The Apparent Acidity Function (H_0) of Polyphosphoric Acid

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The acidity function (H_0) for polyphosphoric acid (PPA) has been redetermined in the range 62–86% P_2O_5 content. Contrary to a previous report,[2] no maximum was found in the curve of H_0 vs. P_2O_5 content. Also, the refractive index vs. P_2O_5 content was found to be essentially linear. Thus, all parameters studied in this paper and the preceding one[5] suggest that the molecular structure of PPA, at least up to 86% P_2O_5, exhibits a regular and continuous change without the incursion of any unique species. The pK_a value of 2,4-dinitroaniline has been found to be different in PPA $(pK_a -5.1)$ from that in sulfuric acid $(pK_a -4.4)$. For this and other reasons, H_0 for PPA is called an apparent acidity function.

Temkin and co-workers[2] have stated that the acidity function, H_0, of polyphosphoric acid (PPA) exhibits a maximum at 79.7% P_2O_5 concentration in water (see dotted line, Fig. 1). This statement suggests the interesting possibility that a relatively more acidic molecular species in PPA is accumulating in the medium up to the percentage mentioned. The most likely species is pyrophosphoric acid (79.8% P_2O_5). Another possibility is that a species which is relatively unreactive to base indicators is accumulating and at 79.7% dominates competing factors. On the other hand, analysis of PPA by paper chromatography[3] and by ion exchange chromatography[4] has shown that no such abrupt molecular changes take place and suggest to the contrary that PPA is a mixture of linear polyphosphate chains with anhydride linkages in which the polymeric species uniformly increase or decrease in concentration as the phosphorus pentoxide content of the PPA is varied. For example, Jameson found that PPA of 80.5% P_2O_5 content contained approximately 14% orthophosphoric acid, 38% pyrophosphoric acid, 23% tripolyphosphoric acid, 13% tetra-, 7% penta-, 2% hexa-, 1% hepta- and 0.2% octapolyphosphoric acid. As the phosphoric anhydride concentration increased, the concentration of the higher molecular weight polyacids was found to increase at the expense of the lower molecular weight polyacids. Also in the previous work of this Laboratory[5] PPA seemed to exhibit a regular and continuous change with phosphorus pentoxide content suggesting that no particular species was accumulating. These studies included an examination of a rearrangement rate, specific gravity and viscosity changes. The first two were rather insensitive parameters, and the third still was continuous but further noteworthy in exhibiting remarkable increases in viscosity as the phosphorus pentoxide content became higher than 82%.[6]

In this paper, a fourth parameter was first examined, the change of refractive index with concentration.[7] The refractive index method, although again not particularly sensitive, was found to be the easiest method of determining P_2O_5 con-

tent of PPA. The results are given in Table I of the Experimental section. Since some difficulty was encountered in correlating the refractive index of PPA with percentage P_2O_5 content, the results recorded are statistical ones accumulated over a number of years. And the interesting conclusion is that the refractive index shows an essentially linear relationship to the phosphorus pentoxide content. Thus another parameter again supports the conclusion that PPA undergoes a continuous and regular molecular change with increasing P_2O_5 concentration.

The further conclusion was inescapable that the work of Temkin and co-workers[2] had to be repeated since only their work on the H_0 determination with indicators supported the case for non-continuity. The method of Hammett and Deyrup[8] was used to extend the acidity scale already determined in dilute phosphoric acid by Heilbronner and Weber[9] and by Temkin and co-workers[2] into the region of 62–86% phosphorus pentoxide content. Their data are in good agreement below 62% P_2O_5, and only Temkin's data[2] above this concentration are in doubt. Our H_0 values (Fig. 1, bold line) are based on the experimentally determined pK_a values of the indicators 2,4-dinitroaniline and 2-bromo-4,6-dinitroaniline in the concentration ranges 62–81% and 79–86%, respectively. Figure 2 illustrates how the pK_a values of the indicators above (curves F and G) are based on Heilbronner and Weber's work in the lower concentration ranges (curves A through E). As usual in the Hammett method, eq. 1 was used with the data in Fig. 2 to determine pK_a values.

$$pK_a{}^B - pK_a{}^C = -\log C_B/C_{BH^+} + \log C_K/C_{CH^+} \quad (1)$$

The following were calculated[10]: pK_a 2,4-dinitroaniline in PPA $= -5.1$, pK_a 2-bromo-4,6-dinitroaniline in PPA $= -6.8$. The value for 2,4-dinitroaniline differs considerably from its value of -4.38[12] determined in aqueous sulfuric and perchloric acids. To furnish a comparison of our technique with that of others, the pK_a value of

(1) Taken from the Ph.D. thesis of R. G. D. to be published in 1961.
(2) A. I. Gel'bshtein, G. G. Shcheglova and M. I. Temkin, *Doklady Akad. Nauk, S.S.S.R.*, **107**, 108 (1956); C. A., **50**, 13180 (1956); quoted by M. Kilpatrick, *J. Chem. Ed.*, **37**, 402 (1960).
(3) A. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956).
(4) R. F. Jameson, *J. Chem. Soc.*, 752 (1959).
(5) D. E. Pearson and R. M. Stone, *J. Am. Chem. Soc.*, **83**, 1715 (1961).
(6) See also J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958.
(7) This study was begun first by Dr. R. M. Stone[5] but brought to its present stage of reproducibility by the authors of this paper.

(8) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).
(9) E. Heilbronner and S. Weber, *Helv. Chim. Acta*, **32**, 1513 (1949).
(10) The pK_a and H values used throughout this paper are based ultimately on the pK_a of p-nitroaniline (curve A, Fig. 2) being +1.11, the accepted value for previous studies.[2,9] If the newly recommended pK_a value[11] for p-nitroaniline $(pK_a +0.99)$ is adopted, correction of the pK_a and H_0 values can be made by subtracting 0.12 from each figure.
(11) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 1 and 935 (1957).
(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.
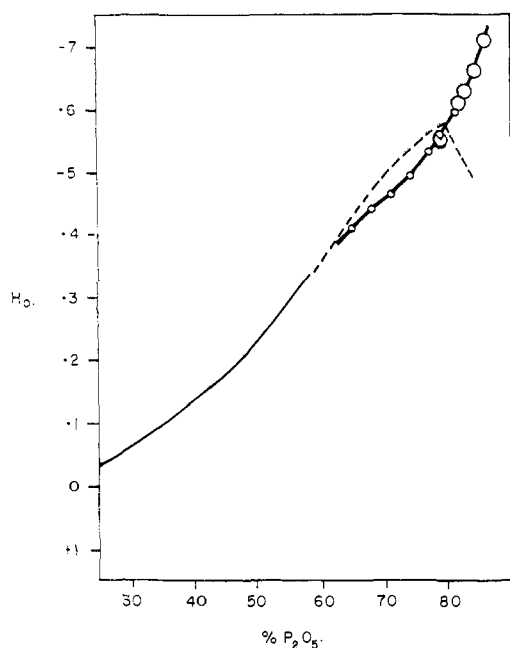
Fig. 1.—H_0 of PPA[10]: ———, solid line, data of Heilbronner and Weber[9] at 19 ± 2°; --------, data of Temkin, et al.,[2] at 20°; line with circles, our data at 25°.

2,4-dinitroaniline was redetermined in sulfuric acid and the pK_a of −4.34 found to be in excellent agreement with former workers.[2,12] The change in pK_a apparently is real and suggests a different type or a greater degree of solvation of the indicator salt (BH$^+$) in PPA than in sulfuric acid.[13] Thus, one of the primary requisites of the Hammett derivation of the H_0 acidity function, i.e., that the pK_a value of a given indicator be found constant in all media, is not obeyed in the more concentrated ranges of the P_2O_5–H_2O system. Another requirement also is not followed, namely, that the curve of 2-bromo-4,6-dinitroaniline (curve G, Fig. 2) does not parallel that of the preceding indicator. Nevertheless, useful estimates of the pK_a values can be made, and from them apparent H_0 values can be calculated from the eq. 2.

$$H_0 = pK_a{}^B + \log C_B/C_{BH^+} \qquad (2)$$

The H_0 values for 25° are shown in Fig. 1 and Table IV.[14] While it is true that the H_0 values in PPA given here suffer from not providing a quantitative acidity scale for comparison with other media, nevertheless they should provide a useful and practical acidity scale for this medium in that what happens to the indicator in PPA is likely to happen to the substrate material under investigation. The extent of usefulness will be determined by how accurately the acidity scale predicts rates of reactions

(13) Heilbronner and Weber[9] also found deviation in the pK_a of two indicators used in phosphoric acid. However, the deviations were small and in the opposite direction from our deviation.

(14) It is emphasized that H_0 is temperature dependent.[2] As an example, McNulty and Pearson[15] have reported that the rate of rearrangement of acetophenone oximes in sulfuric acid at 50° is correlative with H_0 except for a slight drift. This drift is now attributed to the fact that H_0 values for 25° were used rather than those for 50°.[2] Use of the H_0 values at 50° gives a perfectly linear relationship.

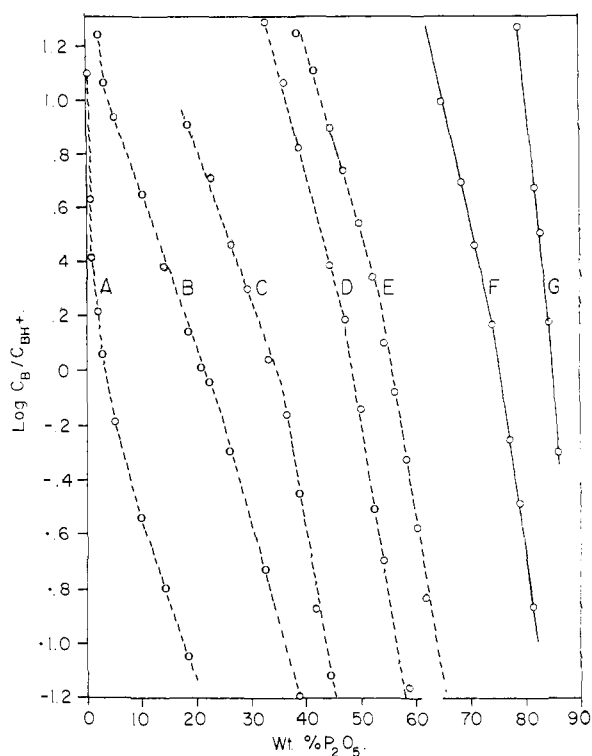(15) P. J. McNulty and D. E. Pearson, J. Am. Chem. Soc., 81, 612 (1959).

Fig. 2.—Plot of log C_B/C_{BH^+} vs. acid concentration as % P_2O_5; curves A through E from ref. 9: A, p-nitroaniline; B, o-nitroaniline; C, p-chloro-o-nitroaniline; D, p-nitrodiphenylamine; E, 2,4-dichloro-6-nitroaniline; F, 2,4-dinitroaniline; G, 2-bromo-4,6-dinitroaniline.

in PPA.[16] Also, it can be stated now with confidence that no maximum occurs in the apparent H_0 acidity function of PPA up to 86% P_2O_5 but rather that the apparent H_0 values rise steadily as the phosphorus pentoxide concentration is increased.

The question arises as to what data misled Temkin and co-workers.[2] The indicator they used in the questionable range 62–86% P_2O_5 content was benzalacetophenone (chalcone). It was found in this Laboratory that chalcone underwent profound changes in PPA even at room temperature as shown in Fig. 3.[18] The protonated peak at 420 mμ disappears with time ($C1$, $C2$, $C3$ in Fig. 3) and is replaced by another peak at 280 mμ. If the Russian workers utilized the 420 mμ band, as they were likely to do using the Pulfrich photometer, they would observe a smaller salt (BH$^+$) concentration because of the side reactions which consume chalcone. This would make it appear that more of the free base form was present and consequently that the acidity of PPA was less. Even the spectrum (B) in PPA of low P_2O_5 content (79.7%) shows the peak characteristic of one of the reaction products. The reaction products of

(16) Apparently, Temkin and co-workers[17] have found that the decomposition rate of formic acid in PPA reaches a maximum at 79.7% P_2O_5, the same P_2O_5 content for maximum protonation in their indicator study. Our work suggests that a factor other than acidity is responsible for a maximum in the decomposition rates.

(17) A. I. Gel'bshtein, G. G. Shcheglova and M. I. Temkin, Zhur. Fiz. Khim., 30, 2267 (1956); C. A., 51, 9272 (1957).

(18) Chalcone has been suspected previously to be a poor indicator for H_0 determinations.[11] Also Temkin[2] stated he could not use the indicator above 60°.
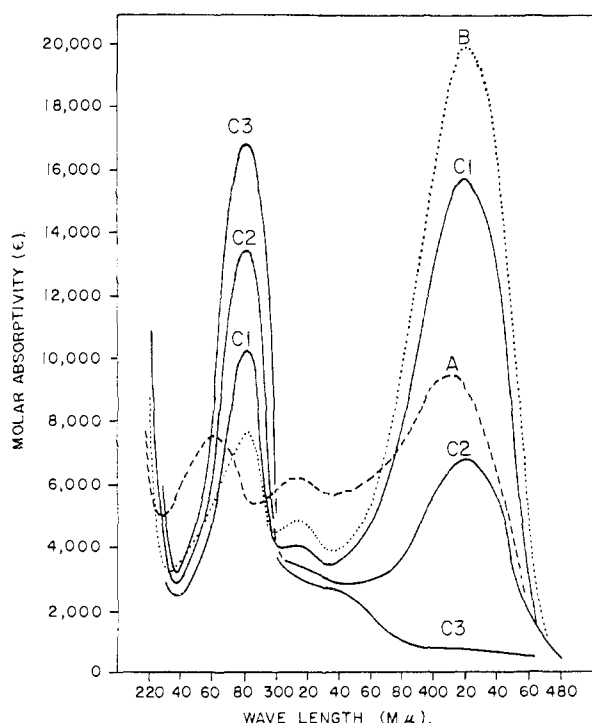
Fig. 3.—Ultraviolet spectra of chalcone showing formation of interfering compounds: A, chalcone in 70.0% P_2O_5 (scan made 2 days after solution prepared); B, chalcone in 79.7% P_2O_5 (scan made 3 days after solution prepared); C's, chalcone in 82.7% P_2O_5, C1 (immediate scanning), C2 (3 days later), C3 (1 day additional with heating on the steam-bath).

chalcone with PPA were diverse and complex in structure and probably resemble those described for the reaction of dypnone with PPA.[19] One of them had a marked blue fluorescence in aqueous solution.

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Experimental

General Comments.—A Cary recording spectrophotometer, model 14, and 1-cm., matched quartz cells were used for all spectrophotometric measurements. The spectrophotometer was located in an air-conditioned room. All transfers and operations involving PPA were made in a dry-box.[20] Melting points were taken on a Kofler hot-stage microscope apparatus.

Polyphosphoric Acid (PPA).—Weighed amounts of phosphorus pentoxide (Baker and Adamson, reagent grade) and orthophosphoric acid (Mallinckrodt, 85% H_3PO_4) were mixed in a flask within a dry-box. After the initial vigorous action had subsided, the heterogeneous mixture was heated on a hot-plate until homogeneous. Several weeks at about 150° was required for the more concentrated samples to dissolve. The orthophosphoric acid from various sources including the above was quite erratic as to color formation. Sometimes it gave almost colorless samples of PPA, at other times straw-colored samples.[21] In the latter case it was

better to add water rather than phosphoric acid to phosphorus pentoxide. After equilibration of the samples, the acid strength was determined as percentage phosphorus pentoxide by means of potentiometric titration of an aliquot which was dissolved in water and hydrolyzed by heating.[22] The end-point occurred in the region about pH 4.5. Because of the high viscosity of PPA, all aliquots and dilutions were made on a weight basis. When necessary, the formula of Van Wazer[6] was used to obtain densities in order to convert indicator solutions to molar concentrations.

$$D_{25°}{}^{PPA} = 0.0167(\%P_2O_5) + 0.66$$

The refractive index measurement was found to be the easiest method for determining the P_2O_5 content of PPA. At worst, the measurement was accurate to the nearest 0.5%, particularly in the range 82–87% P_2O_5. In this range the boundary line between light and dark fields of the Abbe refractometer occasionally was fuzzy. If the liquid was allowed to remain in the refractometer for about 0.5 hour, the boundary line usually became sharper. As the line became sharper, the refractive index readings increased and leveled off to the correct reading. No etching of the refractometer was noted after several years of rather frequent usage. The refractive index and % P_2O_5 showed a linear relationship given by the equation

$$\% \ P_2O_5 = 522.09 n^{25}{}_D - 685.07$$

For convenience, points from this equation are given in Table I.

TABLE I

REFRACTIVE INDEX vs. PERCENTAGE PHOSPHORUS PENTOXIDE[a]

$n^{25}{}_D$	P_2O_5, %	$n^{25}{}_D$	P_2O_5, %	$n^{25}{}_D$	P_2O_5, %
1.4272	60.0	1.4481	71.0	1.4673	81.0
1.4291	61.0	1.4500	72.0	1.4683	81.5
1.4310	62.0	1.4520	73.0	1.4692	82.0
1.4329	63.0	1.4539	74.0	1.4702	82.5
1.4348	64.0	1.4558	75.0	1.4711	83.0
1.4367	65.0	1.4577	76.0	1.4721	83.5
1.4386	66.0	1.4597	77.0	1.4730	84.0
1.4405	67.0	1.4616	78.0	1.4740	84.5
1.4424	68.0	1.4635	79.0	1.4750	85.0
1.4443	69.0	1.4654	80.0	1.4759	85.5
1.4462	70.0	1.4664	80.5	1.4769	86.0

[a] Error estimated at ±0.25% up to 78% P_2O_5 content and ±0.5% above.

2,4-Dinitroaniline.—The indicator, Eastman Kodak Co. practical grade, was recrystallized once from ethanol and once from toluene; m.p. 182°, pK_a −4.34 in 66.7% aqueous sulfuric acid,[23] reported[12] pK_a −4.38. The purified crystals were dissolved in PPA of 81% P_2O_5 to make a 0.01 molar solution. The large crystals required several weeks at 40–50° to dissolve completely.

trans-Benzalacetophenone was recrystallized from methylcyclohexane and then aqueous methanol with resulting needles, m.p. 58.5–59°. The ultraviolet spectrum in 95% ethanol was identical to that reported (λ_{max} 228 and 308 mμ).[24] The changes in ultraviolet spectrum when dissolved in PPA are shown in Fig. 3. When 1 g. of benzalacetophenone and 50 g. of PPA were warmed for a considerable period and then diluted with ice, an oily product together with some starting material was obtained by filtration. The filtrate contained a blue fluorescent compound. Since

(19) R. W. Roeske, D. B. Bright, R. L. Johnson, W. J. De Jarlais, R. W. Bush and H. R. Snyder, J. Am. Chem. Soc., 82, 3128 (1960).

(20) These precautions were not completely necessary. Expedient and prudent transfers of large amounts in the laboratory air seem feasible.

(21) The straw-color, probably originating from organic contamination, can be removed by the addition of a few drops of 30% hydrogen peroxide followed by warming of the sample. In a study of this nature, however, the addition of peroxide would be detrimental.

(22) According to the experience of Van Wazer[6] and our own, PPA need not be hydrolyzed to obtain the phosphorus anhydride concentration because only the first acid hydrogen atom is titrated. In the linear polymer of PPA all phosphorus atoms have at least one strong acidic hydrogen, and hydrolysis generates only a second or third weak acidic hydrogen.

(23) $-5.11(H_0) = pK_a + \log (1990/13707 - 1990)$ at 348 mμ; ϵ_B determined in 36% aqueous sulfuric acid.

(24) W. B. Black and R. E. Lutz, J. Am. Chem. Soc., 75, 5990 (1953).

the products appeared to be difficult to obtain pure and to be complex in nature, similar to those obtained from dypnone,[19] no attempt was made to identify them. It was noted that the blue fluorescent material could be produced even at room temperature.

2-Bromo-4,6-dinitroaniline.—The Eastman Kodak Co. practical grade chemical was recrystallized once from alcohol and once from toluene, as needles, m.p. 153.5–154.5°. The powdered crystals were dissolved in PPA (83% P_2O_5) to make a 0.01 molar solution. The process was very slow requiring many weeks of occasional agitation at 50° or several days at 100°. Duplicate stock solutions were made for each indicator.

Determination of H_0.—An aliquot of the indicator solution (0.01 molar) was added to PPA of the desired P_2O_5 concentration to give a solution about 10^{-4} molar. Absorbance measurements were made directly on these dilutions using PPA of the P_2O_5 concentration in the reference cell and recorded in the spectral range 500 to 200 mμ. The absorptivity ϵ was calculated by the equation

$$\epsilon \equiv A \text{ (absorbance)/molar concn. of indicator}$$

The quantity $\log C_B/C_{BH^+}$ is related to the absorptivity by the following equation where ϵ_B is the molar absorptivity of the free base

$$\log C_B/C_{BH^+} = \log \epsilon/\epsilon_B - \epsilon$$

For the indicator 2,4-dinitroaniline the free base form was shown to be the only one present in PPA below 60% P_2O_5 by absence of the band for the salt form (BH^+). However, determination of the molar absorptivity ϵ_B at several acid strengths in the dilute acid region revealed that the indi-

TABLE II
MOLAR ABSORPTIVITY OF 2,4-DINITROANILINE AT 25 ± 2°

P_2O_5, %	Molar concn. of indicator × 10^4	A	λ_{max}, mμ	ϵ
20.0	0.932	1.295	347.5	13,900[a]
35.0	1.237	1.666	349	13,470[a]
50.0	1.171	1.543	350	13,180[a]
60.0	1.3524	1.753	352	12,932[a]
	0.6441	0.836	352	12,980[a]
65.0	1.0412	1.209	354	11,612
	0.6151	0.719	353.5	11,689
68.0	1.5368	1.635	354	10,640
	0.6412	0.680	354	10,605
71.0	1.3914	1.315	354.5	9,449
	0.8699	0.823	355	9,464
74.0	2.0921	1.562	354	7,466
	1.1553	0.878	354	7,600
77.0[b]	3.8420	1.742	354	4,530
	2.4440	1.097	354	4,489
79.0[c]	4.9475	1.528	353	3.088
81.2[c]	5.1067	0.757	351	1,482

[a] No BH^+ was found to be present in these concentrations. The small trend in values is a solvent effect on the free base. [b] The Beer–Lambert law, $A = \epsilon c$, was tested extensively at this concentration and was shown to be a linear relationship which passed through the origin; less vigorous tests are available at each point at which duplicate analyses were made. [c] The λ_{max} has shifted toward the ultraviolet because of some slight interference from the large neighboring "protonated peak"; such interference is negligible at the other concentrations in this table.

TABLE III
MOLAR ABSORPTIVITY OF 2-BROMO-4,6-DINITROANILINE AT 27 ± 2°

P_2O_5, %	Molar concn. of indicator × 10^4	A	λ_{max}, mμ	ϵ
71.0	1.2750	1.628	361	12,753[a]
	0.4667	0.600	361	12,856[a]
79.0	1.2374	1.502	360	12,138
	0.6888	0.835	360	12,129
81.8	1.1212	1.179	360.5	10,520
	0.5751	0.608	360.5	10,573
82.6	1.6991	1.664	361	9,793
	1.0437	1.014	361	9,720
84.4	1.6344	1.251	362	7,657[b]
	1.8056	1.368	362	7,579[b]
	1.7265	1.330	361	7,703
85.7	1.6126	0.730	356.5[c]	4,528
	1.0225	0.429	348[c]	4,460

[a] Only free base present. [b] Duplicate determinations by dilution of same stock solution. [c] The λ_{max} has shifted toward the ultraviolet because of some slight interference by the large neighboring "protonated peak"; such interference was negligible at the other concentrations in this table.

TABLE IV
H_0 OF THE P_2O_5-H_2O SYSTEM IN THE RANGE 62–86% P_2O_5 AT 25–27°[10]

P_2O_5, % 2,4-DNA, indicator	H_0	P_2O_5, % 2-Br-4,6-DNA, indicator	H_0
65.0	−4.1[a]	79.0	−5.55[b]
68.0	−4.4	81.8	−6.15
71.0	−4.65	82.65	−6.3
74.0	−4.95	84.4	−6.65
77.0	−5.35	85.7	−7.1
79.0	−5.6		
81.2	−6.0		

[a] Limits of error ±0.15 for 2,4-DNA. [b] Limits of error ±0.2 for 2-Br-4,6-DNA.

cator exhibited a definite medium effect. The variation in ϵ_B was corrected by extrapolation of the linear relationship between ϵ_B and P_2O_5 content in the dilute acid region to the critical range of 60–80% P_2O_5 content. The following ϵ_B values were obtained by this extrapolation: 65% P_2O_5, 12,860; 68% P_2O_5, 12,760; 74%, 12,670; 77%, 12,610; 79%, 12,570; 81.18%, 12,510. Some precedent for this method of extrapolation has been found.[25,26]

The other indicator, 2-bromo-4,6-dinitroaniline, also exhibited a medium effect and in this case the value for ϵ_B was taken for the free base peak in PPA of 71% P_2O_5 content—just outside the critical range of 75–86% P_2O_5.

Tables II and III are a summary of the experimentally determined values of molar absorptivities (ϵ) at various acid concentrations.

The H_0 values were calculated from the data of Tables II and III by the method outlined in the discussion. These values are given in Table IV and illustrated in Fig. 1.

(25) H. H. Jaffé and R. W. Gardner, J. Am. Chem. Soc., **80**, 319 (1958).

(26) K. N. Bascombe and R. P. Bell, J. Chem. Soc., 1096 (1959).