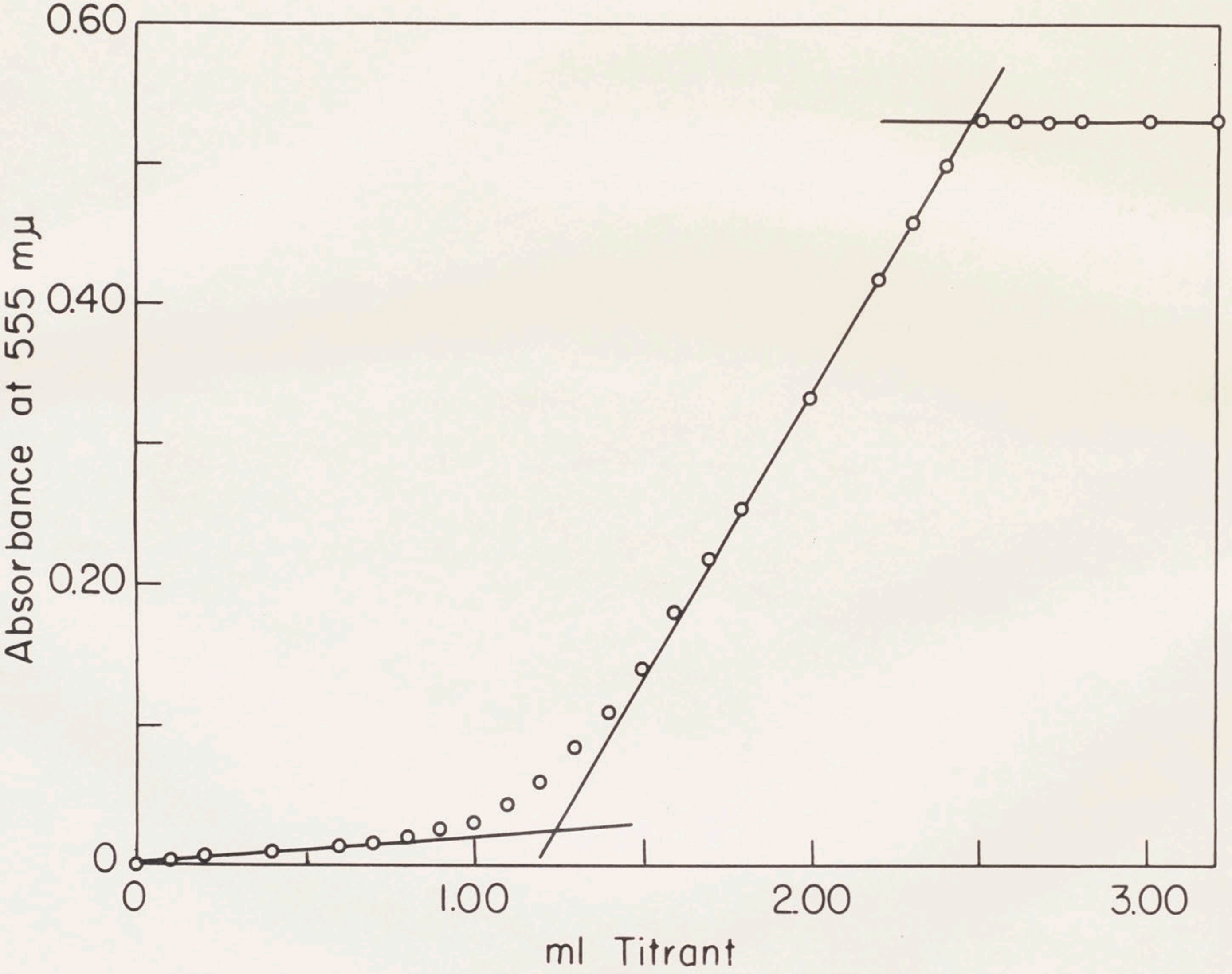
a sharp potentiometric end-point. One photometric and one potentiometric titration on aliquots of the sample would give the first component and the total acidity, respectively, and the second component could then be obtained by difference.

A more favorable example is the differentiating titration of para and meta nitrophenol, shown in Figure 4. Here the stronger acid, p-nitrophenol, forms a phenolate ion which absorbs at shorter wavelengths than the m-nitrophenolate ion. Thus no change in wavelength is needed during the titration, and a sharp second break is obtained. At this wavelength (555mμ) the titrant no longer absorbs and hence the titration curve is horizontal after the second break. In this case the components are very similar in acidic strength, the difference in pK_a values in water being only 1.2 (Table V). For this reason the first break is quite rounded but the equivalence point can nevertheless be accurately located by extrapolation. A potentiometric curve shows no perceptible inflection in this case (Figure 9).

However, the titration of para and meta nitrophenol also serves as an illustration of the fact that a change in solvent has a relatively small effect on the separation of two acids of the same charge type, provided that no leveling reaction occurs with the solvent. Goddu and Hume (27) obtained an almost equally good separation of these two phenols by titrating with sodium hydroxide in aqueous solution. Hence, in cases where the weakest

Figure 4

Photometric Titration of a Mixture of p-Nitrophenol (0.509 meq.) and m-Nitrophenol (0.503 meq.) in Isopropanol with 0.395 M Tetrabutylammonium Hydroxide


0.60
0.40
0.20
0
Absorbance at 555 mμ
0
1.00
2.00
3.00
ml Titrant

component is strong enough to give a good end-point in water little is to be gained by going to a non-aqueous solvent, provided that the components are of the same charge type. If they are not, the change in dielectric constant may have a profound effect on their relative strengths (36).

Figures 5 and 6 illustrate the capability of the photometric titration method to resolve multicomponent mixtures. The former figure shows the titration curve for a mixture of diphenyl phosphate, 2,4-dinitrophenol, p-nitrophenol and m-nitrophenol. The first two breaks are obtained at 505mμ where 2,4-dinitrophenolate and p-nitrophenolate absorb while diphenyl phosphate, the strongest acid, does not. Hence the absorbance of the solution, which was adjusted to zero at the beginning of the titration, remains at this level until the 2,4-dinitrophenol begins to react. A change in the slope of the curve marks the point where titration of p-nitrophenol sets in. The absorption of m-nitrophenolate would be too intense at this wavelength to permit location of the third and fourth breaks, and the wavelength is therefore changed to 555mμ . The slit is adjusted to give zero absorbance at the new setting, and the titration is continued to obtain two additional breaks.

Figure 6 shows the titration curve obtained for a solution containing diphenyl phosphate, pentachlorophenol, 2,4,6-trichlorophenol and 1-naphthol. In this case the first three breaks are obtained at 384 mμ , where only pentachlorophenolate and

Figure 5

Photometric Titration of a Mixture of Diphenyl Phosphate (0.277 meq.), 2,4-Dinitrophenol (0.301 meq.), p-Nitrophenol (0.509 meq.) and m-Nitrophenol (0.503 meq.) in Isopropanol with Tetrabutylammonium Hydroxide

—○—○— Titrated at 505 mμ
—△—△— " " 555 "

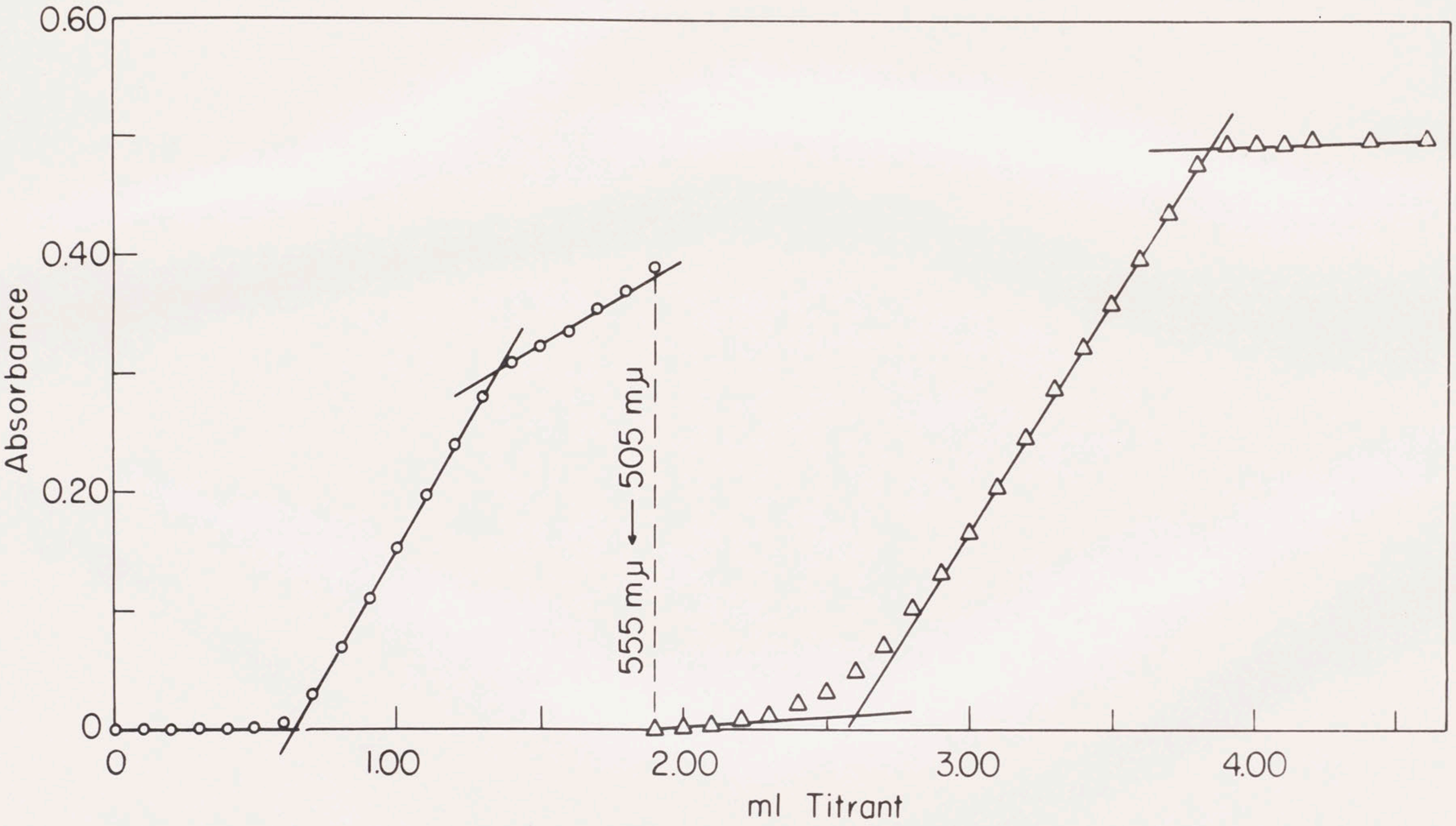
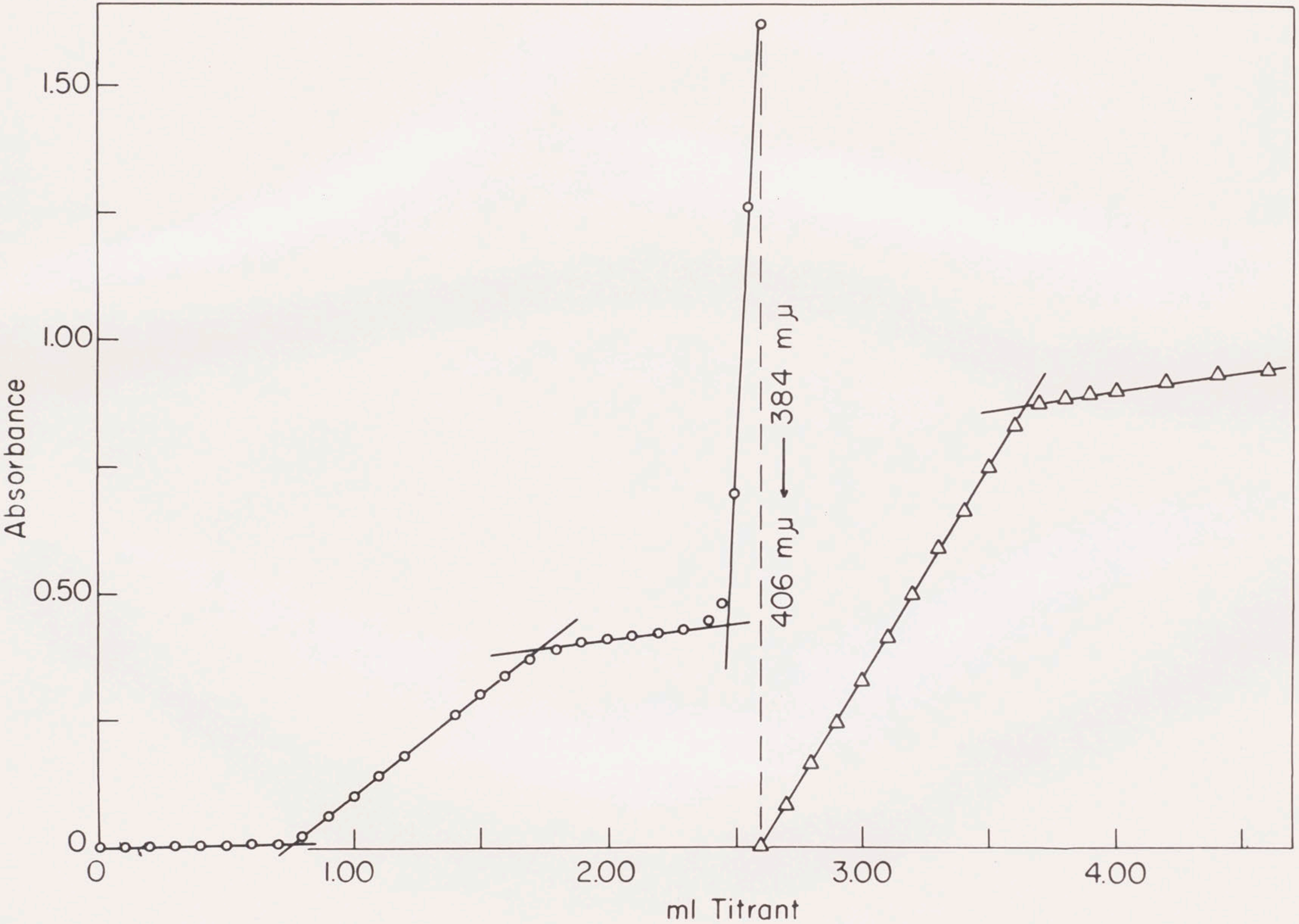

0.60
0.40
0.20
0
Absorbance
0
1.00
2.00
3.00
4.00
ml Titrant
555 mμ ← 505 mμ

Figure 6

Photometric Titration of a Mixture of Diphenyl Phosphate (0.318 meq.), Pentachlorophenol (0.418 meq.), 2,4,6-Trichlorophenol (0.291 meq.) and 1-Naphthol (0.462 meq.) in Isopropanol with Tetrabutylammonium Hydroxide

—○—○— Titrated at 384 mμ

—△—△— " " 406 "



1.50
1.00
0.50
0
Absorbance
406 mμ ← 384 mμ
0
1.00
2.00
3.00
4.00
ml Titrant

1-naphtholate absorb, the latter very strongly. The wavelength is then changed to 406 mμ to obtain the final break, which is quite sharp.

Table V summarizes some of the more successful differentiating titrations. Other mixtures, which could not be adequately resolved, include 1- and 2-naphthol and 2,4-dichlorophenol and p-chlorophenol. In general, it must be considered quite difficult to obtain a successful differentiation of two halogenated phenols if the difference in the number of halogen substituents is only one. This is to be expected since Table V shows that the difference in aqueous pK_a values is only 1.5 - 1.7 in such cases. In reading the table it should be remembered that the phenols were commercial materials. Hence the deviations from 100% in the last column should not be taken to indicate an error of that magnitude.

In most of the mixtures titrated the components were present in roughly equal amounts. The titrations become more difficult if one of the components is present in a large excess. A 1:10 mixture of o-chlorophenol and phenol gave a titration curve indicating an o-chlorophenol content of 14.1 mole percent as compared to the calculated 9.3 mole percent. Such titrations may be of little quantitative value but they constitute a quick method of checking the purity of materials or the extent of reaction in a manufacturing process. It should be remembered that potentiometric or visual titrations offer no indication whatsoever of the existence of two or more components in such cases.

TABLE V

DIFFERENTIATING TITRATIONS OF ACID MIXTURES IN ISOPROPANOL

Components	$pK_a(H_2O)$	Milliequivalents		%Purity
		Taken[a]	Found[b]	
Diphenyl phosphate	Strong	0.318	0.320	100.6
Pentachlorophenol	4.0	0.418	0.408	97.4
2,4,6-Trichlorophenol	6.0	0.219	0.296	101.7
1-Naphthol	9.5	0.462	0.462	100.0
Diphenyl phosphate	Strong	0.277	0.269	97.9
2,4-Dinitrophenol	4.0	0.301	0.299	99.7
p-Nitrophenol	7.1	0.509	0.498	97.6
m-Nitrophenol	8.3	0.503	0.486	96.6
p-Nitrophenol	7.1	0.509	0.494	97.1
m-Nitrophenol	8.3	0.503	0.486	96.6
2,4,6-Trichlorophenol	6.0	0.291	0.300	103.1
2,4-Dichlorophenol	7.7	0.484	0.466	96.3
o-Chlorophenol	8.4	0.521	0.529	101.5
Phenol	9.9	0.506	0.506	100.0

a: Assuming pure compounds

b: Calculated on basis of minimum titrant molarity 0.395 except for diphenyl phosphate, pentachlorophenol and 2,4-dinitrophenol for which 0.421 was used. No solvent blank subtracted.

d. Comparison with Potentiometric Titration Curves:

A few potentiometric titrations were performed for the purpose of comparison, using the equipment described in Section B3. Figure 7 shows the potentiometric titration curve for phenol in isopropanol, showing an inflection of about 50 millivolts. Obviously the exact equivalence point is not easy to locate in a case like this. Figure 8 shows the curve obtained for a mixture of 2,4,6-trichlorophenol and 2,4-dichlorophenol. Here the inflection between the two components is barely perceptible while the second break is quite satisfactory. As pointed out in discussing the corresponding photometric curve (Figure 3) this constitutes a case where a combination of the photometric and potentiometric methods may be advantageous, since the second photometric break is difficult to obtain because of spectral overlap of the components.

Figures 9 and 10 show potentiometric titration curves for four-component mixtures corresponding to those in Figures 5 and 6. In both cases only three distinct inflections are obtained instead of four. Figure 9 shows no break whatsoever between p-nitrophenol and m-nitrophenol while Figure 10 shows a barely perceptible inflection between pentachlorophenol and 2,4,6-trichlorophenol.

Several investigators (15, 26) have pointed out that sharper potentiometric breaks can be obtained in non-aqueous solvents if the aqueous potassium chloride in the calomel electrode is replaced

Figure 7

Potentiometric Titration of Phenol (1.012 meq.) in Isopropanol with 0.395 M Tetrabutylammonium Hydroxide

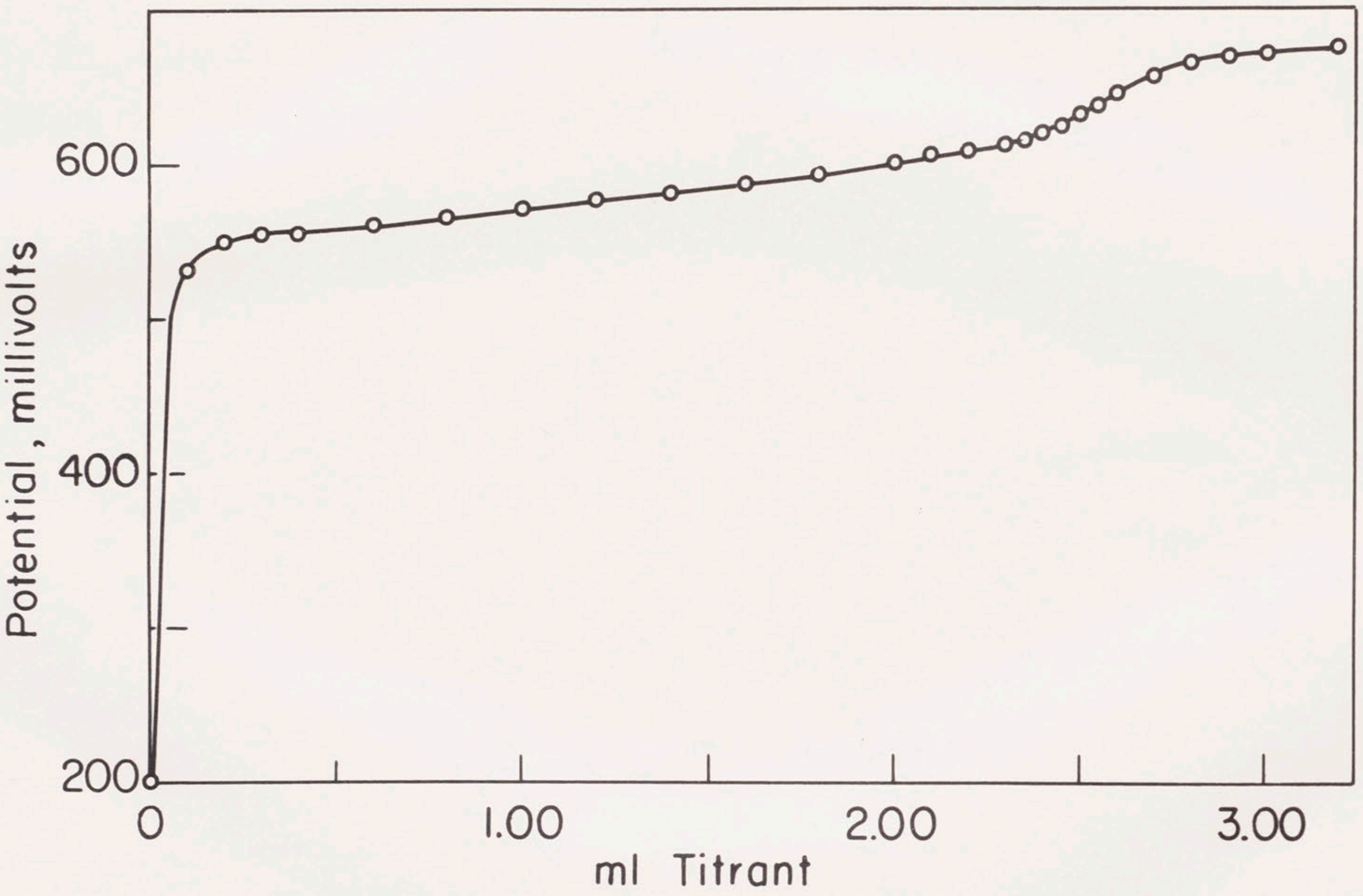

Potential, millivolts
600
400
200
0
1.00
2.00
3.00
ml Titrant

Figure 8

Potentiometric Titration of a Mixture of 2,4,6-Trichlorophenol (0.291 meq.) and 2,4-Dichlorophenol (0.484 meq.) in Isopropanol with 0.395 M Tetrabutylammonium Hydroxide

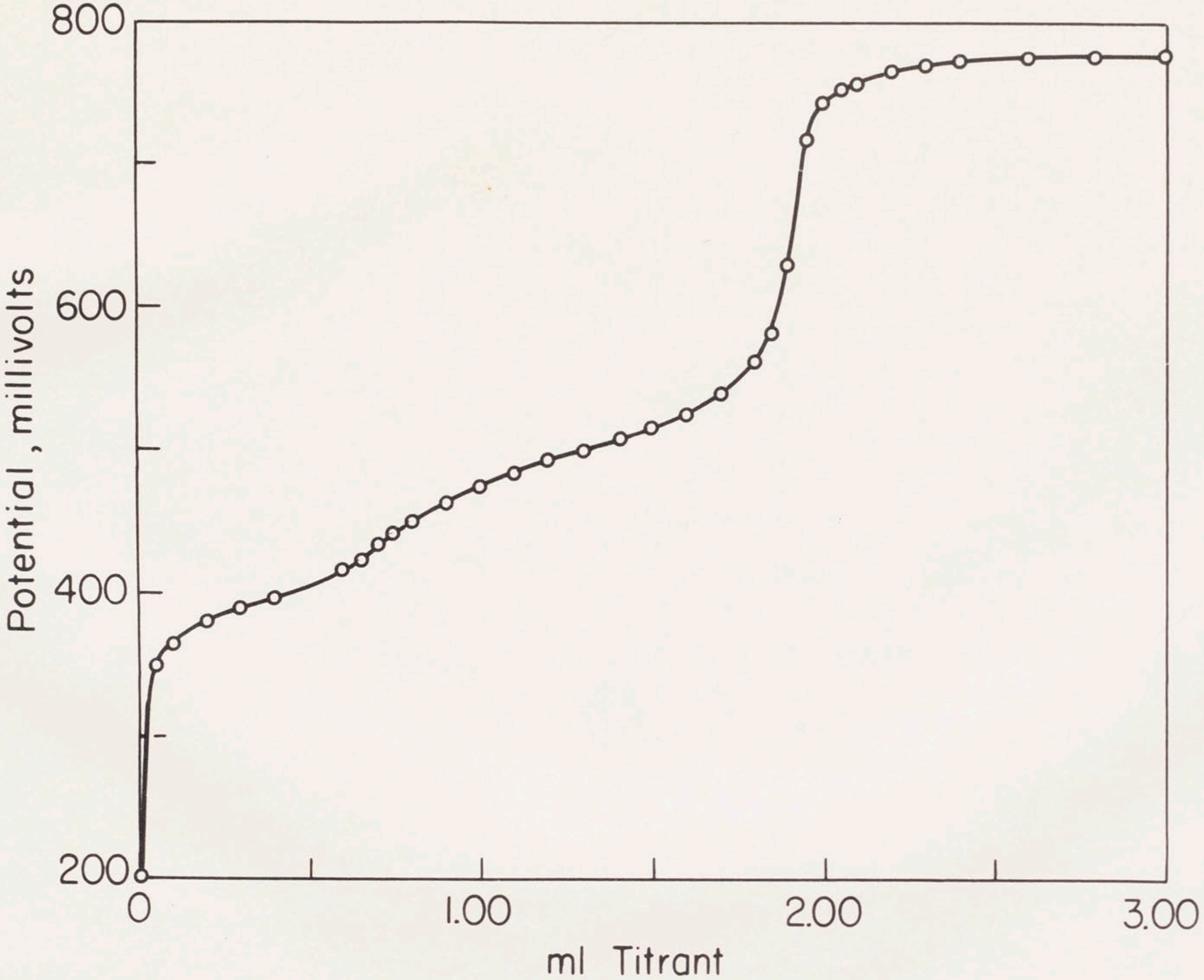

800
600
400
200
Potential, millivolts
0
1.00
2.00
3.00
ml Titrant

Figure 9

Potentiometric Titration of a Mixture of Diphenyl Phosphate (0.261 meq.), 2,4-Dinitrophenol (0.301 meq.), p-Nitrophenol (0.509 meq.) and m-Nitrophenol (0.503 meq.) in Isopropanol with Tetrabutylammonium Hydroxide

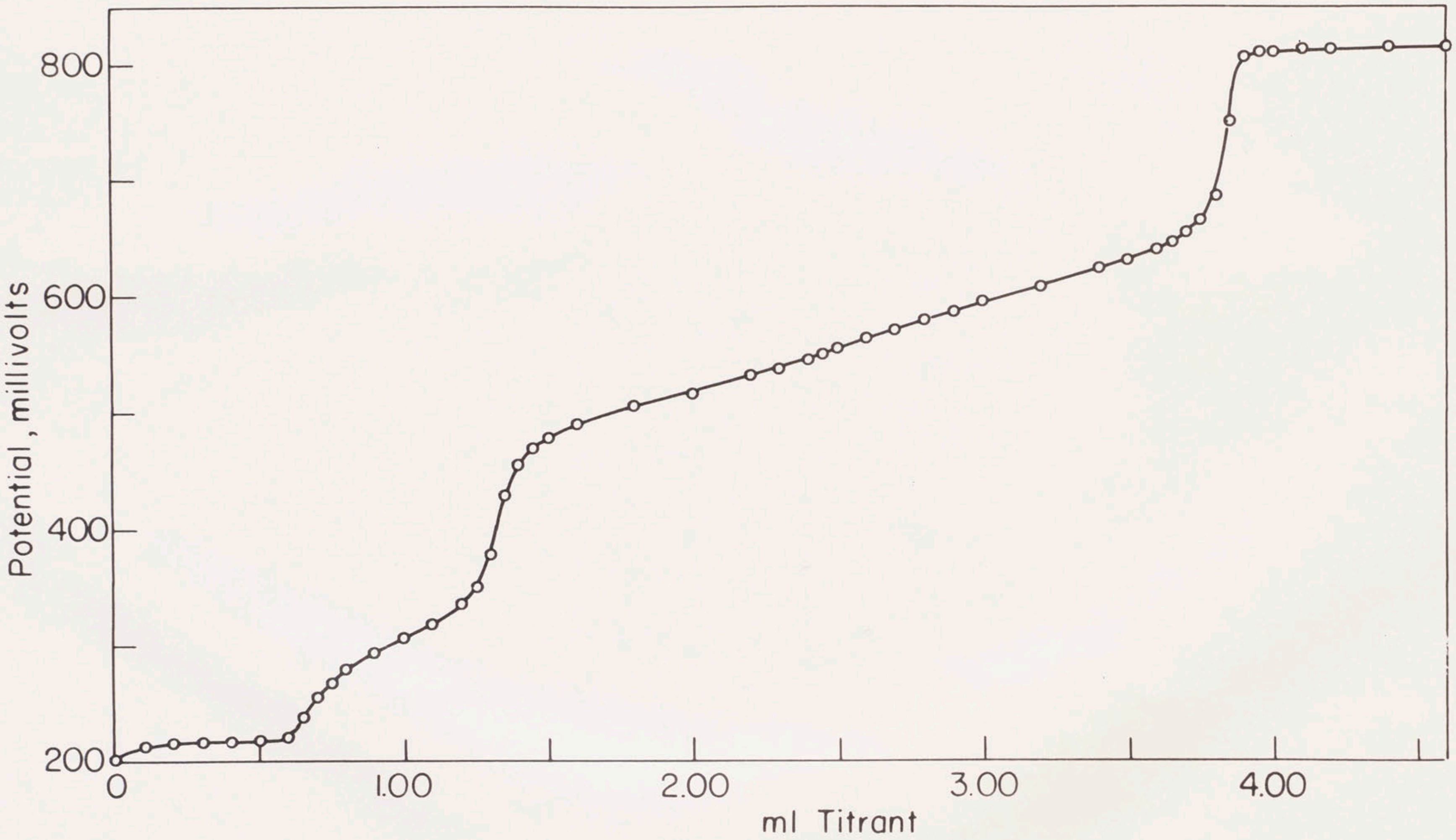
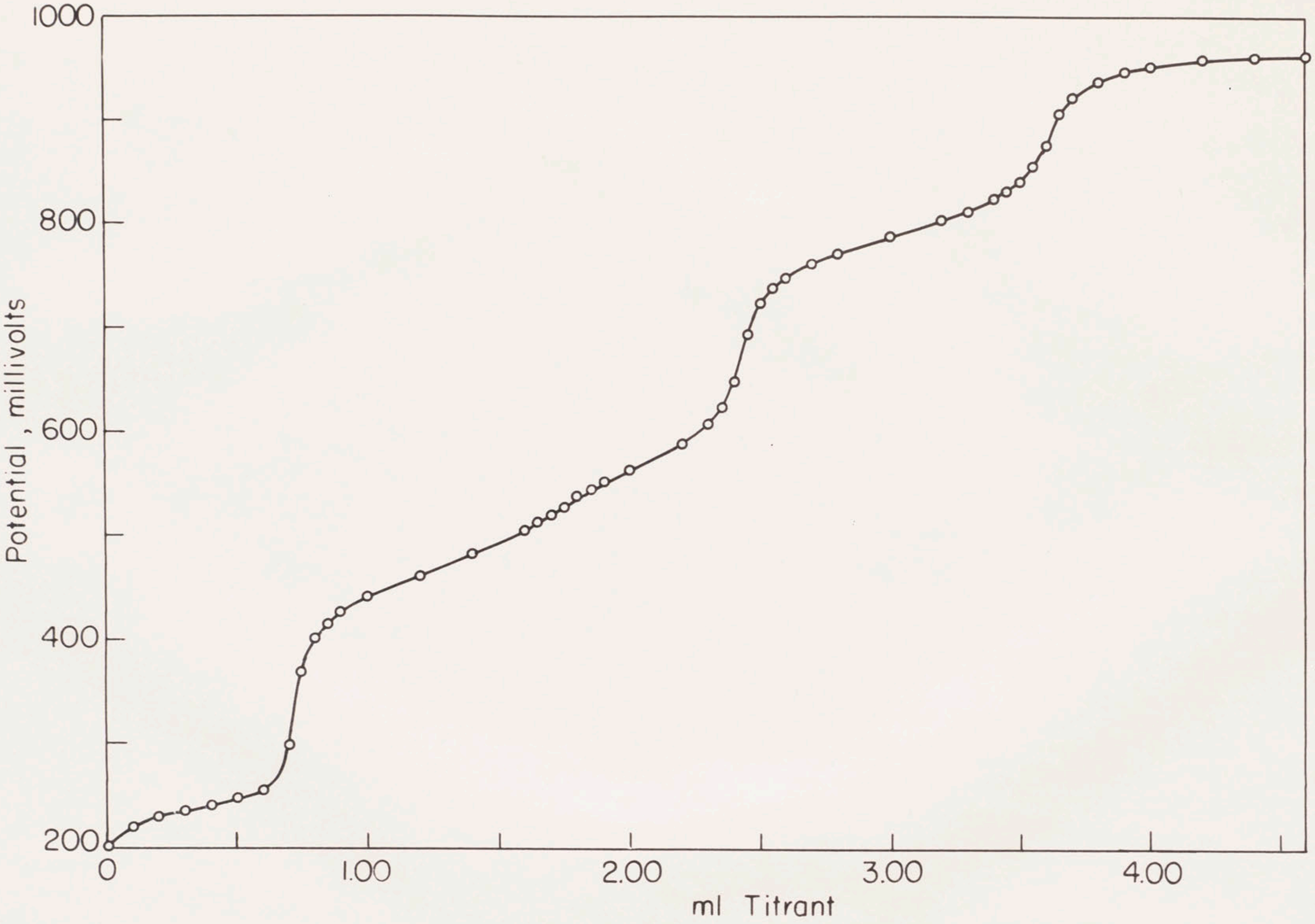

800
600
400
200
Potential, millivolts
0
1.00
2.00
3.00
4.00
ml Titrant

Figure 10

Potentiometric Titration of a Mixture of Diphenyl Phosphate (0.313 meq.), Pentachlorophenol (0.400 meq.), 2,4,6-Trichlorophenol (0.291 meq.) and 1-Naphthol (0.472 meq.) in Isopropanol with Tetrabutylammonium Hydroxide


1000
800
600
400
200
Potential , millivolts
0
1.00
2.00
3.00
4.00
ml Titrant

with an alcoholic solution in order to prevent water from diffusing into the system. In the present study the calomel electrode contained aqueous potaasium chloride and this may have had a detrimental effect on the final breaks obtained. However, the breaks between different components should be largely unaffected by traces of water and it is therefore felt that the potentiometric curves offer a valid comparison with the photometric ones, at least for the differentiating titrations.

e. Anomalous Photometric Titration Curves for Phenols:

In an earlier section it was pointed out that most phenols gave a nonlinear photometric curve, similar to that in Figure 2, when titrated in isopropanol. It was first thought that the curvature was due to impurities in the solvent but titrations of varying amounts of phenol in a constant volume of solvent revealed that this was not the case. It seemed very improbable that so many phenols would all contain enough of a non-absorbing stronger acid to cause the observed type of curvature. Light leakage would have caused a curvature in the opposite direction and could therefore be excluded as a possible explanation. Hence, everything seemd to indicate that the non-linear curve shape was a characteristic feature of the neutralization of phenols for which a chemical explanation had to be sought.

In 1957 van der Heijde (37) reported that phenols give anomalous potentiometric curves when titrated in pyridine. They exhibit an inflection at the half-neutralization point, indicating the presence of two species of different acidic strength. As an explanation for this phenomenon van der Heijde suggested the formation of a 1:1 complex between phenolate ion and untitrated phenol, and this theory is strongly supported by the recent potentiometric and conductometric studies of Harlow and Bruss (33, 11). These investigators confirmed the results of van der Heijde by titrating phenols and carboxylic acids potentiometrically in benzene, toluene and gasoline, thereby often encountering inflections at half-neutralization. In addition, they performed conductometric titrations of phenols in benzene, xylene, toluene, carbon tetrachloride, pyridine, acetone and methyl isobutyl ketone, using both alternating and direct current methods. It was found that those phenols which showed an inflection at half-neutralization in a potentiometric curve gave conductometric curves with a more or less pronounced maximum at the same point.

Bruss and Harlow (11) used a number of alkali base titrants in addition to tetrabutylammonium hydroxide in their conductometric studies. The latter type of titrant was the only one which could be used in benzene, xylene, toluene and carbon tetrachloride since precipitation resulted with alkali bases. On the other hand, no end-points could be obtained with the quaternary ammonium titrant in solvents of intermediate dielectric constant, such as pyridine, acetone or methyl isobutyl ketone. Neither titrant type gave conductometric end-points for phenols in ethanol, methanol or isopropanol.

In order to explain the non-linear conductometric curves Bruss and Harlow assumed that the phenolate ions formed in the beginning of the titration react with untitrated phenol to form a hydrogen-bonded complex anion of the type earlier suggested for partly neutralized carboxylic acids in nonpolar solvents (2, 42, 54, 71). In solvents of low dielectric constant this complex anion forms an ion-pair with the titrant cation, and the conductance of the solution is determined by the dissociation of this ion-pair. During the first half of the titration the bulky complex is the predominating anionic species and the dissociation constant of the ion-pair is relatively large since it depends on the ionic size (50, 51). Hence the conductance of the solution increases up to the half-neutralization point. Further titration results in the formation of an increasing amount of free phenolate ions which form a more strongly bonded ion-pair with the titrant cation because of their smaller size as compared to the phenol-phenolate complex. As a result the number of free ions actually decreases during the second half of the titration and a corresponding decrease in conductance is observed. At the end-point a second increase in conductance occurs due to the appearance of excess titrant.

In solvents of intermediate dielectric constant the tetrabutylammonium hydroxide titrant in isopropanol gave neither conductance maxima nor distinguishable end-points, in contrast to sodium or potassium base titrants. The absence of a maximum indicates that the effect of the size of the anion on the conductance is rather small when the titrant cation is a quaternary ammonium ion. This is to be expected since the bulky tetraalkylammonium ion forms weaker ion-pairs in low-dielectric media than do the sodium or potassium ions (50, 51). If the dielectric constant is very low, as in benzene, the tetraalkylammonium titrant gives conductance maxima because of the more extensive ion association.

The theory of an acid-anion complex as explanation for the conductance maxima is supported by the finding that no such maxima are observed for phenols which are sterically hindered or intramolecularly hydrogen-bonded, as for example 2,6-di-<u>tert</u>-butyl-4-methylphenol and o-nitrophenol, respectively. Also, the presence of more than one percent of a hydrogenbonding solvent, such as isopropanol, was found to eliminate the conductance maxima, presumably by breaking up the complex anion. In fact, Bruss and Harlow obtained conductance maxima in solvents like toluene only when they used 1.0 N tetrabutylammonium hydroxide since a more dilute titrant apparently introduced too much isopropanol into the solution. The same was true for the inflection at half-neutralization in the potentiometric titration of phenol in toluene (33).

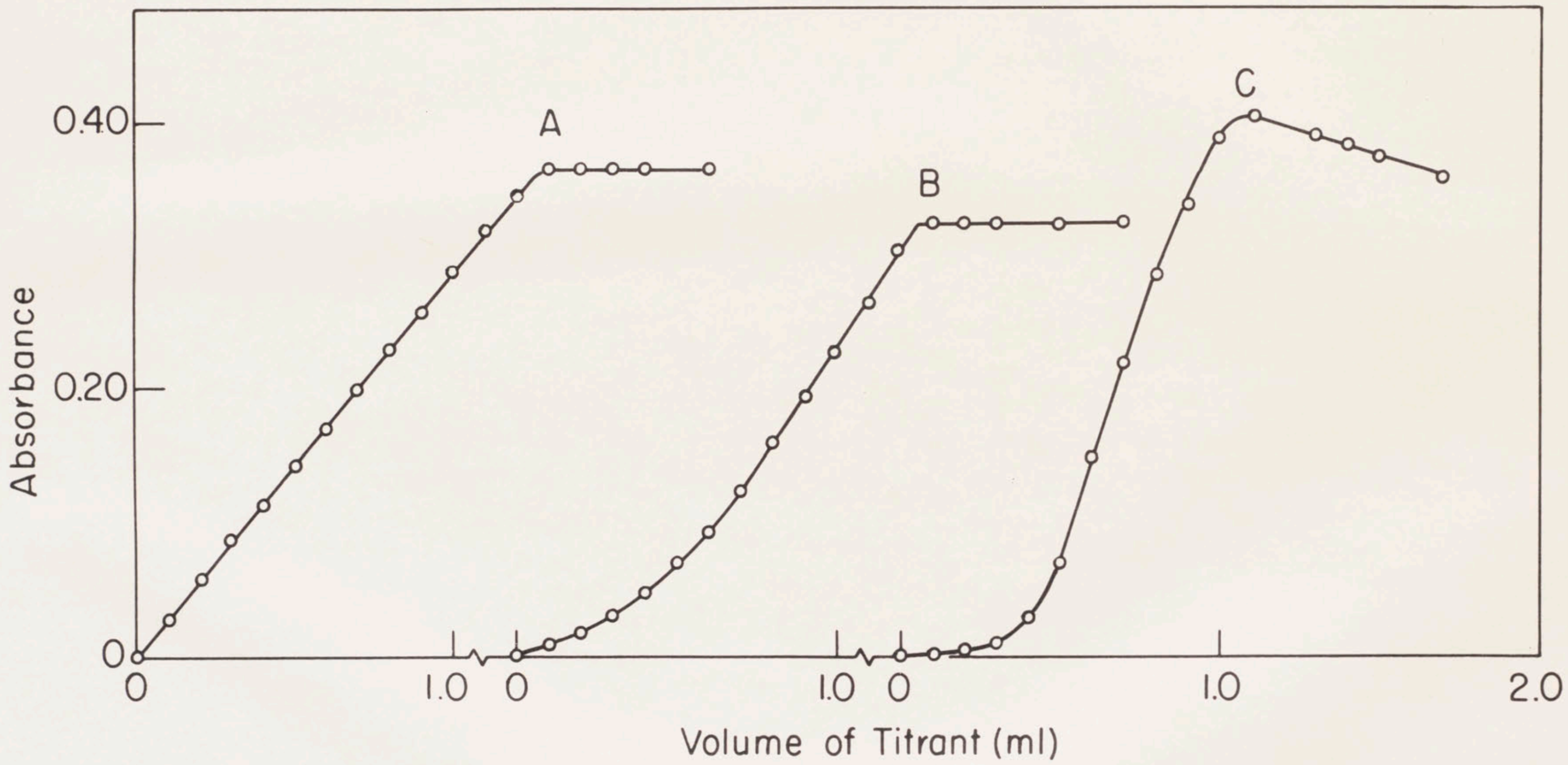
It is difficult to escape the thought that the non-linearity observed in photometric titration curves for phenols indicates the formation of phenol-phenolate complexes even in pure isopropanol, contrary to the conclusions of Harlow and Bruss. Hydrogen bonding is not normally assumed to have a significant effect on absorption spectra in the ultraviolet or visible region, while drastic changes are known to occur in the infrared (3, 53). However, the hydrogen bonds formed between a phenol and the corresponding phenolate ion are undoubtedly much stronger than those between two neutral molecules, and they may be very nearly symmetrical (14). Under these conditions an effect on the electronic absorption spectrum would not be surprising (5, 6). In any event, it appears that the absorption characteristics of the phenolate ions formed in the beginning of a titration are closer to the characteristics of the phenol than is the case for phenolate ions formed during the latter part of the titration. Hence, a non-linear titration curve results.

In order to test the theory, a number of photometric titrations were performed in solvents other than isopropanol. In Figure 11, A and B are the photometric curves of m-nitrophenol in 5:105 mixtures of isopropanol-ethanol and isopropanol-benzene, respectively, while C is the corresponding curve in initially pure benzene. Tetrabutylammonium hydroxide in isopropanol was used as titrant in all cases and hence some isopropanol was introduced during the titration. It is seen that curve A is linear while B and particularly C show pronounced curvature. This is according to expectation since the dielectric constant and hydrogen-bonding capability of the solvent decrease in going from A to C, which

Figure 11

Photometric Titration Curves of m-Nitrophenol in Different Solvents when Titrated with 0.395 M Tetrabutylammonium Hydroxide in Isopropanol

A. 0.503 meq. in 5:105 Isopropanol-Ethanol (535 mμ)
B. 0.503 " " 5:105 Isopropanol-Benzene (560 ")
C. 0.415 " " Benzene (560 mμ)


Absorbance
0.40
0.20
0
A
B
C
0
1.0
0
1.0
0
1.0
2.0
Volume of Titrant (ml)

should increase the stability of the phenol-phenolate complex correspondingly.

A similar dependence of the titration curve on the solvent was found for phenol, p-chlorophenol and p-bromophenol.

Figure 12 compares the photometric titration curves of ortho and para nitrophenol in a 5:105 mixture of isopropanol and benzene. o-Nitrophenol, which is intramolecularly hydrogenbonded, does not show the anomalous curvature while p-nitrophenol does. Since both are quite similar in acidic strength the geometric configuration must be the explanation for their deviating behavior. However, in pure benzene even o-nitrophenol showed a slight curvature, indicating that complex formation occurred to some extent in this solvent even though Bruss and Harlow (11) did not detect it from the conductometric titration curve.

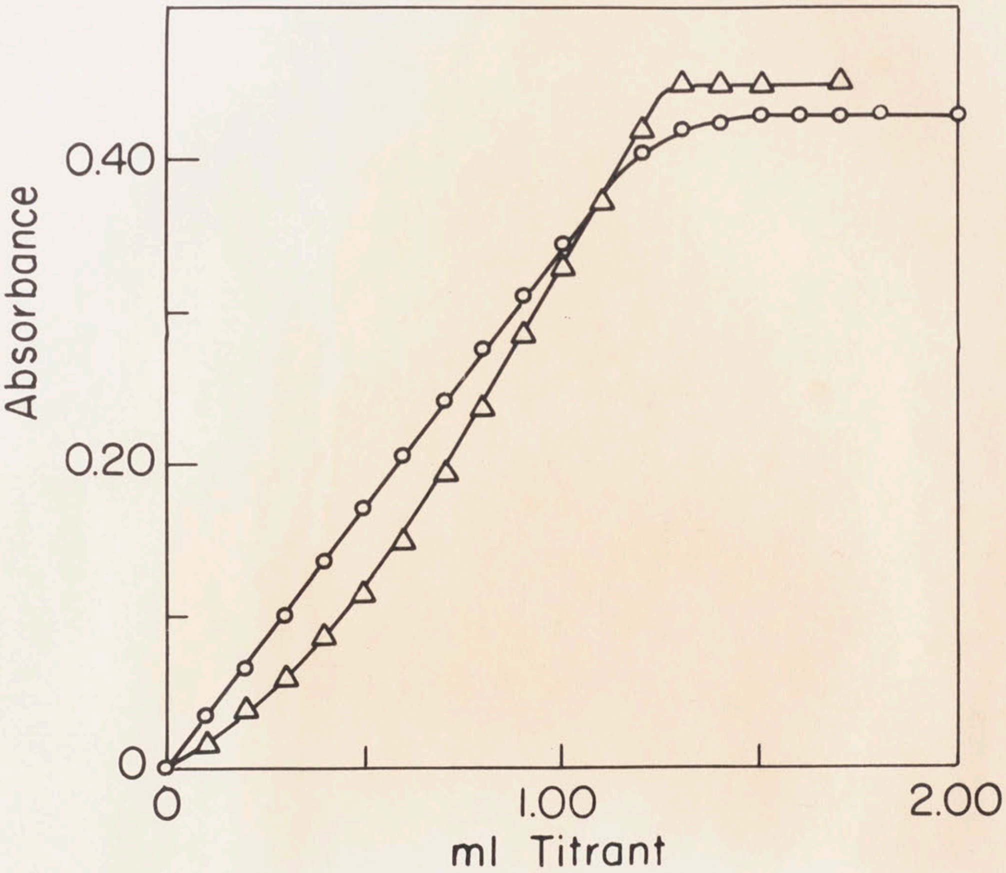
These experiments lend strong support to the theory that the non-linear photometric titration curves of phenolic compounds are caused by the formation of phenol-phenolate complexes which have absorption characteristics intermediate to those of the phenol and the free phenolate ion. Since the photometric curves give evidence for the existence of such complexes even in pure isopropanol while potentiometric and conductometric titrations show no such indication if the solvent contains more than one percent of isopropanol (33, 11) it is obvious that the photometric method is the most sensitive detector for these phenomena. This is natural, since the mid-point inflection in a potentiometric curve

Figure 12

Photometric Titrations of o-Nitrophenol (0.505meq.) and p-Nitrophenol (0.509meq) in 5:105 Isopropanol-Benzene with 0.395 M Tetrabutylammonium Hydroxide

—○—○— o-Nitrophenol at 545 mμ

—△—△— p-Nitrophenol at 490 mμ


Absorbance
0.40
0.20
0
0
1.00
2.00
ml Titrant

depends on the slight difference in acidity between phenol and phenol-phenolate complex and the maximum in a conductometric curve arises from the difference in dissociation constants of two ion-pairs. On the other hand, the photometric technique measures the absorbance, a quantity which is directly related to the complex rather than to some secondary phenomenon.

It is possible that the complex formation affects the shape of the photometric titration curve of phenols by shifting the phenolate absorption to slightly shorter wavelengths, an effect which has been reported to result from hydrogen bonding (6). Since the titration wavelength is chosen near the long-wavelength edge of the phenolate absorption band, such a shift would cause the observed type of curvature. Another explanation is suggested by the recent work of Forbes et al. (19, 20, 21) according to which hydrogen bonding may affect the absorption intensity in the ultraviolet region without causing significant shifts in absorption wavelengths. It seems probable that further study of complexes of this type may throw new light on the nature of strong hydrogen bonds. Apparently the simple electorstatic model needs modification in many cases (53).

A quantitative study of the relative stabilities of different phenol-phenolate complexes by comparison of photometric titration curves is complicated by several factors. Such a study should preferably be performed in an inert solvent such as benzene, where extensive complex formation occurs. If the titrant is made up in another solvent, e.g., isopropanol, the change in solvent composition during the titration may lead to spectral shifts which change the shape of the titration curve. This effect is illustrated in Figure 13, which compares the photometric titration curve of phenol in benzene (circles) with that in a 5:105 mixture of isopropanol and benzene (triangles). Both titrations were performed at the same wavelength, 332 mμ. It is seen that the curve in benzene shows a more pronounced curvature but also reaches a much higher absorbance value than does the curve in isopropanol-benzene despite the roughly equal phenol concentrations. Also, the former curve does not level off at a constant absorbance reading after the end-point but passes through a maximum, and approaches asymptotically the limiting value of the curve in the 5:105 mixture. The explanation for this phenomenon is that the phenolate absorption spectrum is shifted to shorter wavelengths by the introduction of isopropanol with the titrant in the case where the solvent initially consists of pure benzene. In the other case the solvent already contains about five per cent isopropanol and the relative change in composition during the titration is therefore much smaller. Hence the spectral shift is so small that no change in absorbance is observed after the end-point.

Another illustration of the effect of a change in solvent composition during the titration is given by curve C in Figure 11, which shows a negative slope after the equivalence point.

The possibility of such spectral shifts should always be

Figure 13

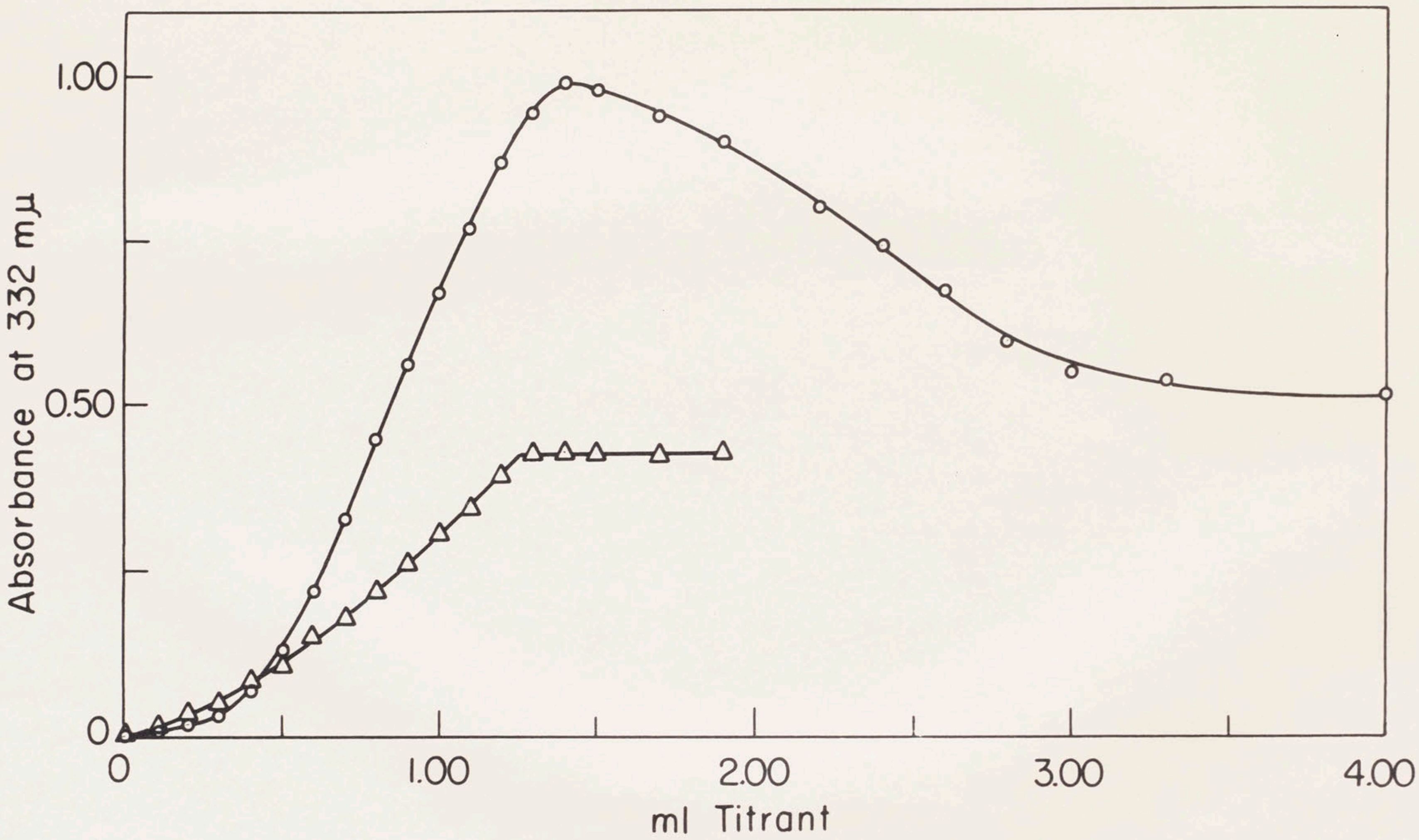
Photometric Titrations of Phenol with

0.395 M Tetrabutylammonium Hydroxide

in Isopropanol

—○—○— 0.544 meq. in Benzene at 332 mμ

—△—△— 0.506 meq. in 5:105 Isopropanol-Benzene at 332 mμ


Absorbance at 332 mμ
1.00
0.50
0
0
1.00
2.00
3.00
4.00
ml Titrant

borne in mind in interpreting photometric titration curves in cases where the sample and titrant solvents differ. In the phenol example, it is obvious that a correction for the spectral change should be applied to obtain the true titration curve. The best solution would be to prepare a titrant in pure benzene but this is a difficult task which apparently has never been accomplished.

Also, the degree of non-linearity of the titration curves may not be a valid relative measure of the complex formation since the spectral effect of the hydrogen bonding probably varies from one phenol to the other. Complete recordings of absorption spectra of phenols at different stages of neutralization are needed to elucidate these problems. Here, again, experimental problems arise due to the relatively rapid oxidation of phenols in basic solutions.

Because of these difficulties a quantitative study of phenol-phenolate complexes was felt to be beyond the scope of the present investigation. However, this can be expected to become a fruitful field for future research.

D. PHOTOMETRIC TITRATION OF BASES

1. Solvents

The possibility of titrating bases in non-aqueous solvents has been known for many years and a large number of basic compounds are now routinely determined by potentiometric or visual titration in solvents such as acetonitrile, dioxane or glacial acetic acid (23). Some workers have recommended the use of mixed solvents such as dioxane-acetic acid (60) and the "G-H" solvents (58). The latter type consists of ethylene glycol mixed with some solvent for hydrocarbons, e.g., isopropanol. Occasionally other solvents are used, such as benzene, chlorobenzene, nitrobenzene, chloroform, carbon tetrachloride, methanol, ethanol, ethyl ether, ethyl acetate, petroleum ether and nitromethane (25, 69, 70). For titration of certain extremely weak bases, acetic anhydride (65) and formic acid (32) have been used as solvents.

A good solvent for titration of basic substances should have little or no basic character itself in order not to compete with the dissolved base for titrant protons. From this viewpoint an acidic solvent, e.g., glacial acetic acid, is ideal, since it has a very low proton-accepting tendency. Glacial acetic acid is indeed one of the most widely used solvents for titration of basic substances. However, acetic acid reacts with strong bases converting them into the corresponding acetates, thereby eliminating any difference in basic strength between them. This effect is known as leveling, since the bases are leveled to the strength of the acetate ion. For this reason it is advantageous to use a non-acidic solvent, such as acetonitrile or dioxane, for differentiating titrations of mixtures containing one or more strong bases. However, the greater basicity of such solvents makes them less suitable than glacial acetic acid for titration of very weak bases. Hence, the choice of solvent depends on the base or base mixture to be titrated. For most purposes either acetonitrile or glacial acetic acid can be used. These two solvents were selected for use in the present study because they have good optical and solvent properties and are commercially available at reasonable cost. Occasionally chloroform, acetone and benzene were used in mixtures with acetic acid.

2. Titrants

For titration of weak bases it is clearly advantageous to use as strong an acid as possible. Since perchloric acid is the strongest avilable acid, it is used almost exclusively as titrant in non-aqueous titrations of bases. Acids such as hydrogen chloride and p-toleunesulfonic acid are sometimes used, but they are much weaker and are therefore useful only for relatively strong bases.

Glacial acetic acid and dioxane have been used most frequently as solvents for the perchloric acid titrant. Acetonitrile is reported to give an unstable titrant (52) and this finding was verified in the present study. Water, introduced with the 70-72% perchloric acid normally used in preparing the titrant, hydrolyzes acetonitrile in the strongly acidic solution. The primary product of this hydrolysis is acetamide, a weakly basic compound which decreases the sharpness of the end-points. If the titrant is allowed to stand for a period of several months the hydrolysis proceeds further to form ammonium acetate, with eventual precipitation of ammonium perchlorate. In half-molar perchloric acid in acetonitrile, interfering amounts of acetamide were observed to form within a couple of days. The interference manifested itself in rounded photometric breaks for compounds which normally gave sharp end-points. Addition of acetamide to freshly prepared titrant led to the same effect and it was therefore concluded that the aging phenomenon was caused by acetamide.

Interestingly enough, the poor breaks obtained with an old perchloric acid titrant in acetonitrile could be markedly improved by titrating not in pure acetonitrile, but in a mixed solvent containing at least twenty percent acetic acid. In pure acetic acid no detrimental effect of the acetamide in the titrant could be observed in titrating moderately weak bases. The reason for this behavior is apparently that a large amount of acetic acid in the solvent decreases the basicity of acetamide by hydrogen-bond formation.

Due to the instability of the perchloric acid titrant in acetonitrile practically all titrations in the present investigation were performed using titrants made up in glacial acetic acid.

This solvent has the additional advantage that a completely anhydrous titrant can be prepared simply by adding the calculated amount of acetic anhydride, as determined by Karl Fischer titration (23, 43). The anhydrous titrant is slightly yellowish but no detrimental absorption was observed in titrations. For most purposes it is not necessary to remove the water introduced with the concentrated perchloric acid but for titration of very weak bases it is advantageous to do so.

Many workers appear to avoid using a perchloric acid titrant made up in glacial acetic acid for differentiating titrations in non-acidic solvents in order not to cause leveling of the bases. However, in a photometric titration a relatively small amount of concentrated titrant is added to a large volume of sample solution, and thus no leveling is normally observed due to introduction of acetic acid with the titrant. Perchloric acid dissolved in glacial acetic acid was used successfully for differentiating titrations in acetonitrile.

However, it should be remembered that spectral shifts may occur as a result of changes in solvent composition when the titrant and sample solvents differ. In such cases distorted photometric titration curves may result, as discussed and exemplified in connection with the phenol titrations. No drastic example of such spectral shifts was encountered in titrating bases but the possibility should nevertheless be borne in mind.

The perchloric acid titrants were standardized by visual titration of potassium acid phthalate in glacial acetic acid, using crystal violet as indicator. For most titrations 0.4 - 0.5 molar titrants were used. Less concentrated perchloric acid solutions were prepared by dilution of stronger titrants.

3. Titrations

a. Titration Technique:

In the photometric titrations of bases either the Beckman Model B or DU spectrophotometer was used, depending on the wavelength region needed. Both instruments were adapted for titrations as described in Section B1. The sample volume was 100 - 110 ml. and the titrant addition normally 1 - 3 ml. The small dilution effect on the absorbance readings was neglected in plotting the titration curves.

b. Titration of Single Bases:

In discussing the different possible shapes of photometric titration curves Goddu and Hume (28) pointed out that it is advantageous to have a decrease rather than an increase in absorbance during the titration. The former type of curve is less susceptible to errors resulting from dilution and light leakage than the latter. It is therefore fortunate that a large and important group of compounds, the aromatic amines, give this favorable curve shape. Figures 38-41 in the Appendix show a few selected absorption spectra of such compounds. In most cases only the spectrum of the basic form is shown, since the acidic form does not absorb in the region of the long-wavelength absorption peak of the basic form. The reason is that this absorption band is due to transitions involving the non-bonding electrons on the nitrogen atom. These electrons are tied up by protonation which therefore eliminates the absorption band.

Bases such as pyridine, quinoline and their derivatives give photometric curves in which the absorbance increases during the titration, since protonation in these cases results in a shift of the absorption to longer wavelengths. An example is given by the titration of 8-chloroquinoline, shown in Figure 14. The absorption spectra of the acidic and basic forms of this compound are shown in Figure 42 in the Appendix.

Figure 15 shows the photometric titration curve of m-nitroaniline in acetic acid. The break is quite sharp despite the weak basicity of m-nitroaniline $[pK_b(H_2O) = 11.55]$. p-Nitroaniline $[pK_b(H_2O) = 13.02]$ can still be titrated but it gives a somewhat rounded break. For titration of such weak bases it is advantageous to use absolutely dry acetic acid as solvent and remove all water from the titrant. o-Nitroaniline $[pK_b(H_2O) = 14.28]$ cannot be titrated even in absolutely anhydrous acetic acid, while 4-methyl-2-nitroaniline [estimated $pK_b(H_2O) = 13.5$] is titratable.

From these results it appears that bases with an aqueous pK_b value not greater than about 13.5 give useful breaks in photometric titrations at the 10^{-2} molar level when glacial acetic acid is used as solvent. In this connection it should be

Figure 14

Photometric Titration of 8-Chloroquinoline (0.794 meq.) in Glacial Acetic Acid with 0.4391 M Perchloric Acid

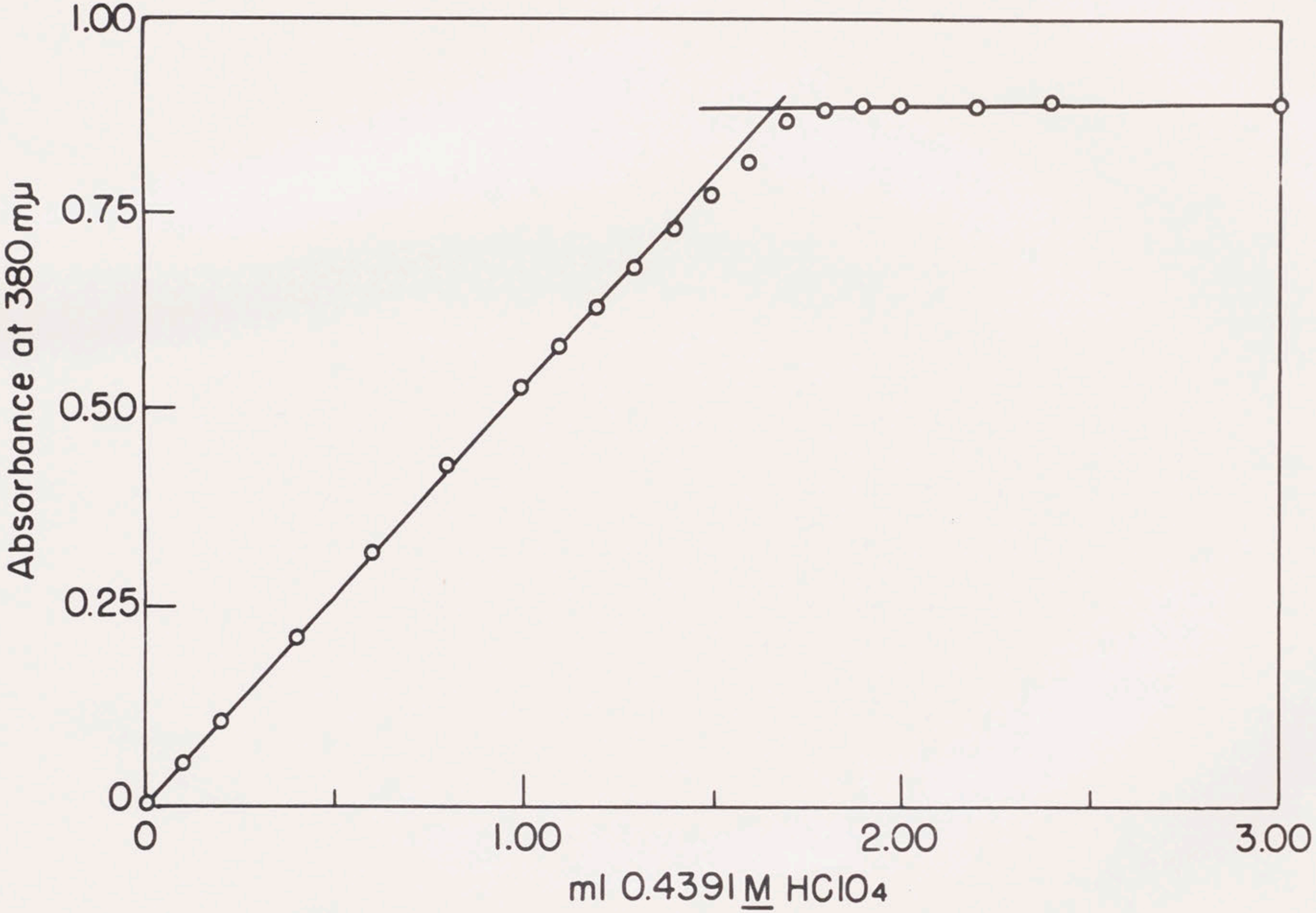
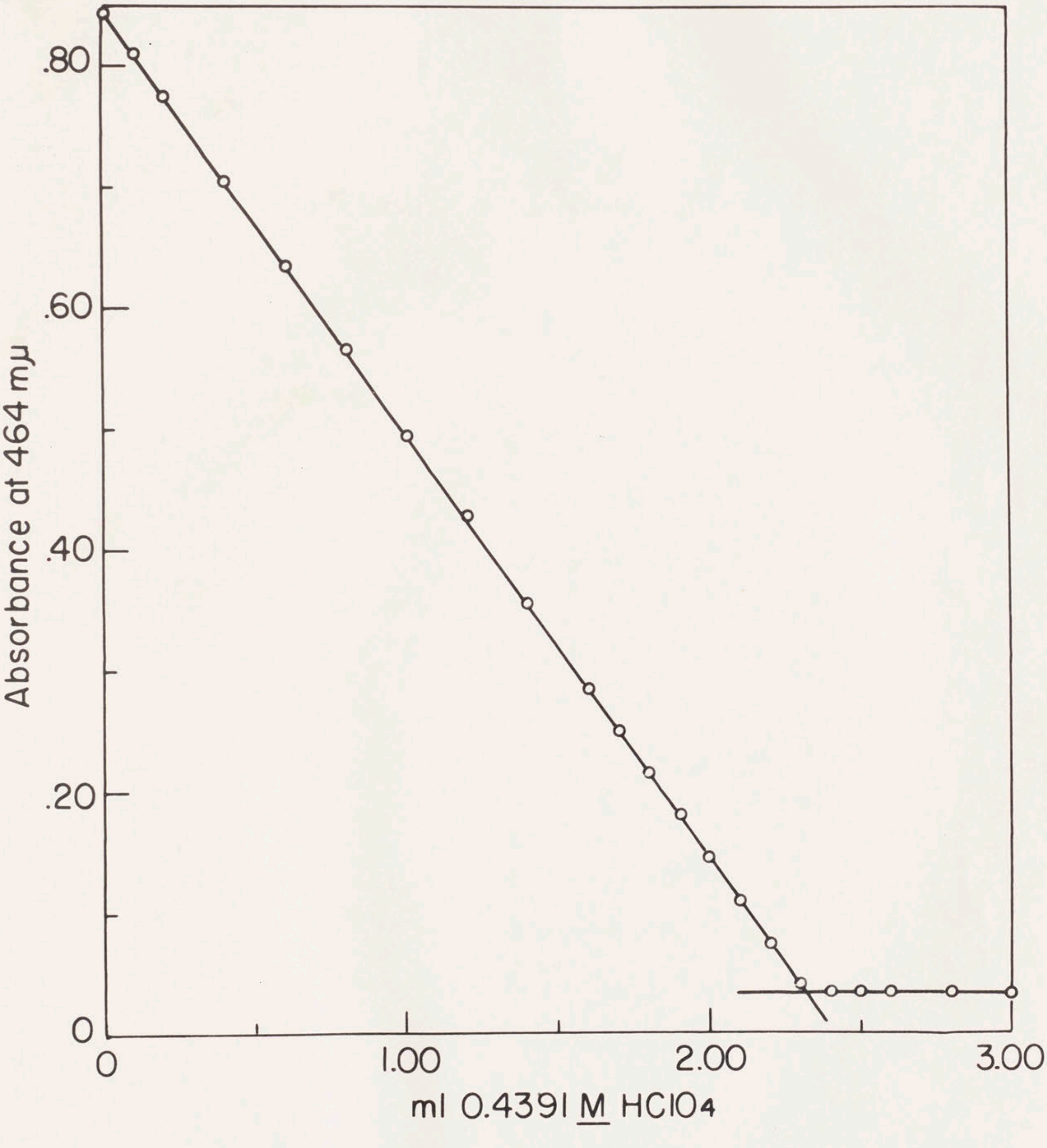

1.00
0.75
0.50
0.25
0
Absorbance at 380 mμ
0
1.00
2.00
3.00
ml 0.4391 M HClO4

Figure 15

Photometric Titration of m-Nitroaniline (1.019 meq.) in Glacial Acetic Acid with 0.4391 M Perchloric Acid


.80
.60
.40
.20
0
Absorbance at 464 mμ
0
1.00
2.00
3.00
ml 0.4391 M HClO4

pointed out that Higuchi and his co-workers (41, 62) have demonstrated that very weak non-absorbing bases, such as urea $\left[pK_b(H_2O) = 13.82\right]$, can be determined by photometric indicator titrations in acetic acid if special plotting techniques are used. These techniques involve calculation and plotting of the ratio of acidic to basic form of the indicator, a procedure which is more time-consuming than direct plotting of the absorbance of the solution, the method employed in the present study. For absorbing bases the latter method yields results which compare very favorably with potentiometric titrations, as shown in a later section. Since the photometric indicator titration techniques of Higuchi et al. are applicable to non-absorbing bases which are too weak to give a potentiometric end-point it can be concluded that the photometric methods are superior to potentiometry for titration of extremely weak bases.

Relatively strong bases, such as N,N-diethylaniline $\left[pK_b(H_2O) = 7.48\right]$, are completely protonated by glacial acetic acid and no change in absorbance would be observed in this solvent since the titration would involve only acetate ions which do not absorb at any useful wavelength. In such cases one can add a weaker indicator base to the acetic acid solution or perform the titration in a non-acidic solvent, e.g., acetonitrile. There are also a large number of bases which are only partially protonated by glacial acetic acid, and these compounds can be determined by direct photometric titration in either type of solvent.

Table VI presents some results of photometric titrations of aromatic amines in acetic acid and acetonitrile. The generally close agreement between calculated and observed titrant consumption indicates that the photometric method gives accurate results.

c. Differentiating Titrations:

The previous section demonstrated the usefulness of the photometric technique for titration of single bases. However, the method probably has its greatest potential uses in the field of differentiating titrations of mixtures containing components of similar basic strength. Figure 16 gives the photometric titration curve for a mixture of 2-methyl-5-nitroaniline and 4-methyl-2-nitroaniline. Since these two bases are very similar in strength and also extremely weak both photometric breaks are rounded, but a comparison with a potentiometric titration of a similar mixture (Figure 21) leaves no doubt about the superiority of the photometric technique. Figure 17 shows the titration of a mixture of 2,4-dichloroaniline and 4-methyl-2-nitroaniline, a case where even the photometric method is pushed somewhat beyond its limit. Here, the error for the first component is -5.5% and that of the second 8.7%. However, the corresponding potentiometric curve (Figure 22) shows no differentiation whatsoever and an only barely perceptible inflection after the second component.

The curves in Figures 16 and 17 illustrate photometric titrations in which only the weaker component absorbs at the selected

TABLE VI

PHOTOMETRIC TITRATIONS OF SINGLE BASES IN ACETONITRILE AND ACETIC ACID USING 0.4-0.5 M PERCHLORIC ACID TITRANTS IN ACETIC ACID

Compound	Solvent	Titrant Consumption Calculated	Titrant Consumption Observed	%Deviation
Aniline	Acetonitrile	1.98	2.00	+1.0
N,N-Dimethylaniline	"	2.03	1.99	-2.0
N,N-Diethylaniline	"	1.00	1.00	0.0
p-Chloroaniline	"	1.97	1.95	-1.0
m-Chloroaniline	"	1.05	1.05	0.0
o-Chloroaniline	"	1.99	1.97	-1.0
o-Chloroaniline	Acetic Acid	2.17	2.19	+0.9
p-Chloroaniline	"	2.41	2.41	0.0
2,4-Dichloroaniline	"	2.30	2.34	+1.7
2,5-Dichloroaniline	"	2.30	2.37	+3.0
m-Nitroaniline	"	2.32	2.32	0.0
p-Nitroaniline	"	2.31	2.34	+1.3
N,N-Dimethyl-m-nitroaniline	"	2.29	2.30	+0.4
N,N-Dimethyl-p-nitroaniline	"	2.36	2.42	+2.5
2-Methyl-5-nitroaniline	"	2.29	2.29	0.0
4-Methyl-2-nitroaniline	"	2.29	2.31	+0.9

Figure 16

Photometric Titration of a Mixture of
2-Methyl-5-nitroaniline (0.502 meq.)
and 4-Methyl-2-nitroaniline (1.007 meq.)
in Glacial Acetic Acid with 0.4391 M
Perchloric Acid

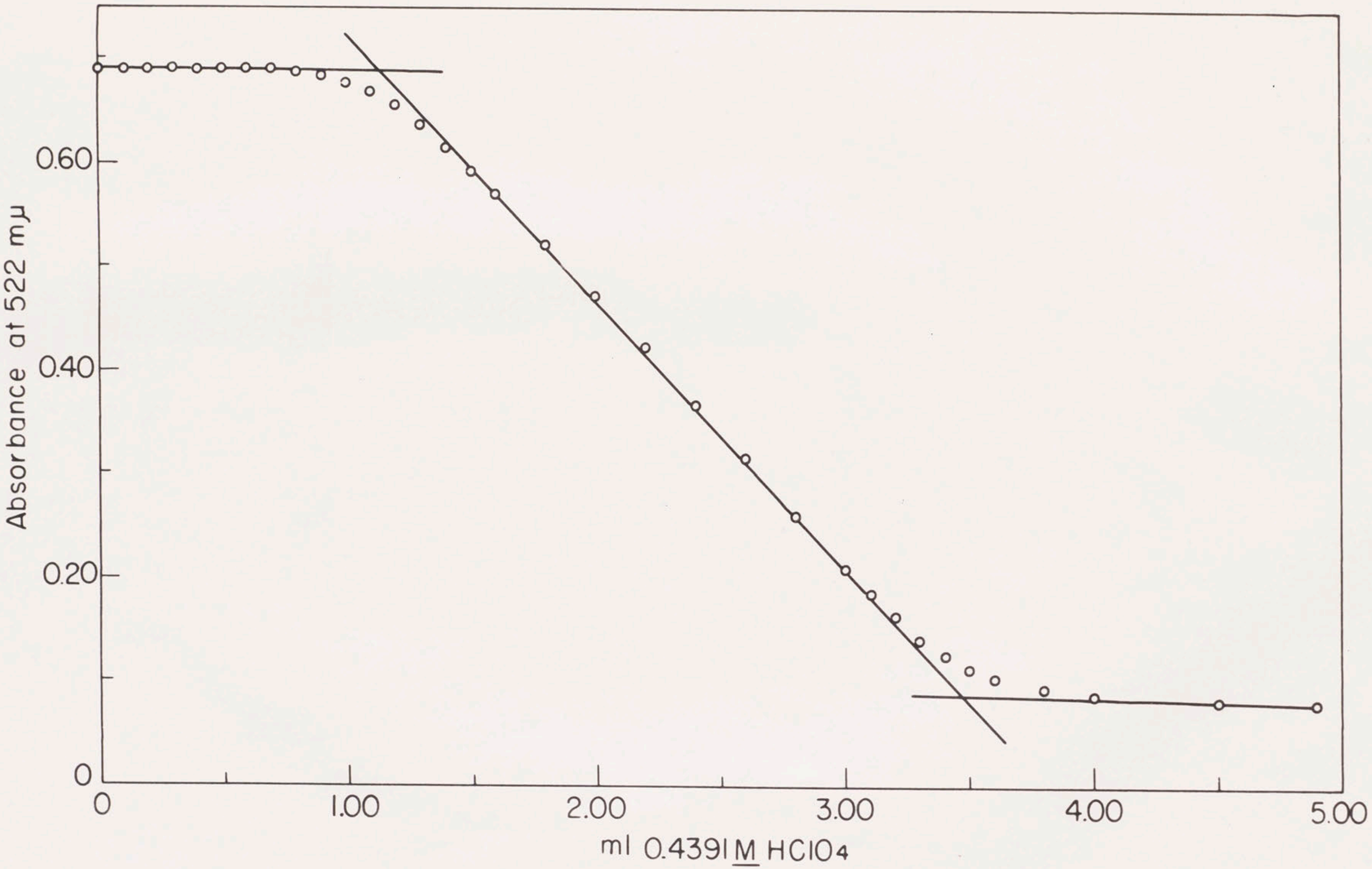
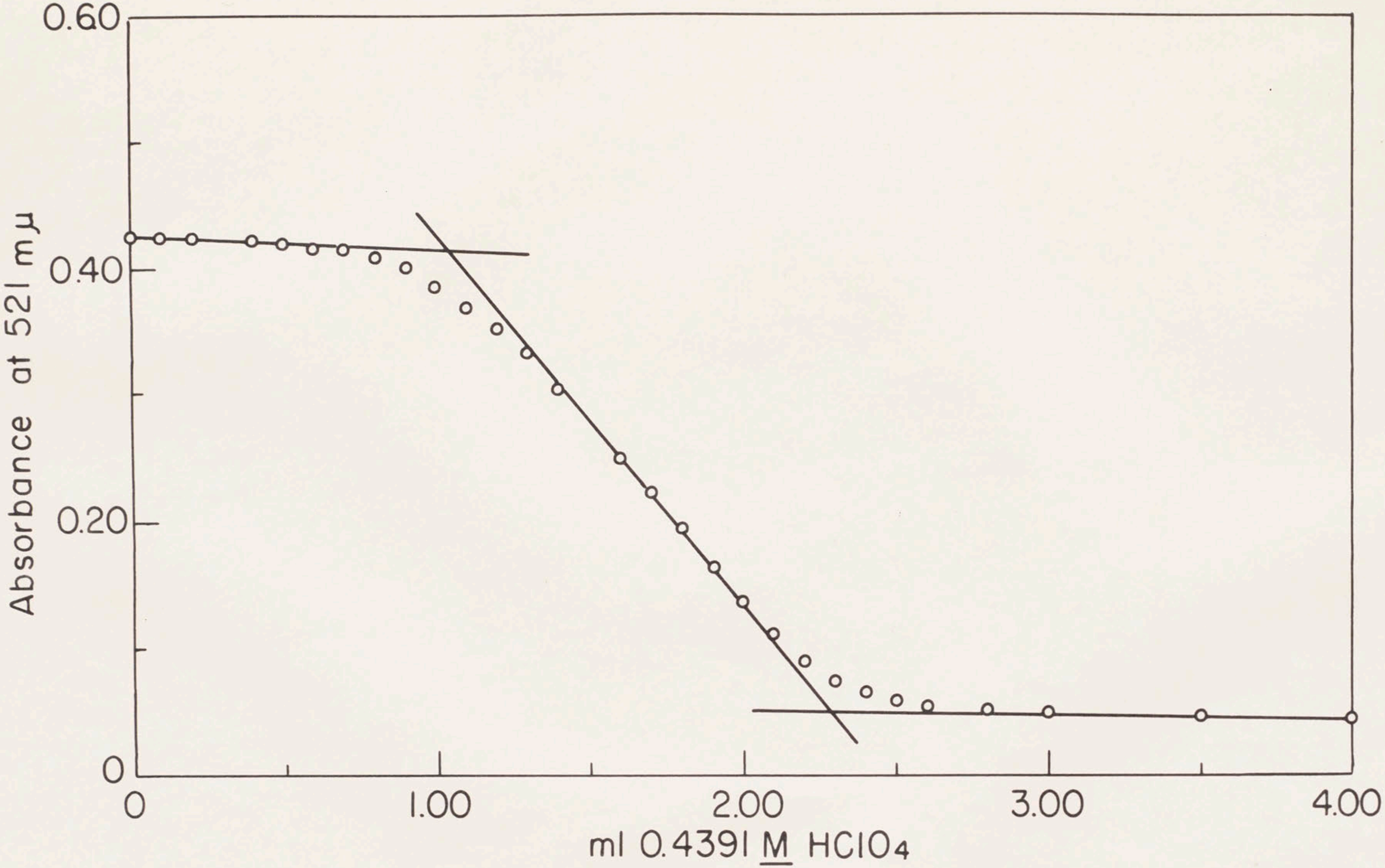

Absorbance at 522 mμ
0.60
0.40
0.20
0
0
1.00
2.00
3.00
4.00
5.00
ml 0.4391 M HClO4

Figure 17

Photometric Titration of a Mixture of
2,4-Dichloroaniline (0.483 meq.) and
4-Methyl-2-nitroaniline (0.504 meq.)
in Glacial Acetic Acid with 0.4391 M
Perchloric Acid


0.60
0.40
0.20
0
Absorbance at 521 mμ
0
1.00
2.00
3.00
4.00
ml 0.4391 M HClO4

wavelength. This situation is encountered when the weaker component absorbs at longer wavelengths than the stronger one. There are, however, a number of cases in which the reverse is true, as illustrated by Figure 38 in the Appendix which shows the basic absorption spectra of aniline $\left[pK_b(H_2O) = 9.42\right]$ and N,N-diethylaniline $\left[pK_b(H_2O) = 7.48\right]$ in acetonitrile. Here the absorption of the weaker component is obscured by that of the stronger one. Fortunately, the absorption of N,N-diethylaniline is shifted to shorter wavelengths upon protonation, thus making the aniline absorption accessible to measurement. Hence, breaks can be obtained for both components by changing to a shorter wavelength after obtaining the first break, as shown in Figure 18. The major drawback of this wavelength-change technique is that the untitrated residue of the first component absorbs quite strongly at the shorter wavelength and causes nonlinearity of the titration curve, since it is titrated faster than the weaker component. In the present case, where the final break is quite sharp, this nonlinearity introduces little uncertainty since the readings close to the end-point can be used for extrapolation. If the second break were rounded the curvature would have a detrimental effect on the accuracy of the titration of the second component. In spite of such occasional difficulties, wavelength changes were found extremely useful in differentiating titrations of aniline derivatives.

Figure 18

Photometric Titration of a Mixture of N,N-Diethylaniline (0.512 meq.) and Aniline (1.014 meq.) in Acetonitrile with 0.5115 M Perchloric Acid

—○—○— Titrated at 337 mμ

—△—△— Titrated at 320 mμ

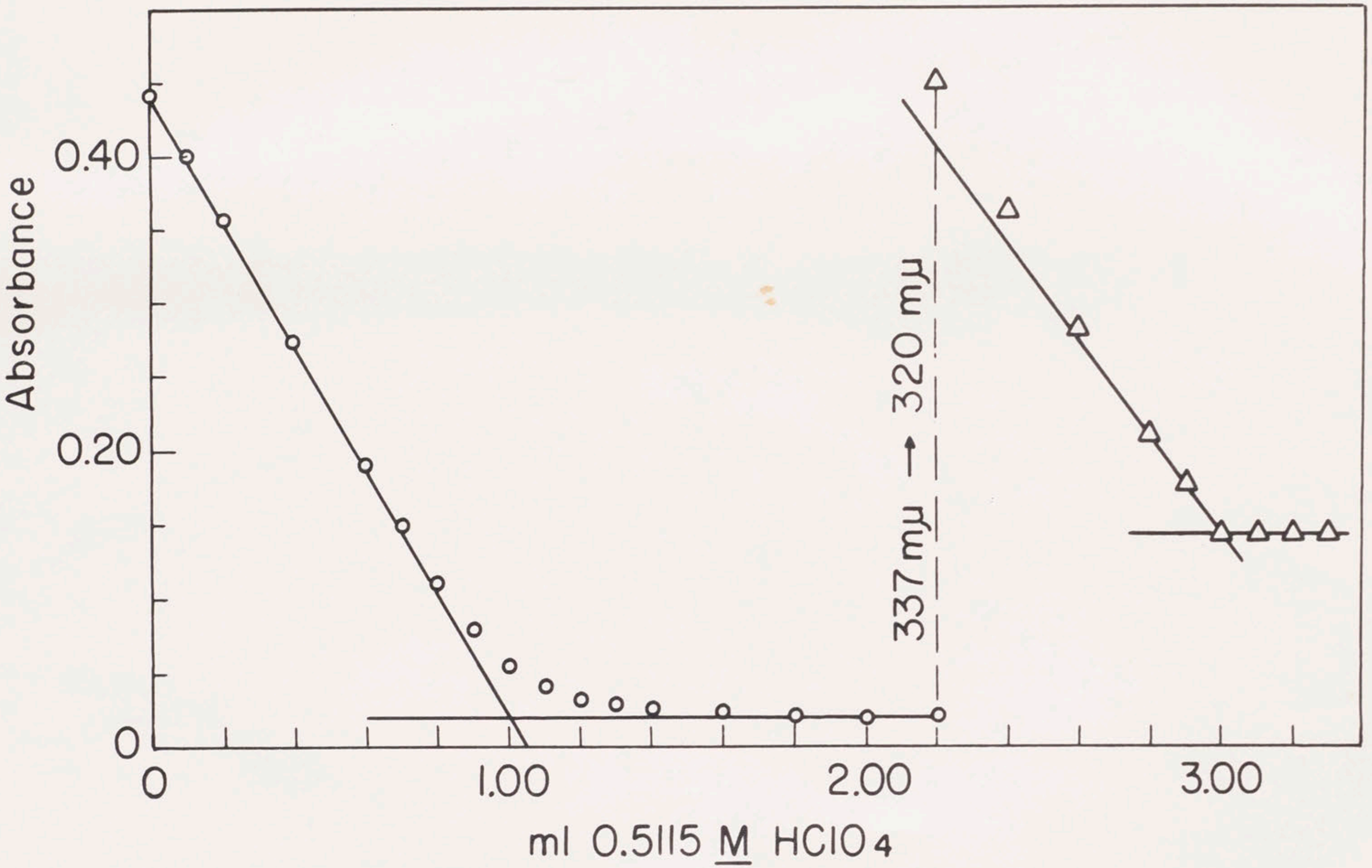

Absorbance
0.40
0.20
0
0
1.00
2.00
3.00
ml 0.5115 M HClO4
337 mμ → 320 mμ

Figure 19 illustrates the photometric titration, in acetic acid, of a three-component mixture consisting of p-chloro-N,N-diethylaniline, o-chloroaniline and 2,5-dichloroaniline. The first break is obtained at 341 mμ where only p-chloro-N,N-diethylaniline absorbs. The wavelength setting is then changed to 327 mμ where the absorption of 2,5-dichloroaniline can be measured while the middle component, o-chloroaniline, absorbs at slightly shorter wavelengths. Although the first two breaks are quite rounded, this titration compares very favorably with the corresponding potentiometric curve (Figure 23) which shows only two poor inflections.

Differentiating titrations of bases in glacial acetic acid must probably be restricted to mixtures containing no more than three components since the available basicity range in this solvent is limited by the leveling effect on strong bases. If the non-leveling solvent acetonitrile is used, even four-component mixtures can be titrated, as illustrated in Figure 20. This figure shows the photometric curve for a mixture of di-n-butylamine, N,N-diethylaniline, aniline and o-chloroaniline. The first two breaks are obtained at 337 mμ , where only the second component, N,N-diethylaniline, absorbs. At the shorter wavelength both aniline and o-chloroaniline absorb, the latter compound more strongly than the former. The marked curvature before the third break is due to the titration of the last traces of N,N-diethylaniline, i.e., the same phenomenon which was discussed in connection with Figure 18.

Figure 19

Photometric Titration of a Mixture of p-Chloro-N,N-diethylaniline (0.407 meq.), o-Chloroaniline (0.951 meq.) and 2,5-Dichloroaniline (0.506 meq.) in Glacial Acetic Acid with 0.4391 $\underline{M}$ Perchloric Acid

—○—○— Titrated at 341 mμ

—△—△— Titrated at 327 mμ

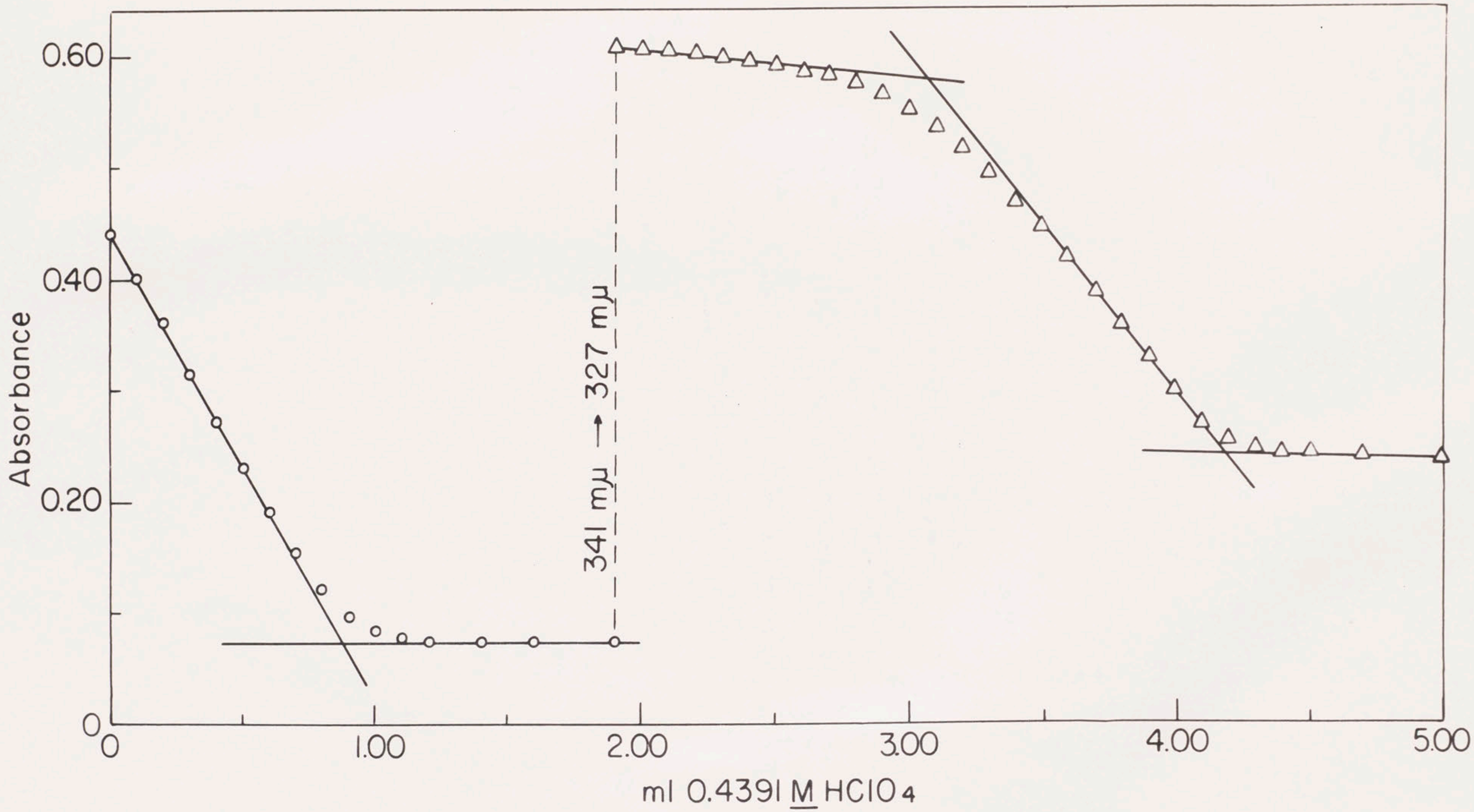
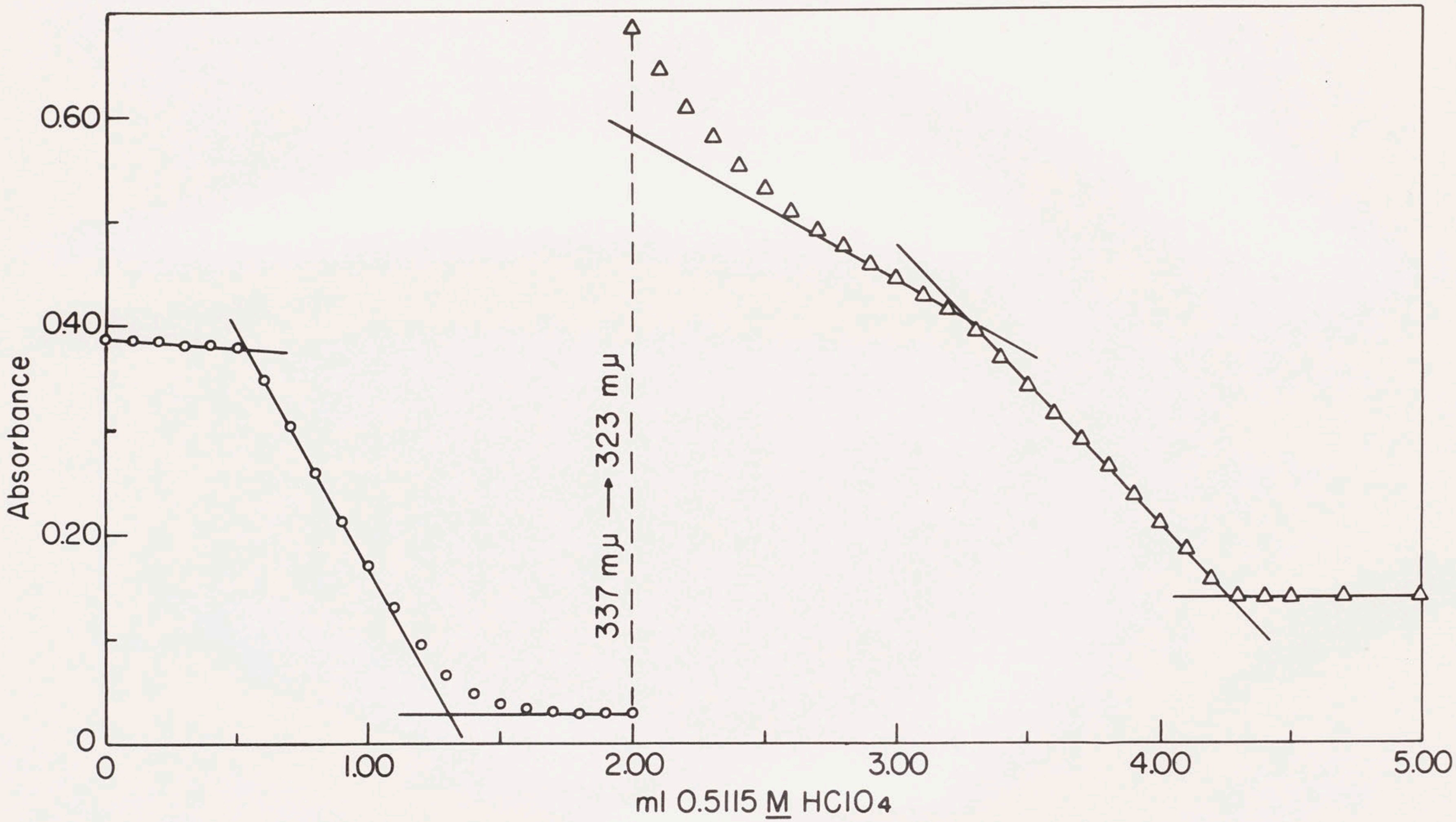

Absorbance
0.60
0.40
0.20
0
0
1.00
2.00
3.00
4.00
5.00
341 mμ → 327 mμ
ml 0.4391 M HClO4

Figure 20

Photometric Titration of a Mixture of Di-n-butylamine (0.283 meq.), N,N-Diethylaniline (0.409 meq.), Aniline (1.014 meq.) and o-Chloroaniline (0.509 meq.) in Acetonitrile with 0.5115 M Perchloric Acid

—○—○— Titrated at 337 mμ

—△—△— Titrated at 323 mμ



0.60
0.40
0.20
0
Absorbance
0
1.00
2.00
3.00
4.00
5.00
ml 0.5115 M HClO4
337 mμ ⟶ 323 mμ

Tables VII and VIII present some results of differentiating photometric titrations in acetonitrile and acetic acid, respectively. Considering that most of the titrated materials were Eastman White Label grade, and hence not of highest purity, the agreement between calculated and observed breaks is satisfactory in most cases. In titrations of bases of very similar strength, such as aniline and m-chloroaniline (Table VII), o-chloroaniline and 2,5-dichloroaniline or o-chloroaniline and 2,4-dichloroaniline (Table VIII) relatively large deviations are observed. However, the photometric results are far better than those obtainable by other titration methods which give little or no differentiation in such cases.

On the basis of these results it appears that photometric differentiation of two bases is possible if the difference between their aqueous pK_b values is 1.5 or greater. In the case of o-chloroaniline and 2,4-dichloroaniline ΔpK_b is only about 0.8, showing that analytically useful, though less reliable, breaks can be obtained even in such situations.

The above statements refer to mixtures in which the components are of comparable concentrations. If one component is present in large excess, the differentiation can be expected to become more difficult.

d. Comparison with Potentiometric Titrations:

Reference has already been made to some potentiometric titration curves which were obtained for the sake of comparison. The

TABLE VII

DIFFERENTIATING TITRATIONS OF BASES IN ACETONITRILE USING 0.4-0.5 M PERCHLORIC ACID TITRANTS IN ACETIC ACID

Components	$pK_b(H_2O)$	Titrant Consumption Calculated	Titrant Consumption Observed	%Deviation
N,N-Diethylaniline	7.5	1.00	1.00	0.0
Aniline	9.4	1.98	2.00	+1.0
p-Chloroaniline	10.0	1.97	1.95	-1.0
o-Chloroaniline	11.4	1.99	1.96	-1.5
Aniline	9.4	1.95	1.96	+0.5
5-Nitro-1-naphthylamine	11.2	0.57	0.56	-1.8
Sodium acetate	9.2	2.20	2.23	+1.4
5-Nitro-1-naphthylamine	11.2	0.57	0.56	-1.8
Di-n-butylamine	2.6	0.55	0.53	-3,6
N,N-Diethylaniline	7.5	0.80	0.78	-2.5
Aniline	9.4	1.98	1.97	-0.5
o-Chloroaniline	11.4	0.99	0.99	0.0
Aniline	9.4	1.98	1.91	-3.5
m-Chloroaniline	10.5	1.05	1.11	+5.7

TABLE VIII

DIFFERENTIATING TITRATIONS OF BASES IN ACETIC ACID USING 0.4-0.5 <u>M</u> PERCHLORIC ACID TITRANTS IN ACETIC ACID

Components	$pK_b(H_2O)$	Titrant Consumption		%Deviation
		Calculated	Observed	
Pyridine	8.8	1.41	1.43	+1.4
o-Chloroaniline	11.4	1.08	1.08	0.0
p-Chloro-N,N-diethylaniline	9.5^*	1.16	1.10	-5.2
o-Chloroaniline	11.4	2.17	2.23	+2.8
o-Chloroaniline	11.4	1.08	1.04	-3.7
2,5-Dichloroaniline	12.5	1.15	1.19	+3.5
o-Chloroaniline	11.4	1.08	1.12	+3.7
2,4-Dichloroaniline	12.2	1.24	1.20	-3.2
2-Methyl-5-nitroaniline	12.0^*	1.14	1.14	0.0
4-Methyl-2-nitroaniline	13.5^*	2.29	2.33	+1.7
p-Chloro-N,N-diethylaniline	9.5^*	0.93	0.88	-5.4
o-Chloroaniline	11.4	2.17	2.18	+0.5
2,5-Dichloroaniline	12.8	1.15	1.13	-1.7

* Estimated values

apparatus used in these titrations has been described in section B1. With regard to the possible effect of the aqueous potassium chloride solution in the calomel electrode the reader is referred to the discussion in connection with the potentiometric titrations of acids.

Figures 21 and 22 illustrate potentiometric titrations of two-component mixtures consisting of very weak bases. These two figures can be compared with the corresponding photometric titrations in Figures 16 and 17.

Potentiometric titration curves for multicomponent mixtures are shown in Figures 23 and 24. The first curve, obtained by titration of a mixture of p-chloro-N,N-diethylaniline, o-chloroaniline and 2,5-dichloroaniline in glacial acetic acid, shows only two inflections instead of three and even these are too small to permit accurate location of the equivalence points. Figure 24, which illustrates the potentiometric titration of a four-component mixture in acetonitrile, shows a curve with only two satisfactory inflections. Here the first break is rather sharp because of the relatively strong basicity of the first component, di-n-butylamine.

e. Photometric Titrations at Lower Concentrations:

The majority of the titrations in the present study were performed on solutions containing $5\text{x}10^{-3}$ to $1\text{x}10^{-2}$ molar bases. This concentration level was chosen mainly because of convenience, since many samples could be weighed out directly while the use of

Figure 21

Potentiometric Titration of a Mixture of 2-Methyl-5-nitroaniline (0.502 meq.) and 4-Methyl-2-nitroaniline (1.007 meq.) in Glacial Acetic Acid with 0.4391 <u>M</u> Perchloric Acid

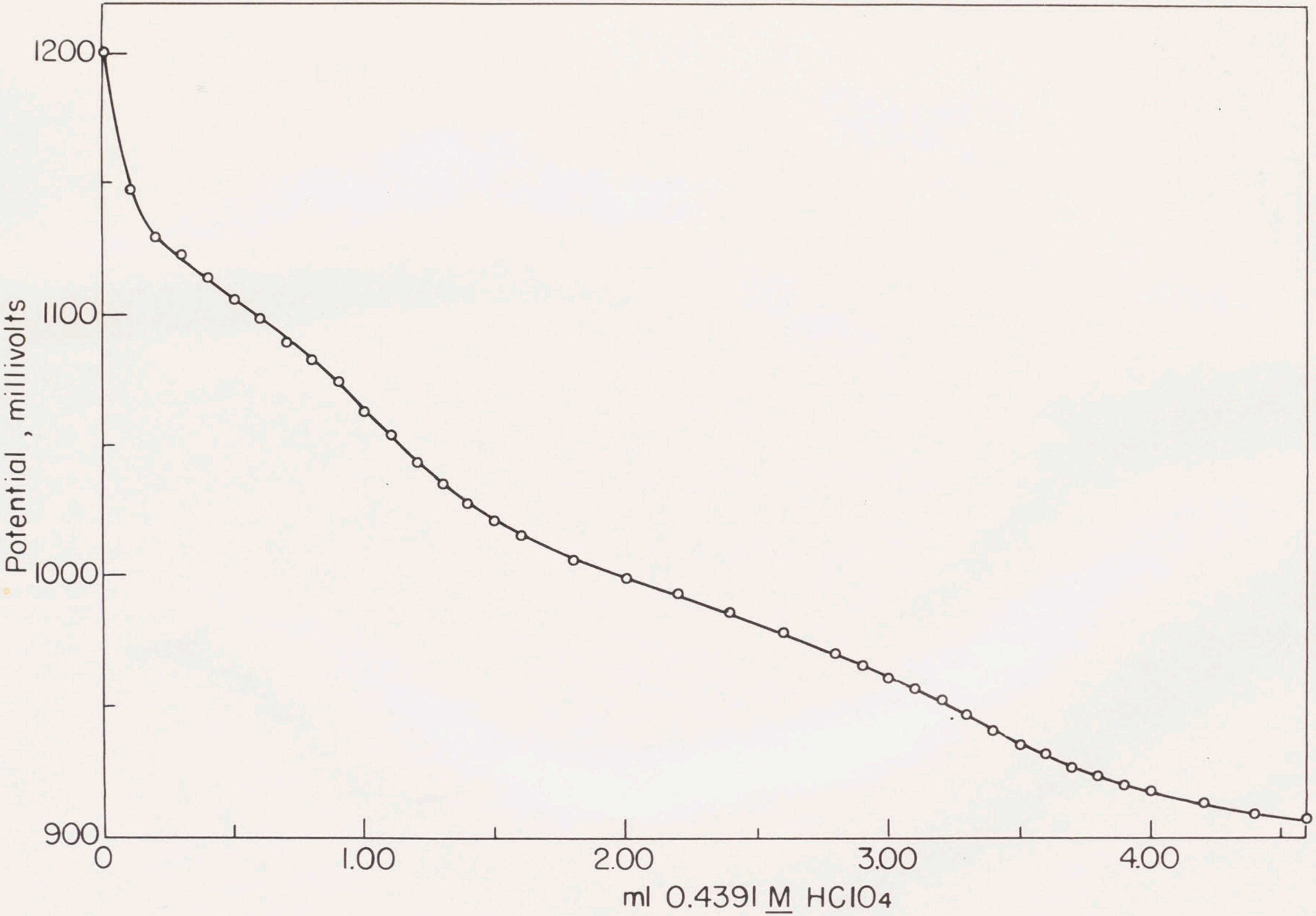

1200
1100
1000
900
Potential , millivolts
0
1.00
2.00
3.00
4.00
ml 0.4391 M HClO₄

Figure 22

Potentiometric Titration of a Mixture of 2,4-Dichloroaniline (0.452 meq.) and 4-Methyl-2-nitroaniline (0.504 meq.) in Glacial Acetic Acid with 0.4391 M Perchloric Acid

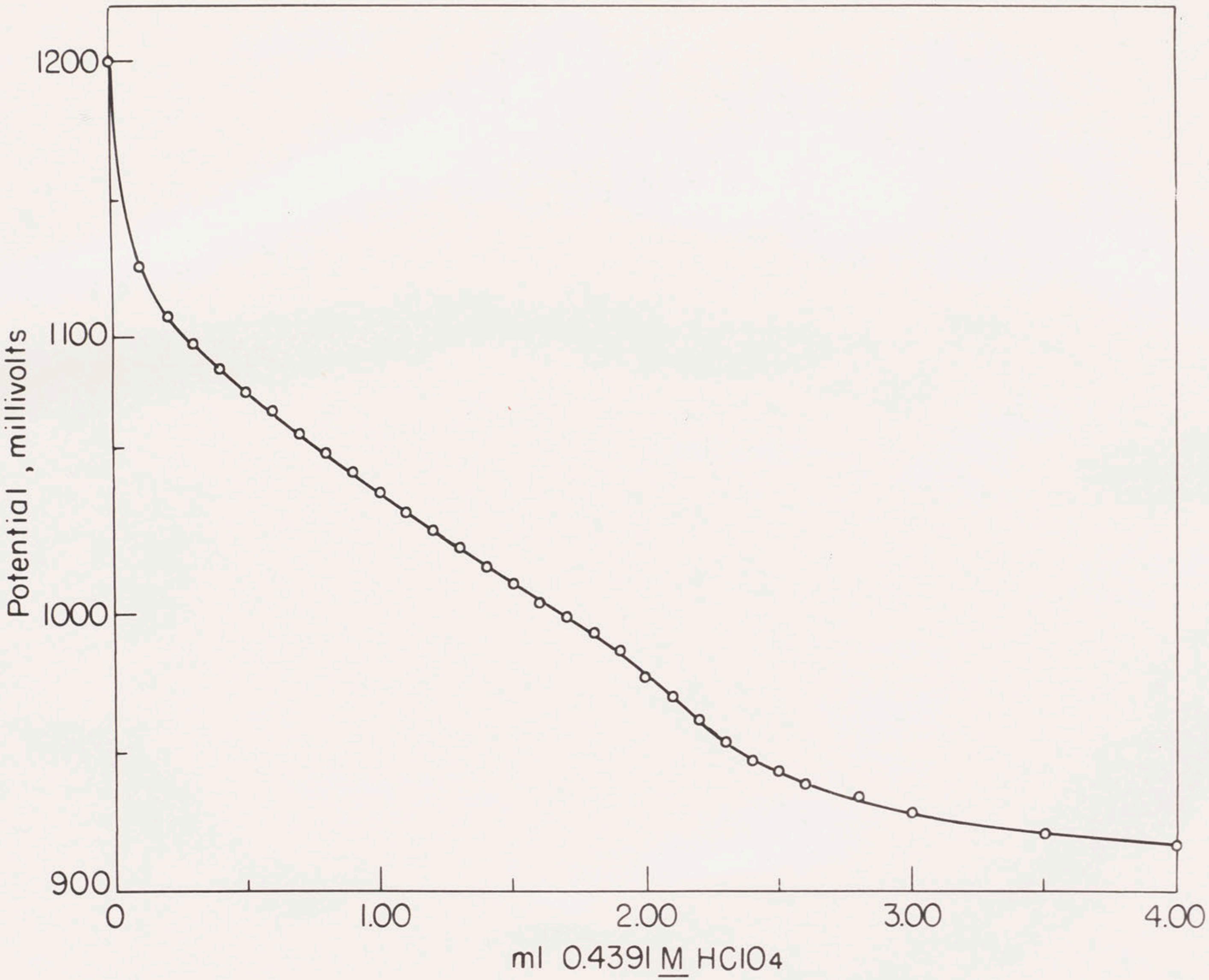

1200
1100
1000
900
Potential , millivolts
0
1.00
2.00
3.00
4.00
ml 0.4391 M HClO4

Figure 23

Potentiometric Titration of a Mixture of p-Chloro-N,N-diethylaniline (0.407 meq.), o-Chloroaniline (0.951 meq.) and 2,5-Dichloroaniline (0.506 meq.) in Glacial Acetic Acid with 0.4391 M Perchloric Acid

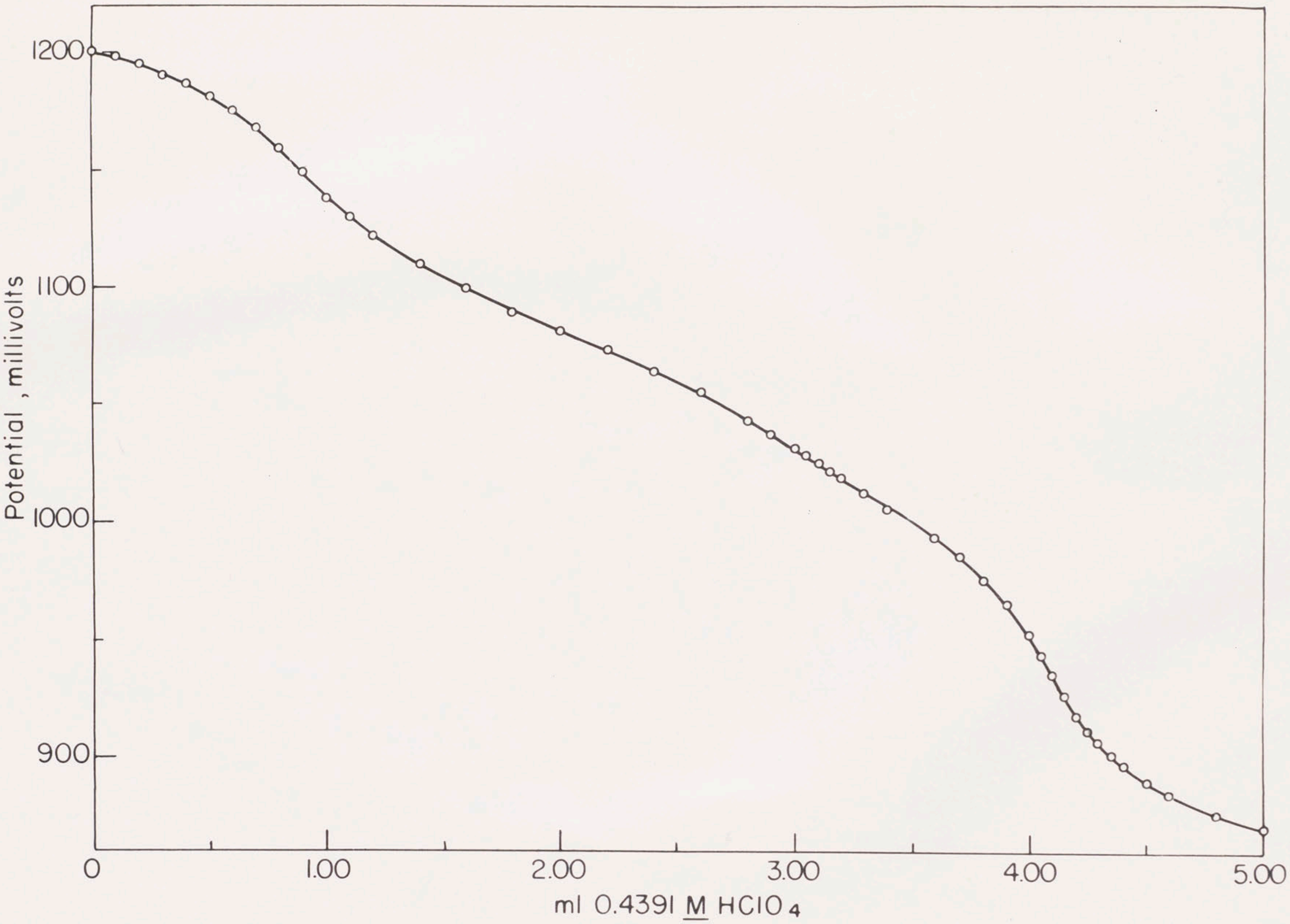
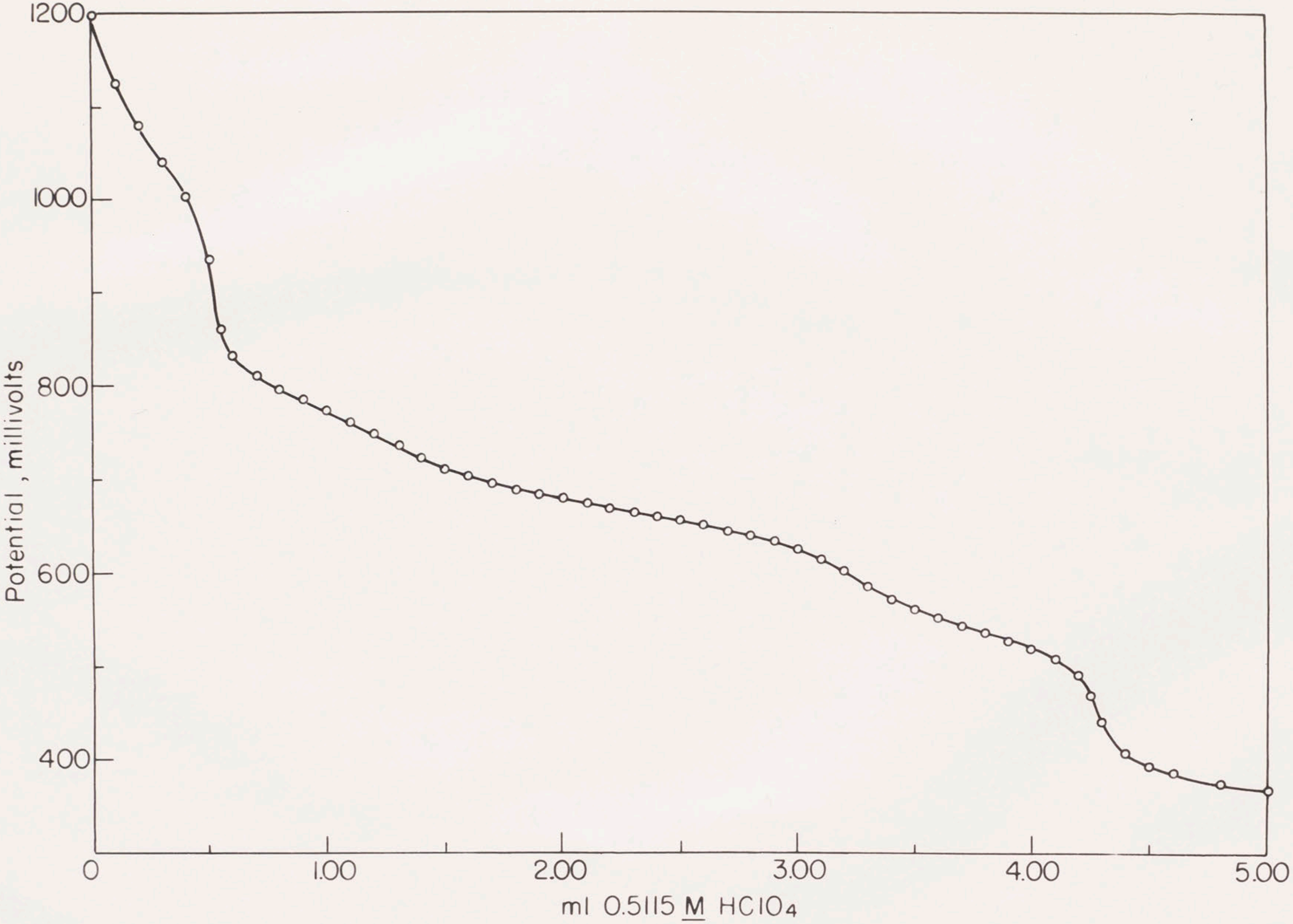

1200
1100
1000
900
Potential , millivolts
0
1.00
2.00
3.00
4.00
5.00
ml 0.4391 M HClO4

Figure 24

Potentiometric Titration of a Mixture of Di-n-butylamine (0.283 meq.), N,N-Diethylaniline (0.409 meq.), Aniline (1.014 meq.) and o-Chloroaniline (0.509 meq.) in Acetonitrile with 0.5115 M Perchloric Acid


1200
1000
800
600
400
Potential , millivolts
0
1.00
2.00
3.00
4.00
5.00
ml 0.5115 M HClO4

a lower concentration level would have necessitated dilutions. Reilley and Schweizer (63) titrated a few relatively strong bases in acetic acid at concentrations around 5×10^{-4} M and this was obviously far from the lower limit of titratability. In the present study 5-nitro-1-naphthylamine, a comparatively weak base $[pK_b(H_2O) = 11.2]$ was successfully titrated in the 10^{-4} molar range using acetic acid as solvent. For stronger bases the lower concentration limits of titratability may be set by their molar absorptivities, or by basic impurities in the solvent, rather than by incompleteness of the titration reactions. The molar absorptivity at the basic peak falls between 2000 and 20,000 liter/mole cm. for most aromatic amines. A value around 2,500 is typical for the stronger amines such as aniline and N,N-diethylaniline, while the weaker bases, such as the nitroanilines, often exhibit a more intense absorption. A simple calculation shows that a 4×10^{-5} molar solution of a base with a molar absorptivity of 2,500 gives a maximum absorbance reading of 0.5 when measured in a cell with 5 cm. light-path. Obviously a dilution below 4×10^{-5} would soon give such low absorbance readings that no reliable titration curve could be obtained. In such situations the molar absorptivity of the base may well become the limiting factor. The more strongly absorbing amines, on the other hand, are usually so weakly basic that they cannot be titrated at extreme dilutions. It is obvious that small basic impurities in the solvent, such as ammonia in glacial acetic acid, become increasingly important when very dilute bases are titrated. However, it should be remembered that visual and potentiometric titrations tend not to give sharp end-points in dilute solutions and there is no doubt that the photometric method is superior to these techniques in spite of its limitations.

f. Anomalous Photometric Titration Curves:

Most of the bases studied in the present investigation gave photometric titration curves in close agreement with the expected linear shapes. However, a few exceptions were encountered, the most drastic being the titration curves of p-chloroaniline and p-nitroaniline in glacial acetic acid (Figure 25). Close inspection of the curves of a considerable number of other bases in acetic acid revealed curvature of the same type to a much smaller degree. One of the bases exhibiting a moderate curvature was o-chloroaniline, a compound which also was titrated by Reilley and Schweizer (63). It is interesting to note that these authors state that the end-point for o-chloroaniline had to be extrapolated from readings close to the break, since earlier readings gave poor results. The shape of the beginning of the titration curve was not shown but it seems reasonable to assume that the curvature was of the type encountered in the present study.

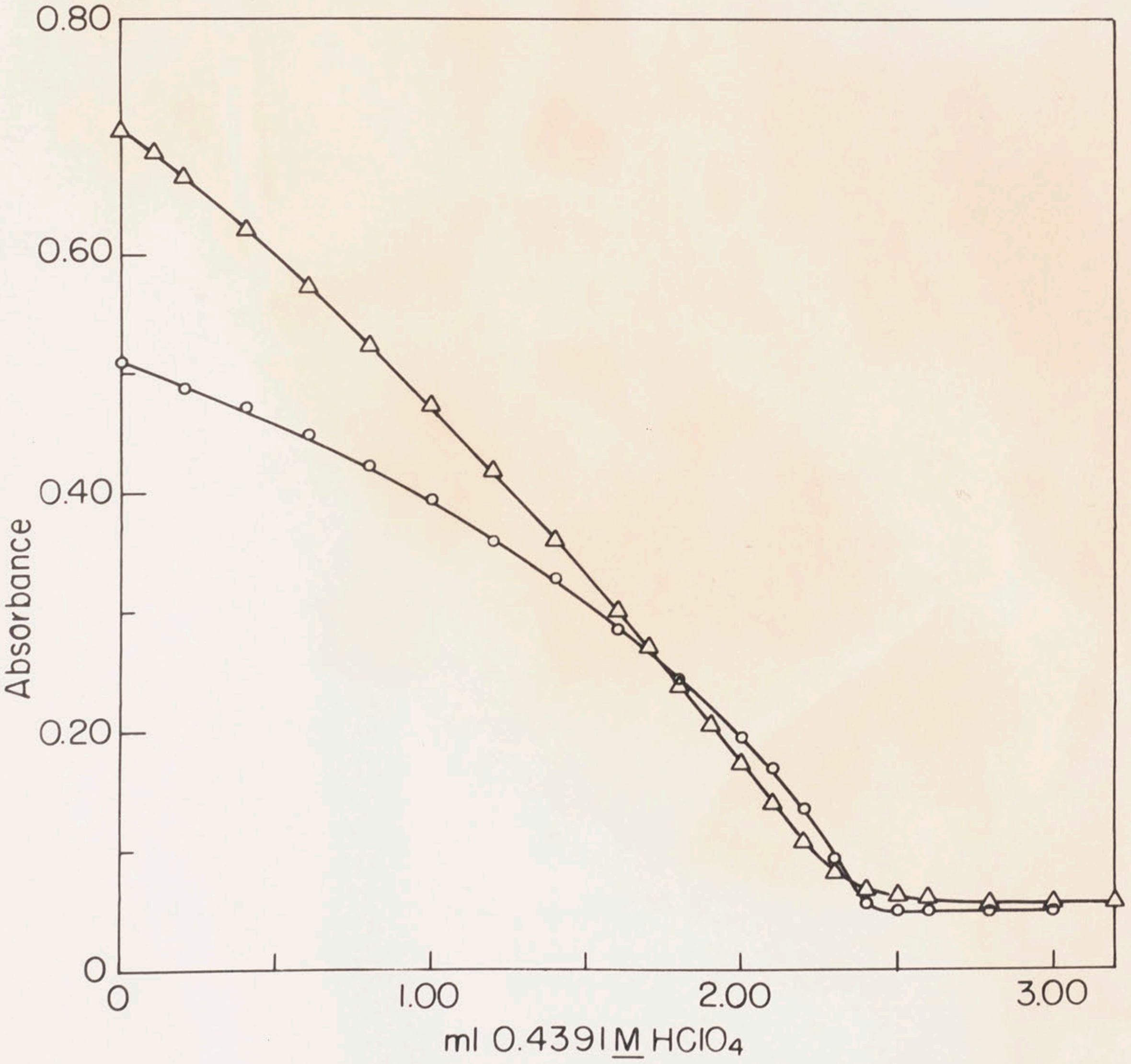
Some nonlinearity of the observed type would be expected to result from light leakage or dilution effects. However, light

Figure 25

Photometric Titrations of p-Chloroaniline (1.053 meq.) and p-Nitroaniline (1.016 meq.) in Glacial Acetic Acid with 0.4391 M Perchloric Acid

—○—○— p-Chloroaniline at 327 mμ

—△—△— p-Nitroaniline at 448 mμ


0.80
0.60
0.40
0.20
0
Absorbance
0
1.00
2.00
3.00
ml 0.4391 M HClO4

leakage would have caused similar deviations in all titrations with the same initial absorbance, regardless of which base was titrated or which solvent was used. The dilution corrections were much too small to account for the observed curvature. Impurities in the samples were considered as a third possible explanation. This, too, had to be discarded since both p-chloroaniline and p-nitroaniline gave theoretical end-points and the known spectra and the basic strengths of their isomers excluded these as possible impurities.

The possibility that the anomalies in the titration curves could be due to ion-pair and ion-aggregate formation was first considered. At the relatively high concentration level used, (10^{-2}M), the ions resulting from the neutralization of a base with perchloric acid in glacial acetic acid undoubtedly are highly associated (46, 51) and it seems reasonable to assume that the degree of association increases as more ions are formed during the titration. However, Kolthoff and Bruckenstein (46) claim that the absorption spectrum of a protonated base in glacial acetic acid is independent of whether it exists as a free ion, or as part of an ion-pair, or a higher ionic aggregate. Slight changes in the acidic spectrum would, in any event, not be observed at the titration wavelength where only the basic form absorbs.

Measurement of the absorption spectrum of p-nitroaniline at different stages of neutralization confirmed the titration results, indicating a nonlinear transition from the basic to the acidic form. No significant spectral evidence for the existence of a third species was found. The readings obtained during photometric titrations were stable and it therefore seemed unlikely that the curvature was caused by air oxidation or some other side reaction.

Hence no satisfactory explanation for the exceptional titration curves could be found at the time they were first encountered. However, later experiences with photometric titrations of phenols suggest an explanation analogous to the theory which accounts for the nonlinear titration curves of these compounds in isopropanol and benzene. In those solvents potentiometric, conductometric, and now photometric evidence indicates the existence of very stable hydrogen-bonded complexes between phenols and phenolate ions. The strong hydrogen bond apparently affects the absorption characteristics of the phenolate ion, causing a nonlinear curve, since the concentration of the complex goes through a maximum at half-neutralization.

In applying an analogous reasoning to an aromatic amine dissolved in glacial acetic acid we have to remember that the base will be partly protonated by the solvent. Even the unreacted base is undoubtedly associated with the solvent through hydrogen bonding. Titration of the base results in formation of an anilinium ion which is a stronger acid than acetic acid, because its conjugate base is weaker than the acetate ion. Hence it seems reasonable to assume that the anilinium ions tend to displace the acetic acid molecules from their hydrogen bonds with the untitrated aniline derivatives, thereby forming N^+-H---N bonds. It is known that the shortest (and strongest) hydrogen bonds have the longest covalent bond distances (14) indicating that the proton is relatively loosely bound. Hence, the anilinium ions formed from a weaker base might be expected to form stronger bonds than those formed from a stronger base, since the weaker base gives a stronger conjugate acid, i.e., a more loosely bound proton. On the other hand, the strength of the hydrogen bond between an aniline and the corresponding anilinium ion must also depend on the electron density around the nitrogen atom of the aniline molecule. This electron density decreases with decreasing basic strength of the amine, an effect which should counteract the bond-strengthening effect of the increased acidity of the corresponding anilinium ion to some extent.

The hydrogen-bonded phenol-phenolate complexes are weaker acids than the free phenols, as indicated by inflections at the half-neutralization point in potentiometric titrations (33, 37). Correspondingly, one would expect a strongly hydrogen-bonded aromatic amine to be a weaker base than the free (or more loosely hydrogen-bonded) amine. This could be at least part of the explanation for the pronounced non-linearity of the photometric titration curve of p-chloroaniline. This compound is largely protonated by glacial acetic acid, as indicated by the much lower basic absorption peak in this solvent compared to the basic spectrum in acetonitrile (Figure 39 in the Appendix). Since the dissociation into free ions is negligibly small at the titration concentration (10^{-2}M), the degree of protonation by the solvent is to a first approximation governed by the following equilibrium:

$$ArNH_2 + HAc \rightleftharpoons ArNH_3^+Ac^-$$

Titration of the solution with perchloric acid leads to formation of anilinium ions in excess of the acetate concentration. Since these anilinium ions are comparatively loosely bonded to the very weakly basic perchlorate ions they may be expected to combine with unprotonated amine molecules to form a hydrogen-bonded complex which is a weaker base than the original amine. This effective weakening of the unprotonated base by complex formation would cause a decrease in the degree of protonation by the solvent during the titration, thereby accounting for the observed curve shape.

The above explanation assumes that the basic spectrum of the aniline molecule is unaffected by the formation of a complex with the anilinium ion. This is probably not strictly true, since the titration curve of p-chloroaniline shows a distinct, though smaller, curvature even in the non-protonating solvent acetonitrile. Likewise, the very weak base p-nitroaniline is not extensively protonated by glacial acetic acid and a change in the degree of protonation can therefore hardly account for the nonlinear titration curve of this compound. Further support for the existence of alterations in the ultraviolet spectrum due to hydrogen band formation is given by the reaction of 4-dimethylamino-4′-nitrostilbene with hydrogen chloride in benzene solution, which system was investigated in the indicator study which constitutes the final part of this thesis. All available evidence indicates that the complex formation leads to an increase in absorption intensity at the basic peak, a phenomenon of the type recently reported by Forbes et al. (19,20, 21). It is possible that a slight shift in peak wavelength also occurs, but this would probably be toward shorter wavelengths (6), causing a decrease in absorbance at the titration wavelength, which is chosen near the long-wavelength edge of the absorption band. If such a shift occurs, its effect must therefore be more than compensated by an increase in absorption intensity resulting from the hydrogen bond.

Forbes and Templeton (21) discuss various mechanisms by which intermolecular hydrogen bonding may affect the absorption intensity in the case of benzoic acid. However, the theory of such interactions is so undeveloped that no reliable explanation can be offered at the present time.

On the basis of the above considerations it is suggested that anomalous photometric titration curves of aromatic amines are caused by the formation of strong hydrogen bonds between the amines and their conjugated acids. The complex formation apparently changes the basic absorption spectrum sufficiently to cause a nonlinear titration curve. If the titration is performed in an acidic solvent, such as acetic acid, the weaker basicity of the complex, as compared to the original amine, may cause a decrease in the degree of protonation by the solvent during the titration. This additional effect tends to increase any nonlinearity resulting from changes in absorption wavelength or intensity due to the hydrogen bond.

E. SUMMARY OF PHOTOMETRIC ACID-BASE TITRATIONS IN NON-AQUEOUS SOLVENTS

1. Applicability

The results presented in this thesis show that the photometric titration technique can be applied successfully to the analysis of large groups of acids and bases in non-aqueous solutions. Among these are phenolic compounds, aromatic amines, and heterocyclic aromatic nitrogen bases. The method can probably be used equally well for direct titration of many other types of compounds, such as substituted benzoic acids and polynitroaromatic compounds. Furthermore, most non-absorbing acids and bases can be titrated photometrically if a suitable indicator compound is added.

As expected, it was found particularly advantageous to use the photometric method for titration of very weak acids and bases and for difficult differentiating titrations. In such situations the photometric technique is distinctly superior to potentiometric titration. However for titrations of relatively strong acids and bases the latter method may give more precise results, since the uncertainty of photometric measurements is comparatively high.

The necessity of using transparent solvents in photometric titrations restricts the choice of solvent more than in the case of other titration methods. For photometric titration of bases, such excellent solvents as glacial acetic acid and acetonitrile are quite useful. The solvent situation is not as good for titration of acidic compounds, since several excellent solvents absorb strongly in the ultraviolet region. However, it has been shown that the photometric technique makes it possible to use solvents in which the potentiometric method would given poor end-points. For example, phenol gives a good photometric break in isopropanol, while basic solvents such as ethylenediamine and pyridine are recommended for potentiometric titrations of this compound. In general, isopropanol appears to be an excellent solvent for photometric titrations of acids.

Use of the photometric method requires no change in the titrants normally employed in non-aqueous acid-base titrations. Perchloric acid titrants in acetic acid and tetraalkylammonium bases in isopropanol are recommended for photometric as well as potentiometric titrations.

The present study confirms the results of Goddu and Hume (27, 28) according to which very satisfactory photometric titrations can be performed using ordinary beakers of glass or Vycor as titration cells. This simple system compares very favorably with the complicated arrangements described in the literature (61,66,63).

2. Use of Photometric Titrations for Study of Hydrogen Bonding.

Anomalous curve shapes encountered in titrating phenols and aniline derivatives demonstrate the ability of the photometric technique to yield chemical information about acid-base systems in addition to analytical data. It appears that the anomalies found in the present study are due to the formation of strongly hydrogen-bonded complexes during the titration. In combination with spectral studies at various stages of neutralization, the photometric titration method can be expected to become a powerful tool in studying the formation of hydrogen bonds. The relation between absorption intensity and hydrogen bonding appears to constitute a particularly challenging field for future research along these lines.

3. Practical Recommendations for Photometric Acid-Base Titrations

When available, the pK values of acids and bases in water can be used as a rough guide in predicting their behavior in photometric titrations. It appears that acids with aqueous pK_a values as high as 10 give satisfactory end-points when titrated with tetraalkylammonium hydroxide in isopropanol solution at the 10^{-2} molar level. Still weaker acids could possibly be titrated, though none was tried in the present study.

It appears possible to obtain quantitative photometric differentiation of two acids in isopropanol provided that there is a difference of about 1.5 units between their aqueous pK_a values.

Useful breaks may be obtained in some cases where this difference is still smaller. However, in the case of phenol derivatives, spectral overlap may make it difficult to obtain a good final photometric break even though the break between the components is satisfactory. In situations where the spectral difficulties cannot be overcome by changing the wavelength setting during the titration, it may be possible to perform a potentiometric titration on an aliquot of the sample to obtain the total acidity while a photometric titration provides differentiation of the components.

Bases can be expected to give useful photometric breaks in glacial acetic acid at the 10^{-2} molar level if their pK_b values in water lie below 13.5. For the weakest bases $[pK_b(H_2O) = 12.5 - 13.5]$ the use of absolutely anhydrous solvent and titrant is recommended. Stronger bases appear to give equally good end-points with ordinary glacial acetic acid as solvent and perchloric acid titrants from which the water has not been removed with acetic anhydride.

If the aqueous pK_b value of a base is lower than about 10, it cannot be determined by direct photometric titration in acetic acid, since it is completely protonated by the solvent. It can be titrated if a weaker indicator base is added, but it is often simpler to use a non-leveling solvent such as acetonitrile. In this solvent, however, bases with aqueous pK_b values greater than about 11.5 can be expected to give rounded breaks. Titrations in acetonitrile should be performed with a perchloric acid titrant made up in glacial acetic acid, since perchloric acid titrants in acetonitrile are unstable due to hydrolysis of the solvent.

For differentiating titrations of bases with aqueous pK_b values below 11.5, acetonitrile is the preferred solvent because of the absence of leveling effects. If the mixture contains both strong and very weak components it may be necessary to perform two titrations: one in acetonitrile to distinguish between the stronger bases, and one in acetic acid to obtain a reliable break for the weakest component. If no leveling occurs, a useful photometric differentiation of two bases can be anticipated if their aqueous pK_b values differ by about 1.5 units.

In titrating mixtures of aromatic amines, changes in wavelength setting during the titration are generally more helpful than in the case of phenolic compounds. The reason is that the transparency of an amine sokution increases while that of a phenol solution decreases upon neutralization.

A few words about the adjustment of the initial absorbance reading before a photometric titration may be in order. If the absorbance at the selected wavelength is known to increase during the titration, the instrument is preferably set to read zero absorbance against the sample solution before the titrant addition is begun. In this way an unnecessarily high final absorbance reading is avoided. On the other hand, if the absorbance is known to decrease upon titration, it is advantageous to zero the instrument against the pure solvent before adding the sample.

When the wavelength setting is changed in the middle of a differentiating titration, it may be necessary to open the slit and increase the sensitivity in order to obtain a sufficient light level. The instrument is again set to read zero absorbance if a further increase in absorption is expected, a situation encountered in titrating phenol mixtures. In the more favorable case of a mixture of aromatic amines, the shifts to shorter wavelengths can usually be performed without changing slit or sensitivity settings.

Tables IX and X give recommended titration wavelengths for a number of acids and bases, respectively. The wavelength values refer to 10^{-2} molar solutions, titrated in a beaker having an inside diameter of about 5 cm. Shorter wavelengths should be chosen if more dilute solutions are titrated using the same light-path. Most of the aqueous pK values included in the tables are based on references 4, 68, 22, 30, and 38 in the bibliography. In a few cases, where no literature data could be found, estimates were made on the basis of values for related compounds.

TABLE IX

RECOMMENDED TITRATION WAVELENGTHS FOR 10^{-2} M PHENOLIC COMPOUNDS IN ISOPROPANOL

Compound	$pK_a(H_2O)$	Titration Wavelength[1]
o-Bromophenol	8.4	342 mμ
p-Bromophenol	9.3	342
m-Chlorophenol	9.0	333
o-Chlorophenol	8.4	337
p-Chlorophenol	9.4	341
2,4-Dibromophenol	7.7*	359
2,4-Dichlorophenol	7.7	351
2,4-Dinitrophenol	4.0	507
1-Naphthol	9.5	408
2-Naphthol	9.7	408
m-Nitrophenol	8.3	570
o-Nitrophenol	7.2	541
p-Nitrophenol	7.1	495
Pentachlorophenol	4.0*	387
Phenol	9.9	329
2,4,6-Trichlorophenol	6.0	360

1. Five centimeter path length

* Estimated values

TABLE X

RECOMMENDED TITRATION WAVELENGTHS FOR 10^{-2} M BASES

Compound	$pK_b(H_2O)$	Titration Wavelength[1]	
		Acetonitrile	Acetic Acid
Aniline	9.4	319 mμ	---- mμ
m-Chloroaniline	10.5	325	----
o-Chloroaniline	11.4	324	320
p-Chloroaniline	10.0	333	327
p-Chloro-N,N-diethylaniline	9.5*	----	342
2-Chloropyridine	13.3	----	294**
8-Chloroquinoline	11.2	----	380**
2,4-Dichloroaniline	12.2	----	335
2,5-Dichloroaniline	12.8	----	328
N,N-Diethylaniline	7.5	337	----
N,N-Dimethylaniline	8.9	334	----
N,N-Dimethyl-m-nitroaniline	11.0*	----	518
N,N-Dimethyl-p-nitroaniline	12.5*	----	485
2-Methyl-5-nitroaniline	12.0*	----	470
4-Methyl-2-nitroaniline	13.5*	----	520
m-Nitroaniline	11.5	----	464
p-Nitroaniline	13.0	----	448
5-Nitro-1-napthylamine	11.2	555	555

1. Five centimeter path length

* Estimated values

** Absorbance increases during titration

III. INDICATOR STUDIES IN SOLVENTS OF LOW DIELECTRIC CONSTANT

A. INTRODUCTION

An inspection of the literature dealing with acid-base reactions in low-dielectric media makes it clear that the thinking of many chemists still is hampered by attempts to apply principles of aqueous chemistry to these completely different systems. Although it is now generally agreed that extensive ion association occurs in solvents of low dielectric constant, relatively few investigators seem to realize that this necessitates a drastic revision of theories which were established for high-dielectric media. For example, many chemists still believe that a basic indicator, which is partly protonated when dissolved in glacial acetic acid, can be converted completely into its basic form by adding a strong base, such as sodium acetate. This would be true in water, but in acetic acid the common-ion effect can only suppress the dissociation of the indicator acetate into free ions while the concentration of the ion-pair form cannot be decreased (46). Another source of confusion has been the shape of potentiometric titration curves in low-dielectric media. Here, again, many workers have tried to apply the concepts of "strong" and "weak" electrolytes from aqueous chemistry without realizing their inadequacy in solvents where extensive ion association occurs.

For the solvent glacial acetic acid such problems as those mentioned above have been largely solved by the brilliant studies of Kolthoff and Bruckenstein (46,8,9,47,10). These authors combined spectrophotometry and potentiometry and thereby succeeded in developing quantitative expressions for acid-base equilibria in this medium. Since it appeared that the methods employed in the spectrophotometric part of their investigation might be applicable in non-acidic solvents of low dielectric constant a study was undertaken to explore this possibility. In the following, the pertinent parts of the Kolthoff-Bruckenstein theory will be described and discussed and some attempted applications to acid-base systems in low-dielectric media will be reported.

B. THE SPECTROPHOTOMETRIC METHOD OF KOLTHOFF AND BRUCKENSTEIN

1. Derivation of an Expression for the Reaction of a Weak Acid With a Weak Indicator Base

For the reaction of a weak indicator base, I , with a relatively weak acid, HX, Kolthoff and Bruckenstein (46) derived an expression which appears generally useful. The indicator base is assumed to be so weak that it is not significantly protonated by the solvent, and the acid is assumed to exist mainly in its unionized, i.e. molecular, form. The last assumption is justified for acids as strong as hydrogen chloride and p-toluenesulfonic acid in glacial acetic acid.

The reaction between the indicator and the acid can be written as follows:

$$I + HX \rightleftharpoons IH^+X^- \rightleftharpoons IH^+ + X^- \qquad (1)$$

The first step in this reaction, the formation of the ion-pair form of the indicator salt, is governed by the ionization (formation) constant

$$K_i^{IHX} = \frac{[IH^+X^-]}{[I][HX]} \qquad (2)$$

while the dissociation of the ion-pair depends on the dissociation constant $$K_d^{IHX} = \frac{[IH^+][X^-]}{[IH^+X^-]} \qquad (3)$$

The experiments of Kolthoff and Bruckenstein indicate that the different protonated forms of the indicator base, IH^+X^- and IH^+, both have the same absorption spectrum and molar absorptivity. Hence, if the sum of the two acidic forms, denoted $\Sigma\,[IH^+]$, can be measured spectrophotometrically, the concentration of the free indicator base, $[I]$, can be obtained by subtracting $\Sigma\,[IH^+]$ from the total concentration of indicator added. On the other hand, the total concentration of acid added is equal to $\Sigma[IH^+] + C_{HX}$ where C_{HX} is given by the expression

$$C_{HX} = [HX] + [H^+X^-] + [H^+] \qquad (4)$$

The concentrations of ionized and dissociated acid, $[H^+X^-]$ and $[H^+]$, respectively, are assumed to be negligibly small compared to $[HX]$ and hence

$$C_{HX} \approx [HX]\ . \qquad (5)$$

Under these conditions, the over-all dissociation constant of the acid, defined as

$$K_{HX} = \frac{[H^+]\,[X^-]}{[HX] + [H^+X^-]} \qquad (6)$$

simplifies to

$$K_{HX} = \frac{[H^+]\,[X^-]}{[HX]} \qquad (7)$$

The experimentally measurable ratio of acidic to basic form of the indicator can be expressed as follows:

$$\frac{\Sigma\,[IH^+]}{[I]} = \frac{[IH^+] + [IH^+X^-]}{[I]} = \frac{[IH^+X^-]}{[I]}\left[1 + \frac{[IH^+]}{[IH^+X^-]}\right]. \qquad (8)$$

Substitution of K_i^{IHX} and K_d^{IHX} into equation 8 gives

$$\frac{\Sigma[IH^+]}{[I]} = K_i^{IHX}\,[HX]\left[1 + \frac{K_d^{IHX}}{[X^-]}\right] \qquad (9)$$

An expression for $[X^-]$ is obtained from the rule of electroneutrality which yields

$$[X^-] = [H^+] + [IH^+] \qquad (10)$$

in acid solution where the concentration of acetate ions can be neglected. Equation 10 can be transformed into

$$[X^-] = \sqrt{K_{HX}\,[HX] + K_d^{IHX}\,[IH^+X^-]} \qquad (11)$$

and further to

$$[X^-] = \sqrt{[HX]} \times \sqrt{K_{HX} + K_d^{IHX}\,K_i^{IHX}\,[I]} \qquad (12)$$

When the expression for $[X^-]$ given by equation 12 is substituted into equation 9 and both sides of the equation are divided by $\sqrt{[HX]}$ we obtain

$$\frac{\Sigma[IH^+]}{[I]\sqrt{C_{HX}}} = K_i^{IHX}\sqrt{C_{HX}} + \frac{K_i^{IHX}\,K_d^{IHX}}{\sqrt{K_{HX} + K_i^{IHX}\,K_d^{IHX}\,[I]}} \qquad (13)$$

in which $[HX]$ is replaced by C_{HX}, since C_{HX} is approximately equal to $[HX]$ for a weak acid (equation 5).

Equation 13 contains only known or experimentally measurable concentrations and it can therefore be used for evaluation of the different equilibrium constants which govern the reaction of HX with I.

It should be pointed out that the derivation of Kolthoff and Bruckenstein assumes that concentrations are equal to activities. This appears to be a fairly good assumption since the indicator studies are performed in very dilute solutions.

2. Experimental Technique

Kolthoff and Bruckenstein invented a clever experimental design which greatly facilitates the use of equation 13. It consists of adding varying amounts of indicator to solutions containing fixed concentrations of HX (the concentration of the acid is much greater than that of the indicator) and determining the concentrations of the acidic and basic forms of the indicator after each addition. An interpolation plot of $\sum [IH^+]$ versus $[I]$ is then constructed, in which each fixed acid concentration gives a separate curve. From this graph one can interpolate values of $\sum [IH^+]$ corresponding to chosen values of $[I]$. This is very useful since an inspection of equation 13 reveals that the last term becomes a constant if $[I]$ can be hald constant. For a given value of $[I]$ equation 13 can be represented by a straight line $y = mx + b$ where

$$y = \frac{\sum [IH^+]}{[I]\sqrt{C_{HX}}} \quad , \quad x = \sqrt{C_{HX}} \, , \quad m = K_i^{IHX}$$ and the intercept

$$b = \frac{K_i^{IHX} \, K_d^{IHX}}{\sqrt{K_{HX} + K_i^{IHX} \, K_d^{IHX} \, [I]}} \quad .$$ If several different constant values of $[I]$ are chosen, each value should give a straight line whose intercept with the y-axis depends on the magnitude of $[I]$. All the lines should have the same slope, given by K_i^{IHX}, and

hence a family of parallel straight lines should be obtained.

It is possible to determine K_{HX} and K_d^{IHX} from the intercepts b of the different straight lines by writing

$$b^2 = \frac{[K_i^{IHX} K_d^{IHX}]^2}{K_{HX} + K_i^{IHX} K_d^{IHX} [I]} \qquad (14)$$

or

$$[I]b^2 = K_i^{IHX} K_d^{IHX} - \frac{K_{HX}}{K_i^{IHX} K_d^{IHX}} b^2 \qquad (15)$$

Equation 15 shows that a plot of $[I]b^2$ versus b^2 should yield a straight line with a slope equal to $- \frac{K_{HX}}{K_i^{IHX} K_d^{IHX}}$ and an intercept given by $K_i^{IHX} K_d^{IHX}$. Since K_i^{IHX} is known from the plot of equation 13 the values of K_d^{IHX} and K_{HX} can be calculated from the plot of $[I]b^2$ versus b^2.

3. Limitations of Equation 13

Inspection of equation 13 reveals that it has some obvious limitations which were not discussed by Kolthoff and Bruckenstein. The square root in the last term is the sum of two terms, and it is instructive to study the effect of changes in the relative magnitudes of these two terms.

a. $K_{HX} \gg K_i^{IHX} K_d^{IHX} [I]$:

In this case the latter term can be neglected and equation 13 takes the form

$$\frac{\Sigma\,[IH^+]}{[I]\sqrt{C_{HX}}} = K_i^{IHX}\sqrt{C_{HX}} + \frac{K_i^{IHX}\,K_d^{IHX}}{\sqrt{K_{HX}}} \qquad (16)$$

Only one straight line is obtained for different constant values of [I] since the intercept no longer depends on [I]. Hence the values of K_d^{IHX} and K_{HX} cannot be obtained in this situation.

b. $K_{HX} \ll K_i^{IHX}\,K_d^{IHX}\,[I]$:

If K_{HX} is much smaller than the second term under the square root it can be neglected and equation 13 takes the form

$$\frac{\Sigma\,[IH^+]}{[I]\sqrt{C_{HX}}} = K_i^{IHX}\sqrt{C_{HX}} + \sqrt{\frac{K_i^{IHX}\,K_d^{IHX}}{[I]}} \qquad (17)$$

Different straight lines are obtained in plotting equation 13 in this situation, but it is seen that the plot of $[I]b^2$ versus b^2 gives a constant value equal to $K_i^{IHX}\,K_d^{IHX}$, independent of b^2. In this case the ionization and dissociation constants of the indicator salt can be determined, but the dissociation constant of the acid can obviously not be evaluated.

c. $K_{HX} \approx K_i^{IHX}\,K_d^{IHX}\,[I]$:

From the above considerations it is clear that all the three constants in equation 13 can be evaluated only if the two terms under the square root are of comparable magnitude. This rather obvious restriction makes the combination of acid and indicator quite critical, as will be shown later by some attempted applications of the method.

4. Complications Due to Higher Ionic Aggregates

The above treatment assumes that the ions occur only as free or in the form of ion-pairs. Actually, Kolthoff and Bruckenstein found that higher ionic aggregates are formed in glacial acetic acid as the ionic strength is increased. Such association reactions remove some of the simple ion-pair form of the indicator salt, thereby shifting the equilibrium toward increased protonation. Complications of this type would preclude the use of equation 13 since this expression does not consider higher ionic aggregates. On the other hand, expansion of the theory is complicated by the fact that the exact nature of the polyionic species is unknown. Probably a number of different species, such as triple and quadruple ions, are involved. Hence, a multitude of equilibria must be considered and the evaluation of the various constants becomes difficult or impossible.

Kolthoff and Bruckenstein were able to avoid the problem of higher ionic aggregates by working at such low indicator concentrations ($< 10^{-5}$ M) that no significant formation of polyionic species occurred. However, Bruckenstein (7) pointed out that complications due to such aggregates may be expected at still lower concentrations in solvents of lower dielectric constant than that of acetic acid (6.15). This prediction is verified by the experiments presented in the following.

C. APPLICATIONS OF THE KOLTHOFF-BRUCKENSTEIN METHOD TO ACID-BASE SYSTEMS IN LOW-DIELECTRIC MEDIA

1. Apparatus

The equipment employed in the present study was similar to that used by Kolthoff and Bruckenstein (46). The spectrophotometric measurements were performed with the Beckman Models B or DU, using cylindrical silica cells with a light-path of 5.00 or 10.00 cm. For addition of indicator solutions to the cells a 0.1-ml. Gilmont ultramicroburet was used.

2. Solvents and Chemicals

a. Solvents:

The glacial acetic acid used in repeating one of the experiments of Kolthoff and Bruckenstein (46) was purified according to a method developed by Keily (43). The method involves reaction of moisture-containing acetic acid with the calculated amount of acetic anhydride, in the presence of some sulfuric acid catalyst, and subsequent distillation of the anhydrous solvent through a two-foot Vigreaux column. Glacial acetic acid prepared using this method contained less than 0.002% water, as determined by Karl Fischer titration. In order to duplicate the conditions of Kolthoff and Bruckenstein as closely as possible the water content of the solvent used in the experiment was adjusted to about 0.03% by addition of reagent grade acetic acid with a water content of 0.2%.

Dry benzene was prepared by fractional distillation of Mallinckrodt Analytical Reagent material from phosphorus pentoxide. Chlorobenzene and o-dichlorobenzene were Eastman White Label products. The latter solvent was purified by fractional distillation when used for preparation of solutions containing hydrogen chloride. Otherwise both solvents were used without further purification. The acetonitrile was a Carbide and Carbon Chemicals product dried over Molecular Sieves (Linde Air Products).

b. Acids :

The p-toluenesulfonic acid was an Eastman White Label product which assayed 99.90% as monohydrate. The water of crystallization was not removed since Kolthoff and Bruckenstein (47) found that it had no detrimental effect on the experiment.

Hydrogen chloride solutions were prepared from the gaseous material of The Matheson Co., East Rutherford, N.J.

Anhydrous diphenyl phosphate was prepared from the dihydrate (Dow Chemical Company) according to a method of Davis and Hetzer (18). The dihydrate, containing a pink impurity, was heated to boiling for a short period in a 4:1 mixture of cyclohexane and benzene. When an excess of diphenyl phosphate was added, most of the pink impurity remained adsorbed on the undissolved material while the nearly colorless supernatant could be decanted. The solution was then digested with charcoal and filtered. More cyclohexane was added to the solution which was cooled and seeded with a few crystals of the impure diphenyl phosphate. The white crystals obtained assayed 99.82% anhydrous diphenyl phosphate when titrated with sodium hydroxide in a water-ethanol mixture.

c. Indicator Bases :

p-Naphtholbenzein, Ethyl Red, and 8-quinolinol were Eastman White Label products. 4-Dimethylamino-4'-nitrostilbene was synthesized from p-dimethylaminobenzaldehyde and p-nitrophenylacetic acid according to the method of Pfeiffer (59) and recrystallized from benzene.

3. Reaction of p-Naphtholbenzein with p-Toluenesulfonic Acid in Glacial Acetic Acid

Kolthoff and Bruckenstein (46) applied equation 13 to the reactions of the weak indicator base p-naphtholbenzein (hereafter denoted PNB) with p-toluenesulfonic acid (HTs) and hydrogen chloride in glacial acetic acid. It was felt desirable to repeat one of these experiments in order to test the method under conditions where it was known to be applicable. p-Toluenesulfonic acid was selected for the test experiment.

The acidic and basic absorption spectra of PNB (Figure 43 in the Appendix) were found to be in substantial agreement with those reported by Kolthoff and Bruckenstein (46). However, the long-wavelength acidic peak was found to occur at 615 $m\mu$ instead of 625 $m\mu$ and its molar absorptivity was 3.08×10^4 liters/mole cm. rather than 2.86×10^4 liters/mole cm. as reported by Kolthoff and Bruckenstein. These authors point out that Smith and Elliot (64) obtained the quite different values 640 $m\mu$ and 1.06×10^4, respectively, for the same compound. Since Eastman White Label products were used in all cases it appears that the purity of this material has improved during recent years. Clearly, the purity of the indicator used in the present study cannot be guaranteed in view of these findings but the fact that it gave a higher molar absorptivity than those measured by previous investigators seems to indicate that it was purer than earlier available products.

In the experiment PNB was added as a 1.97×10^{-3} $\underline{M}$ solution to a 5-cm. cell containing 14.0 ml of a p-toluenesulfonic acid solution. Five different concentrations of p-toluenesulfonic acid were chosen, ranging from 2.16×10^{-4} $\underline{M}$ to 3.02×10^{-3} $\underline{M}$. The indicator was added with a 0.1000 ml. Gilmont ultramicroburet and absorbance measurements at the acidic peak (615 mμ) were made on the Beckman B spectrophotometer at indicator additions of 0.0100, 0.0200, 0.0400, 0.0600 and 0.0800 ml. The results are summarized in Table XI which shows the concentration of protonated indicator, $\Sigma\,[IH^+]$, in p-toluenesulfonic acid solutions of different concentrations as a function of the total amount of PNB added. The concentration of unprotonated indicator, $[I]$, is obtained by subtracting $\Sigma\,[IH^+]$ from the total PNB concentration. Figure 26 shows a plot of $\Sigma\,[IH^+]$ versus $[I]$ at the different acid concentrations. The concentration of p-toluenesulfonic acid is so much greater than the indicator concentration that the acid consumed by protonation of the indicator can be neglected. Interpolation in Figure 26 gives the concentrations $\Sigma\,[IH^+]$ corresponding to the chosen $[I]$ values of 2.00, 3.00, 4.00, 5.00 and 6.00 x 10^{-6} $\underline{M}$ as shown in Table XII. Using these data a plot of $\dfrac{\Sigma\,[IH^+]}{[I]\sqrt{C_{HTs}}}$ versus $\sqrt{C_{HTs}}$, according to equation 13 , is constructed (Figure 27). It is seen that a family of parallel straight lines is indeed obtained. The slopes (equal to K_i^{IHX}) and intercepts (b) of these lines are given in Table XIII. From these data it is possible to construct a plot of $[I]b^2$ versus b^2, as shown in Figure 28. The straight line drawn through the points in Figure 28 has a slope of -7.10×10^{-6} and an intercept of 1.07×10^{-3} . By combining these data with the average value 368 for K_i^{IHX} (Table XIII) K_{HX} and K_d^{IHX} can be calculated. In Table XIV the results are compared with those

TABLE XI

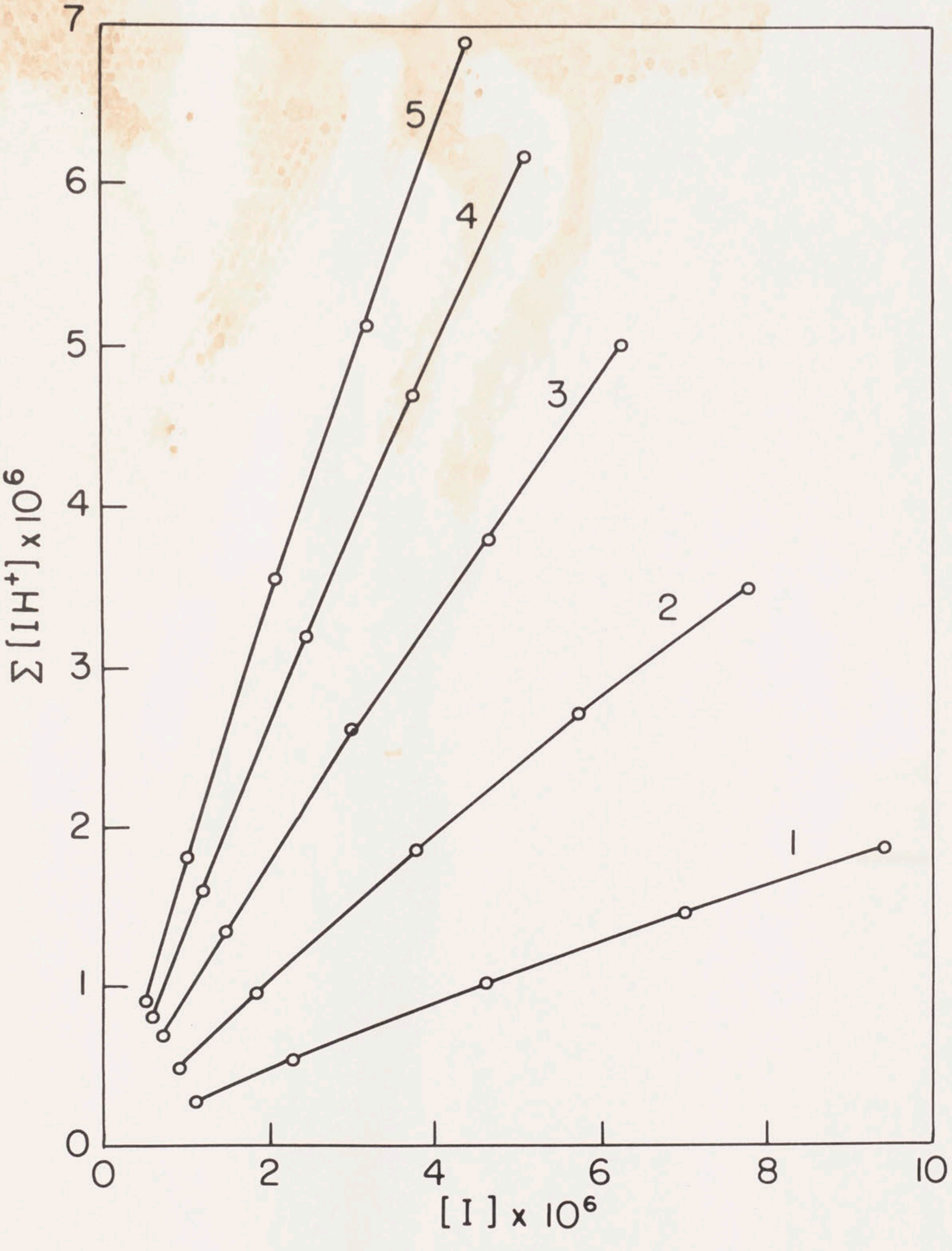
REACTION OF p-TOLUENESULFONIC ACID WITH p-NAPHTHOLBENZEIN IN GLACIAL ACETIC ACID

Total Concentration of PNB	$\sum[IH^+] \times 10^6$ at HTs Molarities of				
$\underline{M} \times 10^6$	2.16×10^{-4}	6.47×10^{-4}	1.29×10^{-3}	2.16×10^{-3}	3.02×10^{-3}
1.41	0.279	0.493	0.694	0.811	0.901
2.81	0.538	0.960	1.34	1.61	1.80
5.63	1.01	1.86	2.61	3.18	3.55
8.44	1.45	2.71	3.79	4.70	5.25
11.26	1.86	3.49	5.01	6.19	6.89

Figure 26

Interpolation Plot for the Reaction of p-Naphtholbenzein with p-Toluenesulfonic Acid in Glacial Acetic Acid

1. 2.16×10^{-4} M p-Toluenesulfonic Acid
2. 6.47×10^{-4} M "
3. 1.29×10^{-3} M "
4. 2.16×10^{-3} M "
5. 3.02×10^{-3} M "



Σ [IH⁺] x 10⁶
[I] x 10⁶
0
1
2
3
4
5
6
7
0
2
4
6
8
10
5
4
3
2
1

TABLE XII

INTERPOLATED VALUES OF $\sum[IH^+]$ IN p-TOLUENESULFONIC ACID SOLUTIONS IN GLACIAL ACETIC ACID

Concentration of Acid	$\sum[IH^+] \times 10^6$ at $[I] \times 10^6$ Equal to				
$\underline{M} \times 10^3$	2.00	3.00	4.00	5.00	6.00
0.216	0.475	0.680	0.890	1.08	1.27
0.647	1.025	1.48	1.95	2.38	2.80
1.29	1.75	2.55	3.32	4.07	4.82
2.16	2.60	3.83	4.98	6.10	-
3.02	3.38	4.87	6.32	-	-

Figure 27

Plot of Equation 13 for the Reaction of p-Naphtholbenzein with p-Toluenesulfonic Acid in Glacial Acetic Acid

—○—○— $[I] = 2.00 \times 10^{-6}$

—△—△— $[I] = 3.00 \times 10^{-6}$

—□—□— $[I] = 4.00 \times 10^{-6}$

—▲—▲— $[I] = 5.00 \times 10^{-6}$

—■—■— $[I] = 6.00 \times 10^{-6}$

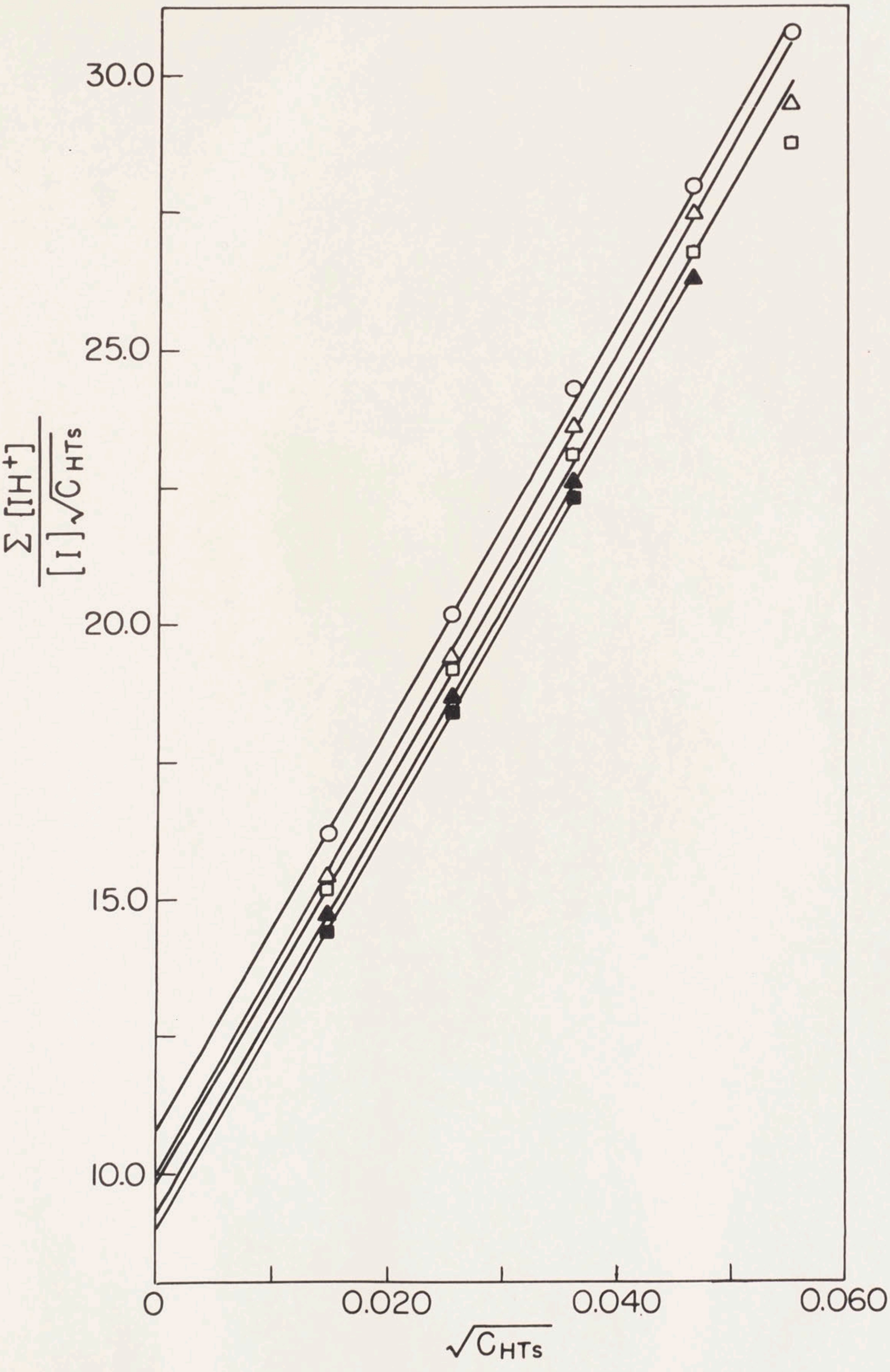

30.0
25.0
20.0
15.0
10.0
0
0.020
0.040
0.060
$\frac{\Sigma\,[IH^+]}{[I]\sqrt{C_{HTs}}}$
$\sqrt{C_{HTs}}$

TABLE XIII

SLOPES AND INTERCEPTS OF THE LINES IN FIGURE 27

[I] M x 10^6	Slope ($=K_i^{IHX}$)	Intercept (=b)
2.00	369	10.8
3.00	375	10.0
4.00	362	9.8
5.00	367	9.3
6.00	369	9.0

Figure 28

Plot of $[I]b^2$ versus b^2 for the Reaction of p-Naphtholbenzein with p-Toluenesulfonic Acid in Glacial Acetic Acid

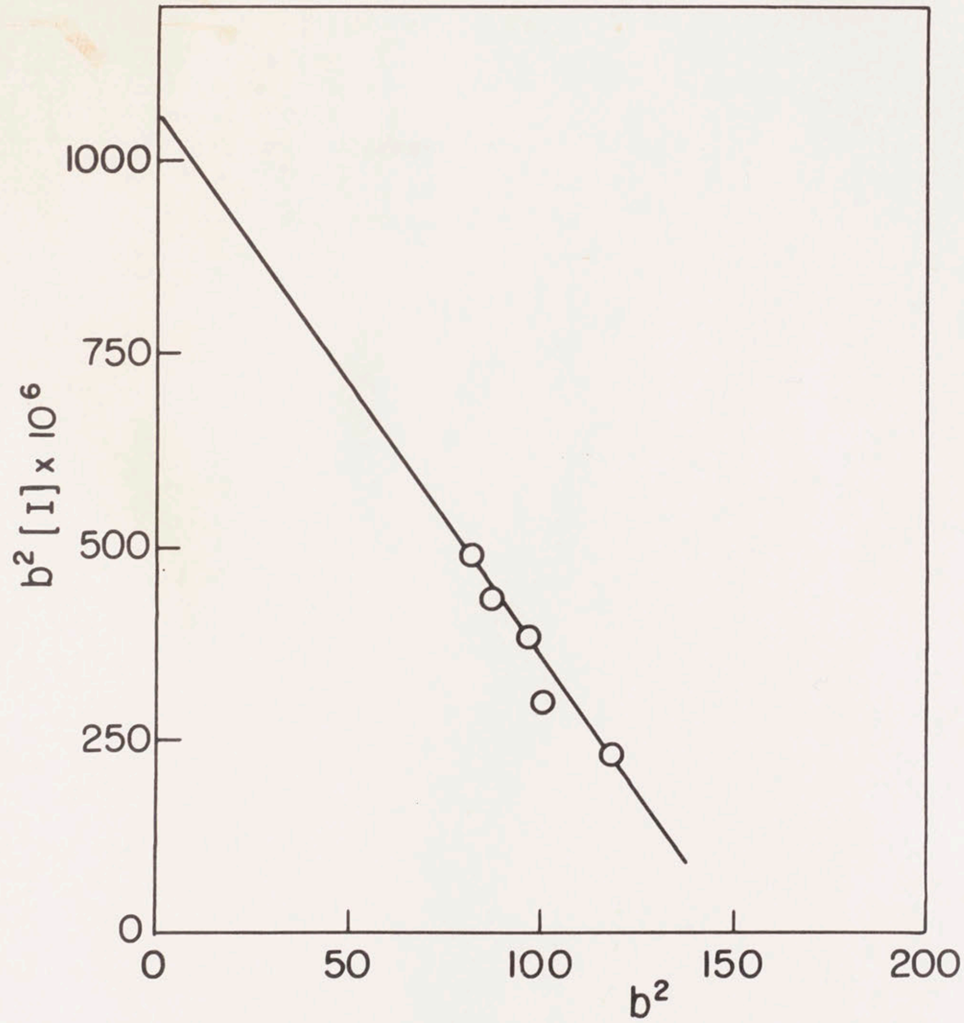

1000
750
500
250
0
$b^2 [I] \times 10^6$
0
50
100
150
200
b^2

TABLE XIV

EQUILIBRIUM CONSTANTS DERIVED FOR THE REACTION OF p-TOLUENESULFONIC ACID WITH p-NAPHTHOLBENZEIN IN GLACIAL ACETIC ACID

Constant	Value Obtained in This Study	Value Obtained by Kolthoff and Bruckenstein
K_{HX}	7.6×10^{-9}	7.3×10^{-9}
K_i^{IHX}	3.7×10^{2}	3.7×10^{2}
K_d^{IHX}	2.9×10^{-6}	4.0×10^{-6}

obtained by Kolthoff and Bruckenstein (46) on the same system. The good agreement indicates that reliable and reproducible results can be obtained in cases where the Kolthoff-Bruckenstein method is applicable.

4. Reaction of 8-Quinolinol With Diphenyl Phosphate in Non-Acidic Solvents

a. Reaction in Chlorobenzene:

After the success in repeating one of Kolthoff's and Bruckenstein's experiments in glacial acetic acid it was decided to test the method in a non-acidic solvent of similar dielectric constant. Chlorobenzene, having a dielectric constant of 5.62 as compared to 6.15 for acetic acid, appeared to be a suitable solvent.

p-Toluenesulfonic acid is very insoluble in aromatic hydrocarbons and could therefore not be studied in chlorobenzene. An acid which is well suited for studies in low-dielectric media is diphenyl phosphate (DPP), a compound which recently has been investigated by Davis and Hetzer (18). It is very soluble in aromatic hydrocarbons and it also forms soluble salts in these solvents. Furthermore, it can be obtained in an anhydrous, easily weighable form. In water, it titrates as a strong acid but Davis and Hetzer (18) found it to be relatively weak in low-dielectric solvents.

The next problem was to find an indicator base suitable for reaction with diphenyl phosphate. p-Naphtholbenzein was found to be too weakly basic in this system. Other indicators, such as p-dimethylaminoazobenzene, were apparently rapidly oxidized and could therefore not be used. In general, it is very difficult to find a strongly basic indicator which at the same time has a high molar absorptivity. The latter property is highly desirable since it makes it possible to use very dilute indicator solutions, thereby avoiding the complications due to formation of polyionic species.

No ideal indicator was found but 8-quinolinol appeared promising in spite of its relatively low molar absorptivity. This compound is quite soluble in low-dielectric media and gives stable and easily distinguishable absorption spectra in its protonated and unprotonated forms. Figure 44 shows its acidic and "neutral" absorption spectra in o-dichlorobenzene. The corresponding spectra in chlorobenzene were quite similar, the broad acidic peak at 380 mμ having a molar absorptivity of 1505 liters/mole cm. as compared to 1467 liters/mole cm. in o-dichlorobenzene. This peak was used for measurement of the concentration of the acidic form of 8-quinolinol, employing the Beckman spectrophotometer Model DU.

The reaction between 8-quinolinol and diphenyl phosphate in chlorobenzene was studied employing the same technique which was used for the system of p-naphtholbenzein and p-toluenesulfonic acid in glacial acetic acid. Because of the low molar absorptivity of 8-quinolinol the indicator concentration was kept as high as 1.56×10^{-5} to 1.25×10^{-4} molar, i.e. about ten times higher than in the previous experiment. The concentration of diphenyl phosphate was varied between 8.64×10^{-5} and 8.64×10^{-4} M. Hence the excess acid was not as large as in the previous case and corrections had to be made for the amount of acid consumed by the indicator.

When the interpolated data were plotted according to equation 13 the lines obtained were not straight but showed a distinct curvature (Figure 29) which made it impossible to obtain reliable

Figure 29

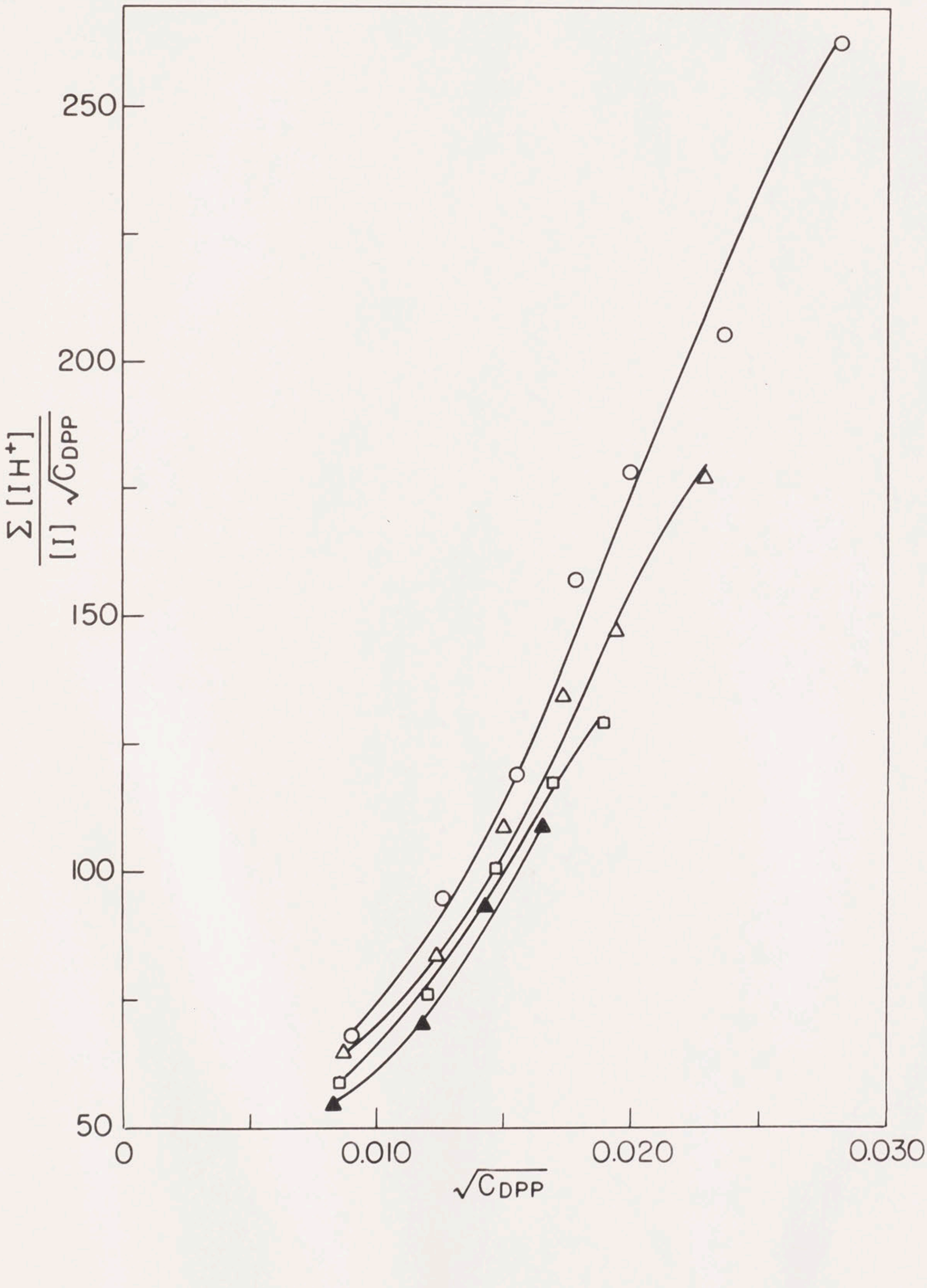
Plot of Equation 13 for the Reaction of 8-Quinolinol with Diphenyl Phosphate in Chlorobenzene

—○—○— $[I] = 1.00 \times 10^{-5}$

—△—△— $[I] = 2.00 \times 10^{-5}$

—□—□— $[I] = 3.00 \times 10^{-5}$

—▲—▲— $[I] = 4.00 \times 10^{-5}$


250
200
150
100
50
$\frac{\Sigma [IH^+]}{[I] \sqrt{C_{DPP}}}$
0
0.010
0.020
0.030
$\sqrt{C_{DPP}}$

intercepts with the y-axis. The curvature indicates that the ratio of acidic to basic form of the indicator increases too rapidly with increasing acid concentration. It appears likely that this phenomenon is due to formation of higher ionic aggregates, since this would lead to an exponential increase in protonation according to the general reaction $I + HX \rightleftarrows IH^+X^- \rightleftarrows [IH^+X^-]_n$.

b. Reaction in o-Dichlorobenzene:

The previous experiment indicated that the dielectric constant of chlorobenzene is too low to permit a study of the reaction between 8-quinolinol and diphenyl phosphate using the Kolthoff-Bruckenstein method. It was therefore decided to try o-dichlorobenzene which has a dielectric constant of 9.93 as compared to 5.62 for chlorobenzene. It has already been mentioned that the molar absorptivity of protonated 8-quinolinol in o-dichlorobenzene was found to be 1,467 liters/mole cm. at 380 mμ.

Figure 30 shows the plot of equation 13 for the reaction of 8-quinolinol with diphenyl phosphate in o-dichlorobenzene. The lines are still curved, indicating that equation 13 is not applicable under the conditions of the experiment. It is interesting to note that the lines are more widely separated and tend toward higher intercepts than was the case in chlorobenzene. This difference will be discussed later.

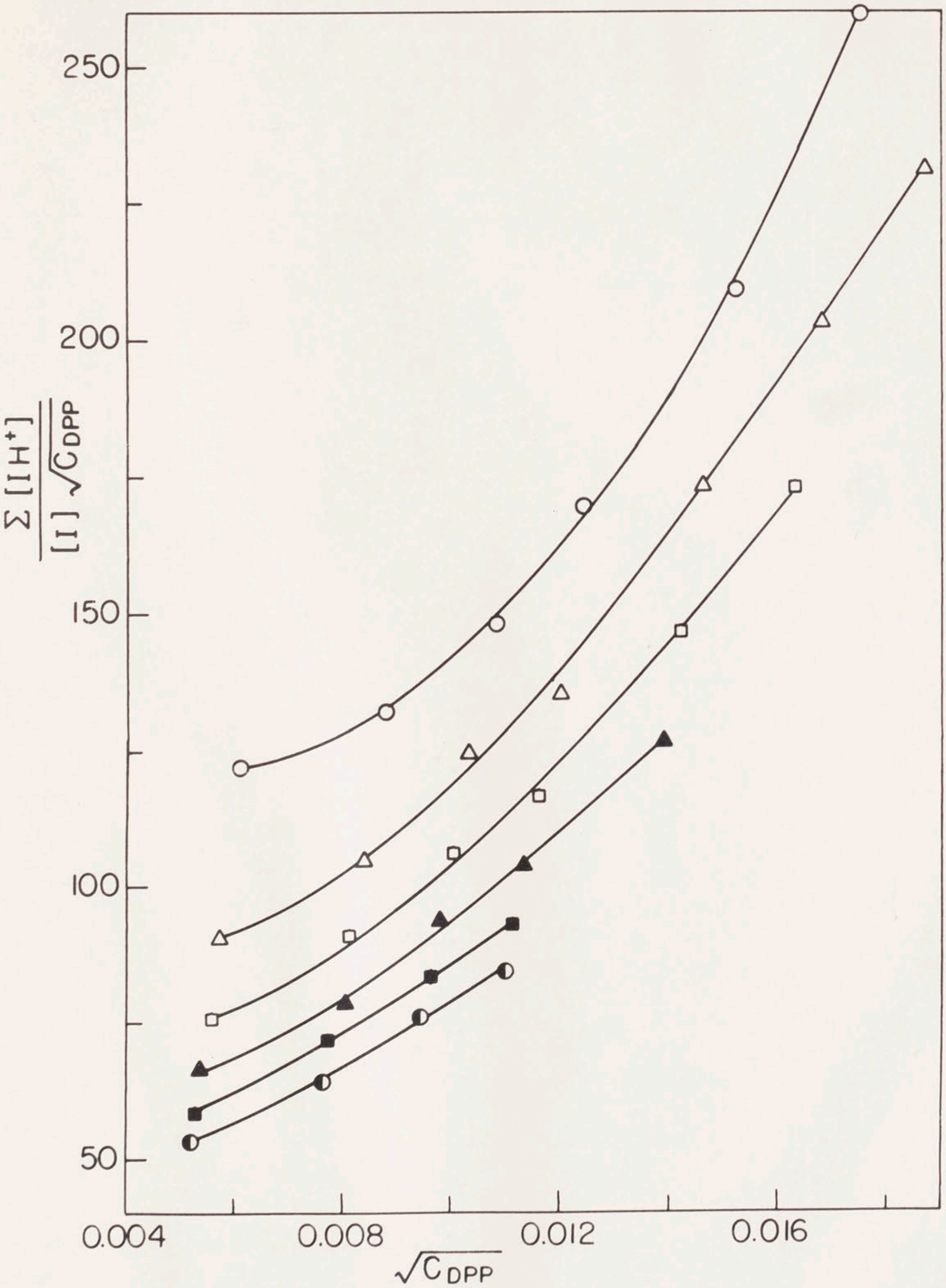
c. Reaction in a 1:4 Mixture of Acetonitrile and o-Dichlorobenzene:

A last attempt to study the 8-quinolinol-diphenyl phosphate system was made in a solvent mixture containing twenty percent acetonitrile (D=37.5) and eighty per cent o-dichlorobenzene (D=9.93)

Figure 30

Plot of Equation 13 for the Reaction of
8-Quinolinol with Diphenyl Phosphate in
o-Dichlorobenzene

—○—○— $[I] = 1.00 \times 10^{-5}$
—△—△— $[I] = 2.00 \times 10^{-5}$
—□—□— $[I] = 3.00 \times 10^{-5}$
—▲—▲— $[I] = 4.00 \times 10^{-5}$
—■—■— $[I] = 5.00 \times 10^{-5}$
—◐—◐— $[I] = 6.00 \times 10^{-5}$


250
200
150
100
50
$\frac{\Sigma [IH^+]}{[I] \sqrt{C_{DPP}}}$
0.004
0.008
0.012
0.016
$\sqrt{C_{DPP}}$

by volume. This mixed solvent should have a dielectric constant around 15 and it was therefore hoped that the tendency toward formation of higher ionic aggregates would be considerably deceased relative to pure o-dichlorobenzene. With the same objective in mind the 8-quinolinol concentration was decreased as far as possible by using 10-cm. cells instead of 5-cm. cells as in the previous experiments. The acidic peak of 8-quinolinol occurred at 375 mμ and had a molar absorptivity of 1555 liters/mole cm.

In spite of all efforts the plot of equation 13 still did not give a family of parallel straight lines (Figure 31). However, the curvature was decreased (note the different scales on the y-axis) and the lines were much more closely spaced than in the previous experiment. They also tended toward lower intercepts.

d. Qualitative Discussion of the Reaction of 8-Quinolinol With Diphenyl Phosphate in Different Solvents :

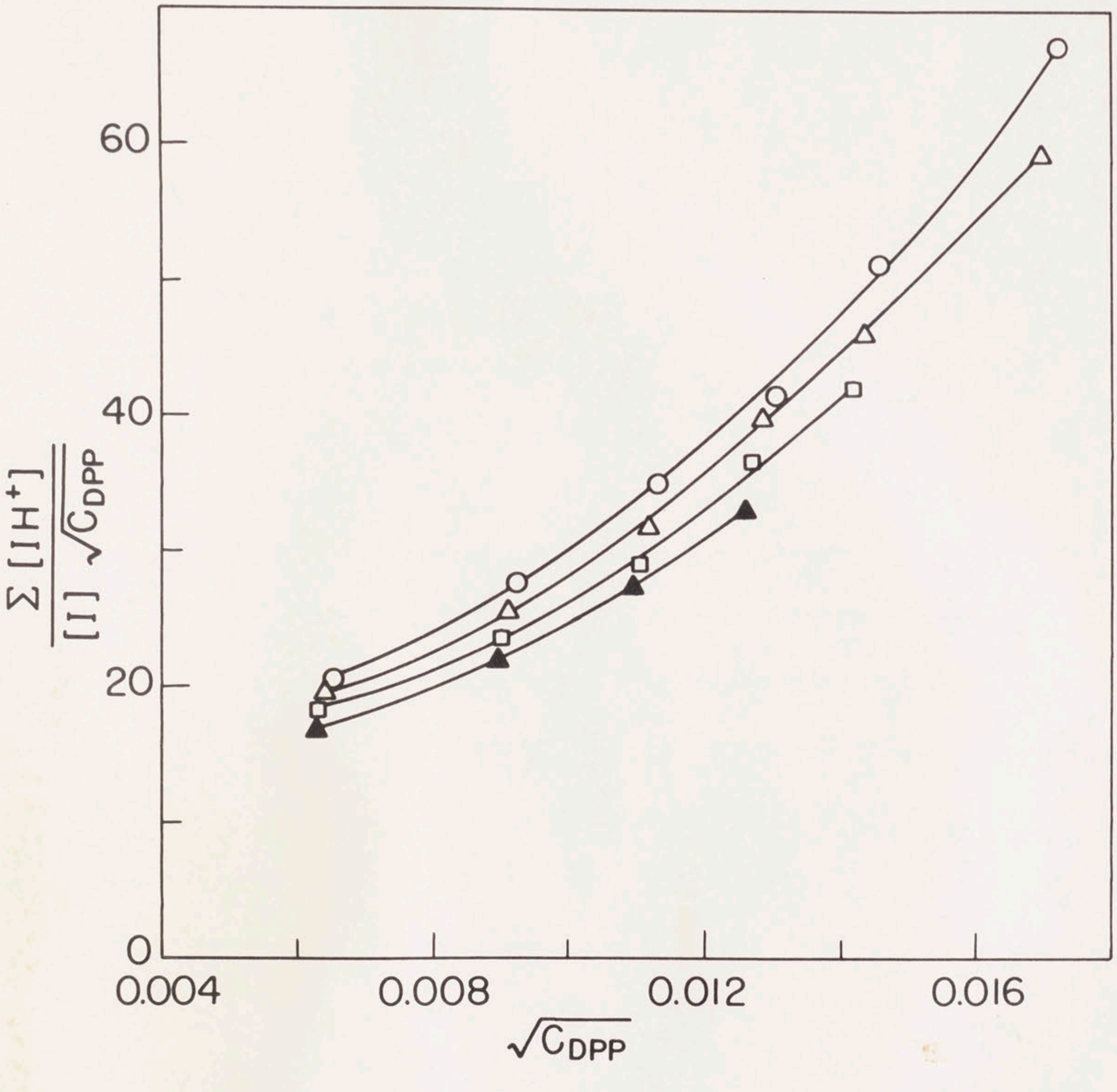
Although the nonlinearity of the plots according to equation 13 makes it impossible to evaluate equilibrium constants for the reaction of 8-quinolinol with diphenyl phosphate, some qualitative conclusions can be drawn from a comparison of the plots for different media.

It has already been pointed out that the spacing of the lines corresponding to different constant values of [I] becomes wider in going from chlorobenzene to o-dichlorobenzene and narrows again in going from o-dichlorobenzene to the mixed solvent containing acetonitrile. This undoubtedly reflects changes in the relative magnitudes of the two terms under the square root in the last term of equation 13. In section 3a it was shown that the lines fuse together when

Figure 31

Plot of Equation 13 for the Reaction of 8-Quinolinol with Diphenyl Phosphate in a 1:4 Mixture of Acetonitrile and o-Dichlorobenzene

—○—○— $[I] = 1.00 \times 10^{-5}$
—△—△— $[I] = 2.00 \times 10^{-5}$
—□—□— $[I] = 3.00 \times 10^{-5}$
—▲—▲— $[I] = 4.00 \times 10^{-5}$



$\frac{\Sigma [IH^+]}{[I]\sqrt{C_{DPP}}}$
0
20
40
60
0.004
0.008
0.012
0.016
$\sqrt{C_{DPP}}$

$K_{HX} \gg K_i^{IHX} K_d^{IHX} [I]$. Correspondingly, the maximum spacing is obtained when $K_{HX} \ll K_i^{IHX} K_d^{IHX} [I]$ (section 3b). It is clear that K_d^{IHX}, the dissociation constant of the ion-pair, should increase with increasing dielectric constant (51), thereby increasing the second term under the square root. If the minimum slopes of the lines in the plots of equation 13 are taken as rough estimates of K_i^{IHX}, one finds values of about 5,000, 6,000, and 2,000, respectively, in going from chlorobenzene to the solvent mixture. The formation constant of the ion-pair of the indicator salt is apparently relatively unaffected in going from chlorobenzene to o-dichlorobenzene. The dissociation constant of the salt, K_d^{IHX}, on the other hand, is incceased in going to a medium of higher dielectric constant. The dissociation constant of the acid is undoubtedly also affected by the increase in dielectric constant but it probably remains quite small due to the relatively nonbasic character of o-dichlorobenzene. Hence the product $K_i^{IHX} K_d^{IHX} [I]$ becomes much larger than K_{HX} in o-dichlorobenzene, and the lines are therefore widely spaced. Actually, this probably approaches a situation where K_{HX} can be neglected (section 3b).

It is interesting to note that K_i^{IHX} appears to decrease in going from o-dichlorobenzene to the mixed solvent (from 6,000 to 2,000). Also, the lines in the plot of equation 13 are very closely spaced for the o-dichlorobenzene-acetonitrile mixture, indicating that K_{HX} has increased in relative importance. This is undoubtedly due to a drastic increase in K_{HX} caused by the addition of the slightly basic solvent acetonitrile (for a discussion of the basic character of acetonitrile, see reference 22). The decrease in K_i^{IHX} can be interpreted in terms of competition from acetonitrile for the proton of diphenyl phosphate.

The magnitude of the intercepts b in the various plots of equation 13 determines the product $K_i^{IHX} K_d^{IHX}$ by affecting the product $[I]b^2$ (see equation 15). However, the spacing of the b values is also important, since it determines the slope of the line in the plot of $[I]b^2$ versus b^2, hence affecting the intercept.

The above discussion has implicitly assumed that the theory of Kolthoff and Bruckenstein would be applicable to the 8-quinolinol-diphenyl phosphate system, provided that it could be studied at such a low concentration level that the complications due to higher ionic aggregates would be eliminated. Although conditions were never found under which the theory would have been strictly applicable the nature of the deviations was such as to support this assumption. It could perhaps be argued that no polyionic species should be formed in the mixed solvent with a dielectric constant of about 15. However, Kraus (51) states that conductance data show the existence of polyionic structures in all solvents with dielectric constants less than about 15 or 20.

5. Reaction of 4-Dimethylamino-4'-nitrostilbene With Diphenyl Phosphate

Since the failure of 8-quinolinol as an indicator was attributed to its relatively low molar absorptivity which necessitated the use of comparatively high concentrations, new efforts were made to find an indicator base with more intense absorption. 4-Dimethylamino-4'-nitrostilbene, an indicator studied by Higuchi et al. (40), seemed to show promise, and it was decided to study its reaction with diphenyl phosphate in o-dichlorobenzene.

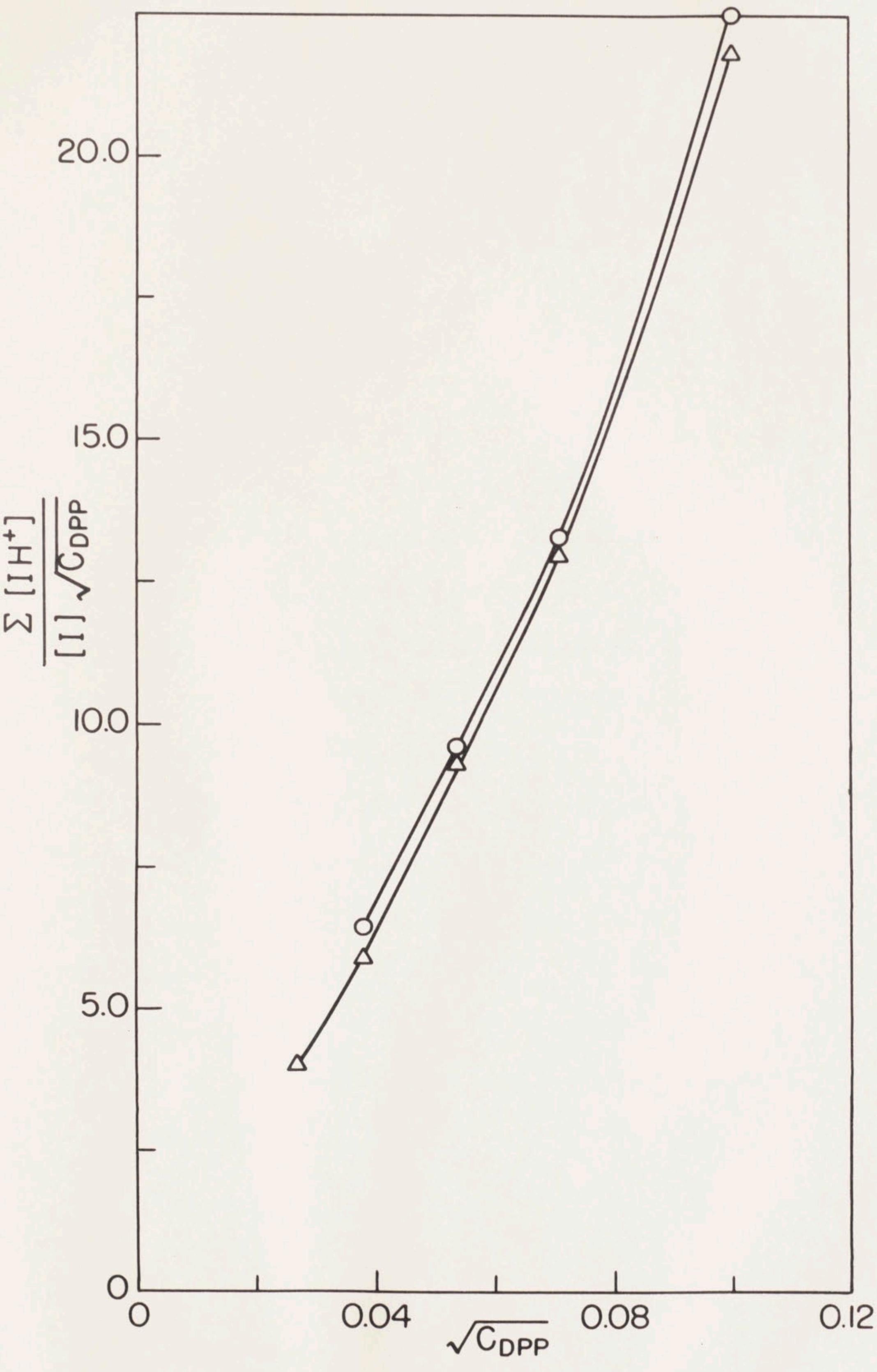
The acidic and basic absorption spectra of 4-dimethylamino-4'-nitrostilbene in benzene are shown in Figure 45 in the Appendix. In this solvent the basic peak occurs at 427.5 mμ and has a molar absorptivity of 2.888×10^4 liters/mole cm. The corresponding values for the basic form in o-dichlorobenzene are 445 mμ and 2.603×10^4 liters/mole cm. The absorbance at 445 mμ was measured on the Beckman Model B spectrophotometer to follow the reaction between 4-dimethylamino-4'-nitrostilbene and diphenyl phosphate in o-dichlorobenzene. Five-centimeter cells were used. The high molar absorptivity of 4-dimethylamino-4'-nitrostilbene made it possible to keep the indicator concentration below 9.94×10^{-6} M while the concentration of diphenyl phosphate ranged from 7.14×10^{-4} M to 1.00×10^{-2} M. The large excess of acid was necessitated by the relatively weak basicity of the indicator. It appears that the high concentration of diphenyl phosphate provided enough ions to cause formation of higher ionic aggregates in spite of the low indicator concentration, since the plot according to equation 13 shows some curvature (Figure 32). In this case the lines corresponding to different values of [I] are practically fused together, showing that $K_{HX} \gg K_i^{IHX} K_d^{IHX} [I]$ (section 3a). From the slope of the lines we estimate $K_i^{IHX} = 200$. This shows that 4-dimethylamino-4'-nitrostilbene is a much weaker base than 8-quinolinol, since the corresponding estimate for the reaction of the latter base with

Figure 32

Plot of Equation 13 for the Reaction of 4-Dimethylamino-4'-nitrostilbene and Diphenyl Phosphate in o-Dichlorobenzene

——○—○— [I] = 1.00×10^{-6}

——△—△— [I] = 2.00 to 6.00×10^{-6}
(all give the same curve)


20.0
15.0
10.0
5.0
0
0
0.04
0.08
0.12
$\sqrt{C_{DPP}}$
$\frac{\Sigma [IH^+]}{[I] \sqrt{C_{DPP}}}$

diphenyl phosphate in o-dichlorobenzene was 6,000. Obviously, an indicator base of intermediate strength would be needed for reaction with diphenyl phosphate.

6. Reaction of 4-Dimethylamino-4'-nitrostilbene With Hydrogen Chloride in o-Dichlorobenzene and Benzene

a. Reaction in o-Dichlorobenzene:

Since 4-dimethylamino-4'-nitrostilbene is a weak indicator base it was hoped that substitution of a stronger acid, such as hydrogen chloride, for diphenyl phosphate would give a system to which the Kolthoff-Bruckenstein method could be applied.

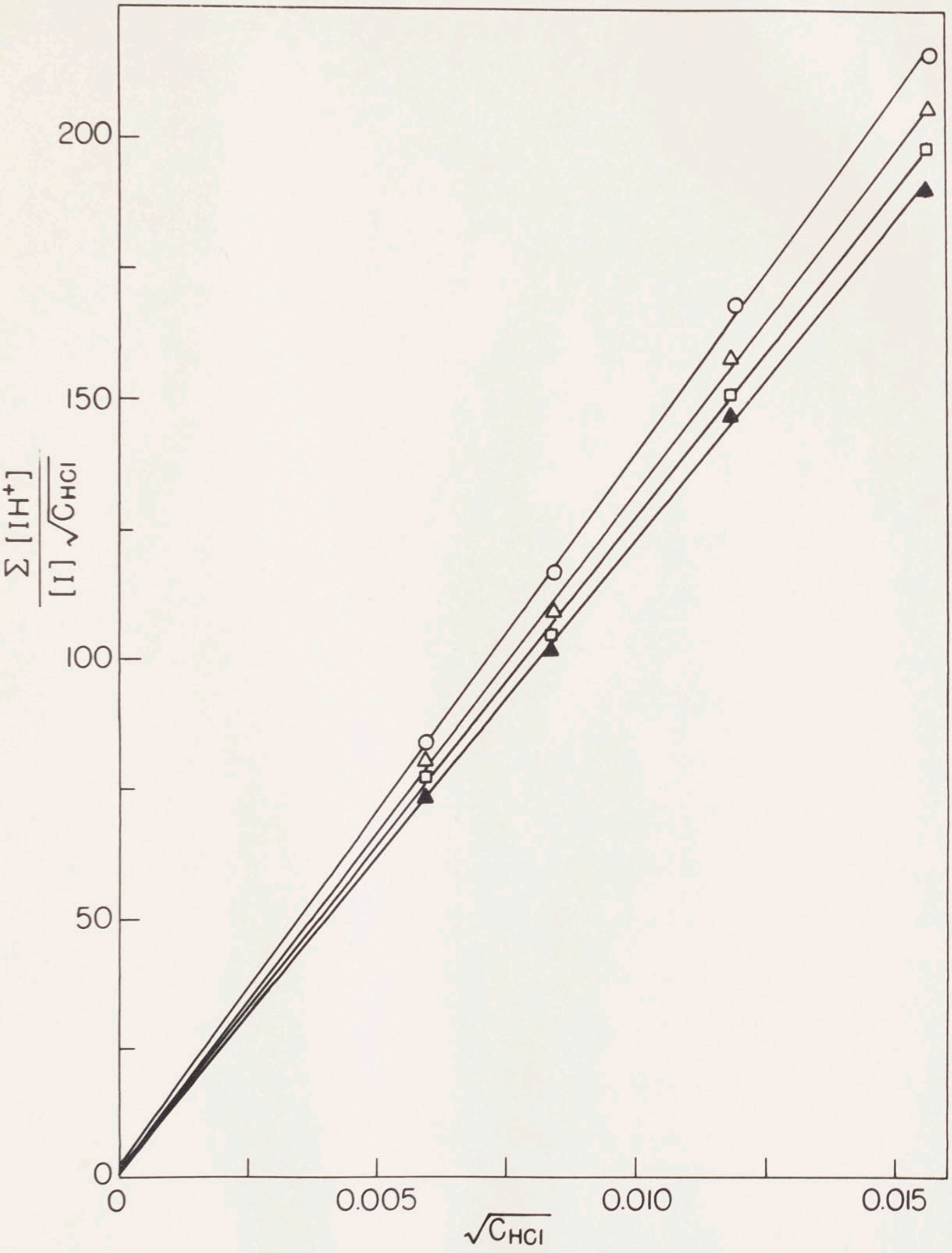
A 0.125 $\underline{M}$ solution of hydrogen chloride (as determined by titration with sodium hydroxide after addition of water) was prepared by passing HCl gas over redistilled o-dichlorobenzene. From this stock solution a 5.00×10^{-4} $\underline{M}$ hydrogen chloride solution was prepared by dilution.

In studying the reaction between 4-dimethylamino-4'-nitrostilbene and hydrogen chloride the indicator concentration ranged from 1.24×10^{-6} $\underline{M}$ to 9.94×10^{-6} $\underline{M}$, while the acid concentration was varied from 3.57×10^{-5} $\underline{M}$ to 5.00×10^{-4} $\underline{M}$. Corrections were made for the amount of acid consumed by the indicator. Figure 33 shows the resulting plot of equation 13. The lines are seen to be relatively straight but they are not parallel and it is therefore impossible to obtain significant intercepts. From the minimum slope in Figure 33 a value of about 12,000 is estimated for K_i^{IHX}. This indicates that hydrogen chloride is much stronger than diphenyl phosphate which gave a value of about 200.

Figure 33

Plot of Equation 13 for the Reaction of
4-Dimethylamino-4'-nitrostilbene with
Hydrogen Chloride in o-Dichlorobenzene

—○——○— $[I] = 1.00 \times 10^{-6}$
—△——△— $[I] = 1.50 \times 10^{-6}$
—□——□— $[I] = 2.00 \times 10^{-6}$
—▲——▲— $[I] = 2.50 \times 10^{-6}$


200
150
100
50
0
$\frac{\Sigma\,[IH^+]}{[I]\,\sqrt{C_{HCl}}}$
0
0.005
0.010
0.015
$\sqrt{C_{HCl}}$

The near success of this experiment confirms the importance of working at low concentration levels of both acid and indicator. However, the fact that the concentrations used were of the same magnitude as those used in the successful study of the reaction of p-naphtholbenzein with p-toluenesulfonic acid in glacial acetic acid seems to indicate that the formation of polyionic species constitutes a worse problem in aromatic hydrocarbons than in acetic acid. The most important reason is probably the smaller tendency of aromatic solvents to solvate ions. Since it is a general rule that decreased solute-solvent interaction leads to increased solute-solute interactions (50,51) one would expect increased ion association in aromatic solvents as compared to acetic acid.

b. Reaction in Benzene:

Although the previous experiences with solvents of higher dielectric constant made it seem very unlikely that the Kolthoff-Bruckenstein method would be applicable to acid-base systems in benzene (D=2.28), it was decided to perform one experiment in this solvent for the purpose of comparison. The reaction of hydrogen chloride with 4-dimethylamino-4'-nitrostilbene was chosen because of the low concentration levels possible in this system.

It has already been mentioned that the basic peak of 4-dimethyl-4'-nitrostilbene in benzene occurs at 427.5 mμ and has a molar absorptivity of 2.888×10^4 liters/ mole cm.

The hydrogen chloride concentrations used ranged from 2.29×10^{-5} <u>M</u> to 3.20×10^{-4} <u>M</u> while the maximum concentration of indicator added was 7.77×10^{-6} <u>M</u>. Figure 34 shows the plot of equation 13 for

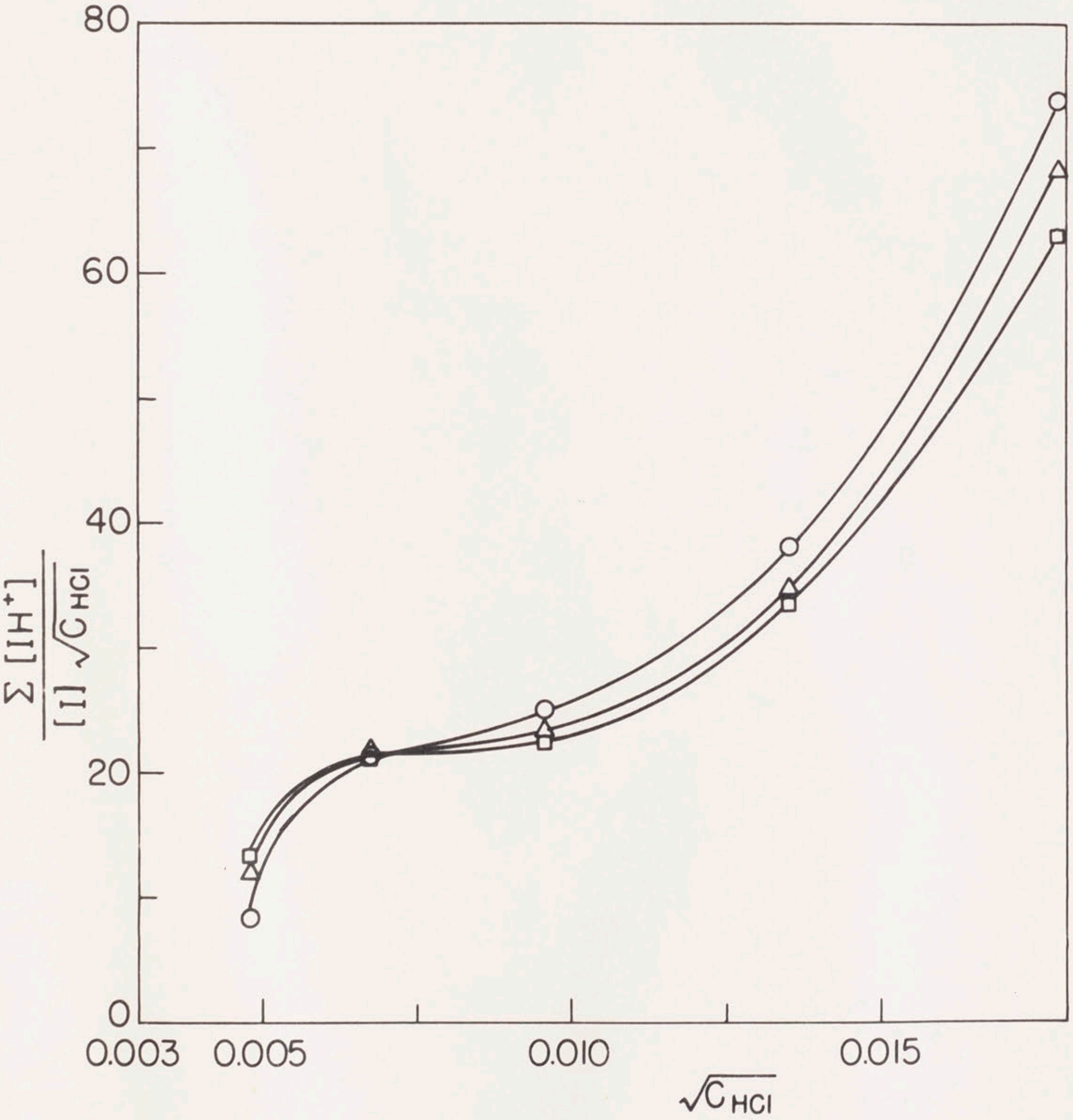
Figure 34

Plot of Equation 13 for the Reaction of 4-Dimethylamino-4'-nitrostilbene and Hydrogen Chloride in Benzene

—○—○— $[I] = 1.00 \times 10^{-6}$

—△—△— $[I] = 2.00 \times 10^{-6}$

—□—□— $[I] = 3.00 \times 10^{-6}$

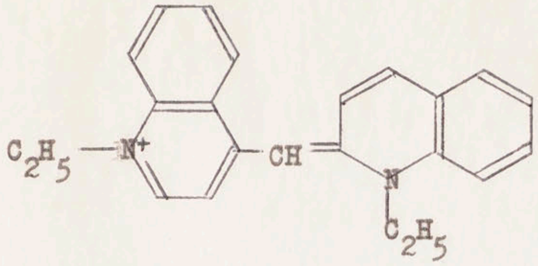

80
60
40
20
0
$\frac{\Sigma\,[IH^+]}{[I]\,\sqrt{C_{HCl}}}$
0.003
0.005
0.010
0.015
$\sqrt{C_{HCl}}$

this system. It is seen that the plot shows a strong curvature of the expected type at higher values of the acid concentration. At low acidity, however, a pronounced curvature in the opposite direction is observed. The curves for different values of [I] cross in an intermediate acidity region.

The unexpected trend at low acidity indicates a phenomenon which had not been encountered in indicator experiments in solvents of higher dielectric constant. A comparison with the anomalous photometric titration curves sometimes encountered with aromatic amines suggests that the new effect is caused by formation of a hydrogen bonded complex between protonated and unprotonated indicator species. The hydrogen bond appears to affect the absorption spectrum of the basic form, causing an apparent decrease in the ratio of acidic to basic form of the indicator. This effect is undoubtedly operative also at higher acid concentrations but it is overcome by the formation of higher ionic aggregates, a process which shows an exponential increase with ionic strength.

7. Effect of Charge on Ion Association

All the indicator bases used in the previous experiments were of the uncharged type which produces monovalent positive ions upon protonation. In searching for a strongly basic indicator with intense absorption, the characteristics of a charged base, ethyl red, were briefly investigated. Since the unprotonated form of this indicator carries a positive charge (see the structure below) protonation results in the formation of a divalent ion. Higuchi et al. (40), who studied a number of indicators in buffer solutions in glacial acetic acid, reported that ethyl red was the strongest base among



Ethyl Red

the indicators which they tested. Since 4-dimethylamino-4'-nitrostilbene, one of the indicators used in the present study, was also investigated by Higuchi et al., ethyl red appeared to show some promise. However, when tested in reactions with diphenyl phosphate and hydrogen chloride in o-dichlorobenzene it was actually found to be a weaker base than 4-dimethylamino-4'-nitrostilbene, contrary to the report of Higuchi et al. The explanation for this discrepancy is apparently that the presence of up to 0.05 molar buffers in the acetic acid solutions studied by Higuchi et al. caused a more extensive formation of higher ionic aggregates in the case of ethyl red than for uncharged bases. This led to an increased degree of protonation for ethyl red which erroneously was attributed to a stronger basicity of this compound. Support for this suggestion is given by Figure 35, which compares the effect of sodium perchlorate on the concentration of the basic form of ethyl red and 4-dimethylamino-4'-nitrostilbene, respectively, in glacial acetic acid. The very low solubility of ethyl red in acetic acid made it impossible to prepare a solution of exactly known concentration and the ethyl red curve is therefore compared with curves for two different concentrations of 4-dimethylamino-4'-nitrostilbene, which are so chosen that they bracket the

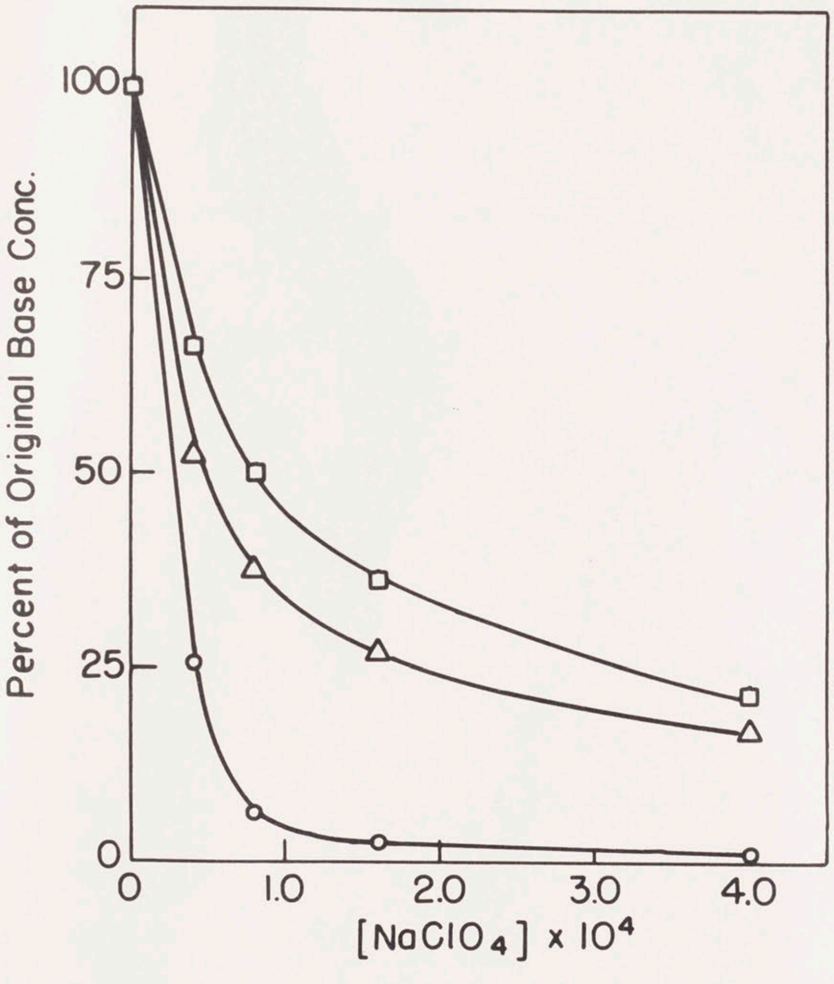
Figure 35

Effect of Sodium Perchlorate on the Concentrations of the Basic Forms of Ethyl Red and 4-Dimethylamino-4'-nitrostilbene in Glacial Acetic Acid

—○—○— Ethyl Red (total concentration $\leq 3.4 \times 10^{-5}$ M)

—□—□— 4-Dimethylamino-4'-nitrostilbene (4.47×10^{-5} M)

—△—△— 4-Dimethylamino-4'-nitrostilbene (8.94×10^{-6} M)


Percent of Original Base Conc.
100
75
50
25
0
0
1.0
2.0
3.0
4.0
[NaClO4] x 10^4

unknown concentration of ethyl red. It is obvious that the concentration of the basic form of ethyl red decreases faster than that of the uncharged indicator when sodium perchlorate is added to the solution.

It should be pointed out that the increased protonation upon salt addition, illustrated in Figure 35, is not entirely due to increased formation of polyionic species. It has long been known (49,39,45,9,47) that so-called "neutral" salts may affect the acidity of solutions in glacial acetic acid. In the present case, addition of sodium perchlorate caused an excess of hydrogen ions because of the smaller dissociation constant of sodium acetate as compared to perchloric acid. These compounds have dissociation constants in acetic acid of 2.09×10^{-7} and 1.35×10^{-5}, respectively (9). Hence the acetate ions formed by autoprotolysis of acetic acid are tied up as undissociated sodium acetate to a larger extent than the corresponding hydrogen ions are consumed in formation of undissociated perchloric acid. The increase in acidity upon addition of such a salt as sodium perchlorate can be detected potentiometrically, and it also increases the degree of protonation of a basic indicator. This phenomenon, which is formally similar to hydrolysis in water solutions, should always be remembered in working with glacial acetic acid solutions.

8. Conclusions of the Indicator Study

The above experiments show that great difficulties are encountered in attempting to apply the Kolthoff-Bruckenstein method in solvents other than glacial acetic acid. Apparently there is no hope for a successful application of this technique in solvents such as benzene where ion association is very extensive. In media such as o-dichlorobenzene the method may prove useful for studying relatively weak acids provided that sufficiently strongly basic indicators with intense absorption can be found. The last condition is imperative since the concentrations of both the indicator and the acid must be kept as low as possible in order to avoid complications due to formation of higher ionic aggregates.

Very interesting comparisons of acid-base reactions in different solvents could be performed using the technique of Kolthoff and Bruckenstein and it is therefore unfortunate that its application is so severely restricted by complicating factors. In particular, the method would make it possible to separate, to a certain extent, effects due to the dielectric constant from those of the acidic or basic character of the solvent.

APPENDIX

SELECTED ABSORPTION SPECTRA OF INDICATOR BASES AND COMPOUNDS DETERMINED BY PHOTOMETRIC TITRATION

Figure 36

Absorption Spectra of 1.62×10^{-4} M Phenol and 1.39×10^{-4} M 2,4,6-Trichlorophenol in Isopropanol in Their Acidic and Basic Forms. Spectra Recorded on the Cary Recording Spectrophotometer Model 11 MS using 1.00-cm. Cells

———————— Phenol (Acidic Form)

— — — — Phenol (Basic Form)

— - — - — 2,4,6-Trichlorophenol (Acidic Form)

— · · — · · — 2,4,6-Trichlorophenol (Basic Form)

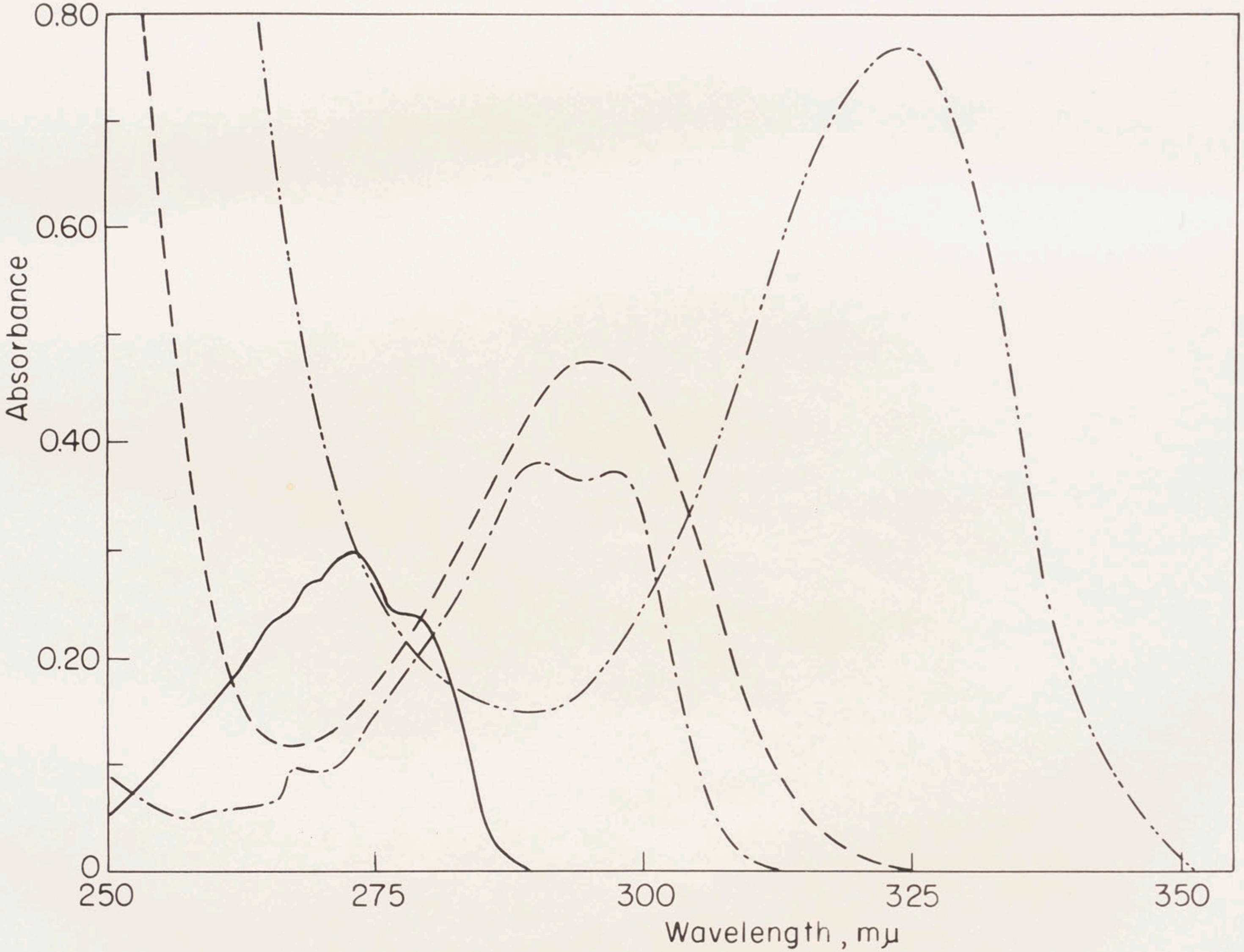

0.80
0.60
0.40
0.20
0
Absorbance
250
275
300
325
350
Wavelength , mμ

Figure 37

Absorption Spectra of 1.61×10^{-4} $\underline{M}$ 1-Naphthol and 4.07×10^{-5} $\underline{M}$ p-Nitrophenol in Isopropanol in Their Acidic and Basic Forms. Spectra Recorded on the Cary Recording Spectrophotometer Model 11 MS using 1.00-cm. Cells

———————— 1-Naphthol (Acidic Form)
— — — — 1-Naphthol (Basic Form)
—·—·— p-Nitrophenol (Acidic Form)
—··—··— p-Nitrophenol (Basic Form)

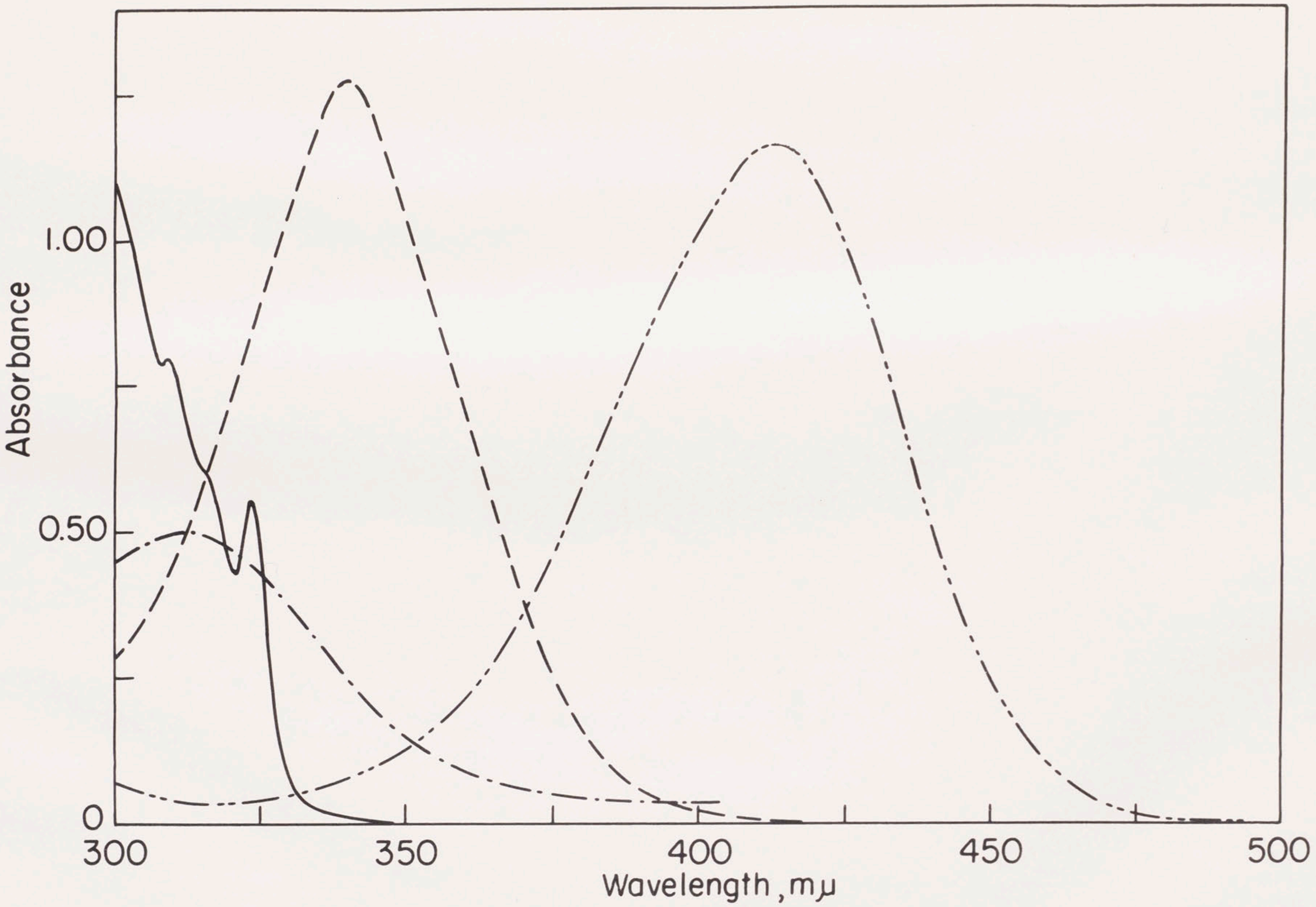

Absorbance
1.00
0.50
0
300
350
400
450
500
Wavelength, mμ

Figure 38

Absorption Spectra of 4.06 x 10^{-4} *M* Aniline and 4.09 x 10^{-4} *M* N,N-Diethylaniline in Acetonitrile. Spectra Measured on the Beckman Spectrophotometer Model DU using 1.00-cm.-Cells

—○—○— Aniline (Basic Form)

—□—□— N,N-Diethylaniline (Basic Form)

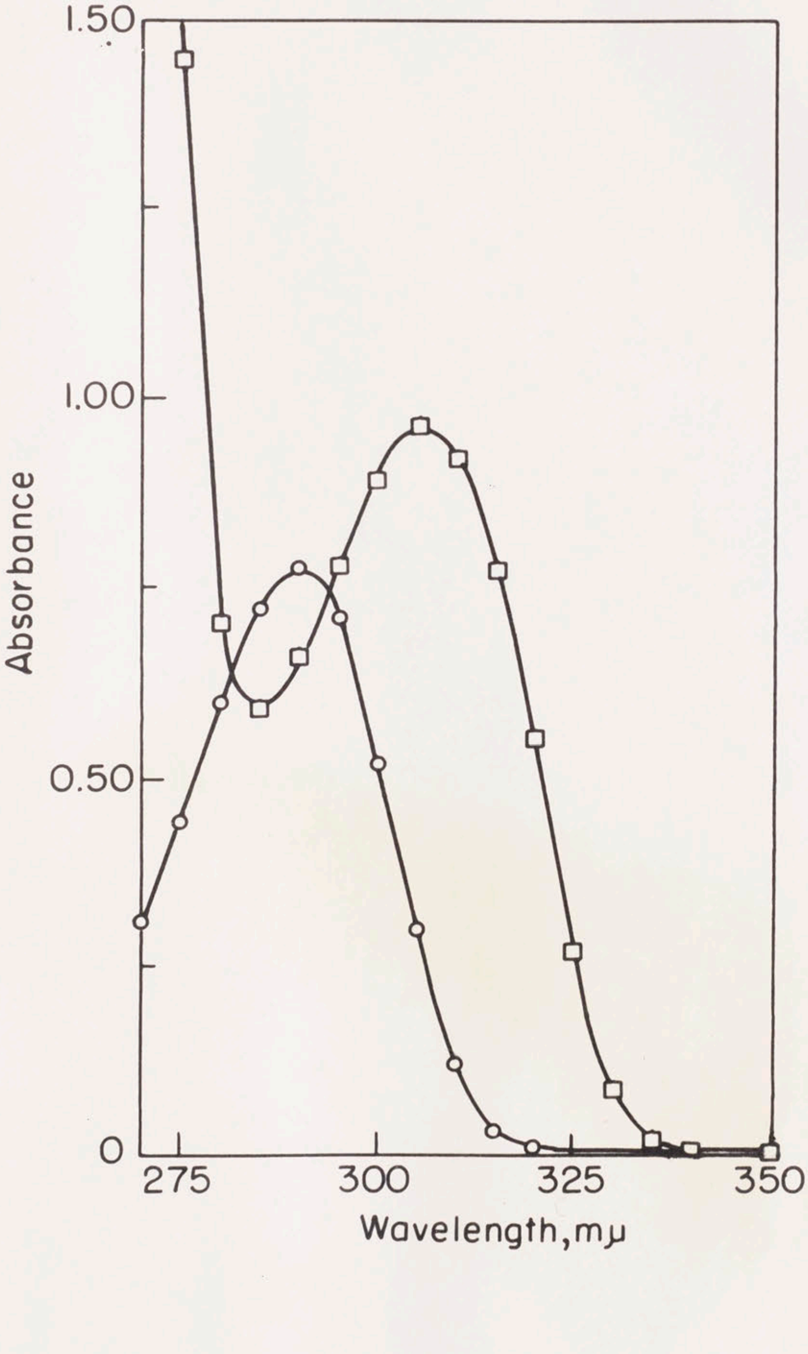

1.50
1.00
0.50
0
Absorbance
275
300
325
350
Wavelength, mμ

Figure 39

Absorption Spectra of the Basic Forms of Monochloroanilines, Measured on the Beckman Spectrophotometer Model DU Using 1.00-cm. Cells

—○—○— o-Chloroaniline 4.07 x 10^{-4} $\underline{M}$ in Acetonitrile

—□—□— m-Chloroaniline 4.32 x 10^{-4} $\underline{M}$ in Acetonitrile

—△—△— p-Chloroaniline 4.03 x 10^{-4} $\underline{M}$ in Acetonitrile

—▲—▲— p-Chloroaniline 4.00 x 10^{-4} $\underline{M}$ in Acetic Acid

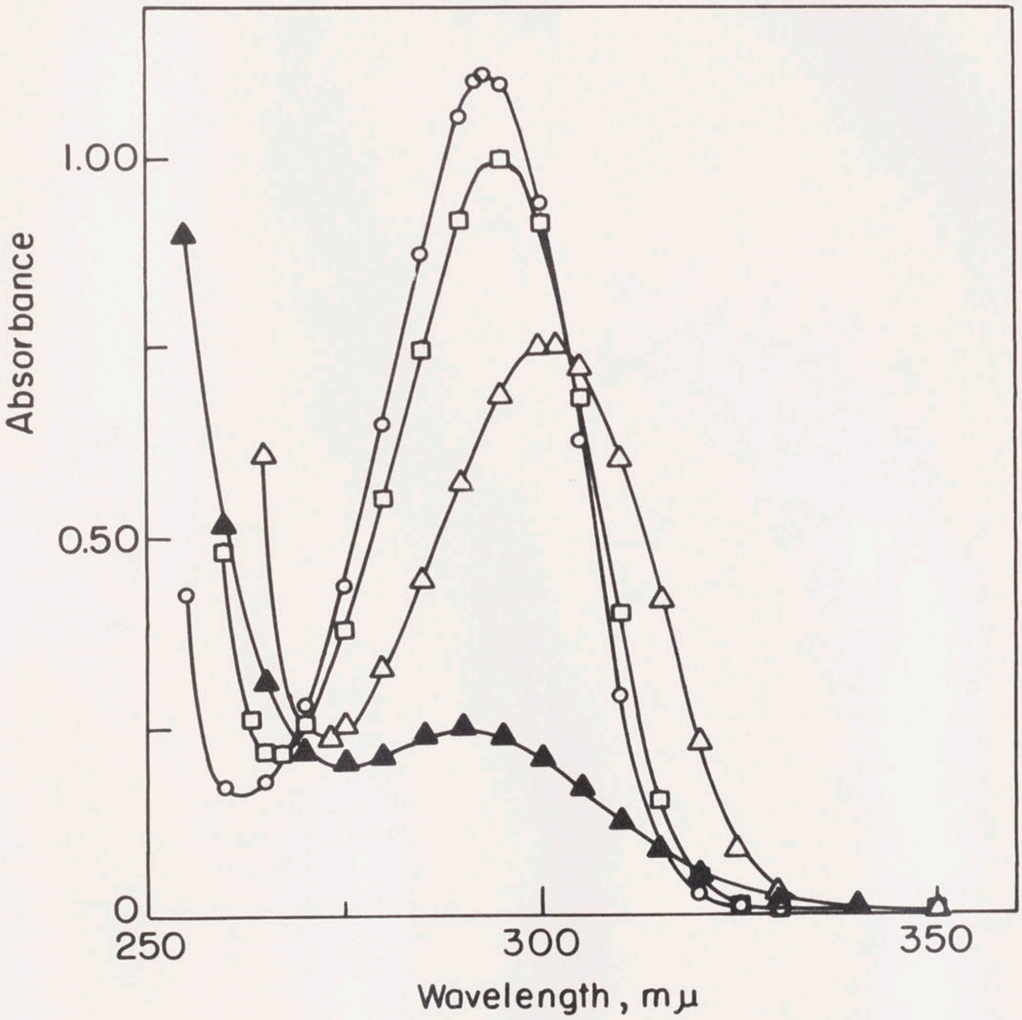

Absorbance
1.00
0.50
0
250
300
350
Wavelength, mμ

Figure 40

Absorption Spectra of the Basic Forms of Some Nitroanilines in Acetic Acid. Spectra Recorded on the Cary Recording Spectrophotometer Model 11 MS Using 1.00-cm. Cells, or on the Beckman Model DK 2 Using 0.100-cm. Cells

———— p-Nitroaniline (6.40×10^{-5} M ; Cary, 1-cm. Cell)

– – – – – – N,N-Dimethyl-p-nitroaniline (6.40×10^{-5} M ; Cary, 1-cm. Cell)

— ·· — ·· — m-Nitroaniline (1.60×10^{-4} M ; Cary, 1-cm. Cell)

— · — · — 4-Methyl-2-nitroaniline (1.0×10^{-3} M ; Beckman DK 2, 0.1-cm. Cell)

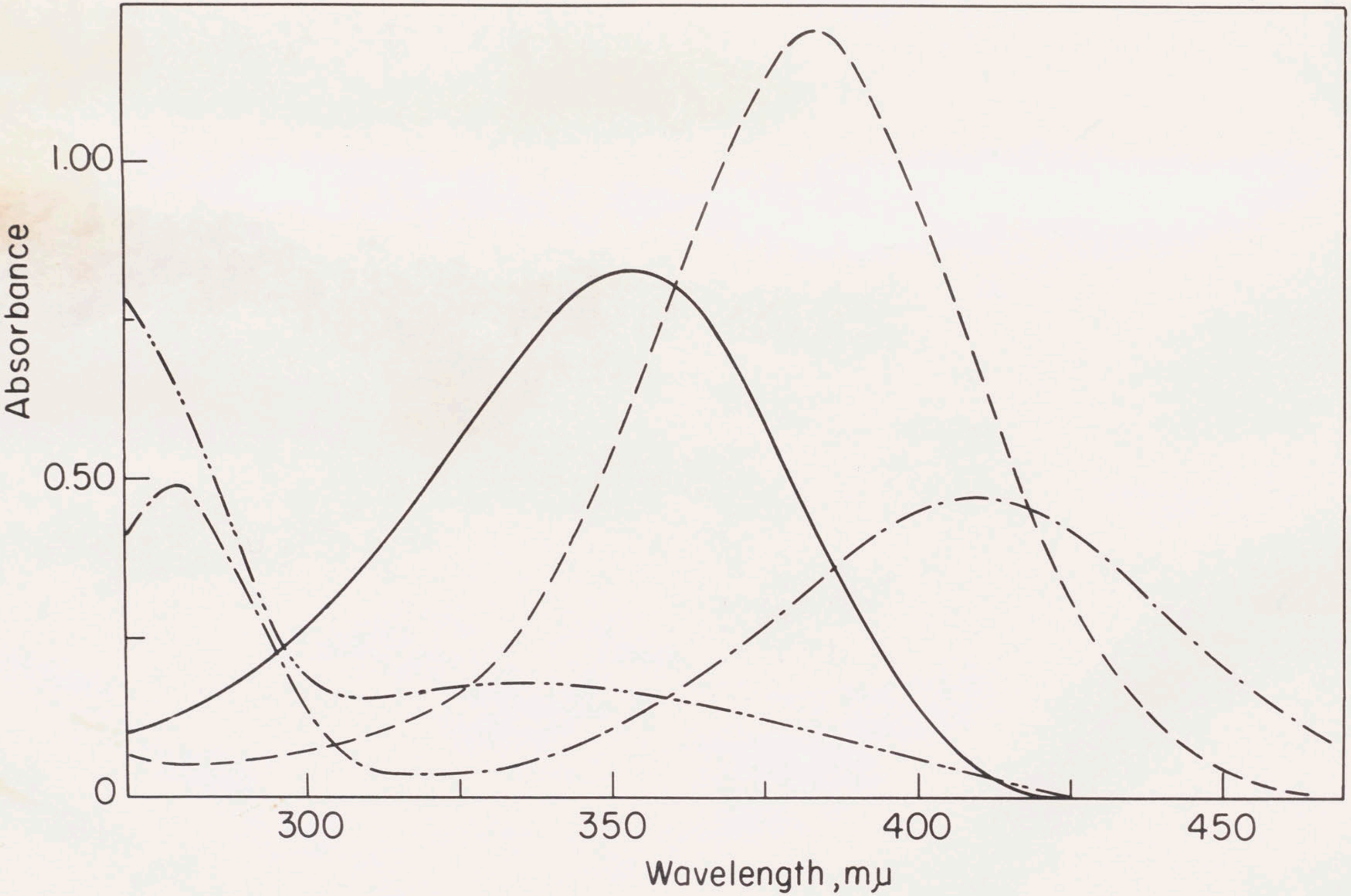
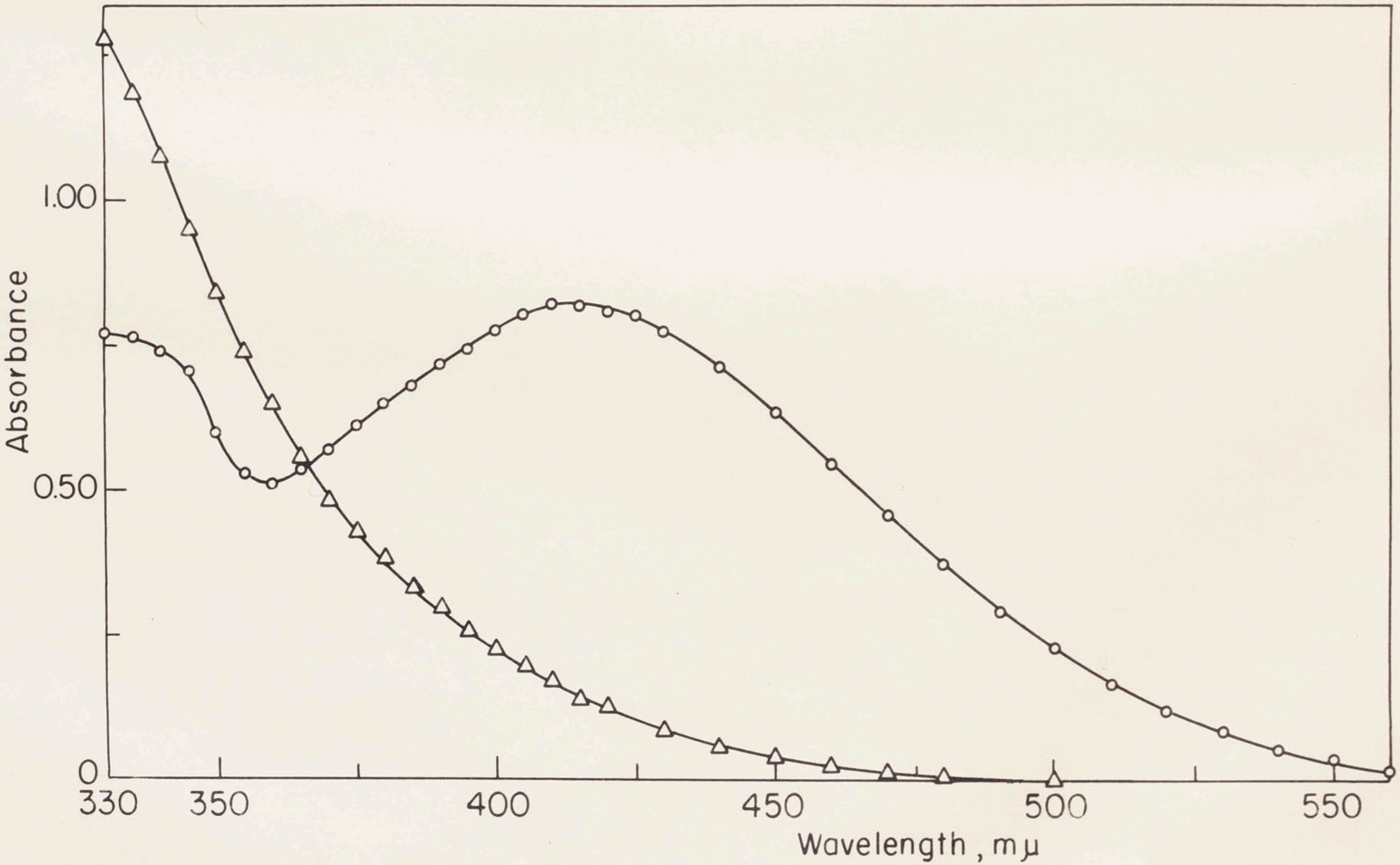

Absorbance
1.00
0.50
0
300
350
400
450
Wavelength , mμ

Figure 41

Absorption Spectra of 3.2×10^{-4} M
5-Nitro-1-naphthylamine in Acetonitrile,
Measured on the Beckman Spectrophotometer
Model DU Using 1.00-cm. Cells

—○—○— Basic Form
—△—△— Acidic Form



Absorbance
1.00
0.50
0
330
350
400
450
500
550
Wavelength , mμ

Figure 42

Absorption Spectra of 2.54×10^{-4} *M* 8-Chloroquinoline in Acetic Acid Measured on the Beckman Model DU Spectrophotometer Using 1.00-cm. Cells

—○—○— Basic Form

—△—△— Acid Form

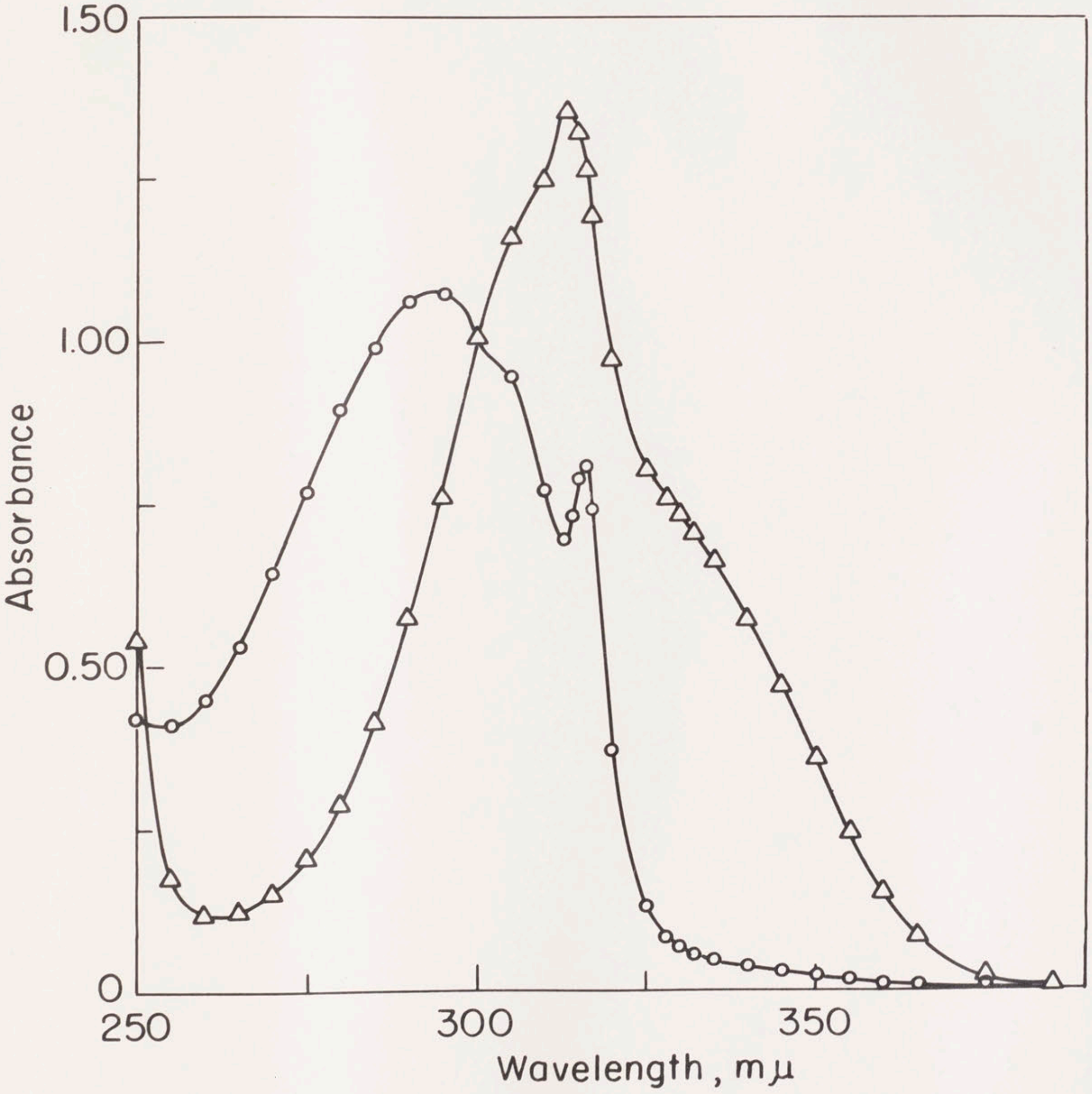

1.50
1.00
0.50
0
Absorbance
250
300
350
Wavelength, mμ

Figure 43

Absorption Spectra of 7.04×10^{-6} M p-Naphtholbenzein in Acetic Acid, Measured on the Beckman Spectrophotometer Model B Using 5.00-cm. Cells

—○—○— Basic Form

—△—△— Acidic Form

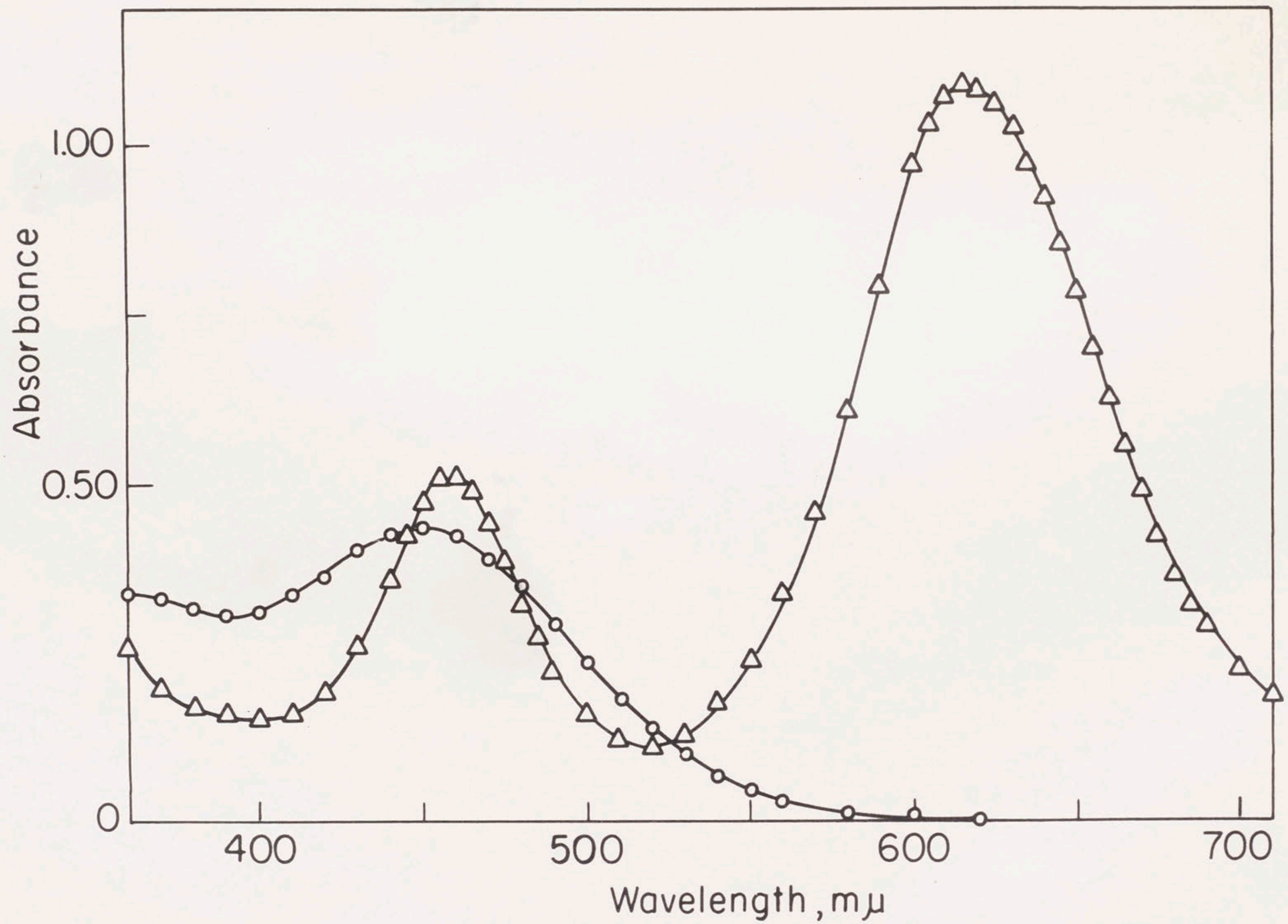

Absorbance
1.00
0.50
0
400
500
600
700
Wavelength, mμ

Figure 44

Absorption Spectra of 7.80×10^{-5} M 8-Quinolinol in o-Dichlorobenzene, Measured on the Beckman Spectrophotometer Model DU Using 5.00-cm. Cells

—○—○— Basic Form

—△—△— Acidic Form

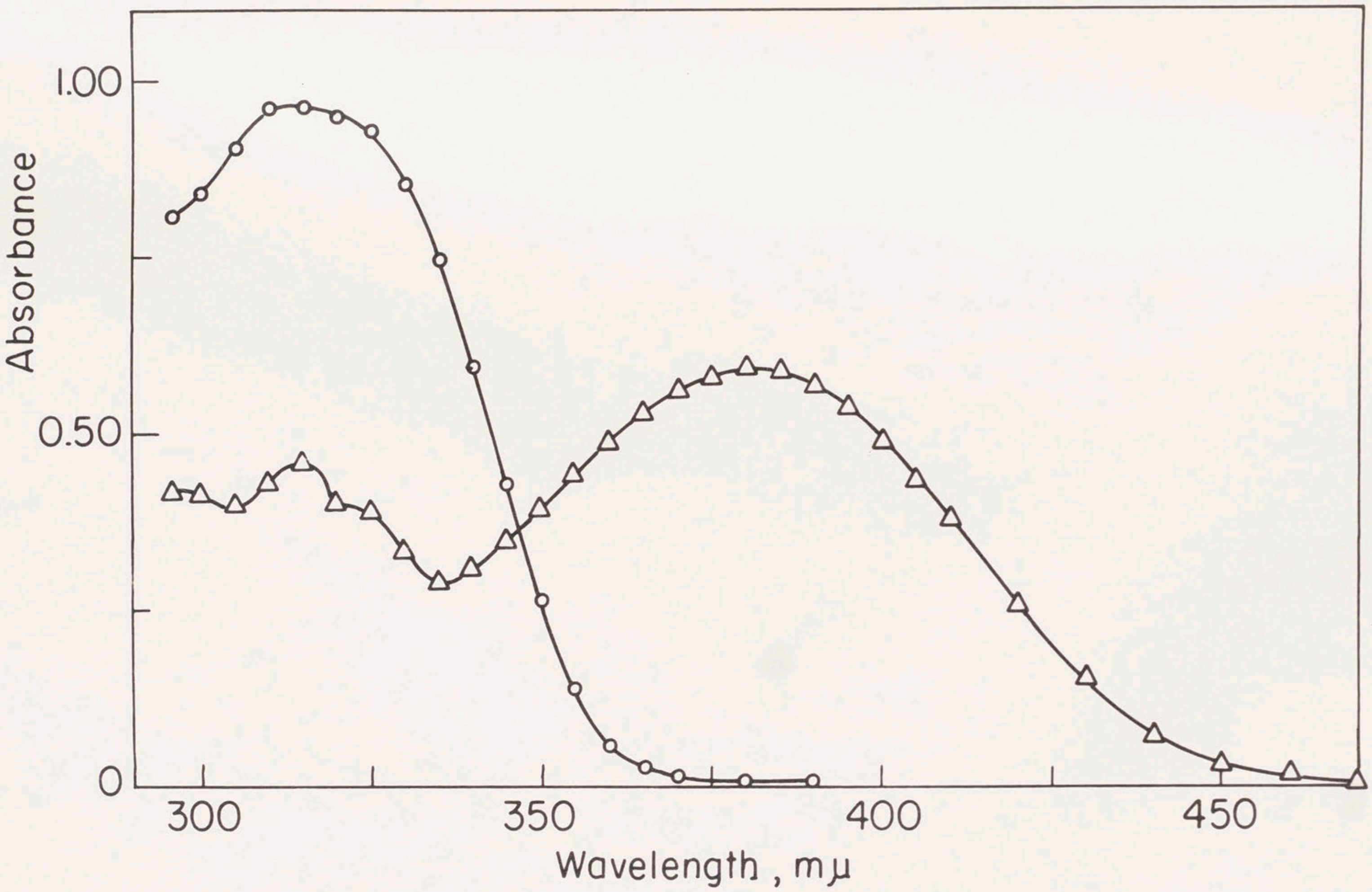

1.00
0.50
0
Absorbance
300
350
400
450
Wavelength , mμ

Figure 45

Absorption Spectra of 7.77×10^{-6} *M*
4-Dimethylamino-4'-nitrostilbene in
Benzene, Measured on the Beckman
Spectrophotometer Model B Using
5.00-cm. Cells

—○—○— Basic Form
—△—△— Acidic Form

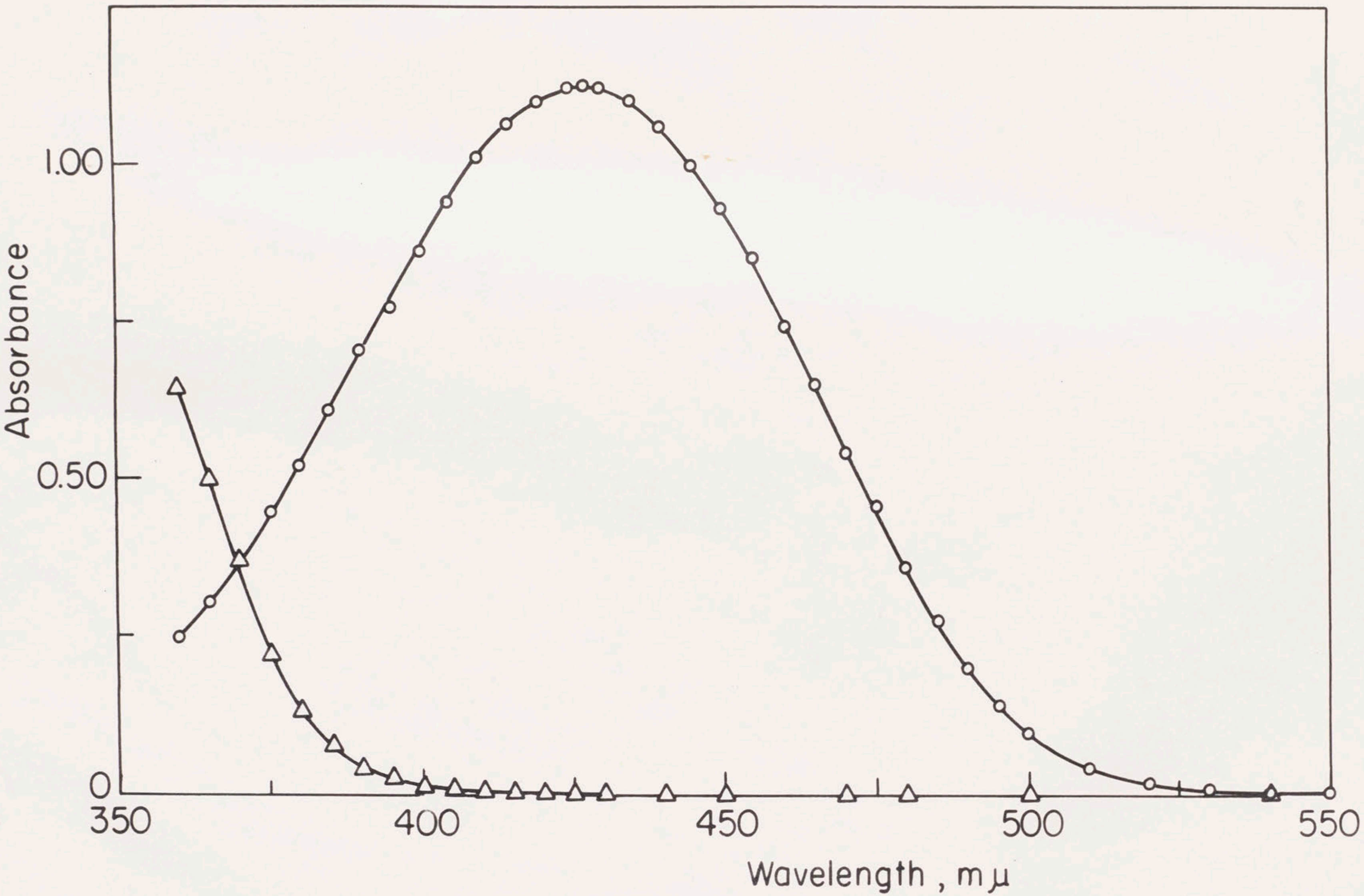
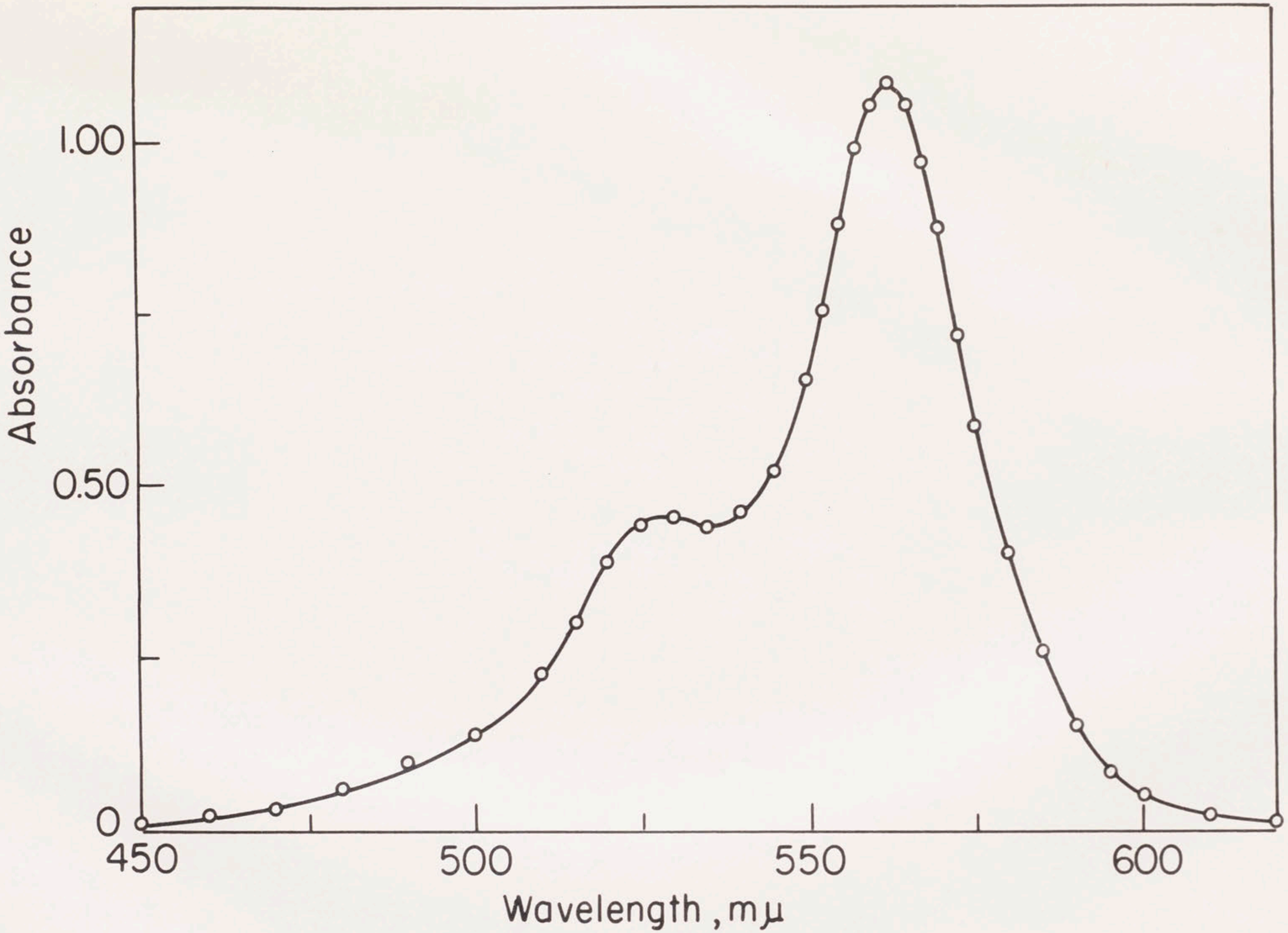

Absorbance
1.00
0.50
0
350
400
450
500
550
Wavelength , mμ

Figure 46

Absorption Spectrum of About 2.5×10^{-6} M Ethyl Red in o-Dichlorobenzene, Measured on the Beckman Spectrophotometer Model B Using 5.00-cm. Cells (The Acidic Form Does Not Absorb in This Wavelength Region)


Absorbance
1.00
0.50
0
450
500
550
600
Wavelength , mμ

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