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THE DETERMINATION OF OVERLAPPING DISSOCIATION CONSTANTS FOR DIBASIC ACIDS

AND

ZIRCONIUM CHLORANILATE COMPLEXES

by

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PREFACE

During a study of complexing agents for zirconium it was found that chloranilic acid possessed promise as a colorimetric reagent for that element. It was therefore decided to determine the formulae and stability of the zirconium chloranilate complexes as a matter of practical and theoretical interest. A determination of the acid constants of chloranilic acid was required because of its appreciable ionization in the solutions that were employed. In the course of this determination a spectrophotometric method was developed which appeared to have general applicability for dibasic acids with overlapping acid constants. In order to test this method it was also used in two other similar cases.

Consequently, the thesis is presented in two distinct parts. The first part is devoted to the determination of overlapping acid constants and the second to the formulae and stability constants of the zirconium chloranilate complexes.

TABLE OF CONTENTS

PART TWO

PART ONE

THE SPECTROPHOTOMETRIC DETERMINATION OF OVERLAPPING DISSOCIATION CONSTANTS FOR DIBASIC ACIDS

INTRODUCTION

The ionization equilibria of dibasic acids are usually discussed in terms of thermodynamic ionization constants, K_1 and K_2, in which

$$K_1 = \frac{a_{H^+} \cdot a_{HA}}{a_{H_2A}} \quad \text{and} \quad K_2 = \frac{a_{H^+} \cdot a_A}{a_{HA}}$$

where a_{H^+} is the activity of hydrogen ion and a_{H_2A}, a_{HA} and a_A are respectively the activities of the undissociated, singly-dissociated and doubly-dissociated forms of the dibasic acid.* Experimentally thermodynamic ionization constants are seldom determined directly due to the effects of ionic strength. In spectrophotometric work only the concentrations of the forms H_2A, HA and A are observed although the activity of hydrogen ion is, of course, observed in terms of pH. Therefore, in discussing the problem of determining overlapping ionization constants it seems preferable to express the equilibria in terms of "acidity constants"** in the following manner:

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*In the present representation charges are not attached to the symbols H_2A, HA and A for the sake of brevity and in order not to exclude from consideration the conjugate acids derived from ampholytes and dibasic bases.

**The term "acidity constant" thus defined follows the terminology used by J.N. Brønstad and C.V. King, Z. Physik. Chem. 130, 700 (1927).

$$k_1 = \frac{a_{H+}[HA]}{[H_2A]} \text{ and } k_2 = \frac{a_{H+}[A]}{[HA]}$$

where k_1 and k_2 are the acidity constants, and $[H_2A]$, $[HA]$ and $[A]$ are the molarities of the forms H_2A, HA and A. Such acidity constants should be true constants provided that the ionic strength is maintained at a low, fixed value and the temperature is kept constant. The acidity constants are, of course, related to the thermodynamic ionization constants in the following manner:

$$k_1 = \frac{\gamma_{H_2A}}{\gamma_{HA}} \cdot K_1 \text{ and } k_2 = \frac{\gamma_{HA}}{\gamma_{A}} \cdot K_2$$

where γ_{H_2A}, γ_{HA} and γ_A are the activity coefficients of the forms H_2A, HA and A at the particular ionic strength that is used. It is convenient for simplicity to use the symbol "a" in place of a_{H+} for the activity of hydrogen ion.

In a series of solutions of constant ionic strength, constant temperature and constant total concentration "c" of the dibasic acid and its ions, the equations expressing the equilibria in terms of acidity constants may be combined to yield the following equations to express the variation of $[H_2A]$, $[HA]$ and $[A]$ with variation in the hydrogen ion activity:

(1) $$[H_2A] = \frac{c}{1 + \frac{k_1}{a} + \frac{k_1k_2}{a^2}}$$

(2) $$[HA] = \frac{\frac{k_1}{a}\, c}{1 + \frac{k_1}{a} + \frac{k_1k_2}{a^2}}$$

$$(3) \qquad [A] = \frac{\frac{k_1k_2}{a^2}}{1 + \frac{k_1}{a} + \frac{k_1k_2}{a^2}}$$

The optical density D of such solutions after correction for the light absorption of buffers and other substances that may be present is as follows:

$$(4) \qquad D = L[H_2A]e_1 + L[HA]e_2 + L[A]e_3$$

where L is the inside length of the absorption cell and e_1, e_2 and e_3 are the molar extinction coefficients of H_2A, HA and A, respectively. By combining (1), (2), (3) and (4) one obtains the following expression:

$$(5) \qquad D = \frac{Lc\left[e_1 + \frac{k_1}{a}e_2 + \frac{k_1k_2}{a^2}e_3\right]}{1 + \frac{k_1}{a} + \frac{k_1k_2}{a^2}}$$

The above equation expresses the optical density at a given wave length as a function of hydrogen ion activity. It would seem to offer possibilities for the determination of k_1 and k_2 provided that the acid and its ions had measurable optical densities and e_1, e_2 and e_3 could be determined.

The spectrophotometric determination of e_1, e_2, e_3, k_1 and k_2 of a light-absorbing, dibasic acid is easily accomplished if the species H_2A, HA and A can be quantitatively obtained at appropriate pH's.[1] The problem is somewhat more difficult if the acidity constants k_1 and k_2 overlap, that is, if the species H_2A and A cannot be quantitatively transformed into HA at any pH. In such a case methods involving the potentiometric titration of the dibasic acid may be used.[2,3] However, the determination of k_1 and

k_2 by potentiometric titration in aqueous solutions is difficult or impossible for many sparingly soluble dibasic acids, an example being terephthalic acid.[4] If the dibasic acid is capable of being reversibly oxidized or reduced its acidity constants can be obtained by studying its oxidation or reduction potential as a function of pH in a series of buffered solutions.[5,6]

Since neither of the above potentiometric methods is always applicable, it is of interest to inquire further into the spectrophotometric determination of k_1 and k_2 when k_1 and k_2 overlap. From (2) the fraction of the total acid that is in the form HA is

$$\frac{[HA]}{c} = \frac{\frac{k_1}{a}}{1 + \frac{k_1}{a} + \frac{k_1 k_2}{a^2}} = \frac{1}{\frac{a}{k_1} + 1 + \frac{k_2}{a}} .$$

The maximum value of $\frac{[HA]}{c}$ is observed when

$$\frac{d\,\frac{[HA]}{c}}{da} = \frac{-\left(\frac{1}{k_1} - \frac{k_2}{a^2}\right)}{\left(\frac{a}{k_1} + 1 + \frac{k_2}{a}\right)^2} = 0$$

from which the relation, $a = \sqrt{k_1 k_2}$, can be obtained directly. The maximum obtainable value of $\frac{[HA]}{c}$ is therefore

$$(6) \qquad \max.\frac{[HA]}{c} = \frac{\sqrt{\frac{k_1}{k_2}}}{1 + \sqrt{\frac{k_1}{k_2}} + 1} = \frac{\sqrt{\frac{k_1}{k_2}}}{2 + \sqrt{\frac{k_1}{k_2}}} .$$

Table 1 contains maximum obtainable values of $\frac{[HA]}{c}$ calculated from (6) and sample values of $\frac{k_1}{k_2}$.

Table 1

Values of Max. $\frac{[HA]}{c}$ Calculated from Equation 6

Sample values of $\frac{k_1}{k_2}$	Max. $\frac{[HA]}{c}$ in per cent
100,000.	99.37
10,000.	98.04
1,000.	94.05
300.	89.65
100.	83.33
50.	77.95
25.	71.43
10.	61.25
5.	52.79
2.	41.42

The spectrophotometric determination of k_1 and k_2 implicitly requires the evaluation of e_2 which can only be done by direct measurement if $\frac{[HA]}{c}$ can be made close to unity at some pH. Thus the evaluation of e_2, k_1 and k_2 would appear to require the rather extensive use of successive approximations for their determination in cases for which $\frac{k_1}{k_2}$ is of the order of 300 or less.

HISTORICAL

In the past the spectrophotometric determination of overlapping acid constants for dibasic acids has always involved approximations. The procedure has been to study the optical density as a function of pH at a constant total concentration of the dibasic acid and constant cell length. One method has been to use the method of successive approximations to fit values of e_2, k_1 and k_2 to the data at each wave length.[7] Another method originally developed by Vlès and Gex[8,9,10,11] has had a number of recent applications in studies by various workers of the acid constants of pyrocatechol,[12] of adrenaline,[13] of tyrosine[14] and of l-dihydroxyphenylalanine.[15] A review article has been written by Vlès[10] in which he has appended a bibliography of earlier applications of the method. The most characteristic feature of the method of Vlès and Gex has been their use of a function $\phi = \frac{D'}{D}$ in which D' and D were two optical densities in the system to be taken at the same pH but at two different wave lengths. From (5) their ϕ function thus became

$$\phi = \frac{e_1' + \frac{k_1}{a} e_2' + \frac{k_1 k_2}{a^2} e_3'}{e_1 + \frac{k_1}{a} e_2 + \frac{k_1 k_2}{a^2} e_3} .$$

By taking ϕ values at different pH's in pairs they derived equations with which to calculate k_1 and k_2. However, their method required successive approximations for the determination of overlapping k_1 and k_2 because it did not provide any means for the evaluation of the extinction coefficients, e_2 and e'_2 at the two wave lengths. As a consequence their method offered little advantage over the direct application of successive approximations. Furthermore they made a fundamental mistake in the derivation of their equations. In their scheme of material balance, Vlès and Gex (Ref. 8, p. 71) wrote

$$\begin{array}{lcl} H_2A & \rightleftharpoons & H^+ + HA^- \\ 1-\alpha_1 & & \alpha_1(1-\alpha_2) \\ HA^- & \rightleftharpoons & H^+ + A^{-2} \\ \alpha_1(1-\alpha_2) & & \alpha_1\alpha_2 \end{array}$$

where α_1 and α_2 were the degrees of acid ionization of H_2A and HA^-, respectively. They began the derivation of the equations for their method with an incorrect expression for pH in terms of pk_1, namely,

$$pH = pk_1 + \log \frac{1}{1-\alpha_1}$$

which was later changed in a note of Errata (Ref. 9, p. 171) to read

$$pH = pk_1 + \log \frac{\alpha_1}{1-\alpha_1} .$$

Neither of the above expressions was correct. It should have been

$$pH = pk_1 + \log \frac{\alpha_1(1-\alpha_2)}{1-\alpha_1} .$$

The final equations that were used (Ref. 9, p. 74-5) were consequently incorrect, although the effect on the values of k_1 and k_2 thus obtained was possibly not very great.

A similar mistake in Vlès and Gex's treatment of ampholytes (Ref. 8, p. 81-3) has been corrected by Hughes, Jellinek and Ambrose (Ref. 7, p. 418-20). After deriving the correct expressions for the application of Vlès and Gex's method to ampholytes, Hughes and co-workers[7] used the correct expressions to calculate the dissociation constants of nicotinic acid. The use of successive approximations was required. However, the dissociation constants so obtained were in substantial agreement with the values calculated at one wave length by another method of successive approximations.

A derivation of the correct equations for Vlès and Gex's treatment of dibasic acids has been placed in Appendix A. A brief comparison of values calculated from these equations and from the equations originally derived by Vlès and Gex has also been included in the same place.

Schwarzenbach and Suter used spectrophotometric measurements to confirm their potentiometric measurements of the overlapping acid constants of dibasic quinone-like compounds.[6] In the spectrophotometric part of their work they plotted optical density versus pH. However, neither in the paper that was published[6] nor in the doctoral thesis[16] from which the paper was derived, did they give any account of the method of calculation that was employed in interpreting the spectrophotometric data.

A colorimetric method has recently been developed by Sacconi for the determination of the acidity constant of a colored monobasic acid for which one or both of its forms cannot be quantitatively obtained in solution.[17]

Sacconi claims that the method is also applicable to colored dibasic acids having overlapping acidity constants although the development of the method and its application imply that only one step of dissociation is operative during the determination of the corresponding dissociation constant. Although his method minimizes the effect of the third species in determining k_1 or k_2, an indeterminate error is nevertheless introduced into the determination if $\frac{k_1}{k_2}$ is fairly small. A brief résumé and discussion of his method has been placed in Appendix B.

THEORY OF THE METHOD

Derivation of the Necessary Equations

In the spectrophotometric determination of overlapping k_1 and k_2 by the method to be described buffered solutions of the acid are scanned at constant concentration of the dibasic acid and constant ionic strength, temperature and cell length. The measured optical density is corrected for absorption by the solvent and buffer and plotted against pH at various wavelengths. A wavelength is selected at which the plot of optical density versus pH gives a decided maximum or minimum in the pH range in which the HA species predominates.

In order to illustrate the method and assist in the derivation two synthetic examples of the types of curves sought are presented in Figures 1 and 2. These curves were calculated from (5) using $k_1 = 5 \times 10^{-5}$ and $k_2 = 2 \times 10^{-6}$. The values of Lce_1, Lce_2 and Lce_3 that were used in each case are indicated below the figures. The values of D so calculated are listed in the third and fourth columns of Table 11 in Appendix A. In many actual cases the curves show more favorable maxima or minima than are given in these two illustrations.

For any curve of this type the pH for any point on the curve can be expressed as follows:

(7) $\quad \mathrm{pH} = -\log a_o + \Delta \quad$ and $a = a_o\, 10^{-\Delta}$

where a_o is the hydrogen ion activity at the maximum (or minimum) of the

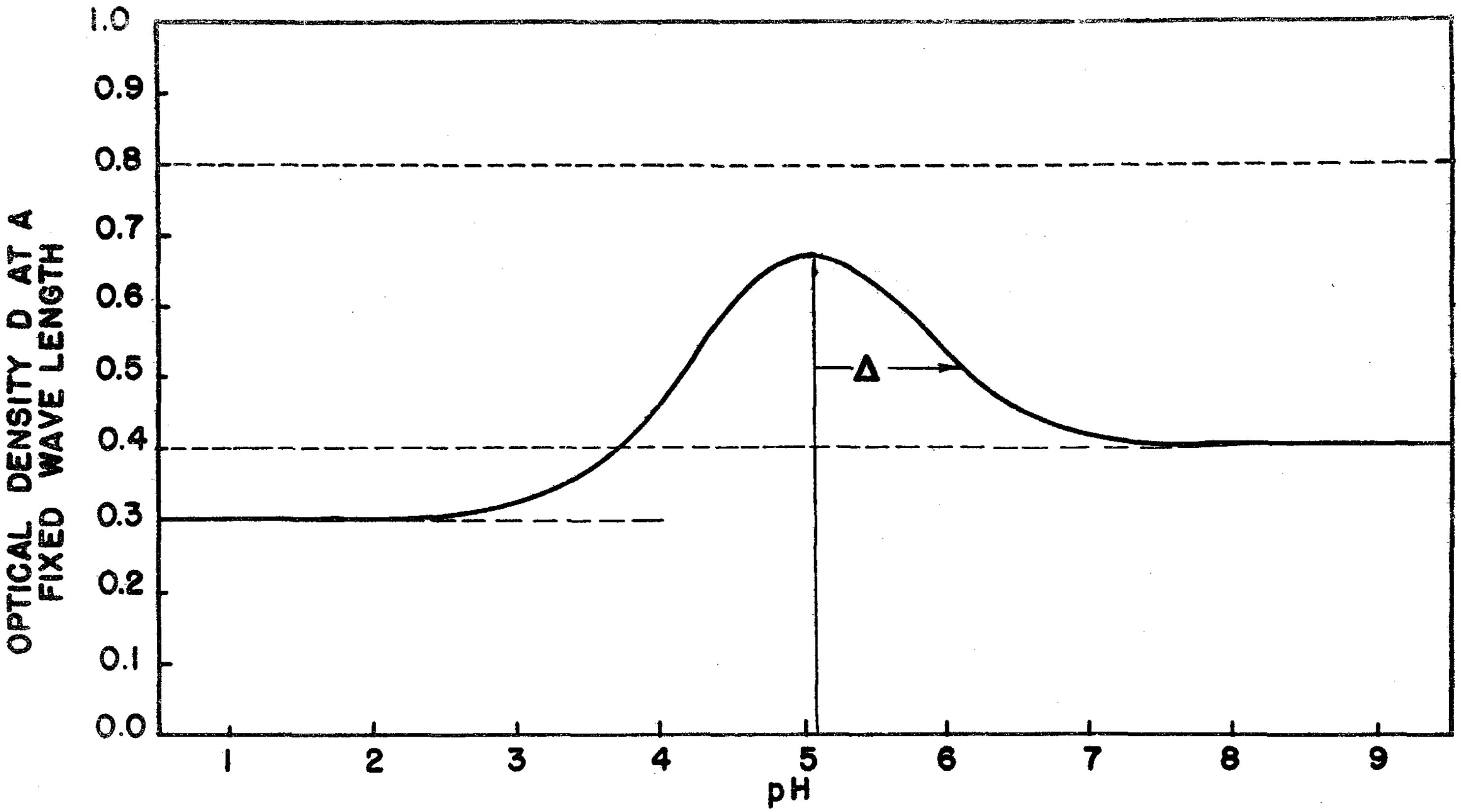

FIG. I PLOT OF OPTICAL DENSITY VS. pH. $K_1=5\times10^{-5}$; $K_2=2\times10^{-6}$. THE VALUES OF $Lc\epsilon_1$, $Lc\epsilon_2$, AND $Lc\epsilon_3$ ARE 0.300, 0.800, 0.400, RESPECTIVELY, FOR WHICH DOTTED HORIZONTAL LINES HAVE BEEN DRAWN.

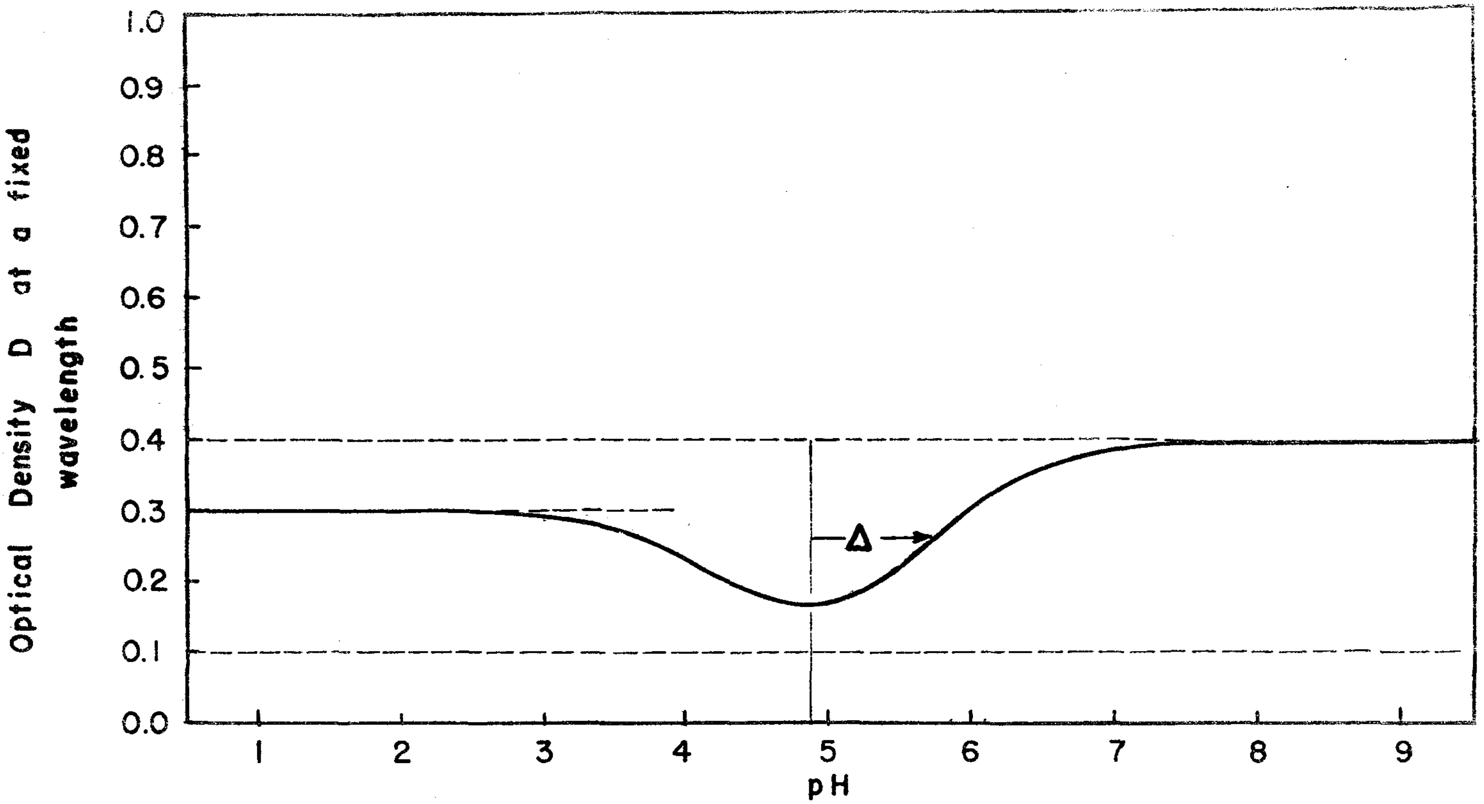

Fig. 2 Plot of Optical Density vs pH. $k_1 = 5 \times 10^{-5}$; $k_2 = 2 \times 10^{-6}$. The values of $Lc\epsilon_1$, $Lc\epsilon_2$ and $Lc\epsilon_3$ are 0.300, 0.100 and 0.400, respectively, for which dotted horizontal lines have been drawn in the figure.

curve as indicated by the vertical line in the figures. The quantity Δ is the horizontal distance from this vertical line to the curve. The term Δ has positive values to the right of the maximum and negative values to the left. The quantity a_o is experimentally measurable for each curve. It remains to be shown what relation it has to the other constants of the curve.

If the plot of optical density versus pH has a maximum (or minimum) it will occur where $\frac{dD}{d\ln a} = 0$ and $\frac{dD}{da} = 0$. Using (5), namely

$$D = \frac{Lc\left[e_1 + \frac{k_1}{a}e_2 + \frac{k_1k_2}{a^2}e_3\right]}{1 + \frac{k_1}{a} + \frac{k_1k_2}{a^2}},$$

$\frac{dD}{da}$ is as follows:

$$\frac{dD}{da} = \frac{Lc\,k_1}{a^2\left[1 + \frac{k_1}{a} + \frac{k_1k_2}{a^2}\right]^2}\left[e_1 - e_2 + \frac{k_1k_2}{a^2}(e_2 - e_3) + 2\frac{k_2}{a}(e_1 - e_3)\right].$$

Hence at the maximum of the curve of D vs. pH the following equation holds true:

$$e_1 - e_2 + \frac{k_1k_2}{a^2}(e_2 - e_3) + 2\frac{k_2}{a}(e_1 - e_3) = 0 \quad .$$

Since the hydrogen ion activity at this point is defined as a_o, the latter equation is better expressed as follows:

$$(8) \qquad e_1 - e_2 + \frac{k_1k_2}{a_o^2}(e_2 - e_3) + 2\frac{k_2}{a_o}(e_1 - e_3) = 0$$

Hence (8) relates a_o to the other constants of the curve, namely, the acid constants and the extinction coefficients.

Expressing the hydrogen ion activity at any point on the curve by (7), namely $a = a_o 10^{-\Delta}$, equation (5) becomes

$$(9) \qquad D = \frac{Lo\left[e_1 + \frac{k_1}{a_o} 10^{+\Delta} e_2 + \frac{k_1 k_2}{a_o^2} 10^{+2\Delta} e_3\right]}{1 + \frac{k_1}{a_o} 10^{+\Delta} + \frac{k_1 k_2}{a_o^2} 10^{+2\Delta}} .$$

For very high values of the hydrogen ion activity and consequently large negative values of Δ, the dibasic acid is entirely in the form H_2A. Hence the left-hand limit D_1 of the curve of D versus pH is

$$(10) \qquad D_1 = Loe_1 \quad .$$

A similar condition applies for low values of (a) and the right-hand limit of the curve is

$$(11) \qquad D_3 = Loe_3 \quad .$$

For example, in Figure 1, $D_1 = 0.300$ and $D_3 = 0.400$. At the maximum of the curve, $a = a_o$ and from equation (9)

$$(12) \qquad D_m = \frac{Lo\left[e_1 + \frac{k_1}{a_o} e_2 + \frac{k_1 k_2}{a_o^2} e_3\right]}{1 + \frac{k_1}{a_o} + \frac{k_1 k_2}{a_o^2}}$$

where D_m represents the maximum optical density at a given wavelength. The quantities D_1, D_m and D_3 can usually be measured with a good degree of accuracy.

Inasmuch as e_2 is not a directly measurable quantity it is desirable to eliminate it from (8), (9) and (12). For this purpose the following terms are defined:

(13) $$\alpha_1 = \frac{D_1}{D_m}$$

(14) $$\alpha_3 = \frac{D_3}{D_m} \; .$$

Substituting from (10) and (12) into (13) one obtains

(15) $$\alpha_1 = \frac{1 + \frac{k_1}{a_o} + \frac{k_1 k_2}{a_o^2}}{1 + \frac{k_1}{a_o} \cdot \frac{e_2}{e_1} + \frac{k_1 k_2}{a_o^2} \cdot \frac{e_3}{e_1}} \; .$$

From (10), (11), (13) and (14)

(16) $$\frac{e_3}{e_1} = \frac{D_3}{D_1} = \frac{\alpha_3}{\alpha_1} \; .$$

Hence (15) becomes

(17) $$\alpha_1 = \frac{1 + \frac{k_1}{a_o} + \frac{k_1 k_2}{a_o^2}}{1 + \frac{k_1}{a_o} \quad \frac{e_2}{e_1} \quad \frac{k_1 k_2}{a_o^2} \quad \frac{\alpha_3}{\alpha_1}} \; .$$

Rearranging (17) one obtains

(18) $$\frac{e_1}{e_2} = \frac{\alpha_1}{1 + (1-\alpha_1)\frac{a_o}{k_1} + (1-\alpha_3)\frac{k_2}{a_o}} \; .$$

From (16) one obtains

(19) $$\frac{e_3}{e_2} = \frac{\alpha_3}{\alpha_1} \cdot \frac{e_1}{e_2} \; .$$

A combination of (18) and (19) gives

$$\frac{e_3}{e_2} = \frac{\alpha_3}{1 + (1 - \alpha_1)\frac{a_o}{k_1} + (1 - \alpha_3)\frac{k_2}{a_o}} . \tag{20}$$

Division of (8) by e_2 yields

$$\frac{e_1}{e_2} - 1 + \frac{k_1 k_2}{a_o^2}\left(1 - \frac{e_3}{e_2}\right) + 2\,\frac{k_2}{a_o}\left(\frac{e_1}{e_2} - \frac{e_3}{e_2}\right) = 0 \quad . \tag{21}$$

The quantity e_2 can now be eliminated from (21) by substitution from (18) and (20).

$$\frac{\alpha_1}{1 + (1-\alpha_1)\frac{a_o}{k_1} + (1-\alpha_3)\frac{k_2}{a_o}} - 1$$

$$+ \frac{k_1 k_2}{a_o^2}\left(1 - \frac{\alpha_3}{1 + (1-\alpha_1)\frac{a_o}{k_1} + (1-\alpha_3)\frac{k_2}{a_o}}\right)$$

$$+ \frac{2\,k_2}{a_o}\left(\frac{\alpha_1 - \alpha_3}{1 + (1-\alpha_1)\frac{a_o}{k_1} + (1-\alpha_3)\frac{k_2}{a_o}}\right) = 0 \quad .$$

By eliminating fractions and rearranging terms the latter equation can be put in the form

$$(1-\alpha_3)\frac{k_1 k_2^2}{a_o^3} + (1-\alpha_3)\frac{k_1 k_2}{a_o^2} + (\alpha_1 - \alpha_3)\frac{k_2}{a_o} - (1-\alpha_1) - (1-\alpha_1)\frac{a_o}{k_1} = 0 \ .$$

Multiplying the latter expression by $a_o^3\,k_1$ and combining terms gives

$$(1-\alpha_3)(k_1k_2)^2 + a_o\left[(1-\alpha_3)k_1 + a_o(\alpha_1 - \alpha_3)\right](k_1k_2) - a_o^3(1-\alpha_1)(k_1 + a_o) = 0 \tag{22}$$

Equation (22) is a quadratic in the quantity (k_1k_2) but k_1 also appears in it separately. If one more relation can be obtained relating k_1 and k_2 to measured quantities, it should be possible to determine both.

Equation (9) can be employed for the latter purpose since D at any point on the curve is a measurable quantity as is also Δ after a_o has been determined. However, it is again necessary to eliminate e_2. For this purpose there is defined the quantity

$$(23) \qquad \beta = \frac{D}{D_m} = \frac{D}{Lce_2} \cdot \frac{Lce_2}{D_m} .$$

Dividing (9) by lce_2 gives

$$\frac{D}{Lce_2} = \frac{\frac{e_1}{e_2} + \frac{k_1}{a_o}10^{+\Delta} + \frac{k_1k_2}{a_o^2}10^{+2\Delta} \cdot \frac{e_3}{e_2}}{1 + \frac{k_1}{a_o}10^{+\Delta} + \frac{k_1k_2}{a_o^2}10^{+2\Delta}} .$$

Substituting from (18) and (20) and rearranging, this equation yields

$$(24) \quad \frac{D}{Lce_2} = \frac{\alpha_1 + \left[1 - \alpha_1 + \frac{k_1}{a_o} + (1-\alpha_3)\frac{k_1k_2}{a_o^2}\right]10^{+\Delta} + \alpha_3\frac{k_1k_2}{a_o^2}10^{+2\Delta}}{\left[1 + \frac{k_1}{a_o}10^{+\Delta} + \frac{k_1k_2}{a_o^2}10^{+2\Delta}\right]\left[1 + (1-\alpha_1)\frac{a_o}{k_1} + (1-\alpha_3)\frac{k_2}{a_o}\right]}$$

Similarly division of (12) by Lce_2 yields

$$\frac{D_m}{Lce_2} = \frac{\frac{e_1}{e_2} + \frac{k_1}{a_o} + \frac{k_1k_2}{a_o^2} \cdot \frac{e_3}{e_2}}{1 + \frac{k_1}{a_o} + \frac{k_1k_2}{a_o^2}}$$

and substitution from (18) and (20) gives

$$\frac{D_m}{Lce_2} = \frac{\alpha_1 + \left[1 + (1-\alpha_1)\frac{a_o}{k_1} + (1-\alpha_3)\frac{k_2}{a_o}\right]\frac{k_1}{a_o} + \alpha_3\frac{k_1k_2}{a_o^2}}{\left[1 + \frac{k_1}{a_o} + \frac{k_1k_2}{a_o^2}\right]\left[1 + (1-\alpha_1)\frac{a_o}{k_1} + (1-\alpha_3)\frac{k_2}{a_o}\right]} .$$

The last equation can be simplified to give

$$(25) \qquad \frac{D_m}{Lce_2} = \frac{1}{1 + (1-\alpha_1)\frac{a_o}{k_1} + (1-\alpha_3)\frac{k_2}{a_o}} \quad .$$

The division of (24) by (25) gives the quantity β:

$$(26) \qquad \beta = \frac{\alpha_1 + \left[1-\alpha_1 + \frac{k_1}{a_o} + (1-\alpha_3)\frac{k_1k_2}{a_o^2}\right]10^{+\Delta} + \alpha_3\frac{k_1k_2}{a_o^2}10^{+2\Delta}}{1 + \frac{k_1}{a_o}10^{+\Delta} + \frac{k_1k_2}{a_o^2}10^{+2\Delta}} .$$

Cross multiplication of (26) gives

$$(27) \qquad k_1 = \frac{a_o}{(1-\beta)}\left[(\beta-\alpha_1)10^{-\Delta} - 1 + \alpha_1 + \left[(\beta-\alpha_3)10^{+\Delta} - 1 + \alpha_3\right]\frac{k_1k_2}{a_o^2}\right] .$$

Combining (27) with (22) permits one to solve for k_1 and (k_1k_2) in terms of measurable quantities.

In order to simplify (22) and (27) for combination, it is convenient to introduce the following terms:

$$(28) \qquad \theta = \frac{1-\alpha_1}{1-\alpha_3}$$

$$(29) \qquad (1-\beta)\rho_1 = (\beta-\alpha_1)10^{-\Delta} + \alpha_1 - \beta$$

$$(30) \qquad (1-\beta)\rho_3 = (\beta-\alpha_3)10^{+\Delta} + \alpha_3 - \beta \quad .$$

Division of (22) by $(1-\alpha_3)$ yields the following equation:

$$(k_1k_2)^2 + a_o\left[k_1 + a_o\left(1 - \left(\frac{1-\alpha_1}{1-\alpha_3}\right)\right)\right](k_1k_2) + a_o^2\left(\frac{1-\alpha_1}{1-\alpha_3}\right)\left[k_1 + a_o\right] = 0 \quad .$$

Substitution of (28) into the above equation gives

$$(31) \qquad (k_1k_2)^2 + a_o\left[k_1 + a_o(1-\theta)\right](k_1k_2) - a_o^2\theta\left[k_1 + a_o\right] = 0 \quad .$$

Substitution of (29) and (30) into (27) yields

$$k_1 = \frac{a_o}{(1-\beta)}\left[(1-\beta)\rho_1 - 1 + \beta + \left[(1-\beta)\rho_3 - 1 + \beta\right]\frac{k_1k_2}{a_o^2}\right]$$

$$(32) \qquad k_1 = a_o\left[\rho_1 - 1 + (\rho_3 - 1)\frac{k_1k_2}{a_o^2}\right] = a_o\rho_1 - a_o + (\rho_3 - 1)\frac{k_1k_2}{a_o}$$

After substituting (32) into (31) there results

$$(k\ k\ )^2 + a_o\left[a_o\rho_1 - a_o + (\rho_3 - 1)\frac{k_1k_2}{a_o} + a_o - a_o\theta\right](k_1k_2)$$

$$- a_o^3\theta\left[a_o\rho_1 - a_o + (\rho_3 - 1)\frac{k_1k_2}{a_o} + a_o\right] = 0$$

which simplifies to the following equation

$$(33) \qquad (k_1k_2)^2 + a_o^2\left[\frac{\rho_1}{\rho_3} - \theta\right](k_1k_2) - \theta\frac{\rho_1}{\rho_3}a_o^4 = 0 \ .$$

A further simplifying substitution is

$$(34) \qquad \phi = \frac{\rho_1}{\rho_3} = \frac{(\beta - \alpha_1)10^{-\Delta} + \alpha_1 - \beta}{(\beta - \alpha_3)10^{+\Delta} + \alpha_3 - \beta} = -\left(\frac{\beta - \alpha_1}{\beta - \alpha_3}\right)10^{-\Delta}$$

Substituting ϕ for $\frac{\rho_1}{\rho_3}$ in (33) one obtains

$$(35) \qquad (k_1k_2)^2 + a_o^2(\phi - \theta)(k_1k_2) - \phi\ \theta a_o^4 = 0 \ .$$

On solving (35) for (k_1k_2) one obtains

$$k_1k_2 = \frac{1}{2}\left[a_o^2(\theta - \phi) \pm \sqrt{a_o^4(\phi - \theta)^2 + 4\phi\theta a_o^4}\right]$$

$$(36) \qquad k_1k_2 = \frac{a_o^2}{2}\left[\theta - \phi \pm (\phi + \theta)\right] \ .$$

Substitution of (13), (14) and (23) into the two expressions of (36) gives

$$(37) \qquad k_1k_2 = a_o^2\,\theta = a_o^2\left(\frac{1-\alpha_1}{1-\alpha_3}\right) = a_o^2\left(\frac{D_m - D_1}{D_m - D_3}\right)$$

and

$$(38) \qquad k_1k_2 = -a_o^2\,\phi = + a_o^2\left(\frac{\beta-\alpha_1}{\beta-\alpha_3}\right)10^{-\Delta} = a_o^2\left(\frac{D-D_1}{D-D_3}\right)10^{-\Delta}$$

of which (38) must be discarded since it gives negative values for (k_1k_2) whenever D lies between D_1 and D_3. Equation 37 is correct.

The substitution of

$$k_1k_2 = a_o^2\left(\frac{1-\alpha_1}{1-\alpha_3}\right)$$

from (37) into (27) gives the following for k_1:

$$(39)\quad k_1 = \frac{a_o}{(1-\beta)}\left[(\beta-\alpha_1)10^{-\Delta} - 1 + \alpha_1 + \left[(\beta-\alpha_3)10^{+\Delta} - 1 + \alpha_3\right]\left(\frac{1-\alpha_1}{1-\alpha_3}\right)\right]$$

or

$$(40)\quad k_1 = \frac{a_o\left[\,(1-\alpha_3)\;(\beta-\alpha_1)10^{-\Delta} + (1-\alpha_1)\;(\beta-\alpha_3)10^{+\Delta} - 2(1-\alpha_1)\;(1-\alpha_3)\right.}{(1-\beta)\;(1-\alpha_3)}\,.$$

Substitution of (13), (14) and (23) into (40) gives the following expression:

$$(41)\quad k_1 = \frac{a_o\left[(D_m-D_3)\;(D-D_1)10^{-\Delta} + (D_m-D_1)\;(D-D_3)10^{+\Delta} - 2(D_m-D_1)\;(D_m-D_3)\right]}{(D_m-D)\;(D_m-D_3)}\,.$$

The division of (37) by (41) gives k_2, of course, since $\frac{k_1k_2}{k_1} = k_2$. Every quantity in (37) and (41) is experimentally measurable. Therefore, the use of these two equations affords a means of calculating k_1 and k_2 from the experimental data without the use of successive approximations.

A simplification of (37) and (41) is possible for the case in which

$D_1 = D_3$. For this case $\alpha_1 = \alpha_3 = \alpha$ and $D_1 = D_3 = D'$. Thus (37) reduces to

(42) $$k_1 k_2 = a_o^2$$

and (39) gives

$$k_1 = \frac{a_o}{(1-\beta)}\left[(\beta-\alpha)(10^{-\Delta} + 10^{+\Delta}) - 2(1-\alpha)\right]$$

(43) $$k_1 = \frac{a_o}{(D_m-D)}\left[(D-D')(10^{-\Delta} + 10^{+\Delta}) - 2(D_m-D')\right] .$$

Since $10^{-\Delta} + 10^{+\Delta} = 2 \cosh(\Delta \ln 10) = 2 \cosh(2.302585\,\Delta)$

(43) may also be put in the following form:

(44) $$k_1 = \frac{2a_o}{(D_m-D)}\left[(D-D')\cosh(\Delta \ln 10) - (D_m-D')\right] .$$

Hence, (42) and either (43) or (44) are applicable in the case in which $D_1 = D_3$. If a wavelength exists at which $D_1 = D_3 = D'$ the curve of D versus pH should be symmetrical as can be shown by combining (42) and (9) to give

(45) $$D = \frac{\frac{k_1}{a_o}(Lce_2) + 2D' \cosh(\Delta \ln 10)}{\frac{k_1}{a_o} + 2 \cosh(\Delta \ln 10)} .$$

Since $\cosh(\Delta \ln 10)$ is an even function of Δ, the quantity D in (45) is also an even function of Δ. Thus whenever $D_1 = D_3$ the plot of optical density versus pH is symmetrical about the maximum (or minimum) of the curve because Δ is defined as being measured from this point.

The foregoing equations of this section show that the present method for determining k_1 and k_2 involves a measurement of D_m in place of an estimate of e_2. However, having obtained k_1 and k_2 by this method one can calculate e_2, or more conveniently Lce_2, by means of (25). Thus

$$Lce_2 = 1 + (1-\alpha_1)\frac{a_o}{k_1} + (1-\alpha_3)\frac{k_2}{a_o} D_m \quad .$$

Substituting (13) and (14) into the above equation gives

$$(46) \qquad Lce_2 = D_m + (D_m - D_1)\frac{a_o}{k_1} + (D_m - D_3)\frac{k_2}{a_o} \quad .$$

Once k_1 and k_2 have been determined, a curve of D versus pH can be most easily calculated using (50) the derivation of which follows. Equation (9), the general expression for the optical density in terms of a_o and Δ, is

$$D = \frac{Lce_1 + \frac{k_1}{a_o} 10^{+\Delta}(Lce_2) + \frac{k_1 k_2}{a_o^2} 10^{+2\Delta}(Lce_3)}{1 + \frac{k_1}{a_o} 10^{+\Delta} + \frac{k_1 k_2}{a_o^2} 10^{+2\Delta}} \quad .$$

Substituting (10), (11) and (46) into the latter expression gives the following:

$$(47)\ D = \frac{D_1 + \left[\frac{k_1}{a_o} D_m + D_m - D_1 + \frac{k_1 k_2}{a_o^2}(D_m - D_3)\right] 10^{+\Delta} + \frac{k_1 k_2}{a_o^2} 10^{+2\Delta} D_3}{1 + \frac{k_1}{a_o} 10^{+\Delta} + \frac{k_1 k_2}{a_o^2} 10^{+2\Delta}} \quad .$$

Substituting $D_m - D_1 = \frac{k_1 k_2}{a_o^2}(D_m - D_3)$ from (37) into (47)

one obtains

$$(48)\ D = \frac{D_1 + \left[\frac{k_1}{a_o} D_m + 2(D_m - D_1)\right] 10^{+\Delta} + \frac{k_1 k_2}{a_o^2} 10^{+2\Delta} D_3}{1 + \frac{k_1}{a_o} 10^{+\Delta} + \frac{k_1 k_2}{a_o^2} 10^{+2\Delta}} \quad .$$

Rearrangement of (48) gives

$$D = D_1 + \frac{\left[\frac{k_1}{a_o}(D_m-D_1) + 2(D_m-D_1)\right] 10^{+\Delta} + \frac{k_1k_2}{a_o^2}(D_3-D_1)10^{+2\Delta}}{1 + \frac{k_1}{a_o}10^{+\Delta} + \frac{k_1k_2}{a_o^2}10^{+2\Delta}} .$$

Substitution of (37) into the latter expression gives

$$(49)\quad D = D_1 + \frac{(D_m-D_1)\left[\frac{k_1}{a_o} + 2\right] 10^{+\Delta} + (D_m-D_1)\left(\frac{D_3-D_1}{D_m-D_3}\right)10^{+2\Delta}}{1 + \frac{k_1}{a_o}10^{+\Delta} + \left(\frac{D_m-D_1}{D_m-D_3}\right)10^{+2\Delta}} .$$

Factoring (49) one obtains

$$(50)\qquad D = D_1 + (D_m-D_1)\left[\frac{\frac{k_1}{a_o} + 2 + \left(\frac{D_3-D_1}{D_m-D_3}\right)10^{+\Delta}}{\frac{k_1}{a_o} + 10^{-\Delta} + \left(\frac{D_m-D_1}{D_m-D_3}\right)10^{+\Delta}}\right] .$$

After the determination of the final values of k_1 and k_2, the quantity a_o can be calculated from (37) and this value of a_o together with (50) can be used to plot calculated values of D over the whole pH range. The degree of agreement of the calculated curve with the experimental points then gives a graphical indication of the consistency of the data.

The Use of Composite Optical Densities

It sometimes happens that no single wavelength can be found at which the plot of optical density versus pH gives a satisfactory maximum or minimum. Such cases are characterized by having small values for one or both of the quantities $|D_m - D_1|$ and $|D_m - D_3|$ at each wavelength for which a maximum or minimum is observed. However, if one of these quantities is large over a portion of these wavelengths and the other is large over a different portion, it is advantageous to combine the data of these two portions of the spectrum.

The manner in which such data are combined is to take a linear combination of the optical densities at each pH. One thus obtains a "composite optical density" C defined by

$$C = g_1D^1 + g_2D^2 + g_3D^3 + \dots \tag{51}$$

where the numbers designate the wavelengths used and the g's are constants chosen in such a manner that the curve of C versus pH has the most favorable maximum or minimum. The "composite extinction coefficients" E_1, E_2, and E_3 for H_2A, HA and A, respectively, are similarly

$$E_1 = g_1e_1^1 + g_2e_1^2 + g_3e_1^3 + \dots \tag{52}$$

$$E_2 = g_1e_2^1 + g_2e_2^2 + g_3e_2^3 + \dots \tag{53}$$

$$E_3 = g_1e_3^1 + g_2e_3^2 + g_3e_3^3 + \dots \tag{54}$$

where the superscripts have the same significance as in (51). Combining (51), (52), (53) and (54) with (5) one obtains

$$C = \frac{Lc\left[E_1 + \frac{k_1}{a}E_2 + \frac{k_1k_2}{a^2}E_3\right]}{1 + \frac{k_1}{a} + \frac{k_1k_2}{a^2}} \; . \tag{55}$$

Equation (55) may be treated in exactly the same manner as (5) in deriving the equations

$$(56) \qquad k_1k_2 = \left(\frac{C_m - C_1}{C_m - C_3}\right)a_o^2$$

and

$$(57) \quad k_1 = \frac{a_o\left[(C_m-C_3)(C-C_1)10^{-\Delta} + (C_m-C_1)(C-C_3)10^{+\Delta} - 2(C_m-C_1)(C_m-C_3)\right]}{(C_m-C)(C_m-C_3)}$$

where

Δ = pH + log a_o

a_o = activity of hydrogen ion at the maximum or minimum of the plot of C versus pH

C_1 = LcE_1 = C when only H_2A is present

C_3 = LcE_3 = C when only A is present

C_m = C at the maximum or minimum of the plot of C versus pH

C = any point on the curve of C versus pH

The individual values chosen for g_1, g_2, g_3, etc., can be either positive or negative. The optimum values obviously depend upon the shapes of the absorption curves. Even if the curve of optical density versus pH possesses a satisfactory maximum or minimum at one or more wavelengths, one can usually obtain more accurate values for k_1 and k_2 by using a composite optical density than one can obtain by using only the data at one wavelength.

The Possible Use of Properties Other than Optical Density

In order for a property to be useful in the measurement of overlapping acidity constants for a dibasic acid, the measured property X must bear the following relation to the concentrations of the respective species:

$$X = x_1[H_2A] + x_2[HA] + x_3[A] \tag{58}$$

where x_1, x_2, and x_3 are characteristic of the species H_2A, HA and A, respectively. Obviously, the measurement for each solution must be performed under the same experimental conditions, or be corrected to the same experimental conditions, and corrections must be made for any effects due to buffers or added salts. If the above prerequisite is met then the analogue of (5) is obtained, namely,

$$X = \frac{c\left[x_1 + \frac{k_1}{a}x_2 + \frac{k_1k_2}{a^2}x_3\right]}{1 + \frac{k_1}{a} + \frac{k_1k_2}{a^2}} \tag{59}$$

where c, the total concentration of the dibasic acid, is the seme value for each solution. A further prerequisite is that the plot of the measured property X versus pH show a maximum or minimum corresponding to the formation of the intermediate species HA. Then the equations that result for k_1k_2 and k_1 are:

$$k_1k_2 = \left(\frac{X_m - X_1}{X_m - X_3}\right)a_o^2 \tag{60}$$

$$k_1 = \frac{a_o\left[(X_m-X_3)(X-X_1)10^{-\Delta} + (X_m-X_1)(X-X_3)10^{+\Delta} - 2(X_m-X_1)(X_m-X_3)\right]}{(X_m-X)(X_m-X_3)} \tag{61}$$

where

$\Delta = pH + \log a_o$

a_o = activity of hydrogen ion at the maximum or minimum of the plot of X versus pH

$X_1 = cx_1 = X$ when only H_2A is present

$X_3 = cx_3 = X$ when only A is present

$X_m = X$ at the maximum or minimum of the plot of X versus pH

$X = $ any point on the curve of X versus pH

Aqueous solutions of optically active dibasic acids usually conform admirably to mathematical expressions of the type given in (58) and (59). The general formula relating observed optical rotation α to tube length L, concentration d in grams per cubic centimeter and specific rotation $[\alpha]$ may be expressed in the following manner:

$$\alpha = Ld\,[\alpha] \tag{62}$$

where $[\alpha]$ is understood to be for a pure substance at a given wavelength of light and a fixed temperature. For solutions of constant total molarity c one has

$$cx_1 = Ld[\alpha_1]$$
$$cx_2 = Ld[\alpha_2]$$
$$cx_3 = Ld[\alpha_3]$$

Substitution of these quantities into (59) gives

$$\alpha = \frac{Ld\left[[\alpha_1] + \frac{k_1}{a}[\alpha_2] + \frac{k_1k_2}{a^2}[\alpha_3]\right]}{1 + \frac{k_1}{a} + \frac{k_1k_2}{a^2}} \tag{63}$$

Vlès and Vellinger have used (63) with a method of successive approximations to obtain k_1 and k_2 for d-tartaric acid,[18] pilocarpine[19] and aspartic acid.[19]

If the plot of optical rotation α versus pH shows a maximum or minimum corresponding to the intermediate species HA, then (60) and (61) may be applied in the form

$$(64) \qquad k_1 k_2 = \left(\frac{\alpha_m - \alpha_1}{\alpha_m - \alpha_3}\right) a_o^2$$

$$(65) \qquad k_1 = \frac{a_o\left[(\alpha_m - \alpha_3)(\alpha - \alpha_1)10^{-\Delta} + (\alpha_m - \alpha_1)(\alpha - \alpha_3)10^{+\Delta} - 2(\alpha_m - \alpha_1)(\alpha_m - \alpha_3)\right]}{(\alpha_m - \alpha)(\alpha_m - \alpha_3)}$$

where $\Delta = \mathrm{pH} + \log a_o$

a_o = activity of hydrogen ion at the maximum or minimum of the plot of α versus pH

$\alpha_1 = \mathrm{Ld}\,[\alpha_1] = \alpha$ when only H_2A is present

$\alpha_3 = \mathrm{Ld}\,[\alpha_3] = \alpha$ when only A is present

$\alpha_m = \alpha$ at the maximum or minimum of the plot of α versus pH

α = any point on the curve of α versus pH

Examples of compounds showing a maximum or minimum corresponding to the species HA in the plot of optical rotation versus pH are found in the amino acids l(-)-leucine and d(+)-methionine.[20] It is well known that the specific rotation of a solution of an optically active substance varies with the wavelength employed, particularly near its absorption bands.[21] Thus it may be profitable to use more than one wavelength in searching for a satisfactory curve of optical rotation versus pH. Furthermore, if data of optical rotation versus pH are obtained at two or more wavelengths, it is possible to combine the data in a composite optical rotation which may show a satisfactory maximum or minimum even though the data at individual wavelengths do not. Such composite optical rotations can be formed and used in a manner exactly analogous to that employed with optical densities.

Another property that might be used is the property of fluorescence. At moderate concentrations the fluorescent substance may appreciably absorb its own fluorescent radiation and the exciting light itself.[22] However, the intensity of the fluorescent light can be taken to be linearly proportional to the concentration at sufficiently low concentrations provided that the intensity of the exciting light is kept constant. At such concentrations one might be able to use the intensity of fluorescence with (60) and (61) to determine k_1 and k_2 of a dibasic acid. Examples of pH-sensitive fluorescent substances are eosin, fluorescein, nicotinic acid, vitamin C and salicylic acid.[23]

The possibility of utilizing magnetic data is suggested by such work as that of Coryell, Stitt and Pauling who have determined the acid constant of ferrihemoglobin by magnetic titration.[24] The relation expressed by (58) corresponds to the Wiedemann mixture law in magnetochemistry.[25] The Wiedemann law appears to hold very well unless unexpected chemical changes such as association take place. The use of magnetic data is experimentally feasible if the dibasic acid or its ions show paramagnetism. Included in this class are some of the simple and complex ions of the transition elements as well as those of the lanthanide and actinide series. The most useful instrument for this purpose is probably the Gouy magnetic balance (Ref. 25, p. 3). As the measured property one could use either the increase in weight of the sample upon the application of a fixed value of the magnetic field or one could use the apparent molar susceptibility. The temperature should be kept constant although the temperature coefficient of susceptibility is only of the order of $\frac{1}{300}$ for most paramagnetic substances at room temperature (Ref. 25, p. 231). Ions containing iron, nickel or a rare earth element, for example, might be investigated in this manner. Examples of inorganic complexes ions for which the successive acid constants lie within a factor of 100 from each other are the diaquotetramine cobaltic cation[26] and the cis diaquodiamine platinous cation.[27]

It is possible, of course, that no plot of a single type of property versus pH can be found to give a maximum or minimum corresponding to the intermediate species HA. In such instances the situation might be remedied by combining two different types of data such as optical density and optical rotation, for example, to form a hybrid composite. If the hybrid composite has the required maximum or minimum it can then be used in (56) and (57) in the usual manner. The different types of data combined in this manner can arbitrarily be brought to the same unit by choosing appropriate units for the weighting factors used in combining them.

ISOPHTHALIC ACID

Materials and Apparatus

The isophthalic acid was originally obtained from the Genesee Research Corporation. In a communication from that company relating to its purity it is stated that impurities of ortho- and tere-phthalic acids

> should be present only in very small amounts since (the) isophthalic acid is made from meta toluidine by Sandmeyer reaction and oxidation of the meta toluidine acid. The only known impurities are inorganic salts that may not be thoroughly washed out; such as, sodium sulphate.*

The isophthalic acid was further purified in this laboratory by metathesis with $BaCO_3$ which produces the soluble salt of isophthalic acid and insoluble barium terephthalate.[28] The solution of barium isophthalate was evaporated to dryness, extracted with cold water and filtered. Barium was removed from the filtrate by precipitation of $BaSO_4$ and isophthalic acid was precipitated in 0.1 molar hydrochloric acid. The isophthalic acid was washed with water and dried for one hour at 105° C. The dimethyl ester prepared[29a] from the purified isophthalic acid gave a melting point of 64-65° C (uncor.).

All solutions used in determining the acidity constants of isophthalic acid were made up in conductance water having a specific conductance of

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*Pastorelle, M.C., Genesee Research Corporation, 100 McKee Road, Rochester 11, New York. (Private communication.) 1950.

less than one micromho per cm.. Formic acid-sodium formate buffers and phosphate buffers were used. The buffer materials, the sodium chloride used to maintain constant ionic strength and the perchloric acid used in the most acidic solutions were of at least C.P. grade. Stock solutions of these materials were filtered if necessary in order to remove slight turbidities or small amounts of foreign matter.

The scanning was done on a Model 12 Cary Recording Spectrophotometer. Matched 50 or 20 millimeter silica cuvettes were used. Values of pH were measured with a Beckman Model G pH meter equipped with that company's No. 290 glass electrode and No. 270 calomel electrode. Beckman buffers of pH 4.00 and 10.00 were used in standardizing the pH meter.

Isophthalic acid at the concentrations used in this investigation was found to give no detectable fluorescence in the ultraviolet or visible region when irradiated with a powerful hydrogen lamp.

Experimental Method

Except in the exploratory experiments all solutions were made up at a constant concentration of isophthalic acid and a constant ionic strength of 0.0302. The value of the concentration of the isophthalic acid was 8.0×10^{-5} molar which was considered to be low enough to insure its remaining in solution at all pH's.* The total formality of formate in the

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*The solubility of isophthalic acid in water at 25° C. is 7.7×10^{-4} molar according to H.E. Stores and R. Fittig.[29b]

solutions buffered with formic acid and sodium formate was kept at 0.030. That was desirable in order to limit the size of the correction that would have to be applied for the optical density of the buffer itself in the region of 2500 to 2450 Ångströms. Thus this correction was never greater than ten per cent of the total optical density. Sodium chloride was added to bring the ionic strength up to 0.0302. The other buffers were practically transparent at these wavelengths.

The pH of each solution containing isophthalic acid was measured. The pH's of scanned and unscanned portions of the same solution were always the same within 0.02 pH units and the pH of the scanned solution was taken as the correct value. The calibration of the pH meter was checked with standard buffer before and after the pH measurement of each sample. The temperature of each sample was 25 ± 1° C. during pH measurement. The effect of possible temperature variations on the pH's of solutions buffered with formic acid and sodium formate was thought to be very small since pK_a for formic acid is constant to 0.001 unit in the range 20-30°C.[30]

Solutions for scanning were made up in pairs, which were identical except that one contained the isophthalic acid and the other only the buffer. The optical density of the acid was taken as the difference between the optical densities of the corresponding pair of solutions. The temperature of each solution was 25 ± 1° C. during scanning.

In using the Cary Spectrophotometer both of the cuvettes were kept in the sample chamber and the reference chamber was left empty. The cuvettes were filled with conductivity water, and the instrument was adjusted to read zero optical density over the spectral range under investigation with the sample cuvette in position.

The reference cuvette was scanned, its tracing being recorded on the scanning sheet. Thereafter the reference cuvette was always scanned prior to the measurement of each solution and, whenever necessary, the instrument was readjusted to give the same tracing for the reference cuvette as was originally recorded. Adjustments for drift in the "zero point" were thus made in an analogous manner to that used with the Beckman Models D and DU Spectrophotometers. Although drift of the Cary Spectrophotometer over a period of hours would otherwise be only of the order of 0.005 optical density units or less, use of the above procedure appeared to be advisable for the most accurate work. All control adjustments on the Cary Spectrophotometer such as slit control, slit sensitivity and damping control were the same for all measurements. The value of the band width was approximately 12 Å.

Experimental Results

Isophthalic acid solutions absorb strongly in the ultraviolet region but not at all in the visible so that measurements were confined to the former region. A preliminary scanning at various pH values were made to find the optimum wavelength region for the spectrophotometric determination. The absorption curves (Figure 3) were obtained using $9.5X10^{-5}$ formal isophthalic acid in a 20 mm. cuvette. The absorption was due principally to the species H_2A at pH 1.92, species HA at pH 4.10, and species A at pH 11.61. From these data it was decided to use wavelengths from 2500 to 2450Å for the determination of the acidity constants.

A series of solutions was made up with a constant isophthalic acid formality of $8.0X10^{-5}$ and a constant ionic strength of 0.0302. They were scanned from 2500 to 2400Å in a 50 millimeter silica cuvette and two wavelengths were selected for the calculations. At one of these wavelengths, 2476.0Å, e_1 appeared to equal e_3, thus allowing the use of (42), (43) and (44). At the other wavelength, 2460.0Å, there was obtained the most favorable maximum in the plot of optical density versus pH. Optical densities at these two wavelengths were obtained at the lowest scanning speed or by "spot" readings at these two wavelengths. Readings obtained by these two methods agreed with each other, thus indicating that the pen was not lagging in tracing out the absorption curve on the lowest scanning speed. The optical densities (D) shown in Table 2 have been corrected for absorption by the buffers. The estimated experimental error in measuring optical densities was approximately ± 0.003 optical density units. The estimated experimental error in measuring pH was approximately ±0.01 pH units.

The plot of optical density versus pH at 2476.0Å (Figure 4) indicated that

$$Dm = 1.164$$

and $D_1 = D_3 = D' = 0.984.$

Hence (42) and (44) were applicable in the form $k_1k_2 = a_o^2$

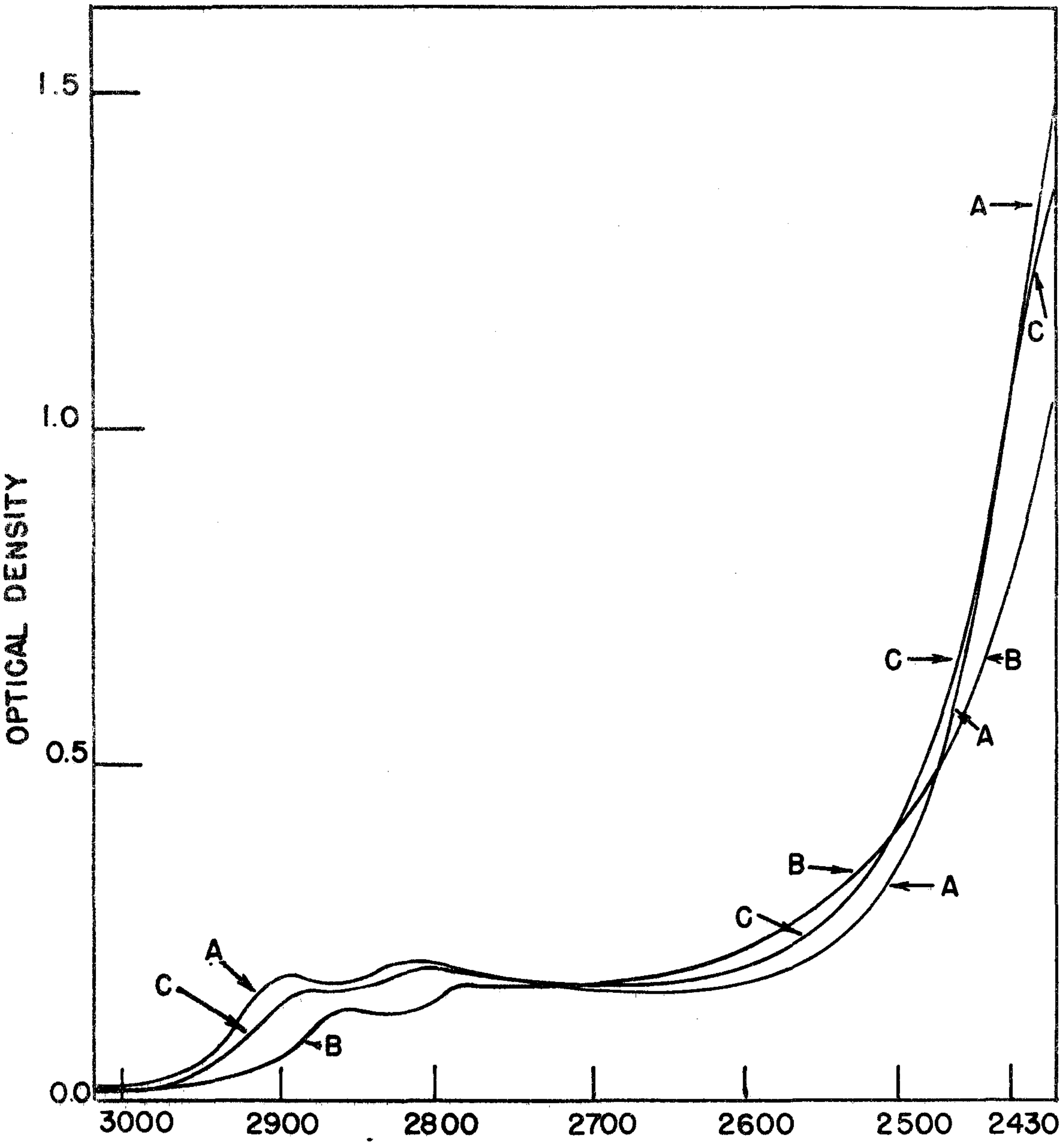


FIG. 3 ABSORPTION CURVES FOR 9.5×10^{-5} FORMAL ISOPHTHALIC ACID IN A 20.00mm CUVETTE.

A: pH 1.92
B: pH 11.61
C: pH 4.10

Table 2.

Optical Densities of 8.0×10^{-5} Formal Isophthalic Acid in 50.00 mm. Cuvettes

pH	D at 2476.0Å	D at 2460.0Å	Buffer
1.58	.987	1.298	($HClO_4$)
1.585	.991	1.297	($HClO_4$)
1.585	.988	1.302	($HClO_4$)
2.49	1.007	1.318	Phosphate
2.725	1.016	1.324	Phosphate
3.03	1.063	1.365	Formate
3.12	1.076	1.375	Phosphate
3.175	1.081	1.383	Formate
3.37	1.109	1.408	Formate
3.37	1.108	1.412	Formate
3.56	1.134	1.435	Formate
3.575	1.141	1.436	Formate
3.75	1.158	1.451	Formate
3.96	1.160	1.447	Formate
3.96	1.167	1.451	Formate
3.96	1.165	1.440	Formate
4.18	1.152	1.421	Formate
4.33	1.142	1.395	Formate
4.34	1.136	1.391	Formate
4.515	1.110	1.341	None
4.535	1.107	1.350	Formate
4.55	1.104	1.346	Formate
4.715	1.078	1.294	Formate
4.91	1.056	1.256	Formate
5.095	1.036	1.233	Formate
7.90	.982	1.149	Phosphate
7.98	.989	1.151	Phosphate
8.72	.982	1.146	Phosphate

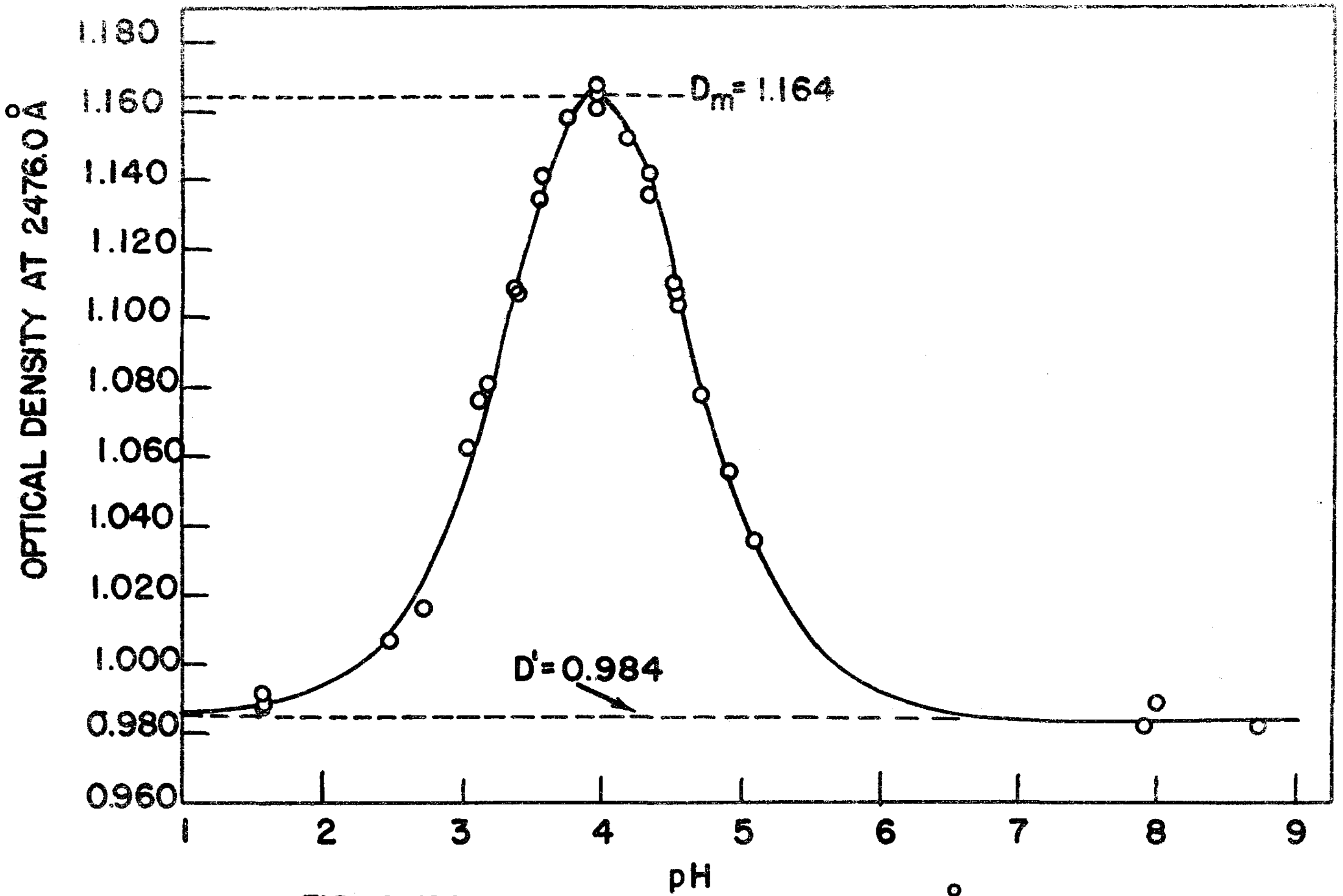


FIG. 4 ISOPHTHALIC ACID AT 2476.0 Å
CIRCLES: EXPERIMENTAL POINTS.
SOLID CURVES: CALCULATED AS
SHOWN LATER.

and $$\frac{k_1}{2a_o} = \frac{(D-0.984)\cosh(\Delta \ln 10) - 0.180}{1.164 - D}$$

where

$$\Delta = \mathrm{pH} + \log a_o = \mathrm{pH} - \mathrm{pH}_o$$

from (7).

Visual estimation of pH_o to 0.05 pH units would be possible in this case but would use only the points near the peak. Instead, it was decided to use as many points as possible since the values obtained for k_1 and k_2 depend markedly upon the value of pH_o. The method was based on the idea that the true value of k_1 would be independent of the pH's used in measuring it. Trial values of pH_o were chosen and for each the function $\frac{k_1}{2a_o}$ was plotted against Δ. The slope of the best straight line through these points was calculated using the method of least squares.[31] Representing the equation of this straight line by

$$\frac{k_1}{2a_o} = y = a + b\Delta$$

the formula for the slope b would be

$$b = \frac{n\sum(\Delta y_o) - \sum\Delta\sum y_o}{n\sum\Delta^2 - (\sum\Delta)^2}$$

in which n was the number of points used, $\sum\Delta$ the sum of Δ over all of the points and y_o was the value calculated for $\frac{k_1}{2a_o}$ for each point used. Values of b calculated at 2476.0Å are shown in Table 5. All points from pH 3.03 to 5.095 were used except those at 3.96.

Table 3.

Values of b for Various Trial Values of pH_o at 2476.0Å

Trial Value of pH_o	Value of b in $\frac{k_1}{2a_o} = y = a+b\Delta$
3.93	+0.182,560
3.945	-0.017,788
3.95	-0.084,285

From these the value of pH_o for which b equals zero was found to be 3.9435.

In using the $pH_o = 3.9435$ and $\Delta = pH-3.9435$ for calculating $\frac{k_1}{2a_o}$ from the data at 2476.0Å, some experimental points were not used. The points at pH 2.49 and 2.725 were not used because they appeared to be in error. The points at pH 3.96 were not used because in general errors in points very close to the maximum give rise to enormous errors in values calculated for k_1. Table 4 shows the values of $\frac{k_1}{2a_o}$ that were obtained and the average value of $\frac{k_1}{2a_o}$. The following are calculated: $\log a_o = -3.9435$, $a_o = 1.139X10^{-4}$

$$k_1 = 2a_o(1.422 \pm 0.245)^*$$

$$k_1 = 2(1.139X10^{-4})(1.422 \pm 0.245)$$

$$k_1 = (3.24 \pm 0.56)X10^{-4}$$

$$k_2 = \frac{(k_1k_2)}{k_1} = \frac{a_o}{2(1.422)} = \frac{1.139X10^{-4}}{2(1.422)}$$

$$k_2 = (4.004 \pm 0.69)X10^{-5}$$

---

*Errors given are standard deviations.

Table 4.

Values Calculated for $\frac{k_1}{2a_o}$ at 2476.0Å with pH$_o$ = 3.9435

pH	D	Δ	$\frac{k_1}{2a^o}$
3.03	1.063	-0.9135	1.4701
3.12	1.076	-0.8235	1.5143
3.175	1.081	-0.7685	1.3607
3.37	1.109	-0.5735	1.2864
3.37	1.108	-0.5735	1.2276
3.56	1.134	-0.3835	1.0800
3.575	1.141	-0.3685	1.6110
3.75	1.158	-0.1935	1.9232
4.18	1.152	+0.2365	1.1280
4.33	1.142	+0.3865	2.0379
4.34	1.136	+0.3965	1.4211
4.515	1.110	+0.5715	1.3287
4.535	1.107	+0.5915	1.3305
4.55	1.104	+0.6065	1.2880
4.715	1.078	+0.7715	1.2287
4.91	1.056	+0.9665	1.4553
5.095	1.036	+1.1515	1.4871

Average $\frac{k_1}{2a_o} = 17\underline{\left|\ 24.1786\right.}$

1.4223

The plot of optical density versus pH at 2460.0Å shown in Figure 5 gave

$D_1 = 1.295$

$D_m = 1.451$

$D_3 = 1.149$

Hence equations 37 and 41 were applicable in the form

$$k_1k_2 = a_o^2\left(\frac{1.451-1.295}{1.451-1.149}\right) = 0.516556a_o^2$$

and

$$\frac{k_1}{a_o} = \frac{(D-1.295)10^{-\Delta}+0.516556(D-1.149)10^{+\Delta}-0.312}{1.451-D}$$

where $\Delta = pH + \log a_o$

Using the same procedure as before, the best value for pH_o was found to be 3.843. Values of $\frac{k_1}{a_o}$ shown in Table 5 were calculated from the above equation at 2460.0 Ångstroms with $pH_o = 3.843$. The standard deviation of these values of $\frac{k_1}{a_o}$ was found to be 0.194. Hence, this data gave

$\log a_o = -3.843$, $a_o = 1.436\text{X}10^{-4}$

$k_1 = (1.856 \pm 0.194)a_o = (1.856 \pm 0.194)(1.436\text{X}10^{-4})$

$k_1 = (2.665 \pm 0.278)\text{X}10^{-4}$

$k_2 = \frac{(k_1k_2)}{k_1}$

$k_2 = (3.994 \pm 0.417)\text{x}10^{-5}$

The experimental results for isophthalic acid at an ionic strength of 0.0302 were therefore as follows:

$k_1 = (3.24 \pm 0.56)\text{x}10^{-4}$ from data at 2476.0 Å

$k_1 = (2.665 \pm 0.28)\text{x}10^{-4}$ from data at 2460.0 Å

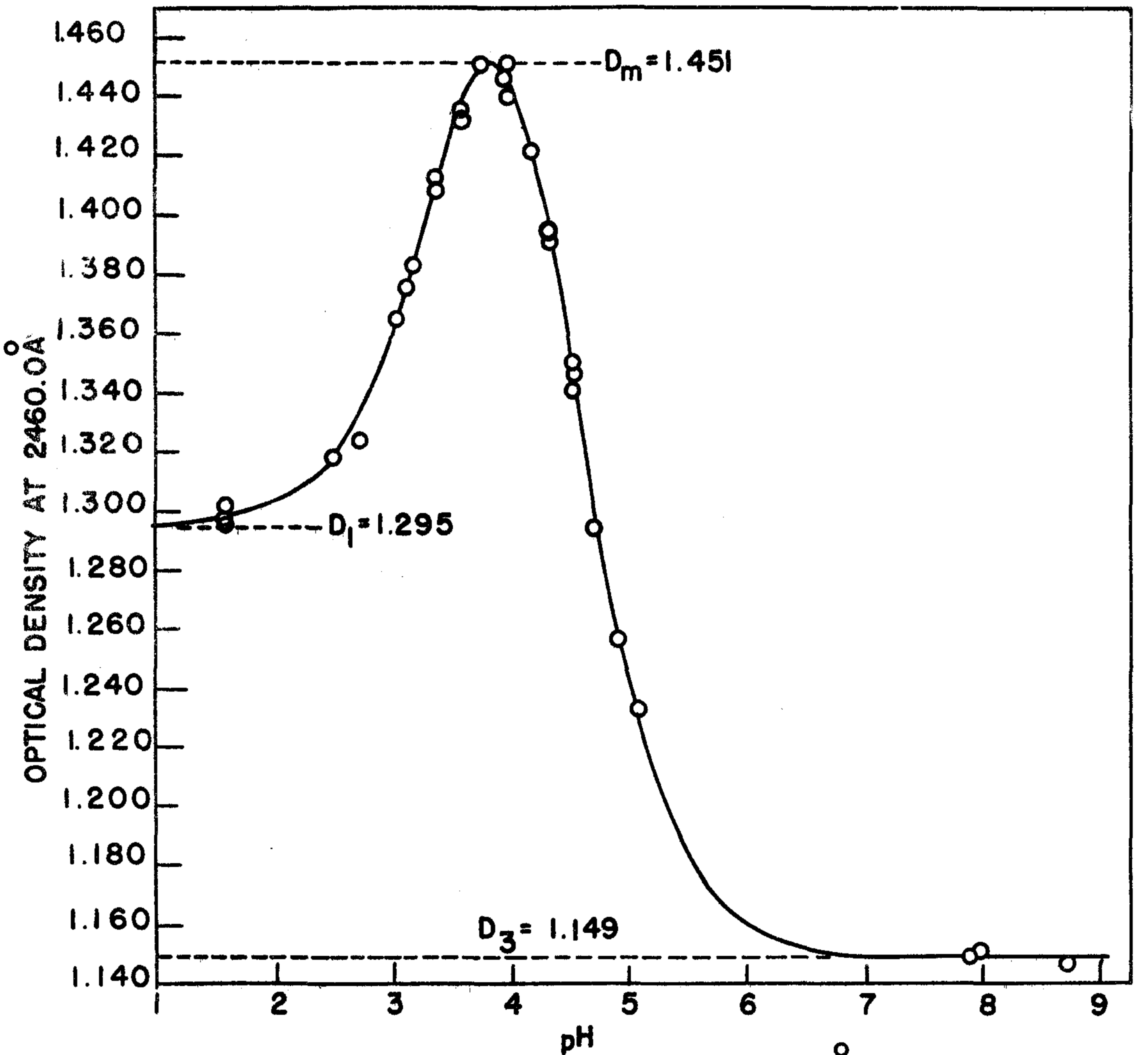


FIG. 5 ISOPHTHALIC ACID AT 2460.0 Å
CIRCLES: EXPERIMENTAL POINTS.
SOLID CURVE: CALCULATED AS
SHOWN LATER.

Table 5.

Values Calculated for $\frac{k_1}{a_0}$ at 2460.0Å with pH_0 = 3.843.

pH	D	Δ	$\frac{k_1}{a_0}$
3.03	1.365	-0.813	1.8634
3.12	1.375	-0.723	1.7480
3.175	1.383	-0.688	1.8188
3.37	1.408	-0.473	1.6005
3.37	1.412	-0.473	2.0873
3.56	1.435	-0.283	2.1009
3.575	1.436	-0.268	1.9553
4.18	1.421	+0.337	1.7088
4.33	1.395	+0.487	1.9745
4.34	1.391	+0.497	1.8525
4.515	1.341	+0.672	1.4893
4.535	1.350	+0.692	2.0797
4.55	1.346	+0.707	2.0601
4.715	1.294	+0.872	1.5648
4.91	1.256	+1.067	1.6901
5.095	1.233	+1.252	2.1087

$$16 \,\underline{)\,29.7027}$$

Average $\frac{k_1}{a_0}$ = 1.8564

$k_2 = (4.004 \pm 0.69)\mathrm{x}10^{-5}$ from data at 2476.0Å

$k_2 = (3.994 \pm 0.42)\mathrm{x}10^{-5}$ from data at 2460.0Å

Combining the two values for k_1 by taking a grand mean (Ref. 30, p. 195-6), the final value for k_1 was calculated as follows:

$$10^{+4}k_1 = \frac{\frac{3.24}{0.56^2} + \frac{2.665}{0.28^2}}{\frac{1}{0.56^2} + \frac{1}{0.28^2}}$$

$$k_1 = 2.78 \times 10^{-4}$$

The standard deviation for the final value of k_1 was

$$\frac{10^{-4}}{\sqrt{\frac{1}{0.56^2} + \frac{1}{0.28^2}}} = 0.25 \times 10^{-4}$$

Hence the final value obtained for k_1 was $(2.78 \pm 0.25) \times 10^{-4}$. The final value obtained for k_2 was similarly found to be $(4.00 \pm 0.36) \times 10^{-5}$. Hence the value of k_1/k_2 obtained for this acid was*

$$\frac{k_1}{k_2} = \frac{(2.78 \pm 0.25) \times 10^{-4}}{(4.00 \pm 0.36) \times 10^{-5}} = 6.95 \pm 0.88$$

The solid curves shown in Figures 4 and 5 were obtained from (50) using

$$k_1 = 2.78 \times 10^{-4}$$

$$k_2 = 4.00 \times 10^{-5}$$

and

$$a_o = \left(\frac{(D_m - D_3)k_1k_2}{(D_m - D_1)}\right)^{1/2} \quad \text{from (37)}$$

---

*In general if there is a function u such that $u = f(x,y)$, and ${}_x$ and ${}_y$ are the standard deviations of x and y, then the standard deviation of the function u is closely approximated by

$$\sigma_u = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \sigma_y^2}$$

where $D_1 = D_3 = 0.984$ and $D_m = 1.164$ at 2476.0 Å, and $D_1 = 1.295$, $D_m = 1.451$ and $D_3 = 1.149$ at 2430.0 Å.
The fact that the points for the unbuffered solution of pH 4.515 gave substantial agreement with the other points and the calculated curves was taken as an indication that the formic acid- sodium formate buffer exerted no specific influence on the dissociation of the isophthalic acid.

Discussion

Constant errors in the measurement of optical density should have little or no effect on the values of k_1 and k_2 calculated by means of the equations used because only differences in optical densities occur in these equations. The effects of individual errors in the measurements are included in standard deviations calculated for the grand mean values of k_1 and k_2. It is estimated that an average additional error of five per cent might be added in order to take into account errors in the determination of pH_o. Hence the values of k_1, k_2, and k_1/k_2 and their probable errors will be taken as

$$k_1 = (2.78 \pm 0.39) \times 10^{-4} \simeq (2.8 \pm 0.4) \times 10^{-4}$$

$$k_2 = (4.00 \pm 0.56) \times 10^{-5} \simeq (4.0 \pm 0.6) \times 10^{-5}$$

$$k_1/k_2 = 6.95 \pm 1.38 = 7.0 \pm 1.4$$

at an ionic strength of 0.0302.

The equations relating the thermodynamic dissociation constants, K_1 and K_2, to the acidity constants k_1 and k_2, are

$$K_1 = (\gamma_{HA}/\gamma_{H_2A})k_1 \text{ and } K_2 = (\gamma_{A}/\gamma_{HA})k_2$$

Since for isophthalic acid the species H_2A is uncharged, its activity coefficient is near to unity. However, due to the salting out effect it is probably advisable to estimate its value from the equation

$$\log \gamma_{H_2A} = C'\mu$$

where C' is the "salting out constant" and μ is the ionic strength.[32] The above equation is a special case of the Hückel equation which may be expressed in the form

$$\log \gamma_i = \frac{-Az_i^2\sqrt{\mu}}{1 + \overset{\circ}{a}B\sqrt{\mu}} + C'\mu$$

where γ_i is the activity coefficient of an i-th species, z_i is its charge, $\overset{\circ}{a}$ is the mean distance of closest approach of ions to the i-th species, and A and B are the constants 0.509 and 0.330×10^8 for aqueous solutions at 25° C.. The effect of the constant C' is small at low ionic strengths since C' is usually between 0.0 and 0.2, and the value of C' can be taken to be approximately the same for each of the species H_2A, HA and A.

For the ions of isophthalic acid the value of $\overset{\circ}{a}$ is estimated to be 5.0×10^{-8} cm. by comparison with experimental values obtained for other ions of similar dimension.[33] Hence for these ions at an ionic strength of 0.0302

$$\log \gamma_i = \frac{-0.509z_i^2\sqrt{0.0302}}{1 + 1.65\sqrt{0.0302}} + 0.0302C'$$

$$\log \gamma_i = -0.0687z_i^2 + 0.0302C'$$

$$\log \gamma_{HA} = -0.0687 + 0.0302C'$$

$$\log \gamma_A = -0.0687 \times 4 + 0.0302C'$$

$$\log(\gamma_{HA}/\gamma_{H_2A}) = -0.0687$$

$$\log(\gamma_A/\gamma_{HA}) = -0.0687x3 = -0.2061$$

The probable error in each of $\log(\gamma_{HA}/\gamma_{H_2A})$ and $\log(\gamma_A/\gamma_{HA})$ might be taken as roughly ten per cent, thus giving

$$(\gamma_{HA}/\gamma_{H_2A}) = 0.8537 \pm 0.0135$$

$$(\gamma_A/\gamma_{HA}) = 0.6222 \pm 0.0295$$

The thermodynamic dissociation constants for isophthalic acid are thus calculated to be

$$K_1 = (0.8537 \pm 0.0135)(2.78 \pm 0.39) \times 10^{-4}$$

$$K_1 = (2.37 \pm 0.34) \times 10^{-4} \simeq (2.4 \pm 0.3) \times 10^{-4}$$

$$K_2 = (0.6222 \pm 0.0295)(4.00 \pm 0.56) \times 10^{-5}$$

$$K_2 = (2.49 \pm 0.37) \times 10^{-5} \simeq (2.5 \pm 0.4) \times 10^{-5}$$

and

$$K_1/K_2 = 9.52 \pm 1.97 \simeq 9.5 \pm 2.0$$

Values of the first ionization constant of isophthalic acid at 25° C. have been obtained by Salm[34] and Ostwald[35]. Salm obtained a value of $k_1 = 3.2 \times 10^{-4}$ at an ionic strength of approximately 2.5×10^{-4} by a colorimetric method using an auxiliary dye indicator. Ostwald found k_1 to be 2.87×10^{-4} at a low ionic strength by conductance measurements. These values probably would have approximated the thermodynamic value K_1 but for the fact that they ignored the second ionization of isophthalic acid. Their values for $k_1 \simeq K_1$ were probably too high due to that fact. Chandler used Ostwald's value for k_1 together with partition studies between water and diethyl ether to obtain values of k_1/k_2.[36] The error in k_1/k_2 resulting from Ostwald's erroneous value for k_1 may have been fairly small due to a compensation of errors. Chandler obtained a value of $k_1/k_2 = 10.8$ at an ionic strength between 0.001 and 0.002. A further source of error in his work must have been the effect of the solubility of the ether in the aqueous phase which amounted to 7.8 per cent by volume.

Maxwell and Partington determined k_1 and k_2 for isophthalic acid by means of electrometric titration.[37,38] They obtained the following values: $k1 = 2.0 \times 10^{-4}$ and $k_2 = 2.0 \times 10^{-5}$ at $\mu = 10^{-3}$;[37] $k_1 = 3.5 \times 10^{-4}$ and $k2 = 3.5 \times 10^{-5}$ at $\mu = 0.03$.[38] It was difficult for them to determine the ionic strength corresponding to each value calculated for k_1 and k_2 because of the changes in ionic strength during the titration. This uncertainty was particularly great for the values at the lower ionic strength. However, at $\mu = 0.03$ the ionic strength was presumably maintained approximately constant by the presence of neutral salts although these writers gave little information on that point.

None of the above investigators gave explicit mention of the probable errors for their values. Arbitrarily assigning the same relative errors to their values as have been estimated for the values obtained in the present investigation, some degree of agreement is obtained between the present values and those of the other investigators. Thus the values of Salm, Ostwald, Chandler, and Maxwell and Partington at ionic strengths of 0.002 or less agree within experimental error with the estimated values of K_1, K_2 and K_1/K_2 taken from the present work. The values of Maxwell and Partington at an ionic strength of 0.03 give a similar degree of agreement with the present values of k_1, k_2 and k_1/k_2 at the same ionic strength.

TEREPHTHALIC ACID

Materials and Apparatus

The terephthalic acid was originally obtained from the Eastman Kodak Company. It was purified by means of its insoluble barium salt in a manner similar to that used by Scheurer and LeFave.[39] The terephthalic acid was finally precipitated with dilute hydrochloric acid, thoroughly washed and dried in a 110°C oven for one hour. All solutions used in determining the acidity constants were made up in conductance water. Other conditions were the same as previously described for isophthalic acid.

Exploratory measurements on the absorption curves for terephthalic acid were made on the Model 12 Cary Recording Spectrophotometer. However, the optical density measurements from which the acidity constants were determined were made on a Beckman Model DU Spectrophotometer.

Terephthalic acid at the concentrations used in this investigation was found to give a bare trace of fluorescence from 4000 to 5000 Å when irradiated with a powerful hydrogen lamp. However, the apparatus used to detect this fluorescence was at least an order of magnitude more sensitive in detecting this effect than the spectrophotometers were. Consequently it was felt that no appreciable error in the determination of the acidity constants would come from this source.

Experimental Method

All solutions of terephthalic acid were made up at the same low concentration, approximately 2.3 X 10^{-5} molar, made necessary by the extremely slight solubility of the acid. The solutions were buffered in the same manner as the isophthalic acid solutions except that the ionic strength was 0.0300. The buffer contributed less than one per cent to the total optical density of the solutions which were made and measured as described previously.

In the exploratory experiments with the Cary Recording Spectrophotometer (see p. 35) the band width was approximately 15Å. Accurate measurements were made with the Beckman DU Spectrophotometer in the usual manner. The reference cuvette was always filled with conductance water. The slit width was kept at 0.100 millimeter corresponding to a band width of approximately 30Å. The temperature of the solution was 25 ± 1°C. during the measurement. A matched pair of 50 mm. silica cuvettes was used in all cases.

Experimental Results

The spectrophotometric work on terephthalic acid was done in the ultraviolet region where the acid and its ions show strong absorption. The useful wavelengths were found by scanning 2.3 X 10^{-5} formal terephthalic acid solutions at pH's of 1.60, 7.97 and 4.06 on the Cary Spectrophotometer. (Figure 6).

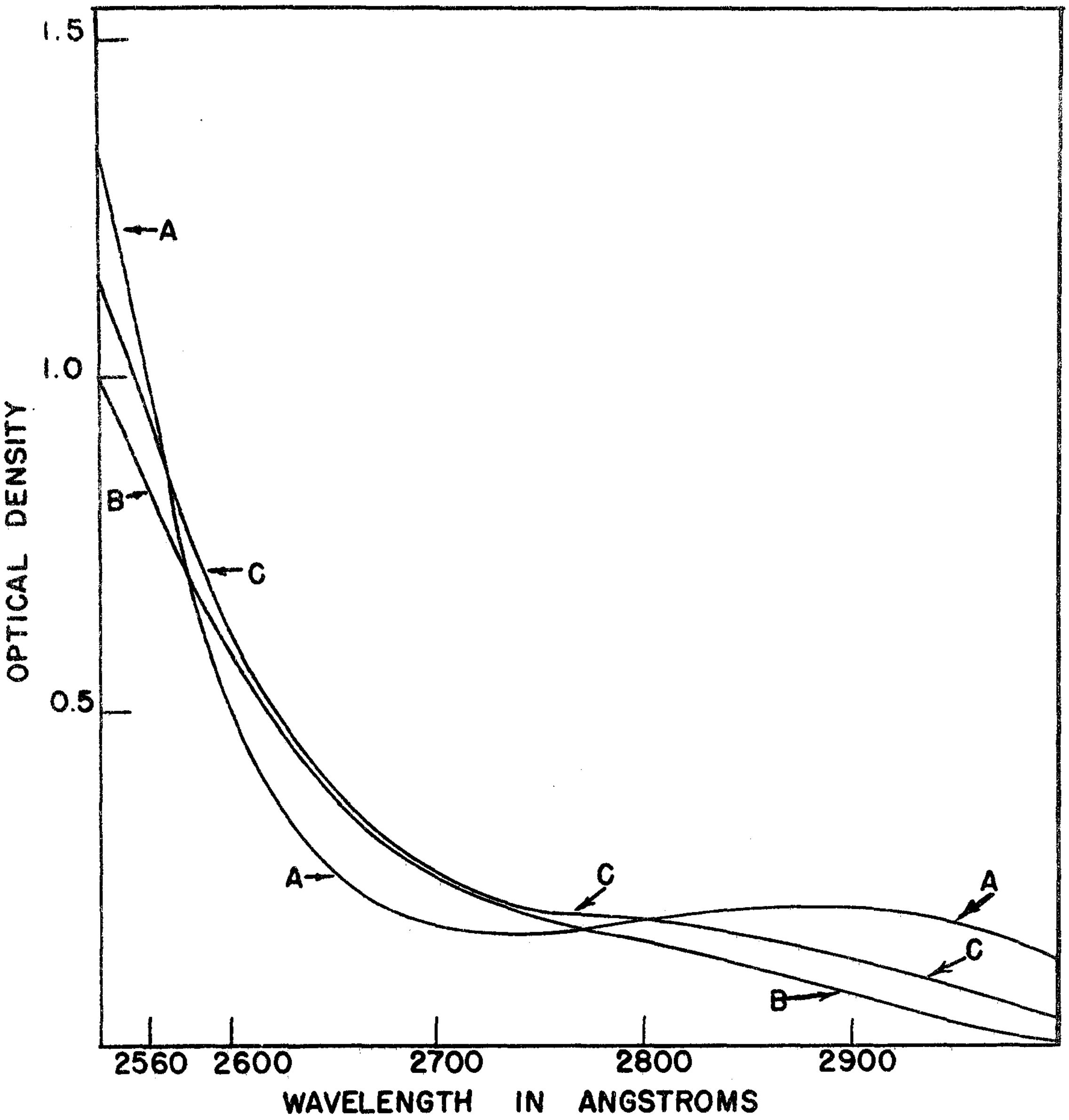


FIG. 6 ABSORPTION CURVES FOR 2.3×10^{-5} FORMAL TEREPHTHALIC ACID IN A 50.00mm CUVETTE.
A: pH 1.60
B: pH 7.79
C: pH 4.06

The curve at pH 4.06 did not rise very far above the other two curves at any wavelength but the best region appeared to be between 2625 and 2575 Å.

A series of buffered solutions of 2.3×10^{-5} formal terephthalic acid were made at pH increments of ~ 0.2 pH units over the intermediate range. In order to obtain proof that the acid was completely in solution at all pH's, a solution was made up with half the usual concentration of terephthalic acid at pH 1.585. The values of D for this solution when multiplied by two should agree closely with those for the solution at pH 1.62 only if the acid was completely in solution in the latter case.

Measurements were made at 2625.0, 2610.0, 2590.0, 2585.0, 2580.0 and 2575.0Å. It was found that the best single wavelength to use was 2590.0Å. The data at all of the other wavelengths were combined into a composite optical density by using (51) with g_1, g_2, g_3, etc., each equal to +1. The values of D and C shown in Table 6 were obtained after correction for the optical densities of the buffers.

At the pH of 1.585 the values of D and C multiplied by two agreed with those at the nearby pH of 1.62. This agreement was taken to indicate that 2.3×10^{-5} formal terephthalic acid was completely in solution at pH 1.62 and also at higher pH values. The reason for believing that such was the case is that the solubility of the acid is least in the most acidic solutions. The values of the net optical density D at 2590.0Å have been plotted against pH in Figure 7. The values of D for the other wavelengths have been plotted against pH in Figure 8 and the values of the composite optical density C have been plotted against pH in Figure 9.

Table 6.

Values of D at 2590.0Å and C for Terephthalic Acid

pH	D at 2590.0Å	C	Buffer
1.585	2 x 0.312 = 0.624	2 x 1.512 = 3.024	($HClO_4$)
1.62	0.622	3.025	($HclO_4$)
2.675	0.642	3.108	Phosphate
3.025	0.666	3.236	Formate
3.03	0.662	3.2125	Formate
3.11	0.675	3.271	Formate
3.38	0.6915	3.341	Formate
3.58	0.701	3.3995	Formate
3.76	0.7105	3.4365	Formate
3.975	0.712	3.453	Formate
4.19	0.709	3.428	Formate
4.35	0.700	3.3235	Formate
4.54	0.686	3.3235	Formate
4.73	0.672	3.258	Formate
4.92	0.659	3.2055	Formate
7.92	0.637	3.094	Phosphate
7.92	0.639	3.097	Phosphate

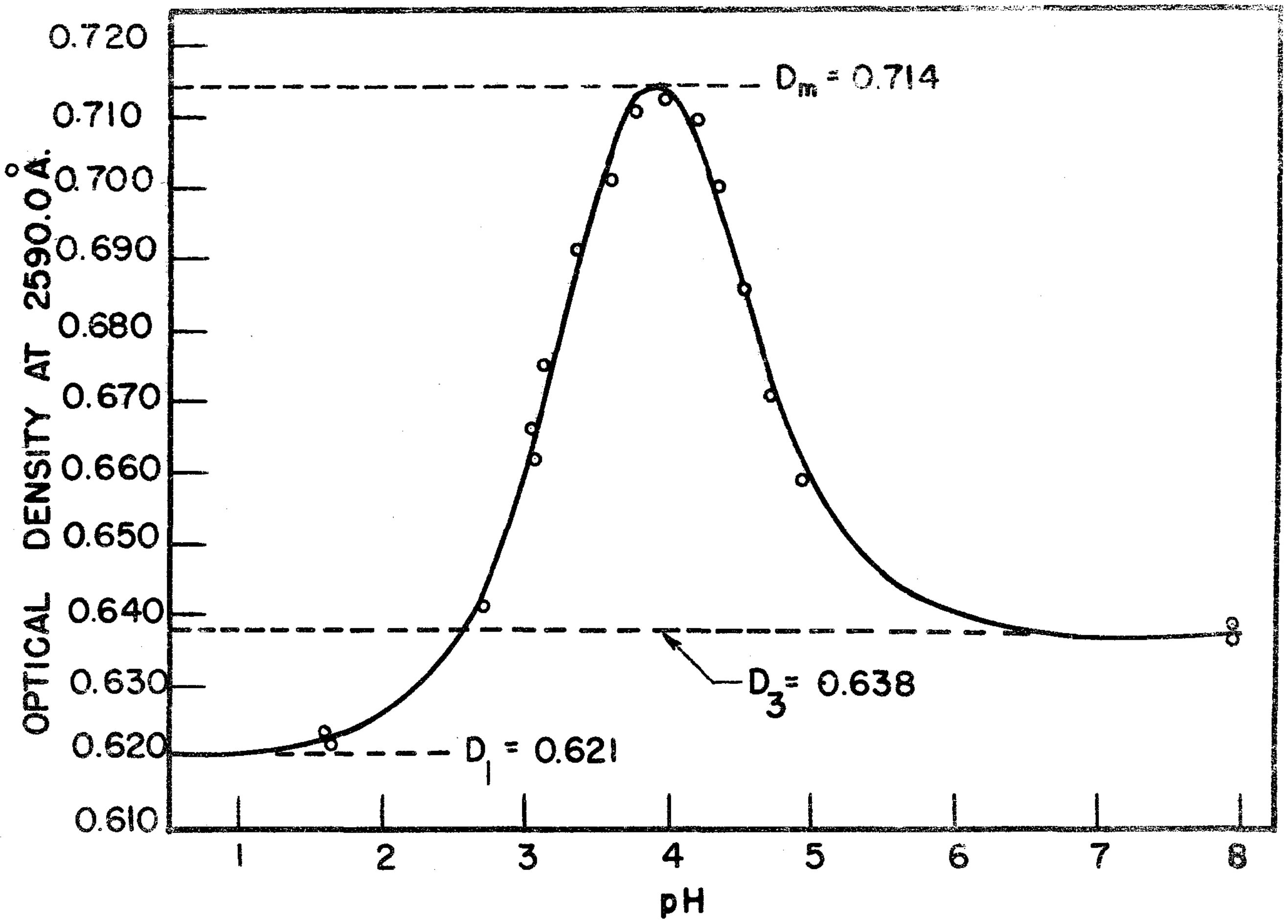


FIG. 7 TEREPHTHALIC ACID AT 2590.0 Å. CIRCLES: EXPERIMENTAL POINTS. SOLID CURVE: CALCULATED AS SHOWN LATER.

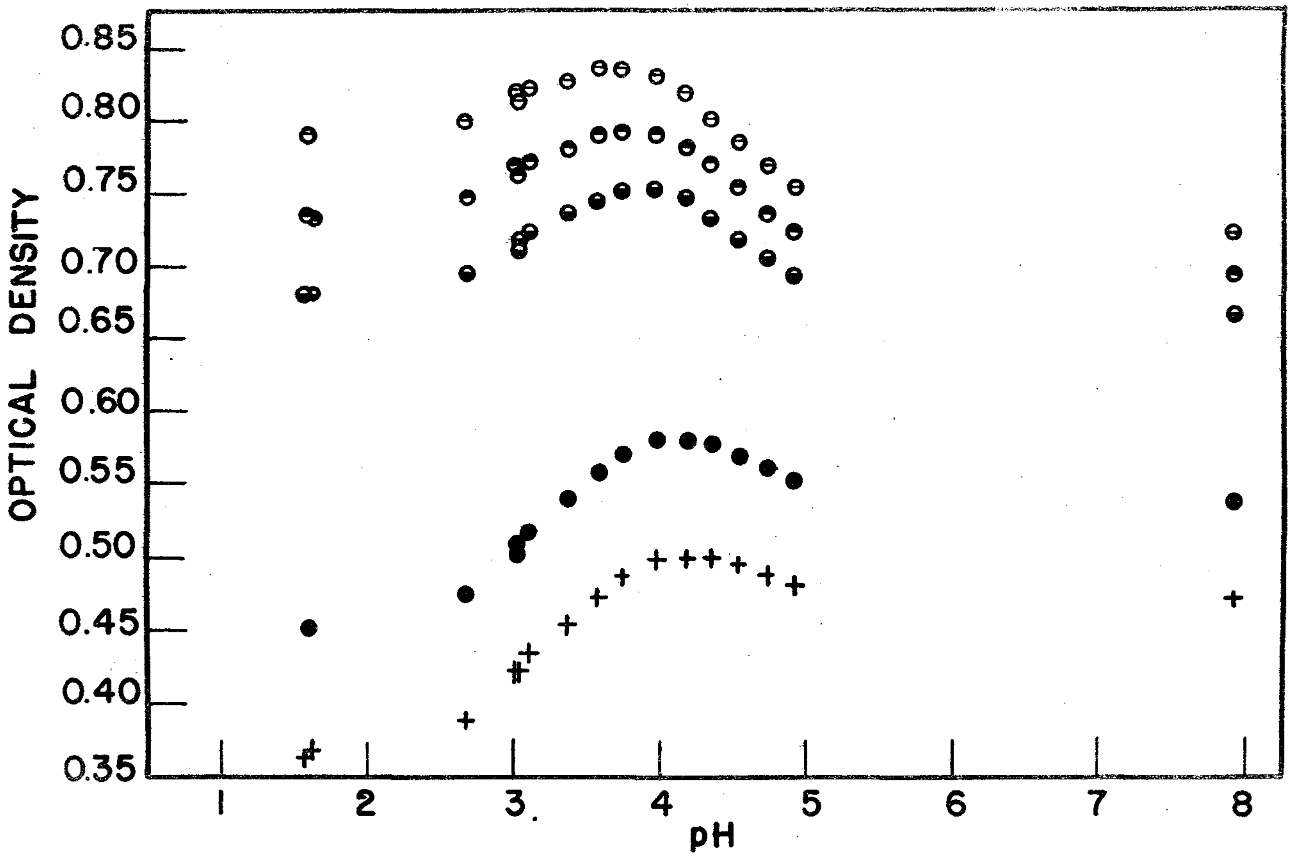


FIG. 8 TEREPHTHALIC ACID

⊖ AT 2575.0 Å
◒ AT 2580.0 Å
◓ AT 2585.0 Å
● AT 2610.0 Å
+ AT 2625.0 Å

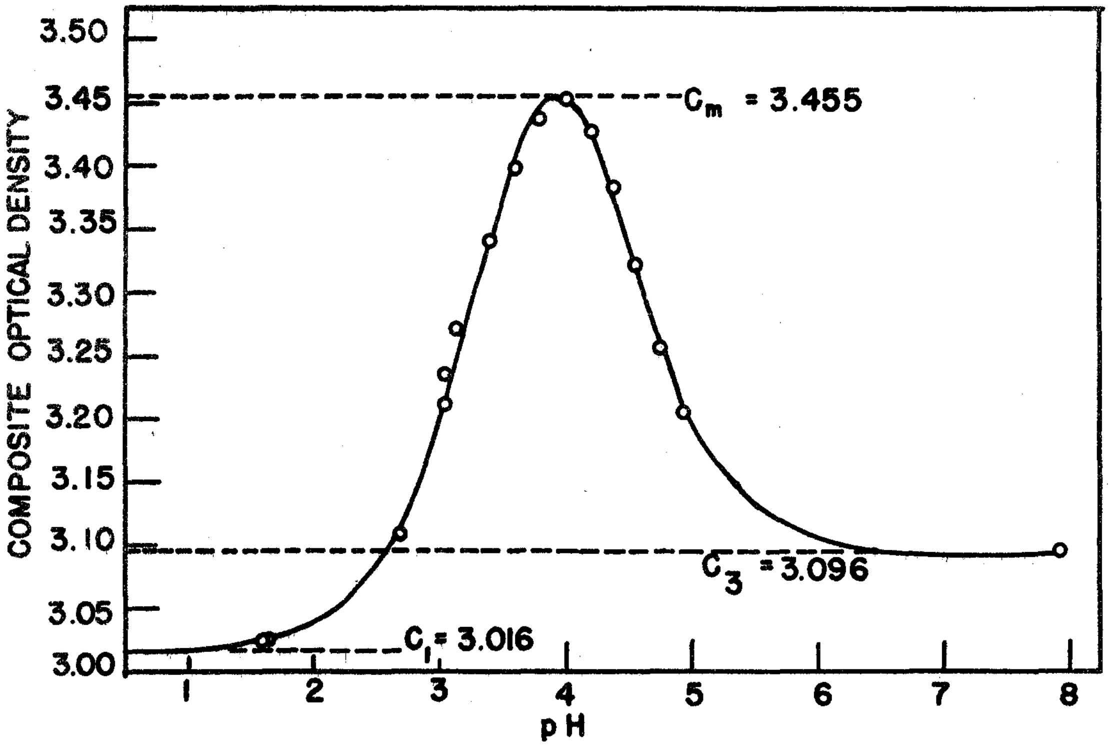


FIG. 9 USE OF COMPOSITE OPTICAL DENSITY FOR TEREPHTHALIC ACID. CIRCLES: EXPERIMENTAL POINTS. SOLID CURVE: CALCULATED AS SHOWN LATER.

The plot of experimental values shown in Figure 7 indicated that at 2590.0Å

$$D_1 = 0.621$$

$$D_m = 0.714$$

and $D_3 = 0.638$

Equations (37) and (41) thus gave

$$k_1k_2 = 1.223{,}684\ a_o^2$$

and

$$\frac{k_1}{a_o} = \frac{(D-0.621)10^{-\Delta} + 1.223{,}684(D-0.638)10^{+\Delta} - 0.186}{0.714-D}$$

where $\Delta = \mathrm{pH} + \log a_o$. Using the least-squares method as before, the best value for pH_o was found to be 3.9026. In obtaining this value the point at pH 3.975 was not used for the reason mentioned in the section on isophthalic acid. For the same reason the points at pH values of 3.76 and 4.19 were not used in obtaining the average value of $\frac{k_1}{a_o}$. The values of $\frac{k_1}{a_o}$ calculated with $\mathrm{pH}_o = 3.9026$ have been placed in Table 7.

The standard deviation from the average value of $\frac{k_1}{a_o}$ was 0.832. Hence the data for terephthalic acid at 2590.0 Ångströms gave the following results:

$$\log a_o = -3.9026,\ a_o = 1.2514 \times 10^{-4}$$

$$k_1 = (2.738 \pm 0.832)a_o = (2.738 \pm 0.832)\ (1.2514 \times 10^{-4})$$

$$k_1 = (3.426 \pm 1.041) \times 10^{-4}$$

$$k_2 = \frac{(k_1k_2)}{k_2} = \frac{1.223{,}684a_o^2}{(2.738 \pm 0.832)a_o} = \frac{1.223{,}684a_o}{(2.738 \pm 0.832)}$$

$$k_2 = \frac{1.223{,}684(1.2514 \times 10^{-4})}{(2.738 \pm 0.832)}$$

$$k_2 = (5.593 \pm 1.699) \times 10^{-5}$$

Table 7.

Values Calculated for $\frac{k_1}{a_o}$ at 2590.0Å with $pH_o = 3.9026$

pH	D	Δ	$\frac{k_1}{a_o}$
2.675	0.642	-1.2276	2.3467
3.025	0.666	-0.8776	3.2921
3.03	0.662	-0.8726	2.3789
3.11	0.675	-0.7926	4.0067
3.38	0.6915	-0.5226	3.0446
3.58	0.701	-0.3226	1.4484
4.35	0.700	+0.4474	3.9106
4.54	0.686	+0.6374	2.9945
4.73	0.672	+0.8274	2.4095
4.92	0.659	+1.0174	1.5479

$$\text{Average } \frac{k_1}{a_o} = \begin{array}{r} 10\,\underline{|27.3801} \\ 2.7380 \end{array}$$

The plot of experimental values of C shown in Figure 9 indicated that the following values should be taken:

$C_1 = 3.016$

$C_m = 3.455$

$C_3 = 3.096$

The use of these values in (56) and (57) gave the following relations:

$$k_1k_2 = \left(\frac{3.455 - 3.016}{3.455 - 3.096}\right) a_o{}^2 = 1.222,841\ a_o{}^2$$

$$\frac{k_1}{a_o} = \frac{(C-3.016)10^{-\Delta} + 1.222,841(C-3.096)10^{+\Delta} - 0.878}{3.455 - C}$$

The best value for pH_o was found to be 3.9038 by the use of the least-squares method. As before data at certain pH values were omitted. Table 8 shows the values of $\frac{k_1}{a_o}$ so calculated.

The results follow:

$$pH_o = 3.9038, \quad a_o = 1.2480 \times 10^{-4}$$

$$k_1 = (2.769 \pm 0.695)a_o = (2.769 \pm 0.695)\ (1.2480 \times 10^{-4})$$

$$k_1 = (3.456 \pm 0.867) \times 10^{-4}$$

$$k_2 = \frac{(k_1k_2)}{k_1} = \frac{1.222,841\ a_o^2}{(2.769 \pm 0.695)a_o} = \frac{1.222,841\ a_o}{(2.769 \pm 0.695)}$$

$$k_2 = \frac{1.222,841\ (1.2480 \times 10^{-4})}{(2.769 \pm 0.695)}$$

$$k_2 = (5.511 \pm 1.383) \times 10^{-5}$$

The experimental results for terephthalic acid at an ionic strength of 0.0300 were therefore as follows:

$k_1 = (3.426 \pm 1.041) \times 10^{-4}$ from data at 2590.0 Å

$k_1 = (3.456 \pm 0.867) \times 10^{-4}$ from the use of C

$k_2 = (5.593 \pm 1.699) \times 10^{-5}$ from data at 2590.0 Å

$k_2 = (5.511 \pm 1.383) \times 10^{-5}$ from the use of C

The grand mean values are:

$k_1 = (3.444 \pm 0.666) \times 10^{-4}$ or $k_1 = (3.4 \pm 0.7) \times 10^{-4}$

$k_2 = (5.544 \pm 1.072) \times 10^{-5}$ or $k_2 = (5.5 \pm 1.1) \times 10^{-5}$

Table 8.

Values Calculated for $\frac{k_1}{a_o}$ using C with $pH_o = 3.9038$

pH	C	Δ	$\frac{k_1}{a_o}$
2.675	3.108	-1.2288	1.9624
3.025	3.236	-0.8788	3.6935
3.03	3.2125	-0.8738	2.5176
3.11	3.271	-0.7938	4.0355
3.38	3.341	-0.5238	2.6081
3.58	3.3995	-0.3238	1.9169
4.35	3.384	+0.4462	3.3470
4.54	3.3235	+0.6362	3.0178
4.73	3.258	+0.8262	2.4659
4.92	3.2055	+1.0162	2.1248

$$10\,\overline{)27.6895}$$

Average $\frac{k_1}{a_o} = 2.7690$

$$\frac{k_1}{k_2} = \frac{(3.444 \pm 0.666) \times 10^{-4}}{(5.544 \pm 1.072) \times 10^{-}} = 6.21 \pm 1.70$$

These grand-mean values for k_1 and k_2 were used with (50) and

$$a_o = \left(\frac{D_m - D_3}{D_m - D_1}\right) k_1 k_2$$

to calculate the solid curve of Figure 7 using $D_1 = 0.621$, $D_m = 0.714$ and $D_3 = 0.638$. The same values of k_1 and k_2 were used with the C-analogues of these two equations to calculate the solid curve of Figure 9 using $C_1 = 3.016$, $C_m = 3.455$ and $C_3 = 3.096$.

Discussion

Due to the fact that the relative errors of k_1 and k_2 in the grand means are approximately twice as large for terephthalic acid as they are for isophthalic acid, it seems reasonable to assume that there is involved an average additional error of ten per cent due to uncertainties in the positions of the maxima of the curves. Therefore, k_1, k_2 and $\frac{k_1}{k_2}$ together with their probable errors will be taken as

$$k_1 = (3.44 \pm 1.01) \times 10^{-4} \text{ or } k_1 = (3.4 \pm 1.0) \times 10^{-4}$$

$$k_2 = (5.54 \pm 1.62) \times 10^{-5} \text{ or } k_2 = (5.5 \pm 1.6) \times 10^{-5}$$

$$\frac{k_1}{k_2} = \frac{(3.44 \pm 1.01) \times 10^{-4}}{(5.54 \pm 1.62) \times 10^{-5}} = 6.21 \pm 2.58 \text{ or } \frac{k_1}{k_2} = 6.2 \pm 2.6$$

at an ionic strength of 0.0300.

Calculating activity coefficients as was done for isophthalic acid, there is obtained

$$\frac{\gamma_{HA}}{\gamma_{H_2A}} = 0.8539 \pm 0.0132$$

$$\frac{\gamma_{A}}{\gamma_{HA}} = 0.6226 \pm 0.0295$$

The thermodynamic dissociation constants for terephthalic acid are therefore calculated to be as follows:

$$K_1 = (0.8539 \pm 0.0132)\,(3.44 \pm 1.01) \times 10^{-4}$$

$$K_1 = (2.94 \pm 0.86) \times 10^{-4} \text{ or } K_1 = (2.9 + 0.9) \times 10^{-4}$$

$$K_2 = (0.6226 \pm 0.0295)\ (5.54 \pm 1.62) \times 10^{-5}$$

$$K_2 = (3.45 \pm 1.02) \times 10^{-5} \text{ or } K_2 = (3.5 \pm 1.0) \times 10^{-5}$$

and $$\frac{K_1}{K_2} = \frac{(2.94 \pm 0.86) \times 10^{-4}}{(3.45 \pm 1.02) \times 10^{-5}}$$

or $$\frac{K_1}{K_2} = 8.5 \pm 3.5$$

The first dissociation constant of terephthalic acid has not been previously determined in aqueous solutions because of the very low solubility of the undissociated form. By analogy with other acids the first dissociation constant of terephthalic acid has been estimated to be 1.5 X 10^{-4} (Ostwald, (Ref. 35, p. 377)) and 3.1 X 10^{-4} (Wegscheider[40]), the estimated values presumable being for low ionic strengths. Kuhn and Wassermann have determined the second dissociation constant in aqueous solutions by potentiometric measurements.[41] Due to errors in measuring E.M.F.'s in the dilute solutions that were necessary, Kuhn and Wassermann did not claim much accuracy for their determination. They found k_2 to be approximately 3.5 X 10^{-5} at an ionic strength of 0.12 and a temperature of 16°C. They calculated K_2 to be 1.5 X 10^{-5} at 16° C. but the expressions used for activity coefficients do not appear to be correct.

CHLORANILIC ACID

Materials and Apparatus

"Practical grade" chloranilic acid was obtained from the Eastman Kodak Company and purified in the following manner. Eight grams of the acid were dissolved in a liter of distilled water at the boiling point, and filtered through a fast filter paper on a preheated funnel leaving a brown silt which was discarded. The filtrate was extracted with two 200 ml. portions of benzene in a large separatory funnel at 50° C. The benzene phases, containing only a little chloranilic acid, were discarded. The aqueous phase was cooled in an ice bath yielding bright red crystals of chloranilic acid which were filtered and washed with three 10-ml. portions of water. The crystals were dried at 115° C. to expel the water of hydration.[42] The over-all yield of chloranilic acid was approximately fifty per cent.

The purity of the product was determined by electrometric titration using carbonate-free sodium hydroxide, standardized against G.F. Smith potassium acid iodate.[43] The purities of two different preparations were found to be (99.8 ± 0.3)% by weight.

Since zirconium chloranilate complexes were being investigated in perchlorate solutions at an ionic strength of 2.00, the acid constants of chloranilic acid were studied in the same medium. For reasons related to the zirconium study, commercial lithium perchlorate was not acceptable.

Consequently it was prepared from lithium metal and perchloric acid. Lithium metal obtained from the Belmont Smelting and Refining Works was converted to the hydroxide by its reaction with conductance water in platinum. The hydroxide was neutralized with G.F. Smith double vacuum distilled perchloric acid. The solution was allowed to stand over night in the presence of a slight excess of perchloric acid and was filtered through a sintered glass crucible to remove silica. The filtrate was made exactly neutral by the addition of fresh lithium hydroxide. The resultant lithium perchlorate solution gave only a faint pink color with sodium thiocyanate and dilute hydrochloric acid indicating that very little iron was present. The strength of the solution was determined by evaporating two aliquots to dryness, igniting them at 280° C. for 2.5 hours and weighing the resulting anhydrous lithium perchlorate.[44] This solution was diluted to exactly 2.002 M. A solution of 2.002 M lithium hydroxide was made from lithium metal and conductance water and standardized via its perchlorate. It was stored in a paraffin-lined bottle. A solution of 2.002 M perchloric acid was made up in conductance water from G.F. Smith double vacuum distilled perchloric acid of 72 per cent strength. It was analyzed by titration with the carbonate-free sodium hydroxide mentioned earlier. Solutions that were 1.033×10^{-3} M in chloranilic acid were made up in both standard perchloric acid and the lithium perchlorate.

From scanning data in the ultraviolet region it was found that in a solution 10^{-5} M in chloranilic acid, 10^{-2} M in chlorate and 2 M in perchloric acid, roughly six per cent of the chloranilic acid was oxidized in a thirty-hour period. For this reason the perchlorate solutions were examined to see if chlorate was present and if chloranilic acid was stable. The solutions were tested for the presence of chlorate by the use of potassium iodide and concentrated sulfuric acid.[45] The colors of liberated iodine were faint and may have been due partly to air oxidation, but by comparison with a similarly treated standard it could be estimated that the lithium perchlorate solution had no more than 10^{-3} M chlorate in it and the perchloric acid solution had considerably less than that. Scanning data in the ultraviolet region indicated that over a period of three months there was less than 0.5 per cent oxidation of chloranilic acid in 2M perchloric acid. Similarly in a solution 1 M in both lithium perchlorate and perchloric acid there was less than one per cent oxidation over a period of four days. All of the chloranilic acid-lithium perchlorate solutions were used within four days of their preparation and the possibility of deterioration cannot be considered very serious.

Chloranilic acid at a concentration of 10^{-3} M was found to give no detectable fluorescence when irradiated with a powerful hydrogen lamp. Since the studies with chloranilic acid never involved a higher concentration of it than 10^{-3} M, interference from this source was not expected.

Experimental Method

The 2.002 M lithium perchlorate and perchloric acid solutions were transparent in the portions of the spectrum that were used. Nevertheless the instrument was balanced to zero optical density with 2.002 M lithium perchlorate in both cuvettes. Otherwise the Cary Spectrophotometer was used as it was for isophthalic acid. The band width was approximately

10 Å and the temperature was maintained at 25 ± 1° C during scanning.

Experimental Results

Although the ultraviolet region was not used in determining the acidity constants of chloranilic acid, it was examined to demonstrate that chloranilic acid obeyed Beer's law as shown in Figure 10. Other studies in the ultraviolet and visible regions were found to give no evidence for complexing of lithium by chloranilic acid.

Solutions of 10^{-3} formal chloranilic acid in two molar perchloric acid were orange in color. Singly-ionized chloranilic acid was a dark magenta color and the doubly-ionized species was a much lighter magenta color. Absorption curves such as those shown in Figure 11 were obtained in the visible region with the use of a 50 mm. cuvette and a chloranilic acid formality of 1.033×10^{-4}. The principal species of curve C was singly-ionized chloranilic acid.

Since the study of zirconium chloranilate complexes was conducted entirely on the basis of concentrations, it was desired also to study the constants of chloranilic acid in these terms. Hence k_1 and k_2 for chloranilic acid were defined to be

$$k_1 = \frac{[H^+]\ [HCh^-]}{[H_2Ch]} \quad \text{and} \quad k_2 = \frac{[H^+]\ [Ch^=]}{[HCh^-]}$$

where the brackets indicated the concentrations of the hydrogen ion and the three species obtained from chloranilic acid. The equations previously developed for the determination of k_1 and k_2 could be used by replacing

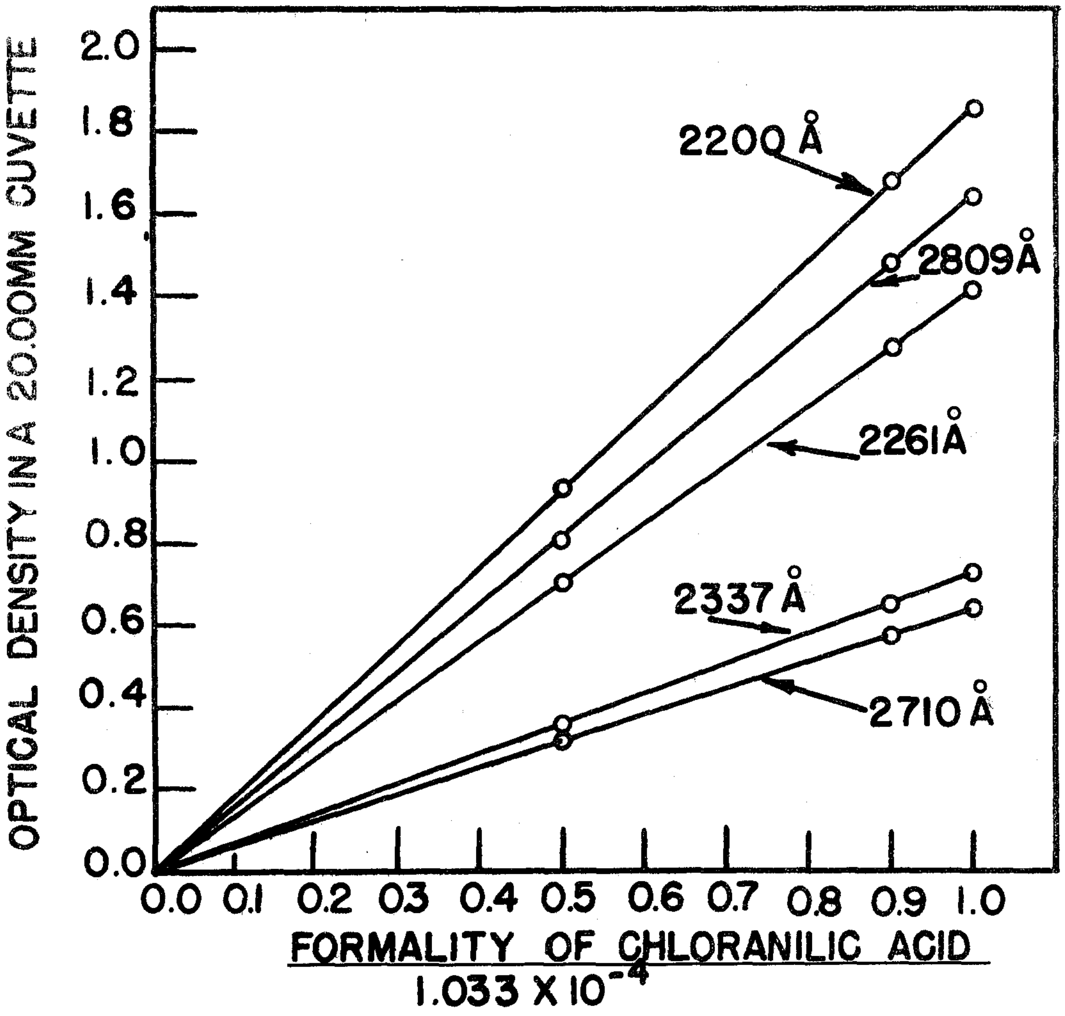


FIG. 10 TEST OF BEER'S LAW FOR CHLORANILIC ACID IN 2.002 M PERCHLORIC ACID.

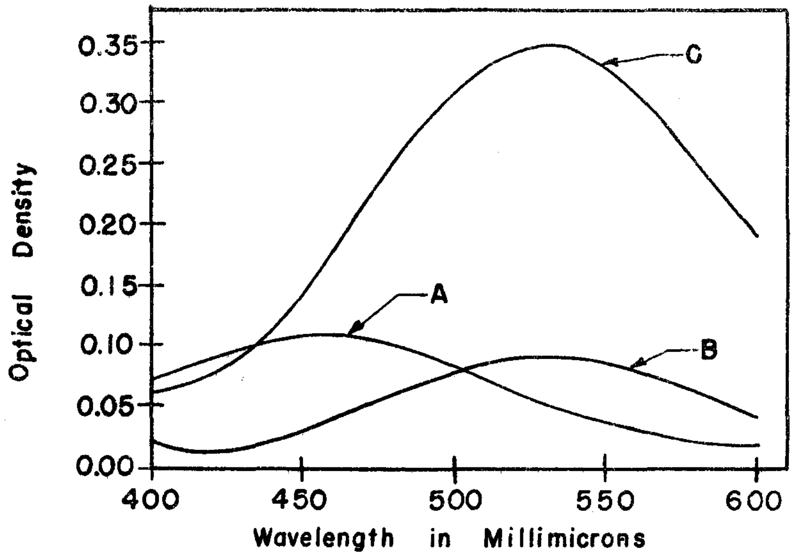


Fig. 11 Absorption Curves for 1.033×10^{-4}
Formal Chloranilic Acid in 50 mm. Cuvettes.
A: 2.00 M $[H^{+}]$
B: 5.0×10^{-11} M $[H^{+}]$
C: 2.00×10^{-2} M $[H^{+}]$

(a) by $[H^+]$ and a_o by $[H^+]_o$.

The acid constants defined above were determined at a wavelength of 496.0 millimicrons where a satisfactory maximum was obtained in the plot of optical density versus - log(true $[H^+]$). The solutions contained 1.033×10^{-4} formal chloranilic acid in lithium perchlorate-perchloric acid solutions at an ionic strength of 2.002. Control of the hydrogen ion concentration was obtained by including the appropriate amount of perchloric acid or lithium hydroxide while the solutions were being made up. The contribution of hydrogen ion from the chloranilic acid had to be taken into account in order to calculate the true hydrogen ion concentrations at low acidities. The experimental data together with the values of (true $[H^+]$)were the values shown in Table 9. The values of (true $[H^+]$) were calculated with the aid of successive approximations. For this purpose values of k_1 and k_2 were initially calculated from points of higher acidity and these values of k_1 and k_2 were used to estimate the contribution of hydrogen ion from chloranilic acid at each acidity. The plot of the last two columns of Table 9 is shown in Figure 12. The calculation of the curve will be described later.

In the use of equations 37 and 41, the following values were used:

$D_1 = 0.075$

$D_m = 0.298$

$D_3 = 0.077$.

(The value of D_1 was obtained with the aid of successive approximations to be described later.) The resulting equations were:

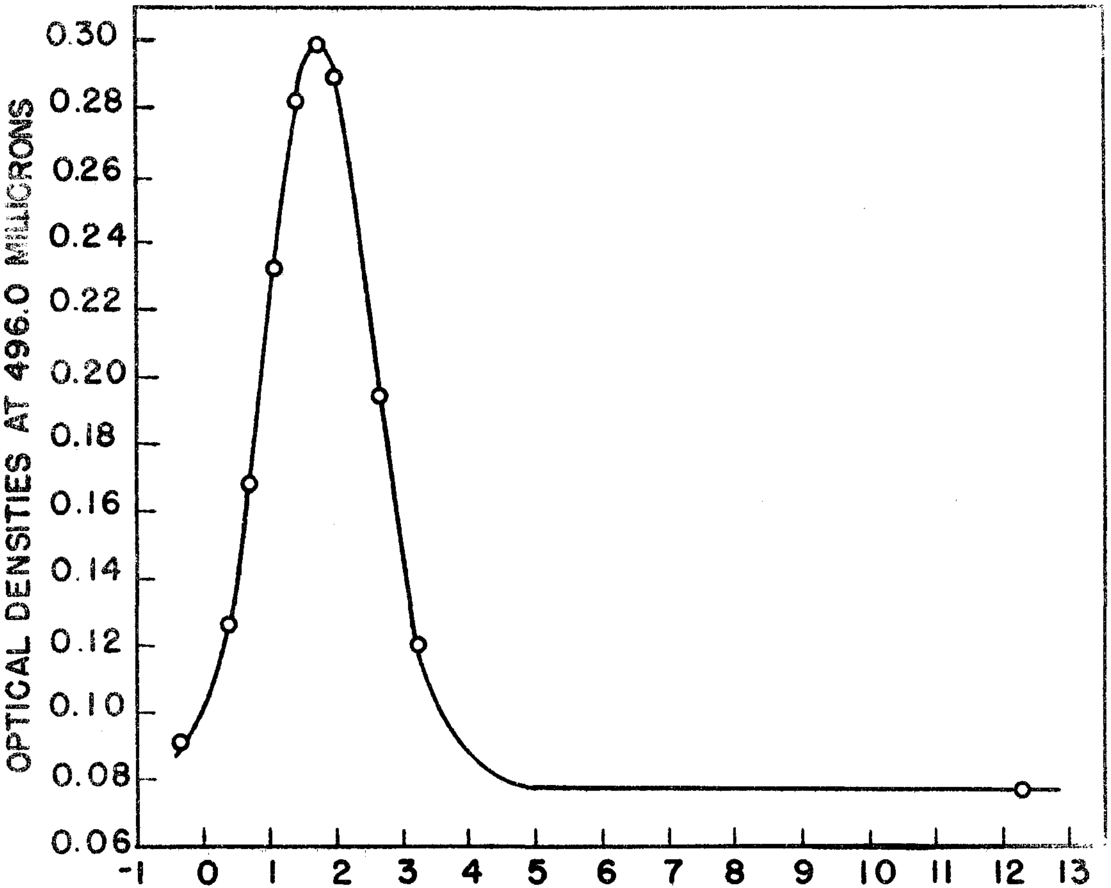


FIG. 12 OPTICAL DENSITIES OF CHLORANILIC ACID AT VARIOUS ACIDITIES. CIRCLES: EXPERIMENTAL POINTS.

Table 9.

Optical Densities of 1.033×10^{-4} Formal Chloranilic Acid in a 50.00 mm. Cuvette

Added $[H^+]$	Added $[OH^-]$	True $[H^+]$	-log(true $[H^+]$)	D at 496.0 m
2.002	-	2.002	-0.3015	0.091
0.4004	-	0.4004	0.3975	0.126
0.2002	-	0.2002	0.6985	0.168
0.08008	-	0.08014	1.0962	0.232
0.04004	-	0.04012	1.3966	0.282
0.01802	-	0.01811	1.7421	0.298
0.01001	-	0.01013	1.9944	0.289
2.002×10^{-3}	-	2.169×10^{-3}	2.6637	0.194
4.004×10^{-4}	-	5.928×10^{-4}	3.2271	0.120
-	0.0200	5.05×10^{-13}	12.297	0.077

$$k_1k_2 = \left(\frac{0.298-0.075}{0.298-0.077}\right)\left([H^+]_o\right)^2 = 1.009,050\left([H^+]_o\right)^2$$

and

$$\frac{k_1}{[H^+]_o} = \frac{(D-0.075)10^{-\Delta} + 1.009,050(D-0.077)10^{+\Delta} - 0.446}{0.298 - D}$$

where $\Delta = -\log(\text{true } [H^+]) + \log(\text{true } [H^+]_o)$.

Using the previously outlined method of least squares the best value for $-\log(\text{true } [H^+]_o)$ was found to be 1.759. The points that were used for this purpose were those shown in Table 10. In taking the average of values of $\frac{k_1}{[H^+]_o}$ at $-\log [H^+]_o = 1.759$, the points with $D = 0.282$ and $D = 0.289$ were omitted because they were too close to the peak to give accurate values for $\frac{k_1}{[H^+]_o}$. The results according to this method were

$$\frac{k_1}{[H^+]_o} = (4.685 \pm 0.250) \text{ , } [H^+]_o = 1.742 \times 10^{-2}$$

$$k_1 = 0.0816 \pm 0.0044$$

$$k_2 = \frac{(k_1k_2)}{k_1} = \frac{1.009,050\ [H^+]_o}{(4.685 \pm 0.250)}$$

$$k_2 = 0.00375 \pm 0.00020$$

The probable errors in the above values for k_1 and k_2 were probably a little higher than indicated due to an uncertainty in the value of $-\log [H^+]_o$.

Prior to the development of the equations used above, the constants for chloranilic acid were calculated by a method of successive approximations. Since the values changed very slowly this procedure was extremely tedious involving 54 sets of such approximations. The method involved the use of equation (5) in various forms:

Table 10.

Values Calculated for $\frac{k_1}{[H^+]_o}$ with $-\log(\text{true}[H^+]_o) = 1.759$

$-\log(\text{true}[H^+]_o)$	D	Δ	$\frac{k_1}{[H^+]_o}$
0.3975	0.126	-1.3615	4.2357
0.6985	0.168	-1.0605	4.8540
1.0962	0.232	-0.6628	4.7009
1.3966	0.282	-0.3624	7.5401
1.9944	0.289	+0.2354	5.1431
2.6637	0.194	+0.9047	4.9692
3.2271	0.120	+1.4681	4.6654

$$(5)\ D = \frac{Lce_1 + \frac{k_1}{[H^+]}(Lce_2) + \frac{k_1k_2}{[H^+]^2}(Lce_3)}{1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}}$$

$$(5')\ D = \frac{D_1 + \frac{k_1}{[H^+]}(Lce_2) + \frac{k_1k_2}{[H^+]^2}D_3}{1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}}$$

The value of D_3 was obtained directly from the data to be 0.077. However, the values of k_1, k_2, Lce_2, D_1 and the true $[H^+]$ were calculated by successive approximations. For the first approximation it was assumed that

D_1 was equal to D_3 and that the curve was symmetrical. The position of maximum optical density was visually estimated to be $-\log [H^+]_o \simeq 1.71$ which was also taken to be the value of $-\frac{1}{2}\log k_1k_2$. The resulting trial value of k_1k_2 was 3.80×10^{-4}. Taking points in pairs the quantity (Lce_2) was eliminated from (5'). Using $k_1k_2 = 3.80 \times 10^{-4}$ in the latter equation together with points on the left-hand side of the peak, an average value was calculated for k_1. These values of k_1 and k_1k_2 were substituted in the following form of (5'):

$$Lce_2 = D + \frac{[H^+]}{k_1}(D - D_1) + \frac{(k_1k_2)}{k_1\,[H^+]}(D - D_3)$$

which, using the four highest points on the curve, gave an average value for Lce_2. This in turn was substituted in another form of (5'):

$$k_1 = \frac{[H^+]\left(1 + \frac{k_1k_2}{[H^+]^2}\right)(D - 0.077)}{Lce_2 - D}$$

Points on the left-hand side of the peak were used in the latter equation to calculate a new average value for k_1. This quantity and the average value of Lce_2 were again substituted into (5') in the form:

$$k_2 = \frac{[H^+]\left[Lce_2 - D - \frac{[H^+]}{k_1}(D - 0.077)\right]}{D - 0.077}$$

This equation with points on the right-hand side of the peak gave an average value for k_2. Multiplying this average value of k_2 by the average value for k_1 a new value for k_1k_2 was obtained which was used in the next approximation. The above procedure was used for several sets of approximations, new values for the values of true $[H^+]$ being calculated occasionally.

In the next approximations the following method was found to be more expeditious:

(1.) Use $Lce_2 = D + \left(\frac{[H^+]}{k_1} + \frac{k_2}{[H^+]} \right)(D - 0.077)$ with the four highest points of the curve to obtain an average value for Lce_2.

(2.) Use this value of Lce_2 in

$$k_1 = \frac{\left[[H^+] + \frac{k_1 k_2}{[H^+]} \right](D - 0.077)}{Lce_2 - D}$$

together with points on the left-hand side of the peak to obtain an average value for k_1.

(3.) Use these average values of k_1 and Lce_2 in

$$k_2 = [H^+] \left[\frac{Lce_2 - D}{D - 0.077} - \frac{[H^+]}{k_1} \right]$$

together with points on the right-hand side of the peak to calculate an average value of k_2.

(4.) Multiply these two values of k_1 and k_2 together for the value of (k_1k_2) to use in the next approximation.

A new value for D_1 was then calculated from (5') using points from the two most acidic solutions and obtaining 0.075 for the average value of D_1.

In the remaining 15 approximations the following modified equations were used:

(1.) Use $Lce_2 = D + \frac{[H^+]}{k_1}(D - 0.075) + \frac{k_2}{[H^+]}(D-0.077)$ together with the four highest points of the curve to obtain an average value for Lce_2.

(2.) Use this value of Lce_2 in

$$k_1 = [H^+]\left(\frac{D-0.075}{Lce_2-D}\right) + \frac{k_1k_2}{[H^+]}\left(\frac{D-0.077}{Lce_2-D}\right)$$

together with points on the left-hand side of the peak to obtain an average value for k_1.

(3.) Use these average values of k_1 and Lce_2 in

$$k_2 = [H^+]\left[\left(\frac{Lce_2 - D}{D - 0.077}\right) - \frac{[H^+]}{k_1}\left(\frac{D - 0.075}{D - 0.077}\right)\right]$$

together with points on the right-hand side of the peak to calculate an average value for k_2.

(4.) Multiply these two values of k_1 and k_2 together for the value of (k_1k_2) to use in the next approximation.

It was found necessary to use a calculating machine in the above approximations because of the very slow manner in which the final values for k_1, k_2, and Lce_2 were approached. Another calculation of D_1 gave the same value, that is, 0.075. The values of $[H^+]$ corrected for contributions from the chloranilic acid were recalculated occasionally until they no longer changed appreciably.

The final values that were obtained were:

$Lce_2 = 0.394$

$k_1 = 0.0839 \pm 0.0036 \simeq 0.084 \pm 0.004$

and $k_2 = 0.00378 \pm 0.00013 \simeq 0.0038 \pm 0.0001$

These values of k_1 and k_2 agreed within the range of their standard deviations with the values calculated by the use of (37) and (41). The above values of Lce_2, k_1, k_2 and D_1 were substituted into (5') from which the curve of Figure 12 was then calculated. This set of values for the constants of chloranilic acid was used in the study of zirconium chloranilate complexes.

Discussion

In view of the large ionic strength at which the acid constants of chloranilic acid were determined, it did not seem possible to estimate its thermodynamic dissociation constants with any degree of accuracy.

Schwarzenbach and Suter[6] determined the acidity constants

$$k_1 = \frac{a_{H^+} \cdot [HCh^-]}{[H_2Ch]} \text{ and } k_2 = \frac{a_{H^+} \cdot [Ch^=]}{[HCh^-]}$$

of chloranilic acid by studying the reduction potential of the acid as a function of pH and also by spectrophotometric measurements. The values that they gave were

$k_1 = 0.14$ and $k_2 = 0.00066$.

They did not specify the ionic strength at which these were determined nor did they indicate that it was kept constant. They did mention, however, that buffer solutions of high capacity were used. Nevertheless, the ionic strengths of their solutions were probably less than 2. This and their use of hydrogen ion activities instead of concentrations should have made their values of both k_1 and k_2 lower than those from the present investigation. However, their k_1 is 70% higher and their k_2 is about one-sixth the present value. It is believed that their E.M.F. measurements did not give very accurate values for k_1 and k_2 because they did not have many points in the pH range at which the singly-ionized species was predominant. They did not specify how they interpreted their spectrophotometric data.

GENERAL DISCUSSION

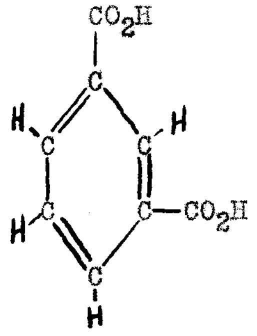
For high accuracy in applying this method it is apparent that a curve of optical density or composite optical density versus pH should have a maximum or minimum for which $|D_m - D_1|$ and $|D_m - D_3|$ or $|C_m - C_1|$ and $|C_m - C_3|$ have large values. From (41) it can also be seen that errors in points close to D_1, D_m or D_3 give rise to very large errors in the calculated value of k_1. It seems advisable to use points near D_m only for estimating D_m and pH_o. Two or more points should be used in determining the values of D_1, D_m and D_3. Buffer solutions should, of course, be fairly transparent in the region of the spectrum in which they are to be used. In the present investigations formate buffers of 0.03 molar concentration had optical densities of roughly 0.1 at 2450 Å and increasingly higher optical densities at lower wavelengths. Sager and co-workers indicate that 0.01 molar acetate buffers may be used above 2200 Å and 0.01 molar citrate buffers may be used above 2300 Å.[46]

A discussion of chemical groups that lead to absorption in the visible or ultraviolet region is found in the text by Brode (Ref. 23, Ch. 5). The present investigations of isophthalic and terephthalic acids were made possible by the strong absorption of the benzene nucleus in the ultraviolet region. There are innumerable substances which might be investigated. Among these are triphenylmethane dyes such as crystal violet. The value of $\frac{k_1}{k_2}$ for crystal violet has been found to be 4, very distinct color changes being in evidence for each step of the equilibria.[47] Other examples are found among the phthaleins. The value of $\frac{k_1}{k_2}$ for the two colorless forms of phenolphthalein that precede the colored form has been reported to be 4 by Rosenstein.[48] This equilibria might be investigated in the ultraviolet region. Many amino acids have overlapping acid constants and also absorb light in the ultraviolet or visible regions. Tyrosine[14] and l-dihydroxyphenylalanine[15] have been cited as examples.

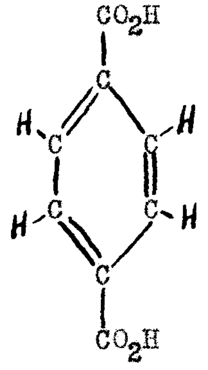
If the acidic groups of a dibasic acid are equivalent and do not interact by means of resonance or hydrogen bonding, the following equation by Bjerrum[49] relates $\frac{K_1}{K_2}$ to the distance r ($\mathring{A}$) between the groups

$$\log \frac{K_1}{K_2} = \log 4 + \frac{3.08}{r} .$$

The equation is based on electrostatic effects. Knowing r, an approximate value for $\frac{K_1}{K_2}$ can be calculated and, conversely, knowing $\frac{K_1}{K_2}$, a value for r may be calculated. For example, values calculated for r in isophthalic acid (I) and terephthalic acid (II)



(I)

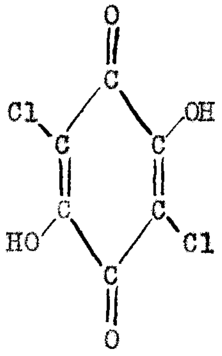


(II)

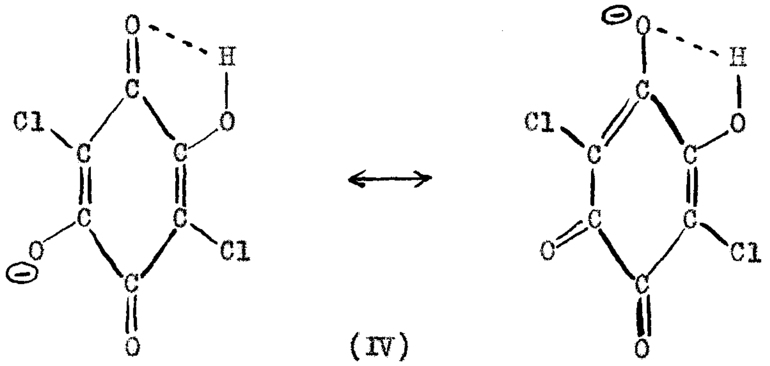
are thus 8.1 and 9.8 $\mathring{A}$ which are not far from the accepted values.

Resonance interaction between the acidic groups in these examples do not greatly affect the values of K_1/K_2.

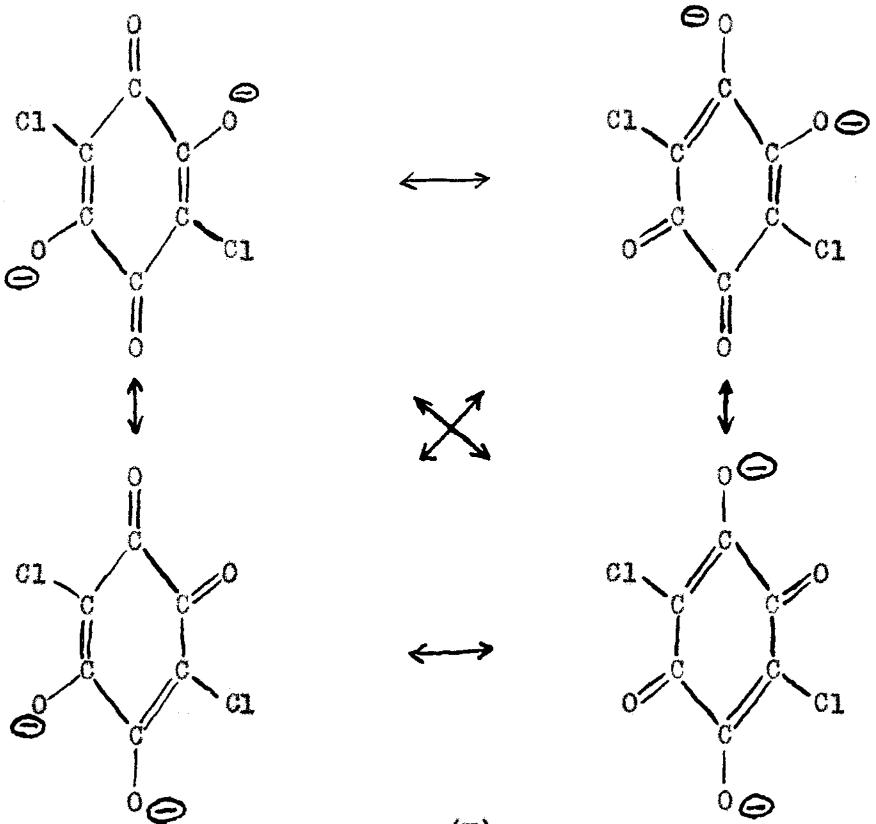
However, K_1/K_2 for chloranilic acid must be influenced by the relative resonance stabilizations of H_2Ch (III), HCh^- (IV), and Ch^{-2} (V)[6] as well as by electrostatic effects.



(III)



(IV)



(V)

Since K_1/K_2, the ratio of the thermodynamic constants, would be larger than $k_1/k_2 = 22.2$ observed at the ionic strength of 2, the resonance effect preferentially stabilizes the intermediate species in this case. This must be due partly to the fact that the right-hand resonance form of (IV) effectively reduces r and allows strong hydrogen-bonding to the negatively charged oxygen atom.

SUMMARY

1. The subject of the spectrophotometric determination of overlapping acidity constants for a dibasic acid has been reviewed. Equations have been derived by means of which such determinations can be made without the use of successive approximations. A brief discussion has been given of the possibility of utilizing other types of data for the same purpose.

2. The acidity constants of isophthalic acid at an ionic strength of 0.0302 have been determined from spectrophotometric studies in the ultraviolet region. The acidity constants have been found to be $k_1 = (2.8 \pm 0.4) \times 10^{-4}$ and $k_2 = (4.0 \pm 0.6) \times 10^{-5}$ from which the thermodynamic dissociation constants have been calculated to be $K_1 = (2.4 \pm 0.3) \times 10^{-4}$ and $K_2 = (2.5 \pm 0.4) \times 10^{-5}$.

3. Similarly the acidity constants for terephthalic acid at an ionic strength of 0.0300 have been found to be $k_1 = (3.4 \pm 1.0) \times 10^{-4}$ and $k_2 = (5.5 \pm 1.6) \times 10^{-5}$. From these values the thermodynamic dissociation constants have been calculated to be $K_1 = (2.9 \pm 0.9) \times 10^{-4}$ and $K_2 = (3.5 \pm 1.0) \times 10^{-5}$.

4. Acid constants in terms of concentrations have been determined for chloranilic acid by means of spectrophotometric studies in the visible region at an ionic strength of 2.002. The values obtained by means of the

equations mentioned above were $k_1 = 0.0816 \pm 0.0044$ and $k_2 = 0.00375 \pm 0.00020$. The same experimental data were used in a much longer method using successive approximations to give the values of $k_1 = 0.0839 \pm 0.0036$ and $k_2 = 0.00378 \pm 0.00013$.

5. A brief discussion has been included regarding the experimental application of the spectrophotometric method.

APPENDIX A

In deriving the correct equations for the application of the method of Vlès and Gex to a dibasic acid, it is convenient to put their ϕ function

$$\phi = \frac{e_1' + \frac{k_1}{a} e_2' + \frac{k_1 k_2}{a^2} e_3'}{e_1 + \frac{k_1}{a} e_2 + \frac{k_1 k_2}{a^2} e_3}$$

in the form

$$\phi = \frac{\frac{a}{k_1} e_1' + e_2' + \frac{k_2}{a} e_3'}{\frac{a}{k_1} e_1 + e_2 + \frac{k_2}{a} e_3} .$$

Making the substitutions $pH = -\log a$, $pk_1 = -\log k_1$ and $pk_2 = -\log k_2$, the latter equation for ϕ becomes

$$\phi = \frac{e_1' \, 10^{pk_1 - pH} + e_2' + e_3' \, 10^{pH - pk_2}}{e_1 10^{pk_1 - pH} + e_2 + e_3 \, 10^{pH - pk_2}} .$$

Clearing of fractions in the latter equation gives

$$\phi \, e_1 \, 10^{pk_1 - pH} + \phi \, e_2 + \phi \, e_3 \, 10^{pH - pk_2}$$
$$= e_1' \, 10^{pk_1 - pH} + e_2' + e_3' \, 10^{pH - pk_2} .$$

Collecting like terms in the latter equation one obtains

$$10^{pk_1}(e_1' - \phi \, e_1) 10^{-pH} + 10^{-pk_2}(e_3' - \phi \, e_3) 10^{pH} = \phi \, e_2 - e_2' .$$

The latter equation is valid at any value of ϕ for which there is a corresponding value of pH. Hence at values ϕ_1 and ϕ_2 one has the following equations

$$10^{pk_1}(e_1' - \phi_1 e_1)10^{-pH_1} + 10^{-pk_2}(e_3' - \phi_1 e_3)10^{pH_1} = \phi_1 e_2 - e_2'$$

$$10^{pk_1}(e_1' - \phi_2 e_1)10^{-pH_2} + 10^{-pk_2}(e_3' - \phi_2 e_3)10^{pH_2} = \phi_2 e_2 - e_2'.$$

Making the substitutions $x = 10^{pk_1}$, $y = 10^{-pk_2}$ and

$$\alpha_1 = (e_1' - \phi_1 e_1)10^{-pH_1} \qquad \alpha_2 = (e_1' - \phi_2 e_1)10^{-pH_2}$$

$$\gamma_1 = (e_3' - \phi_1 e_3)10^{pH_1} \qquad \gamma_2 = (e_3' - \phi_2 e_3)10^{pH_2}$$

$$\delta_1 = \phi_1 e_2 - e_2' \qquad \delta_2 = \phi_2 e_2 - e_2'$$

one obtains

$$x\alpha_1 + y\gamma_1 = \delta_1$$

$$x\alpha_2 - y\gamma_2 = \delta_2$$

The solution of the latter pair of equations is

$$x = \frac{\begin{vmatrix} \delta_1 & \gamma_1 \\ \delta_2 & \gamma_2 \end{vmatrix}}{\begin{vmatrix} \alpha_1 & \gamma_1 \\ \alpha_2 & \gamma_2 \end{vmatrix}} = \frac{\delta_1\gamma_2 - \delta_2\gamma_1}{\alpha_1\gamma_2 - \alpha_2\gamma_1}$$

$$y = \frac{\begin{vmatrix} \alpha_1 & \delta_1 \\ \alpha_2 & \delta_2 \end{vmatrix}}{\begin{vmatrix} \alpha_1 & \gamma_1 \\ \alpha_2 & \gamma_2 \end{vmatrix}} = \frac{\alpha_1\delta_2 - \alpha_2\delta_1}{\alpha_1\gamma_2 - \alpha_2\gamma_1}$$

Since

$$k_1 = \frac{1}{x} = \frac{\alpha_1\gamma_2 - \alpha_2\gamma_1}{\delta_1\gamma_2 - \delta_2\gamma_1}$$

the following expression is obtained for k_1:

$$k_1 = \frac{(e_1' - \phi_1 e_1)(e_3' - \phi_2 e_3)10^{-pH_1+pH_2} - (e_1' - \phi_2 e_1)(e_3' - \phi_1 e_3)10^{-pH_2+pH_1}}{(\phi_1 e_2 - e_2')(e_3' - \phi_2 e_3)10^{pH_2} - (\phi_2 e_2 - e_2')(e_3' - \phi_1 e_3)10^{pH_1}} .$$

Since

$$k_2 = y = \frac{\alpha_1 \delta_2 - \alpha_2 \delta_1}{\alpha_1 \gamma_2 - \alpha_2 \gamma_1}$$

the following expression is obtained for k_2:

$$k_2 = \frac{(e_1' - \phi_1 e_1)(\phi_2 e_2 - e_2')10^{-pH_1} - (e_1' - \phi_2 e_1)(\phi_1 e_2 - e_2')10^{-pH_2}}{(e_1' - \phi_1 e_1)(e_3' - \phi_2 e_3)10^{-pH_1+pH_2} - (e_1' - \phi_2 e_1)(e_3' - \phi_1 e_3)10^{-pH_2+pH_1}} .$$

The above equations can be used to calculate k_1 and k_2 from any two values of ϕ provided that the extinction coefficients are known or can be estimated.

In Table 11 are given optical density values for a hypothetical dibasic acid at two different wave lengths. The acidity constants are defined as being $k_1 = 5 \times 10^{-5}$ and $k_2 = 2 \times 10^{-6}$. The values of D were calculated from (5) using the values of Lce_1, Lce_2 and Lce_3 that are shown in the table. The values of ϕ are shown in the last column of the table. The plot of ϕ versus pH is shown in Figure 13. Since the tabulated values of ϕ are absolutely correct by definition, one can use the values of pH and ϕ of the table to test the validity of equations for evaluating the acidity constants. The results of the test for k_1 as calculated by the above equation and as calculated by the corresponding equation by Vlès and Gex (Ref. 8, p. 74) are shown in Table 12.

Table 11.

Calculated Values of D and ϕ for $k_1 = 5 \times 10^{-5}$ and $k_2 = 2 \times 10^{-6}$

a	pH	D with $Lce_1 = 0.300, Lce_2 = 0.800$ and $Lce_3 = 0.400$	D with $Lce_1 = 0.300, Lce_2 = 0.100$ and $Lce_3 = 0.400$	ϕ = ratio of third column to fourth column
1.0×10^{-1}	1.00000	.300,250	.299,900	1.001,167
1.0×10^{-2}	2.00000	.302,488	.299,005	1.011,649
1.0×10^{-3}	3.00000	.324,067	.290,487	1.115,990
1.0×10^{-4}	4.00000	.466,225	.234,437	1.988,701
6.3×10^{-5}	4.20066	.519,560	.214,115	2.426,546
2.5×10^{-5}	4.60206	.621,519	.178,481	3.482,270
1.7×10^{-5}	4.76955	.651,090	.170,864	3.810,574
1.1×10^{-5}	4.95861	.669,650	.170,298	3.932,225
6.7×10^{-6}	5.17393	.669,876	.181,223	3.696,418
4.0×10^{-6}	5.39794	.648,101	.205,063	3.160,497
2.5×10^{-6}	5.60200	.613,514	.235,135	2.609,199
1.0×10^{-6}	6.00000	.531,788	.300,000	1.772,627
1.0×10^{-7}	7.00000	.419,036	.385,706	1.086,413
1.0×10^{-8}	8.00000	.401,990	.398,507	1.008,740
1.0×10^{-9}	9.00000	.400,200	.399,850	1.000,875

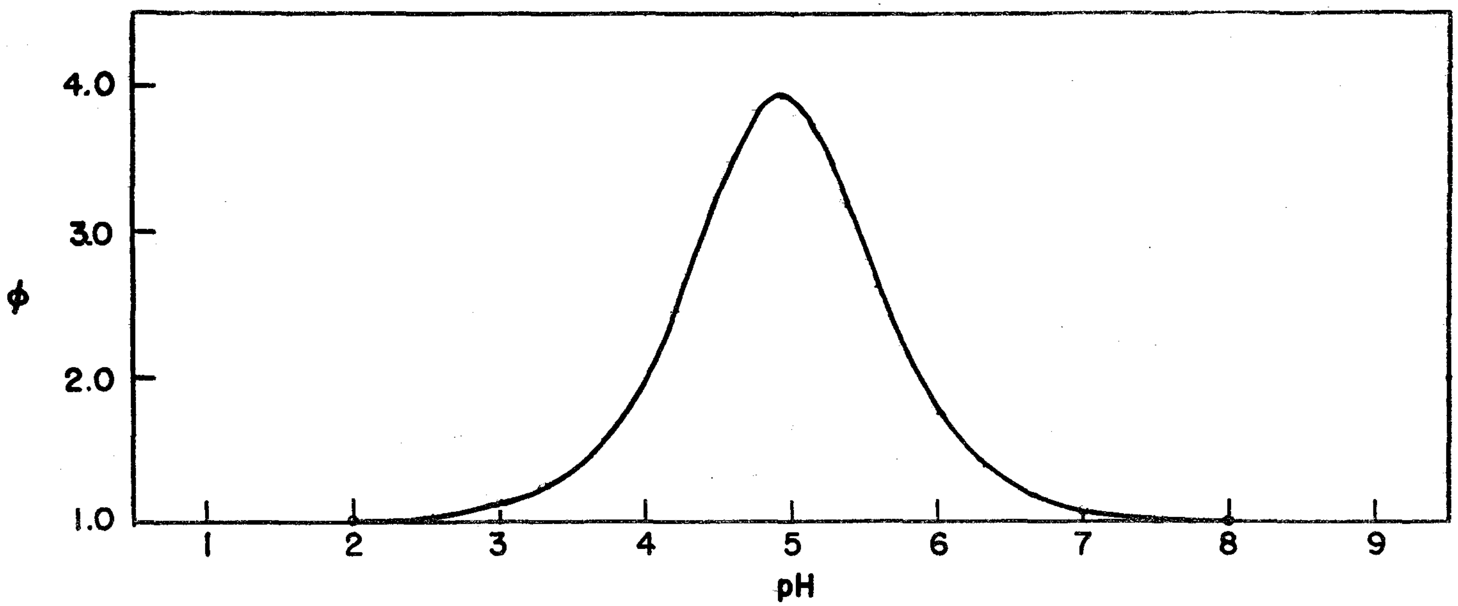


Fig. 13 Plot of φ vs pH for the hypothetical acid having k_1=5 x 10 & k_2=2 x 10.

Table 12.

Values of k_1 calculated from Table 11

Points used		Values of k_1 calculated from the present equation	Values of k_1 calculated from Vlès and Gex's equation
pH	ϕ		
4.76955 5.17393	3.810,574 3.696,418	4.9999×10^{-5}	5.3787×10^{-5}
4.60206 5.17393	3.482,270 3.696,418	4.9998×10^{-5}	5.3237×10^{-5}
4.20066 5.60206	2.426,546 2.609,199	5.0000×10^{-5}	5.3731×10^{-5}

Hence values of k_1 calculated from the equation derived above agree with the originally assumed value of exactly 5×10^{-5} within the limits of error of the arithmetical calculations. The fact that the equation of Vlès and Gex gives consistently different values for k_1 than 5.000×10^{-5} indicates that their equation is in error.

APPENDIX B

The equipment used in Sacconi's method[17] consists essentially of two joined wedge cells having a total light path (L) equal to that of a third cell as shown in Figure 14. Equal concentrations of the acid under investigation are placed in each of the three cells. In the example to be considered here the acidity in the upper wedge cell is made high enough to convert the dibasic acid completely into the form H_2A. The hydrogen ion activity in the other wedge cell and in the single cell are adjusted to values of a_1 and a_2, respectively, with $a_2 > a_1$. The value chosen for a_1 is such that an appreciable color of HA is produced in the lower wedge cell, but it is assumed that none of the species A is produced. The equilibria in the lower wedge cell and the single cell are

$$k_1 = a_1\left(\frac{[HA]}{[H_2A]}\right)_1 \text{ and } k_1 = a_2\left(\frac{[HA]}{[H_2A]}\right)_2 ,$$

respectively. Since the total concentration of the dibasic acid in each cell is a constant c and only one step of dissociation is assumed to be operative, Sacconi assumes that each of the parentheses in the latter pair of equations encloses only one unknown variable. (The question of to what degree this assumption is valid will be discussed presently.) A point N along the line AD is found at which the light transmitted through the joined wedge cells matches the light transmitted through the third cell. The ratio $\frac{AN}{AD}$ is then used to calculate k_1.

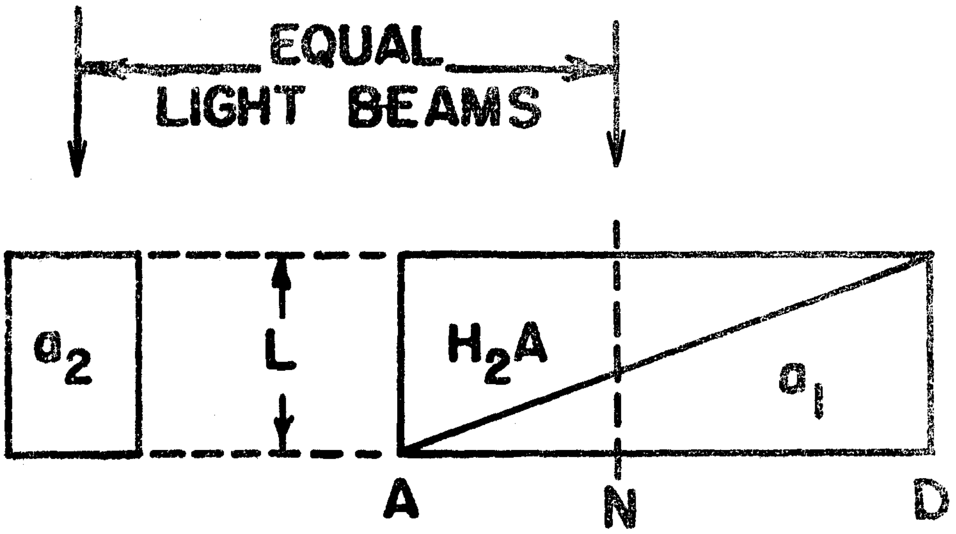


FIG. 14 EXPERIMENTAL ARRANGEMENT FOR SACCONI'S METHOD

Sacconi applied the above procedure for the determination of k_1 of mononitroquinol for which he found $pk_1 = 7.64$ and $pk_2 = 10.06$.[17] Thus, $\frac{k_1}{k_2} = 263$ and there was some overlapping in this case. The value chosen for a_1 in using the above method was such that there was 0.6 per cent of the species A present in the lower wedge cell. Using a slight variation of this method for determining k_1 of mononitroquinol the value of a_1 was taken at such a value that there was 1.8 per cent of the species A in the lower wedge cell. Using an analogous procedure for determining k_2 for mononitroquinol the least basic solution had 1.2 per cent of the undesired species H_2A present. In the latter case he stated that none of the species H_2A was present and in the other two cases mentioned he ignored the presence of the A species. However, the errors introduced into the calculated values of k_1 and k_2 for mononitroquinol were probably fairly small in this case because of the weak degree of overlapping between k_1 and k_2.

For the determination of k_1 and k_2 of a dibasic acid having $\frac{k_1}{k_2} < 200$, the effect of the undesired species becomes more serious in the use of Sacconi's method. Thus, in the determination of k_1 by the method outlined the presence of the A species has a twofold effect. Firstly, it diminishes the concentration and intensity of color of the H_2A-HA combination in the lower wedge cell. Secondly, it introduces a new color in the lower wedge cell due to the A species. The error so introduced into the measurement must depend partly upon the relative colors of H_2A, HA and A. In the determination of k_1 by the above method a value of a_1 is desired such that a high concentration of HA and a low concentration of A are present in the lower wedge cell. The maximum concentration of HA would occur when $-\log a_1 = pH_1 = \frac{1}{2}(pk_1 + pk_2)$ but there would also be a considerable concentration of A at that pH. Thus lower values of pH_1 must be employed. Figures 15 and 16 show the percentages of the forms A and HA in the lower wedge cell for various values of $(pH_1 - \frac{1}{2}(pK + pK\ )$ and $\frac{k_1}{k_2}$. Although the value of pH_2 must be lower than pH_1, the percentage of HA in the left-hand cell must still be appreciable for an accurate measurement. Thus, for low values of $\frac{k_1}{k_2}$ one is probably limited to values of pH_1 indicated in Figures 15 and 16. It is seen that appreciable concentrations of A must coexist with the values of HA required in the lower wedge cell. This factor introduces an error into the determination of k_1 if $\frac{k_1}{k_2}$ is very small. Furthermore the method loses something in sensitivity because the color of the species HA is not developed as much as possible. Similar considerations apply in the determination of k_2 using Sacconi's method. Thus, although his method involves no approximations in the calculations, it ignores an effect which may be serious if $\frac{k_1}{k_2}$ is small.

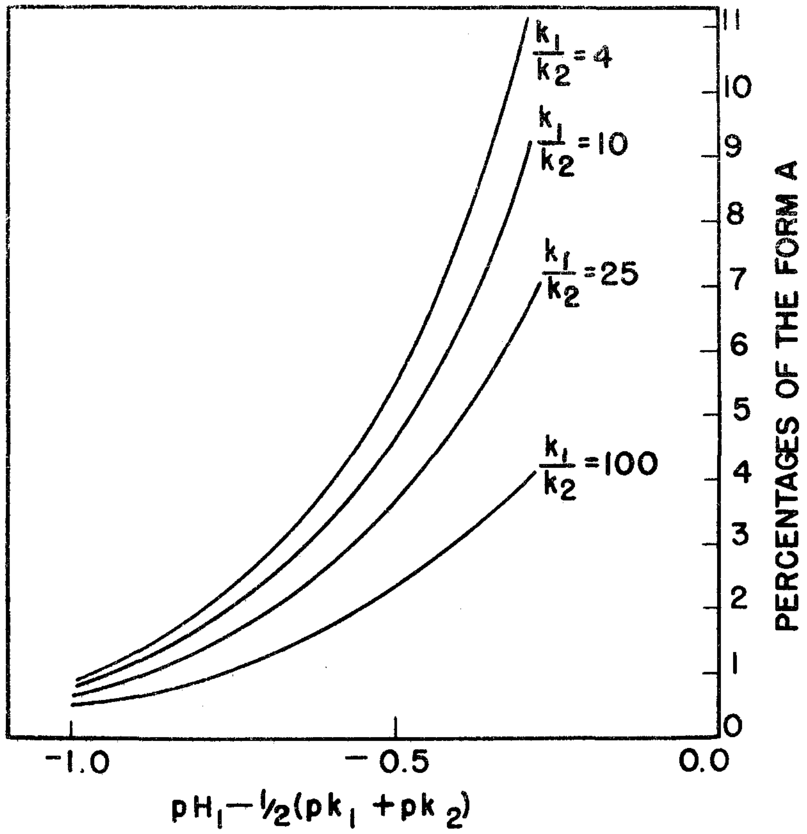


FIG.15 PERCENTAGES OF A IN THE LOWER WEDGE CELL.

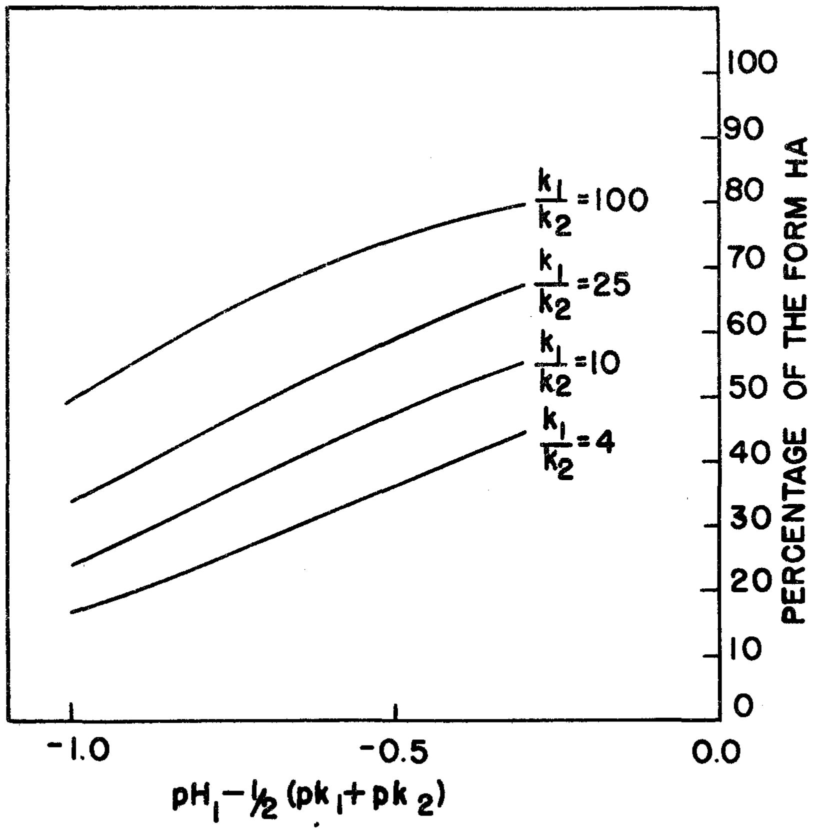


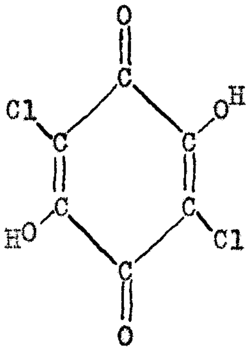
FIG.16 PERCENTAGES OF HA IN THE LOWER WEDGE CELL.

PART TWO

ZIRCONIUM CHLORANILATE COMPLEXES

INTRODUCTION

The reactions of chloranilic acid (I) with zirconium were studied in order to extend the knowledge of the chemistry of that element and in order to find whether or not chloranilic acid could be used as a colorimetric reagent for zirconium.



(I)

The experiments consisted of spectrophotometric studies of the zirconium chloranilate complexes, electrical migration experiments, analysis of a zirconium chloranilate precipitate and the development of a spectrophotometric method for determining zirconium.

Recent studies of the aqueous chemistry of zirconium by Connick and co-workers[50,51] have indicated that in very dilute solutions of zirconium in two molar perchlorate-perchloric acid solutions the principal species is Zr^{+4}. At higher concentrations of zirconium simultaneous hydrolysis and polymerization of zirconium were found. They found that polymerization began at approximately 10^{-3} molar zirconium in 2 molar perchloric acid and at approximately 10^{-4} molar zirconium in 1 molar perchloric acid. In order to keep the ionic strength and as a consequence the activity coefficients constant they used lithium perchlorate at a molarity equal to two minus the concentration of perchloric acid. It has been found[52] that in hydrochloric acid-lithium chloride solutions of constant ionic strength the activity coefficients of the hydrochloric acid remain constant even if the concentration of hydrochloric acid is varied from 10^{-3} to 3.

The results of the experiments of Connick and McVey[50] were reported entirely in terms of concentrations. Since the activity coefficients were presumably constant it was felt that each equilibrium constant would also be virtually constant. It was decided to use the same ionic strength and acid-salt pair in the present investigation of the complexing action of chloranilic acid on zirconium. From this it could be expected both that the equilibrium constants in terms of concentrations would be constant and that little, if any, zirconium would be complexed by the perchlorate ion. Furthermore, using the data of Connick and Reas[51] it was possible to estimate closely the fraction of uncomplexed zirconium that was in the form of the monomer.

MATERIALS AND APPARATUS

The work of Connick and McVey[50] had shown that most inorganic anions complex zirconium to some extent with chloride ion being one of the weakest complexing anions. Consequently it was decided to prepare zirconium perchlorate from zirconyl chloride. In this manner a trace of chloride ion left in the zirconium perchlorate would not interfere in the complexing experiments. A pure grade of zirconyl chloride octahydrate was kindly supplied for this purpose by Dr. K.A. Walsh.* Zirconium hydroxide was precipitated from 100 ml. of 0.033 M zirconyl chloride by the addition of a slight excess of ammonium hydroxide. The precipitate was washed with distilled water until the washes gave only a very faint opalescence when treated with nitric acid and silver nitrate. The zirconium hydroxide was dissolved in 2.003 M perchloric acid, the solution was filtered and made up to exactly 250 ml. with 2.003 M perchloric acid. Aliquots were assayed for zirconium by precipitating the hydroxide with ammonium hydroxide, filtering and igniting to the oxide at 800° C. This solution was diluted with the standard perchloric acid to give a solution containing 1.033×10^{-3} molar zirconium perchlorate in 2.003 M perchloric acid. Similar solutions of chloranilic acid were made up in the manner described in part one of this thesis. The preparation of the two molar

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*Dr. Walsh gave the following figures for the purity of this compound: $\frac{Hf}{Zr} \simeq 0.018$, Si $\simeq$ 0.05%, Fe $\simeq$ 15-20 p.p.m. and Ti $<$ 20 p.p.m.

perchloric acid has also been described.

It was found that recrystallized commercial lithium perchlorate contained enough sulfate to complex zirconium appreciably. For this reason all lithium perchlorate was either prepared from lithium metal plus water followed by neutralization with perchloric acid as described previously or by the method of Richards and Willard.[44] The latter method consisted essentially of heating G.F. Smith lithium perchlorate at 270-280° C. in a stream of dry air for four hours. The desired stock solution of two molar lithium perchlorate was then made up directly from the anhydrous salt. The above fusion of lithium perchlorate apparently expelled sulfate in the form of sulfuric acid since the use of the fused salt gave the same experimental results as did the laboratory prepared lithium perchlorate.

The Zr^{95} activity used in the electrical migration experiments was obtained in the form of a carrier-free, 1 M hydrochloric acid solution from the Oak Ridge National Laboratories. The activity as received contained roughly five millicuries each of Zr^{95} and the Cb^{95} daughter in $1\frac{1}{2}$ ml. of solution. The Zr^{95} was extracted into benzene with three equal volumes of 0.02 M thenoyltrifluoroacetone (TTA) in benzene thus effecting a separation from Cb^{95} since the latter activity is not extractable in this manner.[50] The benzene phase was then diluted 10-fold with benzene and shaken with two 3-ml portions of 2.003M perchloric acid. The resulting carrier-free Zr^{95} activity in 2.003 M perchloric acid was used within a three week period from the time of its preparation.

The Model 12 Cary Spectrophotometer was used for most of the studies with some exceptions as noted.

EXPERIMENTAL METHOD

The Cary Spectrophotometer was always first balanced to zero optical density with the solvent (i.e., $HClO_4 + LiClO_4$) in position. Subsequent optical density readings were then due to zirconium chloranilate complexes and chloranilic acid inasmuch as zirconium perchlorate was found to be transparent in the spectral regions that were used. In the work on the 1:1 complex the reference cuvette was kept in the reference chamber. The drift in the zero point readings never exceeded 0.01 optical density units during a series of measurements, but corrections for drift were applied whenever it was observed to take place. The absorption curves for the 1:1 complex were such that errors due to drift were not serious, but the work on the second complex required the best absolute accuracy obtainable. Thus for the study of this complex the instrument was used in the manner described in the work on isophthalic acid. The band width was approximately 10 Å and the temperature of each solution during scanning was 25±1°C.

In the analytical work on an insoluble compound that formed in concentrated solutions, measurements were made on a Model DU Beckman Spectrophotometer at 5500 and 3400 Å using the tungsten lamp. The band width was 10 Å at 5500 Å and 15 Å at 3400 Å. The Corning No. 9863 filter was used at the latter wavelength. The temperature of the solutions during measurement was 30 ± 3°C.

The electrical migration experiments were performed in a cell made by bending a filter stick of fine porosity into a U shape with the porous disc at the bottom of the U. The inside diameter of the glass tubing was 10 mm. and the overall width of the U tube was 45 mm. A bright platinum foil 5 mm. wide was suspended in each arm of the U tube to serve as an electrode. Voltage was supplied by a 6-volt lead storage battery connected in series with a variable resistor which was adjusted to give the desired voltage across the cell.

The measurement of Zr^{95} activity was accomplished with a mica-window Geiger-Mueller tube connected with an Instrument Development Laboratories amplifier and scaler. Each sample to be counted was measured through a 30 mg./cm.^{2} aluminum absorber and a 190 mg./cm.^{2} aluminum absorber, the difference being taken as due to Zr^{95} activity. This method of measurement was shown by absorption curves on freshly separated Zr^{95} and the equilibrium mixture of Zr^{95}- Cb^{95} to be the most effective way of measuring the Zr activity without influence from the Cb^{95}. This method of measuring Zr^{95} activity in the presence of Cb^{95} has also been employed by Huffman and Beaufait.[53]

THE 1:1 COMPLEX

Mixtures of comparable amounts of zirconium and chloranilic acid in 1 or 2 M perchloric acid were found to give a wine violet color at concentrations from 5×10^{-5} to 2×10^{-4} molar. At concentrations of roughly 2×10^{-4} to 5×10^{-4} molar zirconium in the presence of excess chloranilic acid, a wine red color was obtained that did not appear to be the sum of the wine violet color and the color of uncombined chloranilic acid. Since a second complex seemed to exist at the latter concentrations, it was decided to investigate the complex responsible for the wine violet color in more dilute solutions. This will be referred to as the first complex and the wine-red as the second in the following discussion.

Job's method of continuous variations was used to determine the zirconium-to-chloranilic acid ratio of the first complex. A series of solutions in 2.003 M perchloric acid were prepared having a chloranilic acid concentration of $1.033 \times 10^{-4}(\frac{x}{10})$ and a zirconium concentration of $1.033 \times 10^{-4}(1 - \frac{x}{10})$ for values of x from 0 to 10. These solutions were scanned in the ultraviolet region in a 9.965 mm. cuvette. The plot at several wavelengths of $(D - \frac{x}{10} D_{x=10})$ versus x gave a maximum or minimum at $x=5$ as shown in Figure 17. This indicated that the zirconium-to-chloranilic acid ratio was unity in this complex.

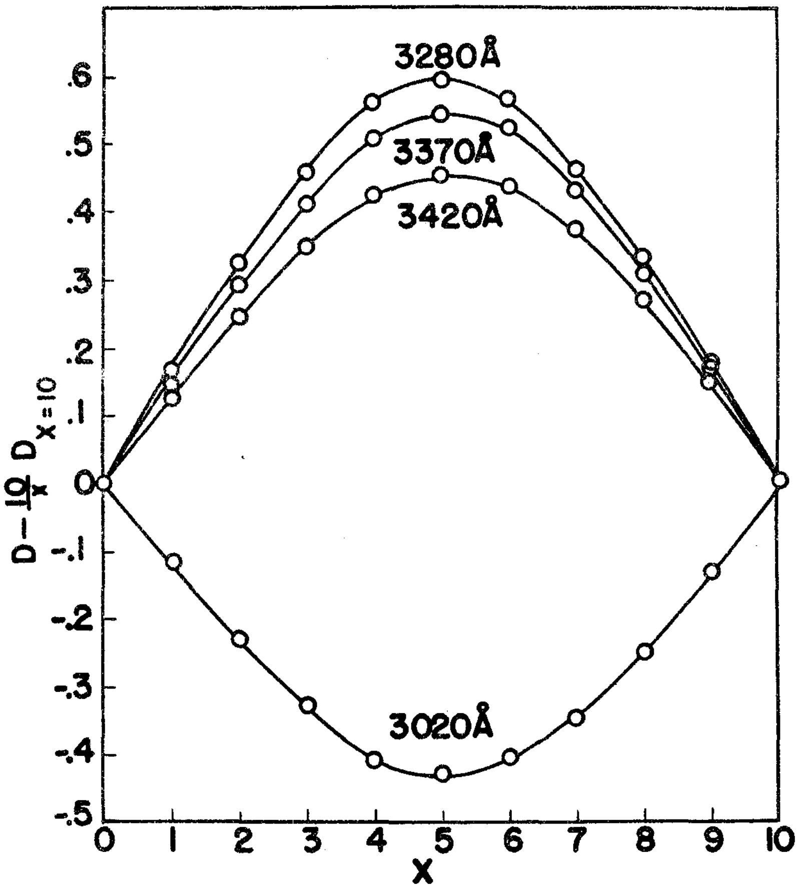

FIG. 17 THE IDENTIFICATION OF THE 1:1 ZIRCONIUM CHLORANILATE COMPLEX. $\frac{X}{10}$ = FRACTION OF CHLORANILIC ACID.

A series of solutions were scanned in order to demonstrate that the 1:1 complex obeyed Beer's law. The solutions were prepared in 2.003 M perchloric acid having a 1.033×10^{-3} molar excess of zirconium. The excess zirconium was necessary in order to prevent the formation of any of the second complex which was later proved to have a lower zirconium-to-chloranilic acid ratio. The concentration of the 1:1 complex was varied from 1.033×10^{-6} to 1.033×10^{-4}. The results obtained using a 20 mm. cuvette were as shown in Figure 18. The chloranilic acid was more than 99 per cent in the form of the 1:1 complex in this series of solutions.

In studying the formation constant of the 1:1 complex the formality of the chloranilic acid was kept at 1.033×10^{-5} while that of the zirconium was varied from 1.033×10^{-5} to 1.033×10^{-3}. The total molarity of perchloric acid and lithium perchlorate was 2.003. Three series of experiments were performed at perchloric acid concentrations 2.003, 1.502 or 1.001 molar. At concentrations of zirconium at which the equilibrium was measurable the zirconium was entirely in the form of the monomer as could be shown from the data of Connick and Reas.[51] Assuming the zirconium monomer to be Zr^{+4}, the equilibrium under study could be represented in the following manner:*

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*If the formula of the monomer in these solutions should be $Zr(OH)^{+3}$ or $Zr(OH)_2^{+2}$, the only effect it would have on the results of the present investigation would be to require a corresponding change in the formulae of the complexes. Present evidence indicates that under these conditions the monomer is at least mostly Zr^{+4}.[50] The effect of its possibly being a mixture of Zr^{+4} and $Zr(OH)^{+3}$ is treated in the discussion at the end of this section.

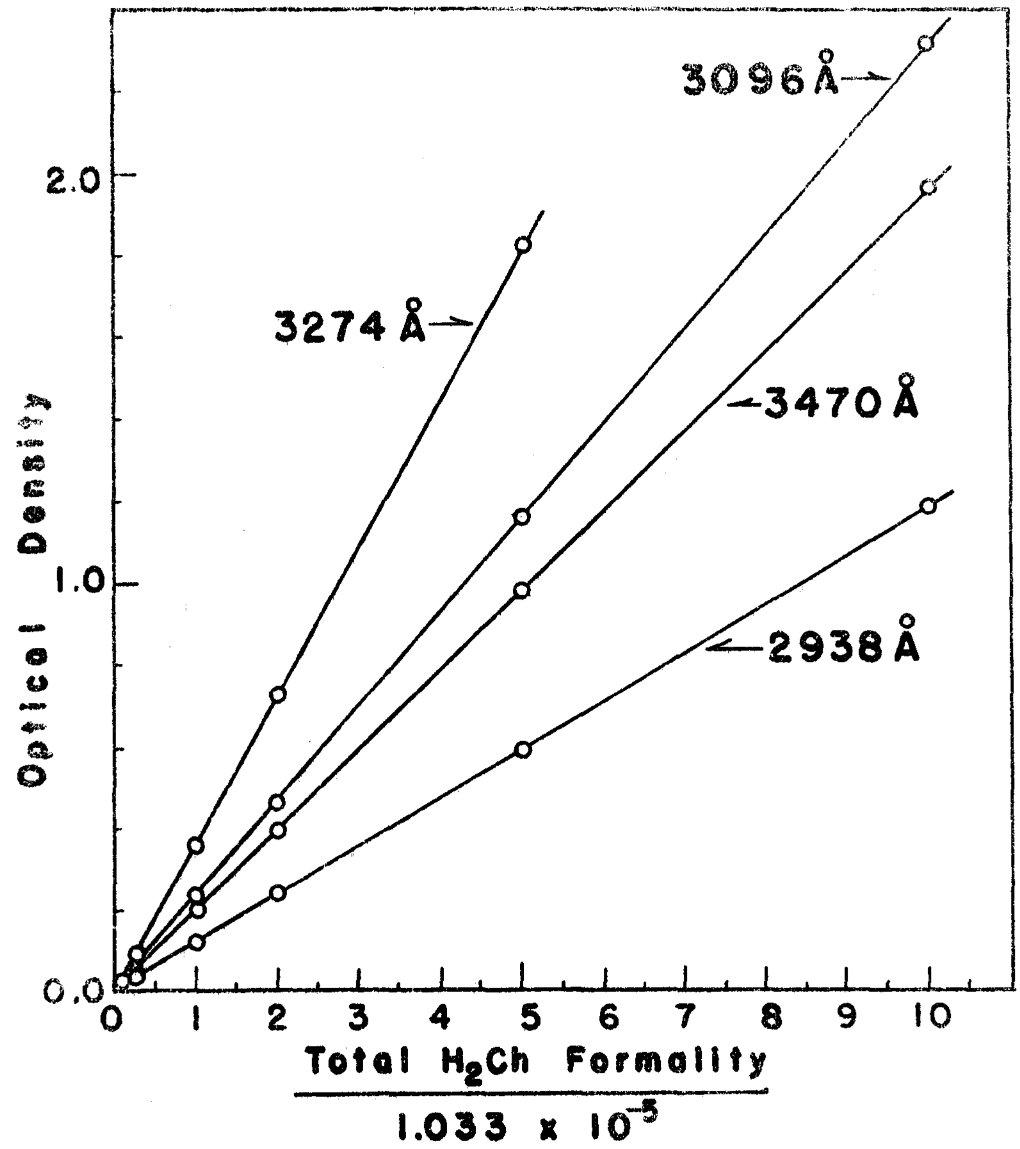


Fig. 18 Test of Beer's Law for the 1:1 Complex

(66) $Zr^{+4} + H_2Ch \rightleftharpoons (Zr\,H_{2-n}\,Ch)^{+4-n} + nH^{+}$

where the charge on the complex of course depends upon the value of n.

Representing 1.033×10^{-5} by the symbol (c) and assuming αc to be the concentration of the 1:1 complex, the formality of uncombined chloranilic acid is $c(1-\alpha)$. This quantity in combination with (1) gives the following expression for the concentration of undissociated chloranilic acid

$$[H_2Ch] = \frac{c(1-\alpha)}{1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}} \tag{67}$$

where k_1 and k_2 are the acid constants for chloranilic acid. The values that will be used are: $k_1 = 0.0839$ and $k_1k_2 = 3.17 \times 10^{-4}$. In 1 or 2 M perchloric acid the term $\frac{k_1k_2}{[H^+]^2}$ is negligible and will be neglected. Expressing the total formality of the zirconium as cy, that of uncomplexed zirconium is $c(y-\alpha)$. The formation constant in terms of concentrations is then

$$K_1 = \frac{c\alpha\,[H^+]^n\left(1 + \frac{k_1}{[H^+]}\right)}{c^2(y-\alpha)(1-\alpha)} = \frac{[H^+]^n\left(1 + \frac{k_1}{[H^+]}\right)}{c} \cdot \frac{\alpha}{(y-\alpha)(1-\alpha)} \tag{68}$$

The following quantity (ρ) is experimentally determined at each value of the hydrogen ion concentration

$$\rho = \frac{\alpha}{(y-\alpha)(1-\alpha)} \tag{69}$$

Combining (69) and (68), the formation constant is expressible as follows:

$$K_1 = \frac{1}{c}\left(1 + \frac{k_1}{[H^+]}\right)[H^+]^n\rho \tag{70}$$

where ρ is a constant for any one value of the hydrogen ion concentration.

Representing the concentration of the 1:1 complex by c_{11} and its molar extinction coefficient by e_{11}, the optical densities of the solutions under study can be expressed as

$$(71)\quad D = Lc_{11}e_{11} + L\,[H_2Ch]\,e_1 + L\,[HCh^-]\,e_2 + L\,[Ch^=]\,e_3$$

where L is the length of the cuvette and e_1, e_2 and e_3 are the molar extinction coefficients of H_2Ch, HCh^- and $Ch^=$ respectively. By means of relations (2), (3) and (67), the sum of the last three terms on the right of (71) can be represented as

$$(72)\quad L\,[H_2Ch]\,e_1 + L\,[HCh^-]\,e_2 + L\,[Ch^=]\,e_3 = \frac{L\,c\,(1-\alpha)}{1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}} \cdot \left(e_1 + \frac{k_1}{[H^+]}\,e_2 + \frac{k_1k_2}{[H^+]^2}\,e_3\right)$$

The optical density D_o with no zirconium present (i.e., $y = o$) is from (5)

$$(73)\quad D_o = \frac{L\,c\left[e_1 + \frac{k_1}{[H^+]}\,e_2 + \frac{k_1k_2}{[H^+]^2}\,e_3\right]}{1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}}$$

and D_o is a constant for a given hydrogen ion concentration. Combining (72) and (73) there is obtained

$$L\,[H_2Ch]\,e_1 + L\,[HCh^-]\,e_2 + L\,[Ch^=]\,e_3 = (1-\alpha)\,D_o$$

which when substituted into (71) gives

$$D = Lc_{11}e_{11} + (1-\alpha)\,D_o$$

Since c_{11} has previously been defined as αc the latter equation becomes

$$(74)\quad D = (Lc\,e_{11})\alpha + (1-\alpha)\,D_o$$

When the chloranilic acid has been completely combined with the zirconium the optical density is $D = Lce_{11}$ which will be represented as D_{11}.

Hence (74) is

$$(75) \quad D = \alpha D_{11} + (1-\alpha)\, D_o$$

which can be rearranged to give

$$(76) \quad D_{11} = \frac{D - (1-\alpha)\, D_o}{\alpha}$$

and

$$(77) \quad \alpha = \frac{D - D_o}{D_{11} - D_o}$$

The absorption curves shown in Figure 19 are representative of the data that were obtained. The 1:1 complex ($y = 25$) showed an absorption maximum at 3280 Å and uncombined chloranilic acid ($y = 0$) showed a peak near 3020 Å. Both wavelengths were used in the calculations. Values of D_{11} were obtained from (76) using solutions having 99 per cent or more of the chloranilic acid in the form of the 1:1 complex. In these solutions the values of α could be estimated with sufficient accuracy with the aid of the rest of the data to allow the evaluation of D_{11} to within 0.5%. At values of D near D_{11} (i.e., at large values of y) the amount of uncomplexed zirconium in the form of the monomer as estimated from the data of Connick and Reas[51] was used in place of y to calculate the value of α.

The data obtained at hydrogen ion concentrations of 2.003, 1.502 and 1.001 have been summarized in Tables 13, 14 and 15. The average values of thus obtained were:

$$\rho = 1.410 \pm 0.023 \quad \text{at} \quad [H^+] = 2.003$$

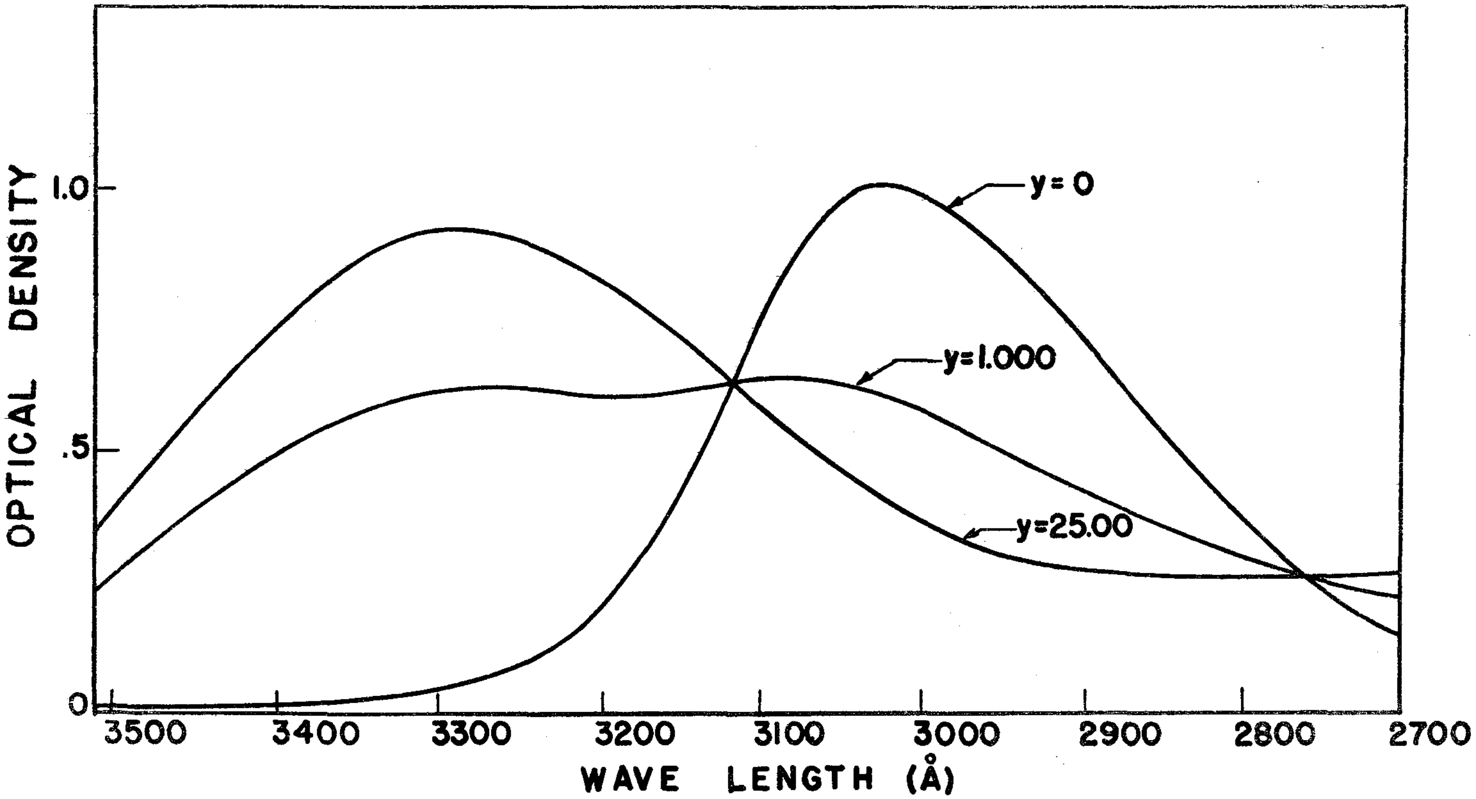


FIG.19 ABSORPTION CURVES OF CHLORANILIC ACID PLUS ZIRCONIUM.
IN 1M $HClO_4$ + 1M $LiClO_4$
LENGTH OF CUVETTE = 50.00 mm.

Table 13.

The 1:1 Zirconium Chloranilate Complex in 2.003 M Acid

	At 3280 Å $D_{11} = 0.947$ $D_o = 0.050$			At 3020 Å $D_{11} = 0.406$ $D_o = 1.043$		
y	D	α	ρ	D	α	ρ
1.00	0.448	0.444	1.437	0.762	0.441	1.411
1.10	0.472	0.470	1.408	0.743	0.471	1.416
1.20	0.499	0.500	1.429	0.730	0.492	1.369
1.25	0.505	0.507	1.384	0.715	0.515	1.445
1.50	0.560	0.568	1.411	0.685	0.562	1.369
2.00	0.638	0.656	1.420	0.625	0.656	1.420
99.0	0.939	-	-	0.411	-	-

Table 14.

The 1:1 Zirconium Chloranilate Complex in 1.502 M Acid

	At 3280 Å $D_{11} = 0.938$ $D_o = 0.050$			At 3020 Å $D_{11} = 0.396$ $D_o = 1.016$		
y	D	α	ρ	D	α	ρ
1.00	0.528	0.538	2.52	0.696	0.516	2.20
1.10	0.552	0.565	2.43	0.669	0.560	2.36
1.25	0.600	0.619	2.58	0.647	0.595	2.24
2.00	0.717	0.751	2.42	0.552	0.748	2.37
74.0	0.930	-	-	0.402	-	-

Table 15.

The 1:1 Zirconium Chloranilate Complex in 1.001 M Acid

y	At 3280 Å $D_{11} = 0.936$ $D_o = 0.051$			At 3020 Å $D_{11} = 0.394$ $D_o = 1.010$		
	D	α	ρ	D	α	ρ
1.00	0.620	0.643	5.04	0.606	0.656	5.54
1.10	0.651	0.678	5.00	0.583	0.693	5.55
1.20	0.682	0.714	5.14	0.564	0.725	5.56
1.30	0.710	0.745	5.27	0.546	0.753	5.58
25.0	0.927	-	-	0.400	-	-

$\rho = 2.39 \pm 0.12$ at $[H^+] = 1.502$

$\rho = 5.34 \pm 0.24$ at $[H^+] = 1.001$

Taking the above ρ values in pairs and solving for n in (70), the three values obtained were n = 1.87, 1.975 and 2.05, the average value for n being 1.97. This was so close to n = 2 that n was assumed to be exactly 2.00. The three average values calculated for K_1 were then

(78)
$$\overline{K_1} = (5.71 \pm 0.09) \times 10^{+5} \quad ([H^+] = 2.003)$$

$$\overline{K_1} = (5.52 \pm 0.23) \times 10^{+5} \quad ([H^+] = 1.502)$$

$$\overline{K_1} = (5.62 \pm 0.25) \times 10^{+5} \quad ([H^+] = 1.001)$$

From these three values the grand mean value $\overline{\overline{K_1}}$ was found to be

(79) $\overline{\overline{K_1}} = (5.69 \pm 0.08) \times 10^{+5}$

The effect of the second complex upon the determination of the stability constant of the 1:1 complex was minimized in the foregoing measurements by having the zirconium in excess. From later measurements it could be calculated that the concentration of the second complex in these solutions was always less than 1.4 per cent, its maximum value being in the 1 M $HClO_4$ solution for which $y = 1$. The effect in 1 M $HClO_4$ decreased in going from $y = 1$ to $y = 1.30$. A comparison of these ρ values at the two wavelengths shows that the values remain constant at 3020 Å, but that they increase at 3280 Å in going from $y = 1$ to $y = 1.3$. Hence the effect of the second complex may have been to give slightly low values for the average ρ at 1 M $HClO_4$ and for the values calculated for n. The effect on the average value of n would not be more than four per cent, so that the assumption that $n = 2$ still appears to be justified. The effect on $\overline{\overline{K_1}}$ would be nil because values of $\overline{K_1}$ at $[H^+] = 1.502$ and 1.001 have only 10-15% weight in determining K_1.

Since the value of n in (66) was found to be 2, the value of $\overline{\overline{K_1}}$ in (79) presumably refers to the reaction

(80) $$Zr^{+4} + H\ Ch \rightleftharpoons ZrCh^{+2} + 2H^+$$

and

(81) $$K_1 = \frac{[H^+]^2\ [ZrCh^{+2}]}{[Zr^{+4}]\ [H_2Ch]}$$

However, it is possible that under these conditions the zirconium monomer and the 1:1 complex undergo partial hydrolysis in the following manner:

$$Zr^{+4} + H_2O = Zr(OH)^{+3} + H^+ \qquad h_o = \frac{[H^+]\,[Zr(OH)^{+3}]}{[Zr^{+4}]}$$

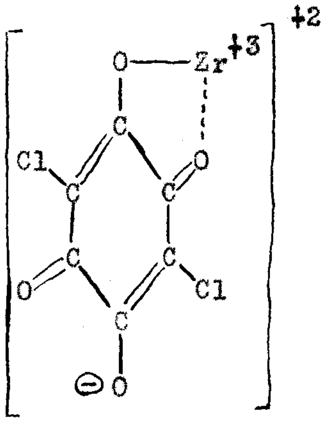
and

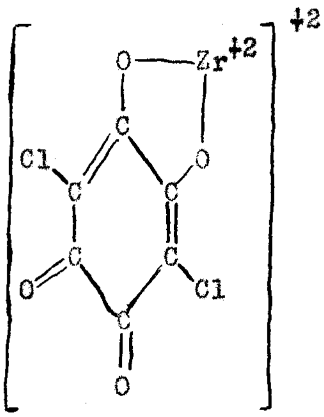
$$ZrCh^{+2} + H_2O = ZrCh(OH)^+ + H^+ \qquad h_1 = \frac{[H^+]\,[ZrChOH^+]}{[ZrCh^{+2}]}$$

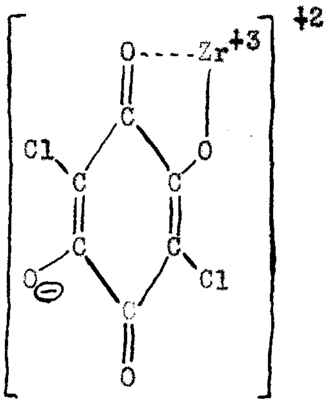
where h_o and h_1 are the respective hydrolysis constants. If this were the case then the measured values $\overline{K_1}$ of (78) would be related to the true constant K_1 of (81) in the following manner:

$$\overline{K_1} = \frac{(h_1 + H^+)}{(h \quad + H^+)} K_1$$

The fact that $\overline{K_1}$ was constant within experimental error over the range of hydrogen ion concentration from 2 to 1 molar appears to indicate one of three things: first, that h_o and h_1 are both large with respect to 2; second, that they are of the order of 1 or 2 and have roughly the same value; or third, that they are both much smaller than 1. The data of Connick and Reas indicate that h_o is less than one and probably less than one-half. If their data are accepted then the present data indicate that the principal 1:1 zirconium chloranilate species is $ZrCh^{+2}$. The structure of this species is probably best represented as a resonance hybrid of the following type







neglecting possible coordinate bonding between the zirconium atom and water molecules. Although the zirconium atom may not necessarily be equidistant from the nearby oxygen atoms it is very likely close enough to each to allow an appreciable contribution from each of the above resonance forms. The similarity between the colors of the 1:1 complex and singly ionized chloranilic acid also suggests the above structure. The bonds from the zirconium in the central structure are probably angular ds bonds or linear sp bonds.[55] It seems unlikely that the above $ZrCh^{+2}$ complex and the Zr^{+4} species should have similar degrees of hydrolysis, the reason being the difference in net charge on the zirconium atom in these two species. It therefore seems reasonable to assume that both h_o and h_1 are considerably less than 1 and that the observed equilibrium is almost entirely as shown in (80).

THE SECOND COMPLEX

The complex responsible for the wine red color was too unstable with respect to the 1:1 complex to be identified by Vosburgh and Cooper's modification[56] of Job's method. Instead it was necessary to see how well trial values for Zr:Ch of the second complex fitted the experimental data.

For the latter purpose a series of solutions was prepared having a total zirconium formality c of 1.033 x 10^{-4} or 2.066 x 10^{-4} and a total chloranilic acid formality of rc where r was varied between 1 and 10. Larger concentrations could not be employed because of the appearance of a precipitate under those conditions. The spectrophotometric measurements were made in the visible using a pair of 50 mm. cuvettes.

At each acidity it was found that the data could best be interpreted in terms of a second complex having a zirconium-to-chloranilic acid ratio of 1:2. The formation of the second complex was assumed to be as follows:

(82) $$ZrCh^{+2} + H_2Ch \rightleftharpoons ZrH_{2-m}\,Ch_2 + mH^{+}$$

and

(83) $$K_2 = \frac{[H^{+}]^{m}\;[ZrCh_2]}{[ZrCh]\;[H_2Ch]} \text{ or } \frac{cK_2}{[H^{+}]^{m}} = \frac{c\;[ZrCh_2]}{[ZrCh]\;[H_2Ch]}$$

where $[ZrCh_2]$ represents the concentration of the second complex no matter what the value of m. From the work on the 1:1 complex, (80) and (81) were assumed to hold with $K_1 = 5.69 \times 10^{+5}$.

The general expression for the optical density was

$$(84)\quad D = L\,[ZrCh_2]\,e_{12} + L\,[ZrCh]\,e_{11} + L\,[H_2Ch]\,e_1 + L\,[HCh]\,e_2 + L\,[Ch]\,e_3$$

where e_{12} was the molar extinction coefficient for the second complex. At each acidity one solution was made up with no zirconium but with the chloranilic acid formality equal to c. From (5) this solution gave the relation

$$L\left(e_1 + \frac{k_1}{[H^+]}e_2 + \frac{k_1k_2}{[H^+]^2}e_3\right) = \frac{D_o}{c}\left(1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}\right)$$

The last three terms of (84) were

$$L\,[H_2Ch]\,e_1 + L\,[HCh]\,e_2 + L\,[Ch]\,e_3$$
$$= L\,[H_2Ch]\left(e_1 + \frac{k_1}{[H^+]}e_2 + \frac{k_1k_2}{[H^+]^2}e_3\right)$$

Combining the latter two expressions with (84) gave

$$(85)\quad D = L\,[ZrCh_2]\,e_{12} + L\,[ZrCh]\,e_{11} + \frac{[H_2Ch]}{c}\left(1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}\right)D_o$$

The equations of material balance were

$$(86)\quad c = [Zr^{+4}] + [ZrCh] + [ZrCh_2]$$

and

$$rc = 2[ZrCh_2] + [ZrCh] + [H_2Ch] + [HCh] + [Ch]$$

The latter equation simplified to

$$(87)\quad rc = 2[ZrCh_2] + [ZrCh] + [H_2Ch]\left(1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}\right)$$

Combination of (87) with (85) gave

$$D = L\left[ZrCh_2\right]e_{12} + L\left[ZrCh\right]e_{11} + \frac{D_o}{c}\left(rc - 2\left[ZrCh_2\right] - \left[ZrCh\right]\right)$$

which upon combining terms gave

$$(88)\quad D = r\,D_o + \frac{1}{c}\left[(Lce_{12} - 2D_o)\left[ZrCh_2\right] + (Lce_{11} - D_o)\left[ZrCh\right]\right]$$

The wavelength chosen, 3847 Å, was one where $Lce_{11} = D_o$ which gave the following relation from (88)

$$(89)\quad \left[ZrCh_2\right] = \frac{(D - rD_o)\,c}{Lce_{12} - 2D_o}$$

Combining (81) and (86) gave

$$(90)\quad \left[ZrCh\right] = \frac{c - \left[ZrCh_2\right]}{1 + \dfrac{\left[H^+\right]^2}{K_1\left[H_2Ch\right]}}$$

Dropping $\frac{k_1k_2}{\left[H^+\right]^2}$ in (87) gave the following expression for $\left[H_2Ch\right]$

$$(91)\quad \left[H_2Ch\right] = \frac{rc - 2\left[ZrCh_2\right] - \left[ZrCh\right]}{1 + \dfrac{k_1}{\left[H^+\right]}}$$

Equations (89), (90) and (91) were used to obtain values for $\frac{ck_2}{\left[H^+\right]^m}$ of (83). Unfortunately the second complex was too unstable to allow the direct measurement of Lce_{12}. The value of $\frac{ck_2}{\left[H^+\right]^m}$ should be a constant at each hydrogen ion concentration. Therefore the experimental values of $\frac{ck_2}{\left[H^+\right]^m}$ were plotted versus r for several trial values of Lce_{12} and the slope of the best straight line through these values was calculated by the method of least squares for each trial value of Lce_{12}. Representing the equation of the straight line by

$$\frac{ck_2}{\left[H^+\right]^m} = y = a + br$$

the correct value of Lce_{12} was taken as the one for which $b = 0$ and the correct value for $\frac{ck_2}{[H^+]^m}$ was taken as (a) at that point. The equations used in calculating (a) and (b) at each value of Lce_{12} were:[31]

$$a = \frac{\sum r^2 \sum y_o - \sum r \sum r y_o}{n \sum r^2 - (\sum r)^2}$$

$$b = \frac{n \sum r y_o - \sum r \sum y_o}{n \sum r^2 - (\sum r)^2}$$

The data at $[H^+] = 2.002$ M and $c = 2(1.033 \times 10^{-4})$ are shown in Table 16 together with the results of the calculations at one trial value of Lce_{12}. The values of (a) and (b) calculated from these data are shown in Table 17. The data and results are similarly summarized in Tables 18 and 19 at $[H^+] = 1.401$ and in Tables 20 and 21 at $[H^+] = 1.001$.

The values obtained from the last six tables mentioned were

(92)

$K_2 = 1332\ (2.002)^m$ and $Lce_{12} = 0.804$

$K_2 = 4130\ (1.401)^m$ and $Lce_{12} = 0.716$

$K_2 = 4980\ (1.001)^m$ and $Lce_{12} = 0.769$

where these values for Lce_{12} are given for $c = 1.033 \times 10^{-4}$. Interpretation of relations (92) on the basis of possible hydrolysis or basic ionization of the $ZrH_{2-m}Ch_2$ complex did not improve the agreement among these expressions for K_2. It was therefore assumed that $ZrH_{2-m}Ch_2$ was a single species and that the correct value of Lce_{12} was the average of the values in (92), namely 0.763. Using this value and recalculating

Table 16.

Optical Density Data for the Second Complex

($[H^+] = 2.002$ M, $c = 2.066 \times 10^{-4}$)

r	D	Values of $\frac{cK_2}{[H^+]^m}$ with Lce$_{12}$ = 1.600
0.00	0.129	-
1.00	0.171	0.275
1.50	0.332	0.279
2.00	0.500	0.280
2.50	0.662	0.286
3.00	0.794	0.270
3.20	0.862	0.284
3.50	0.930	0.272
3.70	0.985	0.276
4.00	1.058	0.275

Table 17.

Values of a and b for Trial Values of Lce$_{12}$

($[H^+] = 2.002$ M)

Lce$_{12}$	a	b
1.700	0.257	-0.00322
1.607 (interpolated)	0.275	0.0000
1.600	0.277	+0.00020
1.500	0.306	+0.00324
1.400	0.325	+0.01359

Table 18.

Optical Density Data for the Second Complex

($[H^+] = 1.401$, $c = 1.033 \times 10^{-4}$)

r	D	Values of $\frac{cK_2}{[H^+]^m}$ with $Lce_{12} = 0.700$
0.00	0.065	-
2.00	0.270	0.460
3.00	0.421	0.437
4.00	0.550	0.443
5.00	0.665	0.461
6.00	0.765	0.470

Table 19.

Values of a and b for Trial Values of Lce_{12}

($[H^+] = 1.401$)

Lce_{12}	a	b
0.700	0.4366	+0.0044
0.716 (interpolated)	0.426	0.0000
0.750	0.4028	-0.0063
0.769	0.3886	-0.0085

Table 20.

Optical Density Data for the Second Complex

($[H^+]$ = 1.001 M, c = 1.033 x 10^{-4})

r	D	Values of $\frac{cK_2}{[H^+]^m}$ with Lce$_{12}$ = 0.770
0.00	0.068	-
2.00	0.303	0.536
2.40	0.373	0.511
3.00	0.470	0.508
3.40	0.528	0.506
4.00	0.608	0.508
6.00	0.822	0.486
9.00	1.098	0.527

Table 21.

Values of a and b for Trial Values of Lce$_{12}$

($[H^+]$ = 1.001 M)

Lce$_{12}$	a	b
0.750	0.5189	+0.0086
0.7688 (interpolated)	0.514	0.0000
0.770	0.5135	-0.0004
0.780	0.5073	-0.0036
0.803	0.4885	-0.0083

the expressions for K_2 there were obtained

$$K_2 = 1472\ (2.002)^m$$

$$K_2 = 3500\ (1.401)^m$$

$$K_2 = 5100\ (1.001)^m$$

Plotting these values of K_2 against the hydrogen ion concentration at which they were obtained, the value of m for which K_2 was most constant was found to be 1.84 ± 0.5. Since this was 2 within experimental error, the true value of m was taken to be exactly 2 and the resulting values for K_2 were thus

$$K_2 = 1472\ (2.002)^2 = 5900.$$

$$K_2 = 3500\ (1.401)^2 = 6870.$$

$$K_2 = 5100\ (1.001)^2 = 5110.$$

The final value for K_2 was taken as the average of the latter three values, namely 5960 ± 720 $\simeq$ 6000 ± 700.

Thus the above calculations indicated the equilibrium involving the second complex was as follows:

$$(93)\quad ZrCh^{+2} + H_2Ch \rightleftharpoons ZrCh_2 + 2H^+$$

$$(94)\quad K_2 = \frac{[H^+]^2\ [ZrCh_2]}{[ZrCh^{+2}]\ [H_2Ch]} = 6000 \pm 700$$

Curves calculated using (93), (94) and $Lce_{12} = 0.763$ (for $c = 1.033 \times 10^{-4}$) have been placed in Figures 20, 21 and 22 along with the experimental points. Although the agreement with the data is not very good, it is better than can be obtained by assuming the second complex to have a zirconium-to-chloranilic acid ratio of 1:3, 2:3 or 3:4. Analogous cal-

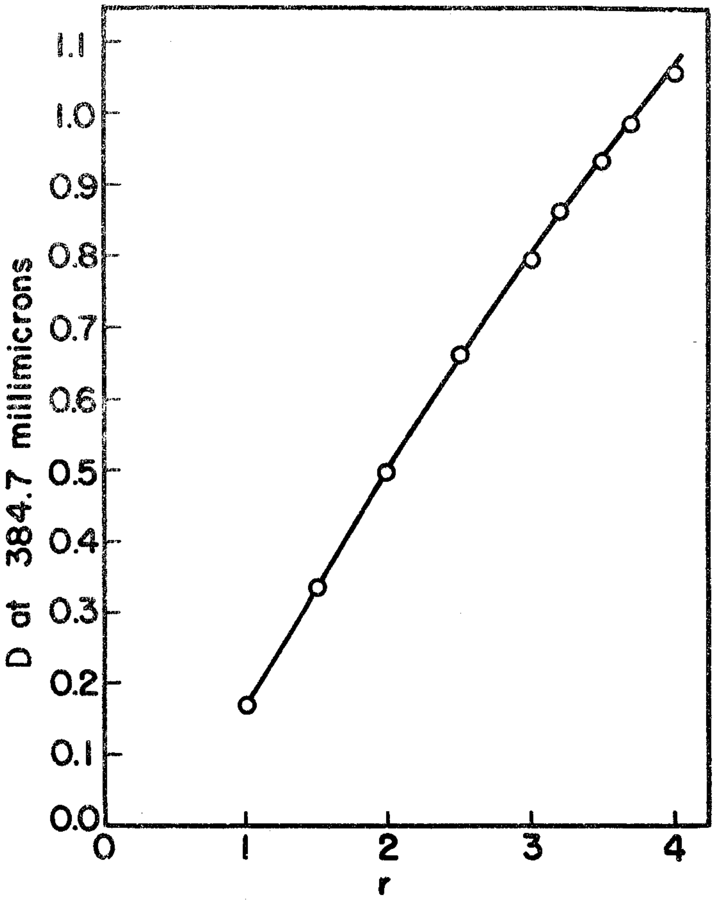


Fig.20 Optical Densities with Excess Chloranilic Acid Present.

$[H^+] = 2.00$

Circle : experimental points.

Curve : calculated on the basis of $ZrCh_2$.

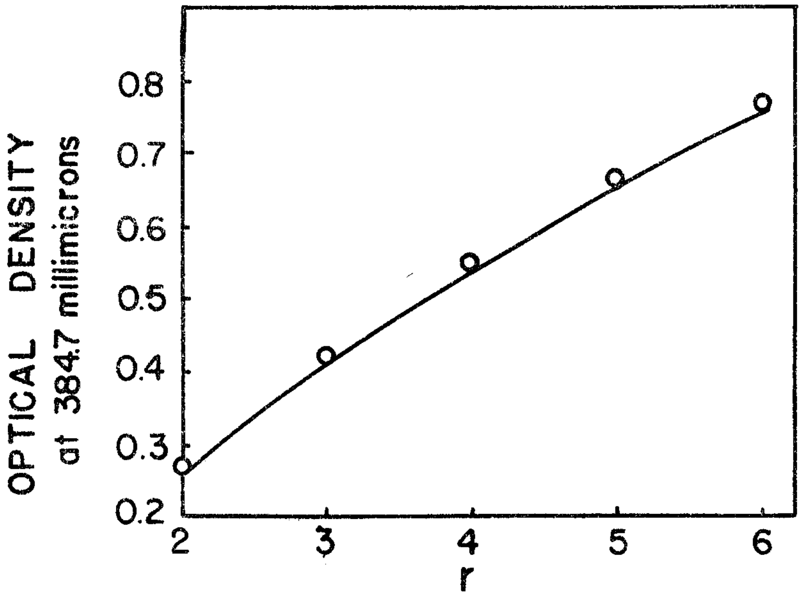


Fig.21 Optical Densities with Excess Chloranic Acid Present.

$[H^+] = 1.40$

Circles: experimental points

Curve: calculated on the basis of $ZrCh_2$

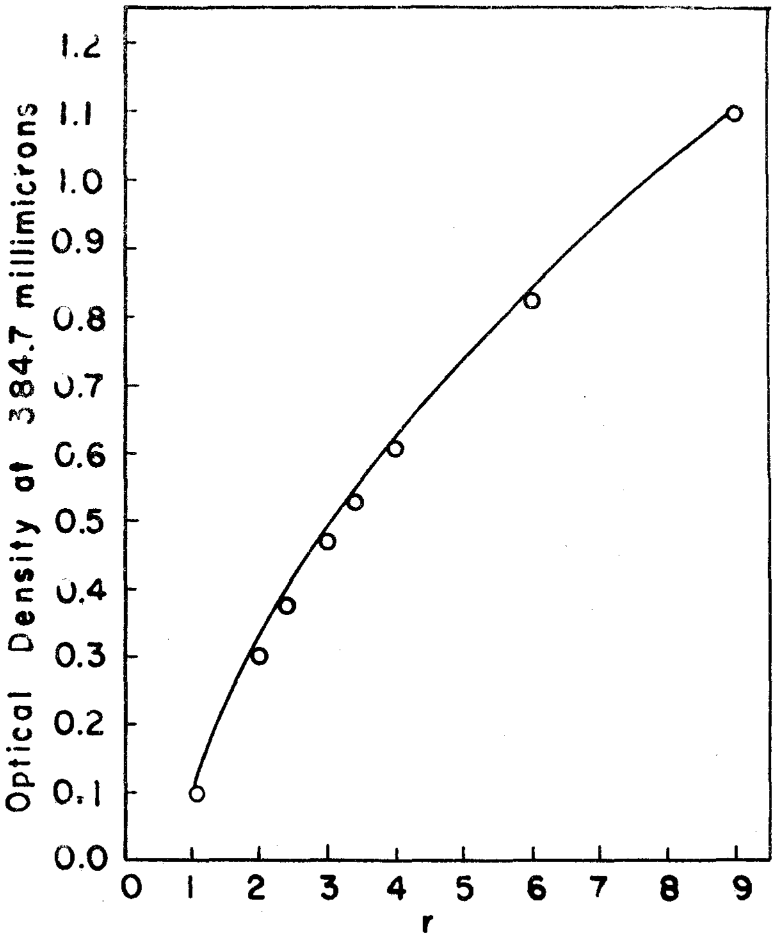


Fig.22 Optical Densities with Excess Acid Present

$[H^+] = 1.00$

Circles: experimental points

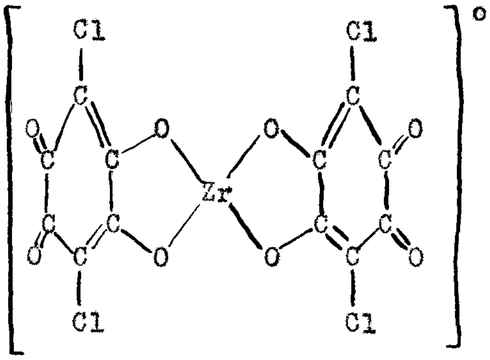
Curve: calculated on the basis of $ZrCh_2$

culations assuming a 1:3 or a 3:4 complex gave such varying values for K_2 and m that these possibilities could easily be discarded. The calculations on the basis of a 2:3 complex gave $m = 2.71 \pm 1.37$ and, assuming m to be 3, $K_2 = (2.27 \pm 0.66) \times 10^{+7}$. The relative standard deviations of these values were roughly twice those calculated for the 1:2 complex. The 2:3 complex was therefore considered to be less likely than the 1:2 complex but it could not be discarded as a possibility. If the 2:3 complex were correct the equilibrium would be as follows:

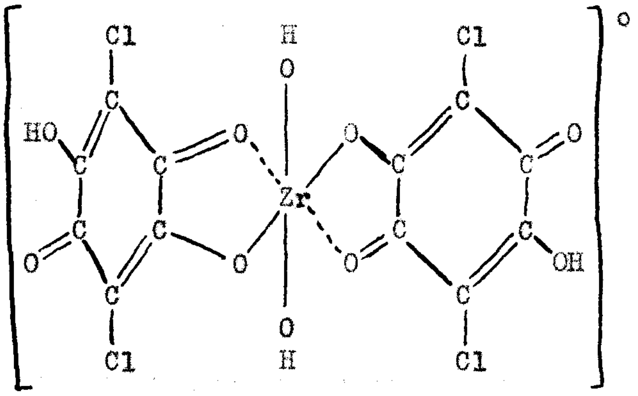
(95) $2ZrCh^{+2} + H_2Ch + H_2O \rightleftharpoons Zr_2(OH)Ch_3^{+} + 3H^{+}$

(96) $$K_2 = \frac{[Zr_2(OH)Ch_3^{+}]\,[H^{+}]^3}{[ZrCh^{+2}]^2\,[H_2Ch]} = (2.5 \pm 0.6) \times 10^{+7}$$

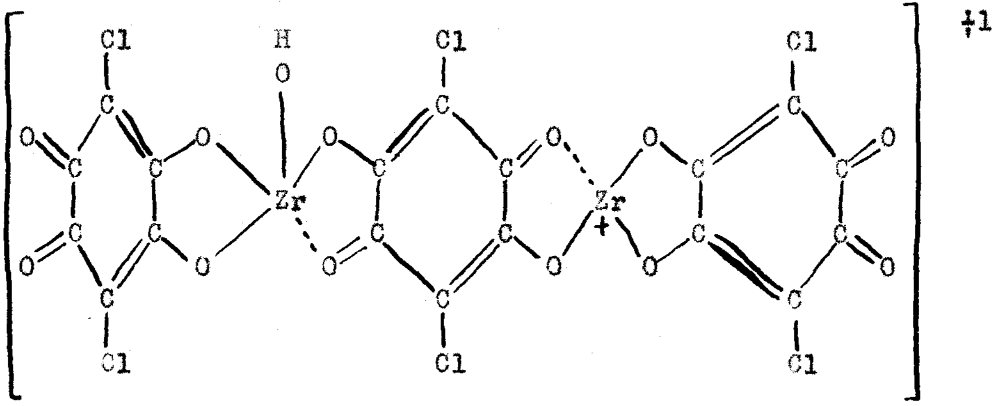
If the equilibrium represented by (93) and (94) are correct, the structure of the second complex is probably



and its resonance structures, if the effect of solvation can be neglected. In the above structure the zirconium atom might use its low lying d and s orbitals to give tetrahedral d^3s bonds, coplanar dsp^2 bonds, or d^2sp bonds directed outward toward the corners of an irregular tetrahedron.[55] Since a coordination number of six is common for zirconium, the following hydrated form might be equally probable for ZrCh$_2$.

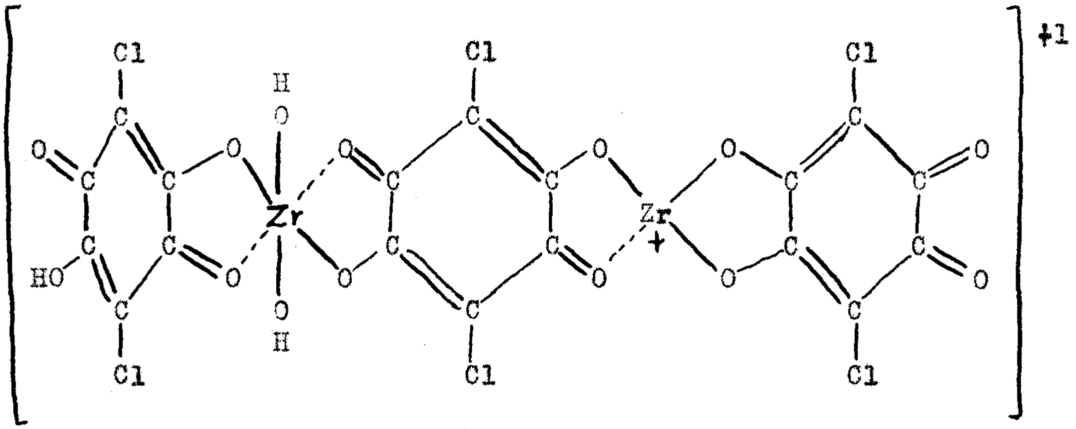


If the equilibria represented by (95) and (96) were correct, the structure of the Zr$_2$(OH)Ch$_3^+$-type complex might be either of the following:



A

or a hydrated form of the above structure such as structure B shown on the following page. Structure B would probably be preferred over structure A because it would not involve a coordination number of five for zirconium.



B

It is possible that the second complex is a mixture of $ZrCh_2$- and Zr_2Ch_3-type species. If this is true it would be difficult to calculate both K_2 for (94) and K_2 for (96) from the present data because of the fact that either or both of the complexes appear to be fairly weak at these concentrations. However, the present data probably indicate that the second complex is principally $ZrCh_2$.

Some electrical migration experiments were performed for the purpose of determining the charge on the second complex. They were run in the absence of lithium perchlorate in order to minimize the specific conductance of the solution, but one molar perchloric acid had to be used to prevent hydrolysis and polymerization of uncomplexed zirconium. The liquid levels in the two arms of the electrical migration cell were made up to the same height with solutions of the same chemical composition, but only one solution had the added Zr^{95} activity. The electrodes were located 2.0 cm. apart. A potential of two volts was applied to the cell for a period of ten hours during which the current remained approximately constant at one milliampere. At the end of this time aliquot portions from each arm of the cell were pipetted into watch glasses, nitric acid was added to destroy organic matter, and the aliquots were evaporated to dryness under an infrared lamp. Counting measurements indicated the percentage of the total Zr^{95} activity that had been transferred through the porous disc. In the experiments with excess chloranilic acid present approximately ten milligrams of solid chloranilic acid was also added to each compartment in order to compensate for oxidation and reduction of this substance. With excess chloranilic acid present roughly 1.5 per cent of the Zr^{95} activity was transferred no matter what the polarity of the electrodes. Without chloranilic acid, less than one per cent of the Zr^{95} activity was observed to migrate from the anode compartment to the cathode compartment. These results indicated that the migration velocity of any zirconium species would be too small to yield reliable data in view of the diffusion effects that were observed. Larger currents were not employed because of excessive changes in acidity and deterioration of the chloranilic acid that would have resulted.

THE ZIRCONIUM CHLORANILATE PRECIPITATE

Solutions having greater than 5 x 10^{-4} formal zirconium and chloranilic acid were found to give a gelatinous, blue-grey precipitate in 2 M $HClO_4$. In preparing the precipitate in order to study its composition solid $ZrOCl_2 \cdot 8H_2O$ and chloranilic acid were dissolved in 200 ml. of 2 M $HClO_4$ in such ratios that the formality of chloranilic acid above that required to form the 1:1 complex was never large enough to exceed the solubility of the acid itself. The solutions were shaken from one to five days in 500 ml. glass-stoppered volumetric flasks and were filtered on a sintered glass filter crucible.

The precipitate was not washed in any manner in order to avoid altering the composition of the precipitate. It was partially dried by continuing the suction from the water aspirator for one hour after the solution had been filtered. The precipitate was still moist but, after mixing, representative samples could be obtained by taking all aliquot portions over a period of five or ten minutes. The amount of chloranilate per milligram of precipitate was obtained by converting the aliquot portion to the 1:1 complex in the presence of 10^{-3} formal zirconium and comparison of its optical density with that of a similar standard solution that was 1.00 x 10^{-4} formal in chloranilic acid. In this method 5.00 ml. of 0.221 M NaOH was added to the aliquot of the precipitate in a 100 ml. volumetric flask and the solution was diluted to approximately 50 ml. with

2.00 M $HClO_4$ after the metathesis to $Zr(OH)_4$ and chloranilate. After the zirconium hydroxide had dissolved, 32.2 mg. of $ZrOCl_2 \cdot 8H_2O$ was added and the solution was diluted to the mark with 2.00 M $HClO_4$. The optical density of the solution was measured at 5500 Å in a 50 mm. cuvette. The measured solutions were 3×10^{-5} to 6×10^{-5} formal in chloranilic acid.

In determining the amount of zirconium per milligram of precipitate, the sample could be digested with HNO_3 and ignited to the oxide. However, 50 mg. of the precipitate was required to give approximately 4 mg. of ZrO_2, a fact that would have required fairly large amounts of materials in preparing the precipitate. It was more convenient to determine the zirconium spectrophotometrically in the presence of a fixed formality of chloranilic acid. For this purpose the sample was metathesized to $Zr(OH)_4$ in a 100 ml. volumetric flask as previously described and brought into solution by the addition of 2.00 M $HClO_4$. A volume of 1.033×10^{-3} M chloranilic acid in 2.00 M $HClO_4$ was added to make the total formality of chloranilic acid 1.033×10^{-4} upon dilution to the mark. The volume of chloranilic acid that was required depended upon the previously found chloranilic acid content of the same precipitate and the size of the sample. The amount of added chloranilic acid was usually about the same as the amount that was already present in the sample. The sample was finally diluted to the mark with 2.00 M $HClO_4$ and measured at 3400 Å in a 1 cm. absorption cell. The standardization curve shown in Figure 23 was obtained at the same final acidity and the same chloranilic acid for-

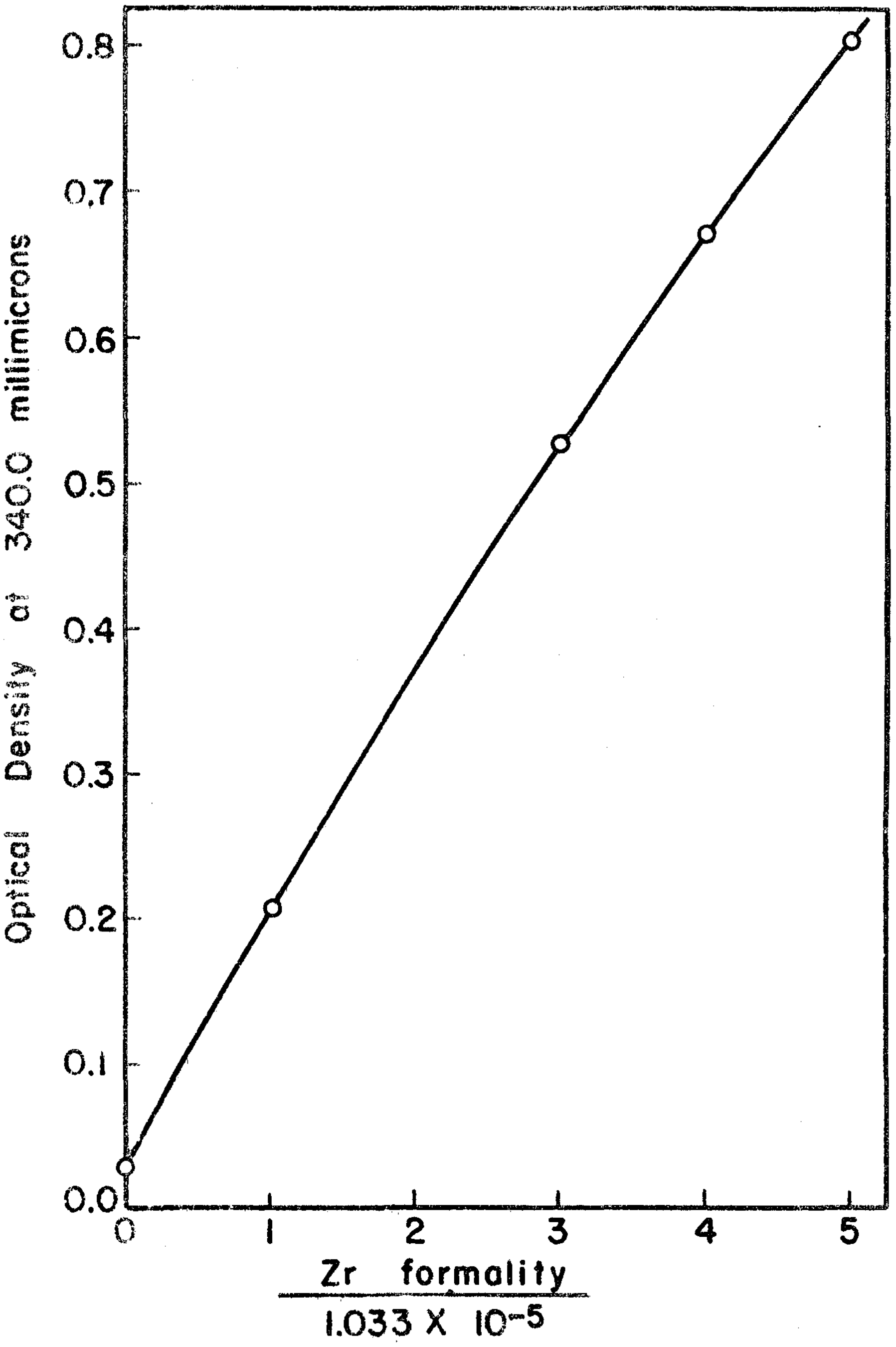
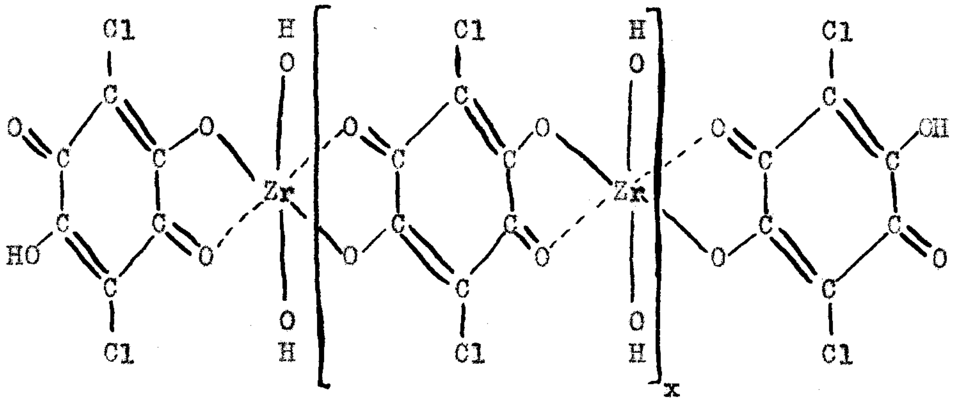


Fig. 23 Standardization Curve for Zirconium

mality of 1.033×10^{-4}. The acidity was 1.89 molar.

Table 22 shows the results of the analyses of the precipitate which has been designated as $ZrCh_n$. The second column indicates the number of days the preparation was shaken before filtration. Columns three and four represent the initial concentrations of the constituents. The last column gives the values found for n, the average of which was 1.24. This value does not correspond to formulae such as $ZrCh_2$, $Zr_2(OH)_2Ch_3$ or $Zr(OH)_2Ch$, but might easily indicate that the precipitate was $Zr_3(OH)_4Ch_4$, $Zr_4(OH)_6Ch_5$, $Zr_5(OH)_8Ch_6$ or $Zr_6(OH)_{10}Ch_7$, the structural formulae of which could be represented by



where $n = \frac{x + 2}{x + 1}$ and $x = 2, 3, 4$ or 5. It therefore appears that the second complex, $ZrCh_2$ and/or $Zr_2(OH)Ch_3^+$, may be the precursor of the insoluble compound just indicated.

Table 22.

Analysis of the $ZrCh_n$ Precipitate

Prep. no.	Time (days)	10^{+3}x [Zr]	10^{+3}x[H_2Ch]	10^{+4}xno. millimoles/mg. of ppt.				Values of n
				Zr (found)	Zr (av.)	H_2Ch (found)	H_2Ch (av.)	
1	3	2.0	2.6	4.12 4.09	4.11	5.40 4.75	5.08	1.24
1	5	2.0	2.6	3.57 3.80	3.68	4.92 4.91	4.91	1.33
2	4	1.0	2.0	7.42 7.07	7.25	7.94 7.86	7.90	1.09
3	1	3.0	2.0	5.40 5.38	5.39	6.44 6.81	6.63	1.23

Av. n $= 1.24 \pm 0.09$

CHLORANILIC ACID AS A COLORIMETRIC REAGENT FOR ZIRCONIUM

Relative to the use of the standardization curve of Figure 23 for the determination of small quantities of zirconium, it may be stated that the indicated values of optical density are reached within fifteen minutes from the time of mixing and that the solutions are true solutions and stable indefinitely. Two of the most currently used colorimetric reagents for zirconium are alizarin and its sulphonated derivative.[57] Both of these reagents give lake suspensions which settle out upon standing. Upon redispersing the alizarin lake by shaking, its transmission curve is claimed to be very nearly the same,[57] but the use of chloranilic acid would involve no such difficulty whatever. Furthermore, the use of alizarin requires a careful adjustment of the acidity and the use of alcohol, neither of which would be required with chloranilic acid. The use of p-dimethylaminoazobenzenearsonic acid for the colorimetric determination of zirconium is time-consuming in that its precipitate with zirconium requires roughly thirty minutes for quantitative precipitation and it must be metathesized in order to liberate the reagent for colorimetric measurement (Ref. 57, p. 62).

Chloranilic acid in 2 M $HClO_4$ gives roughly the same wine violet color with tetrapositive zirconium, hafnium, uranium, thorium and stannic tin but only a weak pink color with tetravalent titanium. Apparently chloranilic acid shows a certain specificity for tetrapositive metal ions. However, ferric ion gives a violet-black color and saturated boric acid

Table 23.

Other Hydroxy-Benzoquinones and Rhodizonic Acid

Reagent and its color in solution	Observed reaction with Zirconium	Remarks
Tetrahydroxyquinone (THQ) (faint yellow)	Bright yellow solution	Zirconium formality was $5x10^{-3}$. Complex was stable above pH 12 for more than 30 minutes. Thorium gave only a very light tan color.
Rhodizonic acid (light tan)	Bright yellow solution	An equal formality of Th^{+4} gave a very light pink color.
Nitranilic acid (yellow color)	Yellow precipitate	Thorium gave a slight color change but no precipitate. $SnCl_4$, $TiOSO_4$ and $Cu\ SO_4$ give no visible reaction.
2,5-Dihydroxy-1,4-Benzoquinone (DHQ) (yellow color)	Rust red precipitate	Thorium gave a magenta precipitate.

SUMMARY

1. Spectrophotometric measurements in 1-2 M perchloric acid solutions of ionic strength 2 have shown the presence of the following equilibrium

$$Zr^{+4} + H_2Ch \rightleftharpoons ZrCh^{+2} + 2H^+$$

$$K_1 = \frac{[ZrCh^{+2}][H^+]^2}{[Zr^{+4}]\,[H_2Ch]} = (5.69 \pm 0.08) \times 10^{+5}$$

where $[Zr^{+4}]$ represents the concentration of the zirconium monomer.

2. Similar studies in the presence of excess chloranilic acid indicated a second complex of the type $ZrCh_2$ or $Zr_2(OH)Ch_3^+$, or possibly a mixture of the two. The best agreement with the data was obtained with the following equations:

$$ZrCh^{+2} + H_2Ch \rightleftharpoons ZrCh_2 + 2H^+$$

$$K_2 = \frac{[ZrCh_2]\,[H^+]^2}{[ZrCh^{+2}]\,[H_2Ch]} = 6000 \pm 700$$

3. A precipitate that formed in these solutions with concentrations of the reactants of roughly 5×10^{-4} molar was shown to have a zirconium-to-chloranilic acid ratio of 1 to 1.24 ± 0.09.

4. A spectrophotometric method was developed for determining zirconium at formalities of roughly 5×10^{-6} to 5×10^{-5} using chloranilic acid and measurement at 3400 Å. Chloranilic acid is briefly compared with other colorimetric reagents for zirconium and other compounds that possess interest are mentioned.

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gives a light pink color. Stannous, ferrous, aluminum, cupric, chromic, cobaltic, manganous, barium and potassium ions give no color reaction at this acidity. In the use of alizarin for determining zirconium positive errors are caused by chromic, ferric and especially titanyl ions. Thorium gives rise to a positive error which can be reduced by raising the acidity. Thus chloranilic acid as compared with alizarin as a reagent for zirconium is subject to less interference from titanium and chromium. The use of alizarinsulfonic acid in a high concentration of hydrochloric acid apparently eliminates interference from titanium, thorium and uranium in determining zirconium, but still has the disadvantage of giving a lake rather than a stably colored solution.[58]

Although chloranilic acid does not have all of the specificity that might be desired in a reagent for zirconium, it does discriminate against titanium to a fair extent. In Table 23 are listed other hydroxy derivatives of p-benzoquinone and rhodizonic acid. The first three compounds give markedly different reactions with zirconium as compared with thorium. Unless otherwise specified the observed reactions were obtained with 0.001 formal zirconium and excess reagent in 2 M $HClO_4$.