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The Synthesis of 2-Carboxyethyl-P, P-Diphenylphosphine and a Study of it as a Potential Chelating Agent

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THE SYNTHESIS OF 2-CARBOXYETHYL-P,P-DIPHENYLPHOSPHINE AND A STUDY OF IT AS A POTENTIAL CHELATING AGENT

Submitted to the Faculty of Ursinus College in partial fulfillment of requirements for Honors in Chemistry.

Approved:

Jane A. Barth

Roger P. Staiger

Signed: Harriet V. Taylor

Harriet V. Taylor

May 11, 1967

ACKNOWLEDGMENTS

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I. INTRODUCTION

In recent years many studies have been made of compounds with chelating ability to determine the stability of these ligand systems. Such investigations have been carried out on amino acids such as N-alkyl (1) and N-aryl (2) glycines. This interest has carried over to other members of the nitrogen family, notably phosphorous.

Several organo-phosphorous acids have been synthesized (3,4). The authors stated that studies of these acids as ligands would be forthcoming, but no further work has been published.

II. HISTORICAL

In 1960, the German chemists, Issleib and Thomas, reported the synthesis of carboxyalkyl-P,P-diphenylphosphines, among which was 2-carboxyethyl-P,P-diphenylphosphine (3). Further work by the same authors appeared in 1961 (5), when they stated that later publications would report a study of these acids as ligands in metal complexes. In 1964, these chemists reported pK values for various carboxyalkylphosphines, among which was the above mentioned acid with pK values in 2:1 ethanol-water of <2.6 and 6.23 (6). No mention has been made of stability constants.

Research has been carried out on nitrogen analogues of the phosphorous compounds. In 1954, studies were made by Basolo and Chen (1) on the chelation of N-alkyl and N-dialkylglycines with Cu(II) and Ni(II). It was found that the ligands exist as zwitterions in solution, yielding two pK values. Formation constants were also determined for various alkyl-substituted glycines. It was found that substituted glycines had less of a tendency to chelate than did glycine itself. Basolo and Chen also determined that the presence of one ligand did not affect the ability of a second molecule of ligand to chelate. This indicates the formation of *trans* complexes.

Also, in 1959, Ch'ên and Chang (2) studied N-arylglycines as ligands with Cu(II) and Ni(II). They found that phenylglycine is less basic than glycine is less basic than N-1-naphthylglycine. They also found that with copper, there was abnormally low stability due to steric hindrance.

In order to calculate stability constants, one needs pK values for the ligand. The method used to calculate the acid dissociation and stability constants was that of Irving and Rossotti (7). These authors define the stoichiometric stability constants for the ligand-proton complex LH_j as ${}^{C}K^{H}_{j} = (LH_j)/(LH_{j-1})(H)$ and for the metal-ligand complex ML_n as ${}^{C}K_n = (ML_n)/(ML_{n-1})(L)$. The overall stability constants, therefore, are ${}^{c}\beta^{H}_{j} = {}^{C}K^{H}_{1}\,{}^{C}K^{H}_{2}\ldots$ and ${}^{C}\beta_n = {}^{C}K_1\,{}^{C}K_2\ldots$. If T_L, T_H, and T_M are the total ligand, proton, and metal concentrations, respectively, in the solution, then for the metal-ligand system,

$$\bar{n} = \frac{\text{total concentration of ligand bound to metal}}{\text{total concentration of metal}}$$

$$= (T_L - \text{concentration of ligand not bound to metal})/T_M$$

and for the proton-ligand system,

$$\bar{n}_H = \frac{\text{total concentration proton bound to ligand}}{\text{total concentration ligand not bound to metal}}$$

$$= \frac{T_H - (H)}{T_L - \bar{n}T_M}$$

Therefore, $\bar{n} = \dfrac{T_L - [T_H - (H)]/\bar{n}_H}{T_M}$ where $\bar{n}$ is the average number of ligands per metal ion.

Titrations were carried out on (1) mineral acid; (2) mineral acid plus ligand; and (3) mineral acid, ligand, plus metal ion. Plots were made of meter reading B *vs.* the volume of base added (see Figure 1). At any pH meter reading the graphs are read to determine the volume of base needed to reach that pH for each titration.

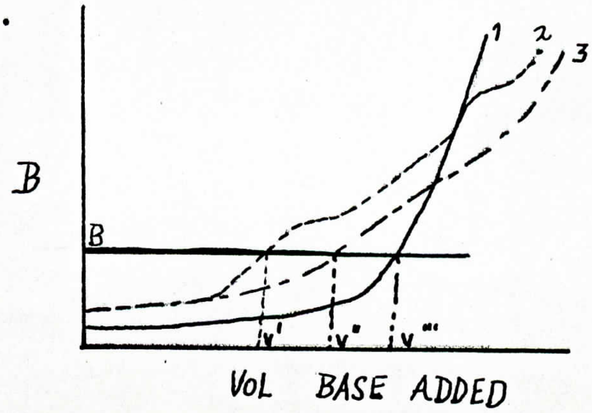


FIG. 1

At any B, $(H') = (H'') = (H''')$ and $T_H = E + yT_L - Na + (OH)$, where E is the concentration of mineral acid, Na is the sodium ion added in titration. When this procedure is used,

$$\bar{n}_H = \frac{yT_L + \frac{(v'-v'')(N+E)}{V+v'}}{T_L} \qquad (1)$$

and

$$\bar{n} = \frac{(v'''-v'')[N + E + T_L(y-\bar{n}_H)]}{(V + v'')\bar{n}_H T_M} \qquad (2)$$

N=base concentration
E=mineral acid concentration
V=initial volume mineral acid
v'=volume base from mineral acid curve
v"=volume base from acid + ligand curve
v'''=volume base from acid, ligand, metal curve

Since by definition

$$pL = \log_{10}\left\{\sum^{c} \beta_j (H)^j / (T_L - \bar{n}T_M)\right\} \qquad (3)$$

it can be shown that

$$pL = \log_{10} \{\Sigma \beta^{H} (1/\text{antilog } B)^j / (T_L - \bar{n}T_M)\}$$

A common method for presenting data is to plot pL <u>vs.</u> $\bar{n}$, a formation curve. However, there are drawbacks to this method that prevent it from being an efficient means of determining stability constants. This method makes use of curve fitting which requires smoothing of data such that full use is not made of available information.

Rossotti and Rossotti (8) and others (9) present several ways of graphing the data to determine stability constants and dissociation constants. If there is one dissociable proton per ligand molecule or one ligand per metal ion, a plot of $\bar{n}/(1-\bar{n})$ <u>vs.</u> B yields a straight line with the intercept equal to β, the pK_a of the acid. All methods can be derived from the equation

$$n = \frac{\sum n \beta_n (L)^n}{\sum \beta_n (L)^n}.$$

For systems in which N = 2, $\bar{n} = \beta_1(L) + 2\beta_2(L)^2 / \{1 + \beta_1(L) + \beta_2(L)^2\}$

This can be rearranged such that $\bar{n}/(1 - \bar{n})(L) = (2 - \bar{n})(L)/(1 - \bar{n})\beta_2 - \beta_1$. Thus a plot of $\bar{n}/(1 - \bar{n})(L)$ *vs.* $(2 - \bar{n})(L)/(1 - \bar{n})$ should yield a straight line with the slope equal to β_2 and the intercept equal to $-\beta_1$, the overall and stepwise stability constants respectively.

III. EXPERIMENTAL

A. Synthesis of 2-carboxyethyl-P,P-diphenylphosphine:

Equipment:

2-necked flask fitted with stirrer, cold-finger condenser with drierite tube, nitrogen inlet, Variac heating unit.

3-necked flask fitted with stirrer, drierite tube, nitrogen inlet, ground-glass fittings to lead to vessel 1 as seen in Figure 2.

Thomas--Hoover melting point apparatus

Perkin-Elmer Infracord 137

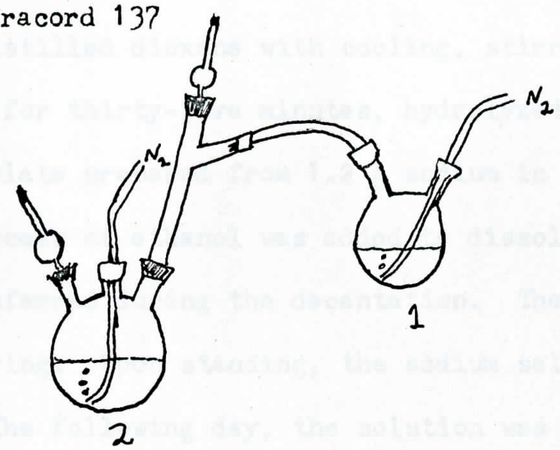


FIG 2

Chemicals:

Sodium, reagent grade

Diphenylchlorophosphine, Alfa Inorganics

2-Bromoethylpropionate, Eastman Organic Chemicals

200 proof ethanol, Pharmco

Dioxane, Fischer, Purified

Hydrochloric acid, sodium hydroxide

Nitrogen, oil pumped

Procedure:

All reactions were conducted under a nitrogen atmosphere.

(1) Purification of Dioxane: Dioxane was purified by refluxing it with sodium until the sodium became molten and shiny. The dioxane was doubly distilled from the sodium as needed.

(2) Preparation of acid: Approximately 150 ml dioxane were refluxed with 5 g of sodium until the sodium became molten, finely divided, and shiny. The solution was cooled and 14 g of diphenylchlorophosphine were added. This solution was refluxed for one hour after it had turned orange. The first reaction vessel was cooled and the excess sodium coagulated by slow stirring.

The above solution was decanted into 11.5 g 2-bromoethylpropionate in 150 ml freshly distilled dioxane with cooling, stirring. The reaction mixture was stirred for thirty-five minutes, hydrolyzed by the addition of 50 ml sodium ethylate prepared from 1.2 g sodium in 50 ml absolute ethanol. A small excess of ethanol was added to dissolve any sodium which had been transferred during the decantation. The solution stood overnight with stirring. Upon standing, the sodium salt precipitated from the dioxane. The following day, the solution was filtered, the mother liquor saved for additional precipitation, and the precipitate dissolved in water. The resulting basic solution was carefully made acidic with hydrochloric acid; and the acid, 2-carboxyethyl-P,P-diphenylphosphine, precipitated. Additional salt was obtained by evaporation of the solvent from the mother liquor at room temperature. Recrystallization was carried out by dissolving the acid in fresh sodium hydroxide and reprecipitating it with dilute hydrochloric acid seven times and from ethanol-water three times. The yield was 75%, melting point 128.5-129.0°C, literature melting point 127-128°C (3).

B. Titrations:

Equipment:

180 ml tall-form beakers fitted with polyethylene cover with holes cut for electrodes, nitrogen inlet, burette tip.

Magnetic stirrer

Beckman Zeromatic pH meter with Beckman glass and calomel electrodes

Wilkens-Anderson water bath

Burette--10 ml graduated in 0.02 ml

Pipets--50 ml, 25 ml--calibrated

Procedure:

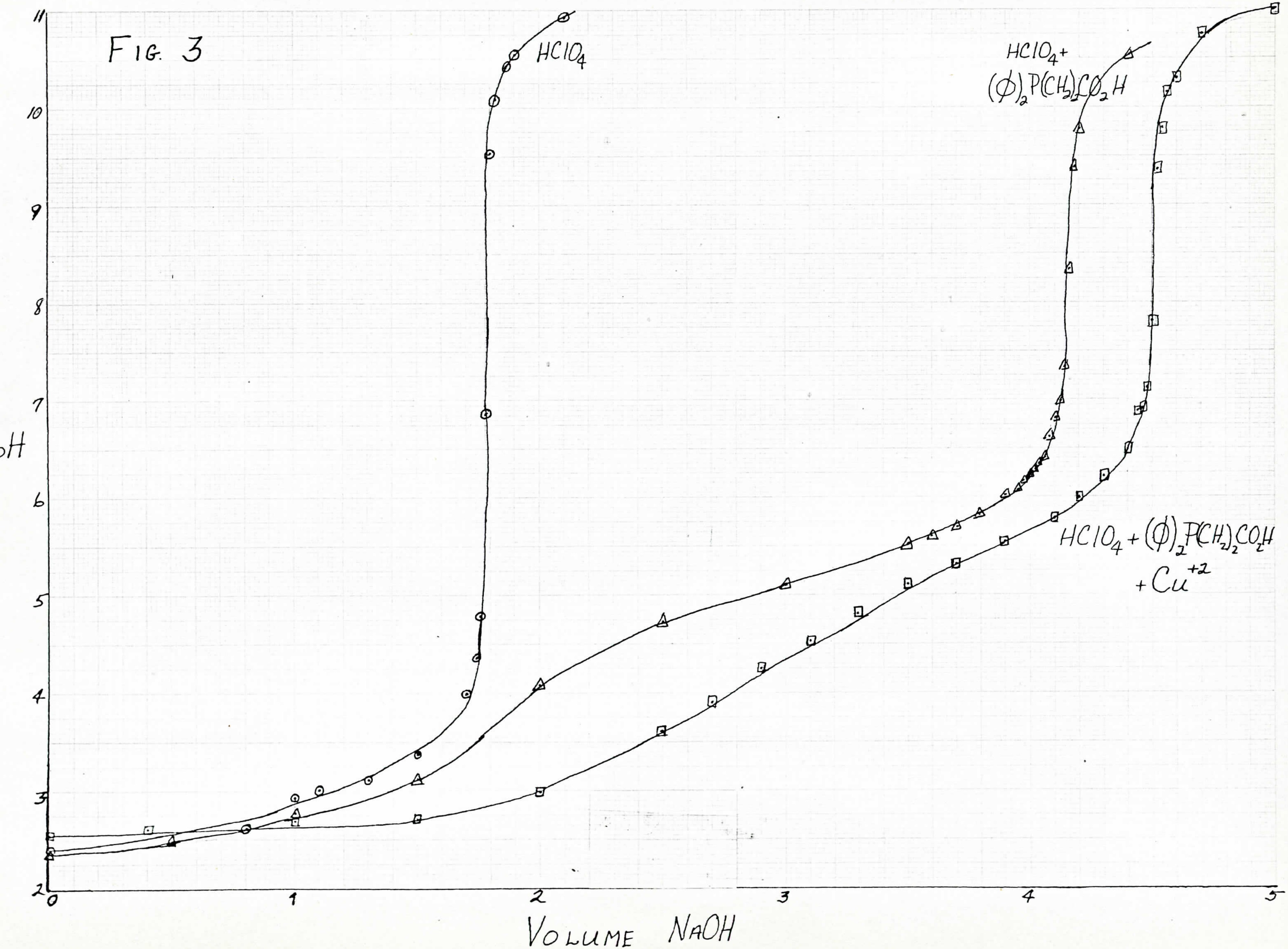
Approximately 0.2 N sodium hydroxide was made from 13.0 ml 50% sodium hydroxide (carbonate free) in two liters of boiled water and stored in a polyethylene bottle. Both burette and stock solution were protected from carbon dioxide with soda lime tubes. It was standardized against potassium acid phthalate, primary standard grade.

Copper perchlorate was synthesized from copper oxide and perchloric acid. The copper was determined electrolytically.

Dilute perchloric acid was made from 62% perchloric acid and was standardized against the standardized sodium hydroxide.

Titrations were carried out using sodium hydroxide vs. 2-carboxyethyldiphenylphosphine, vs. perchloric acid, vs. perchloric plus phosphino-acids, vs. perchloric, phosphino acids, plus copper(II), representing titrations against mineral acid, mineral acid plus ligand, and mineral acid, ligand, and metal ion. All titrations were done in 50% v/v ethanol-water at constant ionic strength (0.1 N sodium perchlorate), under a nitrogen atmosphere, and with stirring. The temperature was controlled at 25°C±.05°. Representative curves are shown in Figure 3.

Fig. 3


HClO$_4$
HClO$_4$ +
$(\phi)_2P(CH_2)_2CO_2H$
HClO$_4$ + $(\phi)_2P(CH_2)_2CO_2H$
+ Cu^{+2}
pH
2
3
4
5
6
7
8
9
10
11
0
1
2
3
4
5
Volume NaOH

IV. DATA

Reagent	Vol. in Analyte*	Concentration
$(C_6H_5)_2P(CH_2)_2CO_2H$	50 ml ethanol	1.25×10^{-3}M
$HClO_4$ in .1M $NaClO_4$	25 ml	1.604×10^{-3}M
$Cu(ClO_4)_2$	25 ml	1.247×10^{-3}
NaOH		2.246×10^{-1}

* The total volume was corrected for contraction: 50 ml water + 50 ml ethanol = 96.48 ml total volume.

B	v'*	v''*	v'''*	$\bar{n}_H$	$\bar{n}$	pL
2.9	1.016	1.093	1.874	0.965	1.524	4.3591
3.0	1.168	1.249	2.017	0.963	1.500	4.2574
3.1	1.289	1.382	2.137	0.958	1.480	4.1566
3.2	1.390	1.490	2.225	0.955	1.444	4.0542
3.3	1.476	1.573	2.313	0,956	1.451	3.9546
3.4	1.535	1.637	2.388	0.954	1.476	3.8561
3.5	1.573	1.684	2.459	0.950	1.528	3.7595
3.6	1.624	1.732	2.528	0.951	1.567	3.6614
3.7	1.656	1.777	2.597	0.946	1.623	3.5649
3.8	1.680	1.823	2.664	0.936	1.682	3.4691
3.9	1.696	1.874	2.725	0.920	1.733	3.3720
4.0	1.708	1.934	2.788	0.899	1.779	3.2753
4.1	1.718	1.997	2.851	0.875	1.828	3.1784
4.2	1.725	2.065	2.919	0.847	1.891	3.0824
4.3	1.730	2.138	2.993	0.827	1.939	2.9857
4.4	1.736	2.216	3.066	0.784	2.035	2.8921
4.5	1.742	2.299	3.142	0.750	2.113	2.7975
4.6	1.746	2.397	3.214	0.707	2.174	2.7013
4.7	1.751	2.503	3.288	0.662	2.233	2.6051
4.8	1.755	2.622	3.362	0.610	2.285	2.5077
4.9	1.758	2.752	3.438	0.554	2.337	2.4123
5.0	1.760	2.892	3.517	0.493	2.396	2.3170

* These volume values are averages of three or more values. Raw data can be found in the Appendix.

V. RESULTS AND DISCUSSION

The steps in the synthesis of 2-carboxyethyl-P,P-diphenylphosphine are as follows:

(1) $2Na + (C_6H_5)_2PCl \longrightarrow NaCl + (C_6H_5)_2PNa\cdot 2Dioxane$

(2) $(C_6H_5)_2PNa + Br(CH_2)_2CO_2C_2H_5 \longrightarrow (C_6H_5)_2P(CH_2)_2CO_2C_2H_5 + NaBr$

(3) $(C_6H_5)_2P(CH_2)_2CO_2C_2H_5 + NaOEt \longrightarrow (C_6H_5)_2P(CH_2)_2CO_2Na$

(4) $(C_6H_5)_2P(CH_2)_2CO_2Na + HCl \longrightarrow (C_6H_5)_2P(CH_2)_2CO_2H + NaCl$

In carrying out the synthesis as described, a 75% yield, melting point 128.5-129.0°resulted. Issleib and Thomas reported a 40% yield, melting point 127-128°C. A comparison of analyses follows:

	Calculated	Issleib and Thomas	Present*
C	70.03	70.22	70.01
H	5.87	5.91	5.93
P	12.00	12.25	11.90
M.W.**	258.3	253.1	260.1

* Analysis by Galbraith Laboratories
** Based on Phosphorous

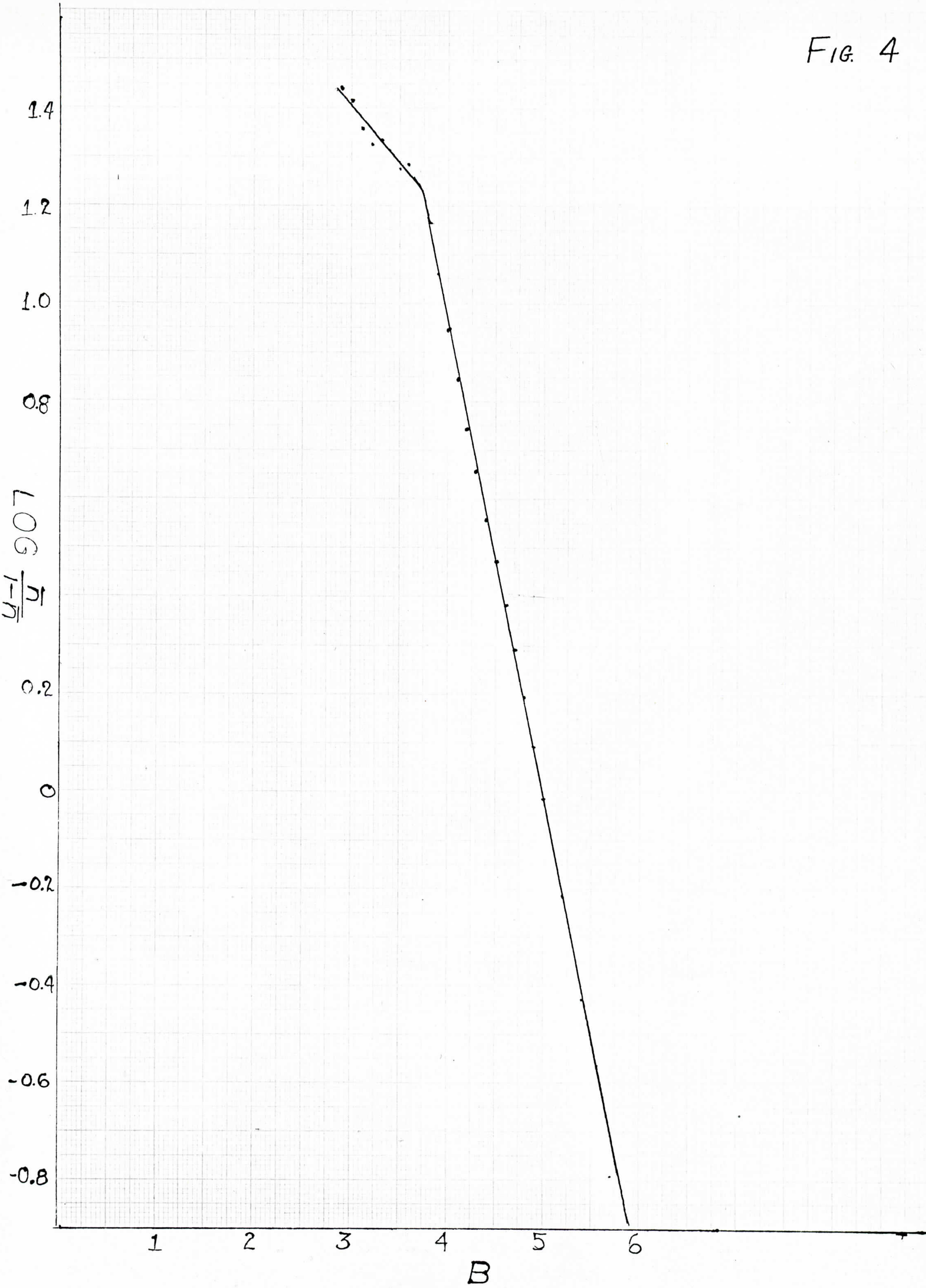
Several factors influenced the yield when contrasted with the original method (3). The authors isolated each intermediate product, changed solvents between steps one and two, used potassium in a 500% excess for the surface reaction, and included in their process two filtrations, a distillation, and a vacuum distillation. In the present synthesis no products were isolated until step three, one solvent was used throughout, the quantity of sodium used was only twice the stoichiometric quantity needed for reaction, and the filtrations and distillations were eliminated.

Reaction times were shortened, 100% ethanol instead of 95% was employed for the hydrolysis by sodium ethylate to prevent decomposition due to water, and the pH of the acidification was controlled because the phosphino-acid appeared to be slightly soluble in excess acid. Besides recrystallization from acid-base, recrystallization from ethanol-water was employed.

When titrations were tried in dioxane-water (50% v/v), in high pH regions the pH decreased as a function of time. Consequently, a shift was made to 50% v/v ethanol-water.

When calculations were carried out and $\bar{n}/(1 - \bar{n})$ was plotted against the meter reading B (see Figure 4), the intercept of the extrapolated straight line portion of the curve (B = 3.7 - 5.9) was 5.20, the pK_a. The sharp angle on the curve may be due to reasons listed below for variations in pK values. In 1964, Issleib and Thomas reported pK values for carboxyalkylphosphines, among them 2-carboxyethyl-P,P-diphenylphosphine (6). The values they listed were <2.6 and 6.23. The above authors carried out the titrations of the sodium salt of the acid in approximately a 2:1 ethanol-water solution with alcoholic HCl. The results of this procedure would not coincide with those of the present study due to differences in experimental conditions. The method used to determine the pK values was that of the half-equivalence point. As with the amino acids, it might be expected that the phosphino-acid might exist in solution as a zwitterion. Issleib and Thomas carried out nuclear magnetic resonance and infra-red spectroscopic studies of the acid and found that they could not unequivocally determine the presence of a zwitterion (6). In the NMR spectra, in tetrahydrofuran a peak for the -OH of the acid appears at a different point from the one in methanol. This could be due to zwitterion character or to an exchange effect between the -OH of the ligand and the solvent,

FIG. 4



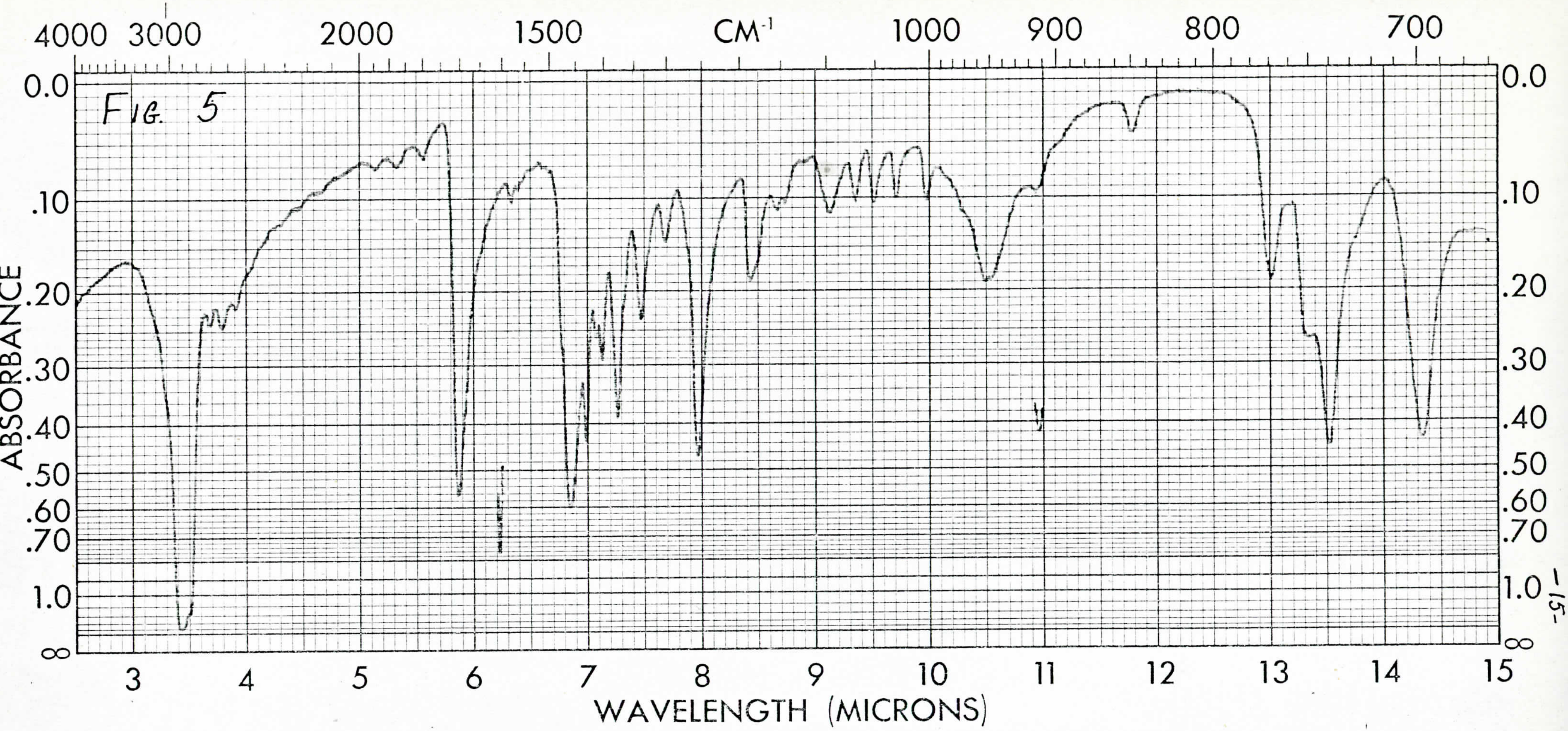
thus giving only one peak in the methanol solution. In the IR study, no peak for the -COO$^-$ appeared, leading to the conclusion that the acid does not exist as a zwitterion; the two forms would be $(C_6H_5)_2P(CH_2)_2CO_2H$ and $(C_6H_5)_2\overset{+H}{P}(CH_2)_2CO_2^-$, (see Figure 5).

A possible explanation of the lack of zwitterion character is that the phenyl groups sterically hinder the proton from bonding to the phosphorous electrons. It has been found that the basicity of substituted phosphines decrease in the order $(C_6H_{11})_3P > (C_2H_5)_3P > (C_6H_5)_3P$ (6). The basicity of the analogous acids should follow the same order. However, the ethyl ester of carboxymethyl-P,P-diphenylphosphine is more basic than expected. This, too, is probably due to steric hindrance. Another explanation for this anomaly is that the phenyl ring π electron clouds absorb the electrons from the phosphorous, and this would not leave them available for bonding with the proton in the zwitterion, thus affecting the basicity.

The same authors report a pK value for the carboxymethyl-P,P-diphenylphosphine as 5.97 compared to that of the ethyl acid as 6.23 (6). The increase in chain length of the alkyl group would cause a decrease in the inductive effect of the phenyl groups, causing a decrease in acidity.

In calculating the stability constants for the phosphino-acid as a ligand, the β value for the acid is the sum of pK values. Because the pK value of the present study does not agree with that found by different researchers, the stability constants determined from the present study would not agree with those of other workers, all other factors being equal. For the present study, the graphs of $\bar{n}$ vs. pL--the formation curve, and for $\bar{n}/(1 - \bar{n})(L)$ vs. $(2 - \bar{n})(L)/(1 - \bar{n})$ appear as Figures 6 and 7. As

FIG. 5



SPECTRUM NO. ______

SAMPLE 2-Carboxyethyl-P,P-diphenylphosphine

ORIGIN ______

PURITY ______

PHASE Nujol

THICKNESS ______

LEGEND ______

1. ______

2. ______

DATE April 23, 1967

OPERATOR H.V. Taylor

REMARKS ______

Polyethylene reference peaks – 6.25 & 11.03μ

SPECTRUM NO. ______

SAMPLE ______

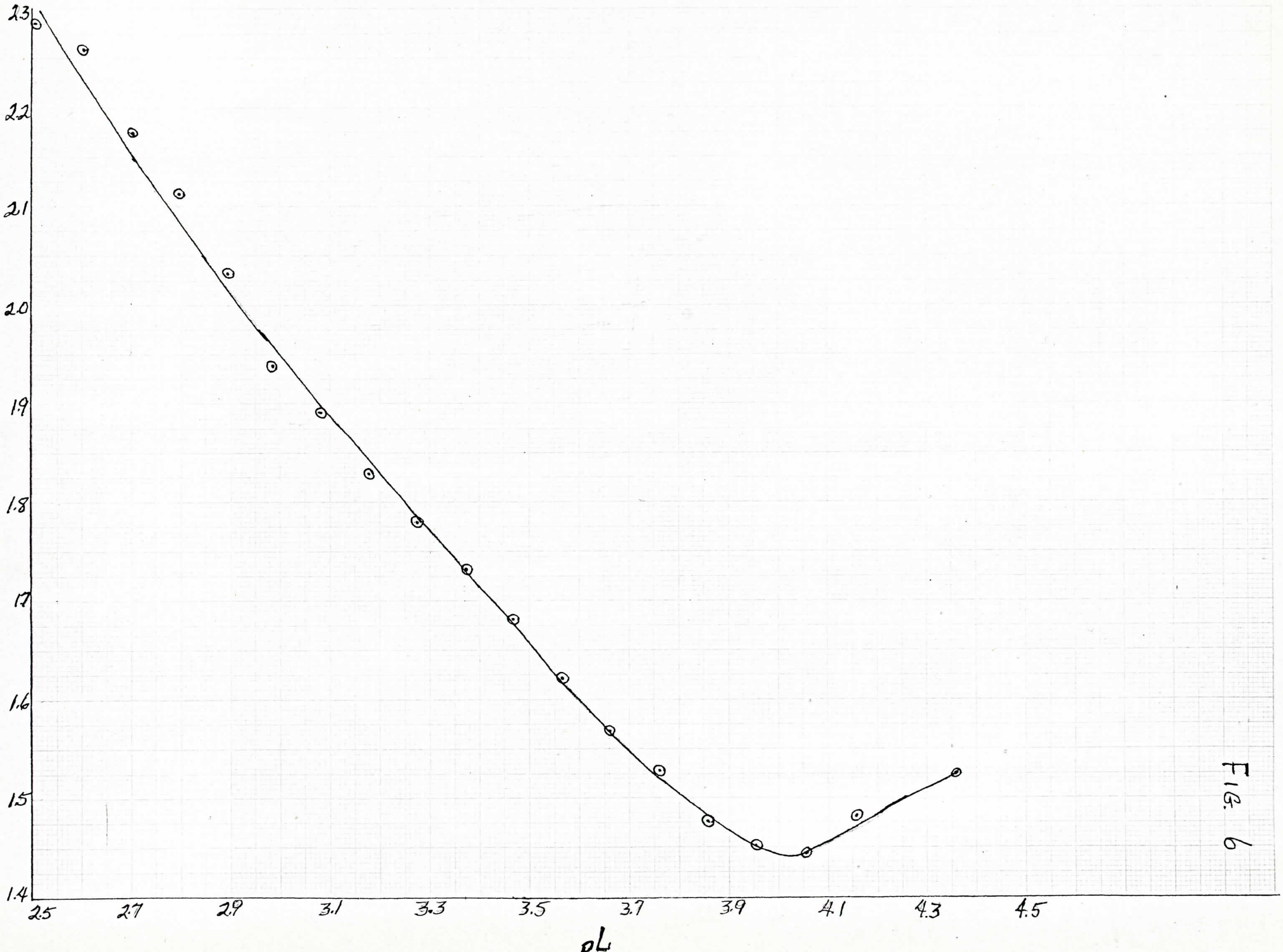
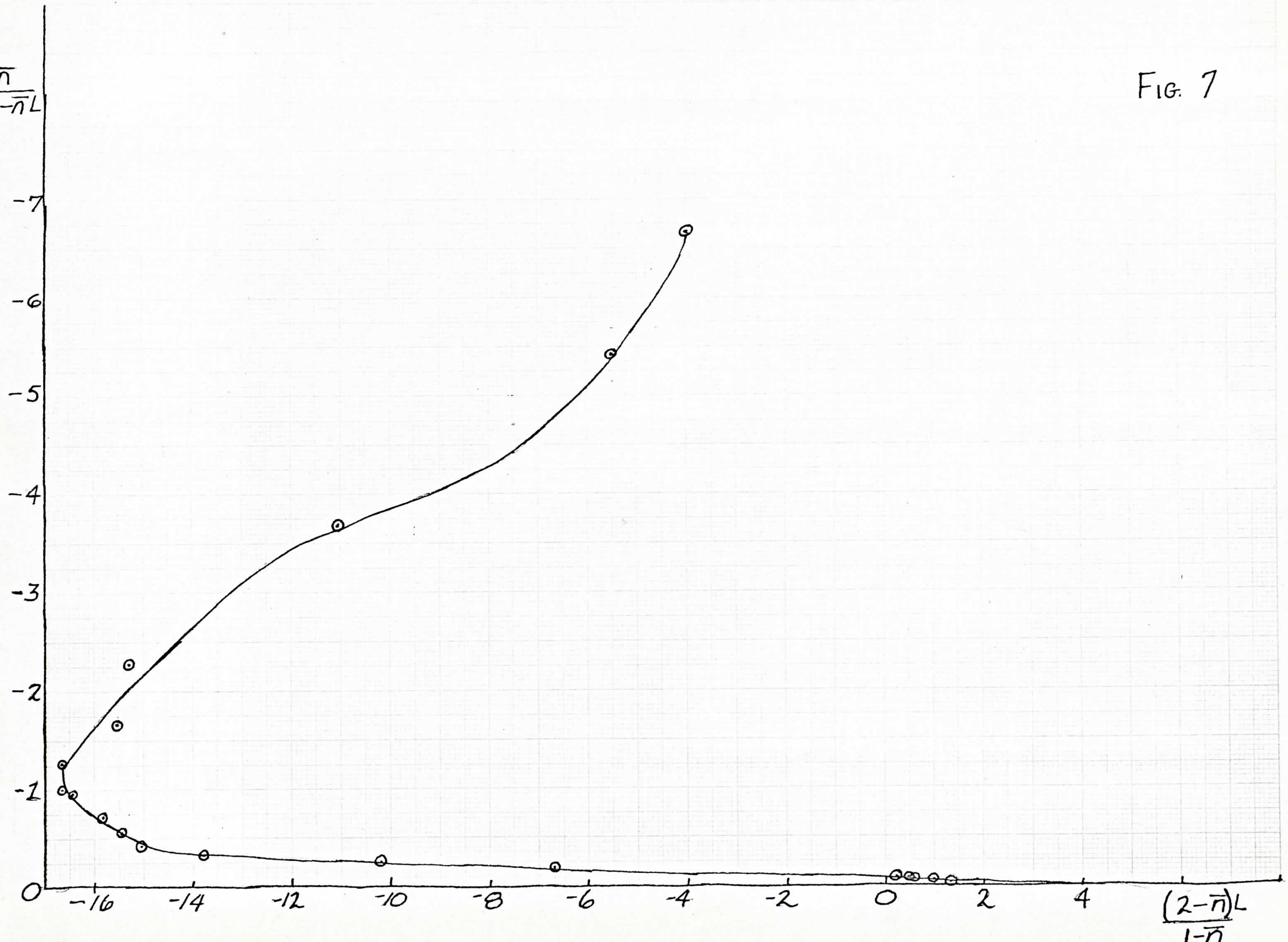
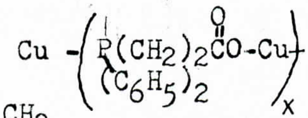
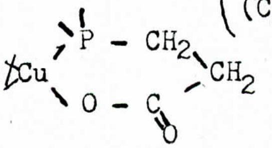
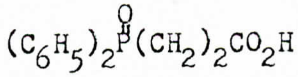


FIG. 6

FIG. 7



can be seen from Figure 7, no conclusive information can be gained as to the stability constants. However, from the titration data, it can be seen that addition of the metal ion did cause a pH lowering, indicating that some complex formed.

There are several possibilities of occurrences in solution that would explain the lack of a straight line for the stability constant curve. The first of these, previously discussed, is the possibility of amphoteric character in the acid. A second possibility is the occurrence of polynuclear species such as  $Cu-\left(\underset{(C_6H_5)_2}{P}(CH_2)_2\overset{O}{\overset{\|}{C}}O-Cu\right)_x$ instead of the anticipated chelate system 2  . Still a third occurrence might be decomposition of the acid in the solution to  $(C_6H_5)_2\overset{O}{P}(CH_2)_2CO_2H$ or to $(C_6H_5)_2PCH_2CH_3$, both of which are known side-products in the synthesis of the acid. A fourth possibility of error could be that the pH of the system and the meter reading in ethanol-water solutions is not a linear function as it should be. In this case, B would not be an effective measure of the hydrogen ion concentration. Van Uitert and Haas demonstrated that dioxane-water systems were linear (10); however, Griswold has shown that dioxane-water solutions are nonlinear under certain conditions (11).

VI. FUTURE WORK

Before any further attempt is made to determine the stability of phosphino acids, the linearity of pH <u>vs.</u> B in the ethanol-water solution should be checked. This is done by plotting pH, as determined by the titration of an acid in water, against meter reading B, as determined by the titration of the same acid in ethanol-water. The resulting plot should be linear. If not, suitable corrections for B must be made in subsequent studies.

In the present study the dielectric constant changed throughout the titrations because equivalent quantities of ethanol were not added with the base to maintain the 50% ratio. A study should be made with the dielectric remaining constant.

Further work on pK values needs to be done to substantiate those from Issleib and Thomas and the present study. Experimental conditions should be maintained identical to those under comparison.

Efforts should be made to determine the stability constants of 2-carboxyethyl-P,P-diphenylphosphine with metals other than copper. Similar studies could be made on analogues of this acid.

An interesting problem arises in considering the thermodynamic quantities associated with the phosphino acid. Studies could be made of pK as a function of temperature to determine enthalpy, and from that, other thermodynamic quantities.

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VIII. APPENDIX

Titrations of 2-carboxyethyl-P,P-diphenylphosphine

Vol. base	B
0.000	4.01
1.000	4.93
2.000	5.33
3.000	5.78
4.000	6.38
4.300	6.69
4.340	6.81
4.400	6.87
4.460	6.89
4.480	7.03
4.500	7.13
4.520	7.19
4.540	7.39
4.560	7.74
4.580	8.90
4.600	9.57
4.650	10.14
4.700	10.40
4.800	10.63

Weight acid: 0.25838 g

Vol. base	B
0.000	3.98
1.000	4.93
2.000	5.41
3.000	5.79
4.000	6.21
4.400	6.97
4.440	7.02
4.480	7.27
4.500	7.30
4.520	7.41
4.540	7.66
4.560	8.21
4.580	9.51
4.600	9.89
4.630	10.19
4.660	10.37
4.710	10.60
4.800	10.72

Weight acid: 0.25831 g

Titrations of perchloric acid

0.000	2.39
0.800	2.61
1.000	2.93
1.100	3.00
1.300	3.12
1.500	3.38
1.700	3.99
1.740	4.36
1.760	4.78
1.780	6.86
1.800	9.53
1.820	10.08
1.868	10.41
2.100	10.92

0.000	2.62
1.000	2.91
1.500	3.31
1.700	3.85
1.720	3.92
1.740	4.30
1.760	4.84
1.780	6.46
1.800	9.50
1.820	9.91

Titrations of 2-carboxyethyl-P,P-diphenylphosphine and perchloric acid

Vol. base	B
0.000	2.36
0.500	2.49
1.000	2.77
1.500	3.12
2.000	4.19
2.510	4.74
3.000	5.11
3.500	5.51
3.600	5.60
3.700	5.70
3.800	5.83
3.900	6.02
3.960	6.07
3.980	6.17
4.000	6.23
4.020	6.29
4.040	6.35
4.060	6.42
4.080	6.62
4.100	6.82
4.120	6.99
4.140	7.34
4.160	8.35
4.180	9.39
4.200	9.78
4.400	10.53

Weight acid: 0.12925 g

Vol. base	B
0.000	2.59
0.500	2.67
1.000	2.95
1.100	2.96
1.500	3.23
1.700	3.51
1.800	3.72
1.900	3.94
2.000	4.08
2.120	4.21
2.200	4.35
2.300	4.49
2.400	4.59
2.500	4.66
2.600	4.81
2.700	4.86
2.800	4.93
2.900	4.99
3.000	5.04
3.100	5.14
3.200	5.22
3.300	5.32
3.400	5.40
3.500	5.47
3.700	5.72
3.840	5.86
3.880	5.93
3.900	5.97
3.920	6.03
3.940	6.08
4.000	6.28
4.040	6.37
4.080	6.51
4.100	6.67
4.120	6.80
4.140	7.06
4.160	7.85
4.180	9.19
4.200	9.69
4.220	9.95
4.260	10.20
4.300	10.34

Weight acid: 0.12917 g

Titrations 2-carboxyethyl-P,P-diphenylphosphine, perchloric acid, copper(II)

Vol. base	B
0.000	2.38
0.500	2.43
1.000	2.54
1.520	2.72
1.700	2.81
1.900	2.91
2.100	3.06
2.300	3.31
2.500	3.55
2.700	3.83
2.900	4.11
3.100	4.39
3.300	4.63
3.500	4.88
3.700	5.11
3.900	5.36
4.100	5.60
4.200	5.75
4.300	5.94
4.400	6.18
4.500	6.51
4.520	6.62
4.540	6.79
4.560	6.95
4.580	7.30
4.600	8.42
4.620	9.44
4.640	9.81
4.680	10.26
4.720	10.41
4.800	10.61
5.000	10.86
5.200	10.99

Weight acid: 0.12927g

Vol. base	B
0.000	2.55
0.500	2.61
1.000	2.69
1.500	2.71
2.000	2.99
2.500	3.60
2.700	3.91
2.900	4.25
3.100	4.53
3.300	4.81
3.500	5.11
3.700	5.32
3.900	5.55
4.100	5.78
4.200	5.98
4.300	6.21
4.400	6.49
4.440	6.88
4.460	6.91
4.480	7.11
4.500	7.82
4.520	9.37
4.540	9.79
4.560	10.15
4.600	10.29
4.700	10.75
4.800	10.73
5.000	11.00

Weight acid: 0.12925 g

Standardization of sodium hydroxide with potassium acid phthalate

Vol. base	B
0.000	5.58
1.000	6.65
2.000	7.03
3.000	7.38
4.000	7.87
4.200	8.02
4.360	8.20
4.420	8.30
4.460	8.38
4.500	8.48
4.540	8.59
4.560	8.63
4.580	8.72
4.600	8.81
4.620	8.94
4.640	9.11
4.660	9.38
4.680	9.81
4.700	10.31
4.720	10.62
4.740	10.84
4.760	10.99
4.810	11.20

Weight acid: 0.21515 g

Vol. base	B
0.000	5.20
1.000	6.03
2.000	6.35
3.000	6.81
4.000	7.30
4.200	7.41
4.300	7.61
4.320	7.69
4.340	7.70
4.420	7.79
4.440	7.82
4.460	7.87
4.480	7.92
4.500	7.99
4.520	8.08
4.540	8.23
4.560	8.38
4.580	8.74
4.600	9.49
4.620	9.92
4.640	10.13
4.660	10.25
4.700	10.49
4.800	10.75

Weight acid: 0.21061 g

0.000	5.21
1.000	6.10
2.000	6.49
3.000	6.82
4.000	7.39
4.300	7.79
4.410	8.15
4.420	8.21
4.440	8.36
4.460	8.54
4.480	8.80
4.500	9.41
4.520	10.03
4.540	10.29
4.600	10.69

Weight acid: 0.20606 g

0.000	5.24
1.000	6.16
2.000	6.56
3.000	6.84
4.000	7.37
4.300	7.73
4.400	8.03
4.420	8.16
4.440	8.28
4.460	8.42
4.480	8.65
4.500	9.03
4.520	9.78
4.540	10.11
4.560	10.31
4.700	10.76

Weight acid: 0.20697 g