# Photometric Studies of Acid–Base Reactions in Low-Dielectric Solvents[1]

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An indicator method developed by Kolthoff and Bruckenstein in glacial acetic acid has been applied to acid-base reactions in o-dichlorobenzene, chlorobenzene, benzene and a mixture of o-dichlorobenzene and acetonitrile. The results indicate that its application is severely limited by complicating association reactions, including formation of higher ionic aggregates, participation of acid molecules in solvating the indicating salt and formation of hydrogen-bonded complexes between protonated and unprotonated indicator species.

## Introduction

The recent studies by Kolthoff and Bruckenstein[2] of acid–base equilibria in glacial acetic acid constitute a landmark in the development of the theory of acid-base reactions in low-dielectric media. In the spectrophotometric part of their investigation[2a] these authors developed a method whereby the dissociation constant of the acid, the formation constant of the ion-pair form of the indicator salt and the dissociation constant of the ion pair could be measured in the reaction between a moderately weak acid and an indicator base. The theory was derived for the case where the indicator base is so weak that it is not significantly protonated by the solvent. Hence it appears that the method should not, in principle, be limited to acidic solvents, and this study was undertaken to explore the possibility of applying it to other low-dielectric media. The essential features of the Kolthoff–Bruckenstein theory which are pertinent to the present study are summarized below.

The low dielectric constant of glacial acetic acid (6.13) permitted Kolthoff and Bruckenstein[2a] to assume that the salt of the acid HX with an indicator base I exists largely in the form of the ion pair IH+X−, the formation constant of which is defined as

$$K_i^{\text{IHX}} = \frac{[\text{IH}^+\text{X}^-]}{[\text{I}][\text{HX}]} \qquad (1)$$

The equilibrium constant for the dissociation of the ion pair into free ions is

$$K_d^{\text{IHX}} = \frac{[\text{IH}^+][\text{X}^-]}{[\text{IX}^+\text{X}^-]} \qquad (2)$$

The total acid concentration $C_{\text{HX}} = [\text{HX}] + [\text{H}^+\text{X}^-] + [\text{H}^+]$ is approximately equal to [HX] for acids even as strong as hydrogen chloride and p-toluenesulfonic acid in glacial acetic acid,[2a] and the over-all dissociation constant of the acid, defined as

$$K_{\text{HX}} = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}] + [\text{H}^+\text{X}^-]} \qquad (3)$$

then simplifies to

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

The absorption characteristics of the protonated indicator were found to be independent of whether it existed as a free ion or as a part of an ion pair or a higher ionic aggregate. Kolthoff and Bruckenstein were able to find experimental conditions under which the concentration of higher aggregates was negligible, and using the symbol $\Sigma[\text{IH}^+]$ to denote the sum $[\text{IH}^+] + [\text{IH}^+\text{X}^-]$, they derived the equation

$$\frac{\Sigma[\text{IH}^+]}{[\text{I}]\sqrt{C_{\text{HX}}}} = K_i^{\text{IHX}}\sqrt{C_{\text{HX}}} + \frac{K_i^{\text{IHX}}K_d^{\text{IHX}}}{\sqrt{K_{\text{HX}} + K_i^{\text{IHX}}K_d^{\text{IHX}}[\text{I}]}} \qquad (5)$$

A clever experimental design permitted evolution of $\Sigma[\text{IH}^+]/[\text{I}]\sqrt{C_{\text{HX}}}$ at chosen constant values of [I], the concentration of the basic form of the indicator, and made it possible to plot $\Sigma[\text{IH}^+]/[\text{I}]\sqrt{C_{\text{HX}}}$ versus $\sqrt{C_{\text{HX}}}$, obtaining a family of parallel straight lines, each constant value of [I] giving a separate line. The slope of these lines is equal to $K_i^{\text{IHX}}$ while the remaining two constants can be obtained from the intercepts by plotting $[\text{I}]b^2$ versus $b^2$ where $b$ is the intercept

$$\frac{K_i^{\text{IHX}}K_d^{\text{IHX}}}{\sqrt{K_{\text{HX}} + K_i^{\text{IHX}}K_d^{\text{IHX}}}\,[\text{I}]}$$

This plot is a straight line with a slope equal to

$$\frac{K_{\text{HX}}}{K_i^{\text{IHX}}K_d^{\text{IHX}}}$$

and an intercept given by $K_i^{\text{IHX}}K_d^{\text{IHX}}$.

From the expression for $b$ it is seen that different intercepts cannot be obtained if $K_{\text{HX}} \gg K_i^{\text{IHX}}$. $K_d^{\text{IHX}}$ [I]. In such a case the parallel lines in a plot of equation 5 fuse together and only $K_i^{\text{IHX}}$ can be determined. On the other hand, $K_{\text{HX}}$ cannot be evaluated if it is negligible in comparison with the product $K_i^{\text{IHX}}K_d^{\text{IHX}}[\text{I}]$. These obvious limitations make the combination of acid and indicator quite critical as shown below.

## Experimental

**Materials.**—The glacial acetic acid was purified by a method[3] which involves reaction of moisture-containing acetic acid with the calculated amount of acetic anhydride, in the presence of sulfuric acid catalyst, and subsequent distillation of the anhydrous solvent through a two-foot Vigreux column. Glacial acetic acid prepared by this method contained less than 0.002% water, as determined by Karl Fischer titration. In order to duplicate the conditions of Kolthoff and Bruckenstein[2a] as closely as possible, the water content of the solvent used in certain experiments was adjusted to 0.03% by addition of reagent grade acetic acid having a water content of 0.2%.

Dry benzene was prepared by fractional distillation of Mallinckrodt Analytical Reagent material from phos-

(1) Abstracted in part from the Ph.D. Thesis of L. E. I. Hummelstedt, Massachusetts Institute of Technology, June, 1959. This work was supported in part by the U. S. Atomic Energy Commission under Contract AT (30-1)905.

(2) (a) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956); (b) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 10 (1956); (c) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2974 (1956); (d) I. M. Kolthoff and S. Bruckenstein, *ibid.*, **79**, 1 (1957); (e) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **79**, 5915 (1957).

(3) H. J. Keily, Ph.D. Thesis, Massachusetts Institute of Technology, 1956.

phorus 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).

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 found that it had no detrimental effect on their experiment in glacial acetic acid.[2d]

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.[4] The white crystals obtained assayed 99.82% anhydrous diphenyl phosphate when titrated with sodium hydroxide in a water–ethanol mixture.

p-Naphtholbenzein and 8-quinolinol were Eastman White Label products. 4-Dimethylamino-4'-nitrostilbene was synthesized from p-dimethylamino-benzaldehyde and p-nitrophenylacetic acid according to the method of Pfeiffer[5] and recrystallized from benzene.

**Apparatus.**—The spectrophotometric measurements were performed with the Beckman Models B or DU spectrophotometers, 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.

**Procedure.**—The experimental design was essentially that of Kolthoff and Bruckenstein.[2a] A total of 0.100 ml. indicator solution was added in 0.0100- or 0.0200-ml. increments to the acid solution in the 5- or 10-cm. cell, the absorbance of the solution being measured after each addition. Since the volume of the solution was 14.00 or 28.00 ml., depending on the cell used, the dilution due to the addition of indicator was negligible. The procedure was repeated at several different acid concentrations.

## Experimental Results and Discussion

In order to test the reliability of the method in our hands, it was first applied to the reaction of p-naphtholbenzein (PNB) with p-toluenesulfonic acid in glacial acetic acid, a system previously studied by Kolthoff and Bruckenstein.[2a] The acidic and basic absorption spectra of PNB were in substantial agreement with those previously reported, but the molar absorptivity of the long-wave length acidic peak was found to be $3.08 \times 10^4$ liters/mole cm. rather than $2.86 \times 10^4$ liters/mole cm. The experimental data for the measurement of $\Sigma[IH^+]$ at molarities of p-toluenesulfonic acid ranging between $2.16 \times 10^{-4}$ and $3.02 \times 10^{-3}$ M for PNB concentrations between 1.41 and $11.26 \times 10^{-6}$ M were treated according to the method of Kolthoff and Bruckenstein. When the results were plotted according to equation 5, a family of parallel straight lines was obtained, as shown in Fig. 1. The slopes $(K_i^{IHX})$ and intercepts $(b)$ of these lines were determined, and a plot of $[I]b^2$ versus $b^2$ gave a satisfactory straight line with a slope of $-7.10 \times 10^{-6}$ and an intercept of $1.07 \times 10^{-3}$. By combining these data with the average value of 368 for $K_i^{IHX}$, $K_{HX}$ and $K_d^{IHX}$ could be calculated. In Table I the results are compared with those obtained by Kolthoff and Bruckenstein on the same system. The good agreement indicates that the method can be expected to give reproducible results in systems to which it is applicable.

(4) M. M. Davis and H. B. Hetzer. *J. Research Natl. Bur. Standards,* **54,** 309 (1955).
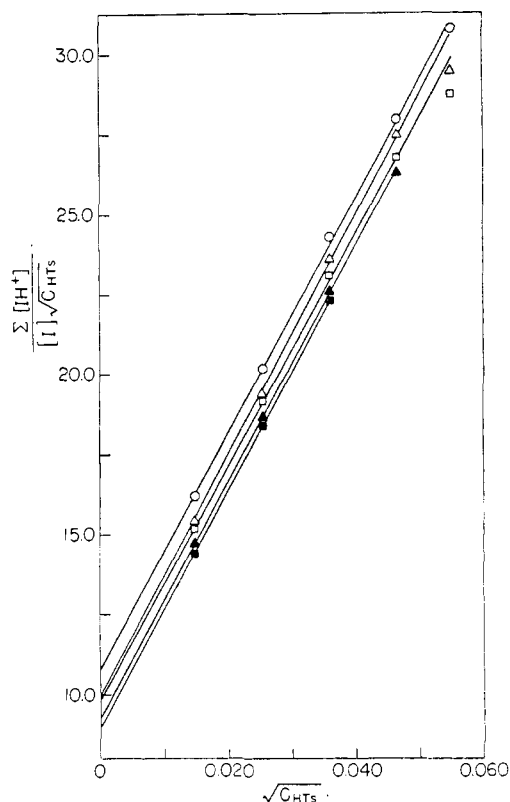
(5) P. Pfeiffer, *Ber.,* **48,** 1796 (1915).



Fig. 1.—Plot of equation 5 for the reaction of p-naphtholbenzein with p-toluenesulfonic acid in glacial acetic acid; concentrations of basic form of indicator $\times 10^6$ M: $\bigcirc$ = 2.00, $\triangle$ = 3.00, $\square$ = 4.00, $\blacktriangle$ = 5.00 and $\blacksquare$ = 6.00.

It was felt that acid–base systems in aromatic solvents such as o-dichlorobenzene (dielectric constant 9.93) and chlorobenzene ($D$ = 5.62) might also be studied by this method. The low solubility of p-toluenesulfonic acid in these solvents made it necessary to use a different acid. Diphenyl phosphate, an acid studied by Davis and Hetzer,[4] is quite soluble in aromatic hydrocarbons, as are many of its salts, and it can be obtained in an anhydrous, easily weighable form. In water, it titrates as a strong acid but Davis and Hetzer found it to be relatively weak in low-dielectric media.

### TABLE I

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

| Constant | This study | Kolthoff and Bruckenstein[2a] |
|---|---|---|
| $K_{HX}$ | $7.6 \times 10^{-9}$ | $7.3 \times 10^{-9}$ |
| $K_i^{IHX}$ | $3.7 \times 10^2$ | $3.7 \times 10^2$ |
| $K_d^{IHX}$ | $2.9 \times 10^{-6}$ | $4.0 \times 10^{-6}$ |

p-Naphtholbenzein was too weakly basic for reaction with diphenyl phosphate and hence a stronger indicator base had to be found. 8-Quinolinol (8-Q) appeared useful although far from ideal. The spectrum of its protonated form in o-dichlorobenzene was found to have a maximum at 380 mμ with a molar absorptivity of 1467 liters/mole cm. This is a low value compared to the corresponding molar absorptivity of p-naphthol-
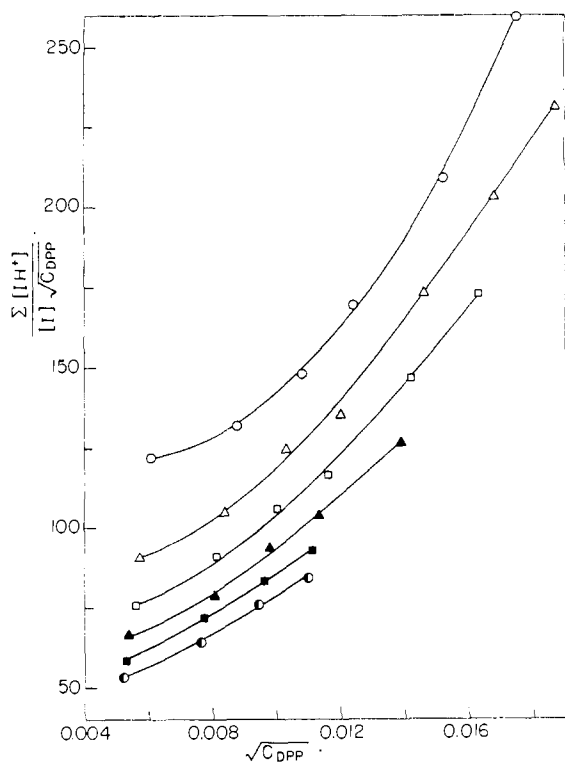
Fig. 2.—Plot of equation 5 for the reaction of 8-quinolinol with diphenyl phosphate in $o$-dichlorobenzene; concentrations of basic form of indicator $\times 10^{-5} M$: $O = 1.00$, $\triangle = 2.00$, $\square = 3.00$, $\blacktriangle = 4.00$, $\blacksquare = 5.00$, $\bullet = 6.00$.

benzein in glacial acetic acid ($3.08 \times 10^4$ liters/mole cm.), and hence it was necessary to use considerably higher concentrations. In studying the reaction between 8-quinolinol and diphenyl phosphate, the indicator concentration was varied between $1.56 \times 10^{-5}$ and $1.25 \times 10^{-4}$ while the concentration of the acid ranged from $4.39 \times 10^{-5}$ to $4.39 \times 10^{-4} M$. Hence, the concentrations were of comparable magnitude and corrections had to be made for the amount of acid consumed in protonating the indicator

$$(C_{HX} = [HX] \text{ added} - \Sigma[IH^+])$$

Figure 2 shows the family of curves obtained in plotting the data from the reaction of 8-quinolinol with diphenyl phosphate in $o$-dichlorobenzene according to equation 5. The lines are not straight and it is, therefore, impossible to obtain meaningful slopes and intercepts. A reason for this deviation from theory is suggested by the dependence of the indicator ratio

$$\frac{\Sigma[IH^+]}{[I]}$$

on the total indicator concentration, shown in Table II and Fig. 3. If the reaction between acid and indicator is assumed to lead to the formation of an undissociated ion pair $IH^+X^-$, the lines in Fig. 3 should coincide and have a slope of unity. If the ion pair dissociates to some extent, the lines would be separate and have slopes less than unity as found for the reaction of $p$-naphtholbenzein with $p$-toluenesulfonic acid in glacial acetic acid.[2a] If, on the other hand, formation of higher ionic aggre-
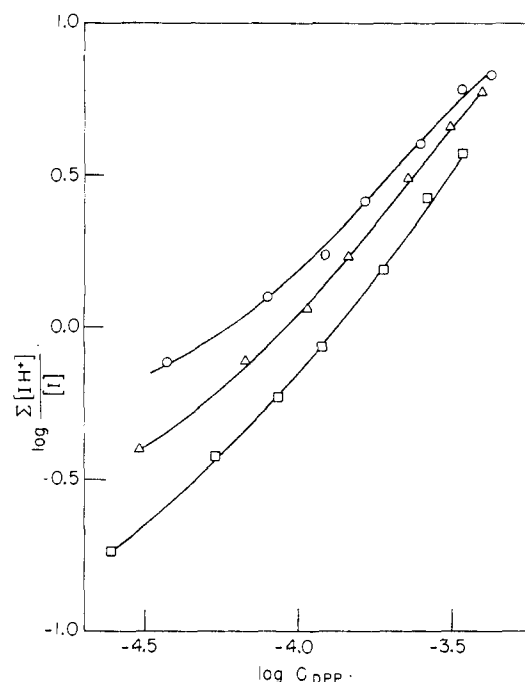


Fig. 3.—Reaction between 8-quinolinol and diphenyl phosphate in $o$-dichlorobenzene as a function of total indicator concentration; 8-quinolinol concentrations: $O = 1.56 \times 10^{-5} M$, $\triangle = 4.68 \times 10^{-5} M$, $\square = 1.25 \times 10^{-4} M$.

gates occurs, the slopes will become greater than unity. The initial slopes of the curves in Fig. 3 are below unity while slopes greater than unity are observed at higher acidities. The lowest initial slope is found for the lowest total indicator concentration, $i.e.$, for the solutions of lowest ionic strength. It appears, therefore, that both dissociation of $IH^+X^-$ into free ions and formation of higher ionic aggregates occur, the latter phenomenon becoming predominant as the total ion concentration increases.

TABLE II

REACTION OF 8-QUINOLINOL WITH DIPHENYL PHOSPHATE IN $o$-DICHLOROBENZENE AT DIFFERENT TOTAL INDICATOR CONCENTRATIONS

| $[8\text{-}Q] =$ $1.56 \times 10^{-5}$ | | $4.68 \times 10^{-5}$ | | $1.25 \times 10^{-4}$ | |
|---|---|---|---|---|---|
| $C_{DPP}$ | $\frac{\Sigma[IH^+]}{[I]}$ | $C_{DPP}$ | $\frac{\Sigma[IH^+]}{[I]}$ | $C_{DPP}$ | $\frac{\Sigma[IH^+]}{[I]}$ |
| $3.71 \times 10^{-5}$ | 0.775 | $3.05 \times 10^{-5}$ | 0.401 | $2.44 \times 10^{-5}$ | 0.185 |
| $7.90 \times 10^{-5}$ | 1.32 | $6.73 \times 10^{-5}$ | 0.786 | $5.34 \times 10^{-5}$ | .382 |
| $1.22 \times 10^{-4}$ | 1.75 | $1.07 \times 10^{-4}$ | 1.17 | $8.53 \times 10^{-5}$ | .593 |
| $1.64 \times 10^{-4}$ | 2.63 | $1.46 \times 10^{-4}$ | 1.72 | $1.18 \times 10^{-4}$ | .870 |
| $2.51 \times 10^{-4}$ | 4.03 | $2.28 \times 10^{-4}$ | 3.07 | $1.88 \times 10^{-4}$ | 1.56 |
| $3.38 \times 10^{-4}$ | 6.09 | $3.13 \times 10^{-4}$ | 4.57 | $2.61 \times 10^{-4}$ | 2.67 |
| $4.26 \times 10^{-4}$ | 6.80 | $3.99 \times 10^{-4}$ | 5.99 | $3.41 \times 10^{-4}$ | 3.77 |

The reaction of 8-quinolinol with diphenyl phosphate was also studied in chlorobenzene ($D = 5.62$) and in a 1:4 mixture of acetonitrile and $o$-dichlorobenzene having a dielectric constant of about 15. Neither system could be analyzed using the method of Kolthoff and Bruckenstein. In chlorobenzene the deviation was larger than in $o$-dichlorobenzene, as would be expected since the lower dielectric constant of the former solvent should increase the tendency toward formation of higher ionic aggregates. The data obtained in the mixed solvent
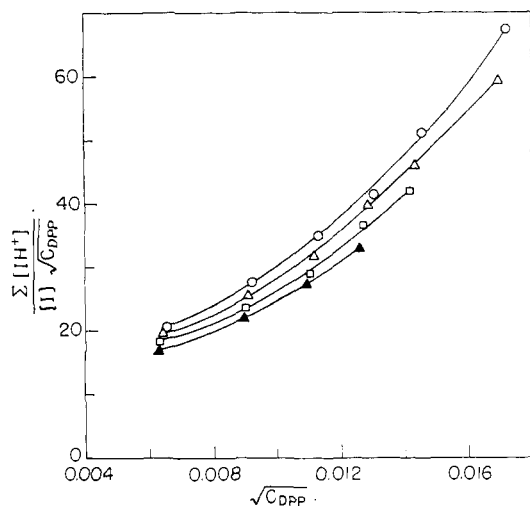
Fig. 4.—Plot of equation 5 for the reaction of 8-quinolinol with diphenyl phosphate in a 1:4 acetonitrile-$o$-dichlorobenzene mixture;   concentration of basic form of indicator $\times$ $10^5$, $M$; $\bigcirc$ = 1.00, $\triangle$ = 2.00, $\square$ = 3.00, $\blacktriangle$ = 4.00.

are plotted according to equation 5 in Fig. 4. Even in this system the lines are somewhat curved, and it is interesting to note that they are much more closely spaced than in $o$-dichlorobenzene (Fig. 2), indicating an increase in the importance of $K_{HX}$ relative to the second term under the square root in equation 5. If the lowest slopes in Figs. 2 and 4 are taken as rough measures of $K_i^{IHX}$, it is seen that addition of acetonitrile to $o$-dichlorobenzene causes a decrease in $K_i^{IHX}$ from about 6000 to 2000. Both these changes undoubtedly are due primarily to the basic character of acetonitrile.[6,7]

The failure of 8-quinolinol as an indicator was attributed to its low molar absorptivity which necessitated the use of relatively high indicator concentrations. Therefore, efforts were made to find an indicator base with more intense absorption. 4-Dimethylamino-4'-nitrostilbene (DNS), an indicator studied by Higuchi, et al.,[8] seemed to show promise, and its reaction with diphenyl phosphate in $o$-dichlorobenzene was studied. The basic form of DNS in this solvent was found to have a molar absorptivity of 2.60 $\times$ $10^4$ liters/mole cm. at 445 m$\mu$ where the protonated indicator does not absorb. This high molar absorptivity made it possible to keep the indicator concentration below 9.94 $\times$ $10^{-6}$ while the concentration of diphenyl phosphate ranged from 7.14 $\times$ $10^{-4}$ to 1.00 $\times$ $10^{-2}$. The large excess of acid was necessitated by the relatively weak basicity of the indicator. Fig. 5 is a plot of equation 5 using the data from the reaction of DNS with diphenyl phosphate in $o$-dichlorobenzene. The lines corresponding to different values of [I] are practically fused into one, showing that

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

From the lowest slope of the lines we estimate

(6) E. J. Forman, Ph.D. Thesis, Massachusetts Institute of Technology, 1957.

(7) (a) G. J. Janz and S. S. Danyluk, J. Am. Chem. Soc., 81, 3846 (1959);  (b) ibid., 81, 3850 (1959);  (c) ibid., 81, 3854 (1959).

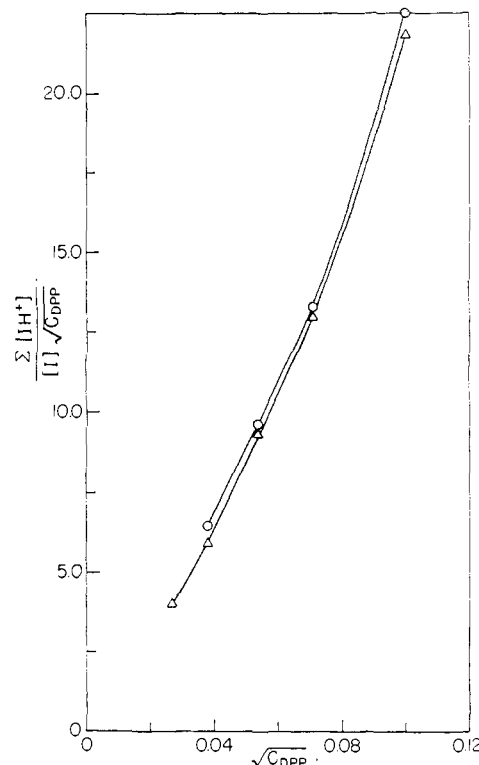(8) T. Higuchi, J. A. Feldman and C. Eehm, Anal. Chem., 28, 1120 (1956).



Fig. 5.—Plot of equation 5 for the reaction of 4-dimethylamino-4'-nitrostilbene and diphenyl phosphate in $o$-dichlorobenzene;   concentration of basic form of indicator, $M$: $\bigcirc$ = 1.00 $\times$ $10^{-6}$, $\triangle$ = 2.00 to 6.00 $\times$ $10^{-6}$ $M$ all give the same curve.

$K_i^{IHX}$ $\approx$ 200. This shows that DNS is a much weaker base than 8-quinolinol, the corresponding estimate for the reaction of the latter base with diphenyl phosphate in $o$-dichlorobenzene being 6000. The curvature of the lines in Fig. 5 is probably in part due to the high acid concentration which contributes to the ionic strength and increases the tendency toward formation of higher ionic aggregates. An alternate explanation will be discussed later.

In view of the weak basicity of DNS it was hoped that substitution of a stronger acid, such as hydrogen chloride, for diphenyl phosphate would give a system to which the method of Kolthoff and Bruckenstein could be applied. The reaction between DNS and hydrogen chloride was studied in $o$-dichlorobenzene at indicator concentrations between 1.24 $\times$ $10^{-6}$ and 9.94 $\times$ $10^{-6}$. In this instance it was possible to keep the acid concentration below 5.00 $\times$ $10^{-4}$, corrections being made for the acid consumed by the indicator. Fig. 6 shows the resulting plot according to equation 5. The lines are relatively straight but they are not parallel, and it is, therefore, again impossible to obtain significant slopes and intercepts. In a plot of

$$\log \frac{\Sigma[IH^+]}{[I]} \text{ versus } \log C_{HCl} \text{ (Fig. 7)}$$

the lines have a slope of 1.10, indicating that formation of multiple ions occurs despite the low ionic strength of the solution. It is interesting to note, however, that the slopes are independent of the
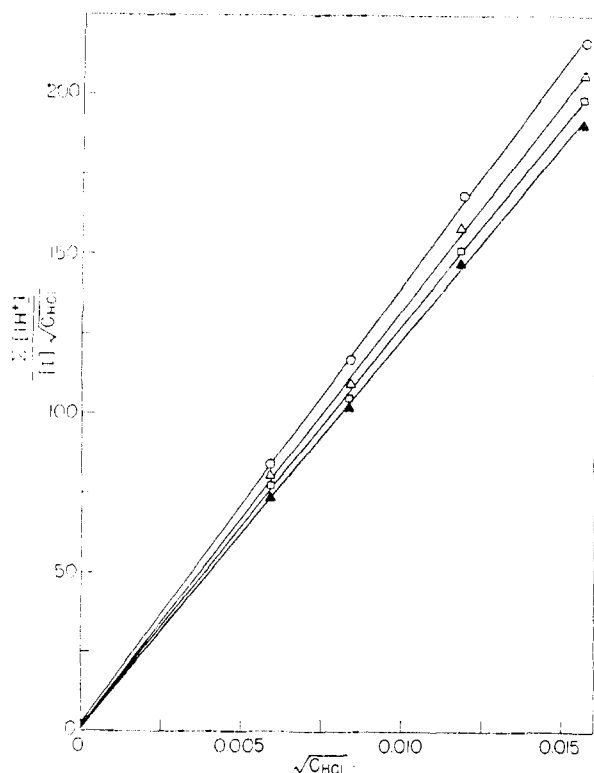
Fig. 6.—Plot of equation 5 for the reaction of 4-dimethyl-amino-4'-nitrostilbene with hydrogen chloride in o-dichlorobenzene; concentration of basic form of indicator × $10^6$, $M$: O = 1.00, △ = 1.50, □ = 2.00, ▲ = 2.50.
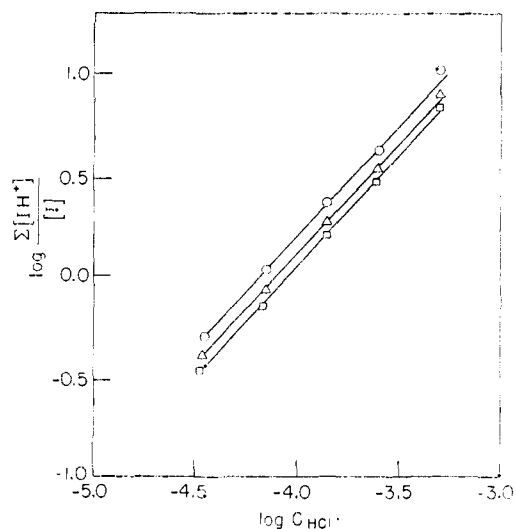


Fig. 7.—Reaction between 4-dimethylamino-4'-nitrostilbene and hydrogen chloride in o-dichlorobenzene as a function of total indicator concentration; DNS concentrations × $10^6$ $M$: O = 1.24, △ = 4.97, □ = 9.94.

total indicator concentration, in contrast to Fig. 3. This suggests that formation of higher ionic aggregates may not be the chief cause of the failure of the HCl–DNS system to obey the theory of Kolthoff and Bruckenstein. An alternate explanation is suggested by the recent study by Van Looy and Hammett[9] of the behavior of sulfuric acid in nitromethane. These authors found that three molecules of sulfuric acid react with each molecule of indicator base when the acid concentration is >0.1 $M$. As the acidity is decreased, reactions involving only one acid molecule begin to occur. Van Looy and Hammett conclude that the lack of hydrogen-bonding capability of nitromethane necessitates association of the indicator salt with acid molecules, and they suggest that the solvating power of a solvent may be more important than its dielectric constant (the dielectric constant of nitromethane is as high as 38) in determining the course of acid-base reactions.

Participation of more then one hydrogen chloride molecule in part of the reactions with DNS would lead to slopes >1 in Fig. 7 without necessitating the assumption of multiple ion formation. (In corresponding plots of reactions of sulfuric acid in nitromethane, Van Looy and Hammett found slopes as large as 3.) It is also quite possible that the same phenomenon plays a role in the reaction of diphenyl phosphate with DNS in o-dichlorobenzene where the maximum acid concentration was as high as

(9) H. Van Looy and L. P. Hammett, J. Am. Chem. Soc., 81, 3872 (1959).

$10^{-2} M$. There, plots of

$$\log \frac{\Sigma[\text{IH}^+]}{[\text{I}]} \text{ versus } \log C_{DPP}$$

also gave slopes independent of the total indicator concentration. The slope increased from 1.04 in $10^{-3} M$ acid to 1.27 in $10^{-2} M$ acid.

The tendency for more than one acid molecule to react with a monoacidic indicator base probably depends strongly on the structure of the acid and the corresponding anion. A diphenyl phosphate anion would appear to be more easily solvated in an aromatic solvent than a chloride ion. Hence hydrogen chloride may well begin to associate with the indicator salt at a lower acid concentration level than does diphenyl phosphate. In general, association of acid molecules with salts would be expected to begin at lower acid concentrations in lower dielectric constant solvents, assuming constant associating power. This phenomenon could, therefore, be important at much lower concentration levels in o-dichlorobenzene ($D = 9.93$) than in nitromethane ($D = 38$).

Although the experiences with solvents of higher dielectric constant made it seem very unlikely that the method of Kolthoff and Bruckenstein would be applicable to acid-base systems in benzene ($D = 2.28$), one experiment was performed in this solvent for the purpose of comparison. The reaction of hydrogen chloride and DNS was chosen because of the feasibility of working with very low concentrations. The absorption peak of the basic form of the indicator occurred at 427.5 mμ in benzene and had a molar absorptivity of 2.89 × $10^4$ liters/mole cm.

The hydrogen chloride concentrations used ranged from 2.29 × $10^{-5}$ to 3.20 × $10^{-4}$ while the highest indicator concentration was 7.77 ×$10^{-6}$. Fig. 8 shows the plot of the data for this system according to equation 5. As expected, a strong curvature is observed at higher values of the acid concentration. At low acidity, however, there is a pro-

nounced curvature in the opposite direction, and 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 in glacial acetic acid[10] suggests that the new effect may be caused by the formation of a hydrogen-bonded complex between protonated and unprotonated indicator species. The hydrogen bond seems to affect the absorption spectrum of the basic form, causing an apparent decrease in the ratio of acidic to basic form of the indicator. It probably also decreases the basic strength of the indicator, thereby decreasing the extent of reaction with the acid. Such effects should be most marked at low values of [I] and $C_{HCl}$, as observed. This new finding serves to emphasize that a multitude of association reactions occur even at very low concentrations in a solvent such as benzene.

## Conclusions

The experimental data indicate that an application of the photometric method of Kolthoff and Bruckenstein to acid–base systems in non-acidic solvents of low dielectric constant is made difficult or impossible by a variety of complicating association reactions. One of these is multiple ion formation, a phenomenon observed even in glacial acetic acid. Another interfering reaction appears to be participation of acid molecules in solvating the indicator salt. It is interesting to note that the early results of La Mer and Downes[11] in benzene might be explained assuming that more than one acid molecule reacts with the indicator base. Finally, association of protonated and unprotonated indicator species seems to occur at least in benzene. It is understandable that association reactions play a more important role in aromatic solvents than in glacial acetic acid, since the latter solvent is more effective as a solvating agent. Very interesting comparisons of acid–base

(10) L. E. I. Hummelstedt and D. N. Hume, *Anal. Chem.*, **32**, 576 (1960).

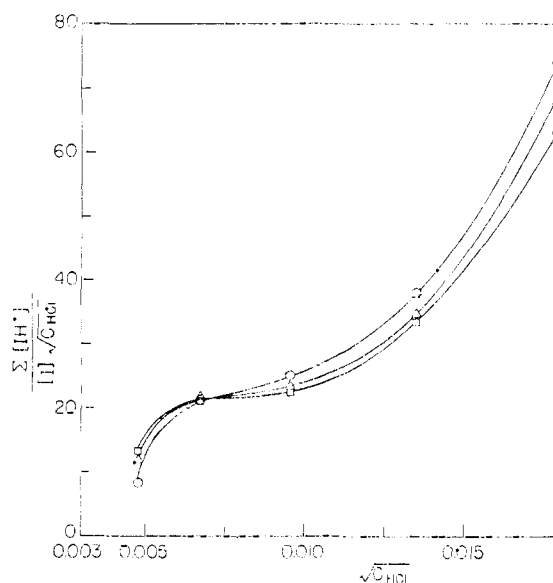(11) V. K. La Mer and H. C. Downes, *J. Am. Chem. Soc.*, **55**, 1840 (1933).



Fig. 8.—Plot of equation 5 for the reaction of 4-dimethylamino-4'-nitrostilbene and hydrogen chloride in benzene; concentrations of basic form of indicator $\times$ 10$^6$, $M$: O = 1.00, $\triangle$ = 2.00, $\square$ = 3.00.

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. Apparently there is no hope for a successful application in solvents such as benzene where association phenomena are very pronounced. 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 from association reactions.