A STUDY OF THE COPOLYMERIZATION AND COPOLYMERS OF ITACONIC ANHYDRIDE AND STYRENE

Thesis for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY

John Constantine Dougas

1959

This is to certify that the

thesis entitled

A STUDY OF THE COPOLYMERIZATION
AND COPOLYMERS OF
ITACONIC ANHYDRIDE AND STYRENE

presented by

JOHN CONSTANTINE DROUGAS

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Major professor

Date April 2, 1959

O-169

o.c.s.

A STUDY OF THE COPOLYMERIZATION AND COPOLYMERS OF ITACONIC ANHYDRIDE AND STYRENE

By

John Constantine Drougas

A THESIS

Submitted to the School for Advanced Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1959

G15233
6/18/61

ACKNOWLEDGMENT

The author expresses his sincere appreciation to Doctor Ralph L. Guile, under whose direction this investigation was accomplished, for his inspiration, guidance, patience, and understanding which made this thesis possible.

He also wishes to make known his debt to Doctor Andrew Timnick for his aid in instrumentation, and for his helpful suggestions.

Appreciation is also extended to the Archer-Daniels-Midland Company, Minneapolis, Minnesota, whose Fellowship Program provided personal financial assistance during the academic years 1956-1958.

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To my Mother and Father

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AN ABSTRACT

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Approved _____

ABSTRACT

Itaconic anhydride and styrene were copolymerized by benzoyl peroxide to form copolymers of varying compositions. The reactivity ratios for this copolymerization were determined in two solvents. In benzene r_2 (itaconic anhydride) = 0.78, r_1 (styrene) = 0.015, and in tetrahydrofuran r_2 = 0.60, r_1 = 0.10. Values determined for the copolymerization in tetrahydrofuran are probably more accurate because of the homogeneous nature of the polymerization but polymerization in benzene yields copolymers that are easier to work with and at a faster rate.

The itaconic anhydride-styrene copolymers were shown to have a highly alternating structure and arranged in a head-to-tail manner. The dibasic acid nature of the itaconic anhydride-styrene segment in the copolymer was established both by potentiometric and high-frequency titrations. Apparent values of pK_1' and pK_2' are 5.7 and 8.8 respectively.

Monoester derivatives were prepared and were shown by high-frequency titrations in all cases to be a mixture of two different monoesters. Apparent values of pK_1'' and pK_2'' for the monomethyl ester are 6.3 and 7.9 respectively.

Diester derivates of the copolymer were prepared.

An optically active derivative was produced from the copolymer and the copolymer was converted to a network polymer which exhibited ion-exchange properties.

The monoethyl and dimethyl ester derivatives of the copolymer do not undergo hydrolysis in aqueous sodium hydroxide at 25°C in about twenty-five hours.

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INTRODUCTION

INTRODUCTION

The copolymers and copolymerization of itaconic anhydride and styrene have been the subject of a number of investigations in this laboratory (1,2,3). The study was originally initiated because of the availability of itaconic anhydride and the research in this laboratory and elsewhere on the apparently similar copolymerization and copolymers of maleic anhydride and styrene (4,5,6). The purpose of this investigation was to determine the reactivity ratios of each of the monomer radicals, to analyze the copolymers for composition and structure, and to prepare derivatives of the copolymers.

This thesis also reports, we believe for the first time, the study of a high frequency titration applied to polymeric polyelectrolytes, an analytical technique made necessary by the limitations of potentiometric titrations when applied to polycarboxylic acids.

HISTORICAL

HISTORICAL

Styrene has been shown to be a useful monomer in many copolymerizations (7,8,9). Itaconic acid, an unsaturated dibasic acid has the structure necessary for the preparation of high-molecular weight thermoplastic materials by polycondensation reactions. These linear products can crosslink through the residual unsaturation. In practice however, vinyl type monomers such as styrene or dimethyl itaconate are polymerized with the polycondensation product, in order to improve the physical properties of the resulting thermosetting resin. The diesters of itaconic acid formed from saturated monohydric alcohols may be polymerized with peroxide catalysts to form thermoplastic homopolymers. They may also be copolymerized with other vinyl type monomers to yield useful, transparent plastics.

Copolymers of itaconic acid or its derivatives with various unsaturated compounds have been found to be excellent viscosity improvers for lubricating oils (10,11).

Copolymers prepared using diallyl itaconate as one of the components are claimed to be useful as ion exchange resins (12,13). Diesters of itaconic acid formed from saturated monohydric alcohols may be copolymerized with monomers such as divinyl benzene. Saponification of these copolymers forms an ion exchange resin.

Itaconic acid and some of its derivatives may be copolymerized with acrylonitrile, vinyl chloride and other vinyl monomers to form polymers useful as textile fibers (14,15).

Copolymers of itaconic acid diesters with styrene or one of the methacrylates yield clear, water-white materials with excellent optical properties which should be useful for the manufacture of lenses and other transparent plastic products (16,17).

Copolymers of itaconic anhydride and vinyl acetate are useful as soil conditioners (18,19).

A search of the literature has indicated that no extensive study of the copolymerization of styrene and itaconic anhydride has been made.

REAGENTS

1. Benzene

Thiophene-free benzene was obtained from the stockroom and shaken for one-half hour with concentrated sulfuric acid. The process was repeated twice with fresh portions of acid. The benzene was then placed over sodium and distilled. The fraction boiling at 80-81°C was used.

2. Tetrahydrofuran

The tetrahydrofuran obtained from the stockroom was purified by treatment with potassium hydroxide, followed by distillation over lithium aluminum hydride. The fraction boiling at 65-66°C was used.

3. Methyl Alcohol

Absolute methanol was placed in a one-liter flask fitted with a large reflux condenser. To this was added 10 g. of magnesium turnings and the mixture refluxed for three hours. The dry alcohol was distilled from the magnesium hydroxide and magnesium methoxide, that part boiling at 64.5-65°C was used in this work.

4. Ethyl Alcohol

The above procedure was applied to absolute ethanol and the fraction boiling at 74.4 to 74.6°C was selected for use in these experiments.

5. Styrene

Commercially available styrene was washed with three successive portions of a 10% sodium hydroxide solution to remove the inhibitor. The styrene was then washed with water until the washings were neutral

to litmus. The styrene was then stored over anhydrous sodium sulfate for 2-3 days, and distilled under reduced pressure in a nitrogen atmosphere. The sample was free of polymer as indicated by the lack of a precipitate on the addition of methanol. The refractive index of the material used was n_D^{20} -1.5340, and the boiling point was 36-37°C at 30 mm. pressure.

6. Unsymmetrical Dimethylsuccinic Acid

This material was purchased from K & K Laboratories, Inc., Long Island City, 1, N. Y.

7. Methylsuccinic Acid

This was obtained from Aldrich Chemical Co., Inc., Milwaukee, 10, Wisconsin.

8. Succinic, Salicylic, Benzoic, Propionic, and Acetic Acids

These were of a C. P. Grade available in this laboratory.

9. Itaconic Anhydride

A mixture of 50 g. (0.39 mole) itaconic acid and 100 ml. acetyl chloride was heated under reflux for one hour, during which time the itaconic acid dissolves. Heating was continued for about fifteen minutes beyond this point. The acetyl chloride-acetic acid mixture was then distilled under reduced pressure (water aspirator 25 mm.) under a nitrogen atmosphere. Two 60 ml. portions of toluene were added consecutively and removed. During the distillation of the toluene and acetic acid mixtures the temperature was kept below 80°C by means of a water bath. This was a critical temperature above which decomposition and polymerization occurred. The syrupy residue was transferred to an Erlenmeyer flask and 100 ml. anhydrous ethyl ether

were added. Approximately 32 g. of itaconic anhydride, m.p. 68-69°C crystallizes. Concentration of the ethereal solution yielded an additional 8.5 g. of crude anhydride, m.p. 63-66°C. About four hours are required for this preparation. The preparation should be continuous up to the point where the ether is added.

The crude itaconic anhydride was recrystallized twice from c.p. chloroform to give a constant melting product, m.p. 68-68.5°C. A good yield of itaconic anhydride was 90% based on itaconic acid.

Itaconic anhydride may be prepared from itaconic acid with thionyl chloride (21), phosphorous pentoxide (22), acetyl chloride (23), or acetic anhydride (24). Itaconic acid is chiefly produced by the submerged culture fermentation of a glucose media by "Aspergillus terreus." A laboratory method of preparation consists in the rapid distillation of citric acid (25).

Determination of Itaconic Anhydride by Reaction with Morpholine

The procedure used was similar to that of Johnson and Funk (57).

A standard (0.8552N) HCl methanolic solution was prepared by the addition of 6N-HCl to a one liter volumetric flask and diluting to the mark with methanol. The HCl should be standardized daily against standard NaOH using phenolphthalein indicator.

An approximately 0.5N-methanolic solution of morpholine was prepared by adding 44 ml. of redistilled morpholine to a one liter reagent bottle and diluting to one liter with methyl alcohol. The bottle was fitted with a two hole rubber stopper. A 50 ml. pipette was inserted in the one hole so that the tip dipped below the solution of the

morpholine. A short piece of glass tubing was inserted through the second hole and a rubber bulb was attached to it.

A methyl yellow-methylene blue mixed indicator was prepared by dissolving 1 g. of methyl yellow and 0.1 g. of methylene blue in 125 ml. of methanol.

Procedure: A 50 ml. aliquot of morpholine was added to each of two 250 ml. glass-stoppered flasks. An accurately weighed sample (0.5 g.) of itaconic anhydride was introduced into one of the flasks. About one hour was allowed for the solution of the itaconic anhydride and then 4 drops of the indicator solution were added to each flask. The solutions were then titrated with standardized HCl to the disappearance of the green color.

The morpholine consumed is represented by titration difference between the blank and sample and this is a measure of the anhydride. The amount of acid originally present in the sample may be determined when the morpholine procedure is used in conjunction with others which measure total acid and anhydride.

The results are summarized in the following table.

TABLE IA

DETERMINATION OF ITACONIC ANHYDRIDE BY REACTION WITH MORPHOLINE

Sample Weight Itaconic Anhydride* g	Ml. 0.8522 N-HCl For Sample	Ml. 0.8522 N-HCl For Blank	Percent Itaconic Anhydride
0.5312	38.22	43.82	100.9
0.5043	38.60	43.82	99.1
0.5261	38.36	43.81	99.4

Sample Calculation:

$$\text{Percent Itaconic Anhydride} = \frac{(\text{ml. HCl Blank} - \text{ml. HCl Sample})(\text{N-HCl}) \times \frac{112}{1000}}{\text{Sample Weight}} \times 100\%$$

*The itaconic anhydride used for these experiments was a sample which had been recrystallized several times from chloroform. M.p. 68-68.5°C.

PART I

A. Evaluation of Monomer Reactivity Ratios in Benzene.

B. Evaluation of Monomer Reactivity Ratios in Tetrahydrofuran.

EXPERIMENTAL

EXPERIMENTAL

A. Evaluation of Monomer Reactivity Ratios in Benzene

A series of copolymerizations of itaconic anhydride and styrene were carried out in benzene at molar ratios of itaconic anhydride/styrene of 10/90, 20/80, 25/75, 40/60, 50/50, 65/35, 75/25, 85/15, 95/5. A typical procedure for the reactions follows.

The copolymerization was carried out in a five hundred milliliter, three-neck, round bottom flask with standard taper ground glass joints. The flask was fitted with a reflux condenser, a nitrogen inlet tube and a mechanical stirrer. The polymerization mixture was protected from moisture by a calcium chloride tube and kept under a nitrogen atmosphere. The flask was charged with three hundred and fifty milliliters (307.6 g.) of benzene and the desired amount of itaconic anhydride was added. To dissolve the itaconic anhydride the mixture was heated, with stirring, at the reflux temperature of benzene (80°C) maintained by use of an oil bath. Approximately thirty minutes were required for the solution of the itaconic anhydride. A sufficient amount of styrene comonomer was then added to the reaction flask to make a total comonomer charge of 0.233 mole. The benzoyl peroxide catalyst, 0.1166 g., was added and the time recorded. When the desired per cent of polymerization was obtained, in about fourteen minutes, the contents of the flask were transferred to a large test tube and immersed in a dry-ice acetone mixture for several minutes to

quench the reaction. The solid copolymer was filtered off with suction and washed with several portions of hot benzene. Finally the solid copolymer was dried at 4-5 mm. pressure at 56°C for twenty-four hours and weighed. Per cent polymerization was calculated as follows:

$$\text{Per cent polymerization} = \frac{\text{weight of polymer}}{\text{total monomer weight}} \times 100$$

The samples from the various copolymerization reactions were submitted for carbon-hydrogen analyses, the results of which were used to calculate the mole per cent of itaconic anhydride in the copolymer. The data for these experiments are listed in Table I. The mole fraction of itaconic anhydride was calculated from the per cent carbon as shown by analysis.

A sample calculation follows:

Assume a sample of copolymer of 100 g.

Let x = g. itaconic anhydride in sample

Then (100-x) = g. styrene in sample

Itaconic anhydride contains 53.6% carbon.

Styrene contains 92.3% carbon.

Therefore

$$0.536\,x + 0.923(100-x) = \text{per cent carbon.}$$

The copolymerization equation

$$(1) \qquad \frac{d[M_1]}{d[M_2]} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1}$$

can be arranged to the form

$$(2) \qquad r_2 = \frac{M_1}{M_2}\left[\frac{m_2}{m_1}\left(1 + \frac{M_1}{M_2}\, r_1\right) - 1\right]$$

where

M_1 = mole per cent styrene in the monomer charge.

M_2 = mole per cent itaconic anhydride in the monomer charge.

m_1 = mole per cent styrene in the copolymer.

m_2 = mole per cent itaconic anhydride in the copolymer.

Substitution in equation (2) for the values of M_1, M_2, m_1, and m_2 was made for the various reactions. There resulted a series of equations which would give straight line graphs when r_1 is plotted against r_2. Assumed values of r_1 (from -0.1 to +0.1) were substituted in equation (2) to give a corresponding value of r_2. A sample calculation is given below using reaction No. I in Table I.

$$r_2 = \frac{M_1}{M_2}\left[\frac{m_2}{m_1}\left(1 + \frac{M_1}{M_2}\, r_1\right) - 1\right]$$

$$r_2 = \frac{9}{1}\left[\frac{50.3}{49.7}\left(1 + \frac{9}{1}\, r_1\right) - 1\right]$$

If $r_1 = 0$; $r_2 = 0.135$

$r_1 = +0.1$; $r_2 = 8.356$

$r_1 = -0.1$; $r_2 = -8.086$

Only two substitutions of r_1 in equation (2) were required to obtain two values of r_2 which would determine the straight line. However, three values of r_1 were used so that the third point on the straight line could serve as a check on the calculations. The values of r_1 versus r_2 were plotted for each of the copolymer compositions and the resulting series of straight lines is shown in Fig. 1.

The r_1 - r_2 values were now used, along with the monomer composition, to calculate the theoretical composition of the increment of polymer formed at a specified monomer composition. These values are shown in the last column of Table I. The equation used to make these calculations is

$$(3) \quad F_2 = (r_2 f_2^2 + f_1 f_2)/(r_2 f_2^2 + 2 f_1 f_2 + r_1 f_1^2)$$

where

F_2 = mole fraction of monomer M_2 in the increment of copolymer formed at a given stage in the polymerization.

f_2 = mole fraction of monomer M_2 in the monomer charge.

f_1 = mole fraction of monomer M_1 in the monomer charge.

r_2 = ratio of the rate constants of M_2^* with monomer M_2 and M_2^* with monomer M_1.

r_1 = ratio of the rate constants of M_1^* with monomer M_1 and M_1^* with monomer M_2.

M_2 is itaconic anhydride.

M_1 is styrene.

A plot of the mole fraction (F_2) of itaconic anhydride in the copolymer versus the mole fraction of itaconic anhydride (f_1) in the monomer mixture is shown in Fig. 2.

The method of Fineman and Ross (20) was also used in the analysis of the copolymerization data to evaluate r_1 and r_2. In their method equation

$$(1) \quad \frac{d[M_1]}{d[M_2]} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad \left(= \frac{m_1}{m_2} \text{ for low conversions} \right)$$

may be rewritten as:

$$f = F \frac{r_1 F + 1}{r_2 + F}$$

where

$$f = \frac{m_1}{m_2} \qquad \text{and} \qquad F = \frac{M_1}{M_2}$$

and by rearranging the terms one obtains:

$$\frac{F}{f}(f - 1) = r_1 \frac{F^2}{f} - r_2$$

A plot of $(F/f)(r - 1)$ as ordinate and (F^2/f) as abscissa is a straight line whose slope is r_1 and whose intercept is $-r_2$. The data are plotted in Fig. 3.

Table II lists the values of the reactivity ratios as determined by the copolymerization equation (2) and the method of Fineman and Ross.

TABLE I

REACTIVITY RATIO DATA FOR ITACONIC ANHYDRIDE-STYRENE COPOLYMERIZATION IN BENZENE

No.	Itaconic Anhydride g.	Styrene g.	Mole Fraction[a]	Conversion[b] Per Cent	Carbon Per Cent	Hydrogen Per Cent	Mole Fraction[c]	Calculated Mole Fraction[d]
1	2.612	21.84	0.100	1.2	72.15	5.67	0.503	0.489
2	5.224	19.40	0.197	3.7	70.29	5.56	0.550	0.529
3	6.524	18.15	0.250	3.1	70.18	5.34	0.553	0.546
4	10.45	14.55	0.400	6.1	66.60	5.00	0.647	0.597
5	13.03	12.10	0.500	7.9	66.98	5.19	0.637	0.636
6	16.97	8.49	0.651	7.8	64.05	5.00	0.712	0.708
7	19.58	6.07	0.749	4.5	62.13	5.04	0.767	0.761
8	22.18	3.63	0.850	4.2	61.57	5.02	0.772	0.843
9	24.79	1.21	0.950	3.8	58.42	4.86	0.869	0.940

[a] Mole fraction itaconic anhydride in the charge.

[b] Per cent conversion based on the weight of polymer obtained.

[c] Mole fraction of itaconic anhydride in the copolymer determined by carbon-hydrogen analysis.

[d] Mole fraction of itaconic anhydride as calculated from the monomer composition and the r_1-r_2 values previously determined.

TABLE II

REACTIVITY RATIOS IN BENZENE

a. By $r_1 - r_2$ plots:

Itaconic Anhydride	0.780
Styrene	0.015

$r_1 r_2 = 0.011$

b. By the method of Fineman and Ross:

Itaconic Anhydride	0.750
Styrene	0.008

$r_1 r_2 = 0.006$

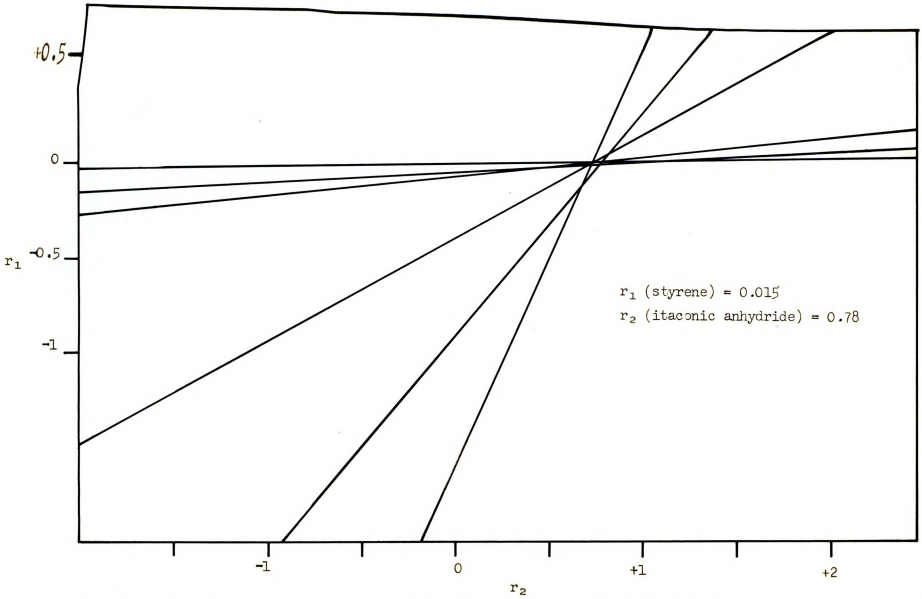


Fig. 1. Reactivity ratios for the copolymerization of itaconic anhydride with styrene in benzene.

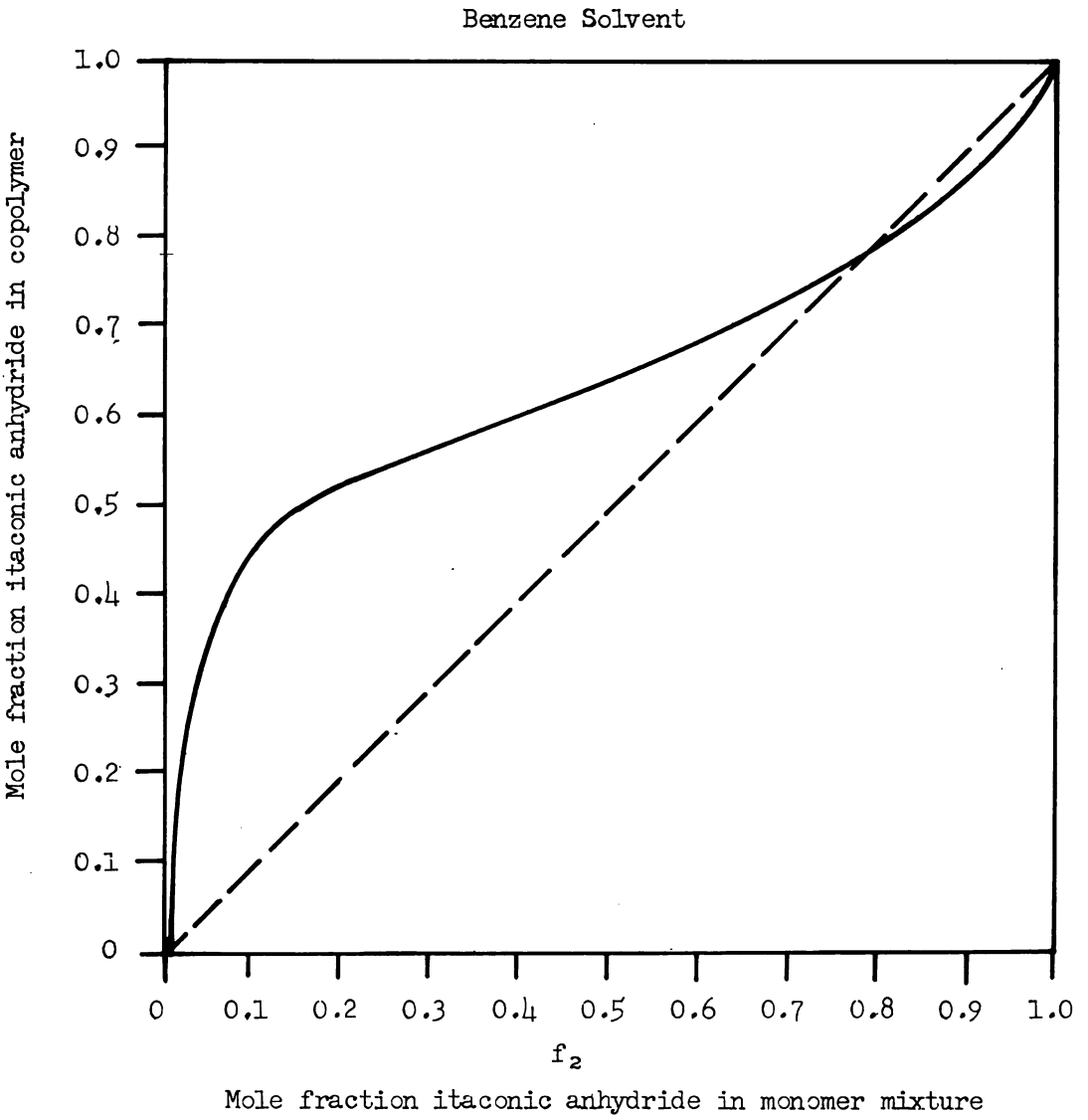


Fig. 2. Copolymer composition curve.

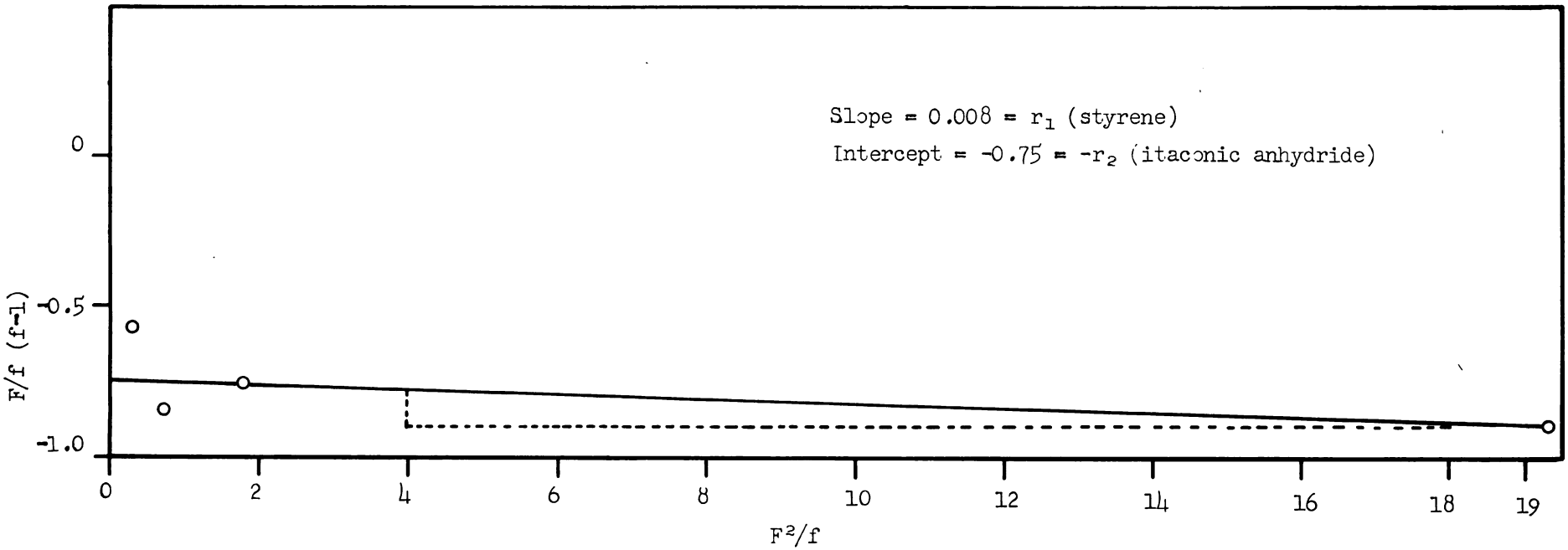


Fig. 3. Reactivity ratios for the copolymerization of itaconic anhydride with styrene in benzene, by the method of Fineman and Ross.

B. Evaluation of Monomer Reactivity Ratios in Tetrahydrofuran

The copolymerizations were carried out at the reflux temperature of tetrahydrofuran (65°C.). The experimental procedure is the same as that used in benzene. After the reaction mixture was removed from the dry-ice acetone bath, the following steps were necessary:

a. Addition of anhydrous diethyl ether to precipitate the copolymer. This appeared to be the only non-solvent yielding a good precipitate. It was necessary that the non-solvent be anhydrous to prevent the hydrolysis of the anhydride ring.

b. Centrifugation and filtration to isolate the copolymer. Due to the finely divided nature of the copolymer, it was necessary to centrifuge the reaction mixture for about ten minutes. After decanting off most of the liquid, the remainder was removed by filtration.

c. The copolymer was then dried at 4-5 mm. at 56°C. for twenty-four hours and weighed. The samples were then submitted for carbon-hydrogen analysis.

The data for these experiments are found in Table III.

The values of r_1 and r_2 were determined as previously described and these were plotted as shown in Fig. 4. The composition of the increment of polymer formed at a specified monomer composition was calculated using equation (3) and the values appear in the last column of Table III. The plot of mole fraction (F_2) of itaconic anhydride in the copolymer versus the mole fraction of itaconic anhydride (f_2) in the monomer mixture is shown in Fig. 5.

The method of Fineman and Ross (20) was also used to evaluate r_1 and r_2 and Fig. 6 shows a plot of the data.

Table IV lists the values of the reactivity ratios as determined by the copolymerization equation and the method of Fineman and Ross.

TABLE III

REACTIVITY RATIO DATA FOR ITACONIC ANHYDRIDE-STYRENE COPOLYMERIZATION IN TETRAHYDROFURAN

No.	Itaconic Anhydride g.	Styrene g.	Mole Fraction[a]	Conversion[b] Per Cent	Carbon Per Cent	Hydrogen Per Cent	Mole Fraction[c]	Calculated Mole Fraction[d]
1	2.61	21.84	0.100	9.5	77.48	6.32	0.365	0.312
2	5.22	19.40	0.197	5.1	74.14	6.04	0.450	0.418
3	6.52	18.15	0.250	7.9	74.02	6.03	0.453	0.456
4	10.45	14.55	0.400	9.1	70.91	5.70	0.533	0.565
5	13.03	12.10	0.500	8.8	68.81	5.88	0.589	0.581
6	16.97	8.49	0.651	13.0	66.63	5.35	0.646	0.660
7	22.18	3.63	0.850	5.3	62.58	5.41	0.753	0.684

[a]Mole fraction itaconic anhydride in the charge.

[b]Per cent conversion based on the weight of polymer obtained.

[c]Mole fraction of itaconic anhydride in the copolymer determined by carbon-hydrogen analysis.

[d]Mole fraction of itaconic anhydride as calculated from the monomer composition and the $r_1 - r_2$ values previously determined.

TABLE IV

REACTIVITY RATIOS IN TETRAHYDROFURAN

a. By $r_1 - r_2$ plots:

Itaconic Anhydride	0.60
Styrene	0.10

$r_1 r_2 = 0.06$

b. By the method of Fineman and Ross:

Itaconic Anhydride	0.60
Styrene	0.095

$r_1 r_2 = 0.058$

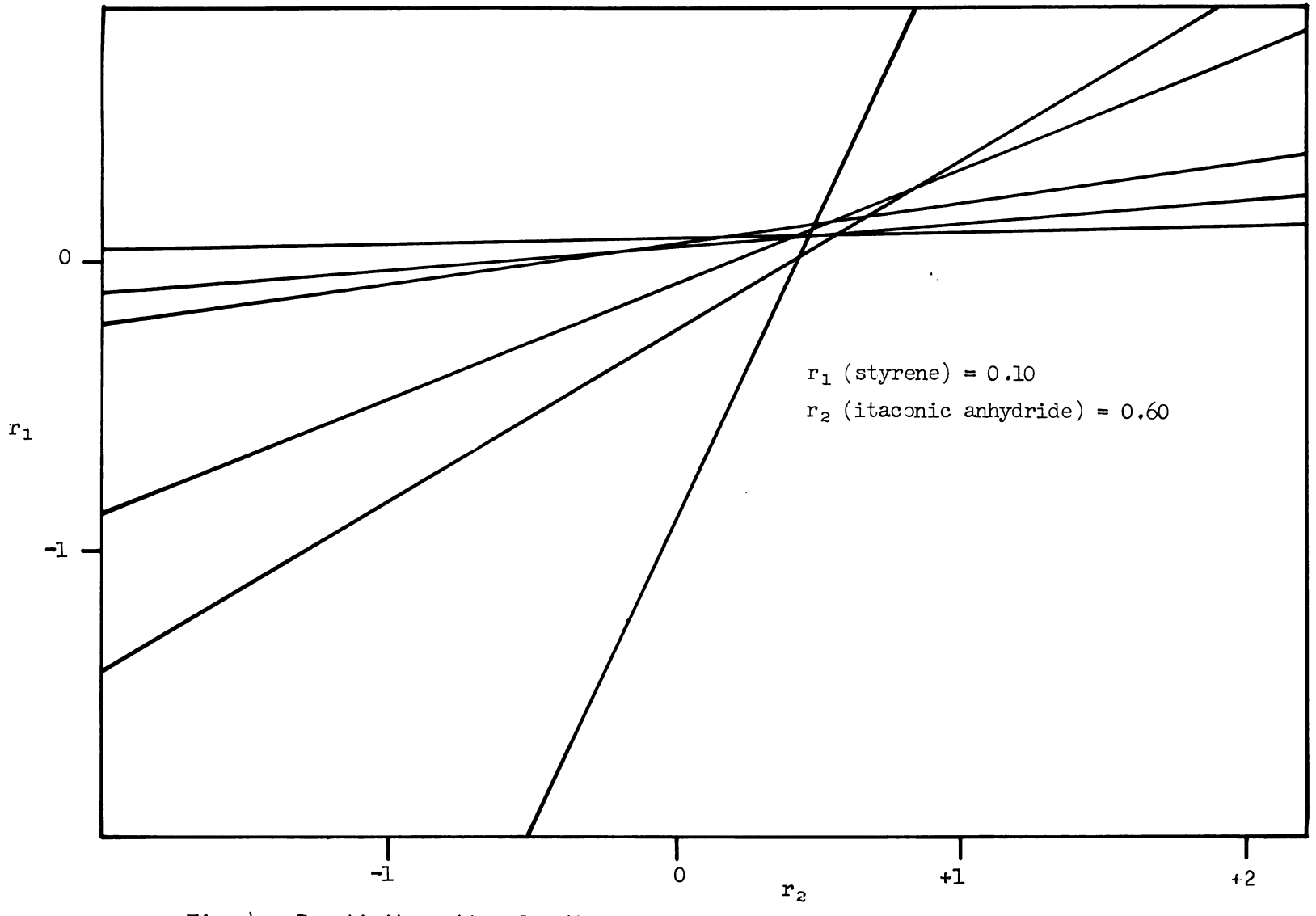


Fig. 4. Reactivity ratios for the copolymerization of itaconic anhydride with styrene in tetrahydrofuran.

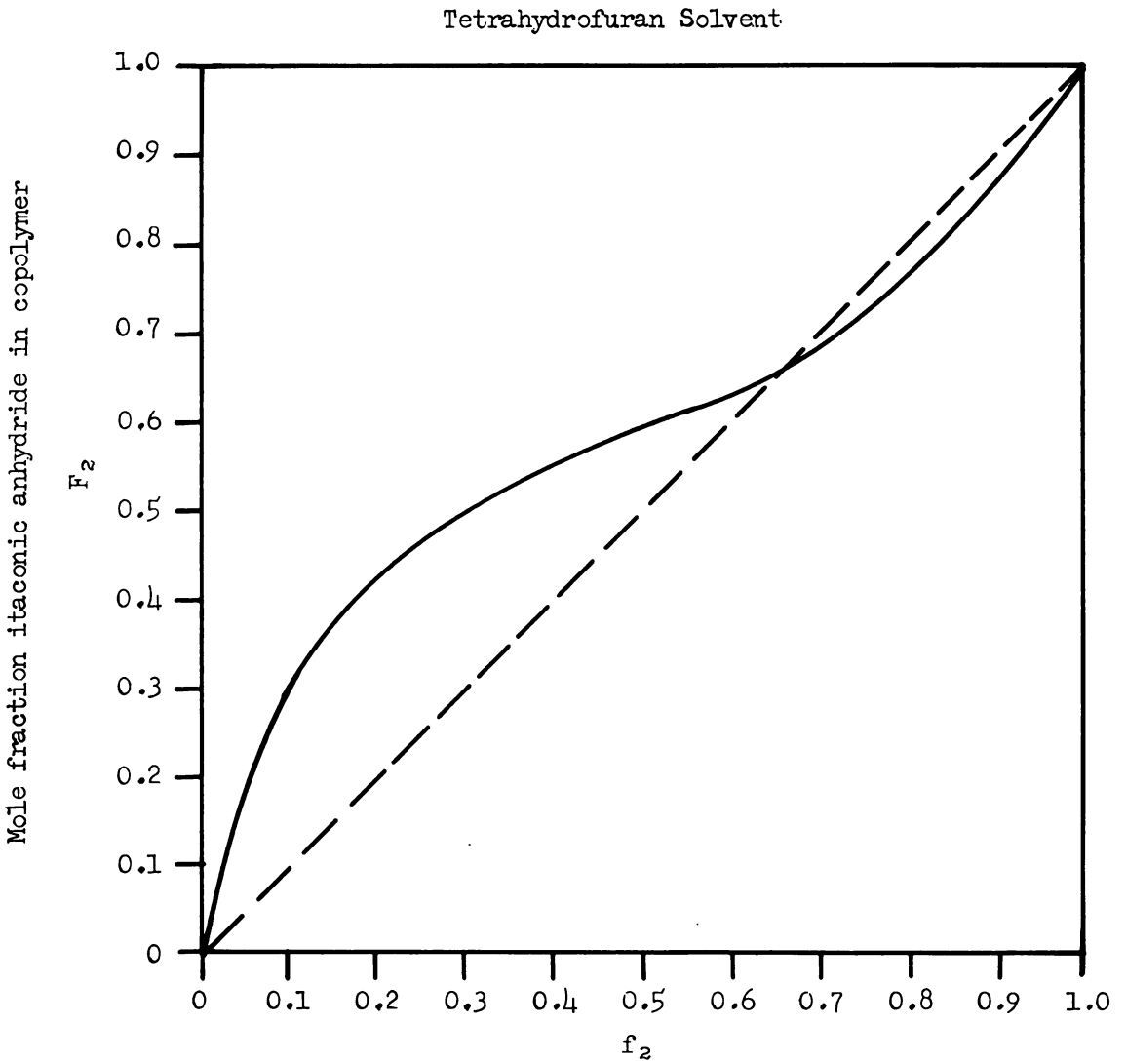


Fig. 5. Copolymer composition curve.

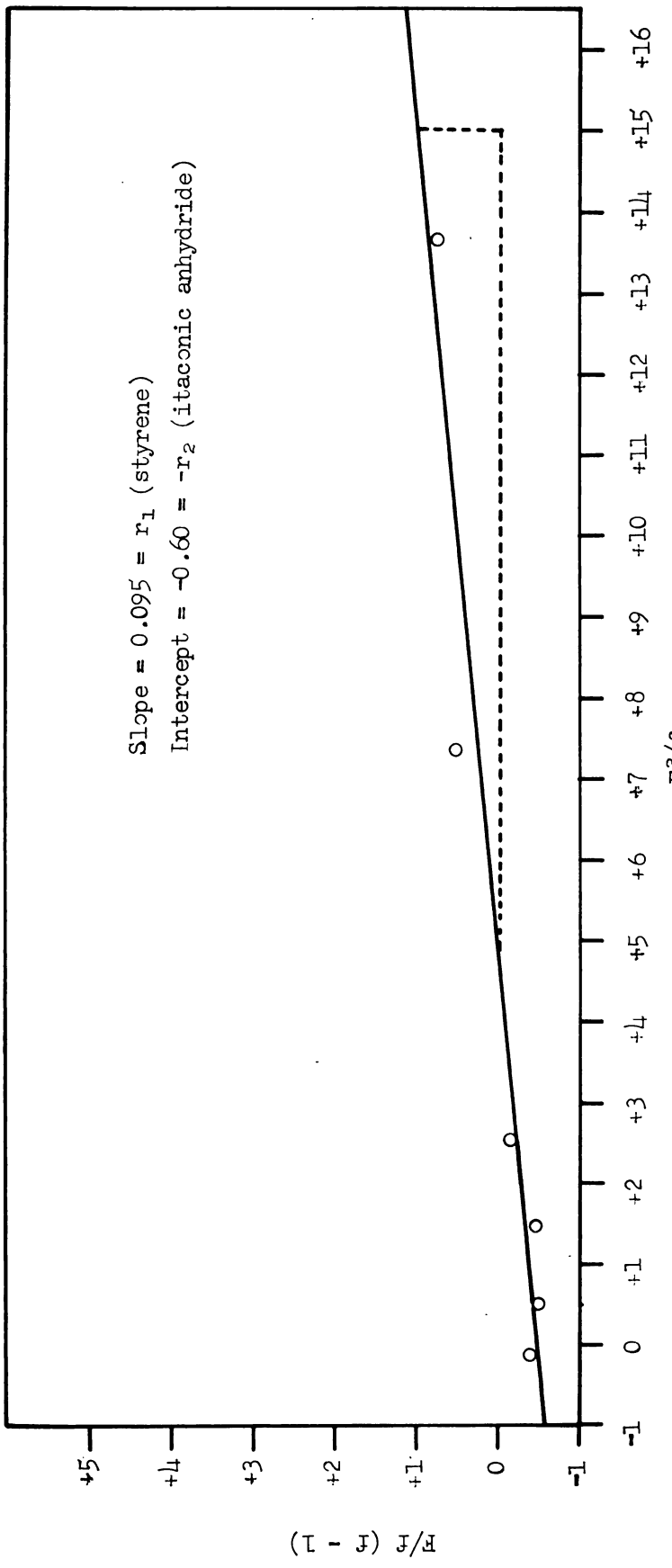


Fig. 6. Reactivity ratios for the copolymerization of itaconic anhydride with styrene in tetrahydrofuran, by the method of Fineman and Ross.

DISCUSSION

DISCUSSION

The composition of a polymeric substance is usually described in terms of its structural units. Generally, these may be defined as groups having a valence of two or more. The structural units are connected to one another in the polymer molecule, or polymeric structure, by covalent bonds. The generation of the entire structure by the repetition of one or a few elementary units, is the basic characteristic of polymeric substances, as implied by the word polymer, meaning many membered.

The structural units may be connected together in any imaginable pattern. In the simplest of polymers, the structural units are connected one to another in linear sequence.

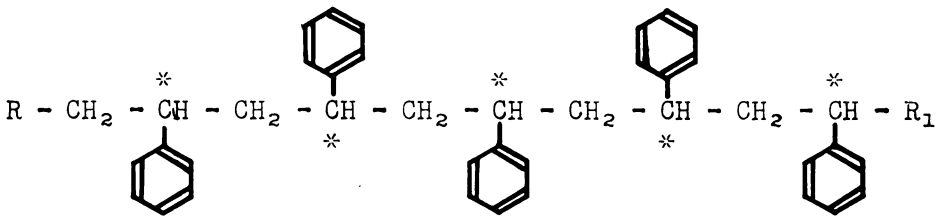
The polymers prepared in this investigation were formed from monomers which enter into two, and only two, linkages with other structural units. The structural units of linear polymers necessarily are bivalent. The ability of the extra electron pair of the ethylenic linkage to enter into the formation of two bonds gives to styrene and itaconic anhydride this interlinking capacity. In accordance with the functionality concept introduced by Carothers (26,27), all monomers which when polymerized may join with two, and only two, other monomers are termed bifunctional. A bifunctional unit is one which is attached to two other units. Linear polymers then are composed of bifunctional units.

Polymeric substances containing two or more structural units combined in a more or less random sequence are called copolymers. A linear copolymer composed of two bifunctional units M_1 and M_2 may be represented in several ways. The structural units may alternate, that is, $-M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2$ - there may be a preponderance of long sequences of like units, $- M_1M_1M_1M_1 -M_1 -M_2--M_2 -M_2 M_2 -M_1M_1$ - or the structural units may be randomly oriented, $-M_1M_2M_2M_1M_2M_1M_1M_1M_2$ -. In the event that the units alternate with perfect regularity the polymer is regarded as a polymer of the repeating unit $-M_1M_2-$. Tendency toward alternation is the rule in copolymerization.

The term copolymerization implies that the monomers combine in the same polymer chain. In the event that the monomers polymerized separately to form molecularly distinct species, each having a different unit, the product would simply be a mixture of polymers and not a copolymer.

A strict application of the foregoing definition would place polystyrene in the class of copolymers since it possesses asymmetric carbon atoms and can have d and l structural units. Since it is formed from a single monomer rather than by copolymerization of a number of monomers, application of the term polymer is justified.

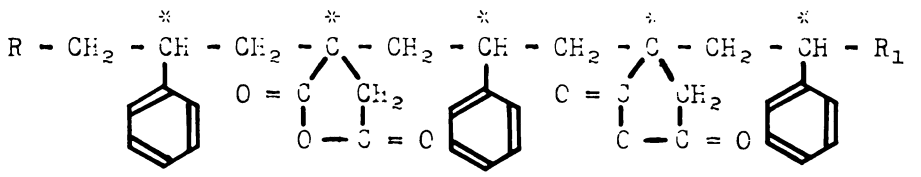
Polystyrene can have the following formula:



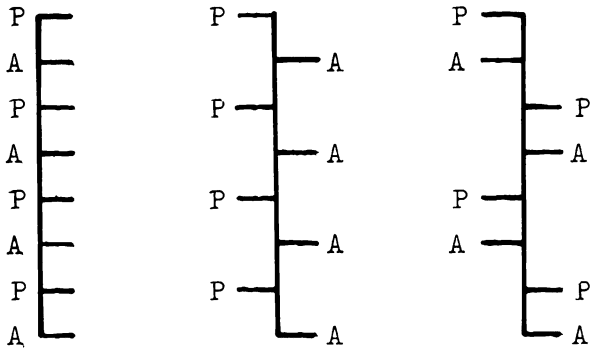
The carbon atoms designated with the asterisks are asymmetric but the polymer molecule does not exhibit optical activity due to internal compensation. The only asymmetric carbon atoms incapable of being internally compensated and thus capable of exhibiting optical activity are those at each end of the polymer chain provided that the chain does not end with two hydrogen atoms. The contribution to the molar rotation of the two terminal carbons is practically negligible due to the extreme length of the polymer chain, therefore the polystyrene molecule does not exhibit optical activity.

In polystyrene the length of the chain interferes with the free rotation to such an extent that the molecule shows a type of geometric isomerism. The phenyl rings in the chain may be so ordered that they are all on the same side of the backbone of the polymer chain. This is called isotactic polystyrene and has been prepared under certain conditions. If the phenyl rings alternate regularly along the polymer chain the resulting polymer is called syndiotactic. Polystyrene with random geometric distribution of the phenyl rings along the polymer chain is termed an atactic polymer.

In the case of the itaconic anhydride-styrene copolymer there exist two types of asymmetric carbon atoms designated with the asterisks below.



As mentioned in the case of polystyrene the only asymmetric carbon atoms which might contribute to the molecular rotation may be those located at the ends of the polymer chain. The internal asymmetric carbon atoms in the body of the polymer chain do not contribute to the optical rotation due to internal compensation. The itaconic anhydride styrene copolymer may have many more possible forms with a wider variation in "tacticity." As yet no attempt has been made to demonstrate degrees of "tacticity" within these copolymers. A few of the theoretical arrangements of the styrene and anhydride rings about the main polymer backbone are as follows:



Work with molecular models indicates no steric considerations that prevent stacking of phenyl and anhydride rings even in a highly stacked configuration although in this condition the backbone of the polymer is very rigid. Molecular model work also indicates that alternate phenyl and anhydride rings are not necessarily at angles of 90° or 180° to each other and to the backbone as shown by plane surface diagrams, but are at definite angles. However, only small variations

from these angles are possible due to steric hindrance between the phenyl and anhydride rings.

According to the classification applied by Carothers (28) the copolymers prepared in this investigation would be called addition polymers since the molecular formula of the structural units is identical with that of the monomers from which the copolymer is derived.

Addition polymerizations of unsaturated monomers leading to the formation of high molecular weight products almost always proceed by chain reaction mechanisms. Initial activation of a monomer or a pair of monomers is followed by the addition of other monomers in rapid succession as in:

$$M \xrightarrow{\text{activation}} M^{*} \xrightarrow{+M} M_2^{*} \xrightarrow{+M} M_3^{*} \longrightarrow \quad \text{etc.}$$

This process continues until the growing chain is eventually deactivated or terminated. The activated center, which is at the growing end of the polymer species, may be a free radical, a carbonium ion or a carbanion. The majority of the investigated vinyl polymerizations proceed by a free radical mechanism. These free radical polymerizations are commonly induced by radicals released by a decomposing peroxide, which is considered the catalyst. The free radicals may also be initiated thermally or photochemically. A large portion of the terminations of polymer chains in free radical polymerization has been shown to be by combination of two growing polymer chains.

The entire polymer molecule is synthesized within a matter of a few seconds or less. At any instant therefore during the polymerization

the reaction mixture consists of unchanged monomer and high polymer. The length of time during which a polymerization is carried out depends on the quantity of polymer desired, (per cent conversion of monomer to polymer) and is nearly unrelated to the molecular weight of the polymers already present or being formed.

There are practically no polymer species at intermediate stages of growth. Polymers that form even in the initial stages of a polymerization reaction compare favorably in molecular weight to those in the polymer mass at an advanced stage of the same polymerization (29). Thus it can be seen that the individual polymer molecules grow while most of the monomers remain unchanged. This is in line with the common feature of vinyl polymerizations that the active center of the kinetic chain is retained by a single polymer molecule during the course of its growth. If the active centers which convert the monomer to polymer were transferred randomly from one molecule to another, all molecular species would participate in combination with other species at all stages of the reaction. All the polymer molecules would then grow more or less simultaneously, and species such as dimers, trimers, and tetramers would be present at early stages in the polymerization and advance in size as the polymerization progresses. These intermediates are practically non-existent, and in the case of styrene the known dimer and trimer are themselves quite inert toward further polymerization (30). Thus it can be concluded that a given molecule is formed by consecutive steps of a single chain process set off by the generation of some active center. From the above considerations

it is apparent that the active center is in some way retained by a growing polymer chain from each addition of a monomer molecule to the next.

The following free radical chain mechanism, first suggested by Taylor and Bates (31) to explain the polymerization of ethylene induced by free radicals in the gas phase and independently proposed by Staudinger (32) for liquid phase polymerizations, offers an explanation for the general features of vinyl polymerizations:

$$R\cdot \xrightarrow{+CH_2 = CHX} R\text{-}CH_2\text{-}\overset{X}{\underset{}{C}}H\cdot \xrightarrow{+CH_2 = CHX} R\text{-}CH_2\text{-}\overset{X}{\underset{}{C}}H\text{-}CH_2\text{-}\overset{X}{\underset{}{C}}H\cdot \rightarrow \text{etc.}$$

As in all chain reactions, the over-all polymerization involves two other processes: 1) chain initiation, which depends on a reaction which introduces free radicals into the system, and 2) chain termination, in which the terminal radical on a growing chain is deactivated.

The number of reactions required to represent the copolymerization of two or more monomers increases geometrically with the number of monomers entering into reaction. The types of chain radicals to be considered is equal to the number of monomers present, and the reaction characteristics of a chain radical are determined almost entirely by the terminal monomer unit, the structure of those before it in the chain being of little importance. In the copolymerization of two monomers, two chain radicals must be distinguished. Addition of the two monomers to each of the radical species introduces four simultaneously occurring propagation reactions.

If the chains are long, the composition of the copolymer and the arrangement of units along the chain are determined almost entirely by the relative rates of the various chain propagation reactions. However, the rate of polymerization depends not only on the rates of the propagation steps but also on the termination reactions. Three different chain-terminating reactions between pairs of radicals should be considered.

The chain propagating reactions occurring when two monomers M_1 and M_2 are present may be written as:

a) $M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$

b) $M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$

c) $M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$

d) $M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$

Where M_1^* and M_2^* represent chain radicals having monomer residues M_1 and M_2 as the terminal, free-radical-bearing units.

Radicals of type M_1^* are formed by initiation of the monomer in (a) and by reaction (d) above. These radicals, M_1^*, are destroyed by reaction (b) and by termination reactions. At the steady state, the rates of appearance and disappearance of these radicals are practically equal. If it is assumed that the chains are long, only the above reactions need be considered since the interest lies in the relative concentrations of the two types of chain radicals. The steady state condition in this approximation reduces to

e) $k_{21} [M_2^*] [M_1] = k_{12} [M_1^*] [M_2]$

The rates at which monomer M_1 and M_2 are used are

f) $$\frac{-d[M_1]}{dt} = k_{11}\,[M_1^*]\,[M_1] + k_{12}\,[M_2^*]\,[M_1]$$

g) $$\frac{-d[M_2]}{dt} = k_{12}\,[M_1^*]\,[M_2] + k_{22}\,[M_2^*]\,[M_2]$$

Solving equation (e) for one of the radical concentrations, substituting this value in (f) and (g) to eliminate one of the radicals, and dividing (f) by (g) we obtain:

h) $$\frac{d[M_1]}{d[M_2]} = \left(\frac{[M_1]}{[M_2]}\right)\left(\frac{r_1[M_1]/[M_2] + 1}{[M_1]/[M_2] + r_2}\right)$$

The quantity $d[M_1]/d[M_2]$ given by equation (h) represents the ratio of the two monomers in that increment of copolymer formed when the ratio of unreacted monomers is $[M_1]/[M_2]$. Therefore by letting $\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2}$ and rearranging one arrives at the previously used equation (2)

(2) $$r_2 = \frac{M_1}{M_2}\left[\frac{m_2}{m_1}\left(1 + \frac{M_1}{M_2}\,r_1\right) - 1\right]$$

where r_1 and r_2 are monomer reactivity ratios defined by

$$r_1 = k_{11}/k_{12}$$

$$r_2 = k_{22}/k_{21}$$

r_1 represents the ratio of the rate constants for the reaction of a radical M_1^* with monomer M_1 and with monomer M_2; r_2 similarly expresses the relative reactivity of an M_2^* radical toward an M_2 monomer compared with an M_1 monomer. The unreacted monomer ratio changes as the polymerization continues, and this gives rise to a continually changing composition of the polymer being formed at each instant.

The compositions of the monomer feed and of the polymer formed may be expressed as mole fractions instead of mole ratios as indicated earlier. If F_1 represents the fraction of monomer M_1 in the increment of copolymer formed at a given instant in the polymerization then,

$$\text{i)} \quad F_1 = \frac{d[M_1]}{d([M_1] + [M_2])} = 1 - F_2$$

and if f_1 and f_2 represent the mole fractions of unreacted monomers in the feed then,

$$\text{j)} \quad f_1 = \frac{[M_1]}{([M_1] + [M_2])} = 1 - f_2$$

Substituting (i) and (j) in

$$(1) \quad \frac{d[M_1]}{d[M_2]} = \frac{M_1}{M_2} \cdot \frac{r_1M_1 + M_2}{r_2M_2 + M_1}$$

there results equation (3):

$$(3) \quad F_2 = (r_2f_2^2 + f_1f_2)/r_2f_2^2 + 2f_1f_2 + r_1f_1^2)$$

The composition of the increment of polymer formed at a specified monomer composition can be readily calculated using equation (3) and the determined reactivity ratios r_1 and r_2. Figures 2 and 5 represent a plot of the mole fraction of itaconic anhydride in the copolymer versus the mole fraction of itaconic anhydride in the monomer mixture. Also plotted on these graphs are the mole fractions of itaconic anhydride in the copolymer as determined from the carbon-hydrogen analysis. These data are listed in the last two columns of Tables I and III and

an inspection of these and the graphs shows that the theoretical mole fractions agree very well with the actual values.

It can be seen that the mole fraction F_2 will not usually equal f_2; and thus F_2 and f_2 will change as the polymerization progresses.

If the two radicals display the same preference for one of the monomers over the other then

$$k_{11}/k_{12} = k_{21}/k_{22}$$

or $r_1 \cdot r_2 = 1$. The broken line in Fig. 2 and 5 represents the case in which $k_{11} = k_{12}$ and $k_{22} = k_{21}$, that is, the two monomers are equally reactive with each radical. In this case $r_1 = r_2 = 1$ and $F_2 = f_2$, that is, the polymer composition is equal to the monomer composition. In the case where the monomer feed contains a mole fraction of 0.4 in itaconic anhydride, the copolymer will contain the same mole fraction in itaconic anhydride.

Wall (33) first indicated the close analogy between the copolymer-monomer mixture composition relationships and vapor-liquid equilibria in binary systems. Wall introduced the term ideal copolymerization for the case where $r_1 \cdot r_2 = 1$, in analogy to the vapor-liquid equilibria for ideal liquid mixtures. In this case the two radicals display the same preference for one of the monomers over the other, and as before

$$k_{11}/k_{12} = k_{21}/k_{22}$$

or

$$r_1 \cdot r_2 = 1$$

Equations (1) and (3) in this case reduce to

$$k) \quad \frac{d[M_1]}{d[M_2]} = r_1 [M_1]/[M_2]$$

and

$$l) \quad F_2 = r_2 f_2/(r_2 f_2 + f_1)$$

The monomer reactivity ratio r_1 in equation (k) corresponds to the ratio of the vapor pressures (P_1°/P_2°) of the pure components of the ideal mixture, and F_1 and f_1 to the mole fractions of component 1 in the vapor and liquid at equilibrium. When $r_1 > 1$ the polymer ("vapor") is richer in M_1 than is the monomer feed; thus the residual mole fraction f_1 must diminish as the polymerization (distillation) proceeds. For $r_1 < 1$ the reverse is true.

In an ideal polymerization the sequence of monomer units must be random. The probability of the occurrence of an M_1 unit immediately following an M_1 unit is the same as for an M_1 unit to follow an M_2 unit. The probability of either unit at any place in the chain is always equal to its mole fraction in an ideal copolymer. This applies to the increment of copolymer formed over a narrow range of conversion and not to the total product. The total product consists of increments of polymer formed at progressively changing monomer ratios.

If the two radicals show different selectivities in their selection of monomers then $r_1 \cdot r_2 = 1$. If $r_1 \cdot r_2 > 1$, the tendency for radicals of a given kind to regenerate themselves is greater than their tendency for alternation. Such a copolymer would contain groups of like units

in greater abundance than in a random copolymer and this tendency increases as the product of $r_1 \cdot r_2$ increases. In the as yet unknown case where both k_{12} and k_{21} are zero, the two monomers might polymerize simultaneously yielding a mixture of two polymers rather than a copolymer containing both units. There appears to be no known example of a free radical propagated copolymerization for which $r_1 \cdot r_2 > 1$. The product $r_1 \cdot r_2$ is almost always less than unity.

Actually cross monomer additions predominate over additions of a like monomer. In the specific case for the copolymerization of itaconic anhydride and styrene in benzene the $r_1 \cdot r_2$ product is 0.011 and for the same copolymerization in tetrahydrofuran the $r_1 \cdot r_2$ product is 0.058.

The small values for r_1 and r_2 correspond to very small rate constants for reactions (a) and (c) on page 33. This condition leads to a copolymer in which the monomer units alternate with near perfect regularity along the chain, and the itaconic anhydride-styrene copolymers are believed therefore to have highly alternating structures.

In figures 2 and 5 the curve crosses the broken line which represents $F_2 = f_2$. At the point of intersection the composition of polymer being formed coincides with that of the monomer mixture and polymerization proceeds without change in composition. Wall (33) designates these critical mixtures as "copolymerization azeotropes." Letting $F_2 = f_2$ in equation (3) we obtain for the critical concentration

$$(f_2)_c = (1 - r_1)/(2 - r_2 - r_1)$$

In benzene $(f_2)_c = 0.81$ calculated

$(f_2)_c = 0.77$ from graph.

In tetrahydrofuran $(f_2)_c = 0.76$ calculated

$(f_2)_c = 0.73$ from graph.

The value of $(f_2)_c$ lies within the permissible range only if both r_1 and r_2 are greater than unity or less than unity.

If one of the reactivity ratios is greater than unity while the other is less than unity, no critical composition exists.

As the polymerization continues, the compositions f_2 and F_2 depart increasingly from that of the azeotrope. The final increment of polymer formed when polymerization is complete would consist entirely of the pure polymer of M_1 or M_2.

If the monomer reactivity ratios are much less than unity the mixture is strongly azeotropic. The copolymer composition approximates that of the azeotrope over a wide range in f_2, and the two units tend to alternate regularly along the chain. The itaconic anhydride-styrene copolymer exhibits a strong tendency towards alternation.

In the determination of the parameters r_1 and r_2, all the procedures depend on careful analysis of the copolymers formed from a series of monomer mixtures at varying concentrations. Since the concentration changes with conversion it is necessary to limit the copolymerization to a conversion to polymer that represents a very small fraction of the monomer mixture. If the monomer mixture is not carried to a low per cent polymerization then the average composition of the copolymer produced over a finite range of conversion must be

calculated. This can be done by the method of Skeist (34). Let $[M] = [M_1] + [M_2]$. The number of moles of M_1 polymerized out of a total of $-d[M]$ moles of monomers converted to polymer is $-F_1 d[M]$. Meanwhile f_1 changes by df_1 and the number of moles of unreacted M_1 changes from $f_1[M]$ to $(f_1 + df_1)([M] + d[M])$. The decrease in moles of M_1 must equal the moles appearing in the newly formed polymer

$$f_1[M] - (f_1 + df_1)([M] + d[M]) = -F_1 d[M]$$

$$d[M]/[M] = df_1/(F_1 - f_1)$$

This may be converted to the integral form from the initial feed composition $(f_1)_0$ to some value f_1

$$([M]/[M]_0) = \int_{(f_1)_0}^{f_1} df_1/(F_1 - f_1)$$

For the values of r_1 and r_2, F_1 may be calculated as a function of f_1 through the use of equation (3). The integration may then be performed graphically to give the degree of conversion. Through a repetition of this process for chosen values of f_1, it is possible to construct the relationship between f_1 and the degree of conversion. The calculations required by this method are indeed laborious and for this reason the experiments were designed to eliminate these calculations. All polymerizations used for the evaluation of reactivity ratios were carried out to a low per cent conversion.

The method selected for this investigation to evaluate r_1 and r_2 is the most widely used (37) and consists in substituting the copolymer and monomer compositions for a single copolymerization in equation (2),

and plotting r_1 versus r_2. This was done for each of several copolymerizations. If there were no experimental error, all of the lines would intersect at the same point, the coordinates of which are the proper values of r_1 and r_2. However, an average point of intersection had to be determined which represented the best experimental pair of r_1 and r_2 values. Theoretical composition curves (Figs. 2 and 5) calculated from r_1 and r_2 values determined in this way are seen to agree very well with the experimentally observed copolymer composition throughout the range of monomer composition. It appears therefore, that one is justified in concluding that the theoretical treatment is correct and that the same rate constant ratios apply at all compositions.

For the copolymerization of itaconic anhydride and styrene in benzene, r_1 (styrene = M_1) is 0.015. This means that the styrene radical is about sixty-seven times more reactive towards the itaconic anhydride monomer than it is towards the styrene monomer. In the same system, r_2 (itaconic anhydride = M_2) has been shown to be 0.780. This means that the itaconic anhydride radical is one and three-tenths times more reactive towards the styrene monomer than towards the itaconic anhydride monomer.

For the copolymerization of itaconic anhydride and styrene in tetrahydrofuran r_1 is 0.1 indicating that the styrene radical is ten times more reactive towards the itaconic anhydride monomer than towards the styrene monomer. In this solvent, r_2 is 0.6 showing that the itaconic anhydride radical is about one and seven-tenths times more reactive towards the styrene monomer than it is towards the itaconic anhydride monomer.

In both cases r_1 and $1/r_2$ are less than unity and greater than unity respectively. This indicates that both radicals prefer different monomers, and lends further evidence to the belief that the itaconic anhydride-styrene copolymer has a highly alternating structure.

The temperature effect on the monomer reactivity ratio is fairly small. In the limited number of cases examined with accuracy (36) the ratio nearly always changes towards unity as the temperature increases. This indicates that a difference in activation energy is responsible, at least in part, for the difference in rate of the competing reactions.

The reactivity ratios r_1 and r_2 are fundamental constants for the free radical polymerization of the two monomers and are expected to be independent of the polymerizing conditions. The fundamental nature of r_1 and r_2 values to describe the free radical copolymerization of two monomers is obvious from the theoretical considerations.

However the constancy of the r_1-r_2 values for a specific copolymerization in a variety of solvents with a variety of free radical catalysts and temperatures has not been systematically studied.

Variations in the r_1-r_2 values might be expected for variations in the type of copolymerization, that is, free radical, cationic, or anionic. Variations would also be expected when comparing polymerizations having different reaction sites.

Copolymerization where polymerization occurs in solution might differ from a copolymerization where polymerization occurs on the surface of the polymer or solid catalyst which might in turn differ from copolymerization where polymerization occurs at a liquid-liquid interface.

This must be expected because of the individual and separate solubilities of any two monomers in solvents (precipitated polymer included) and the individual and separate adsorption of the two monomers by the polymer or catalytic surface.

A different ratio of monomers at a reaction site than the ratio added to the reaction will result in copolymers which when used to evaluate an r_1-r_2 pair experimentally will give an apparent value only.

A strict comparison of the reactivity ratios for the copolymerization of itaconic anhydride with styrene in the two solvents used in this investigation is not, therefore, entirely justified. As previously mentioned, the growing copolymer precipitates as it is being formed in benzene but remains in solution in tetrahydrofuran. Polymer thus precipitated may act as an auxilliary site of reaction. The values of r_1 and r_2 determined in tetrahydrofuran should be closer to the fundamental values than those determined in benzene.

In view of the above mentioned physical difference between the copolymerization in tetrahydrofuran and the copolymerization in benzene it is indeed striking that the values of r_1 and r_2 obtained in the course of this investigation are so close. The values of r_1 in benzene and tetrahydrofuran differ by a factor of only seven, while the values of r_2 in the two solvents are almost identical.

It seems even more significant that the reactivity ratios agree as well as they do in the two different polymerizing media, when one notices the considerable variations observed in the two solvent systems with regard to molecular weights and reaction rates.

The weight average molecular weights, $\overline{Mw}$, were determined by Kangas (35) making use of light scattering phenomena from dilute solutions of the polymers. The light scattering measurements on the itaconic anhydride-styrene copolymer were made in acetone. The following values were obtained:

Solvent	Catalyst	$\overline{Mw}$
Benzene	Benzoyl Peroxide	156,000
Tetrahydrofuran	Benzoyl Peroxide	50,000

A primary factor affecting the molecular weight of a polymer as it is being formed during reaction is chain transfer. The amount of chain transfer depends on the nature of the particular solvent and has been shown to affect the degree of polymerization (49). The more chain transfer the lower the molecular weight of the polymer formed.

Chain transfer is at a minimum in benzene as compared to a large variety of solvents. Although no work has been reported on chain transfer in tetrahydrofuran it would be predicted that transfer reactions would be considerably greater in this solvent than in benzene, a phenomenon that could easily account for the difference in the observed molecular weights.

The copolymerization of itaconic anhydride and styrene has been shown (35) to be about twenty times faster in benzene than in tetrahydrofuran. The values are given in Table V.

In order to explain the difference in the rates of polymerization as observed in the two solvents, the following arguments are presented.

An increase in the over-all rate of polymerization may be affected by:

TABLE V

FIRST ORDER REACTION RATE CONSTANTS

Copolymerization System			
Solvent	Catalyst	k ($Sec.^{-1}$) from Styrene Concentration	from I. A. Concentration
Benzene	Benzoyl Peroxide	1.6×10^{-4}	2.0×10^{-4}
Tetrahydrofuran	Benzoyl Peroxide	9.6×10^{-6}	8.3×10^{-6}

a) An increase in active centers.

b) An increase in propagation steps.

c) A decrease in termination reactions.

The increase in the rate of polymerization in benzene may be attributed to an increase in active centers, due to an induced decomposition of the benzoyl peroxide catalyst. The benzoyl peroxide catalyst has been shown to undergo an induced decomposition in certain solvents (38-40).

A second possible explanation for an increase in active centers and hence an increased rate for the polymerization in benzene solvent may be due to the action of the dead or precipitated polymer acting as a co-catalyst with benzoyl peroxide. This co-catalytic effect has been proposed by Bengough and Norrish (46) to explain certain of their observations in studies on the polymerization of vinyl chloride.

In the presence of a solvent for the polymer, such as tetrahydrofuran, the polymerization proceeds at a somewhat constant rate which decreases in the late stages of the reaction. Dead polyvinylchloride has been shown to act as a co-catalyst with benzoyl peroxide in the polymerization of vinyl chloride. In the absence of benzoyl peroxide the dead polymer does not catalyze the polymerization. It is suggested that the co-catalytic effect of the dead polymer is caused by an increase in the number of centers of polymer growth in the reacting system. These new centers arise from chain transfer reactions between growing polymer chains and molecules of dead polymer resulting in the accumulation of stabilized centers of polymer growth on the surface of

the solid polymer. The revivified polymer grows by addition of monomer until it is finally terminated by chain transfer with monomer, with the production of a mobile free radical.

Only in the case of the polymerization in benzene does the co-polymer of itaconic anhydride and styrene precipitate and therefore only in this case can a co-catalytic effect be expected.

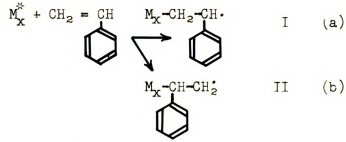
A decrease in the rate of termination will also account for an increase in the over-all rate of polymerization since any given radical will propagate longer and for a given concentration of active nuclei more monomer will be converted to polymer in a given time.

A related dependence of the rate of termination, k_t, on the medium has been observed by Norrish and Smith (41) working with methyl methacrylate, and by Burnett and Melville (42) with vinyl acetate. Rates in poor solvents are high due to a decrease in k_t. This decrease in k_t accounts for the increased rate in polymerization. Actually precipitation of the polymers appears to be responsible for the effect since the growing radicals become imbedded in precipitated droplets, presumably of very small size. This effect causes the suppression of the termination reaction owing to the isolation of the chain radical in one droplet from that in another. This is common in systems yielding polymer which is not soluble in the reaction mixture (43). It is closely related to the fast rates observed in emulsion polymerizations, which are explained on the basis of a decrease in k_t caused by reaction environment.

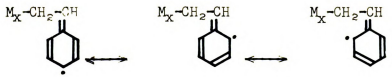
Precipitation of the itaconic anhydride-styrene copolymer from benzene as it was being formed would result in conditions leading to a decrease in k_t and consequently a higher over-all rate. This is not the case for the copolymerization of itaconic anhydride and styrene in tetrahydrofuran from which the copolymer does not precipitate as it is being formed.

A consideration of the structural unit of the styrene-itaconic anhydride polymer molecule is essential at this point.

If the growing polymer radical, M_x^*, were to attack a styrene monomer two product radicals might be formed. They are:



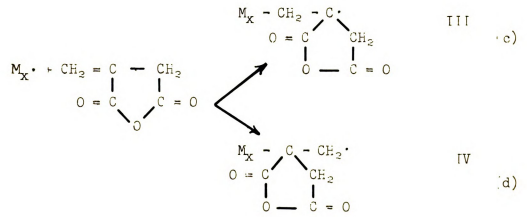
Process (a) should be more favorable since the product radical would have more opportunity for resonance due to the adjacent phenyl ring. Three quinoid resonance structures may be written for the substituted benzyl radical obtained during the course of polymerization:



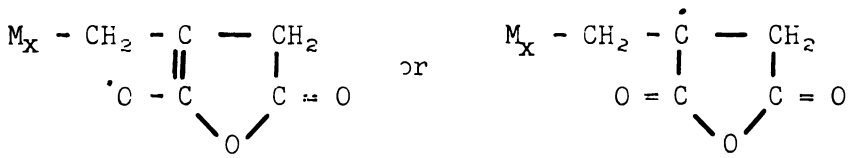
The relative rates of these processes should depend on the stability of the product radicals I and II. In II, the phenyl ring is situated on the beta carbon atom and thus is unavailable for participation

in resonating structures involving the odd electron. Thus I is more probable than II. A comparison of bond strengths in methane and toluene (44) indicates that a benzyl radical as in I is favored by resonance stabilization in the amount of 20 to 25 kcal. per mole. The product radical II is a β-phenylethyl radical analog which should have approximately the same stability as an ethyl or methyl radical. Thus process (a) should be favored over (b) by an energy difference of about 20 to 25 kcal. per mole. Resonance stabilization in the transition state for the monomer addition step will be less than the energy of the product radical, but the activation energy for (a) should be less than that for (b) by about 8 to 10 kcal. per mole which should be enough to cause I to form to the almost complete exclusion of II.

If the growing polymer radical attacks the itaconic anhydride monomer two possible structures would result:



The product radical III could have the following resonance structures:

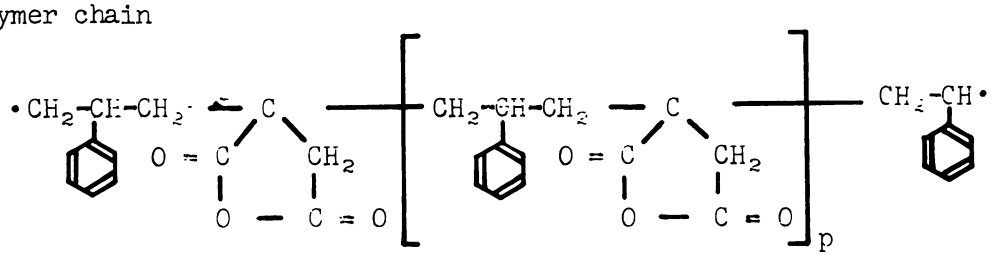


In monomers having the C = O group conjugated with the carbon-carbon double bonds, the above resonance structures describe states of higher energy than those for the radical styrene. thus their resonance energy is smaller. From resonance considerations III would be more stable, and although the resonance stabilizations are less than phenyl they are by no means negligible.

The stabilization of the monomer by substituents must also be considered. The additional resonance structures which are introduced by the presence of the substituent contain fewer bonds than are present in the structure normally written for the monomer; thus these represent higher energy states. Resonance stabilization by the substituent is therefore much less in the monomer than in the corresponding radical. In styrene, the resonance stabilization due to conjugation amounts to about 3 kcal. per mole. The effect of a conjugating substituent in the monomer may be summed up by observing that its influence is much greater in the product radical than in the monomer. In the activated complex which is in an intermediate state between reactants and product, resonance stabilization is appreciably greater than in the monomer reactant, but less than in the product radical. The substituent therefore lowers the activation energy of the reaction and increases the reactivity of the monomer. The conclusion to be drawn is that the more reactive monomers give the least reactive radicals, and the least reactive monomers the most reactive radicals.

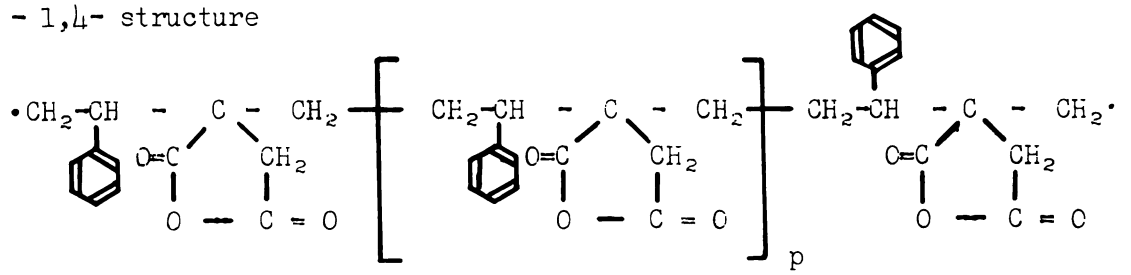
Thus from the previous discussion of reactivity ratios it can be seen that the propagation constant for the more reactive styrene with a styrene radical turns out to be less than that for the less reactive itaconic anhydride monomer with the more reactive itaconic anhydride radical, since this lacks appreciable resonance stabilization.

Successive and alternate addition of monomer molecules in accordance with the preferred processes (a) and (c) will produce the following polymer chain

(A) 

This structure has the units oriented in the same direction and is designated as the head-to-tail or 1,3-structure. In each monomer the $-CH_2-$ is designated as the head.

At the other extreme there is the head-to-head, tail-to-tail, or 1,2 - 1,4- structure

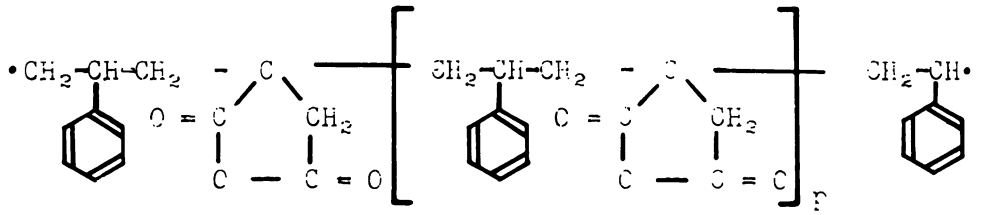
(B) 

The head-to-head structure is impossible based on resonance considerations. Another factor which may favor the head-to-tail arrangement is the steric hindrance offered by the phenyl radical as it

approaches the anhydride ring. A model compound was constructed and this was indeed evident, since it was impossible to construct a unit with a head-to-head arrangement.

A few of the possible configurations which the polymer chain may have when the units are arranged in a head-to-tail construction have been illustrated (page 29). From the previous consideration the structures of the monomers are such as to greatly favor head-to-tail arrangement to the almost complete exclusion of any head-to-head, (tail-to-tail) configuration. Similar lines of reasoning have been and can be applied to many vinyl type homo and hetero copolymerizations. This reasoning has been confirmed in abundant instances by various workers (47,48,49). Detailed analysis of many polymers and some copolymers has failed to reveal one substantiated case of head-to-head (tail-to-tail) structure. The subject is reviewed in detail by Marvel (45).

Until direct evidence to the contrary is obtained, the formula for the unit of the itaconic anhydride styrene copolymer will be considered a head-to-tail structure as illustrated in A:



PART II

Preparation and Analysis of Itaconic Anhydride--Styrene Copolymers and Their Ester Derivatives

A. Preparation of Itaconic Anhydride-Styrene Copolymers.

B. Titration of Itaconic Anhydride-Styrene Copolymers.

C. Determination of Apparent pK' Values.

D. Preparation of Monoester Derivatives of the Itaconic Anhydride-Styrene Copolymers.

1. By Reaction with Alcohols.
2. By Reaction with Dimethyl Sulfate.

E. Titration of the Monoester Derivatives of the Itaconic Anhydride-Styrene Copolymers.

F. Preparation of Diester Derivatives of the Itaconic Anhydride-Styrene Copolymers.

1. Dimethyl Ester of Poly 61:39 (itaconic anhydride co styrene).
2. Methyl Ethyl Diester of Poly 57:43 (itaconic anhydride co styrene).
3. A Partial Diethyl Ester of Poly 61:39 (itaconic anhydride co styrene).
4. Attempted Preparation of a Diester Using Absolute Alcohol and Gaseous Hydrogen Chloride Catalyst.

G. Titration of the Diester Derivatives of the Itaconic Anhydride-Styrene Copolymers.

H. Preparation and Titration of the Homopolymer-Polyitaconic Anhydride.

1. Preparation of Polyitaconic Anhydride.
2. Titration of Polyitaconic Anhydride.

I. Titration of Mixtures

1. Itaconic Anhydride-Styrene Copolymer and a Monoethyl Ester Derivative.
2. Itaconic Anhydride-Styrene Copolymer and Itaconic Anhydride
3. Monoethyl Ester Derivative and Itaconic Anhydride.

J. Titration of Some Dibasic Acids.

Itaconic Acid
Unsymmetrical Dimethylsuccinic Acid
Methylsuccinic Acid
Salicylic Acid-Benzoic Acid Mixture
Propionic Acid-Acetic Acid Mixture

K. Derivatives of the Itaconic Anhydride-Styrene Copolymer.

1. Preparation of an Optically Active Monoester Derivative of Poly 61:39 (itaconic anhydride co styrene).

2. Preparation of a Network Polymer.

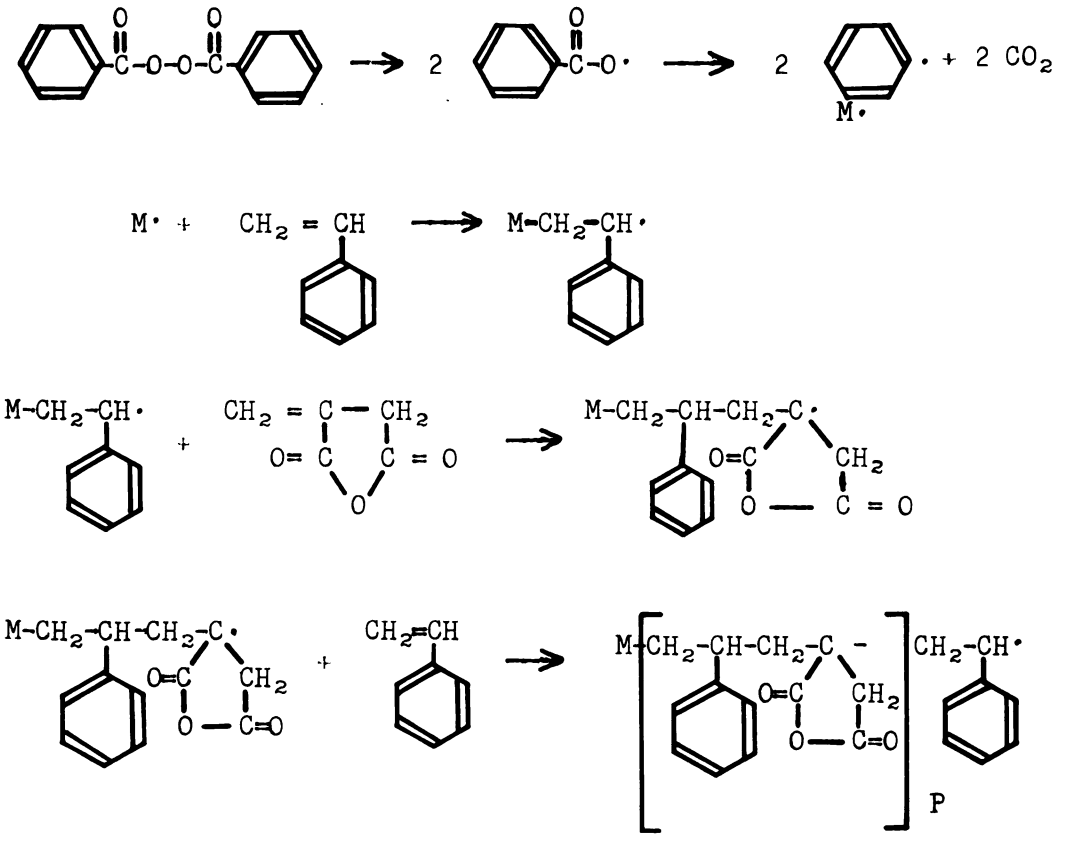
L. Stability to Hydrolysis.

1. Stability to Hydrolysis of the Monoethyl Ester of Poly 61:39 (itaconic anhydride co styrene).

2. Stability to Hydrolysis of the Dimethyl Ester of Poly 61:39 (itaconic anhydride co styrene).

M. Infrared Spectra.

EXPERIMENTAL



A. Preparation of Itaconic Anhydride-Styrene Copolymer.

A. Preparation of Itaconic Anhydride-Styrene Copolymers

The copolymerization was carried out in a one-liter, three-neck, round bottom flask with standard taper ground glass joints. The flask was fitted with a reflux condenser, a nitrogen inlet tube and a mechanical stirrer. The polymerization mixture was protected from moisture by a calcium chloride tube and kept under a nitrogen atmosphere. The flask was charged with 625 ml. of thiophene-free benzene and the desired quantity of itaconic anhydride. To dissolve the itaconic anhydride the mixture was heated, with stirring, at the reflux temperature of benzene (80°C) maintained by use of an oil bath. Approximately thirty minutes were required for the solution of the itaconic anhydride. To the resulting solution was added the styrene and 0.233 g. of benzoyl peroxide dissolved in 75 ml. of benzene. At the end of the reaction, the solid copolymer was removed by filtering with suction, dried, and weighed.

The copolymer was purified by exhaustive extraction with benzene in a Soxhlet extractor for ten days, and then dried under vacuum in a drying pistol at the reflux temperature of acetone. The copolymer was then analyzed for carbon and hydrogen.

The data on the various copolymers prepared are summarized in Table VI.

Itaconic Anhydride in Monomer Mixture g	Styrene in Monomer Mixture g	Copolymer g	Percent Polymerization	Percent Carbon in Copolymer	Weight Percent I.A.* Segments in Copolymer	Mole Percent I.A. Segments in Copolymer	Copolymer Designated as
26.1	24.2	38.5	76.7	67.8	63.3	61.3	Poly 61:39 (itaconic anhydride co styrene)
26.1	24.2	32.4	64.4	69.6	58.3	56.7	Poly 57:43 (itaconic anhydride co styrene)
26.1	24.2	47.3	94.0	69.4	59.1	57.3	Poly 57:43 (itaconic anhydride co styrene)
6.52	18.2	0.78	3.1	70.2	57.1	55.3	Poly 55:45 (itaconic anhydride co styrene)

*I. A. = Itaconic Anhydride

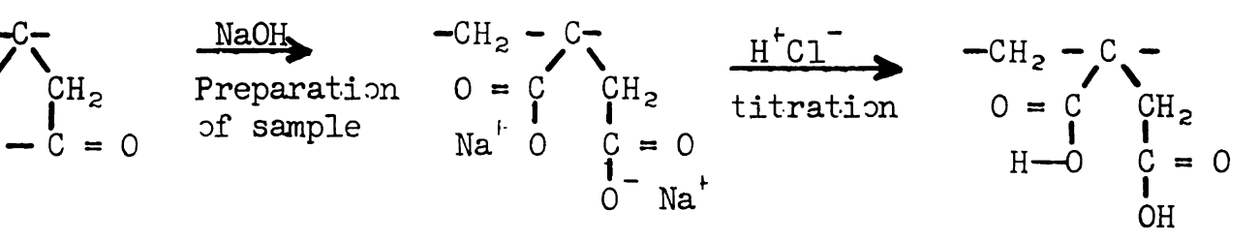
. High Frequency and Potentiometric Titration Procedures for the Itaconic Anhydride-Styrene Copolymers

e titrations were followed with a pH meter and a high frequency ter at the same time.

e hydrogen ion concentration was measured on a line operated pH meter equipped with glass reference and saturated calomel des.

e high frequency titrimeter which was used is one originally d by Johnson and Timnick (50) and later modified by Lai, Mortland, nick (51).

e titrations were performed with the titration apparatus operated megacycles per second. Oscillator tube grid current change was d during the course of the titration. To follow this change a ometer set-up had been designed to follow the potential-drop related to the grid current flow change across a resistor which nected in series with the grid leak resistor. The potential drop this added measuring resistor was compensated with a potentiometer. ent response is expressed throughout this study in terms of ry potentiometer dial units.



accurately weighed sample (approximately 0.2 g.) of the finely
copolymer was dissolved in acetone. To this solution was added
quantity of standard sodium hydroxide and the solution was
on a steam bath to drive off the acetone. There resulted a clear
n of the disodium salt of the copolymer. When the odor of
was gone, the sample was quantitatively transferred to the
ylene cell of the high frequency titrimeter. The sample was
luted with distilled water to a volume of about 180 ml. The
des of the potentiometer were placed in the solution and pro-
was made for mechanical stirring of the solution during the
ion. A glass stirrer was used.

he standard HCl solution was added from a 50 ml. buret in 1 ml.
ents. In the titrations where the HCl titrant was added in 0.5
crements, a 10 ml. buret was used. After each addition of titrant,
two minutes were allowed for the reaction to reach equilibrium.
reading of the potentiometer and the potentiometer dial reading
high frequency titrimeter were simultaneously recorded.

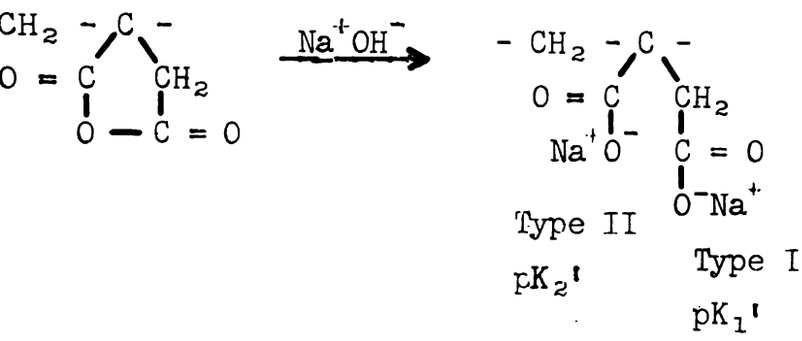
When the copolymer was converted to the free acid form a precipitate
served in the titration cell. Several increments of titrant were
beyond this point to insure the completeness of the titration and
he purpose of plotting the data.

Figures 7 through 14 represent plots of the data obtained in the
tion of the itaconic anhydride-styrene copolymers. Figure 15 is
t of the data for the titration of the maleic anhydride-styrene
ymer. The data are summarized in Table VIII.

igures 9A, 11A, and 15A represent plots of pH versus log $\frac{1 - \alpha}{\alpha}$
o calculate apparent pK' values.

he data used in plotting all the figures in this thesis are
in the Appendix.

n adding sodium hydroxide to the copolymer there result two
ylate ions:



The apparent pK' values are shown in Table VII. The method used
lculate pK' values is shown in C, page 74.

For reference, the carboxylate groups were labeled Type I and
II and considered to have corresponding pK_1' and pK_2' values
ctively. Type I was assigned to that particular carboxylate group,
ased on structural considerations it is believed to be the stronger
Type I carboxylate is attached to a methylene group and is
ier removed from the polymer backbone, whereas Type II is attached
disubstituted carbon atom and is directly attached to the polymer
one. For these reasons Type I carboxylate is probably a stronger
and it is believed to be more easily solvated.

Whenever necessary, the end points determined from the high-
uency titration curves were used to locate accurately the end
ts on the pH titration curves so that apparent pK' values could be

ed. The use of the high frequency end points to locate
ometric end points was especially necessary in locating any
sodium hydroxide, an end point which was completely hidden in
entiometric titration curve.
nce in all cases the calculated pK' values agreed very well with
ead directly from the pH titration curve, only a limited number
values were calculated.

Figure Number	Weight Percent I.A. Segments in Copolymer	Sample Weight g.	pK Values Read Directly from pH Curve pK_1	pK Values Read Directly from pH Curve pK_2	pK Values Calculated pK_1'	pK Values Calculated pK_2'
7	58.3	0.1018	6.3	9.1	---	---
8	58.3	0.2040	5.8	8.9	---	---
9	58.3	0.2004	5.7	8.8	5.6	8.8
10	58.3	0.2005	5.5	7.2	---	---
11	57.1	0.2006	5.8	8.8	5.7	8.8
12	59.1	0.0950	5.9	9.3	---	---
13	63.2	0.0508	7.6	10.7	---	---
14	63.2	0.0490	6.3	9.8	6.3	9.8
15*	48.5	0.2000	4.8	9.9	4.9	9.8

*Maleic Anhydride

Figure Number	Sample Weight g.	Weight Percent I.A.* Segments in Copolymer	NaOH Required Meqs.	NaOH Added Meqs.	Excess NaOH Meqs.		Type I Carboxylate Meqs.		Type II Carboxylate Meqs.		Total Meqs. I.A. Segments from Titration	Total Meqs. I.A. Segments from C-H* Analysis
					Calcd.	Found	Calcd.	Found	Calcd.	Found		
7	0.1018	58.3	1.055	2.638	1.583	1.645	0.530	0.614	0.530	0.446	1.060	1.060
8	0.2040	58.3	2.124	2.638	0.513	0.513	1.062	1.093	1.062	1.031	2.124	2.124
9	0.2004	58.3	2.084	2.084	0	0	1.042	1.019	1.042	1.065	2.084	2.084
10	0.2005	58.3	2.084	1.042	0	0	0.521	0.512	0.521	0.511	1.023	1.042
11	0.2006	57.1	2.046	2.638	0.592	0.617	1.023	1.032	1.023	0.990	2.022	2.046
12	0.0950	59.1	1.003	1.003	0	0	0.501	0.487	0.501	0.565	1.002	1.002
13	0.0508	63.2	0.574	0.574	0	0	0.287	0.287	0.287	0.287	0.574	0.574
14	0.0990	63.2	0.549	0.549	0	0	0.275	0.285	0.275	0.278	0.563	0.550
15†	0.2000	48.5	1.988	1.988	0	0	0.994	0.994	0.994	0.994	1.988	1.988

*I. A. = Itaconic Anhydride; C-H = Carbon-Hydrogen.

†Maleic Anhydride Copolymer.

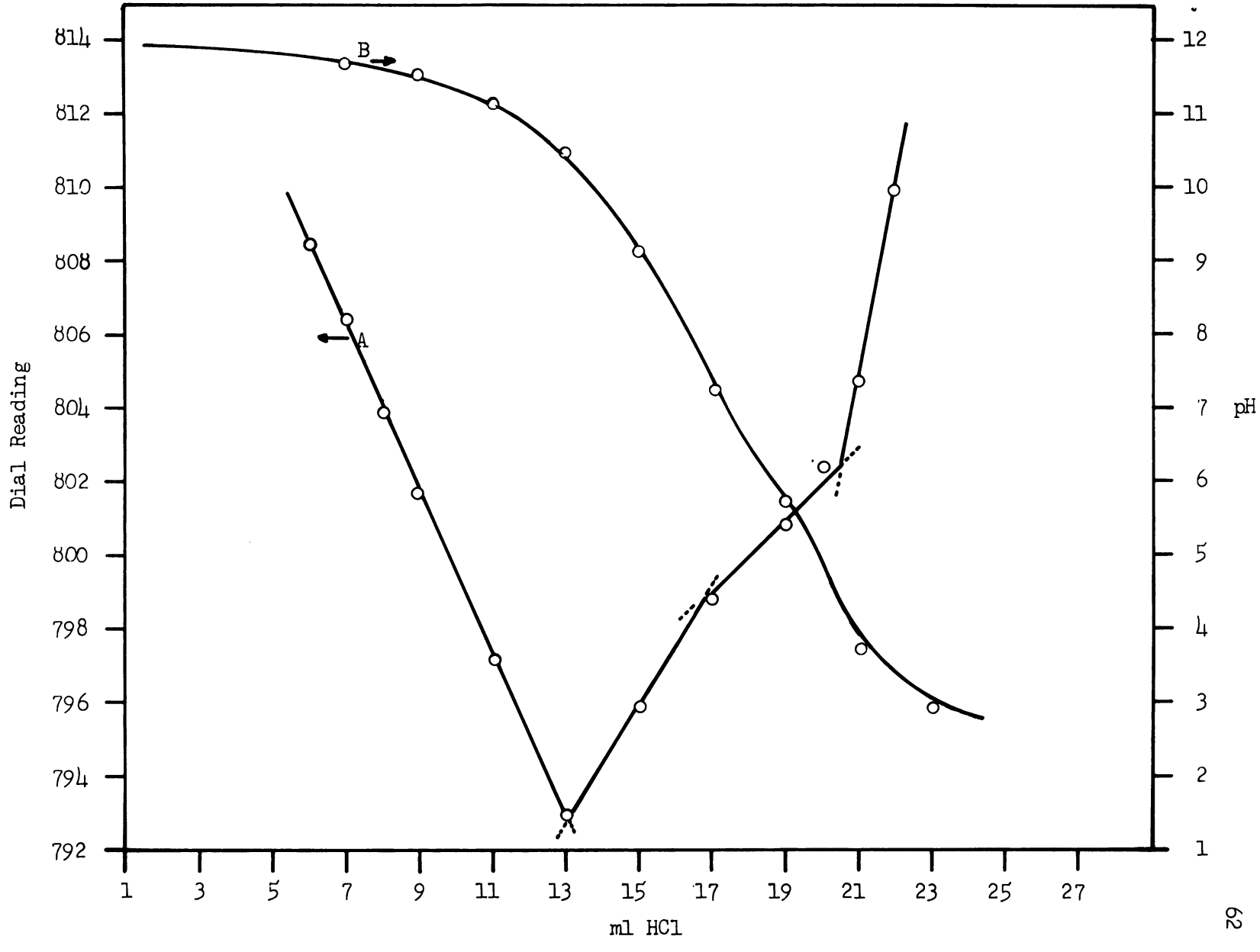


Fig. 7. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

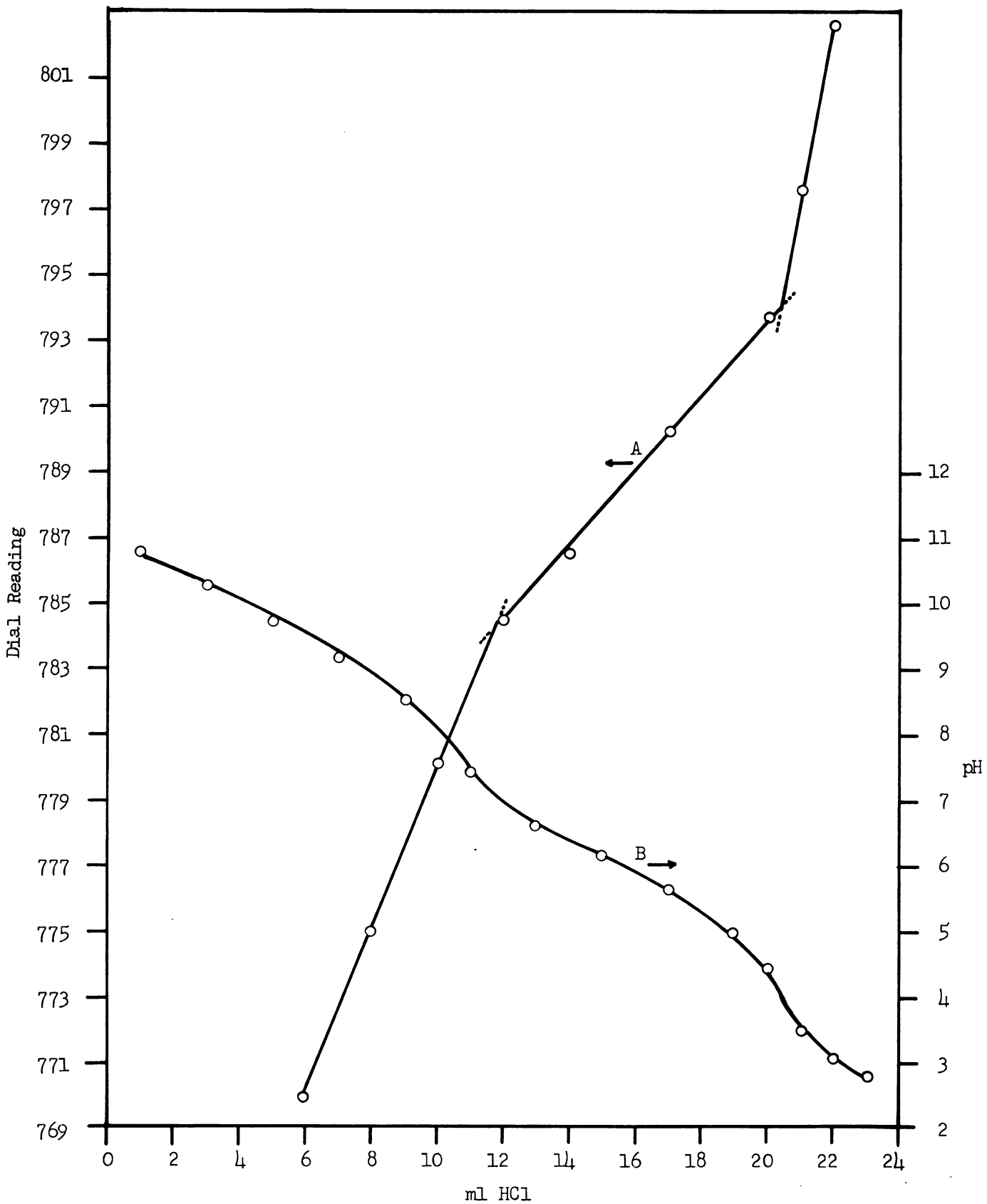


Fig. 8. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

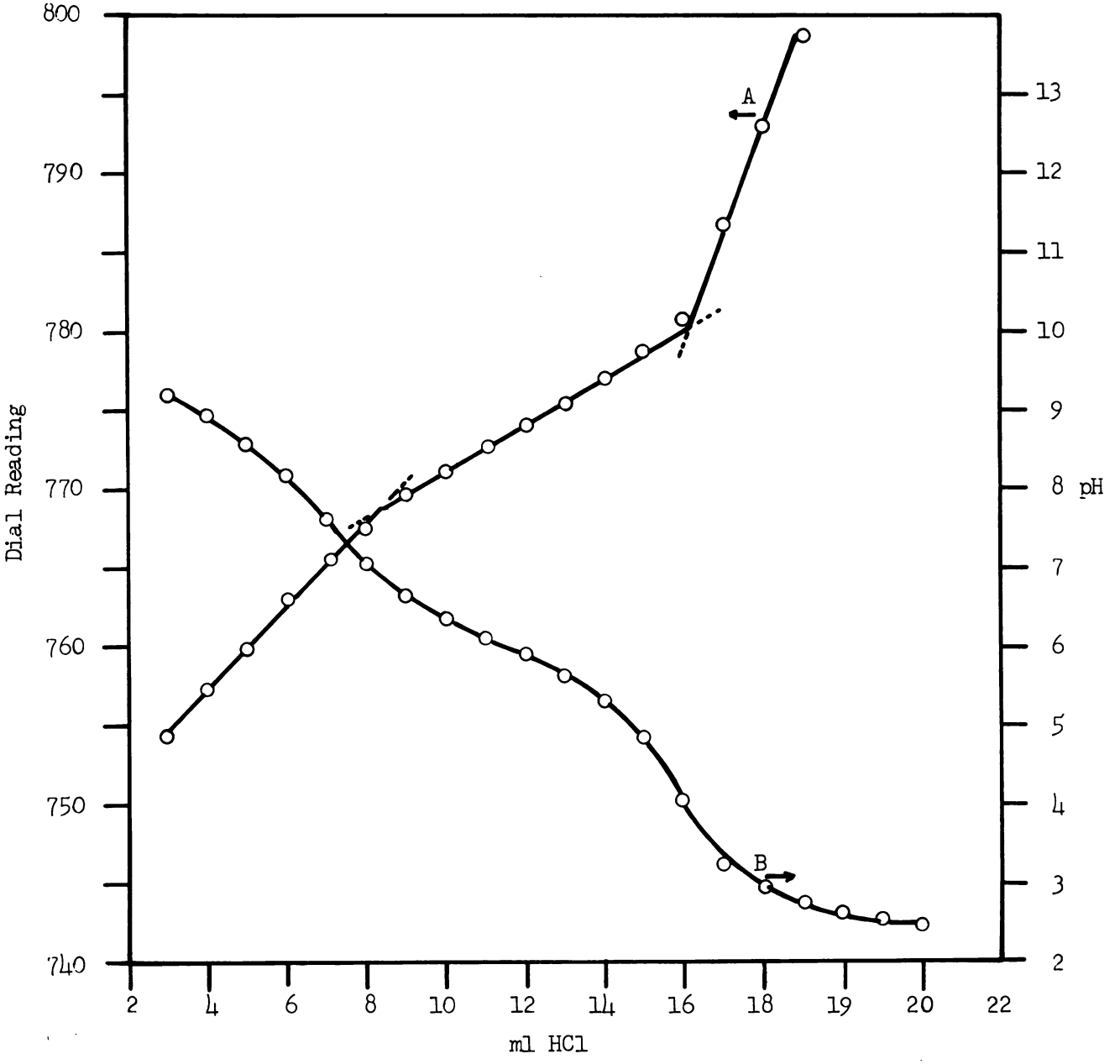


Fig. 9. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

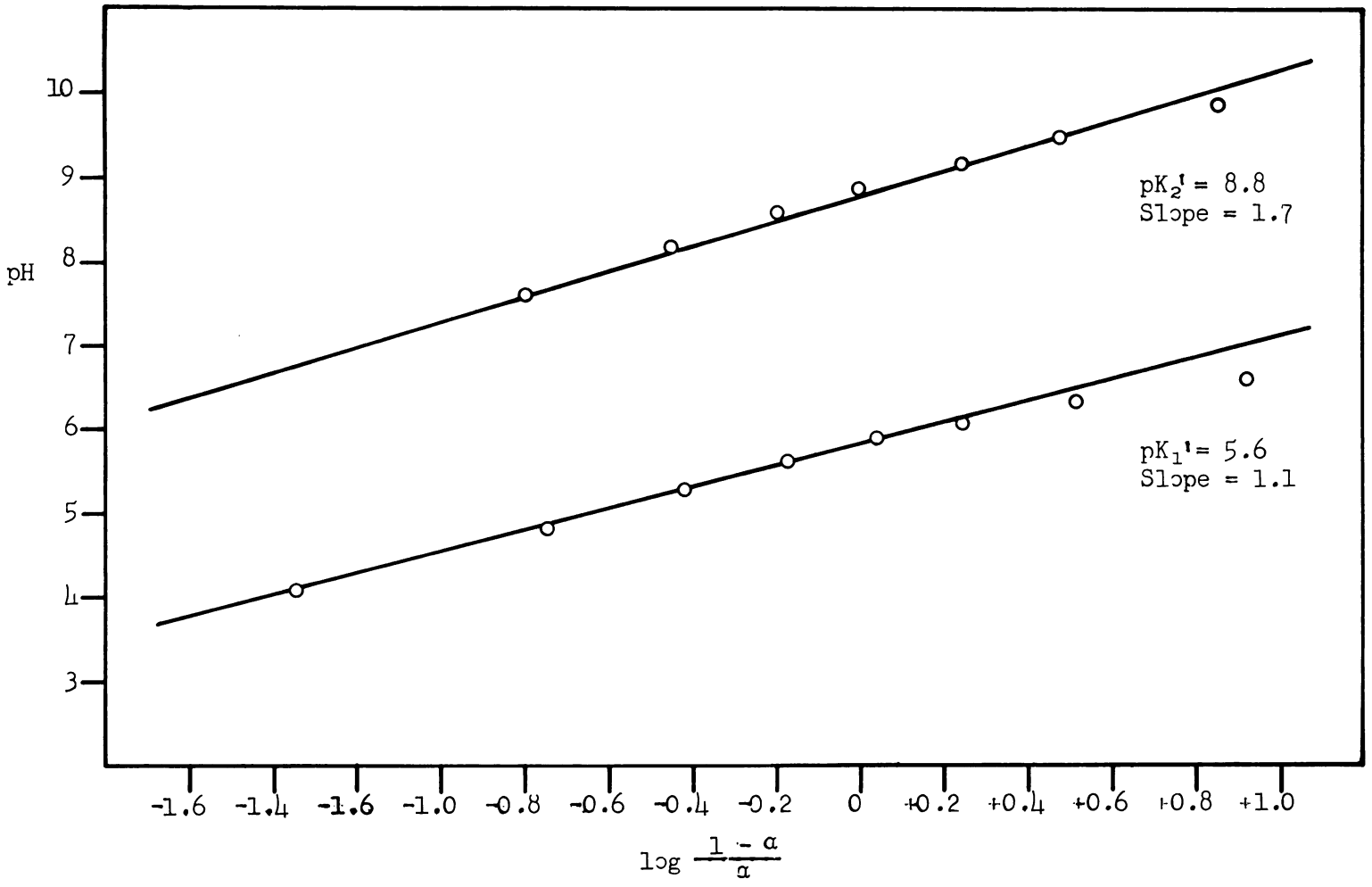


Fig. 9A. Plot of pH vs. $\log \frac{1-\alpha}{\alpha}$ for the titration of Poly. 57:43 (itaconic anhydride co styrene), from the data for the titration in Fig. 9.

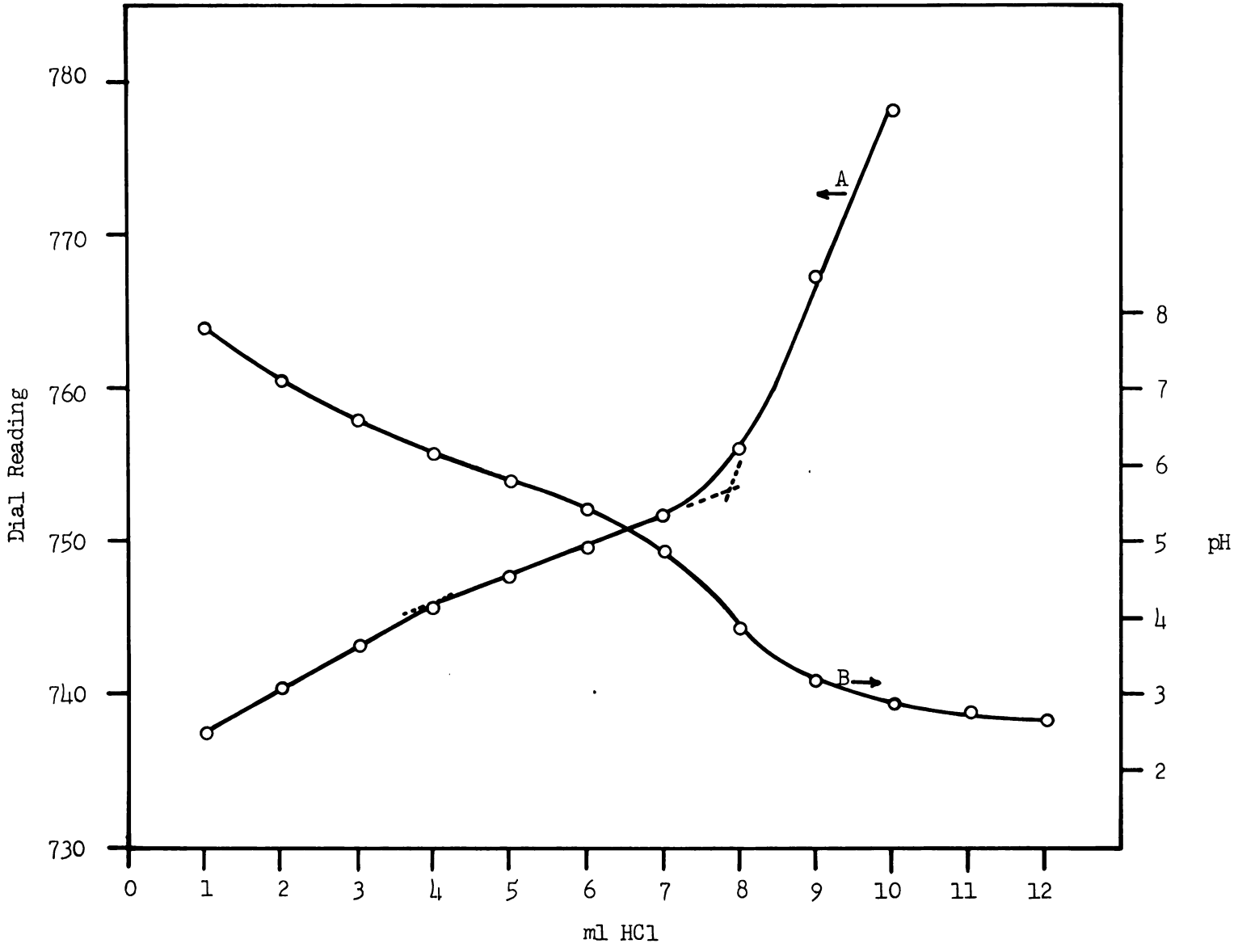


Fig. 10. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

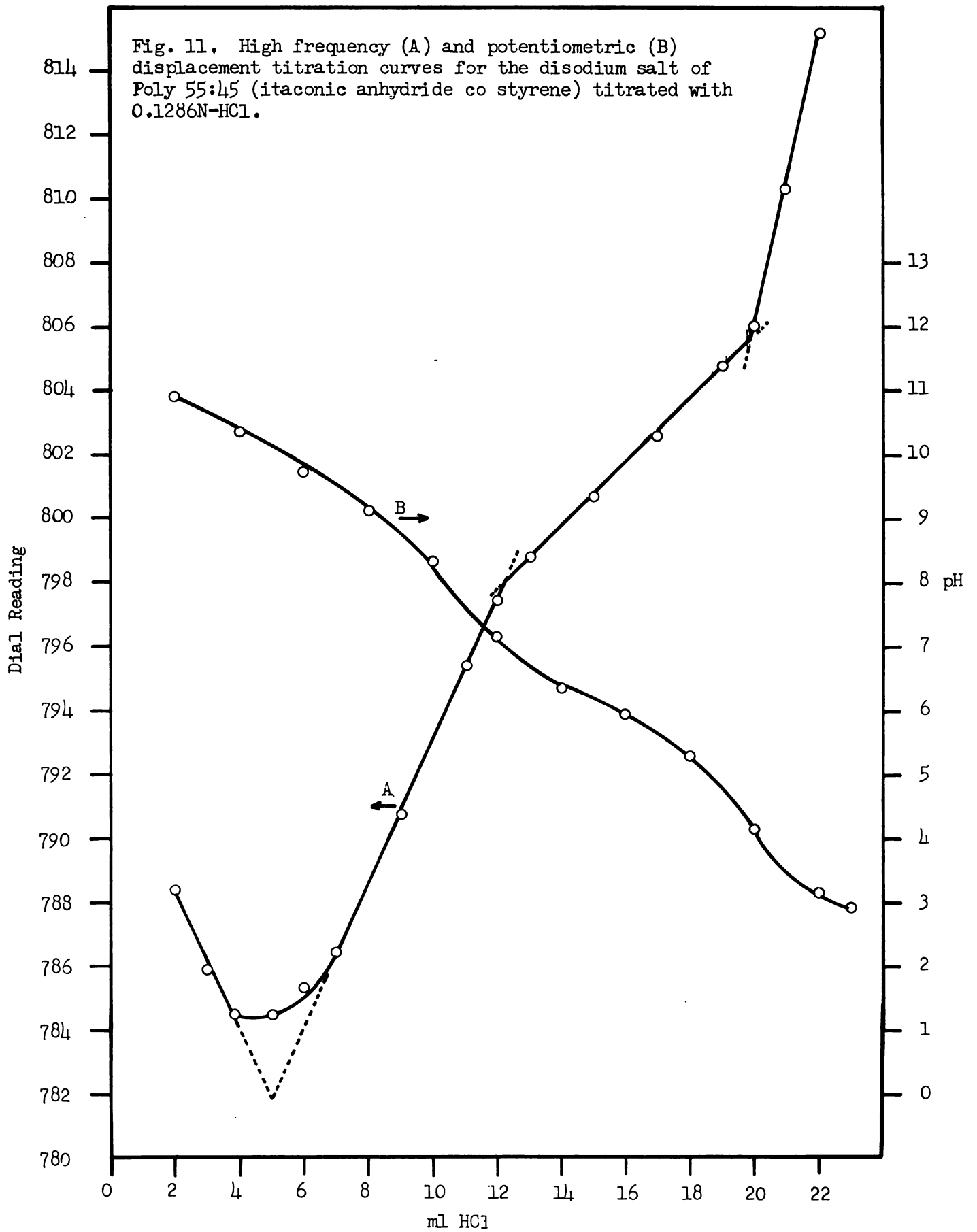


Fig. 11. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of Poly 55:45 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

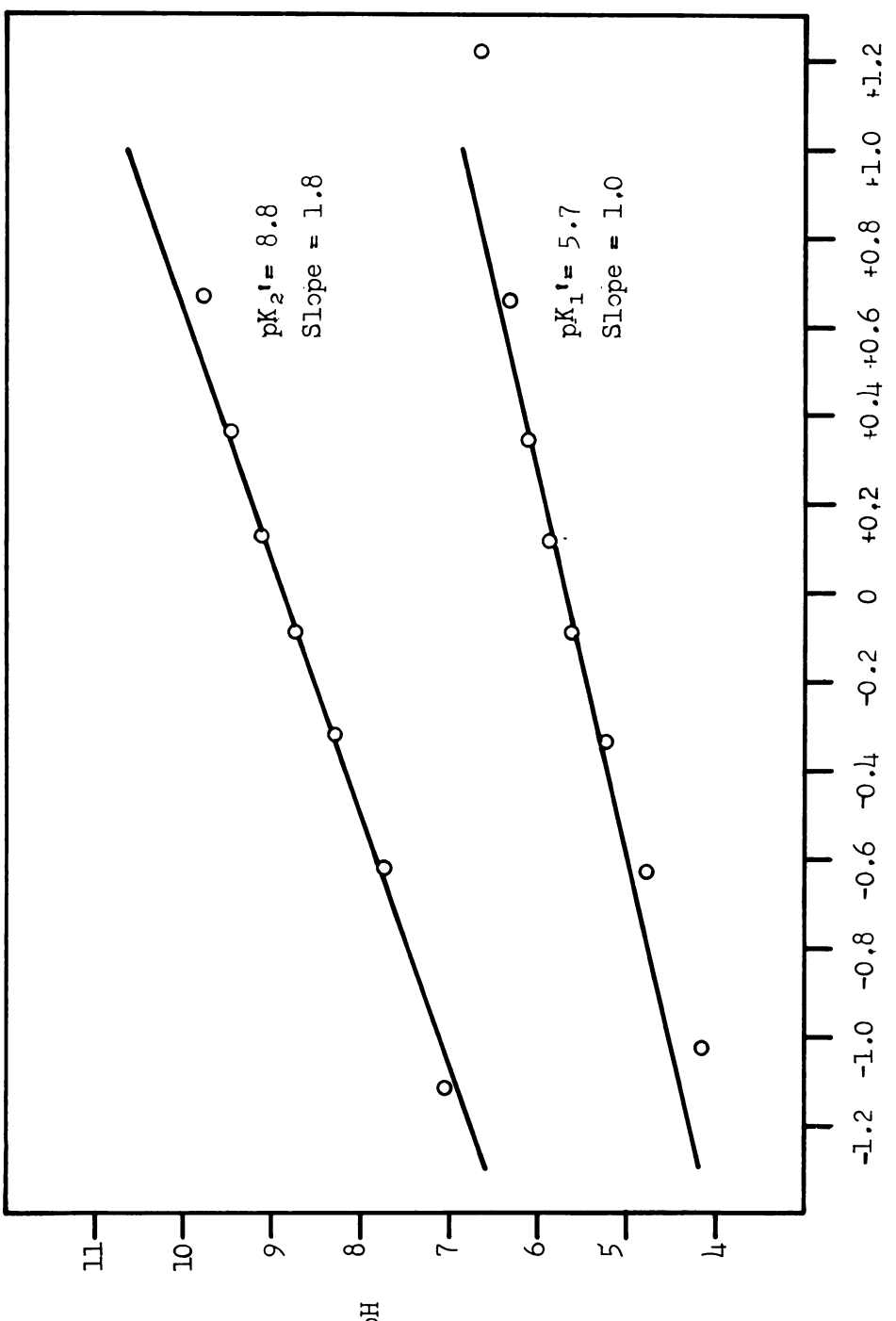


Fig. 11A. Plot of pH vs. $\log \frac{1-\alpha}{\alpha}$ for the titration of Poly 55:45 (itaconic anhydride co styrene), from the data for the titration in Fig. 11.

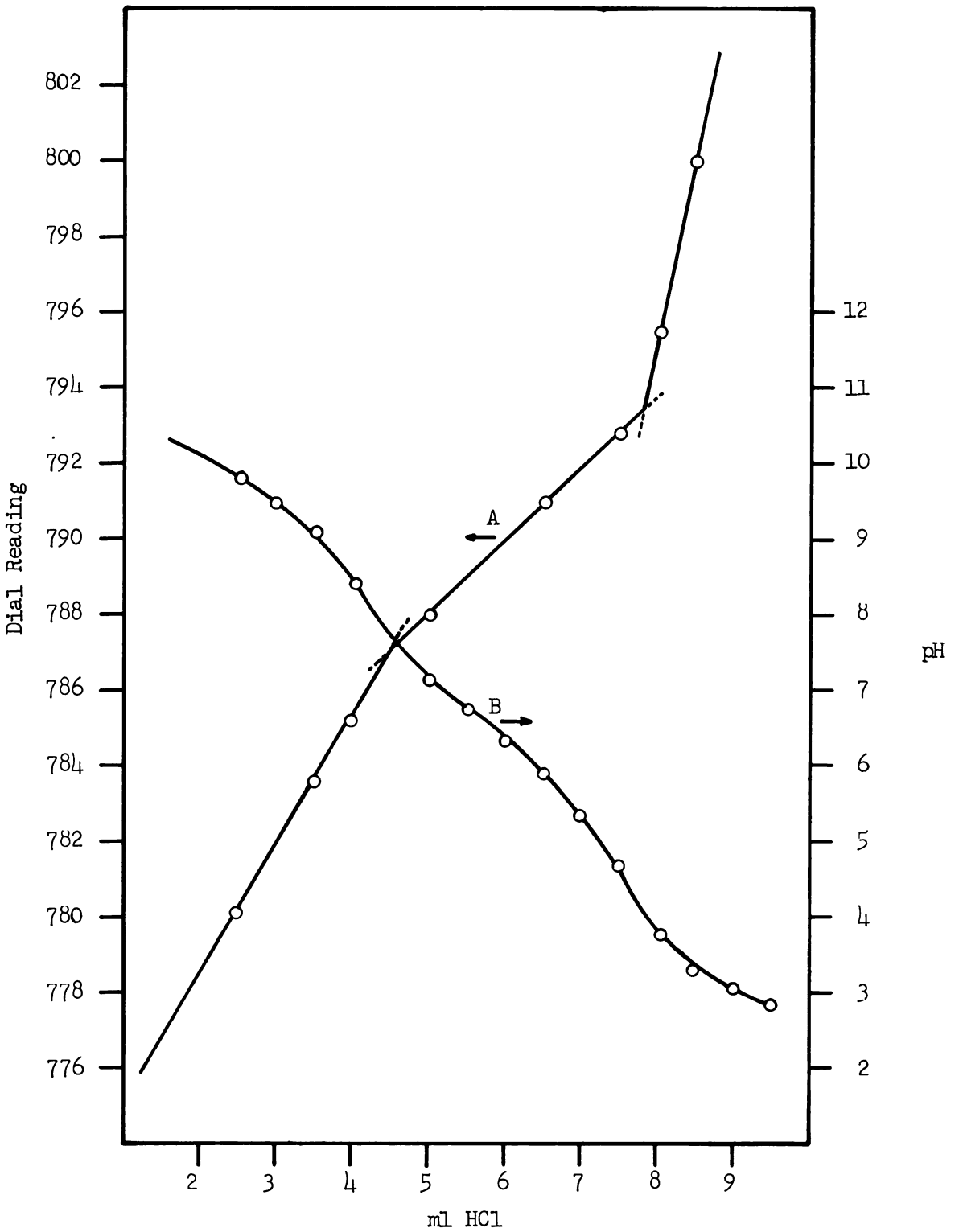


Fig. 12. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

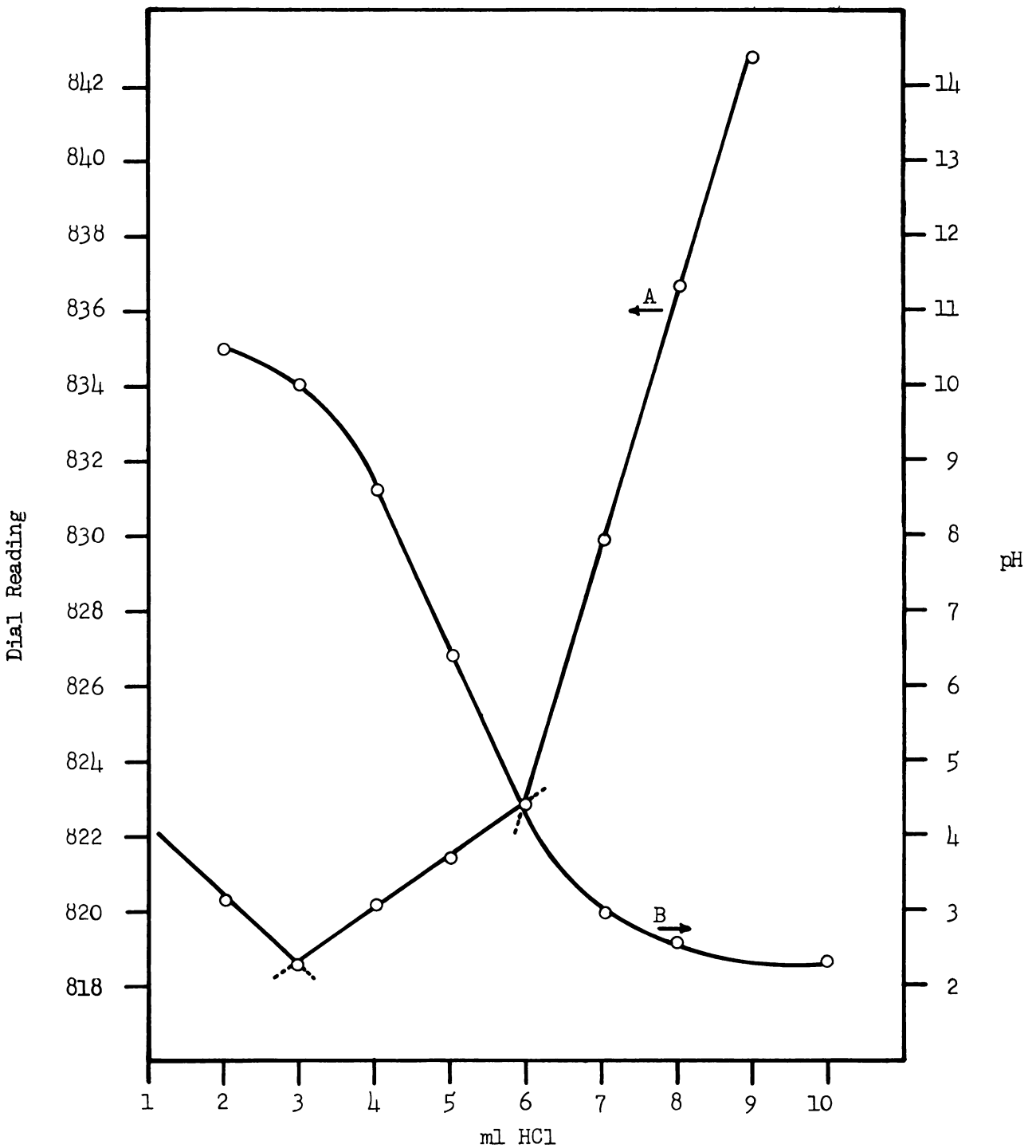


Fig. 13. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of Poly 61:39 (itaconic anhydride co styrene) titrated with 0.09666N-HCl.

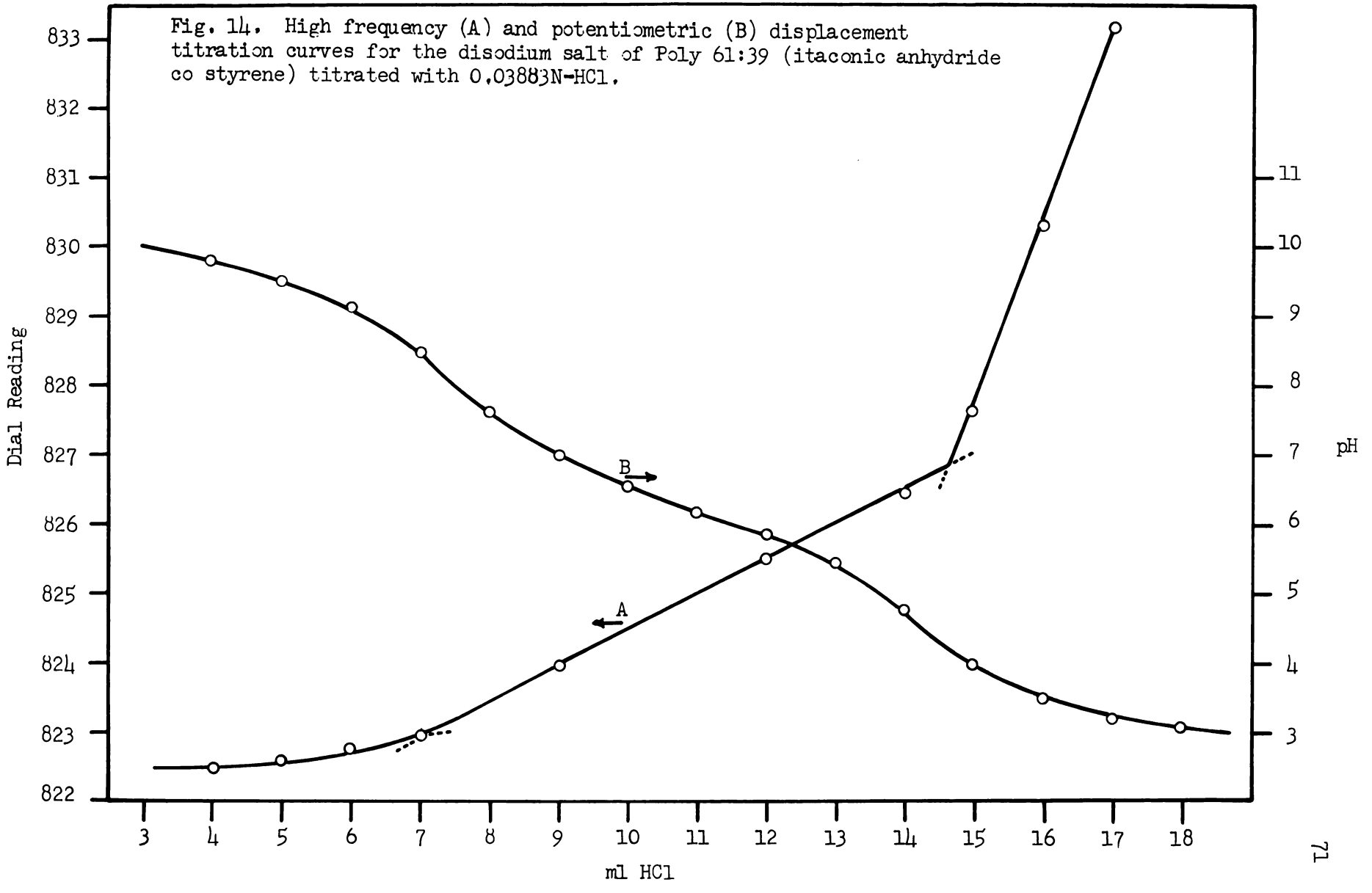


Fig. 14. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of Poly 61:39 (itaconic anhydride co styrene) titrated with 0.03883N-HCl.
Dial Reading
833
832
831
830
829
828
827
826
825
824
823
822
pH
11
10
9
8
7
6
5
4
3
B
A
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
ml HCl
71

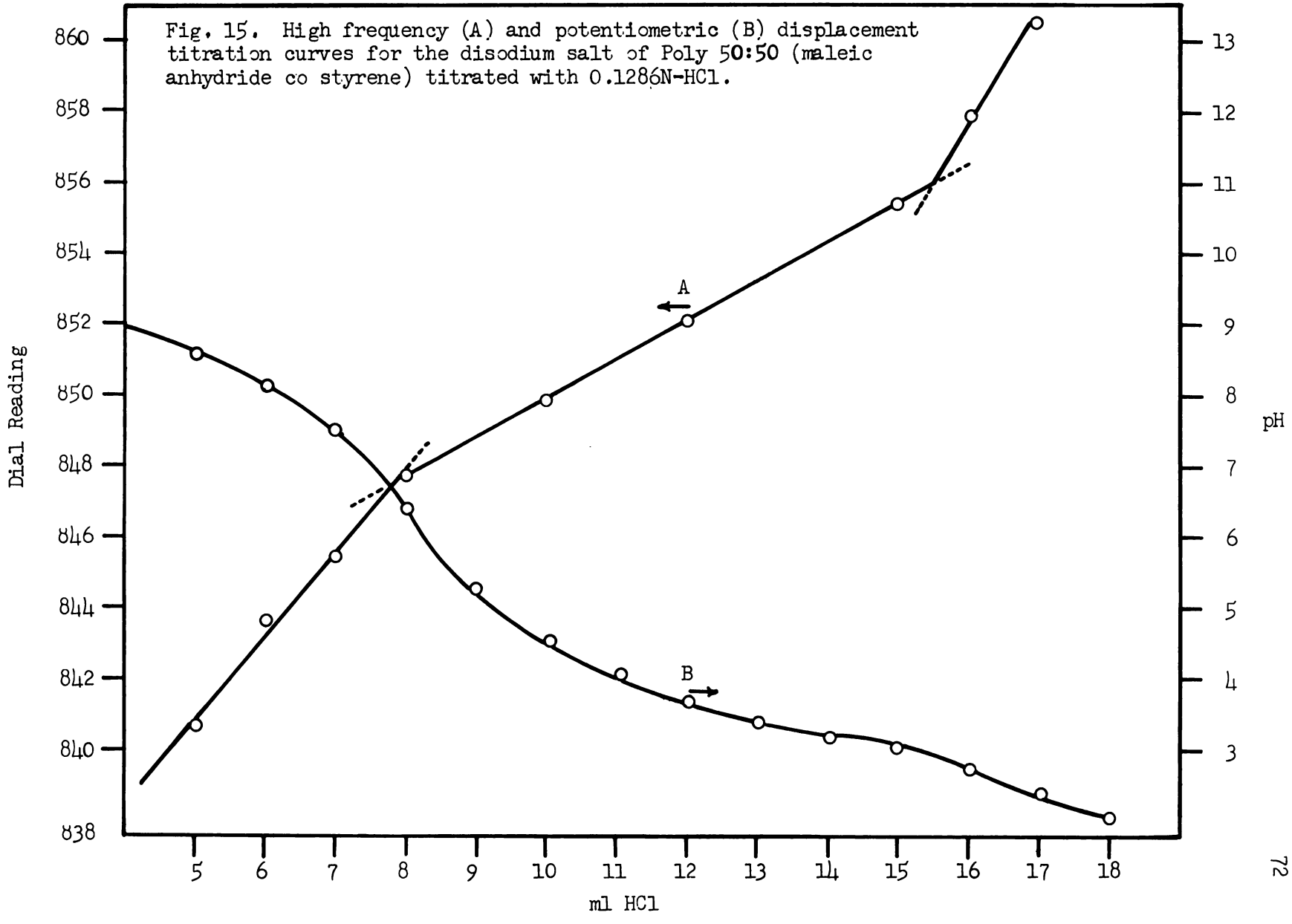


Fig. 15. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of Poly 50:50 (maleic anhydride co styrene) titrated with 0.1286N-HCl.

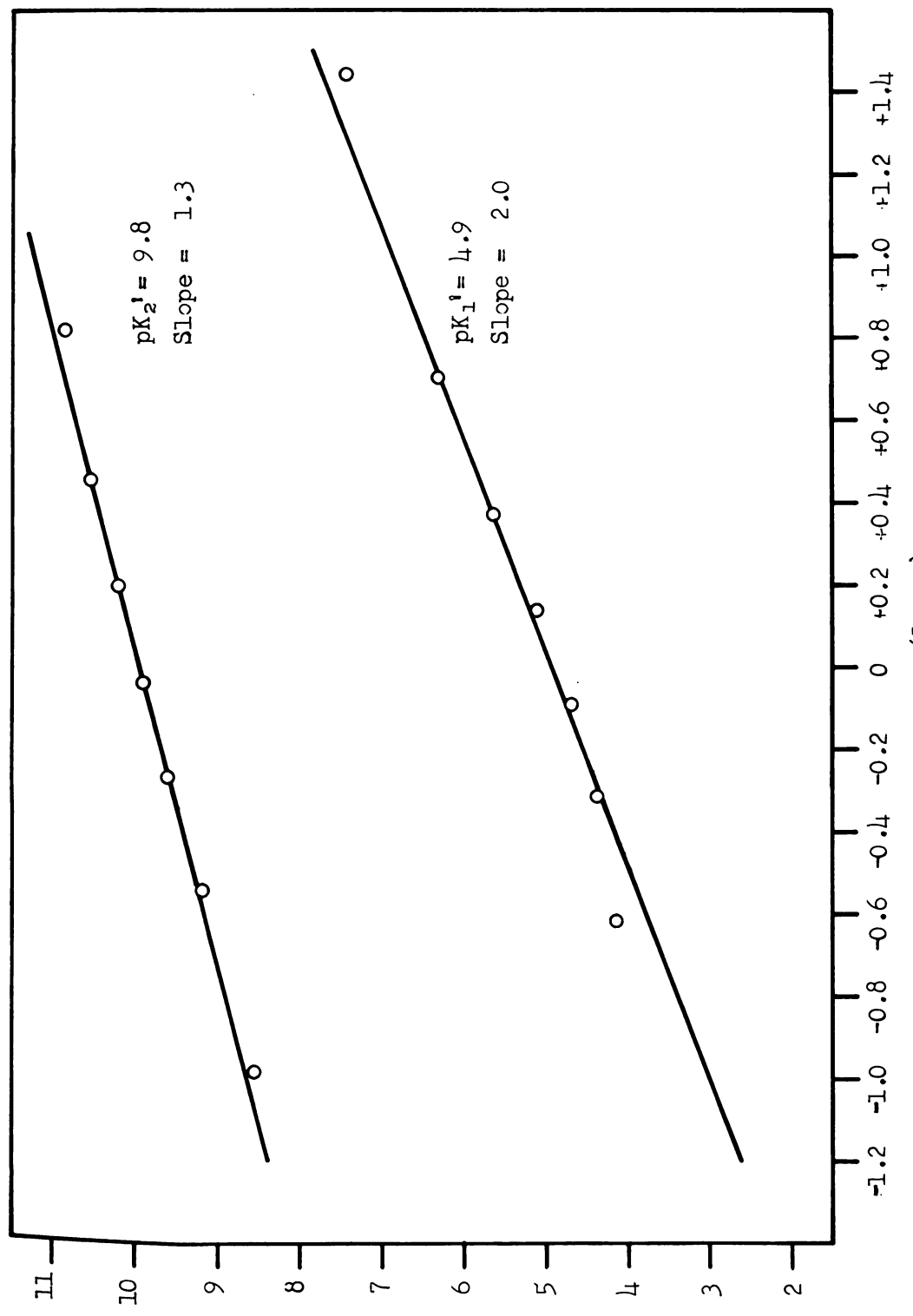


Fig. 15A. Plot of pH vs log $\frac{1-\alpha}{\alpha}$ for the titration of Poly 50:50 (maleic anhydride co styrene), from the data for the titration in Fig. 15.

C. Determination of Apparent pK_1' and pK_2' Values

If we define the primary dissociation constant of the free copolymer acid as:

$$(1) \qquad K_a = \frac{[H^+] \times [HIA^-]}{[H_2IA]}$$

where $[H_2IA]$ is the molar concentration of all itaconic acid segments in the copolymer, $[HIA^-]$ is the molar concentration of all mono-ionized itaconic acid segments in the copolymer and $[H^+]$ is the molar concentration of hydrogen ions. Taking the logarithm of the reciprocals of both sides of equation (1) we have:

$$(2) \quad \log \frac{1}{K} = \log \frac{1}{[H^+]} + \log \frac{[H_2IA]}{[HIA^-]}$$

or

$$(3) \quad pK = pH + \log \frac{[H_2IA]}{[HIA^-]}$$

Rearranging (3) gives

$$(4) \quad pH = pK - \log \frac{[H_2IA]}{[HIA^-]}$$

or

$$(5) \quad pH = pK - \log \frac{(1 - \alpha)}{\alpha}$$

where α is the fraction of mono-ionized itaconic acid segments. If equation (1) is valid, the potentiometric data should conform to the linear equations (4) and (5). Katchalsky and Spitnik (52) have attempted to apply the Henderson-Hasselbach equation -5- to potentiometric data from the titrations of the polymeric acids polymethacrylic acid and polyacrylic acid and have found it necessary to modify it to the form

$$(6) \quad pH = pK - n \log \frac{(1-\alpha)}{\alpha}$$

as the slope of the lines determined by a plot of pH versus $\log \frac{(1-\alpha)}{\alpha}$ for these polymeric acids was not equal to unity.

Garrett and Guile (53) presented the first conclusive evidence as to the polydicarboxylic nature of the maleic anhydride-styrene copolymer. The calculations presented here are similar to those used by these authors.

A plot of the data of pH vs $\log \frac{1-\alpha}{\alpha}$ from aqueous titrations is given in Figures 9A, 11A, 15A, and 16A.

The slope(n) of the curve for the apparent pK_1' is close to unity.

For secondary carboxyls Garrett and Guile (53) have shown that if a correction is made for activity by a procedure similar to that of Katchalsky and Spitnik (52), the slope approaches two.

Since titration curves of the primary carboxyls show no deviation in slope and are similar to univalent acid titrations, pK_1' is a measure of the "fundamental" as well as the "practical" dissociation constant and each of the primary carboxyls may be considered to dissociate independently of the ionization of the others.

The slopes of the secondary titration curves are 1.7, 1.8, and 1.8. The values approach the predicted value of 2 and do not appear to vary.

Previous work (53) revealed a difficulty in measuring pK_2', and it is felt that the difficulty was due to the use of too high a concentration. The present work appears to indicate that the difficulty has been overcome by using more dilute solutions in the titrations and apparent pK_2' values for the ionization of the secondary carboxyl have been found for the maleic anhydride-styrene and itaconic anhydride-styrene copolymers.

In the case of the monoester derivatives, the slope for the primary and secondary carboxylates approaches unity. As expected, this indicates the monobasic acid character of these substances.

Method of Calculation for Date Plotted in
Figures 9A, 11A, 15A, 16A

1. [C] = Total molar concentration of all IA units in sample =

$$\frac{\text{moles IA in copolymer sample}}{\text{liters of solution}}$$

2. $[Na^{+}HIA^{-}]$ = molar concentration of the monosodium salt of the IA units in the copolymer =

$$\frac{\text{ml. of acid titer added x norm. of acid}}{\text{liters of solution}}$$

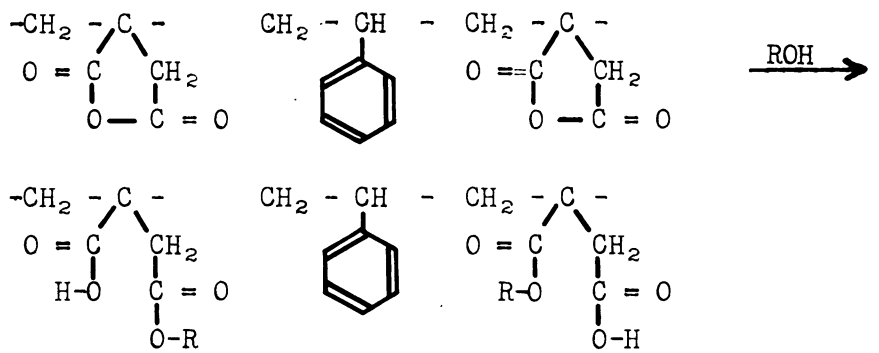
3. $[C] - [HIA^{-}] = [H_2IA]$ or $[C] - [IA^{=}] = [HIA^{-}]$

4. $\text{Log } \frac{[HIA^{-}]}{[H_2IA]} = \log \frac{(1 - \alpha)}{\alpha}$ for primary carboxyl-pK_1'

5. $\text{Log } \frac{[IA^{=}]}{[HIA^{-}]} = \log \frac{(1 - \alpha)}{\alpha}$ for secondary carboxyl-pK_2'

D. Preparation of Monoester Derivatives of the Itaconic Anhydride-Styrene Copolymers

1. By Reaction with Alcohols



A weighed sample (approximately 0.2 g.) of the itaconic anhydride-styrene copolymer was placed in a 250 ml. flask equipped with a reflux condenser. To the flask was added a quantity (from 5 to 15 ml.) of the desired alcohol and the mixture brought to reflux. The copolymer dissolved on reaction with the alcohol. Reflux was continued for several hours after solution to insure complete reaction (1).

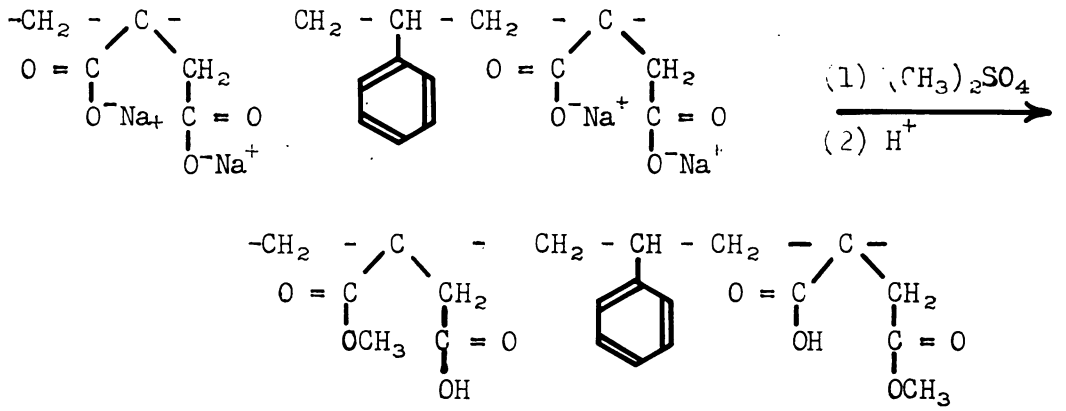
In some cases the monoester derivative was isolated before titration, and this was accomplished in one of two ways.

1. The excess alcohol was removed under reduced pressure.
2. Water was added to the alcohol solution of the monoester resulting in the formation of a precipitate. The monoester derivative was then removed by filtration, washed with ether, and dried under reduced pressure.

The approximate times required to dissolve a 0.2 g. sample of poly 57:43 (itaconic anhydride co styrene) in 5 ml. of the corresponding alcohol at reflux were as follows:

Alcohol	Time in Hours	Temperature °C
Benzyl	0.5	200
Methyl	3	64
Ethyl	5	78
n-Butyl	6	117
2-Methyl-1-butanol	13	130

2. By Reaction with Dimethyl Sulfate



A finely ground sample (0.5 g.) of Poly 61:39 (itaconic anhydride co styrene) was placed in a 250 ml. three-necked flask fitted with a dropping funnel, mechanical stirrer and a reflux condenser. The required amount of sodium hydroxide to form the disodium salt, (54 ml. 0.1044 N) was added to the flask and the stirrer started. About one hour was required for the solution of the itaconic anhydride-styrene copolymer.

When solution was complete, 0.6 ml. of dimethyl sulfate was added through the dropping funnel. When the addition of the dimethyl sulfate

was completed the reaction was heated to reflux and maintained at that temperature for three hours. A precipitate was formed during the course of the reaction. The precipitate was separated by filtering with suction and washed with HCl. The solid product was then washed with distilled water until the washings were free of chloride ion.

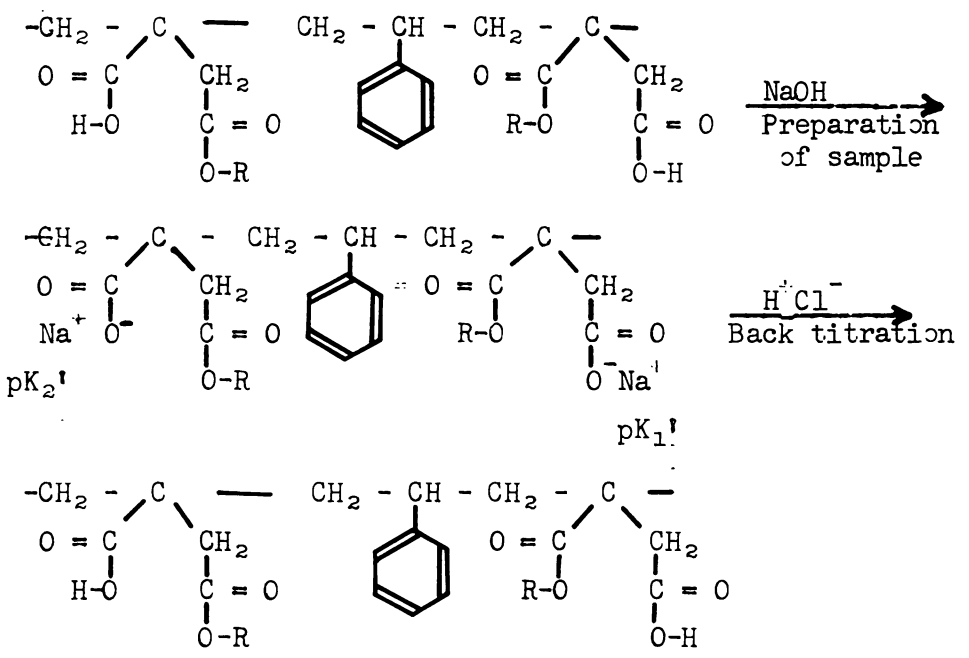
The acid-ester copolymer was then subjected to an exhaustive extraction with water to remove any sodium sulfate that may have been occluded during the precipitation of the product. A Soxhlet extraction apparatus was used and the extraction was continued for 48 hours.

A sample of the acid-ester copolymer was then ignited in a Vycor crucible and a trace of ash remained.

The ash was probably sodium sulfate. In many cases it is virtually impossible to remove inorganic salts from a polymer.

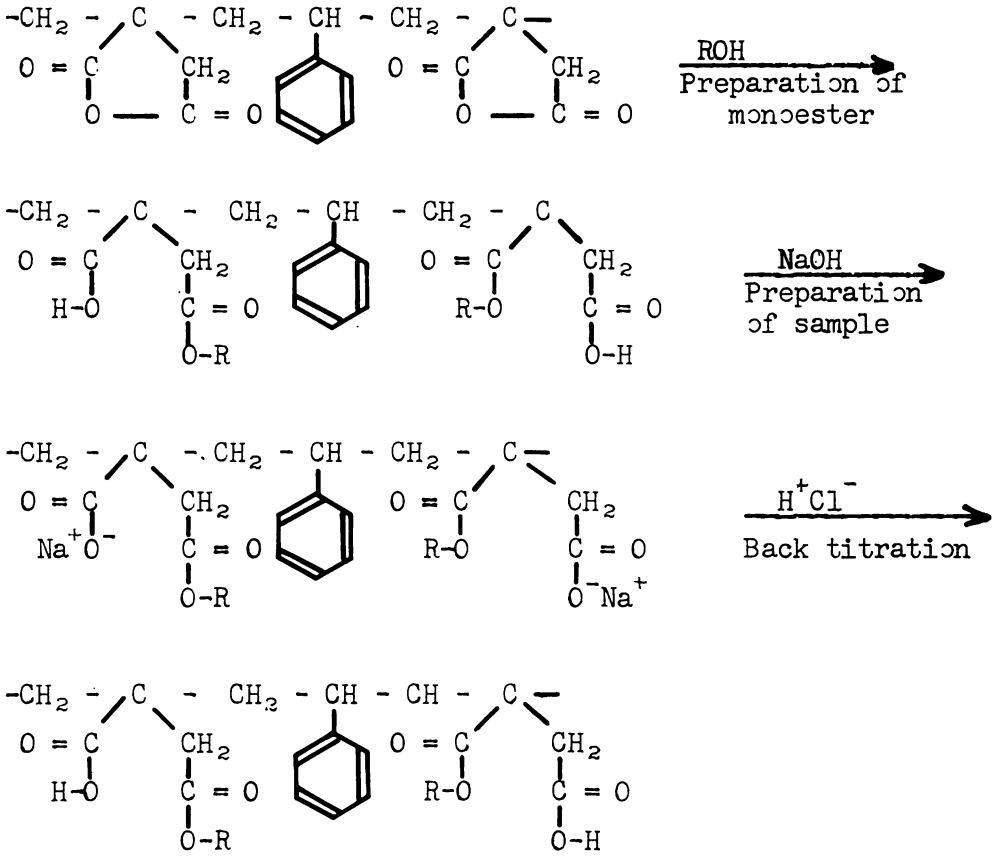
This same difficulty was encountered when a catalytic quantity of sulfuric acid was used to aid esterification.

E. Titration of the Monoester Derivatives of the Itaconic Anhydride-Styrene Copolymers



An accurately weighed sample of the monoester derivative of the itaconic anhydride-styrene copolymer was dissolved in 10 ml. of acetone followed by addition, in the cold, of a known amount of standard sodium hydroxide. The clear solution was then ready for titration.

In the instances where the monoester derivative was not isolated the procedure was as follows:



To an accurately weighed sample of the copolymer was added 20 ml. of the desired alcohol and the mixture heated until solution was obtained. The excess methyl or ethyl alcohol was removed on a steam bath. The solid monoester derivative was dissolved in 10 ml. of acetone,

heating on the steam bath when necessary. The solution was then cooled to room temperature and a known amount of standard sodium hydroxide was added. The clear solution was then ready for the back titration with standard hydrochloric acid.

Figures 16 through 23 represent plots of data obtained in the titration of the monoester derivatives of the copolymers. The data are summarized in Table X.

In the reaction of an alcohol with the anhydride segment of the copolymer two isomeric monoesters result.

Both isomers are evident in all the high-frequency titration curves of the monoester derivatives. The apparent pK' values for the monoester derivatives are tabulated in Table IX. The method used to calculate pK' values is shown in C, page 74.

TABLE IX

APPARENT pK' VALUES FOR THE MONOESTER DERIVATIVES OF THE ITACONIC ANHYDRIDE-STYRENE COPOLYMERS

Figure Number	Weight Percent Monoester Segments in Copolymer	Sample Weight g.	Type Monoester	pK Values Read Directly from pH Curve pK_1''	pK_2''	pK Values Calculated pK_1''	pK_2''
16	62.29	0.2345	Methyl	6.3	7.9	6.4	7.8
17	66.44	0.2022	Ethyl	6.2	7.6	6.1	7.5
18	66.44	0.2534	Ethyl	6.9	8.2	--	--
19	73.19	0.3182	Benzyl	7.1	8.4	--	--
20	71.42	0.2909	2-Methyl-1-butyl	7.1	9.2	--	--
21	70.86	0.0454	Ethyl	6.4	8.5	--	--
22	68.70	0.1955	Methyl	6.2	8.6	--	--
23*	48.50	0.2000	Ethyl	5.5	7.8	--	--

*Maleic Anhydride

TABLE X

SUMMARY OF THE TITRATION DATA FOR THE MONOESTERS OF THE ITACONIC ANHYDRIDE-STYRENE COPOLYMERS

Figure Number	Sample Weight g.	Weight Percent Monoester Segments in Copolymer	NaOH Reqd. Meqs.	NaOH Added Meqs.	Observed Meqs. Monoester Type I	Observed Meqs. Monoester Type II	Total Meqs. of Monoester Segments from Titration	Total Calcd. Meqs. of Monoester Segments	Percent Monoester Type I	Percent Monoester Type II
16	0.2345	62.29	1.06	2.64	0.546	0.524	1.07	1.06	51	49
17	0.2022	66.44	0.844	2.64	0.451	0.469	0.921	0.850	49	51
18	0.2534	66.44	1.07	2.64	0.572	0.528	1.10	1.07	52	48
19	0.3182	73.19	1.06	2.64	0.662	0.688	1.35	1.06	49	51
20	0.2909	71.42	1.04	2.64	0.457	0.413	0.860	1.04	52	48
21	0.0454	70.86	0.207	0.207	0.088	0.112	0.207	0.207	44	56
22	0.1955	68.70	0.929	2.20	0.493	0.437	0.930	0.930	53	47
23	0.2000	48.50	1.00	1.99	0.479	0.541	1.02	1.00	47	53

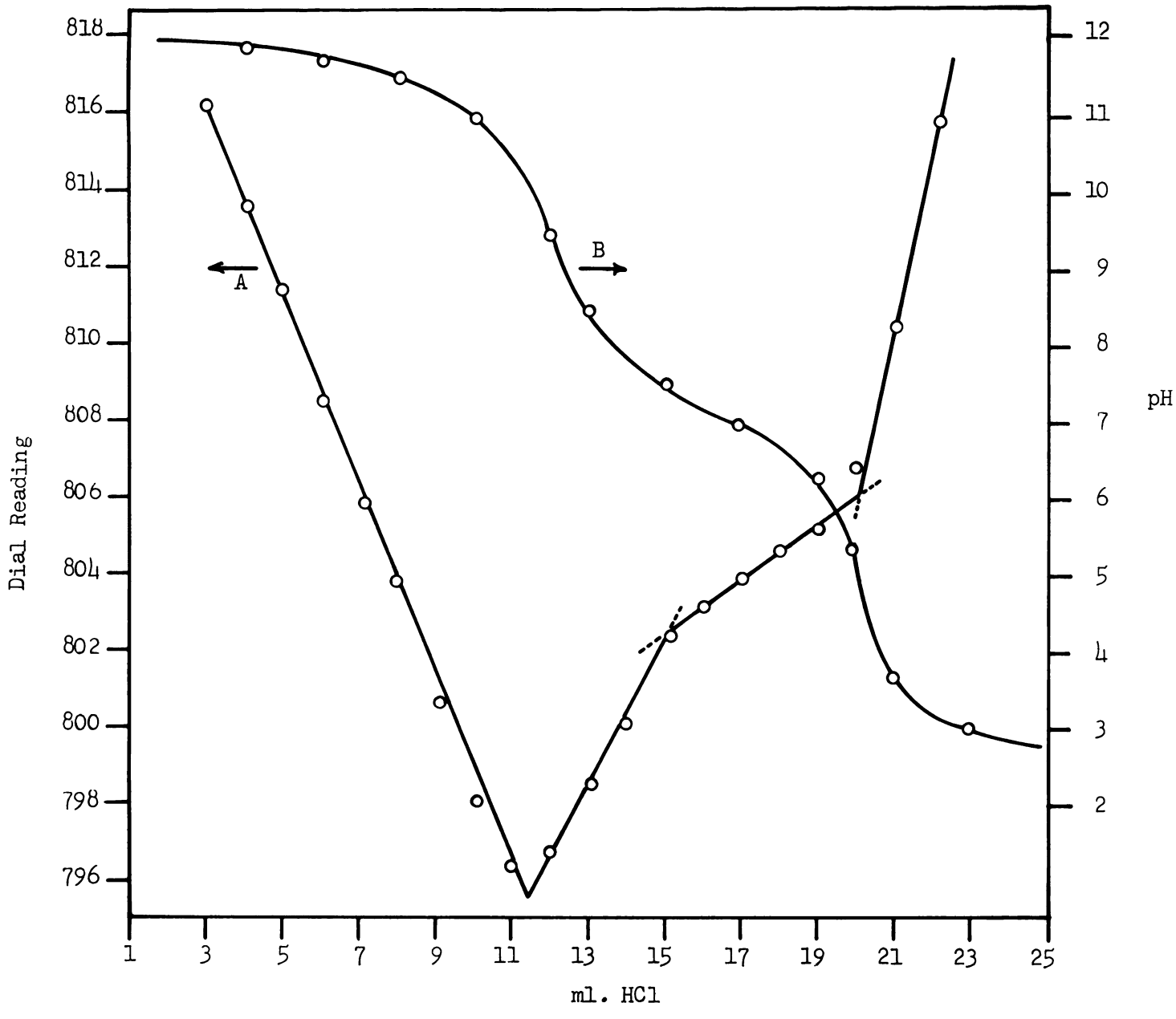


Fig. 16. High frequency (A) and potentiometric (B) displacement titration curves for the sodium salt of the monomethyl ester of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286 N-HCl.

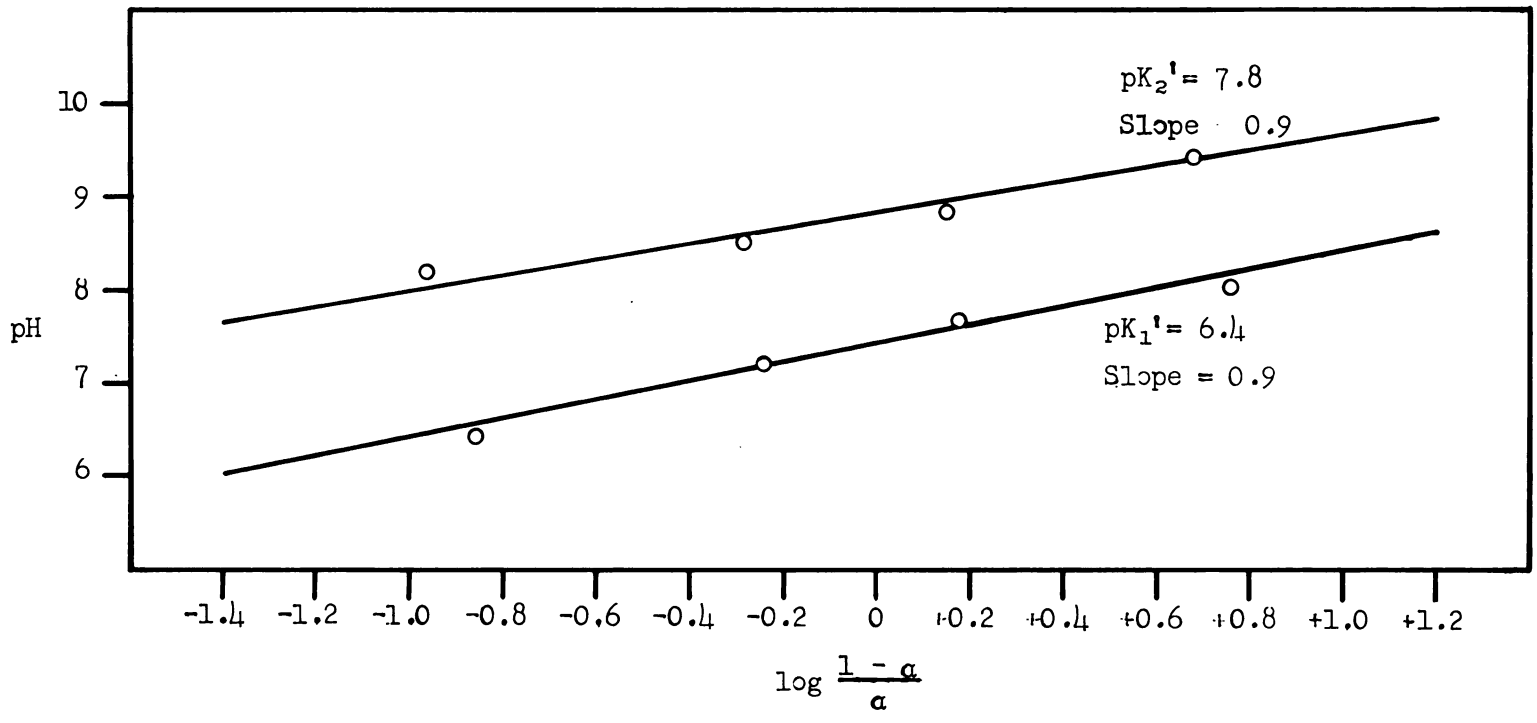


Fig. 16A. Plot of pH vs. log $\frac{1 - \alpha}{\alpha}$ for the titration of the Monomethyl ester of Poly 57:43 (itaconic anhydride co styrene) from the data for the titration in Fig. 16.

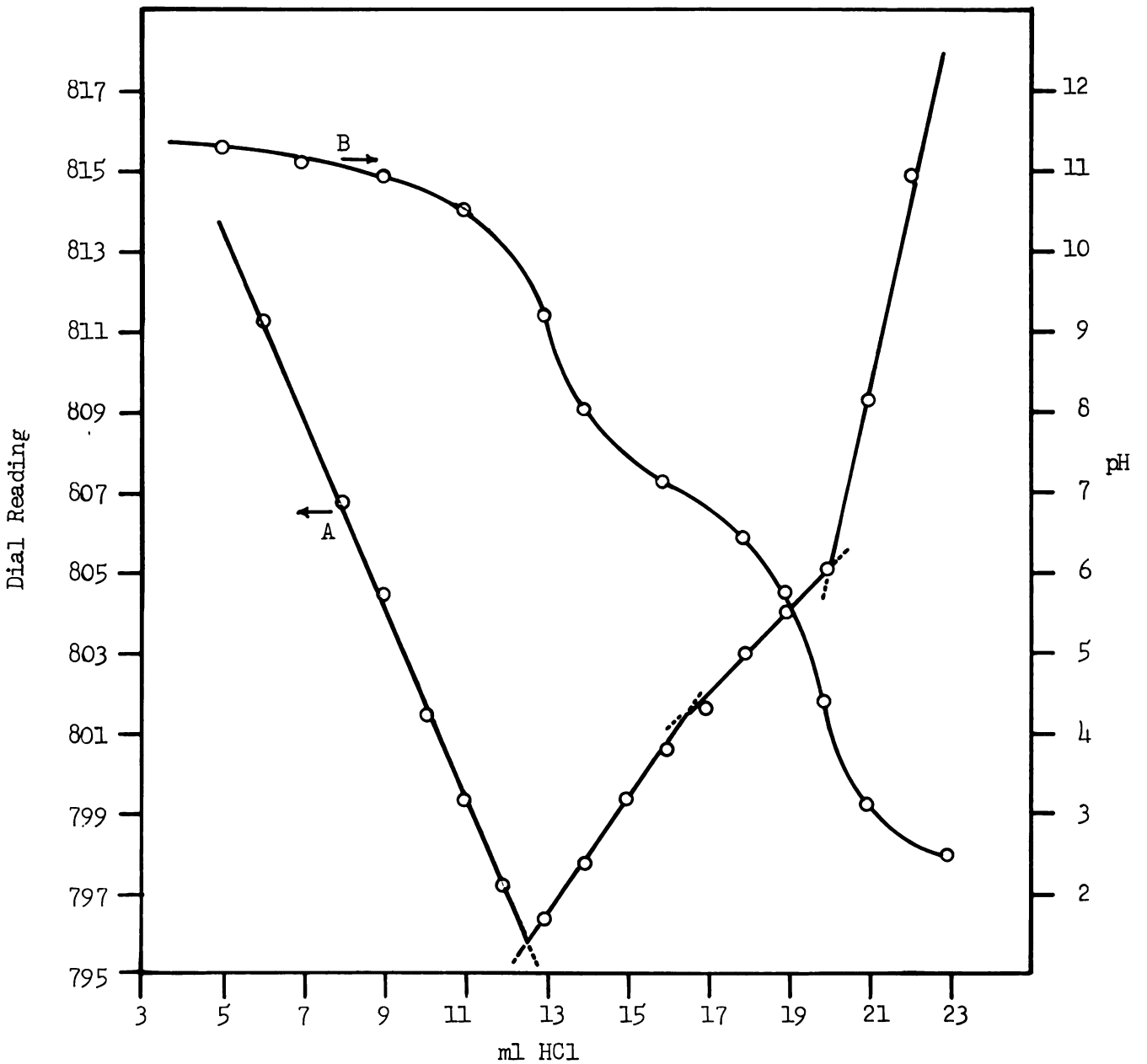


Fig. 17. High frequency (A) and potentiometric (B) displacement titration curves for the sodium salt of the monoethyl ester of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

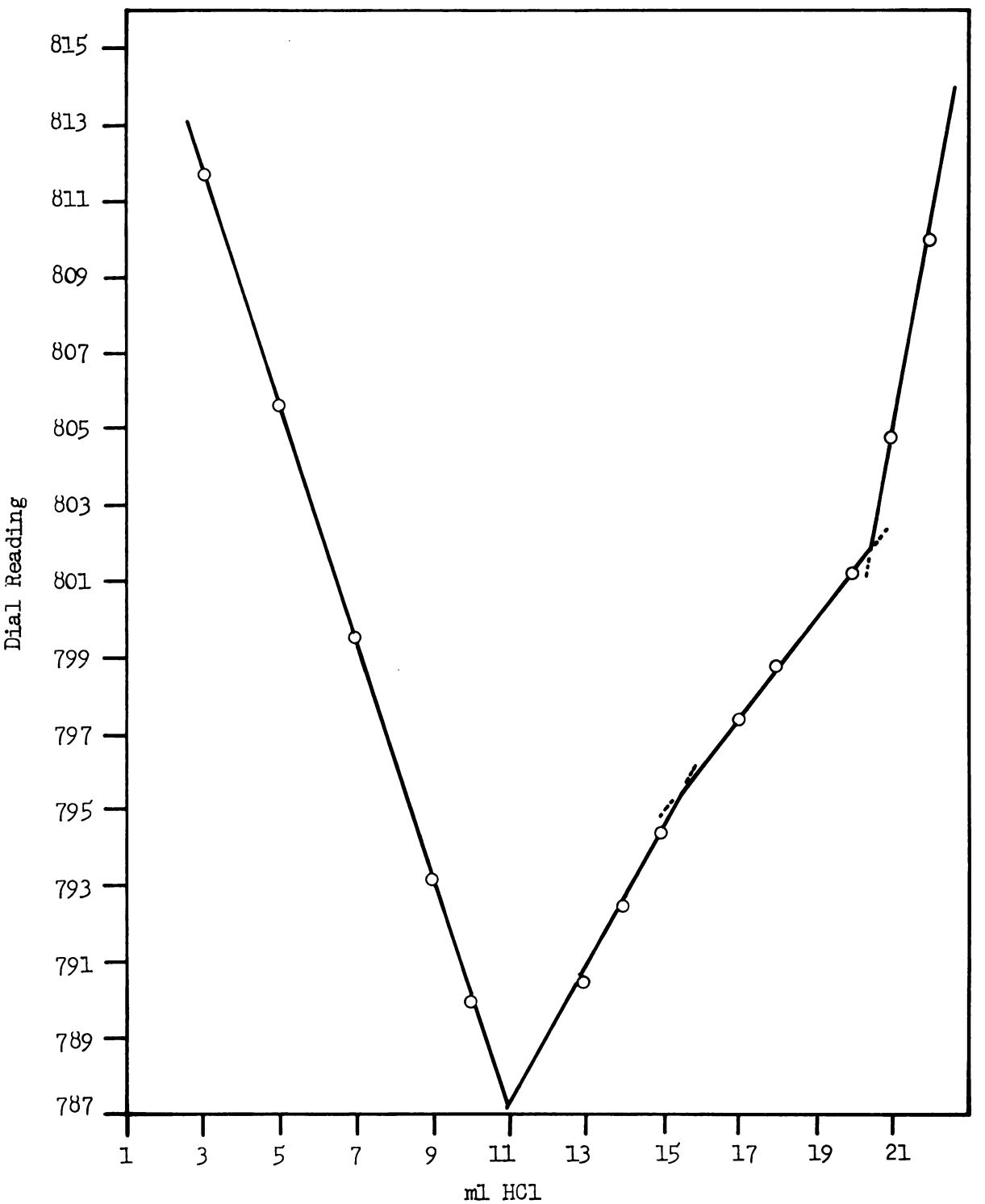


Fig. 18. High frequency displacement titration curve for the sodium salt of the monoethyl ester of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

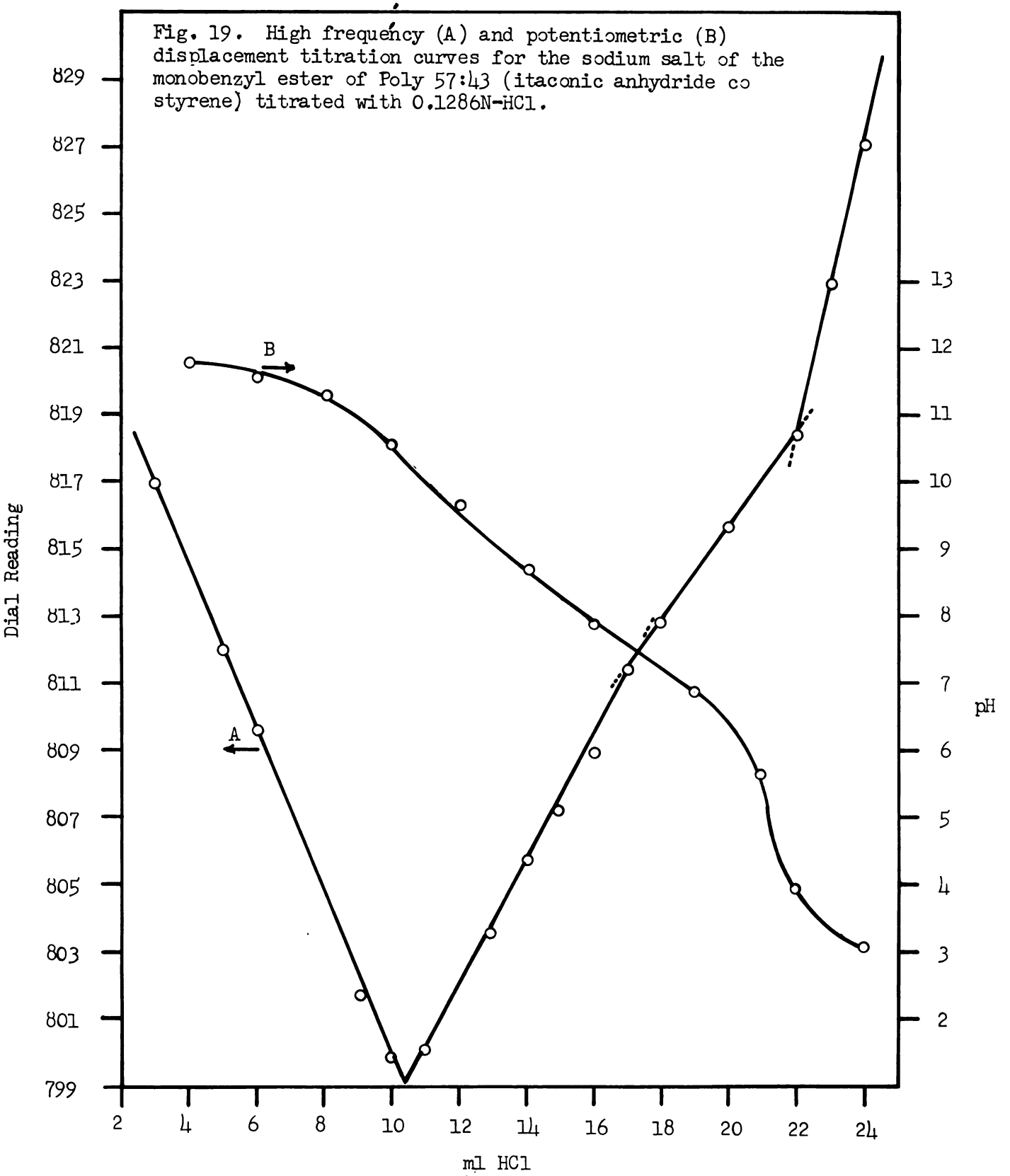


Fig. 19. High frequency (A) and potentiometric (B) displacement titration curves for the sodium salt of the monobenzyl ester of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

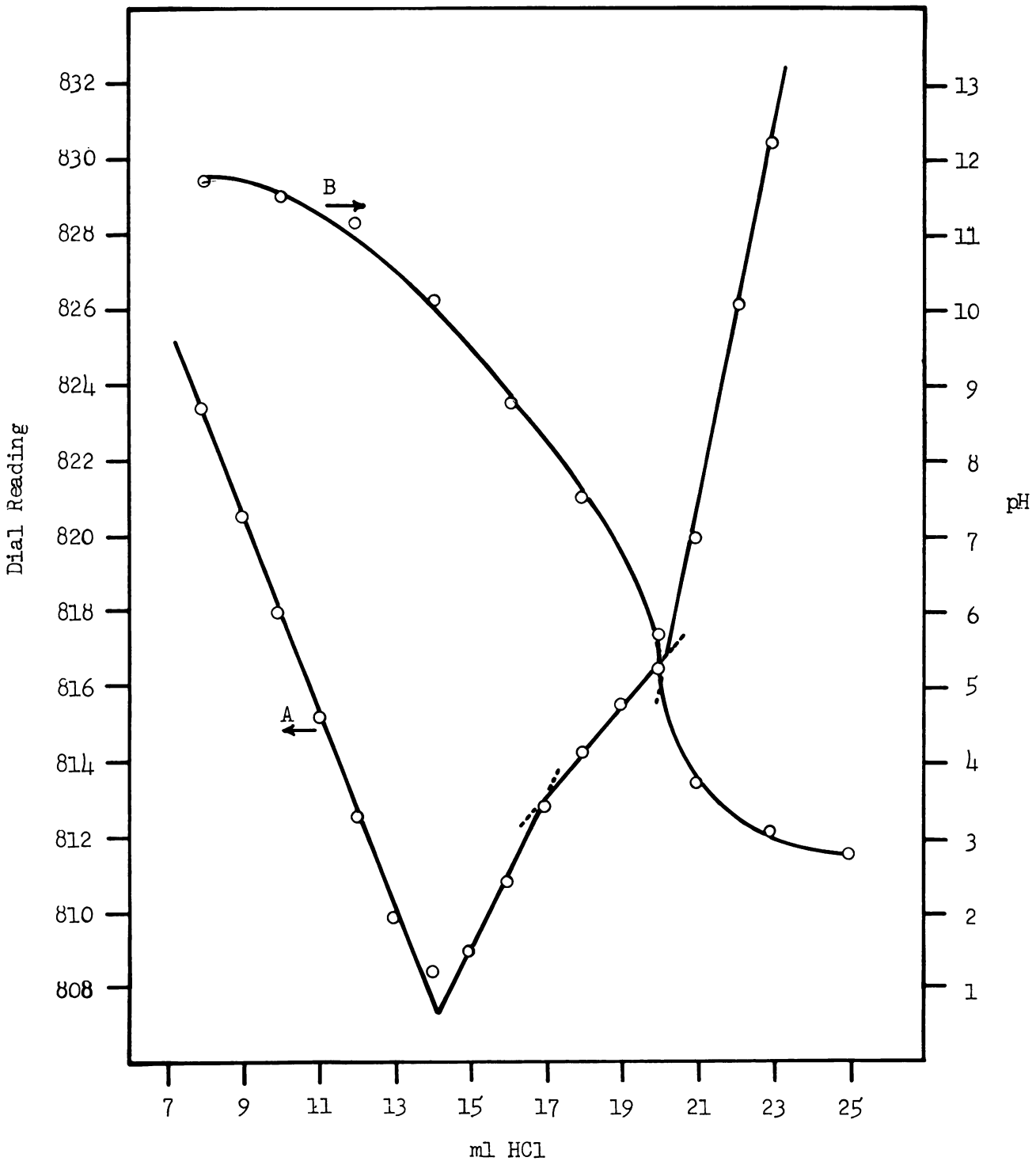


Fig. 20. High frequency (A) and potentiometric (B) displacement titration curves for the sodium salt of the mono-2-methyl-1-butyl ester of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.

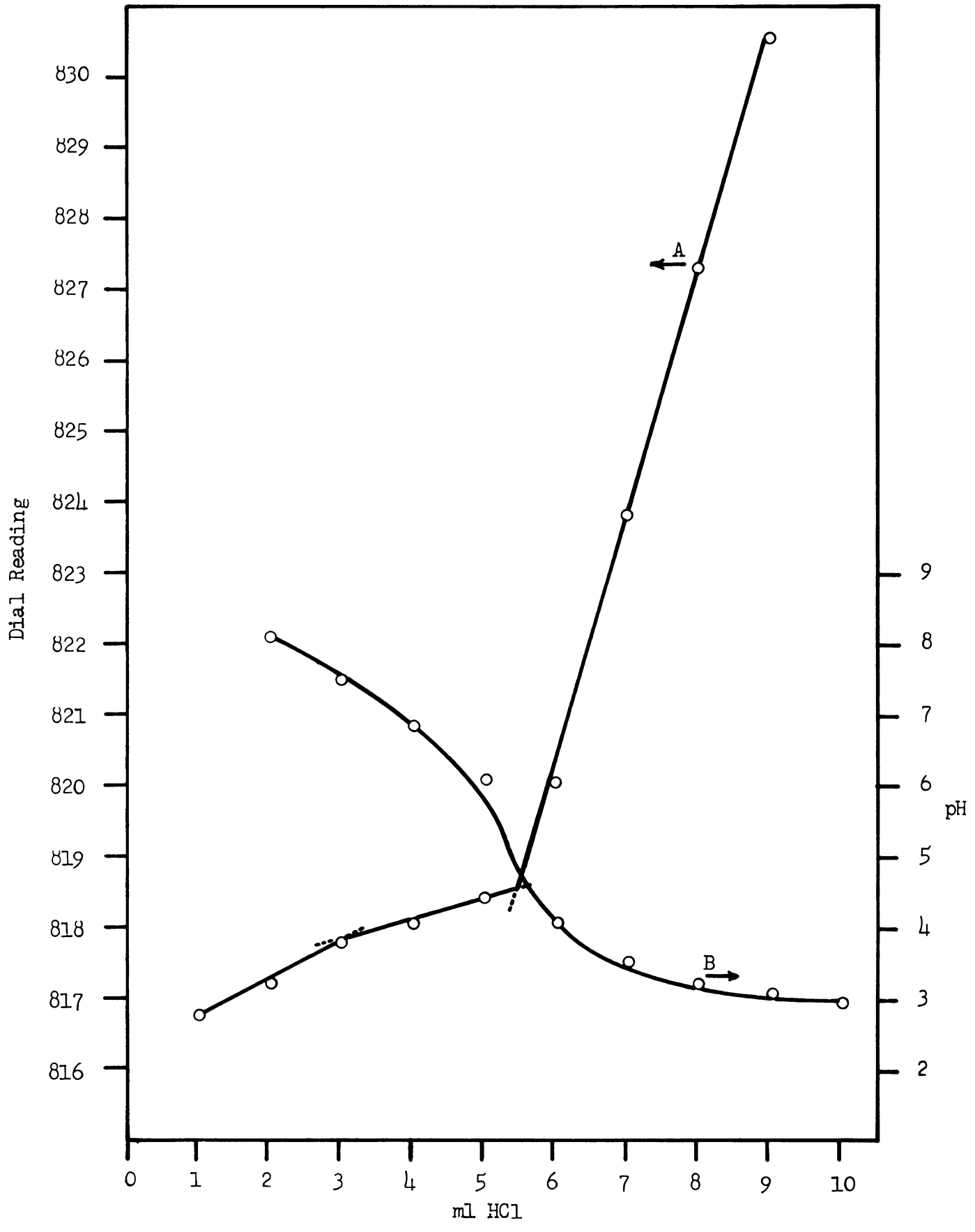


Fig. 21. High frequency (A) and potentiometric (B) displacement titration curves for the sodium salt of the monoethyl ester of Poly 61:39 (itaconic anhydride co styrene) titrated with 0.03883N-HCl.

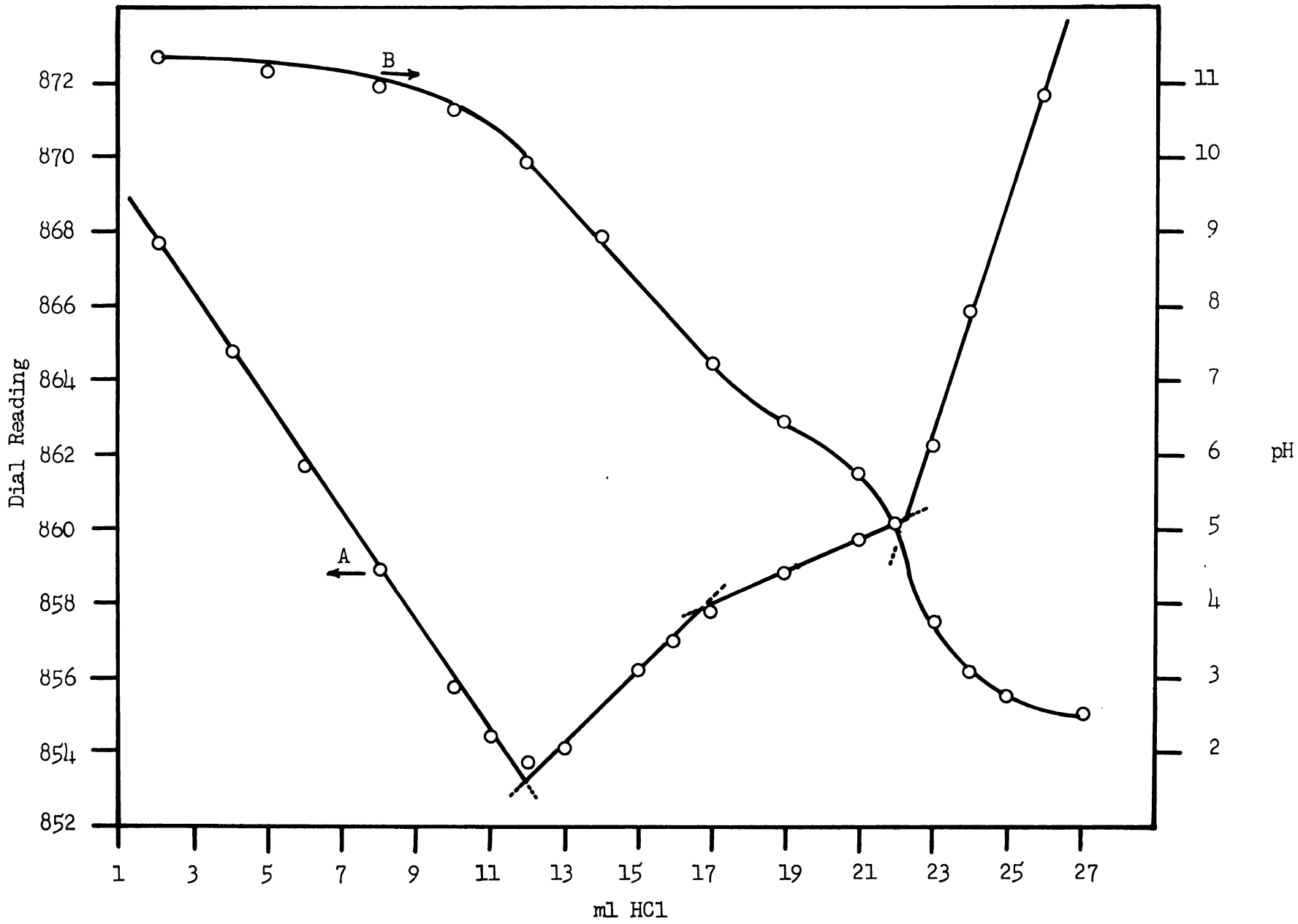


Fig. 22. High frequency (A) and potentiometric (B) displacement titration curves for the sodium salt of the monomethyl ester of Poly 61:39 (itaconic anhydride co styrene) titrated with 0.09744N-HCl.

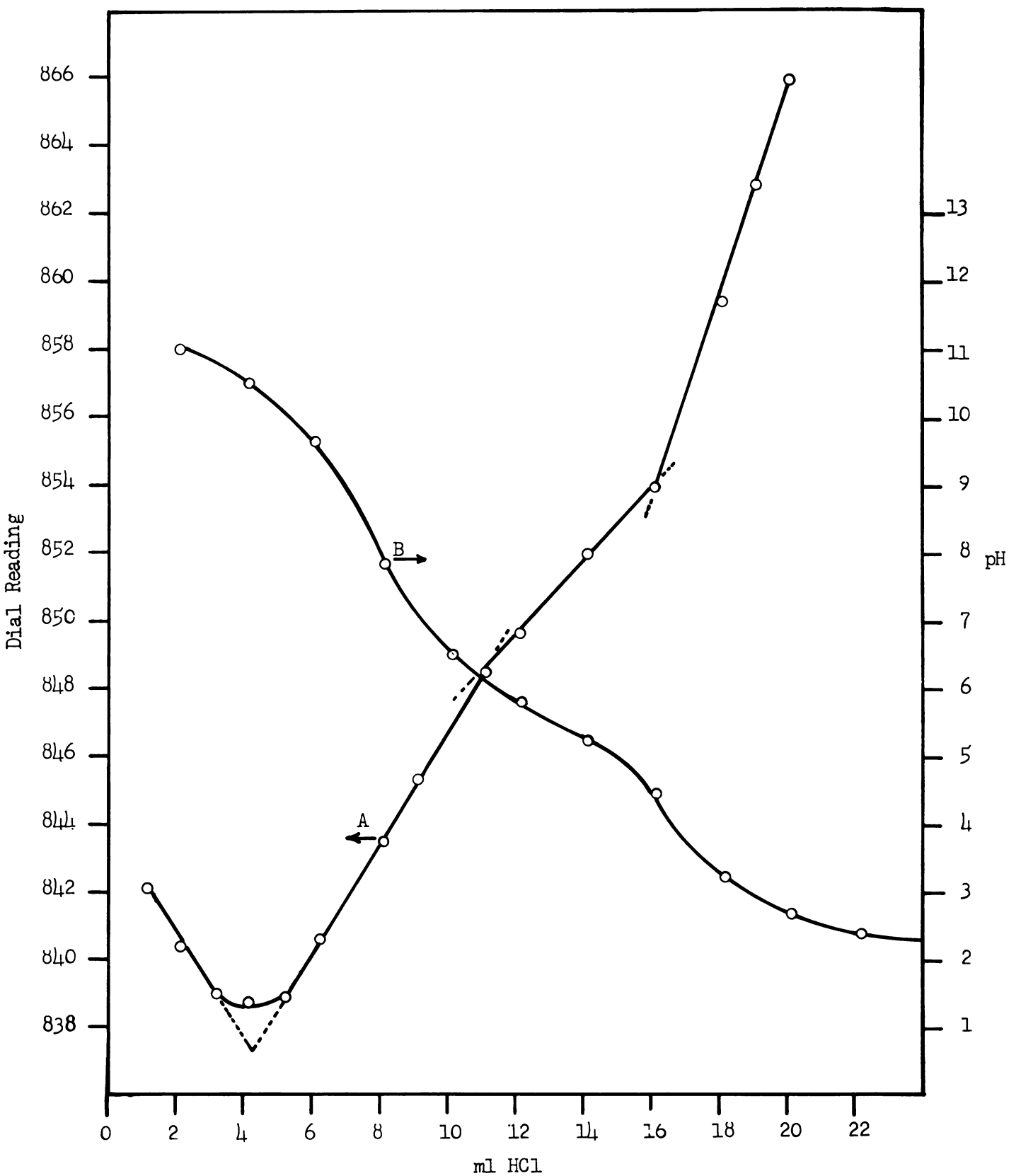
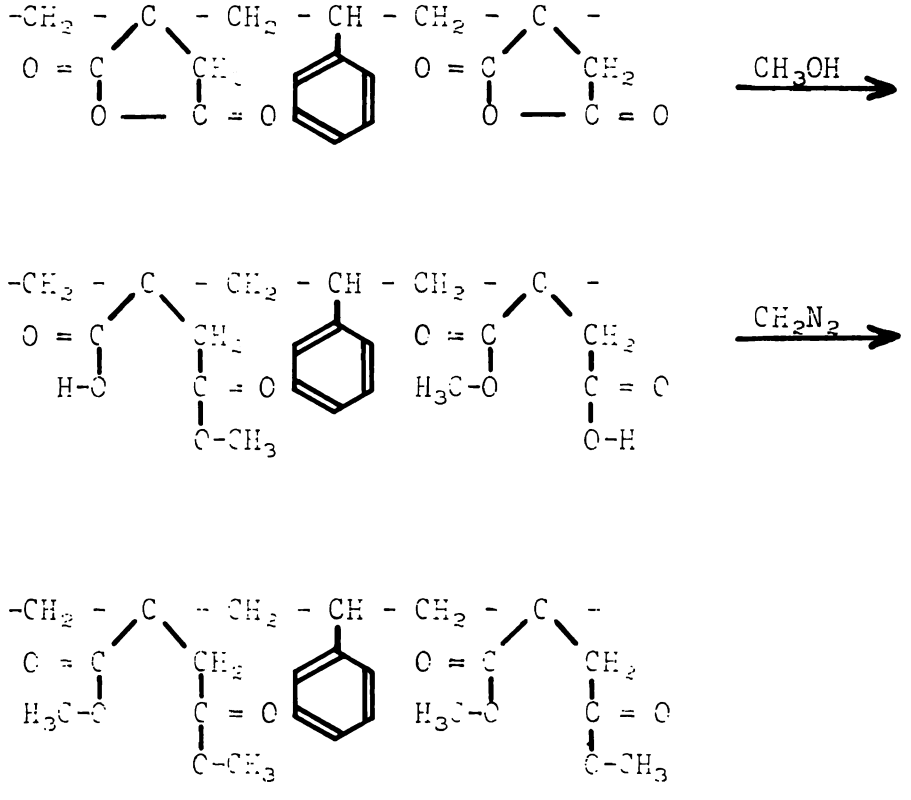


Fig. 23. High frequency (A) and potentiometric (B) displacement titration curves for the sodium salt of the monomethyl ester of Poly 50:50 (maleic anhydride co styrene) titrated with 0.1286N-HCl.

F. Preparation of Diester Derivatives of the Itaconic Anhydride-Styrene Copolymers

1. Preparation of the Dimethyl Ester of Poly 61:39 itaconic anhydride co styrene).



a. Diazomethane Procedure

1) Preparation of Nitrosomethylurea (54)

In a tared one-liter flask there was placed 120 g. (1.5 moles) of a 40 percent aqueous methylamine solution. Concentrated hydrochloric acid was added until the solution was acid to methyl red. Water was then added to bring the total weight to 500 g. and 300 g. of urea were added. The solution was heated gently to boiling and allowed to reflux for three hours. The solution was cooled to room temperature, 100 g. (1.5 moles) of a standard aqueous solution of sodium nitrite was dissolved in it, and it was then cooled to 0°C. The cold methylurea-nitrite solution was added slowly from a dropping funnel to a mixture of 600 g. of ice and 100 g. (1 mole) of concentrated sulfuric acid in a 3-liter beaker surrounded by an efficient freezing mixture. The addition should be at such a rate that the temperature does not rise above 0°C. The reaction mixture was stirred continually during the addition.

The nitrosomethylurea rises to the surface as a crystalline foamy precipitate which was filtered at once with suction and pressed well on the filter. The crystals were stirred to a paste with about 50 ml. of cold water, and then sucked as dry as possible. A sample of the moist crystals was dissolved completely in boiling methanol thus indicating that a rather pure product was obtained. The crystals were then dried in a vacuum desiccator. The yield was about 100 g. or 60 percent of the theoretical amount.

2) Preparation of Diazomethane and Reaction with Copolymer

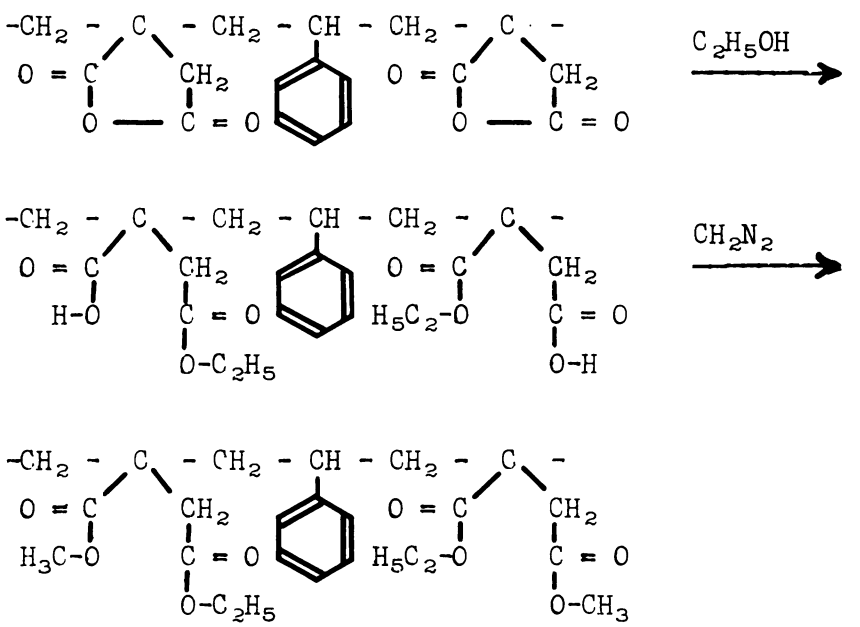
Diazomethane as a gas is explosive. Dissolved in ether it is safe, but even so it is best to prepare it only in small quantities. Only about 0.2 mole was produced at any one time and the reaction flask and receiver always contained considerable quantities of ether in which the diazomethane was generated and collected. The reaction was carried out in the hood. As long as any diazomethane was present, the entire reaction apparatus was completely shielded from the operator by a laminated glass safety shield. The operator was also careful to wear safety glasses at all times during this procedure.

A 500 ml. round-bottomed flask was charged with 60 ml. of 50 percent aqueous potassium hydroxide solution and 200 ml. of ether. The mixture was cooled to 5°C and 20.6 g. (0.2 mole) of nitrosomethylurea was added with shaking. The flask was fitted with a condenser set for distillation. The lower end of the condenser carried an adapter passing through a two-holed rubber stopper and dipping below the surface of a soltuion of 20 ml. of absolute methanol and 40 ml. of anhydrous ether in which the copolymer was dissolved.

To prepare the alcohol-ether solution of the copolymer it was necessary to first dissolve the copolymer in the alcohol followed by addition of the ether. The copolymer is insoluble in ether alone. The solution was contained in a 300 ml. Erlenmeyer flask and cooled in an ice-salt mixture. The exit gases were passed through a second 40 ml. portion of ether likewise cooled below 0°C. The reaction flask was placed in a water bath at 50°C. During the heating the flask was shaken occasionally. The distillation was continued until the ether came over colorless and during the distillation, the diester that formed was

precipitated. Under no circumstances should more than two-thirds of the ether in the reaction flask be distilled. If this should become necessary more ether must be added. The contents of the two receivers were combined and allowed to stand at room temperature for about twenty-four hours to get rid of the excess diazomethane. The ether and alcohol were decanted and the solid derivative was dried under vacuum at the reflux temperature of acetone.

2. Preparation of the Methyl Ethyl Diester of Poly 57:43 (itaconic anhydride co styrene).



a. Diazomethane Procedure

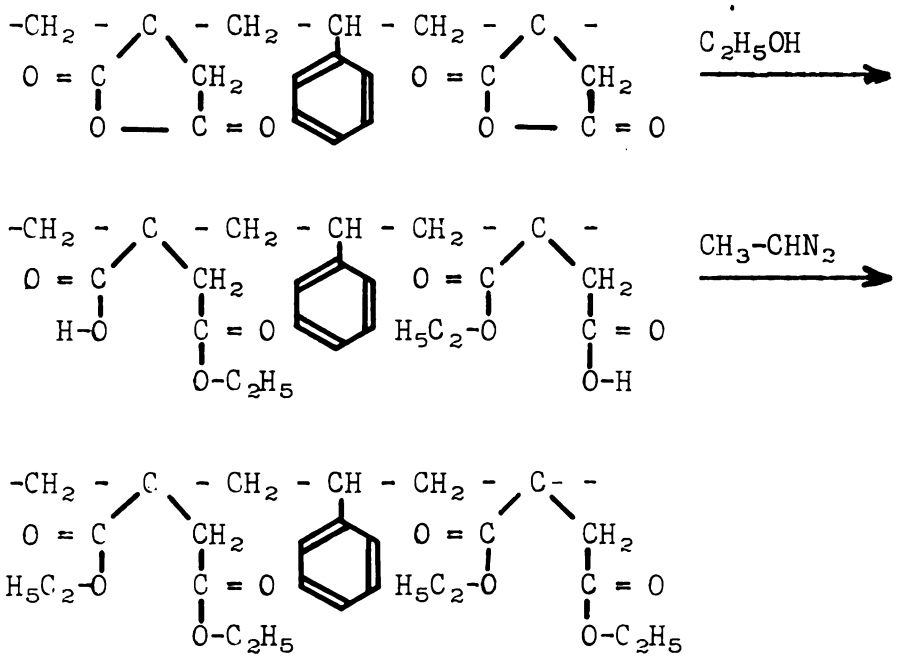
The preparation and distillation of the diazomethane was the same as outlined above with the modification that the diazomethane was now distilled into a solution of 25 ml. of absolute ethyl alcohol and 15 ml. anhydrous ether containing the dissolved Poly 57:43 (itaconic anhydride co styrene). The copolymer was first dissolved in the absolute ethyl

alcohol with gentle heating on the steam bath. The solution now contains the monoethyl ester derivative in ethyl alcohol. The ether was then added to this solution.

The results are as follows:

Found	Calculated
67.4% C	67.4% C
7.2% H	7.9% H

3. Preparation of a Partial Diethyl Ester of Poly 61:39 (itaconic anhydride co styrene).



a. Diazoethane Procedure

1) Preparation of N-Nitroso-β-ethylaminoisobutyl methyl ketone (55).

In a 2-liter three-necked flask, fitted with a mechanical stirrer, a thermometer, and a dropping funnel was placed 2 moles of ethylamine. The flask was surrounded by an ice bath and the stirrer started. When the temperature of the solution dropped to about 5°C, 2 moles of freshly

distilled mesityl oxide were added through the dropping funnel at such a rate that the temperature remained below 20°C. After the addition of the mesityl oxide, the mixture was allowed to stand without cooling for one-half hour.

The solution was then cooled to 10°C by means of an ice bath, and 125 ml. of glacial acetic acid were added through the dropping funnel at such a rate that the temperature remained below 15°C., then an additional 75 ml. of the acid were added rapidly.

The ice bath was removed, and 300 ml. of 8N sodium nitrite were added in about thirty minutes to the stirred solution, which was kept at a temperature of 25-35°C. Stirring was then stopped and the mixture was allowed to stand for twelve hours. Care should be taken to see that the temperature does not exceed 35°C at any time.

The oily layer was separated from the aqueous layer, the aqueous layer was extracted with two 200 ml. portions of ether, and the combined extracts and oil were dried over anhydrous calcium chloride. The drying agent was removed by filtration, the ether distilled by means of a water bath, and finally, all low-boiling material was removed from the mixture on a boiling water bath under the reduced pressure obtained with an aspirator. The nitrosoaminoketone remaining in the flask was considered sufficiently pure for the preparation of diazoethane.

2) Preparation of Diazoethane and Reaction with Copolymer.

Diazoethane is explosive as the gas but is safe when dissolved in ether. Identical precautions as those described in the preparation and use of diazomethane were followed, page 96.

Thirty milliliters of a solution of sodium isopropoxide, prepared from one g. of sodium and 100 ml. of isopropyl alcohol, were placed in a 250 ml. Claisen flask. The flask was provided with a dropping funnel, a condenser, and two receivers cooled in a dry ice bath; the first receiver contained a sample of the itaconic anhydride-styrene copolymer dissolved in 20 ml. of absolute ethyl alcohol to which was added 20 ml. of anhydrous ether. The first receiver was connected to a second one containing 20 ml. of anhydrous ether; the inlet tube of the second receiver dipped below the surface of the ether.

The water bath was heated to 75°C, and one-half of a solution prepared by dissolving 15.8 g. of N-nitroso-β-ethylaminoisobutyl methyl ketone in a mixture of 80 ml. of anhydrous ether and 12 ml. of isopropyl alcohol were added through the dropping funnel at a rate slightly greater than that of the distillation. After the contents of the separatory funnel were added, an additional 15 ml. of the solution of sodium isopropoxide were added; the remainder of the solution of nitroso compound then being added as before. Anhydrous ether was gradually added through the dropping funnel until the ether distillate was colorless.

As the diazoethane was distilled into the first receiver which contained the copolymer dissolved in an alcohol-ether mixture, a precipitate was formed. At the end of the distillation the contents of the two receivers were combined and allowed to stand at room temperature for twenty-four hours to get rid of the excess diazoethane. The ether alcohol solution was decanted and the solid derivative was dried under vacuum at the reflux temperature of acetone.

The results are as follows:

Found	Calculated
65.6% C	66.6% C

A possible explanation for the incomplete esterification may be due to the fact that during reaction the product precipitates. If some free carboxyl groups become imbedded in the precipitated product they thus become unavailable for esterification with diazoethane. This phenomenon of physical impediment to reaction is a rather common occurrence in attempting to carry out reactions with polymers. The procedure probably can be refined to give quantitative results.

4. Attempted Preparation of a Diester Using Absolute Alcohol and Gaseous Hydrogen Chloride Catalyst.

The reaction was carried out in a 500 ml., three-neck, round bottom flask with standard taper ground glass joints. The flask was fitted with an inlet tube attached to a hydrogen chloride cylinder, a reflux condenser the top of which was attached to a distillation head, and an inlet tube attached to a distillation apparatus to permit a continuous distillation of absolute alcohol into the reaction flask.

The itaconic anhydride-styrene copolymer was placed in the reaction flask and absolute methyl (or ethyl) alcohol was distilled directly into the reaction flask. Gaseous hydrogen chloride was passed slowly into the flask and gentle heating was started. The copolymer dissolved in about one hour. When about 200 ml. of alcohol had been distilled into the reaction flask, the distillation of fresh alcohol was stopped and the solution allowed to reflux for four hours. The alcohol in the

reaction flask was removed by distillation to a volume of 100 ml. and freshly distilled absolute alcohol (100 ml.) was distilled into the reaction flask. Gaseous hydrogen chloride was passed intermittently into the reaction flask throughout the process. The reaction was carried out for 96 hours.

Several portions of anhydrous benzene were then added to the reaction flask and the contents distilled. The purpose of the benzene was to aid in the removal of the hydrogen chloride. The alcohol and benzene were finally removed under reduced pressure and the solid product was dried under vacuum.

The carbon-hydrogen analyses indicated that the product in all cases was the monoester derivative.

G. Titration of the Diesters

The finely ground diester derivative of the copolymer was suspended in an acetone-alcohol solution in which the diester was only slightly soluble. An excess of standard sodium hydroxide was added and the titration carried out as previously described.

The titration curves, Figs. 24 and 25, indicate that a diester is present as the curves are typical of those for the titration of a strong base (NaOH) with a strong acid (HCl), with no carboxylate species present.

Fig. 26 is the titration curve for the partial diethyl ester, and the presence of a second break in the high-frequency titration curve indicates that there are some unesterified carboxylate groups in the sample.

The data for these titrations are tabulated in Table XI.

TABLE XI

SUMMARY OF THE TITRATION DATA FOR THE DIESTERS OF THE ITACONIC ANHYDRIDE-STYRENE COPOLYMERS

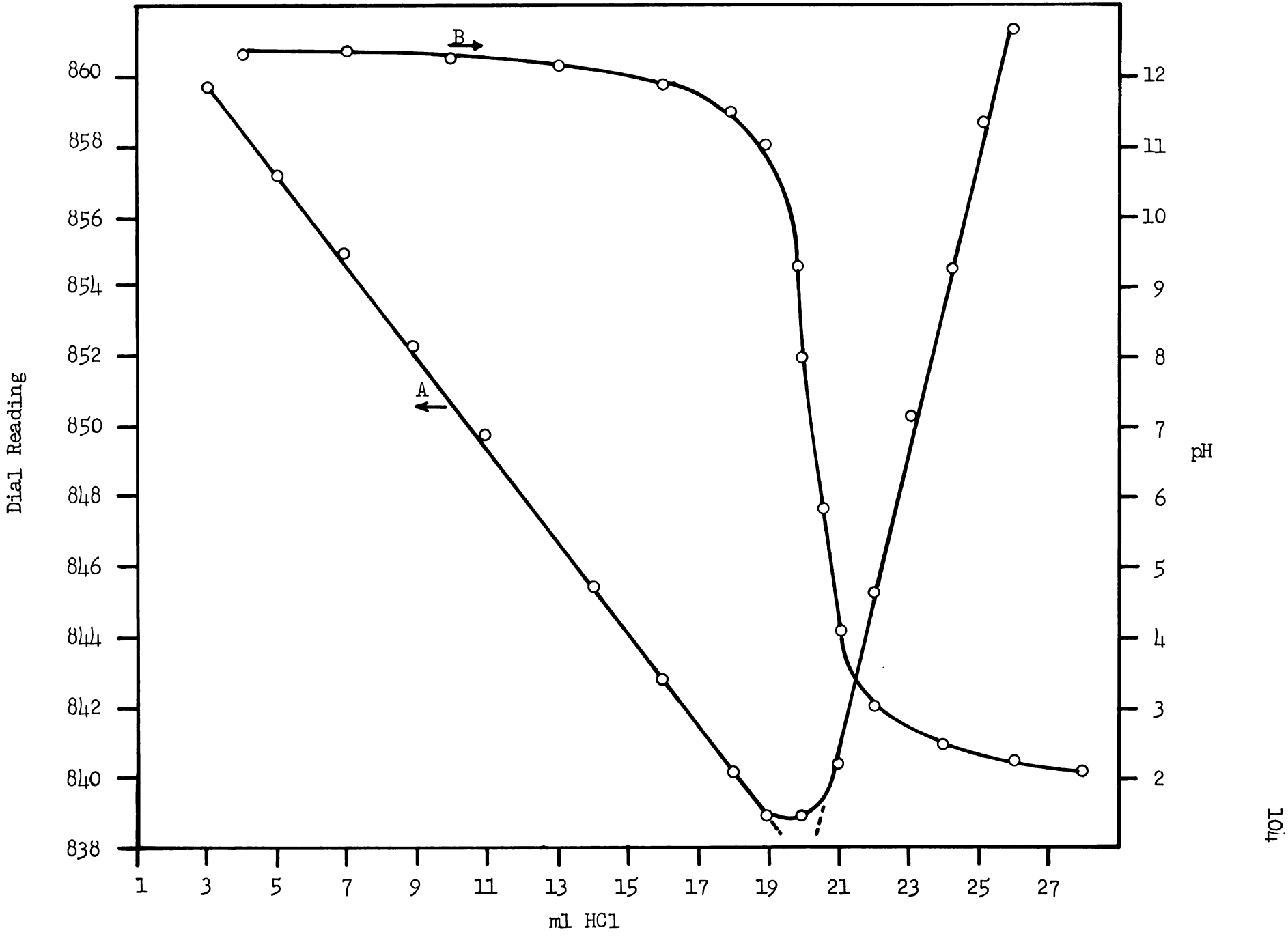
Diesters

Figure Number	Sample Weight g.	Diester of	NaOH Added Meqs.	NaOH Found Meqs.
24	0.1144	Methyl Ethyl Ester of Poly 57:43 (itaconic anhydride co styrene)	2.604	2.604
25	0.2048	Dimethyl Ester of Poly 61:39 (itaconic anhydride co styrene)	2.307	2.307

Partial Diester

Figure Number	Sample Weight g.	Weight Percent Acid-Ester Segment in Copolymer	Designated as	NaOH Required Meqs.	NaOH Added Meqs.	Meqs. of Acid-Ester from Titration	Calcd. Meqs. of Acid-Ester if Monoester	Calcd. Meqs. of Acid if Diester
26	0.1996	70.8	Partial Diethyl Ester of Poly 61:39 (itaconic anhydride co styrene)	0.897	2.26	0.341	0.895	0

Fig. 24. High frequency (A) and potentiometric (B) titration curves for the methyl ethyl diester of Poly 57:43 (itaconic anhydride co styrene) titrated with 0.1286N-HCl.



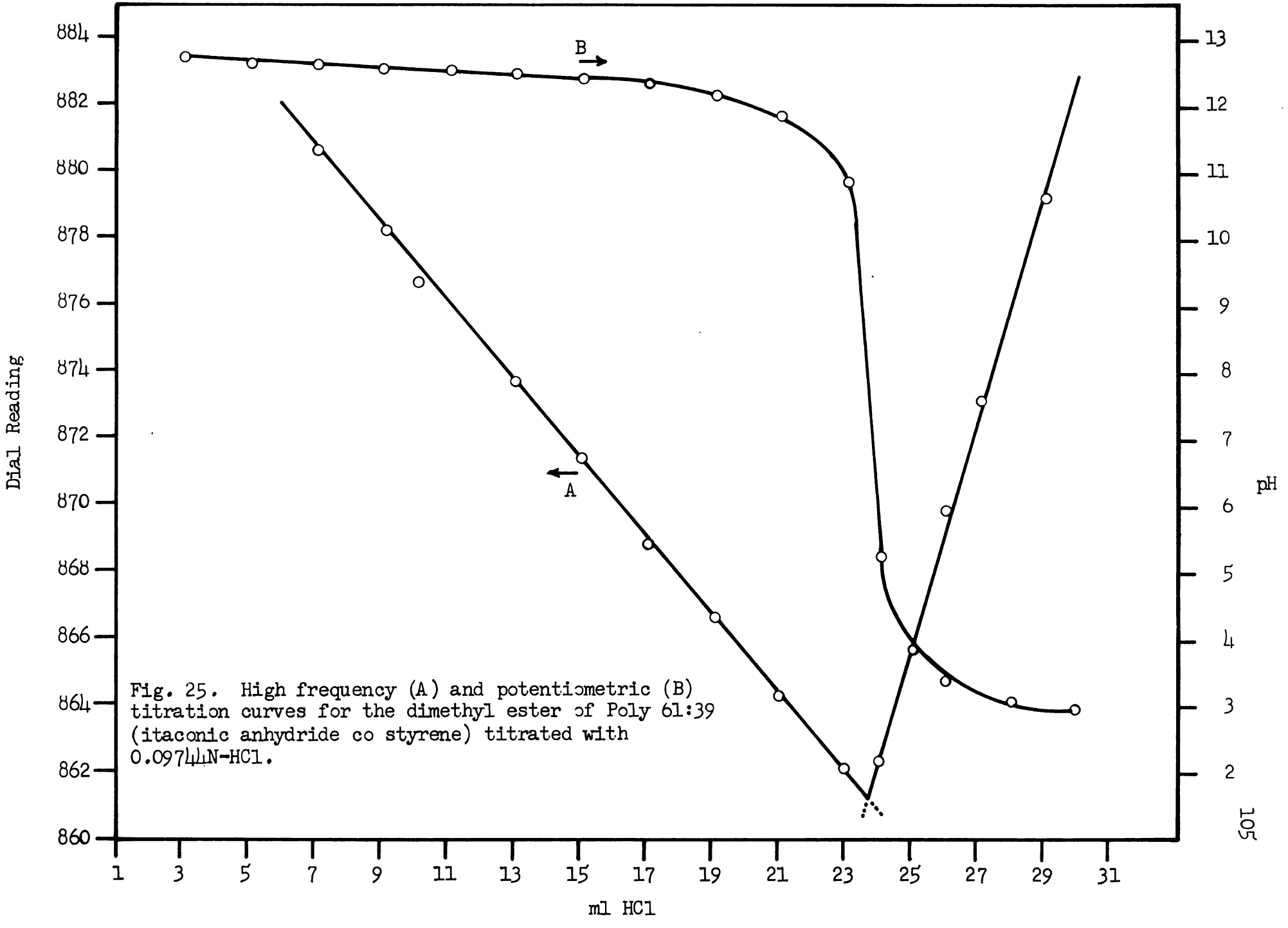
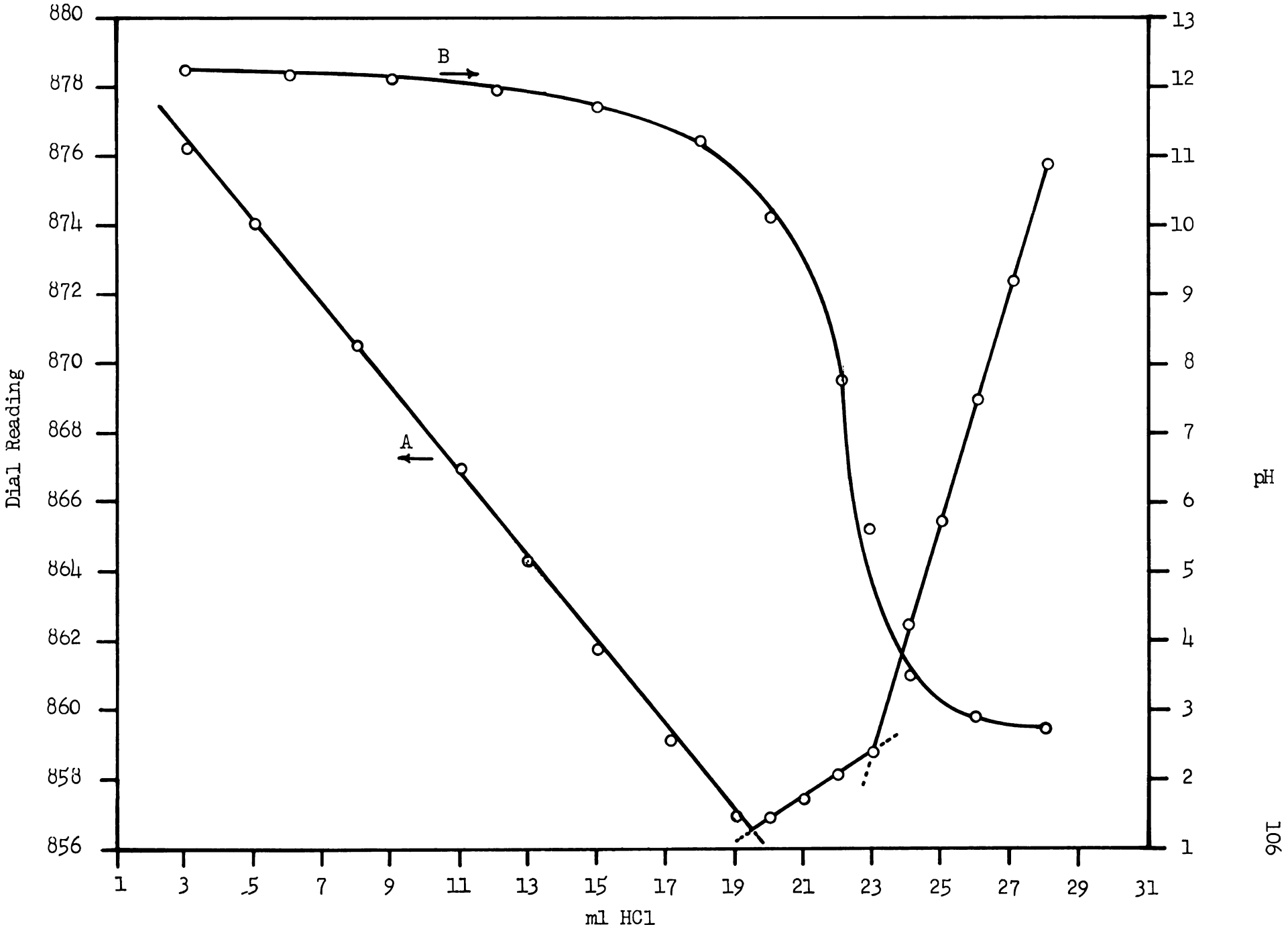


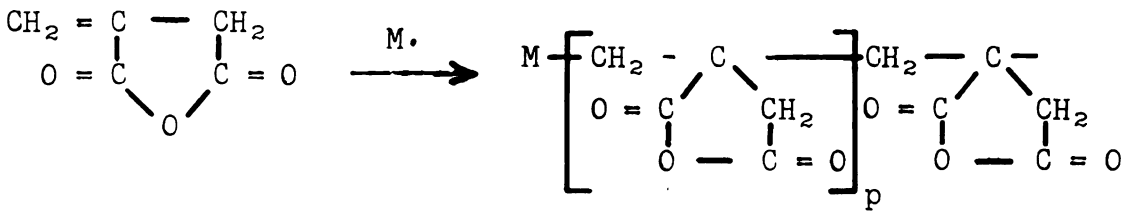
Fig. 25. High frequency (A) and potentiometric (B) titration curves for the dimethyl ester of Poly 61:39 (itaconic anhydride co styrene) titrated with 0.09744N-HCl.

Fig. 26. High frequency (A) and potentiometric (B) titration curves for the partial diethyl ester of Poly 61:39 (itaconic anhydride co styrene) titrated with 0.09744N-HCl.



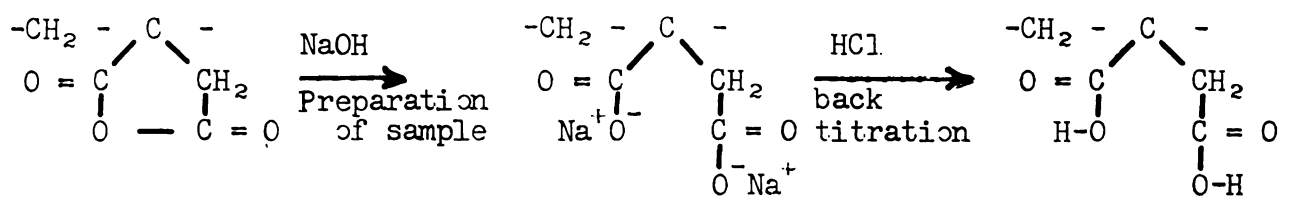
H. Preparation and Titration of the Homopolymer-Polyitaconic Anhydride

1. Preparation of Polyitaconic Anhydride



The polymerization was carried out in a five hundred milliliter, three-neck, round bottom flask with standard taper ground glass joints. The flask was fitted with a reflux condenser, a nitrogen inlet tube and a mechanical stirrer. The polymerization mixture was protected from moisture by a calcium chloride tube and kept under a nitrogen atmosphere. The flask was charged with 307.6 g. of benzene and 15.5 g. of itaconic anhydride. The reaction mixture was heated, while stirred, for one hour at the reflux temperature to dissolve the itaconic anhydride. When solution was complete 0.2 g. of benzoyl peroxide was added and the reaction was permitted to continue for 15 hours. The precipitated polymer was removed and extracted with benzene in a Soxhlet extractor for 96 hours and then dried under vacuum in a drying pistol at the reflux temperature of acetone.

2. Titration of Polyitaconic Anhydride



A sample of the polyitaconic anhydride was dissolved in acetone. To the solution was added a quantity of standard sodium hydroxide and the solution was heated on a steam bath to drive off the acetone. The resulting solution was then titrated with standard hydrochloric acid as previously described.

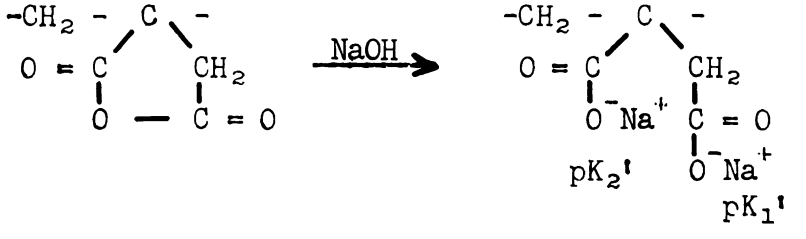
The titration data are plotted in Fig. 32 and listed below.

Sample Weight g.	NaOH Required Meqs.	NaOH Added Meqs.	Calc'd. Meqs. Acid	Found Meqs. Acid from Titration	pK_1'	pK_2'
0.0997	1.780	1.780	1.780	1.675	5.1	7.1

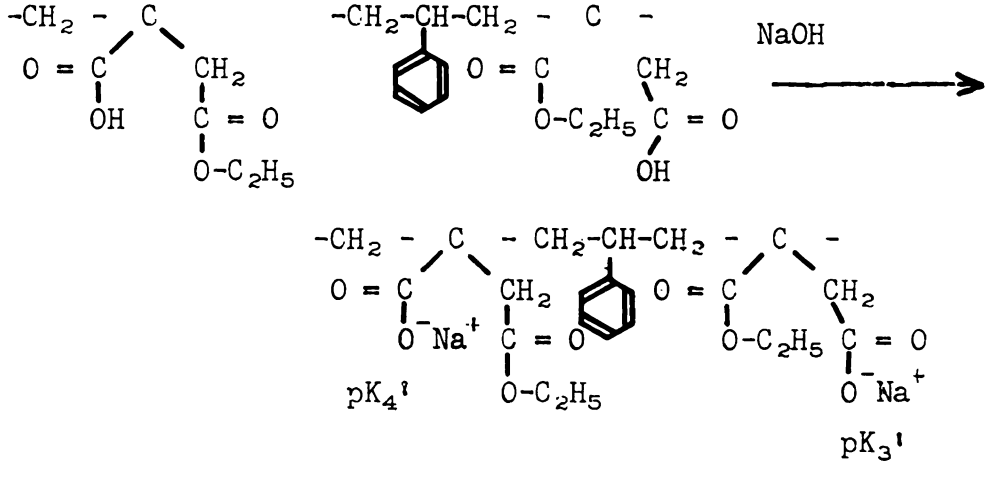
I. Titration of Mixtures

These species are present in the mixtures titrated:

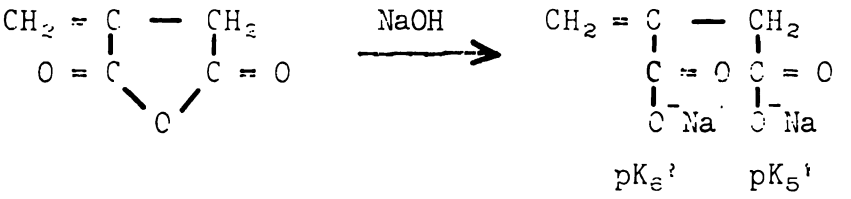
Poly 61:39 (itaconic anhydride co styrene)



Monoethyl ester of Poly 61:39 (itaconic anhydride co styrene)



Itaconic Anhydride



1. Mixture of Poly 61:39 (itaconic anhydride co styrene) and the monoethyl ester of Poly 61:39 (itaconic anhydride co styrene).

There are four acid species in this mixture and therefore four types of carboxylate ions are involved in the back titration.

The titration curve should yield four neutralization breaks and Fig. 27 does show four breaks, (a-d).

a. The break at about 11.8 ml. HCl could be the neutralization of one-half of the disodium salt of the copolymer. The theoretical value is 11.6 ml. HCl.

b. The break at 19 ml. HCl could be the monosodium salt of the copolymer and the neutralization of one type of carboxylate of the monoethyl ester derivative. The theoretical value is 19 ml. HCl.

c. The break at 28 ml. HCl could be the neutralization of both types of carboxylate of the copolymer and one type of carboxylate of the monoethyl ester. The theoretical value is 30 ml. HCl.

d. The break at 36.7 ml. HCl represents the free acid form of the four carboxylate species. It represents the neutralization of the second type of carboxylate of the monoethyl ester derivative. The theoretical value is 36.7 ml. HCl.

TABLE XII

DATA FOR THE TITRATION IN FIGURE 27

(a) Poly 61:39 (itaconic anhydride co styrene) and (b) Monoethyl ester of Poly 61:39 (itaconic anhydride-co styrene).

Substance	Weight Sample g.	Weight Percent I.A. Segment in Copolymer	NaOH Required Meqs.	NaOH Added Meqs.	Total Meqs. of I. A. Segment from Titration	Total Meqs. of I.A. Segment from C-H Analysis
(a)	0.2000	63.2	1.296	1.296		
					3.556	3.560
(b)	0.2900	70.8	2.250	2.250		

	pK_1'	pK_2'	pK_3'	pK_4'
Apparent pK Values from Mixture Titration	6.3	10.3	5.2	8.6
Apparent pK Values from Single Titration	5.7	8.8	6.4	7.8

(a) 1.296 meqs. of NaOH = 13.4 ml. HCl (0.0966 N)

(b) 2.250 meqs. of NaOH = 23.4 ml. HCl (0.0966 N)

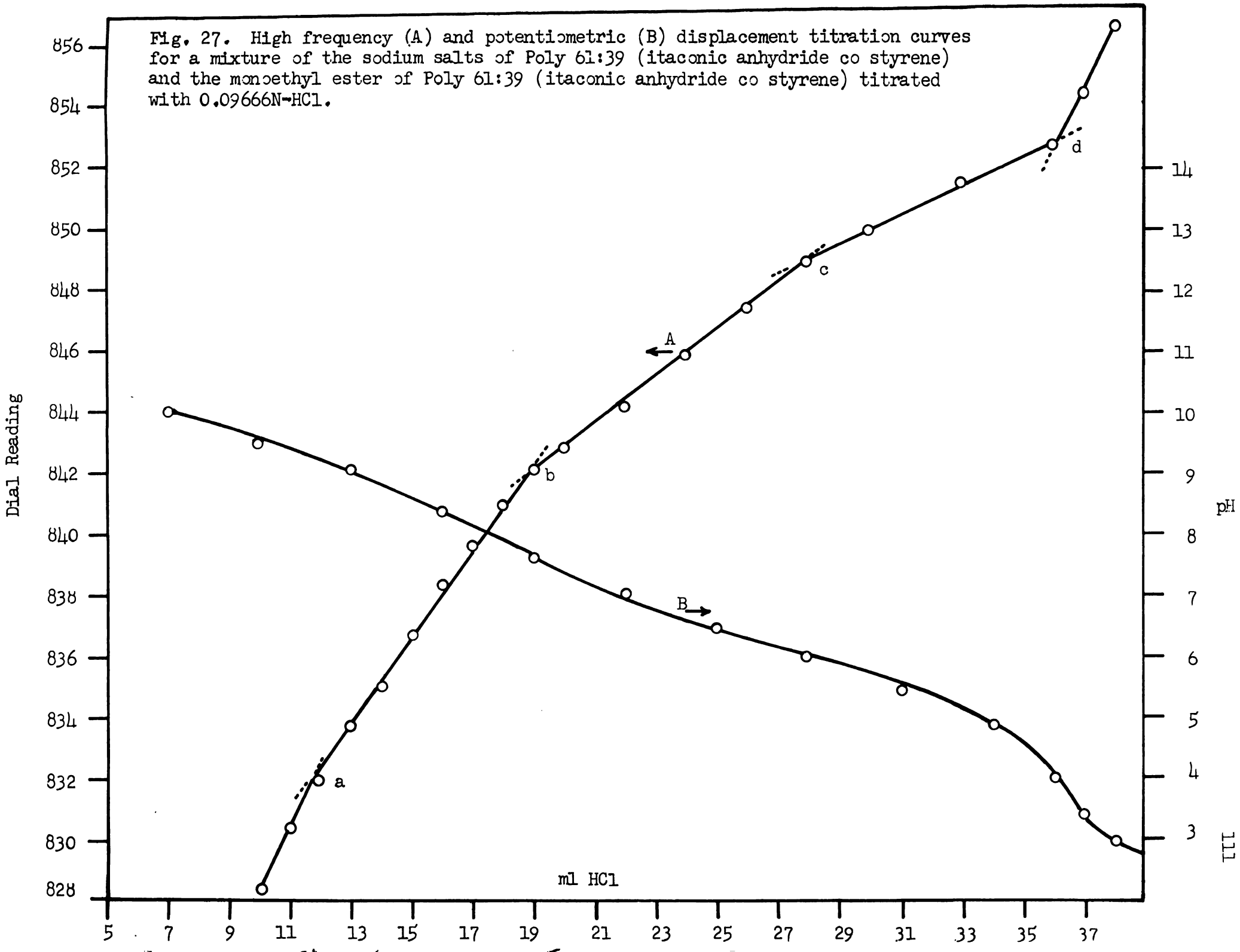


Fig. 27. High frequency (A) and potentiometric (B) displacement titration curves for a mixture of the sodium salts of Poly 61:39 (itaconic anhydride co styrene) and the monoethyl ester of Poly 61:39 (itaconic anhydride co styrene) titrated with 0.09666N-HCl.
Dial Reading
856
854
852
850
848
846
844
842
840
838
836
834
832
830
828
pH
14
13
12
11
10
9
8
7
6
5
4
3
ml HCl
5
7
9
11
13
15
17
19
21
23
25
27
29
31
33
35
37
A
B
a
b
c
d
111

2. Mixture of Poly 61:39 (itaconic anhydride co styrene) and itaconic anhydride.

There are four acid species in this mixture and therefore four types of carboxylate ions are involved in the back titration.

The titration curve should yield four neutralization breaks and Fig. 28 shows five breaks, (e-i).

e. The break at 6.4 ml. HCl could be the neutralization of one type of carboxylate of the disodium salt of the copolymer. The theoretical value is 5.6 ml. HCl.

f. The break at 11.8 could be the neutralization of all the carboxylate in the polymer which is now in the free acid form. The theoretical end point is at 11.3 ml. HCl.

The breaks at g and h are unexplainable in relation to the expected stoichiometry of the titration.

i. The end point at 29.4 ml. HCl represents the free acid form of all the species. The theoretical end point is at 30.0 ml. HCl.

TABLE XIII

DATA FOR THE TITRATION IN FIGURE 28

(a) Poly 61:39 (itaconic anhydride co styrene) and (b) itaconic anhydride.

Substance	Weight Sample g.	Weight Percent I.A. Segment in Copolymer	NaOH Required Meqs.	NaOH Added Meqs.	Total Meqs. of I.A. Segment from Titration	Total Meqs of I.A. Segment from C-H Analysis
a	0.0975	63.2	1.099	1.099		
					2.842	2.920
b	0.1017		1.835	1.835		

	pK_1'	pK_2'	pK_5'	pK_6'
Apparent pK values from Mixture Titration	[9.6]	[11.2]	[4.2]	[6.0]
Apparent pK values from Single Titration	5.7	8.8	4.3	6.5

(a) 1.099 meqs. of NaOH = 11.3 ml. HCl (0.0966 N)

(b) 1.835 meqs. of NaOH = 18.7 ml. HCl (0.0966 N)

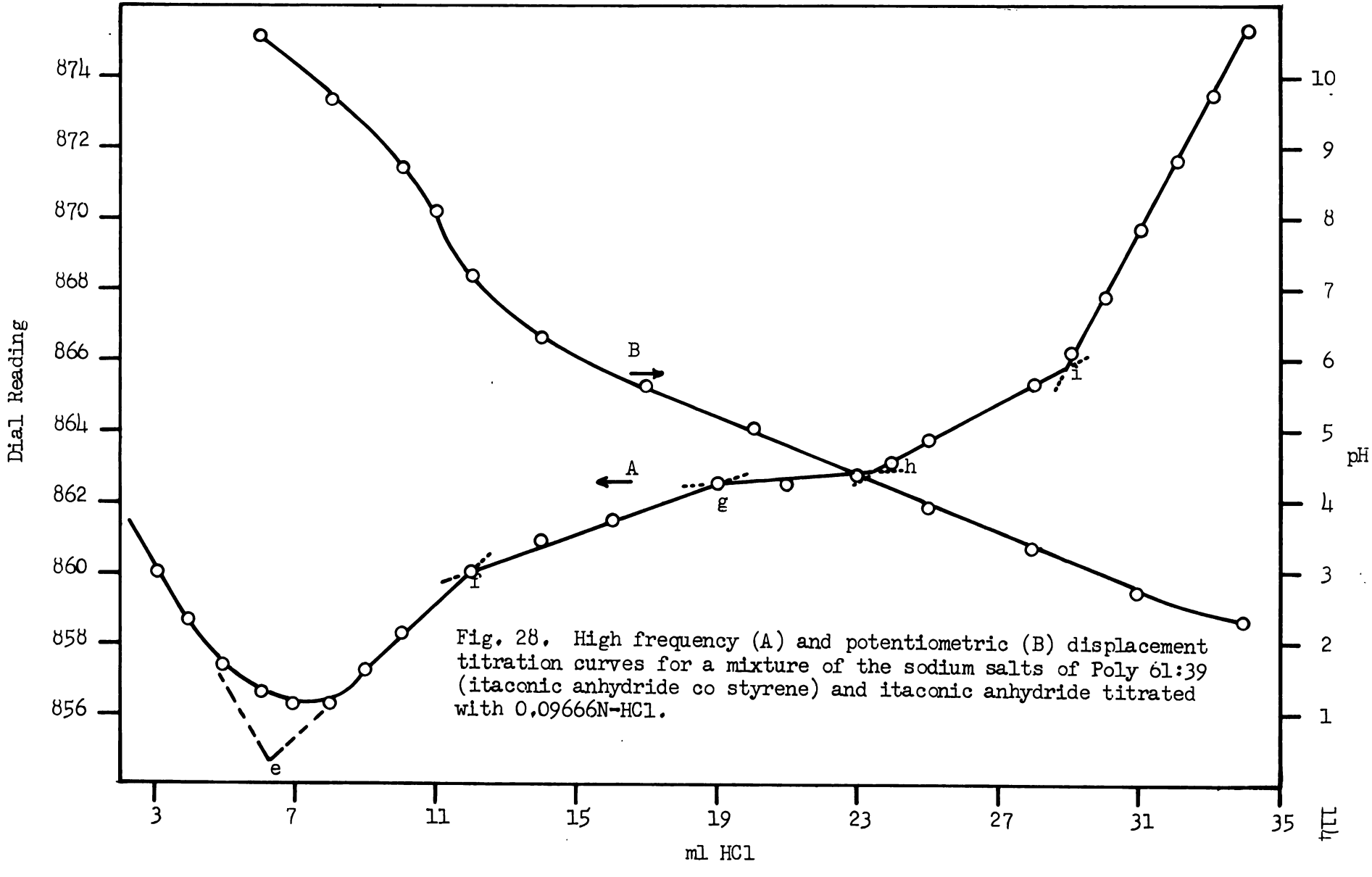


Fig. 28. High frequency (A) and potentiometric (B) displacement titration curves for a mixture of the sodium salts of Poly 61:39 (itaconic anhydride co styrene) and itaconic anhydride titrated with 0.09666N-HCl.

Mixture of Poly 61:39 (itaconic anhydride co styrene) and itaconic anhydride.

There are four acid species in this mixture and therefore four types of carboxylate ions are involved in the back titration.

The titration curve should yield four neutralization breaks and Fig. 29 does show four breaks (j-m). This is a repetition of the titration in Fig. 28, but at a lower concentration of the two substances. Note: In the previous titration of the same mixture at a higher concentration, five breaks were observed and only four were expected. Since the acid functions in the mixture are not titrated independently of each other, the observed effect might be attributed to concentration. It would be expected that in dilute solutions there is less interaction between carboxylate groups than in concentrated solutions.

j. The neutralization break at 3 ml. HCl could be the half neutralization of the copolymer. The theoretical end point is at 3 ml. HCl.

k. The break at 6 ml. HCl could be the complete conversion of the copolymer to the free acid. The theoretical end point is at 5.9 ml. HCl.

l. The break at 12.8 ml. HCl should be the conversion of all the copolymer to the free acid and the neutralization of one-half of the anhydride salt. The theoretical end point is at 10.7 ml. HCl.

m. The end point at 15.5 ml. HCl represents the free acid form of all the species. The theoretical end point is at 15.5 ml. HCl.

TABLE XIV

DATA FOR THE TITRATION IN FIGURE 29

(a) Poly 61:39 (itaconic anhydride co styrene) and (b) itaconic anhydride

Substance	Weight Sample g.	Weight Percent I.A. Segment in Copolymer	NaOH Required Meqs.	NaOH Added Meqs.	Total Meqs. of I.A. Segment from Titration	Total Meqs. of I.A. Segment from C-H Analysis
(a)	0.0205	63.2	0.228	0.228	0.601	0.601
(b)	0.0209		0.373	0.373		

	pK_1'	pK_2'	pK_5'	pK_6'
Apparent pK values from Mixture Titration	[8.2]	[10.0]	[3.8]	[5.7]
Apparent pK values from Single Titration	5.7	8.8	4.3	6.5

(a) 0.228 meqs. NaOH = 5.9 ml. HCl (0.03883 N).

(b) 0.373 meqs. NaOH = 9.6 ml. HCl (0.03883 N).

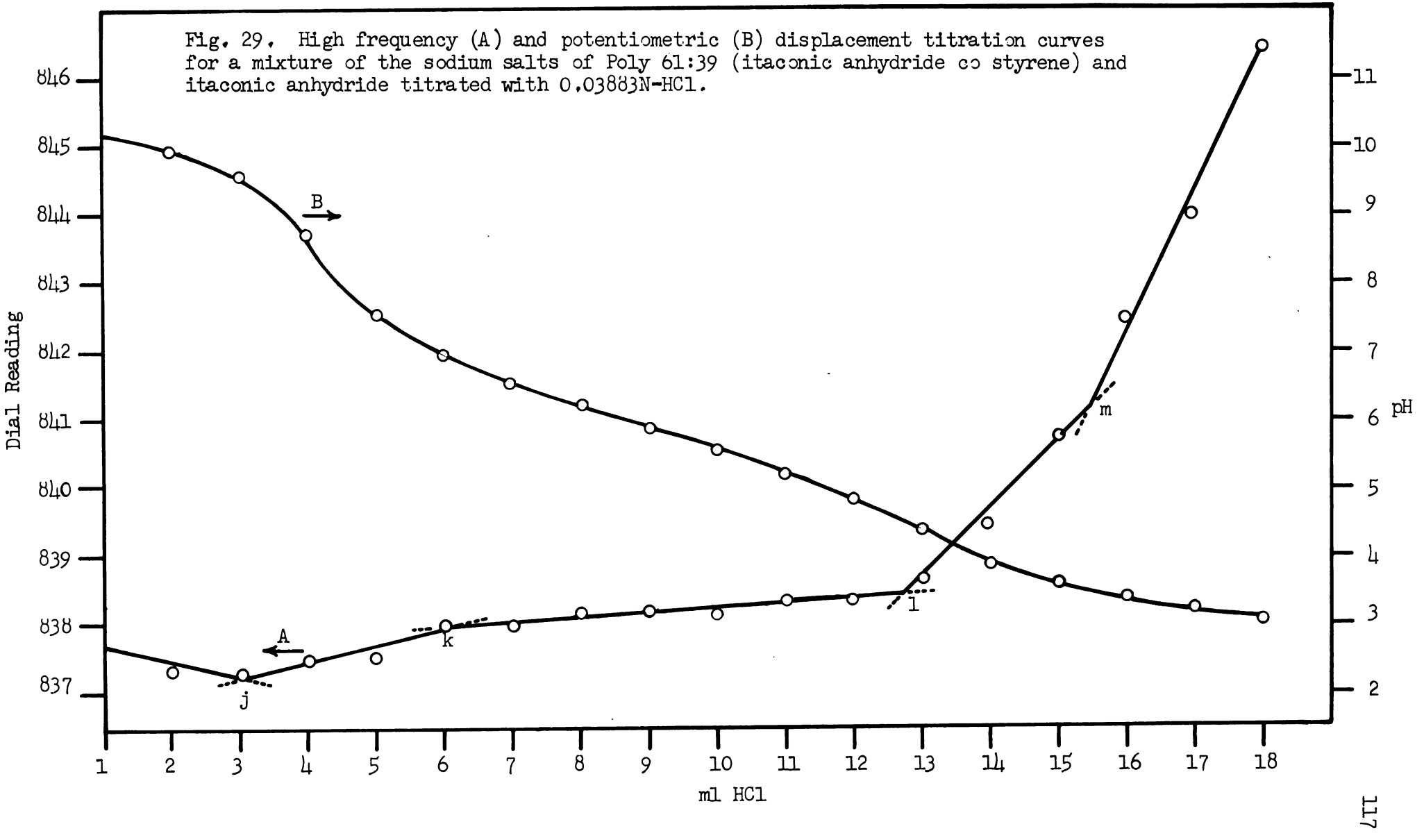


Fig. 29. High frequency (A) and potentiometric (B) displacement titration curves for a mixture of the sodium salts of Poly 61:39 (itaconic anhydride co styrene) and itaconic anhydride titrated with 0.03883N-HCl.
Dial Reading
846
845
844
843
842
841
840
839
838
837
B
A
j
k
l
m
pH
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
ml HCl
117

3. Mixture of Monoethyl ester of Poly 61:39 (itaconic anhydride co styrene) and itaconic anhydride.

There are four acid species in this mixture and therefore four types of carboxylate ions are involved in the back titration.

The titration curve should show four breaks and Fig. 30 does reveal four breaks, (n-q).

n. The neutralization break at 6.7 ml. HCl might represent the complete neutralization of the carboxylate functions in the monoester derivative. The theoretical end point is at 4.8 ml. HCl.

o. The break at 10.3 ml. HCl could be the free acid form of one-half of the anhydride. The theoretical end point is at 9.4 ml. HCl.

p. The break at 14.6 ml. HCl might be the complete conversion of the monoester derivative to the free acid and the monosodium salt of the anhydride. The theoretical end point is at 14.2 ml. HCl.

q. The break at 23 ml. HCl represents the free acid form of all the carboxylate species. The theoretical end point is at 23.6 ml. HCl.

TABLE XV

DATA FOR THE TITRATION IN FIGURE 30

(a) Monoethyl ester of Poly 61:39 (itaconic anhydride co styrene) and (b) itaconic anhydride

Substance	Weight Sample g.	Weight Percent I.A. Segment in Copolymer	NaOH Required Meqs.	NaOH Added Meqs.	Total Meqs. of I.A. Segment from Titration	Total Meqs. of I.A. Segment from C-H Analysis
a	0.1043	70.8	0.467	0.467	2.223	2.282
b	0.1020		1.815	1.815		

	pK_3'	pK_4'	pK_5'	pK_6'
Apparent pK values from Mixture Titration	[7.5]	[10.7]	[4.6]	[6.3]
Apparent pK values from Single Titration	6.4	7.8	4.3	6.5

(a) 0.467 meqs. NaOH = 4.8 ml. HCl (0.0966 N).

(b) 1.815 meqs. NaOH = 18.8 ml. HCl (0.0966 N).

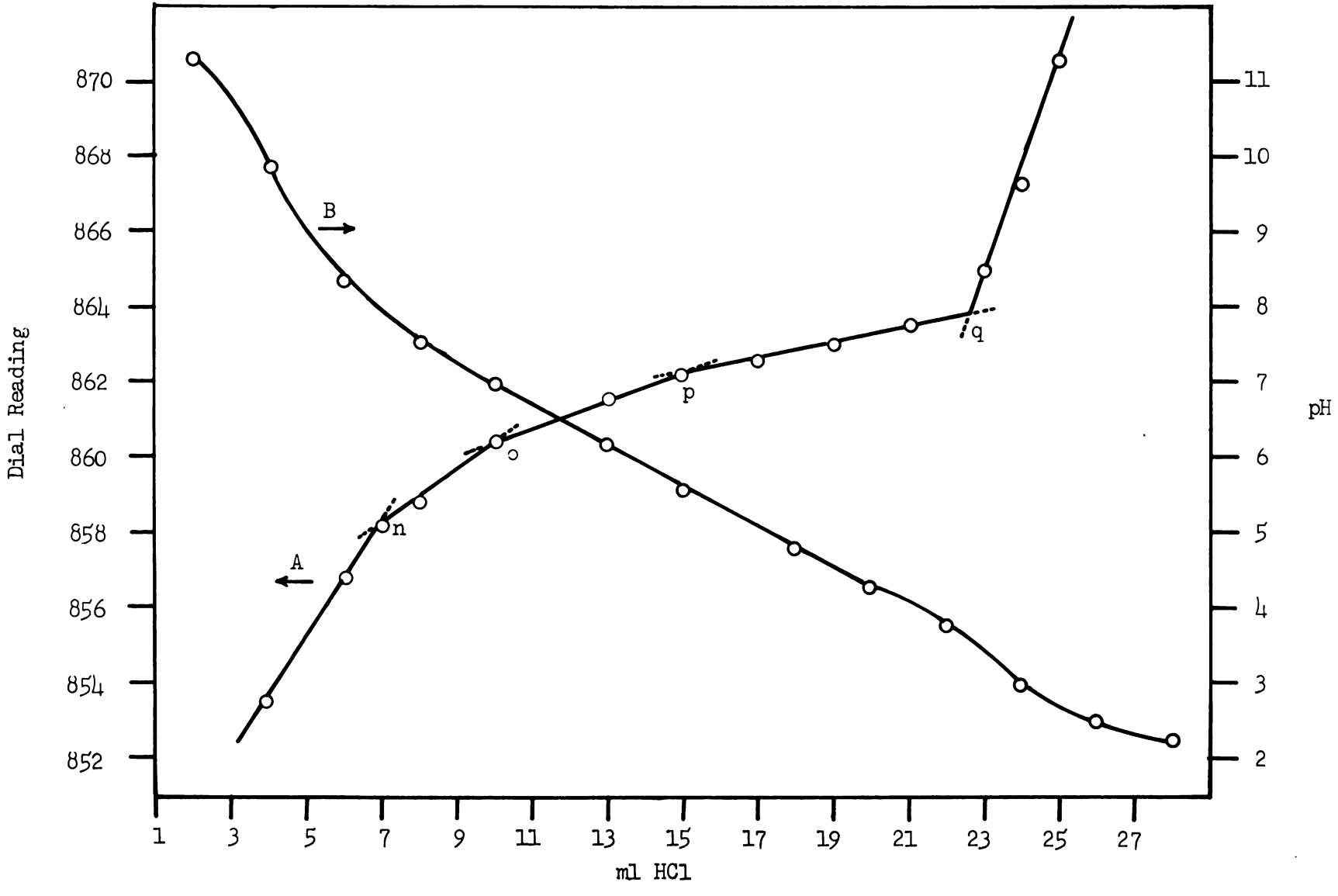
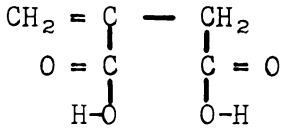
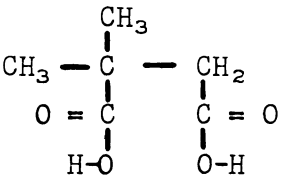


Fig. 30. High frequency (A) and potentiometric (B) displacement titration curves for a mixture of the sodium salts of the monoethyl ester of Poly 61:39 (itaconic anhydride co styrene) and itaconic anhydride titrated with 0.09666N-HCl.

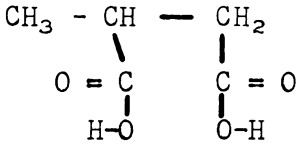
J. Titration of Some Dibasic Acids



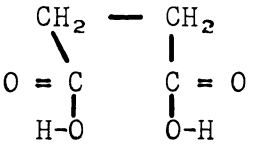
Itaconic Acid



Unsymmetrical Dimethylsuccinic Acid



Methylsuccinic Acid



Succinic Acid

An accurately weighed sample was dissolved in water. For the direct titrations, the volume was adjusted to about 180 ml., with distilled water, and the sample titrated directly with standard sodium hydroxide. The procedure for the titrations has been described in B.

For the back titrations, a known amount of standard sodium hydroxide was added to the solution of the acid in water. The volume was then adjusted to 180 ml., with distilled water, and the sample titrated with standard hydrochloric acid.

It was desired to use a quantity of acid equivalent to the anhydride content of the copolymer. In some cases this amount of acid was satisfactory for titration, but in some instances a larger sample was required.

The back titrations, (displacement titrations), were carried out for two reasons.

The first was to see how the observed pK' values of the back titrations agreed with the literature pK values determined by direct titration of the free acid. By back titration is meant the initial formation of the sodium salt by adding the known amount of the standard sodium hydroxide to the acid sample and titrating with standard hydrochloric acid to the free acid form of the species.

The second reason was to see if the pK' values determined by the titrations for any of these acids resembled the observations made for the itaconic acid segment in the copolymer.

Analysis of this titration data indicates:

1. That direct titrations and back titrations are in most cases equivalent.
2. The itaconic acid segment in the copolymer has a structure resembling that of a substituted succinic acid.

Much difficulty was encountered in the tirration of itaconic acid which in view of the excellent purity of the sample of itaconic anhydride used was unexplainable.

In this connection it should be noted that the itaconic anhydride segment cannot have the original double bond of itaconic anhydride, but is similar to a substituted succinic anhydride.

No particular difficulties were noted in the titration of the succinic acids.

The acetic acid-propionic acid mixture and the benzoic acid-salicylic acid mixture were titrated to determine if the high-frequency titrimeter could resolve each of these two acid species and show two breaks in the titration curve.

The ratio of the ionization constants of acetic and propionic acids is 1.3. It was impossible to observe two breaks in the high-frequency titration curve, and this is probably due to the fact that they are very similar in acidity.

The ratio of the ionization constants of salicylic and benzoic acids is 16.8. The high-frequency titration curve for this mixture shows two breaks. This is the first known instance of the titration, in aqueous medium, of a mixture of acids with such a low ionization constant ratio.

The titration data for these experiments are listed in Table XVII.

The following table includes the pK values observed for the back titrations, the literature values for the pK values of the direct titrations and some observed pK values for direct titrations.

TABLE XVI

pK VALUES OF SOME DIBASIC ACIDS

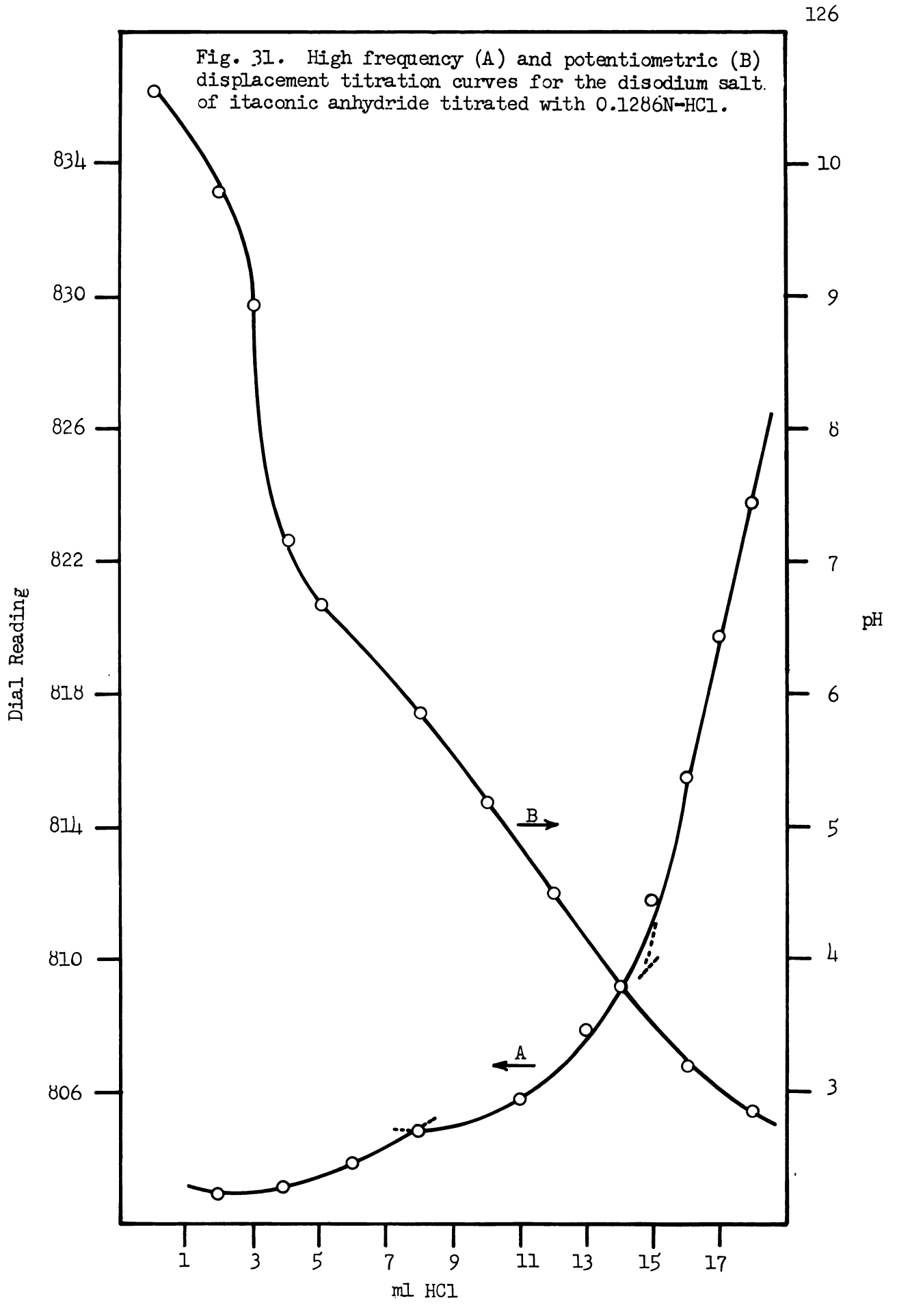
Substance	Observed Values from Back Titrations		Direct Titrations: Literature		Direct Titrations: Observed	
	pK_1'	pK_2'	pK_1	pK_2	pK_1'	pK_2'
Itaconic acid	4.3	6.5	3.8	5.6	3.8	5.5
Methylsuccinic acid	4.2	5.6	unavailable		not measured	
Unsym. dimethylsuccinic acid	4.2	6.4	4.2	6.4	4.2	6.5
Succinic acid	4.1	5.3	4.2	5.6	4.1	5.4
Benzoic acid	4.1	---	4.2	---	not measured	
Salicylic acid	2.8	---	2.8	---	not measured	

TABLE XVII

SUMMARY OF THE TITRATION DATA FOR SOME DIBASIC ACIDS

Figure Number	Substance Weighed	Sample Weight g.	NaOH Required Meqs.	NaOH Added Meqs.	Calc'd. Meqs. Acid		Meqs. Acid from Titration
31	Itaconic anhydride	0.1024	1.828	2.044	1.828		1.762
33	Itaconic acid	0.1038	1.596	1.596	1.596		1.596
34	Unsym. Dimethylsuccinic acid	0.0792	1.085	1.085	1.085		1.046
35	Methylsuccinic acid	0.1020	1.545	1.545	1.545		1.503
36	Succinic acid	0.1237	2.088	2.088	2.088		2.045
37	Salicylic acid	0.1463	1.054	1.054	1.054		0.973
	Benzoic acid	0.1295	1.054	1.054	1.054		1.055
38	Sodium acetate	0.1011	---	---	1.232	2.932	2.915
	Propionic acid	0.1260	1.691	1.691	1.700		

Fig. 31. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of itaconic anhydride titrated with 0.1286N-HCl.



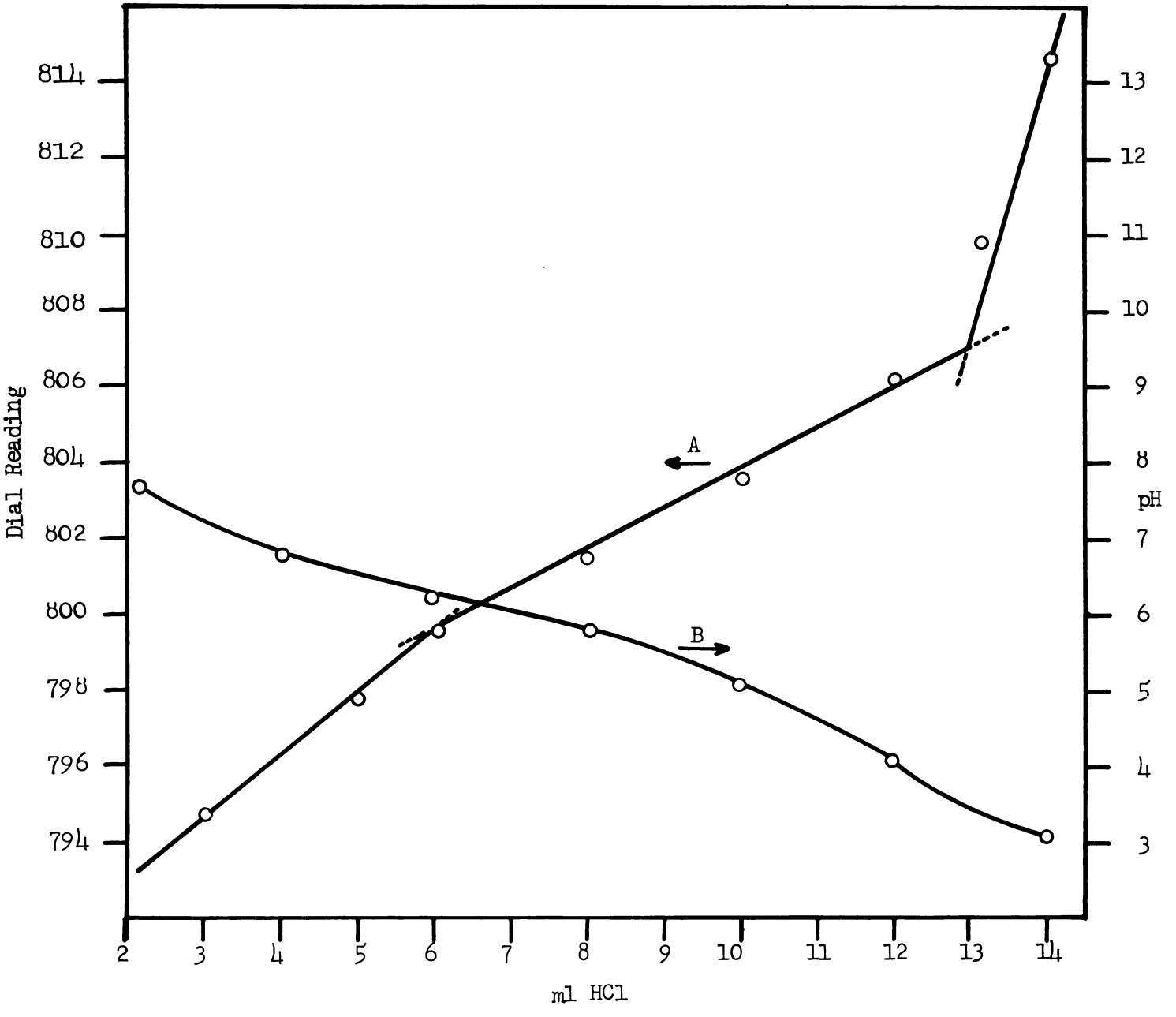


Fig. 32. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of polyitaconic anhydride titrated with 0.1286N-HCl.

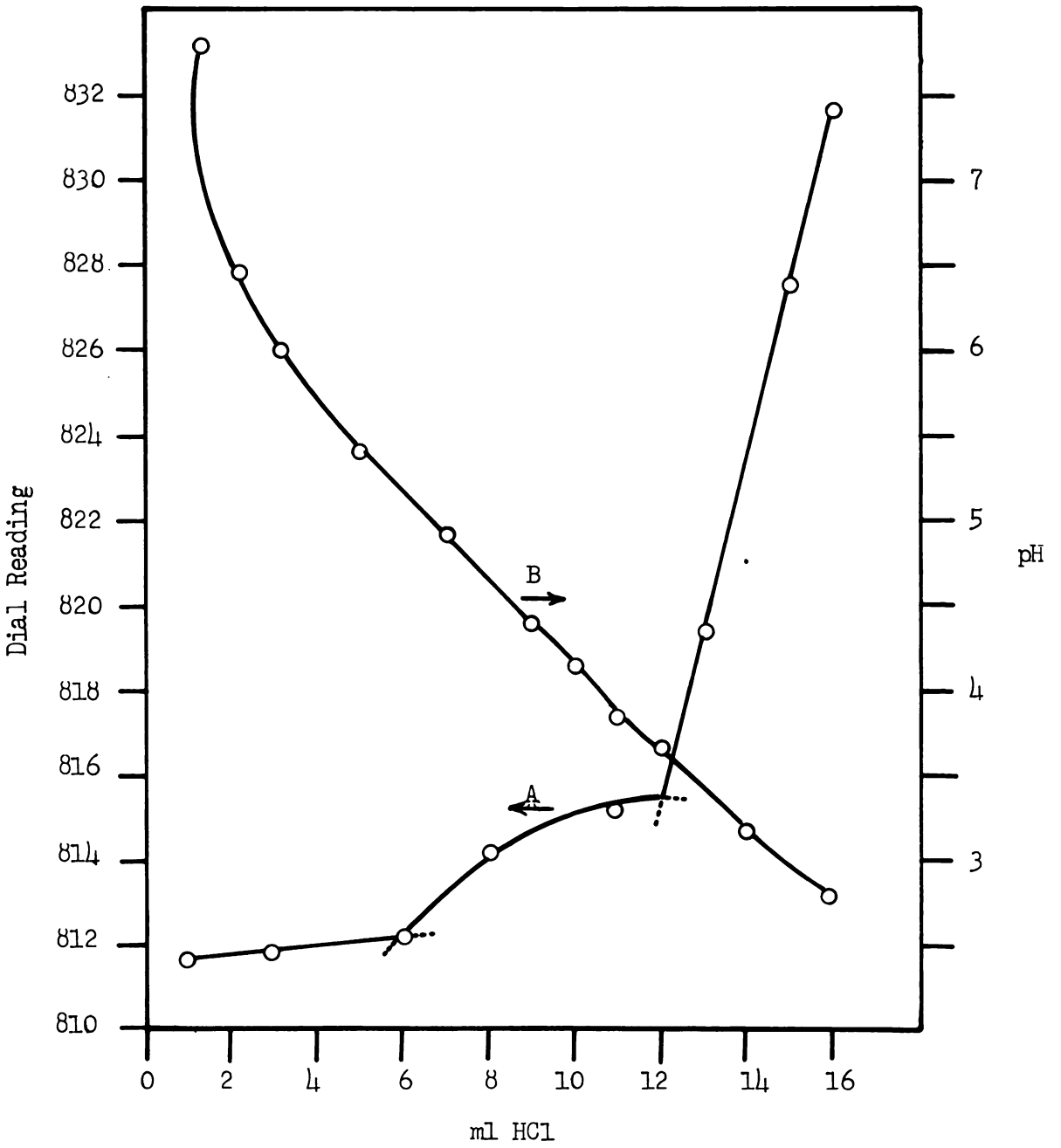


Fig. 33. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of itaconic acid titrated with 0.1286N-HCl.

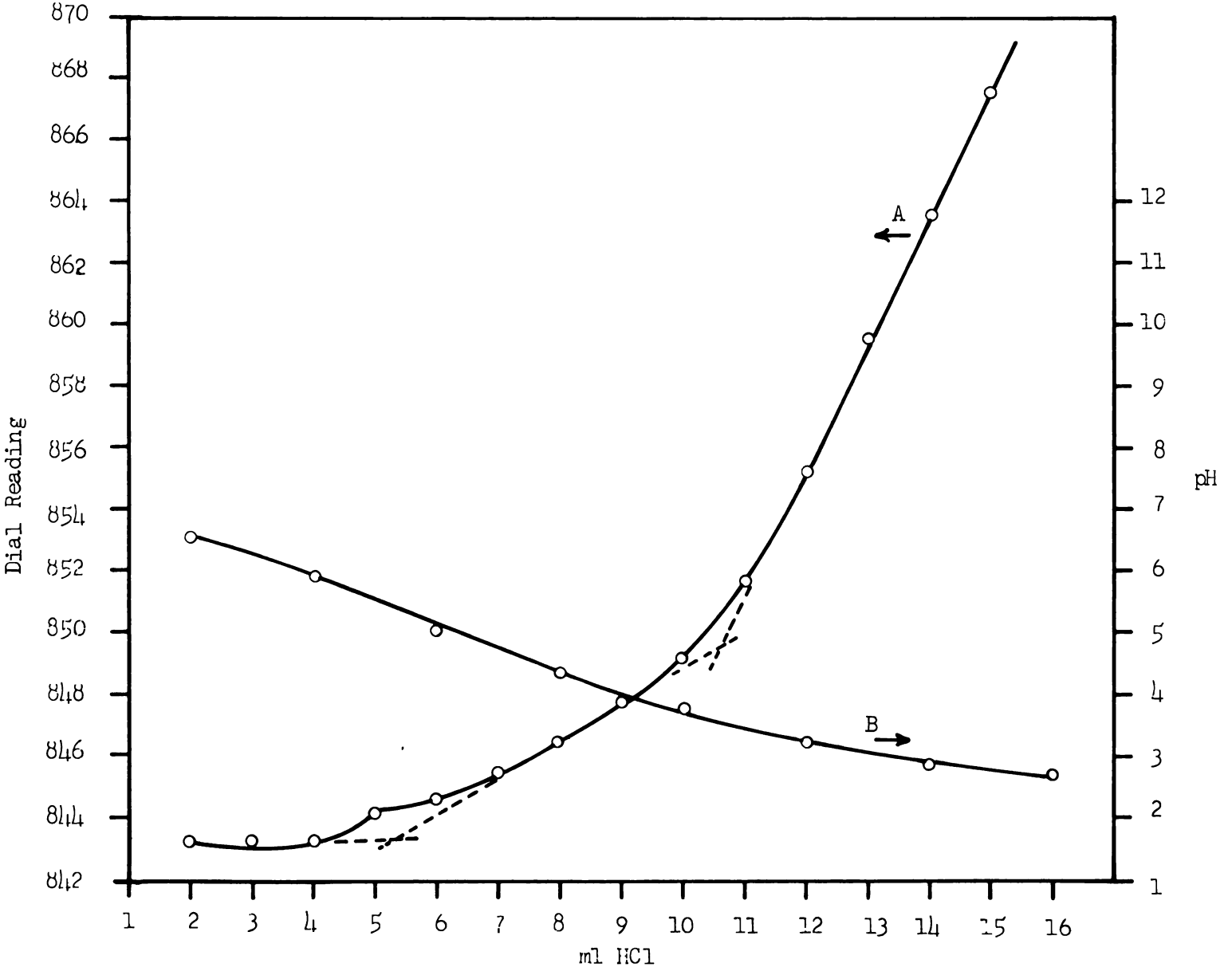


Fig. 34. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of unsymmetrical dimethylsuccinic acid titrated with 0.097[illegible]N-HCl.

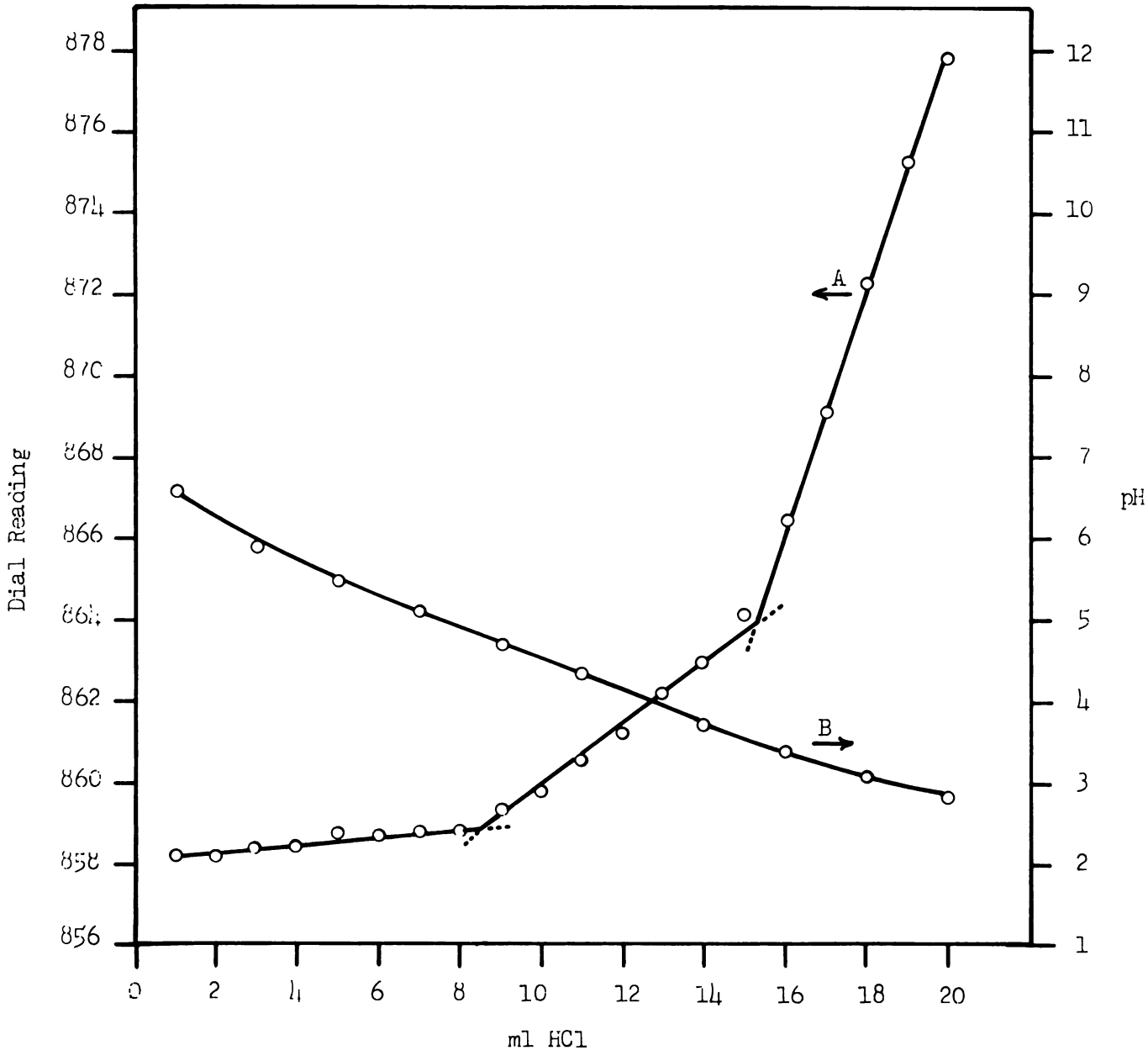


Fig. 35. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of methylsuccinic acid titrated with 0.09744N-HCl.

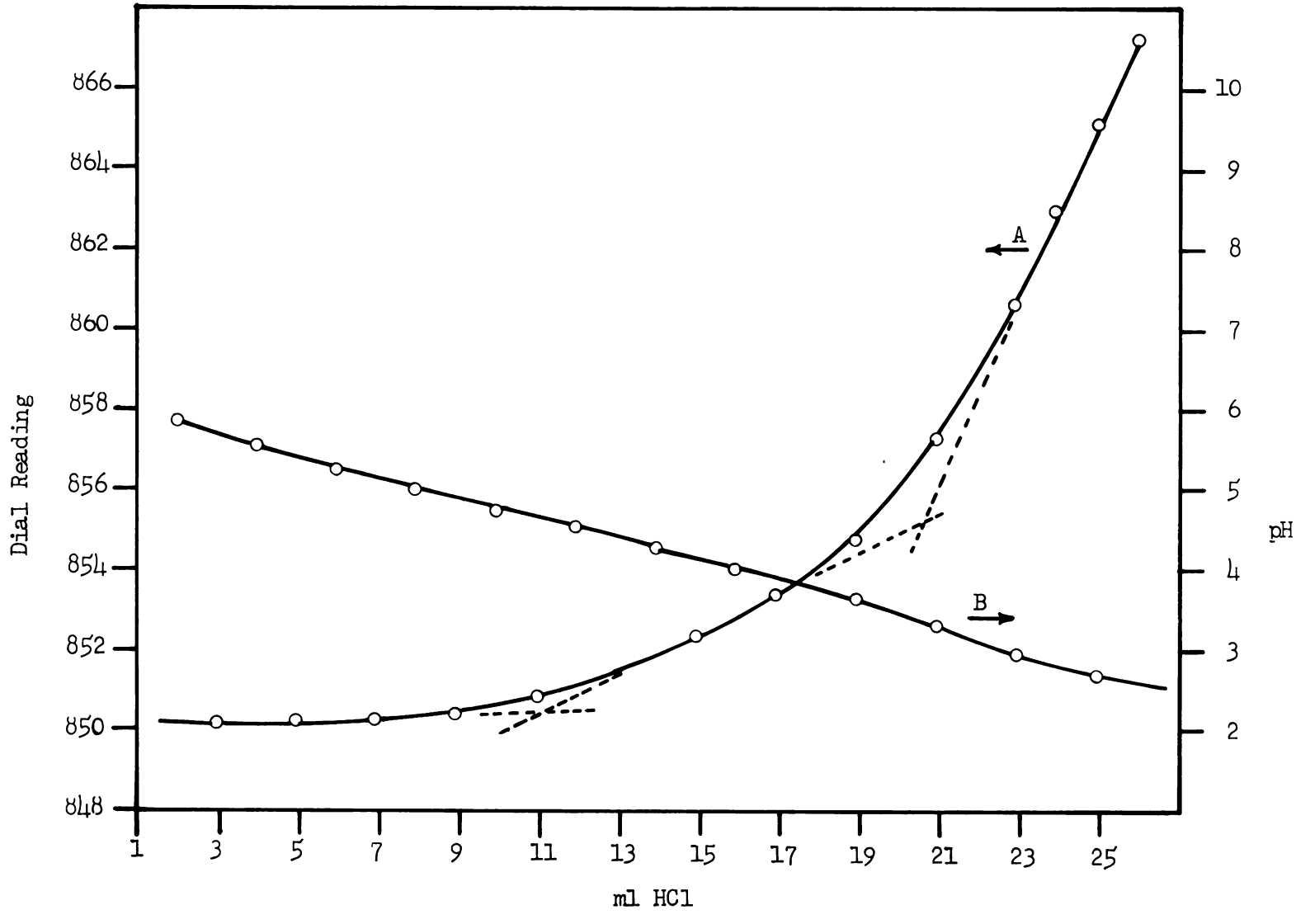


Fig. 36. High frequency (A) and potentiometric (B) displacement titration curves for the disodium salt of succinic acid titrated with 0.09744N-HCl.

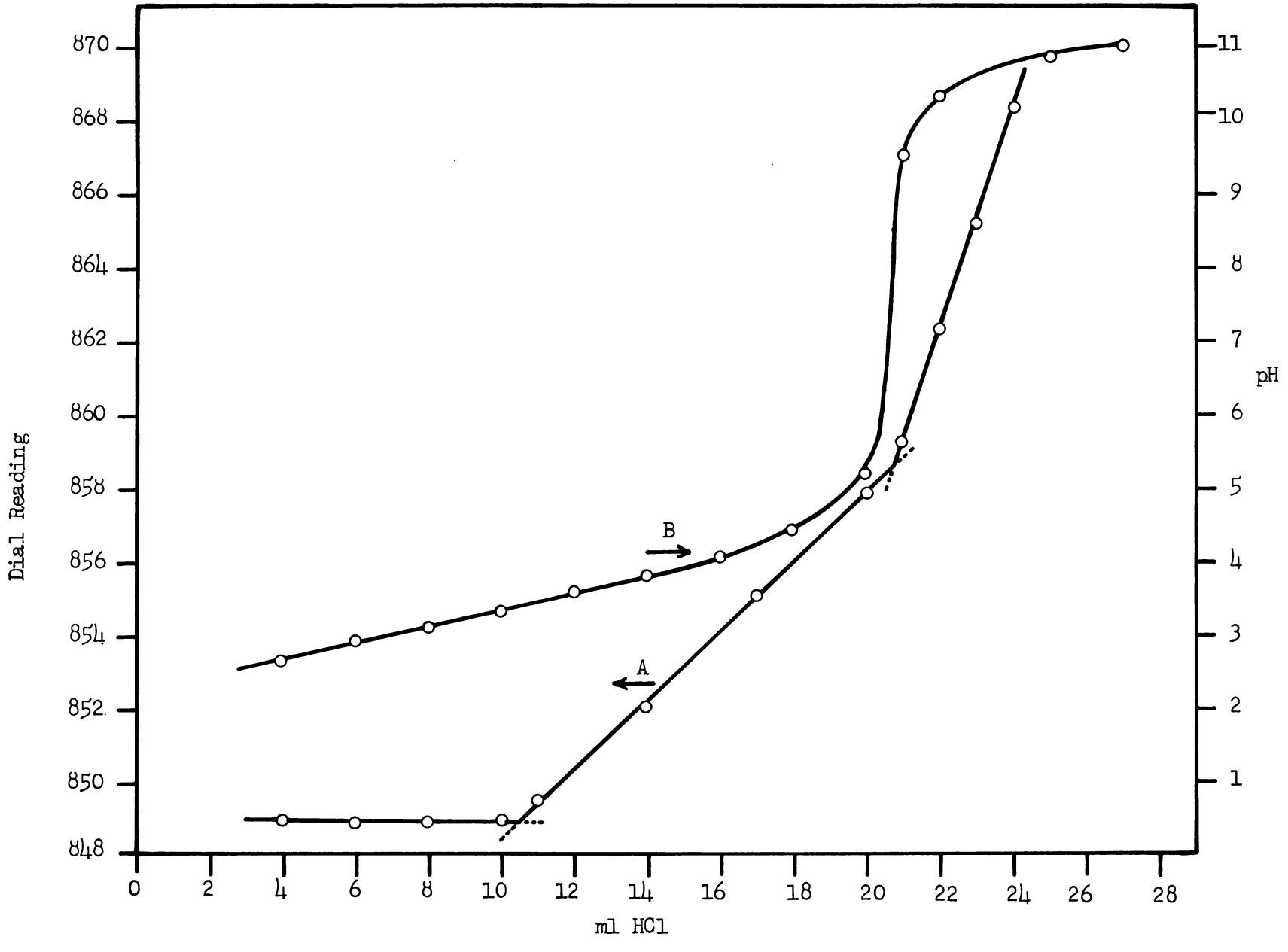


Fig. 37. High frequency (A) and potentiometric (B) displacement titration curves for a mixture of the disodium salts of benzoic and salicylic acids titrated with 0.09744N-HCl.

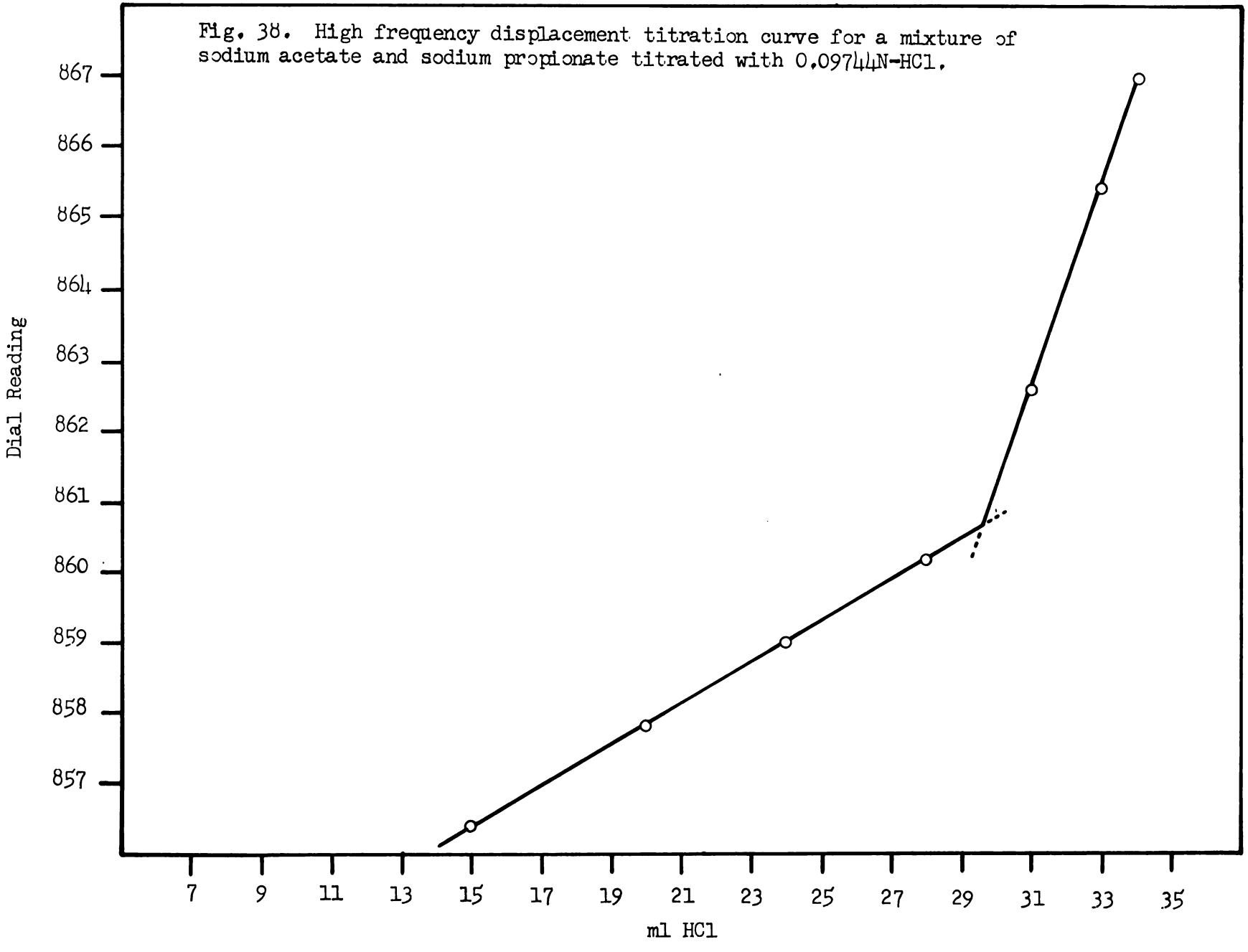
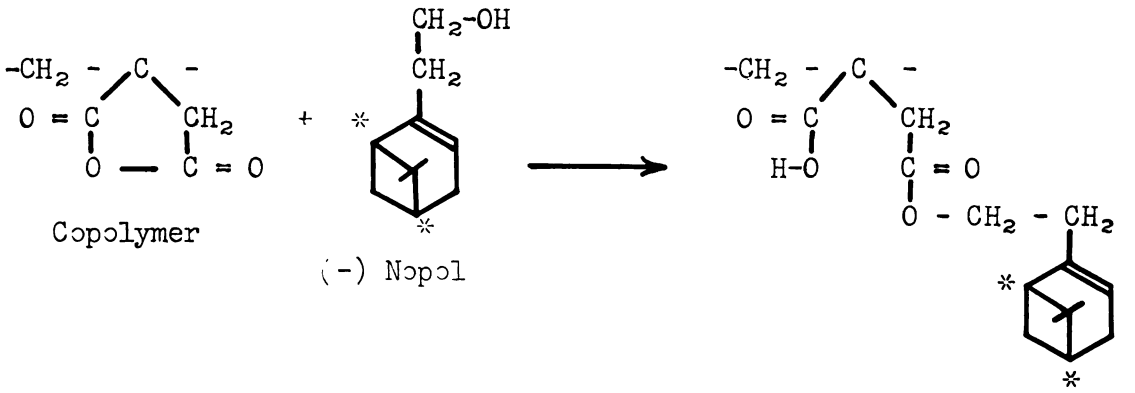


Fig. 38. High frequency displacement titration curve for a mixture of sodium acetate and sodium propionate titrated with 0.09744N-HCl.

K. Derivatives of the Itaconic Anhydride-Styrene Copolymer

1. Preparation of an Optically Active Derivative of Poly 61:39 (itaconic anhydride co styrene).



An optically active monoester derivative of the itaconic anhydride-styrene copolymer was prepared by the reaction of an optically active primary alcohol with the anhydride segment of the copolymer to form a monoester.

The optically active primary alcohol selected was 6,6-dimethyldicyclo-(1,1,3)-hept-2-ene-2-ethanol, having the common name, nopol. The optical rotation of pure nopol is $[\alpha]_D^{25} = -36.5^\circ$ (10 cm. tube). Nopol is formed by the action of β-pinene and formaldehyde (56). Regardless of the source of β-pinene, it occurs as the optically pure levo form.

A weighed sample of the copolymer was dissolved in tetrahydrofuran. A weighed quantity of nopol sufficient to form a monoester was added to the reaction flask. A reflux condenser was attached to the flask and the mixture refluxed for four hours. The solution was cooled and on the addition of water a precipitate was formed. The precipitate was filtered with suction, washed with ether and dried in a drying pistol

at the reflux temperature of acetone. The supernatant showed no optical rotation.

A 1.0449 g. sample of the monoester was dissolved in tetrahydrofuran and the volume of the solution made up to 50 ml. in a volumetric flask. A 10 cm. polarimeter tube was filled with the solution and the rotation was measured with a Rudolph Polarimeter Model 80. The observed rotation was -0.772° and the specific rotation was calculated to be $[\alpha]_D^{22} = -3.69^{\circ}$.

A 1.0059 g. sample of the monoester was dissolved in acetone and the solution made up to a volume of 50 ml. in a volumetric flask. The observed rotation was -1.266° and the specific rotation was calculated to be $[\alpha]_D^{22} = -6.29^{\circ}$.

2. Preparation of a Network Polymer

In a 250 ml. three-neck flask fitted with a reflux condenser, a mechanical stirrer, and a thermometer were placed 4 g. of Poly 61:39 (itaconic anhydride co styrene) and 50 g. of ethylene glycol. On heating the copolymer went into solution and further heating to 170°C the solution began to gel. The gel appeared in about thirty minutes. Heating was continued for one hour after the appearance of the gel. The gel was then removed from the flask with some difficulty and washed thoroughly with ether. The solid product was then dried in vacuo.

The solid derivative was insoluble in a variety of solvents, indicating that a network polymer had formed.

The solid copolymer was finely ground in an agate mortar. To a 0.2782 g. sample of the fine powder were added 2.0880 meqs. of NaOH and

the suspension was allowed to sit for thirty minutes. The suspension was then filtered off and washed with several portions of water. The supernatant was then titrated with standard HCl and 1.3815 meqs. of NaOH were present. Thus 0.7065 meqs. of NaOH were used by the sample.

To the residue was then added 1.9488 meqs. of HCl and after allowing the suspension to sit for thirty minutes the residue was filtered and washed thoroughly. The supernatant was titrated with standard NaOH and 1.2319 meqs. of HCl were present. Thus 0.7169 meqs. of HCl were used by the sample.

It was calculated that 22.5% of all the carboxyl groups in the sample were free, and thus 77.5% of the carboxyl groups were esterified or cross-linked.

L. Stability to Hydrolysis

1. Stability to Hydrolysis of the Monoethyl Ester of Poly 61:39 (Itaconic Anhydride co Styrene).

A finely ground sample (0.1252 g.) of the monoethyl ester derivative was weighed into a conductance cell. To the cell were added 3 ml. of ethyl alcohol to effect solution of the copolymer and also a quantity of conductance water. The cell was allowed to reach a temperature equilibrium of 25 ± 0.1°C in an oil bath. A ten percent excess of 0.1044N-NaOH was then added and the time recorded. The cell was filled to a volume of about 25 ml. The resistance readings were taken over a 25 hour period and are recorded in Table XLIV.

The data indicate that practically no hydrolysis has taken place at 25 ± 0.1°C. for 25 hours.

2. Stability to Hydrolysis of the Dimethyl Ester of Poly 61:39 (Itaconic Anhydride co Styrene).

A finely ground sample (0.0962 g.) of the dimethyl ester was weighed into the conductance cell. The dimethyl ester of the copolymer was not found to be completely soluble in any suitable solvent. A mixture of 5 ml. of ethanol and acetone was added to the cell and some of the diester dissolved and some remained suspended in the system. A quantity of conductance water was added and the cell placed in an oil bath at 25° ± 0.1°C to reach equilibrium. A ten percent excess of 0.1044N-NaOH was added, the volume adjusted to about 25 ml. and the time recorded. The resistance readings were taken over a 31 hour period and are recorded in Table XLV.

The data indicate that practically no hydrolysis has taken place at 25 ± 0.1°C. for 31 hours.

M. Infrared Spectra

Infrared spectra were obtained for polyitaconic anhydride, poly 61:39 (itaconic anhydride co styrene), the monoethyl ester of poly 61:39 (itaconic anhydride co styrene), the monobenzyl ester of poly 57:43 (itaconic anhydride co styrene), the mononopol ester of poly 61:39 (itaconic anhydride co styrene), the dimethyl ester of poly 61:39 (itaconic anhydride co styrene), the partial diethyl ester of poly 61:39 (itaconic anhydride co styrene), styrene, and hexachlorobutadiene.

The spectrum of styrene was determined in hexachlorobutadiene, and the spectrum of hexachlorobutadiene was obtained versus a salt plate. The spectrum of the dimethyl ester of poly 61:39 (itaconic anhydride

co styrene) was obtained in solution in hexachlorobutadiene and also as a mull with this solvent.

The remainder of the spectra were obtained as mulls with hexachlorobutadiene. The instrument used in all cases was the Perkin-Elmer double beam recording spectrophotometer.

The infrared spectra are shown in Figures 39 through 48.

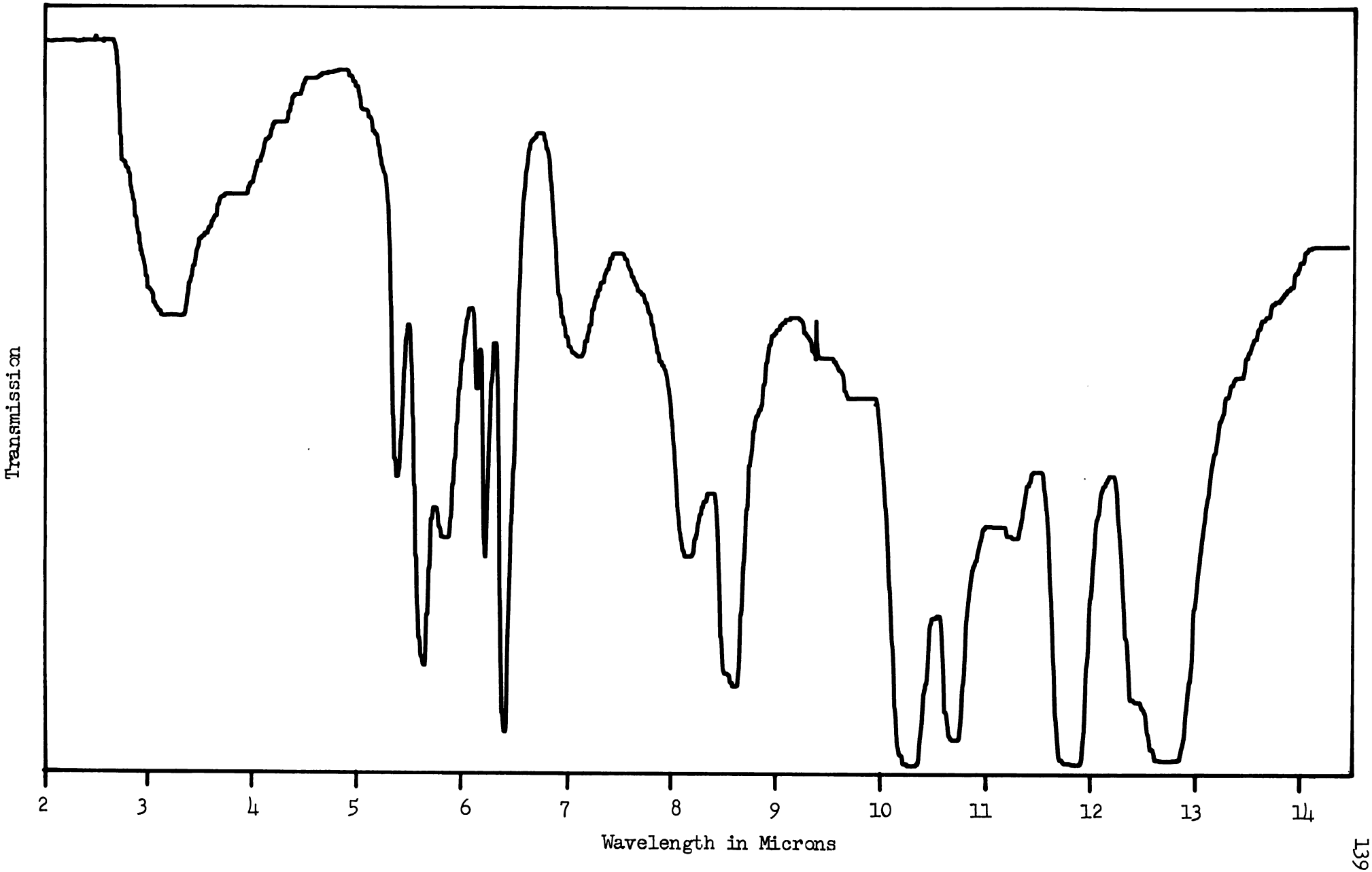


Fig. 39. Infrared spectrum of polyitaconic anhydride mull with hexachlorobutadiene.

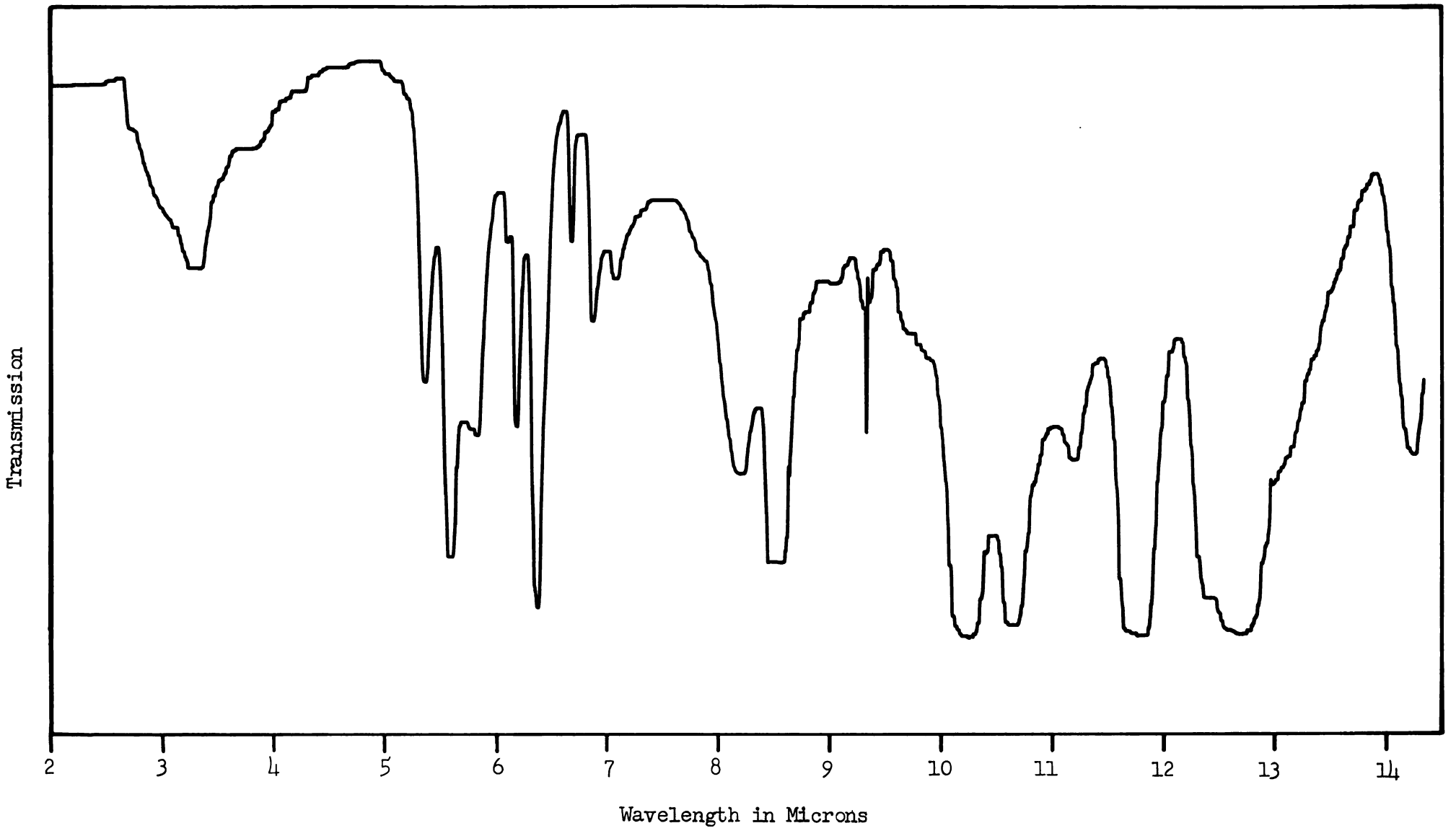
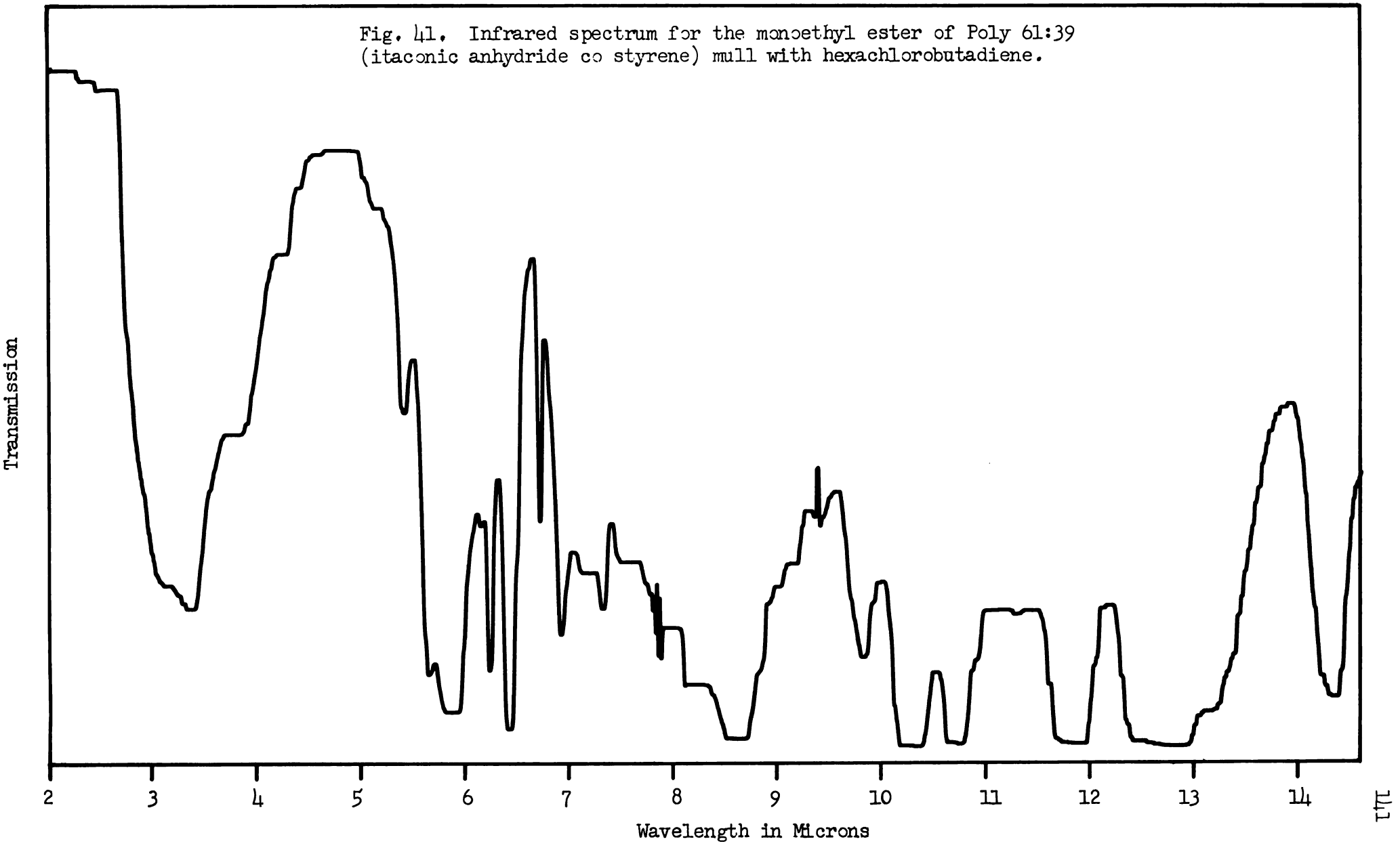


Fig. 40. Infrared spectrum of Poly 61:39 (itaconic anhydride co styrene) mull with hexachlorobutadiene.

Fig. 41. Infrared spectrum for the monoethyl ester of Poly 61:39 (itaconic anhydride co styrene) mull with hexachlorobutadiene.



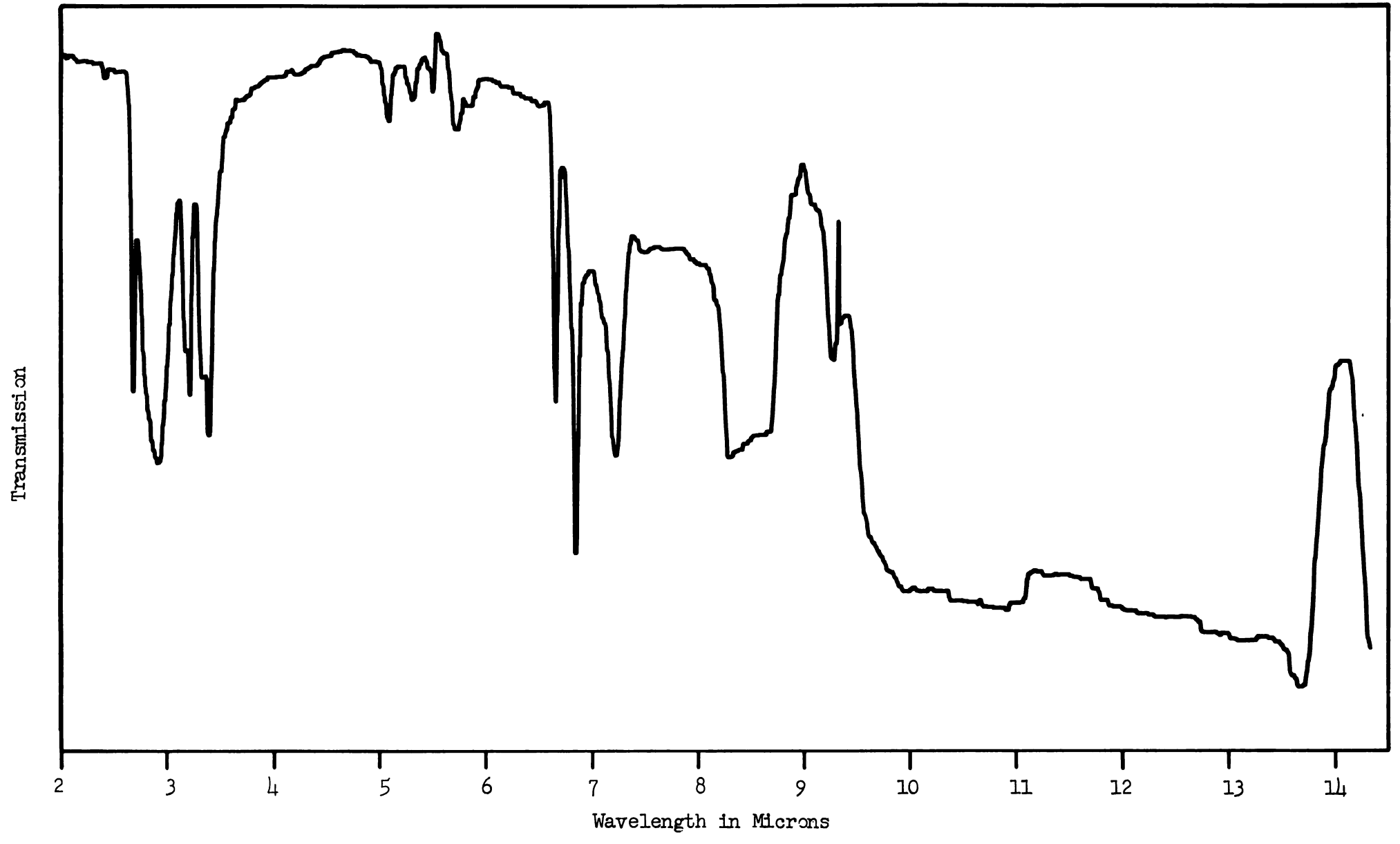
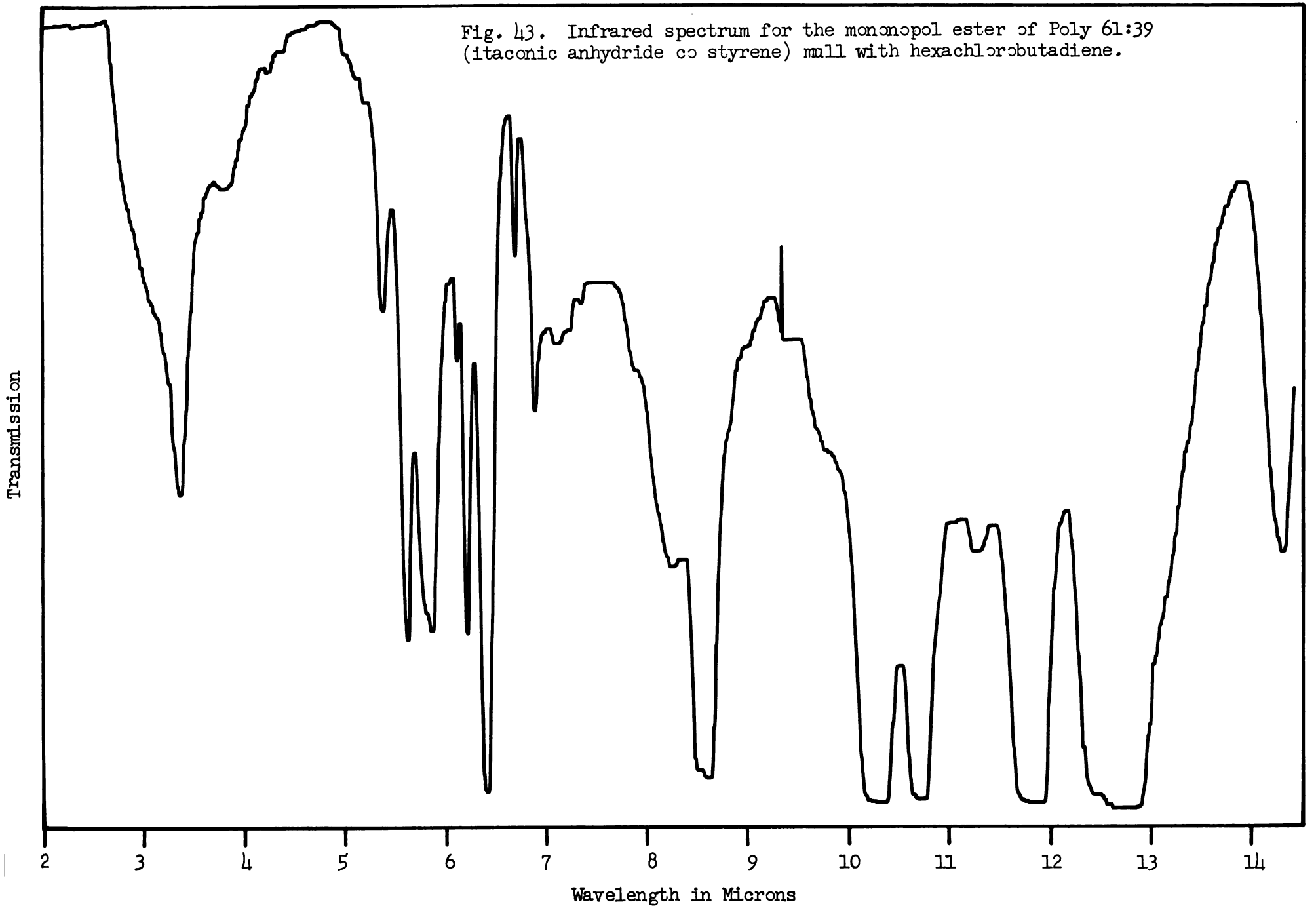


Fig. 42. Infrared spectrum for the monobenzyl ester of Poly 57:43 (itaconic anhydride co styrene) mull with hexachlorobutadiene.

Fig. 43. Infrared spectrum for the mononopol ester of Poly 61:39 (itaconic anhydride co styrene) mull with hexachlorobutadiene.



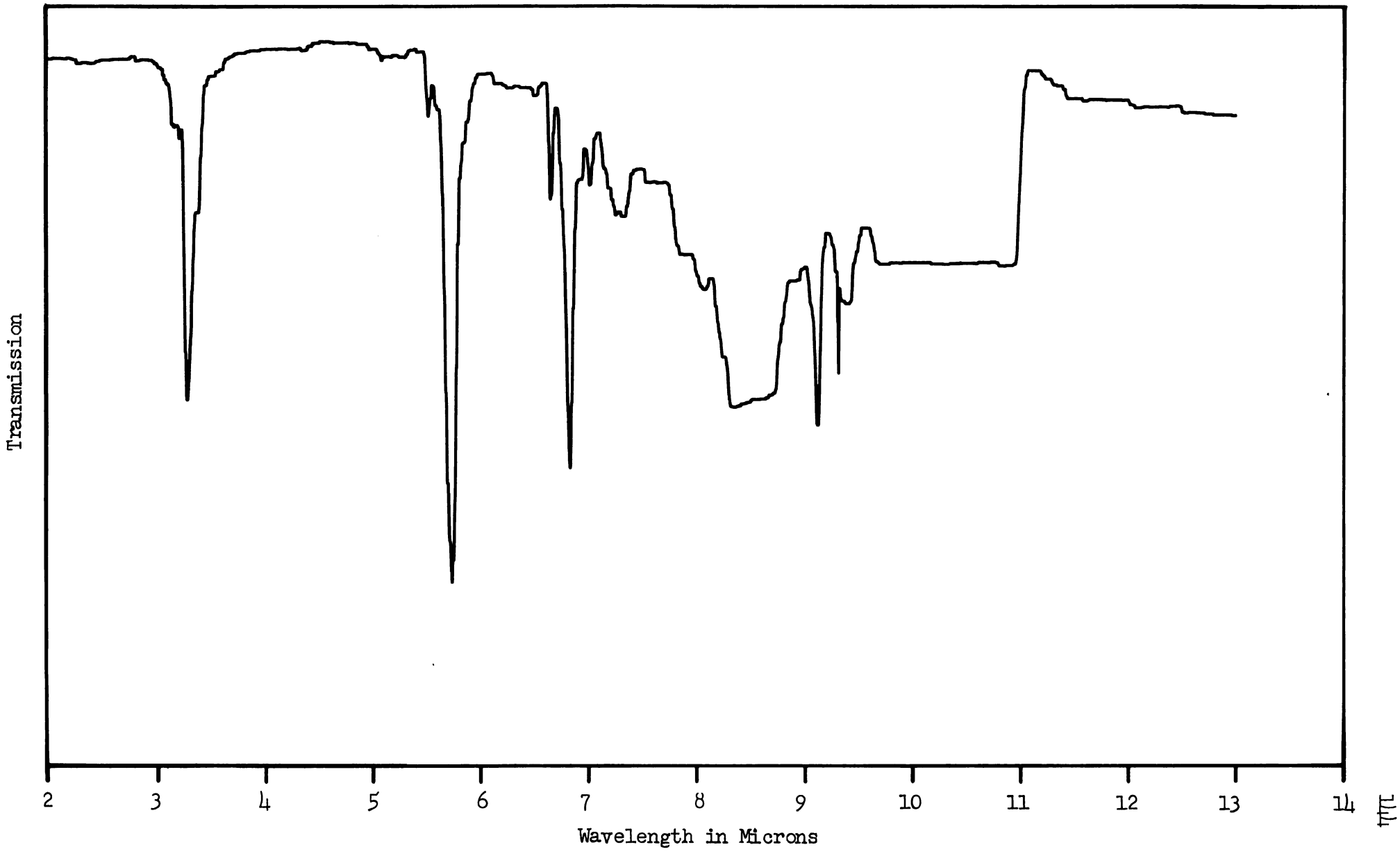


Fig. 44. Infrared spectrum for the dimethyl ester of Poly 61:39 (itaconic anhydride co styrene) in hexachlorobutadiene.

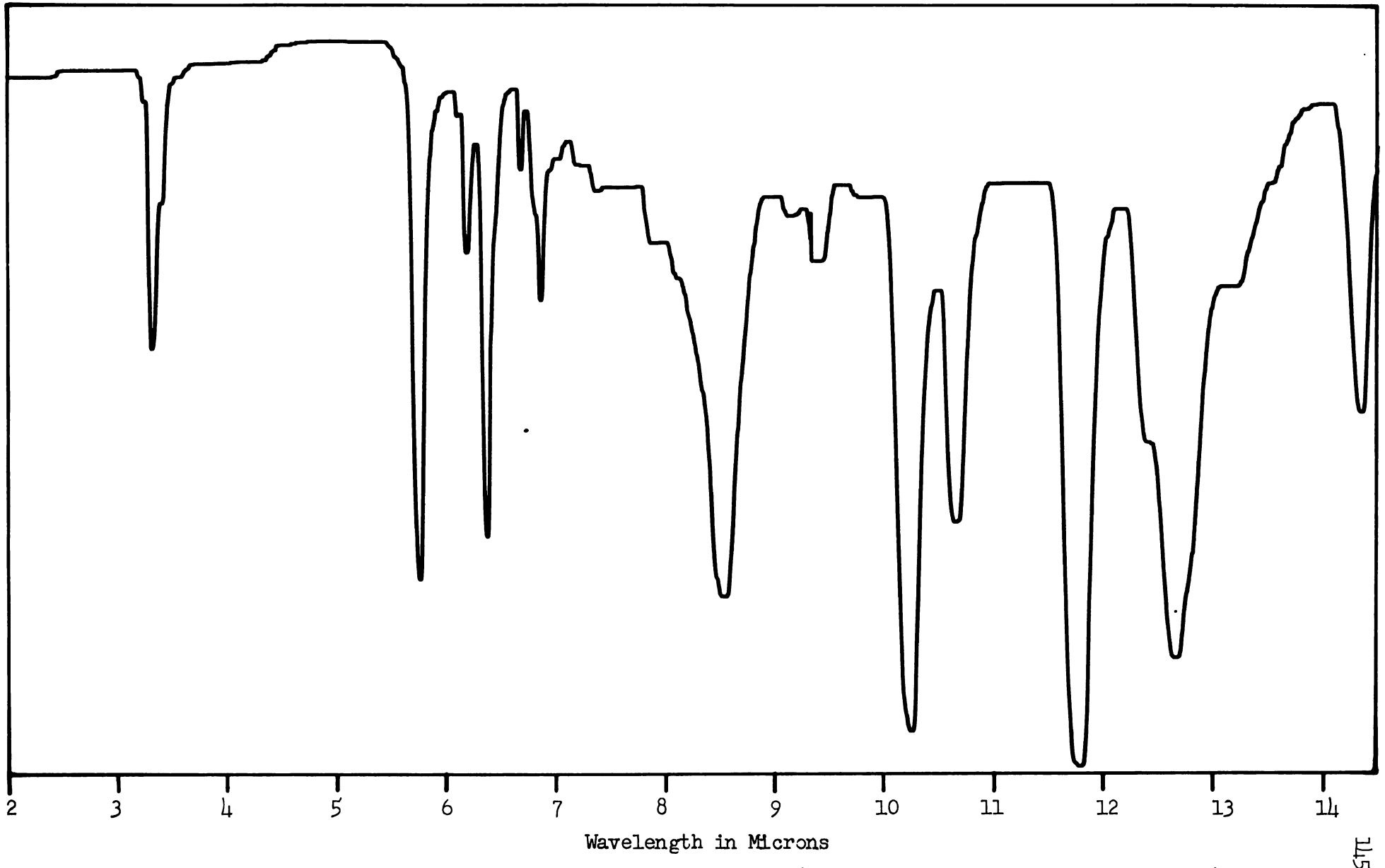


Fig. 45. Infrared spectrum for the dimethyl ester of Poly 61:39 (itaconic anhydride co styrene) mull with hexachlorobutadiene.

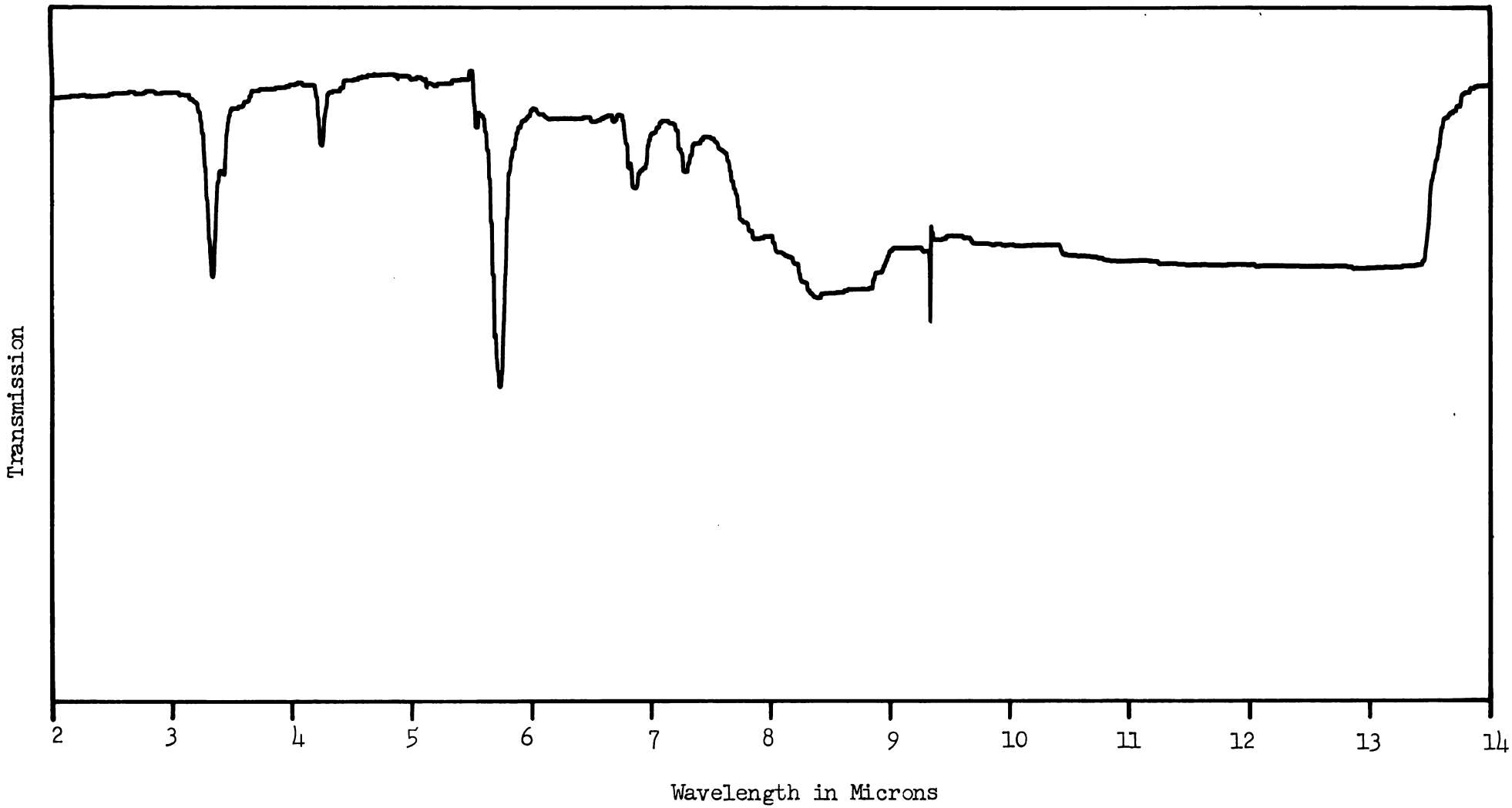


Fig. 46. Infrared spectrum for the partial diethyl ester of Poly 61:39 (itaconic anhydride co styrene) in hexachlorobutadiene.

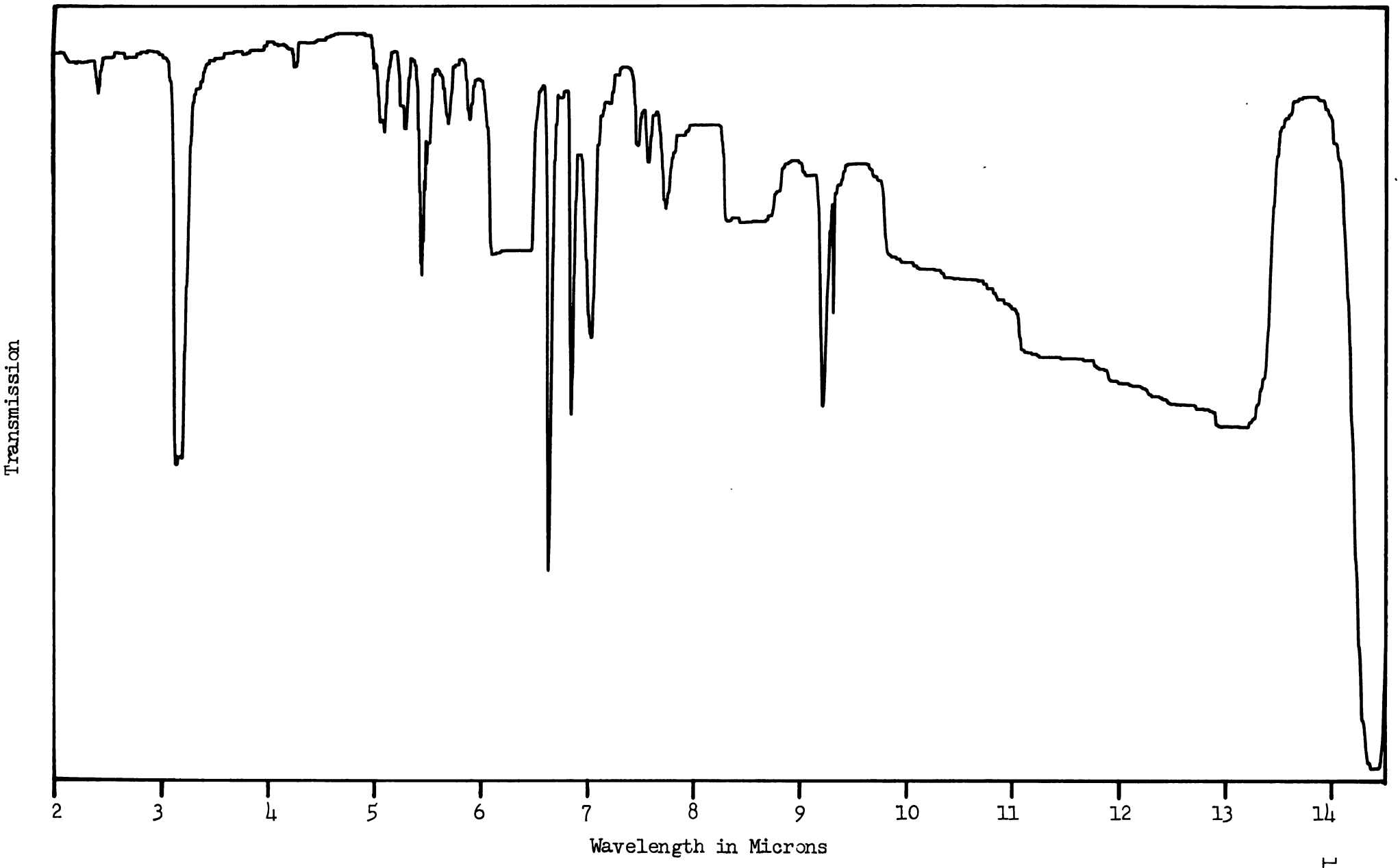


Fig. 47. Infrared spectrum of styrene in hexachlorobutadiene.

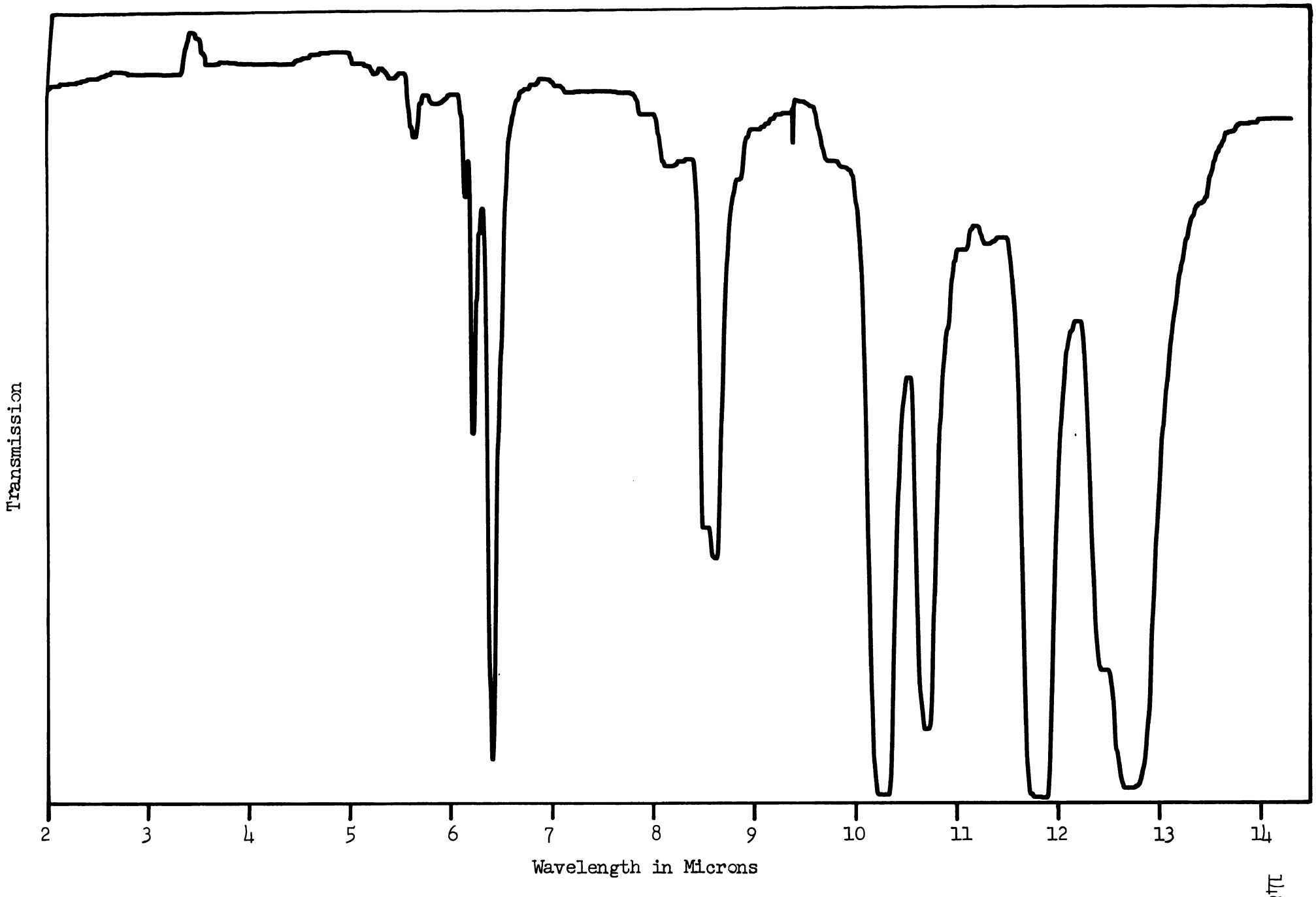


Fig. 48. Infrared spectrum of hexachlorobutadiene versus salt plate.

DISCUSSION

A copolymer of itaconic anhydride-styrene can be prepared from the monomers with the use of almost any free radical catalyst. Benzoyl peroxide was used as the catalyst in these preparations since it is readily available in high purity.

A copolymer of itaconic anhydride-styrene may be prepared in benzene or tetrahydrofuran. Benzene was used as a reaction medium because it possessed certain advantages in that:

1) An insoluble copolymer results which can be readily filtered from the benzene solvent, thus separating it from the soluble monomers.
2) The copolymer produced was a granular white powder.
3) The method gave a greater product yield in a reasonable time due to a faster reaction rate.
4) The course of the reaction could be followed by the extent of precipitation.

The use of tetrahydrofuran as a reaction medium offers several disadvantages.

1) The copolymer produced is soluble and must be precipitated by the addition of the non-solvent ether.
2) This precipitated product was a gelatinous, adhesive mass, difficult to wash, extract, and purify. The copolymers prepared and used for this portion of the work (data tabulated in Table VI) were prepared in benzene using a benzoyl peroxide catalyst.

The monoester derivatives were prepared by reaction of the itaconic anhydride-styrene copolymer with the desired alcohol. Moran and Siegel (58) have shown that in anhydrous solutions organic anhydrides form the monoester of primary alcohols with the speed of ionic reactions. This work supports the views expressed by Moran and Siegel. The reaction of the itaconic anhydride-styrene copolymer with alcohol was indeed rapid. The approximate times required for reaction with various alcohols are listed on page 79. By using a larger quantity of alcohol, or inert solvent, these times may be shortened.

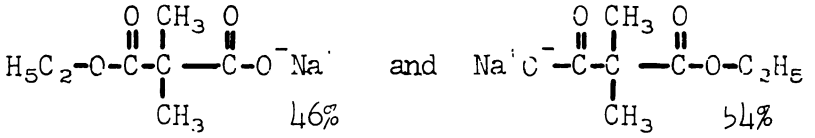
The monoesters of the copolymer were isolated by precipitation with the non-solvent water or by distilling the excess alcohol under reduced pressure. If a large quantity of a monoester derivative is desired, isolation by precipitation with water is preferable since it is rapid and yields a white granular powder which can be easily handled. This investigation has also revealed that no hydrolysis of the monoester derivative occurs under these conditions, see page 136.

A monomethyl ester was prepared from the disodium salt of the itaconic anhydride-styrene copolymer by reaction with dimethyl sulfate. This experiment was carried out for two reasons. The first was to determine if the copolymer could be esterified starting from the acid form. The second reason was to determine if this esterification produced two isomeric acid esters as were produced in the reaction of the copolymer with an alcohol. The high-frequency titration curve, Fig. 22, indicates that two isomeric acid esters are produced by the esterification with dimethyl sulfate. The pK values for this monoester derivative having an anhydride content of 63.2% are: $pK_1^{\prime\prime}=6.2$, $pK_2^{\prime\prime}=8.6$. The pK values

for the monoester derivative prepared by reaction with methanol for the copolymer having an anhydride content of 58.3% are: $pK_1''=6.3$, $pK_2''=7.9$. Thus it appears that the two monoesters prepared by different methods are identical.

As shown on page 78, two isomeric acid esters result when an alcohol reacts with the itaconic anhydride segment of the copolymer. The evidence obtained from the high-frequency titration curves for all the monoester derivatives indicates that both acid ester isomers are present.

LePeletier de Rosanbo (59), isolated two isomeric ethyl esters on reacting unsymmetrical dimethylsuccinic anhydride with sodium ethylate. The values reported are:



The percent of each type of acid ester isomer agrees very well with those reported in this thesis for the isomers obtained by the reaction of the itaconic anhydride segment of the copolymer with an alcohol. The data are tabulated in Table VIII.

Farmer and Kracovski (60) isolated two isomeric ethyl esters on reacting unsymmetrical dimethylsuccinic anhydride with ethyl alcohol.

The preparation of the diester derivatives was accomplished by the reaction of diazomethane with the monoester derivative. With the exception of the hazardous nature of this reagent, this method of preparation appears to be the most favorable at this time. The excess diazomethane presents no problem and there is no impurity to contaminate

the copolymer. One limitation of this procedure is that it does not lend itself to the preparation of diester derivatives in large quantities. No more than 0.2 mole of diazomethane should be produced at any one time, due to the explosive nature of the reagent.

The carbon-hydrogen analysis of the diester derivative prepared with diazomethane agrees well with the calculated value.

One attempt to prepare a diethyl ester derivative by reaction with diazoethane resulted in a partial diester derivative, as shown by carbon-hydrogen analysis. The partial diester precipitated as formed and this might account for the incomplete esterification. Some of the free carboxyl groups were probably imbedded in the precipitated product and were thus unavailable for esterification.

Numerous attempts to prepare a diester derivative employing gaseous hydrogen chloride or sulfuric acid as catalysts failed.

In all cases the monoester derivative was obtained as indicated by carbon-hydrogen analyses and the high-frequency titration curves.

The use of sulfuric acid as a catalyst in the preparation of diester derivatives is not recommended. It was found impossible to purify the copolymer and get it free of sulfur. The inability to remove solid catalysts from the product limited the use of preparative procedures involving these catalysts.

In the case where gaseous hydrogen chloride was passed into the reaction vessel, it was found that it could be removed by the addition of benzene to the reaction flask and distilling under reduced pressure. The product isolated was free of chloride.

The preparation of the optically active monoester derivative of the itaconic anhydride-styrene copolymer was accomplished by reacting the copolymer with the optically active primary alcohol, nopol. The optical activity was measured in acetone and tetrahydrofuran. The specific rotation in acetone was $[\alpha]_D^{22} = -6.29^\circ$ and in tetrahydrofuran $[\alpha]_D^{22} = -3.69^\circ$. The observed difference in the specific rotation may be due to a difference in solvation and association in the respective solvents.

The analysis of the copolymers to determine the composition depends on the determination of the itaconic anhydride segment in the copolymer. The itaconic anhydride-styrene copolymer was dissolved in acetone and a known quantity of standard sodium hydroxide was added to the solution. On heating on a steam bath, the itaconic anhydride segment was completely hydrolyzed to the disodium salt and the acetone was boiled off.

An attempt was made to titrate the itaconic acid segment using phenolphthalein as an indicator, but in all cases the amount of itaconic acid found did not correspond to the theoretical quantity present. Thus it appears that the indicator may be adsorbed on the copolymer. The phenophthalein indicator was observed to change from pink to colorless not at the usual pH range of 8-9, but anywhere in the range of pH 11 to 6.

The use of a line operated Beckman pH meter to titrate the acid segment was then attempted. The titration curve obtained by plotting pH versus ml. of titer revealed the dibasic nature of the itaconic acid segment, but the end points were not very sharp and were not always too close to the theoretical values. A second and major difficulty with

the potentiometric titration is the inability of the instrument to locate the excess sodium hydroxide. The titration of the acid segment depends on the addition of a known excess of base to completely hydrolyze the anhydride. Thus the method used to determine the dibasic acid must also be capable of detecting the excess base. Another difficulty encountered with the use of a potentiometer occurs when the polymer begins to precipitate. When the disodium salt is converted to the free acid form of the copolymer, a precipitate appears. This precipitate tends to adhere to the electrode surface and may lead to inconsistent results.

It was found that a sample weight of copolymer not larger tha 0.3 g. should be used in order to obtain two reasonably good neutralization breaks in the potentiometric titration curve. Previous (5) potentiometric titration work with the maleic anhydride-styrene copolymer was performed using 1 g. samples. The pH titration curves did not show a second neutralization point under these conditions. The potentiometric titration of the maleic anhydride-styrene copolymer was reinvestigated and it was found that the second inflection point does appear in the pH curve, Figure 15, under the conditions of the titration.

The availability of a high frequency titrimeter presented an interesting possibility to adapt this instrument to solutions of polyelectrolytes.

Electrometric methods of analysis include those methods based on the response of electrodes immersed in a solution to concentration changes of ionic species in solution; the reactions at electrodes in contact with electrolyte solution; the passage of electricity through

electrolyte solutions, or some other measurable change in electrical properties. High-frequency titration is a relatively new addition to electrometric methods (61,62).

In high-frequency titrations, the vessel containing the solution to be titrated is placed between the plates of a condenser or in a field of the coil of the tank circuit of an oscillator operating in the megacycle frequency range. Discussions of the theory of the high-frequency method have been published (63,64,65,66).

The distinct advantage of the high-frequency titration method lies in the fact that the "electrodes" do not come into contact with the solution. Contamination of the solution by immersed electrodes or the desensitization of electrodes by adsorption of substances onto the electrodes immersed in solution is thus eliminated.

Preliminary work indicated that the excess of sodium hydroxide could be determined. Thus it was decided to use the high-frequency titrimeter and the pH meter simultaneously. The high-frequency titration end points were used to check and detect the end points determined from the potentiometer. The potentiometer readings were desired for the determination of apparent pK' values.

The data for the titration of the itaconic anhydride-styrene copolymers are tabulated in Table VIII, and plotted in Figures 7 to 15. In all instances where there was an excess of sodium hydroxide added this was determined quite accurately.

The total milliequivalents of the itaconic acid segment as determined from titration are equal in most cases to the theoretical milliequivalents as calculated from the composition of the itaconic anhydride-styrene

copolymer. In some instances the milliequivalents of one type of carboxylate determined by titration do not agree too well with the calculated milliequivalents for the same type of carboxylate. However, the total milliequivalents of the two types of carboxylate determined by high-frequency titration agree very well with the total theoretical milliequivalents of carboxylate.

The advantage of the high-frequency titration method in determining composition of copolymers is that it is rapid and the accuracy is very good under the conditions used in this investigation.

The use of the high-frequency titration method was valuable in the determination of the monoester derivatives. The excess sodium hydroxide was easily located, and the quantity of the monoester-acid segment readily calculated.

A more striking advantage is the ability to determine, with the use of the high-frequency titrimeter, the two isomeric acid esters which are obtained on reacting the itaconic anhydride segment of the copolymer with an alcohol.

The problem of proving the existence of two isomeric acid esters when a simple unsymmetrical anhydride is reacted with an alcohol is complicated. The isolation of the two isomers and their purification is tedious.

In a copolymer, where isolation and recrystallization become impossible, it has been clearly demonstrated, in this investigation, that it is possible not only to show that two isomeric esters are formed when the anhydride reacts with an alcohol, but also to determine

the amount of each type of acid ester formed with the use of the high-frequency titrimeter.

A look at the titration curves of the monoesters, Figures 16-23, shows two distinct breaks beyond the sodium hydroxide excess. The minimum in the high-frequency titration curve represents the excess of sodium hydroxide.

The data for the titration of the monoesters are tabulated in Table X. The table shows that the anhydride ring opens to give almost equivalent amounts of the two isomeric acid esters. The observed and theoretical milliequivalents of the acid segment agree very well in most cases.

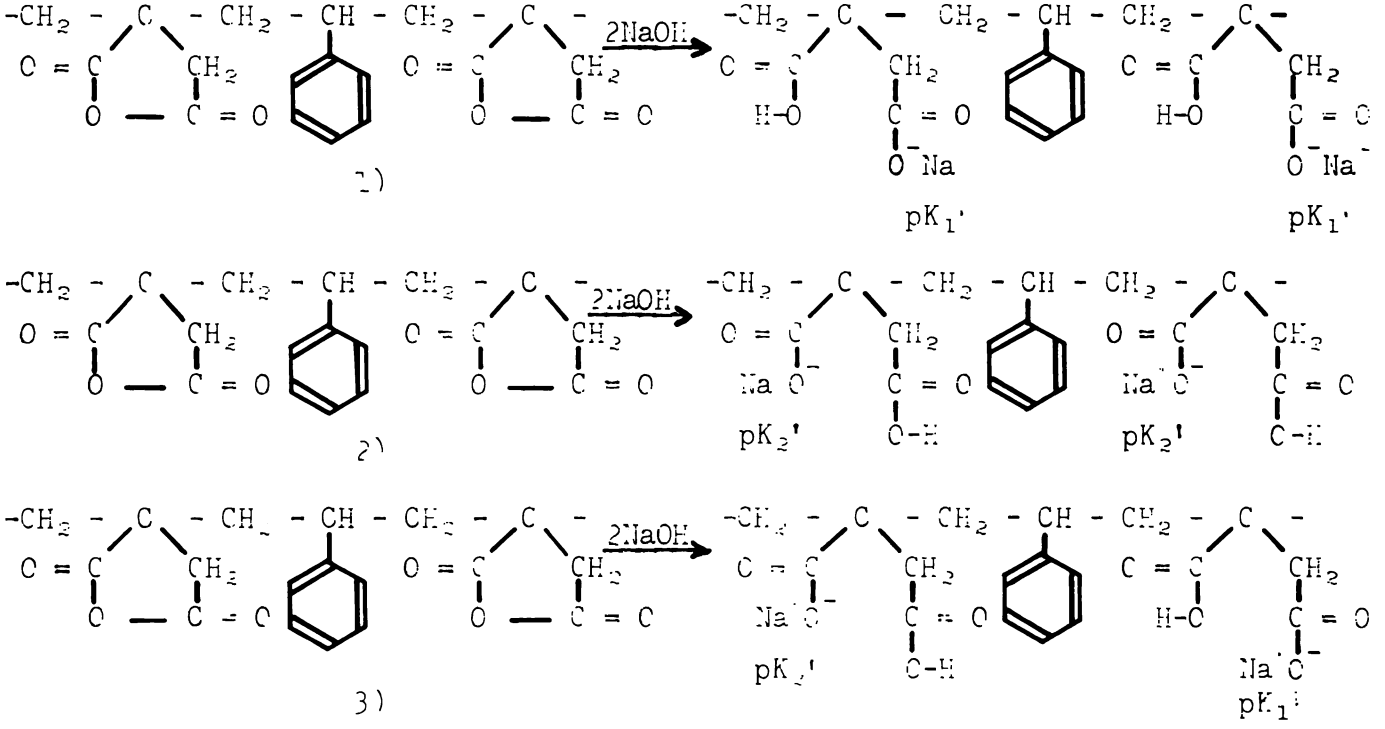
Special attention is called to Fig. 22 which represents the titration of the monomethyl ester of the itaconic anhydride-styrene copolymer prepared by the action of dimethyl sulfate. The high-frequency titration curve indicates that there are two isomeric acid-esters present. Thus the esterification of the anhydride segment with alcohol and the action of dimethyl sulfate on the disodium salt of the itaconic acid segment both lead to two isomeric acid esters.

The apparent pK_1' and pK_2' values for the itaconic anhydride-styrene copolymers and for the maleic anhydride-styrene copolymer are shown in Table VII.

In most cases the agreement of the pK' values read directly from the graph agree well with each other.

The pK_2' value reported for the titration shown in Fig. 10 appears to be low compared to the others in the table. A possible explanation

may lie in the fact that this titration was a little different from the others in that only one-half of the sodium hydroxide necessary to hydrolyze all the anhydride segments was added. The reason for adding one-half of the required sodium hydroxide was to see if the high-frequency titration curve shows two breaks, since the following structures are possible when the sodium hydroxide is added.



A look at Fig. 10 reveals two breaks in the high-frequency titration curve and it is felt that reaction (3) took place when the sodium hydroxide was added. Thus it appears that the titration resembles that of a monobasic acid or the acid species of the monoester derivative. The pK' values for this titration are of the order of magnitude of those determined for the monoester derivatives as shown in Table IX.

The pK' values reported for the titrations shown in Figs. 13 and 14 are somewhat higher than for the other listed values. These titrations involved more dilute solutions. No systematic study has been done as yet to determine if the concentration affects the apparent pK' values of a polyelectrolyte.

The apparent pK' values for the monoester derivatives are shown in Table IX. A look at Fig. 16A shows that the plot of pH versus $\log \frac{1 - \alpha}{\alpha}$ gives a slope approaching unity for the primary and secondary carboxyls. It appears that the monoester derivatives are acting as monobasic acids and one carboxylate ionizes independently of the other.

The titration curves for the diester derivatives are shown in Figures 24 and 25. The high-frequency and potentiometric titration curves indicate the titration of a strong acid (HCl) and strong base (NaOH). In this case there is only a minimum in the high-frequency curve which represents the sodium hydroxide added. There is no free carboxylate in the copolymer. The milliequivalents of sodium hydroxide found by titration are identical to the quantity added. The titration and elemental analysis data indicate the presence of a diester.

Figure 26 represents the titration of the partial diethyl ester prepared in the diazoethane reaction. The carbon-hydrogen analysis of this sample indicates that the diester was not completely formed. A look at Fig. 26 indicates a break in the high-frequency titration curve beyond the sodium hydroxide excess represented by the minimum in the curve. The second break represents the carboxylate which was not esterified. Once again it becomes obvious that the high-frequency titrimeter is a valuable tool in determining composition of copolymers

or their derivatives.

Since it was possible to detect two acid species in the itaconic anhydride-styrene copolymer, in the monoester derivatives of the copolymer, and itaconic acid itself, it was felt that mixtures of these species should be investigated.

In a mixture of any of these two species it was expected that four breaks would be found in the high-frequency titration curves. This indeed was the case in the instances studied, with one exception. Fig. 28 represents the titration of a mixture of poly 61:39 (itaconic anhydride co styrene) and itaconic anhydride. The high-frequency titration curve shows five breaks and only four are expected. A repetition of this titration using more dilute solutions is shown in Fig. 29. In this instance only four breaks are seen in the high-frequency titration curve. Since no systematic study has been conducted dealing with concentration effects in mixtures it is impossible to explain the presence of a fifth break in the case of the more concentrated solution.

In the discussion of each titration in VIII, it was necessary to assume that each of the species was titrated independently of the others present. This is probably not the case, but the observations for the individual breaks agree well with the theoretical values. With this assumption, the five breaks in Fig. 28 can be explained. The total milliequivalents of all acid species in each of the titrations of the mixtures agree well with the calculated values.

The apparent pK' values listed for each of the titration mixtures were read directly from the pH curve making use of the assumption that each carboxylate species is titrated independently. It appears impossible

to calculate the apparent pK' values for this mixture. The pK' values of the mixtures were read for the purpose of comparison with those determined for the separate titration of the particular substance.

It might be mentioned at this point that it appears that the composition of polyamines might be determined with the use of the high-frequency titrimeter.

The titration curves for a number of monomeric dibasic acids and polyitaconic acid are plotted in Figures 30 to 38. The data for the titrations are tabulated in Table XVII.

An interesting instance is a comparison of the titration curve of itaconic acid Figures 31 and 33 and polyitaconic acid Figure 32. The high-frequency titration curve for the monomeric itaconic acid shows a curved effect whereas the high-frequency titration curve for the polyitaconic acid is a straight line. The curved nature of the high-frequency titration curves for monomeric dibasic acids is quite prevalent in all the work done in this laboratory. Only the titration curve of methylsuccinic acid, Figure 36, is a straight line. The milliequivalents of acid found by titration agree well with the theoretical milliequivalents of acid present.

Fig. 37 is a plot of a mixture of benzoic and salicylic acids. The determination of these two acids in aqueous solution was surprising. It represents the first time that a mixture of two acids with a ratio of ionization constants of about 17 has been determined in aqueous solution using the high-frequency titrimeter.

It was impossible to resolve a mixture of acetic and propionic acid. The ratio of the ionization constants of these two acids is about

1.3. No extensive study has been made to determine the limits for the high-frequency titrimeter.

The hydrolysis of the monoethyl ester and of the dimethyl ester was followed conductometrically. The data indicate that the monoethyl ester was not hydrolyzed at 25 ± 0.1°C. for 25 hours. The dimethyl ester does not show any hydrolysis at 25 ± 0.1°C. for 31 hours. The hydrolyses were conducted at 25°C and in aqueous solution to simulate the conditions for the titrations of the monoester and diester derivatives which were done at room temperatures and in aqueous basic solution. Thus it is concluded that no hydrolysis occurred during the titration of the monoester and diester derivatives. The conclusion often found expressed is that the difficulty encountered in forming a diester derivative was due to a reversible hydrolysis with the small quantity of water formed in the esterification. This conclusion is no longer tenable. The difficulty encountered in preparing diesters by a catalytic method is attributed to a steric factor and the equilibrium nature of the esterification reaction.

The infrared spectra of various copolymer derivatives appear in Figures 39 to 48.

The bands for carbonyl groups as a class are the most stable in position, 5.45-5.50 μ. In the region of 5-7 μ these are the strongest in the spectrum (67). This was found to be true in the copolymers investigated, the two absorption bands for the anhydride linkage, 5.38 and 5.62 μ were reasonably constant. The 0.2 μ separation between these two bands (67) was approximately constant in each case.

The shift to higher frequencies for the carbonyl containing anhydrides followed the correlation that this shift was due to ring strain in the five membered ring. The band at 8.3 μ in the spectrum of polyitaconic anhydride and that at about 8.2 μ in the copolymer's spectra were attributed to the C-O-C stretching vibration. The band was shifted in the copolymer and this was probably due to hindrance to stretching by the phenyl groups in the proximity of the five membered ring (68).

The absorptions characteristic to esters arise from C=O and C-O- linkages. These appear approximately in the regions 5.73 to 5.80 μ. The spectra of the esterified copolymers had a common band at about 5.8-5.9 μ. This absorption band was shifted from the normal region of ester C=O and this may be due to the unsymmetrical groups adjacent to the carbonyl carbon.

In the copolymer, the absorption band at about 14.25 μ was attributed to the contribution of the phenyl ring. Through the correlation from open chain vibrations (68) in long chain molecules with methylene groups along the chain a strong band was observed in the region of 14 μ. In this work it was found at 14.2 μ. This band is attributed to a rocking mode of the CH_2 group. The band at 14.2 μ shifted to higher wavelengths with no correlation in the relative amounts of the contributing structures.

An excellent region for the identification of the carboxylic acid in the monoester derivatives lies in the range 3-3.5 μ. The separation of these bands from the absorptions of the C-H stretching vibrations was great enough to prevent any confusion. In the diester preparations.

Figures 44 and 45, this broad band attributed to the carboxylic acid residue has disappeared.

No quantitative evaluation of the linkages involved in the copolymer and its derivatives was made. However, the characteristic linkages present were sufficient to give a qualitative identification.

If a suitable solvent were available, a quantitative determination of the amount of anhydride or its derivatives could be made, thus serving as another tool for the analysis of copolymer composition.

SUMMARY

1. Itaconic anhydride and styrene have been copolymerized in benzene and tetrahydrofuran solvent using benzoyl peroxide as a catalyst.

2. The reactivity ratios for the copolymerization of these two monomers are: In benzene r_2 (itaconic anhydride) = 0.78 and r_1 (styrene) = 0.015. In tetrahydrofuran r_2 = 0.60 and r_1 = 0.10.

3. The copolymer produced in benzene precipitates as it is being formed and is an easily workable white granular powder.

4. The copolymer produced in tetrahydrofuran must be precipitated by a non-solvent and is a gelatinous, adhesive mass which is difficult to purify.

5. The itaconic anhydride-styrene copolymer has a highly alternating structure and the units are arranged in a head-to-tail manner.

6. The high-frequency titration apparatus is a useful tool in the titration of polycarboxylic acids.

7. The composition of the itaconic anhydride styrene copolymers has been determined by carbon-hydrogen analysis and by high-frequency titration.

8. The potentiometric and high-frequency titrations indicate that the itaconic anhydride segment of the copolymer is a dibasic acid. The apparent pK_1' and pK_2' values are 5.7 and 8.8 respectively.

9. Monoester derivatives of the copolymer were prepared by reaction of a primary alcohol with the anhydride segment of the copolymer.

10. The high-frequency titration curves show the monoester derivative to be a mixture of two isomeric acid esters. Apparent values of pK_1'' and pK_2'' for the monomethyl ester are 6.3 and 7.9 respectively.

11. Diester derivatives of the copolymer have been prepared by reaction with diazomethane.

12. An optically active monoester derivative has been prepared by reaction of the anhydride segment of the copolymer with an optically active alcohol.

13. The itaconic anhydride-styrene copolymer has been converted to a network polymer exhibiting ion-exchange properties.

14. The monoethyl and the dimethyl ester derivatives of the copolymer do not undergo hydrolysis in aqueous sodium hydroxide at 25°C in twenty-five hours.

15. The high-frequency titration procedure was applied to the maleic anhydride-styrene copolymer. The apparent values of pK_1' and pK_2' are 4.8 and 9.9 respectively.

16. Itaconic anhydride was polymerized to produce a homopolymer, polyitaconic anhydride.

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APPENDIX

TABLE XVIII

(Data Plotted in Figure 7)

Ml. HCl	Dial Reading	pH
0	816.5	12.05
1	815.5	12.02
2	813.5	11.99
3	813.0	11.95
4	811.7	11.88
5	810.0	11.85
6	808.5	11.78
7	806.5	11.72
8	804.0	11.65
9	801.8	11.55
10	800.0	11.48
11	797.2	11.22
12	795.4	10.98
13	793.0	10.49
14	793.8	9.75
15	795.9	9.12
16	796.5	8.44
17	798.9	7.22
18	800.0	6.32
19	800.9	5.75
20	802.5	4.90
21	804.8	3.71 precipitate
22	810.0	3.22
23	813.0	2.99
24	816.0	2.84

TABLE XIX

(Data Plotted in Figure 8)

Ml. HCl	Dial Reading	pH	
0	768.5	11.05	
1	766.0	10.83	
2	765.0	10.58	
3	765.0	10.31	
4	766.0	10.04	
5	768.0	9.77	
6	769.8	9.48	
7	772.6	9.21	
8	775.0	8.92	
9	778.3	8.56	
10	780.2	8.12	
11	783.0	7.48	
12	784.8	6.98	
13	785.3	6.62	
14	786.5	6.35	
15	787.5	6.15	
16	789.0	5.92	
17	790.3	5.68	
18	791.5	5.40	
19	792.5	5.03	
20	793.8	4.45	
21	797.6	3.49	precipitate
22	802.5	3.05	
23	806.2	2.83	

TABLE XX

(Data Plotted in Figure 9)

Ml. HCl	Dial Reading	pH	
0	750.0	10.08	
1	751.3	9.78	
2	752.5	9.50	
3	754.7	9.23	
4	757.5	8.92	
5	760.0	8.59	
6	763.3	8.19	
7	765.7	7.62	
8	767.7	7.04	
9	769.7	6.63	
10	771.0	6.32	
11	772.8	6.09	
12	774.0	5.90	
13	775.5	5.63	
14	777.0	5.29	
15	779.0	4.87	
16	781.0	4.05	
17	787.0	3.28	precipitate
18	793.3	2.95	
19	799.0	2.77	
20	803.0	2.63	
21	806.4	2.55	
22	808.5	2.47	

TABLE XXI

THIS DATA IS PLOTTED IN FIGURE 9A AND IS FOR THE TITRATION SHOWN IN FIGURE 9

pH	Liters of Solution	[C]	Ml. HCl Added	$[IA^{=}]$	$[HIA^{-}]$	$\log\frac{(1-\alpha)}{\alpha}$
9.78	0.181	0.00576	1	0.00505	0.00071	0.8521
9.50	0.182	0.00573	2	0.00432	0.00141	0.4861
9.23	0.183	0.00570	3	0.00360	0.00210	0.2340
8.92	0.184	0.00567	4	0.00289	0.00278	0.0166
8.59	0.185	0.00564	5	0.00216	0.00348	-0.2072
8.19	0.186	0.00561	6	0.00147	0.00414	-0.4498
7.62	0.187	0.00558	7	0.00077	0.00481	-0.7959
7.04	0.188	0.00555	8	0.00009	0.00546	-1.9594
				$[HIA^{-}]$	$[H_2IA]$	
6.63	0.189	0.00552	9	0.00492	0.00060	0.9138
6.32	0.190	0.00548	10	0.00420	0.00128	0.5160
6.09	0.191	0.00545	11	0.00350	0.00195	0.2539
5.90	0.192	0.00543	12	0.00283	0.00260	0.0370
5.63	0.193	0.00540	13	0.00215	0.00325	-0.1795
5.29	0.194	0.00537	14	0.00146	0.00391	-0.4278
4.87	0.195	0.00535	15	0.00082	0.00454	-0.7476
4.05	0.196	0.00532	16	0.00023	0.00517	-1.3518

TABLE XXII

(Data Plotted in Figure 10)

Ml. HCl	Dial Reading	pH	
0	735.0	8.55	
1	737.8	7.80	
2	740.5	7.05	
3	743.3	6.55	
4	745.5	6.15	
5	747.5	5.78	
6	749.9	5.38	
7	751.5	4.85	
8	756.2	3.82	
9	767.5	3.10	
10	778.8	2.88	precipitate
11	787.0	2.72	
12	794.4	2.58	
13	800.0	2.50	
14	804.0	2.43	
15	807.0	2.35	

TABLE XXIII

(Data Plotted in Figure 11)

Ml. HCl	Dial Reading	pH	
0	792.9	11.25	
1	789.5	11.13	
2	786.4	10.94	
3	783.8	10.69	
4	782.5	10.39	
5	782.5	10.08	
6	783.3	9.75	
7	784.5	9.44	
8	787.0	9.12	
9	788.8	8.75	
10	791.4	8.33	
11	793.5	7.75	
12	795.5	7.12	
13	796.8	6.68	
14	797.6	6.38	
15	798.7	6.15	
16	799.8	5.92	
17	800.5	5.64	
18	801.7	5.30	
19	802.8	4.84	
20	804.0	4.12	
21	808.3	3.38	precipitate
22	813.2	3.12	
23	818.0	2.92	

TABLE XXIV

THIS DATA IS PLOTTED IN FIGURE 11A AND IS FOR THE TITRATION SHOWN IN FIGURE 11

pH	Liters of Solution	[C]	Ml. HCl Added	$[IA^{=}]$	$[HIA^{-}]$	$\log \frac{1-\alpha}{\alpha}$
9.75	0.186	0.005500	1.4	0.004533	0.000967	0.6709
9.44	0.187	0.005470	2.4	0.003820	0.001650	0.3645
9.12	0.188	0.005441	3.4	0.003116	0.002325	0.1271
8.75	0.189	0.005412	4.4	0.002419	0.002993	-0.0925
8.33	0.190	0.005384	5.4	0.001730	0.003654	-0.3247
7.75	0.191	0.005356	6.4	0.001048	0.004308	-0.6139
7.12	0.192	0.005327	7.4	0.000371	0.004956	-1.1261
				$[HIA^{-}]$	$[H_2IA]$	
6.68	0.193	0.005300	8.4	0.005005	0.000295	1.2296
6.38	0.194	0.005273	9.4	0.004320	0.000953	0.6564
6.15	0.195	0.005246	10.4	0.003636	0.001610	0.3537
5.92	0.196	0.005219	11.4	0.002959	0.002260	0.1170
5.64	0.197	0.005192	12.4	0.002293	0.002899	-0.1019
5.30	0.198	0.005167	13.4	0.001632	0.003535	-0.3357
4.84	0.199	0.005141	14.4	0.000981	0.004160	-0.6275
4.12	0.200	0.005115	15.4	0.000330	0.004785	-1.1616

TABLE XXV

(Data Plotted in Figure 12)

Ml. HCl	Dial Reading	pH	
0	776.8	11.08	
1.0	776.2	10.58	
2.0	778.3	10.05	
2.5	780.0	9.77	
3.0	782.3	9.44	
3.5	783.6	9.07	
4.0	785.2	8.36	
5.0	788.0	7.10	
5.5	789.4	6.73	
6.0	790.2	6.32	
6.5	791.0	5.87	
7.0	792.0	5.38	
7.5	792.8	4.67	
8.0	795.5	3.68	precipitate
8.5	800.0	3.25	
9.0	805.3	3.03	
9.5	809.7	2.86	
10.0	813.8	2.76	
10.5	817.8	2.68	
11.0	822.0	2.59	

TABLE XXVI

(Data Plotted in Figure 13)

Ml. HCl	Dial Reading	pH
0	825.7	11.13
1	822.7	10.93
2	820.2	10.53
3	818.6	9.94
4	820.2	8.60
5	821.4	6.37
6	822.8	4.28
7	830.0	2.90
8	836.7	2.61
9	842.7	2.42
10	847.7	2.30

TABLE XXVII

(Data Plotted in Figure 14)

Ml. HCl	Dial Reading	pH
0	822.8	10.50
1	822.5	10.35
2	822.5	10.20
3	822.5	10.00
4	822.5	9.75
5	822.6	9.50
6	822.8	9.15
7	823.0	8.53
8	823.6	7.63
9	824.0	6.95
10	824.8	6.55
11	825.2	6.15
12	825.5	5.85
13	825.8	5.45
14	826.4	4.85
15	827.6	3.95
16	830.3	3.52
17	833.2	3.28
18	835.7	3.12
19	838.4	2.98
20	841.0	2.88

TABLE XXVIII

(Data Plotted in Figure 15)

Ml. HCl	Dial Reading	pH
0	834.7	10.95
1	834.7	10.78
2	835.2	10.53
3	836.5	10.24
4	838.5	9.92
5	840.7	9.58
6	843.8	9.18
7	845.5	8.58
8	847.8	7.43
9	848.8	6.29
10	849.8	5.58
11	851.5	5.03
12	852.0	4.67
13	852.8	4.40
14	854.4	4.20
15	855.5	4.02
16	858.0	3.75
17	861.0	3.38
18	864.5	3.05
19	867.5	2.80
20	871.0	2.64

TABLE XXIX

THIS DATA IS PLOTTED IN FIGURE 15A AND IS FOR THE TITRATION SHOWN IN FIGURE 15

pH	Liters of Solution	[C]	Ml. HCl Added	$[MA^{=}]$	$[HMA^{-}]$	$\log \frac{1-\alpha}{\alpha}$
10.78	0.181	0.005494	1	0.000710	0.004784	0.8286
10.53	0.182	0.005464	2	0.001413	0.004051	0.4574
10.24	0.183	0.005434	3	0.002108	0.003326	0.1981
9.92	0.184	0.005405	4	0.002796	0.002609	-0.0301
9.58	0.185	0.005376	5	0.003476	0.001900	-0.2623
9.18	0.186	0.005347	6	0.004148	0.001199	-0.5400
8.58	0.187	0.005318	7	0.004814	0.000504	-0.9800
				$[HMA^{-}]$	$[H_2MA]$	
7.43	0.188	0.005290	8	0.005108	0.000182	1.4482
6.29	0.189	0.005262	9	0.004400	0.000862	0.7079
5.58	0.190	0.005234	10	0.003700	0.001534	0.3824
5.03	0.191	0.005207	11	0.003008	0.002199	0.1361
4.67	0.192	0.005179	12	0.002320	0.002859	-0.0907
4.40	0.193	0.005153	13	0.001644	0.003509	-0.3293
4.20	0.154	0.005126	14	0.000972	0.004154	-0.6308
4.02	0.195	0.005100	15	0.000308	0.004792	-1.1921

TABLE XXX

(Data Plotted in Figure 16)

Ml. HCl	Dial Reading	pH
0	819.5	11.98
1	818.2	11.95
2	817.0	11.92
3	816.2	11.85
4	813.5	11.82
5	811.5	11.75
6	808.5	11.65
7	805.8	11.56
8	803.8	11.43
9	800.5	11.25
10	798.0	10.95
11	796.4	10.35
12	796.8	9.42
13	798.5	8.45
14	800.0	7.85
15	802.4	7.49
16	803.2	7.22
17	804.0	7.02
18	804.8	6.72
19	805.2	6.26
20	806.9	5.37
21	810.5	3.68
22	815.9	3.22
23	820.0	2.99
24	824.0	2.84

TABLE XXXI

THIS DATA IS PLOTTED IN FIGURE 16A AND IS FOR THE TITRATION SHOWN IN FIGURE 16

pH	Liters of Solution	[C]	Ml. HCl Added	$[HIA^-]$	Type I $[H_2IA]$	$\log \frac{1-\alpha}{\alpha}$
8.45	0.193	0.002728	0.7	0.002262	0.000466	0.6861
7.85	0.194	0.002714	1.7	0.001587	0.001127	0.1486
7.49	0.195	0.002700	2.7	0.000920	0.001780	-0.2867
7.22	0.196	0.002686	3.7	0.000258	0.002428	-0.9739
				$[HIA^-]$	Type II $[H_2IA]$	
7.02	0.197	0.002673	4.7	0.002278	0.000395	0.7610
6.72	0.198	0.002659	5.7	0.001616	0.001043	0.1900
6.26	0.199	0.002646	6.7	0.000963	0.001683	-0.2425
5.37	0.200	0.002633	7.7	0.000315	0.002318	-0.8671

TABLE XXXII

(Data Plotted in Figure 17)

Ml. HCl	Dial Reading	pH
0	821.2	11.46
1	819.0	11.46
2	817.8	11.40
3	816.5	11.35
4	815.0	11.32
5	813.0	11.25
6	811.2	11.18
7	808.7	11.12
8	806.7	11.02
9	804.4	10.90
10	801.5	10.73
11	799.3	10.50
12	797.2	10.10
13	796.3	9.13
14	797.7	8.01
15	799.3	7.40
16	800.5	7.12
17	801.6	6.82
18	803.0	6.43
19	804.0	5.63
20	805.0	4.37
21	809.3	3.10
22	814.9	2.69
23	819.0	2.49
24	822.0	2.35

TABLE XXXIII

(Data Plotted in Figure 18)

Ml. HCl	Dial Reading	pH	
0	818.1	12.28	
1	816.1	12.24	
2	814.1	12.18	
3	811.7	12.11	
4	808.6	12.02	
5	805.6	11.92	
6	802.9	11.85	
7	799.6	11.76	
8	795.9	11.64	
9	793.2	11.47	
10	790.1	11.17	
11	788.0	10.67	
12	788.7	9.66	
13	790.5	8.80	
14	792.6	8.21	
15	794.4	7.87	
16	795.8	7.63	
17	797.4	7.40	
18	798.8	7.13	
19	800.0	6.63	
20	801.2	5.79	
21	804.8	3.82	precipitate
22	810.0	3.33	
23	816.4	3.08	
24	820.5	2.94	

TABLE XXXIV

(Data Plotted in Figure 19)

Ml. HCl	Dial Reading	pH
0	822.8	11.98
1	822.4	11.91
2	819.1	11.86
3	817.0	11.80
4	814.8	11.75
5	812.0	11.67
6	809.6	11.59
7	808.3	11.46
8	803.4	11.29
9	801.5	11.03
10	799.9	10.60
11	800.1	10.12
12	802.8	9.65
13	803.6	9.13
14	805.8	8.70
15	807.2	8.31
16	808.9	8.00
17	811.4	7.68
18	812.8	7.29
19	813.9	6.89
20	815.7	6.47
21	816.8	5.66
22	818.5	3.94
23	823.1	3.35
24	827.1	3.11
25	830.3	2.94

TABLE XXXV

(Data Plotted in Figure 20)

Ml. HCl	Dial Reading	pH
0	833.8	12.08
1	832.5	12.05
2	831.9	12.02
3	831.0	11.98
4	829.9	11.92
5	829.0	11.86
6	827.2	11.82
7	825.5	11.75
8	823.5	11.68
9	820.5	11.60
10	818.0	11.48
11	815.2	11.34
12	812.5	11.12
13	809.9	10.75
14	808.5	10.12
15	809.0	9.39
16	810.8	8.78
17	812.8	8.18
18	814.4	7.52
19	815.6	6.72
20	816.5	5.65
21	820.0	3.75
22	826.2	3.25
23	830.5	3.04
24	833.5	2.89

XXXVI

(Data Plotted in Figure 21)

Ml. HCl	Dial Reading	pH
0	816.0	9.80
1	816.8	8.96
2	817.2	8.10
3	817.8	7.46
4	818.0	6.80
5	818.4	6.15
6	820.0	4.00
7	823.8	3.48
8	827.3	3.22
9	830.5	3.08
10	834.0	2.96

TABLE XXXVII

(Data Plotted in Figure 22)

Ml. HCl	Dial Reading	pH
0	870.4	11.46
1	869.0	11.42
2	867.7	11.37
3	866.2	11.32
4	864.8	11.27
5	863.4	11.22
6	861.7	11.13
7	860.3	11.06
8	859.0	10.98
9	857.4	10.83
10	855.8	10.66
11	854.5	10.40
12	853.8	9.98
13	854.2	9.47
14	855.2	8.97
15	856.3	8.42
16	857.0	7.80
17	857.8	7.24
18	858.5	6.75
19	858.8	6.48
20	859.1	6.12
21	859.8	5.75
22	860.8	5.05
23	862.3	3.73
24	866.0	3.10
25	869.6	2.82
26	871.8	2.67
27	874.4	2.55

TABLE XXXVIII

(Data Plotted in Figure 23)

Ml. HCl	Dial Reading	pH
1	842.3	11.22
2	840.4	11.05
3	839.0	10.82
4	838.8	10.52
5	839.0	10.13
6	840.8	9.70
7	841.6	9.09
8	843.5	7.88
9	845.4	7.00
10	846.8	6.50
11	848.5	6.18
12	849.7	5.85
13	851.0	5.59
14	852.0	5.28
15	853.0	4.93
16	854.0	4.50
17	856.0	3.86
18	859.3	3.24
19	862.8	2.88
20	866.0	2.68
21	869.0	2.52

TABLE XXXIX

(Data Plotted in Figure 24)

Ml. HCl	Dial Reading	pH
0	864.3	12.43
1	862.3	12.42
2	860.8	12.42
3	859.5	12.40
4	858.5	12.38
5	857.3	12.36
6	856.2	12.35
7	855.0	12.33
8	853.5	12.33
9	852.4	12.31
10	851.0	12.27
11	849.9	12.23
12	848.4	12.20
13	847.2	12.15
14	845.5	12.12
15	844.2	12.04
16	842.9	11.93
17	841.5	11.80
18	840.2	11.56
19	839.0	11.05
20	839.0	8.00
21	840.5	4.15
22	845.2	3.05
23	850.4	2.72
24	854.5	2.55
25	858.7	2.44

TABLE XL

(Data Plotted in Figure 25)

Ml. HCl	Dial Reading	pH
0	888.8	12.78
1	887.5	12.78
2	886.5	12.77
3	885.5	12.77
4	884.3	12.73
5	883.2	12.73
6	882.2	12.70
7	880.7	12.68
8	879.2	12.65
9	878.2	12.62
10	876.5	12.58
11	875.5	12.55
12	874.7	12.53
13	873.7	12.48
14	872.5	12.47
15	871.5	12.43
16	870.4	12.38
17	868.7	12.28
18	867.8	12.23
19	866.7	12.16
20	865.5	12.04
21	864.3	11.88
22	863.0	11.58
23	862.3	10.88
24	862.3	5.28
25	865.6	3.73
26	870.0	3.38
27	873.3	3.22
28	876.0	3.08
29	879.2	2.98
30	881.8	2.90

TABLE XLI

(Data Plotted in Figure 26)

Ml. HCl	Dial Reading	pH
0	880.7	12.34
1	878.0	12.29
2	877.0	12.23
3	876.2	12.23
4	875.0	12.23
5	874.0	12.19
6	873.2	12.14
7	872.0	12.14
8	870.6	12.10
9	869.6	12.05
10	868.4	12.04
11	867.0	11.97
12	865.7	11.93
13	864.4	11.87
14	863.3	11.79
15	861.8	11.72
16	860.4	11.58
17	859.0	11.48
18	857.8	11.22
19	857.0	10.78
20	857.0	10.12
21	857.5	9.00
22	858.2	7.74
23	858.8	5.65
24	862.5	3.48
25	865.5	3.18
26	869.0	2.98
27	872.5	2.83
28	874.8	2.75

TABLE XLII

(Data Plotted in Figure 27)

Ml. HCl	Dial Reading	pH
0	803.7	11.65
1	803.3	11.53
2	802.5	11.35
3	801.5	11.08
4	812.8	10.78
5	818.3	10.48
6	820.3	10.24
7	822.6	10.05
8	824.0	9.88
9	826.8	9.69
10	828.4	9.50
11	830.5	9.34
12	832.0	9.20
13	833.8	9.03
14	835.0	8.84
15	836.8	8.63
16	838.5	8.40
17	839.7	8.14
18	841.0	7.91
19	842.1	7.67
20	842.8	7.47
21	843.3	7.27
22	844.2	7.07
23	845.1	6.89
24	845.9	6.68
25	846.7	6.52
26	847.5	6.37
27	848.5	6.18
28	849.0	6.02
29	849.7	5.88
30	850.0	5.68
31	850.5	5.50
32	851.2	5.34
33	851.6	5.14
34	852.0	4.89
35	852.0	4.56
36	852.8	4.02
37	854.5	3.41
38	856.5	2.98
39	858.8	2.78
40	860.8	2.63
41	862.7	2.53
42	864.3	2.43

TABLE XLIII

(Data Plotted in Figure 28)

Ml. HCl	Dial Reading	pH
0	865.4	11.45
1	863.8	11.39
2	862.3	11.30
3	860.0	11.19
4	858.7	11.04
5	857.4	10.84
6	856.6	10.58
7	856.3	10.18
8	856.3	9.70
9	857.3	9.25
10	858.3	8.78
11	859.3	8.10
12	860.0	7.20
13	860.2	6.68
14	861.0	6.33
15	861.2	6.08
16	861.5	5.83
17	862.0	5.63
18	862.0	5.43
19	862.5	5.23
20	862.5	5.02
21	862.5	4.80
22	862.8	4.58
23	862.8	4.36
24	863.2	4.15
25	863.8	3.94
26	864.0	3.74
27	864.4	3.54
28	865.4	3.34
29	866.2	3.14
30	867.8	2.90
31	869.7	2.72
32	871.7	2.57
33	873.6	2.43
34	875.4	2.34
35	877.3	2.25

TABLE XLIV

(Data Plotted in Figure 29)

Ml. HCl	Dial Reading	pH
0	837.7	10.45
1	837.7	10.25
2	837.3	9.95
3	837.3	9.58
4	837.5	8.73
5	837.5	7.55
6	838.0	6.95
7	838.0	6.55
8	838.2	6.22
9	838.2	5.90
10	838.2	5.60
11	838.4	5.23
12	838.4	4.84
13	838.7	4.40
14	839.5	3.98
15	840.8	3.67
16	842.5	3.42
17	844.0	3.24
18	846.4	3.10
19	847.7	2.97
20	850.5	2.88

TABLE XLV

(Data Plotted in Figure 30)

Ml. HCl	Dial Reading	pH
0	854.0	11.72
1	852.8	11.60
2	852.4	11.32
3	852.4	10.82
4	853.5	9.86
5	855.4	9.09
6	856.8	8.35
7	858.2	7.84
8	858.8	7.50
9	859.5	7.23
10	860.4	6.97
11	860.8	6.72
12	861.2	6.45
13	861.5	6.17
14	862.0	5.88
15	862.2	5.58
16	862.2	5.28
17	862.5	5.00
18	863.0	4.77
19	863.0	4.53
20	863.3	4.28
21	863.6	4.08
22	864.0	3.78
23	865.0	3.40
24	867.2	2.98
25	870.5	2.72
26	873.5	2.52
27	876.7	2.38
28	880.0	2.28
29	882.8	2.19

TABLE XLVI

(Data Plotted in Figure 31)

Ml. HCl	Dial Reading	pH
0	803.8	10.55
1	803.5	10.23
2	802.8	9.80
3	802.8	8.95
4	803.0	7.18
5	803.5	6.68
6	803.8	6.46
7	804.4	6.13
8	804.8	5.87
9	804.8	5.55
10	805.0	5.20
11	805.9	4.87
12	806.4	4.51
13	807.9	4.20
14	809.0	3.80

TABLE XLVII

(Data Plotted in Figure 32)

Ml. HCl	Dial Reading	pH
0	789.2	9.30
1	791.2	8.72
2	793.7	7.78
3	794.7	7.15
4	796.6	6.78
5	797.8	6.53
6	799.5	6.28
7	800.4	6.05
8	801.5	5.79
9	802.8	5.49
10	803.5	5.10
11	805.0	4.60
12	806.5	4.10
13	810.0	3.55
14	814.8	3.14
15	821.0	2.86
16	826.6	2.69
17	830.5	2.58
18	833.8	2.47
19	835.8	2.39
20	837.2	2.32

TABLE XLVIII

(Data Plotted in Figure 33)

Ml. HCl	Dial Reading	pH
0	814.4	10.80
1	811.8	9.97
2	811.8	6.48
3	811.8	5.98
4	812.3	5.66
5	812.3	5.40
6	812.3	5.18
7	813.8	4.93
8	814.3	4.65
9	815.0	4.40
10	815.2	4.15
11	815.2	3.85
12	816.8	3.64
13	819.5	3.40
14	822.3	3.18
15	827.6	2.98
16	831.7	2.80
17	836.0	2.66

TABLE XLIX

(Data Plotted in Figure 34)

Ml. HCl	Dial Reading	pH
0	843.3	9.32
1	843.3	7.03
2	843.3	6.58
3	843.5	6.28
4	843.5	5.97
5	844.2	5.60
6	844.6	5.08
7	845.5	4.62
8	846.5	4.40
9	847.8	4.04
10	849.2	3.78
11	851.8	3.52
12	855.4	3.27
13	859.7	3.08
14	863.7	2.93
15	867.7	2.82
16	871.3	2.73

TABLE L

(Data Plotted in Figure 35)

Ml. HCl	Dial Reading	pH
0	858.4	9.53
1	858.2	6.56
2	858.2	6.13
3	858.4	5.87
4	858.4	5.66
5	858.7	5.48
6	858.7	5.28
7	858.8	5.08
8	858.8	4.88
9	859.3	4.68
10	859.8	4.50
11	860.5	4.32
12	861.2	4.16
13	862.2	3.98
14	863.0	3.78
15	864.2	3.62
16	866.4	3.40
17	869.0	3.22
18	872.3	3.05
19	875.3	2.93
20	877.7	2.83

TABLE LI

(Data Plotted in Figure 36)

Ml. HCl	Dial Reading	pH
0	850.2	6.48
1	850.0	6.08
2	850.2	5.87
3	850.2	5.68
4	850.3	5.53
5	850.3	5.40
6	850.3	5.28
7	850.3	5.14
8	850.3	5.02
9	850.4	4.89
10	850.8	4.77
11	850.8	4.64
12	851.4	4.53
13	851.4	4.41
14	851.4	4.28
15	852.4	4.18
16	852.8	4.04
17	853.4	3.90
18	854.0	3.78
19	854.8	3.64
20	855.8	3.48
21	857.3	3.32
22	858.8	3.13
23	860.7	2.97
24	863.0	2.80
25	865.2	2.68
26	867.3	2.58
27	869.0	2.50

TABLE LII

(Data Plotted in Figure 37)

Ml. HCl	Dial Reading	pH
0	858.4	2.37
1	855.8	2.43
2	853.3	2.51
3	851.5	2.58
4	849.9	2.67
5	849.0	2.77
6	848.5	2.86
7	848.5	2.96
8	848.5	3.07
9	848.5	3.18
10	849.0	3.30
11	849.5	3.41
12	850.2	3.53
13	851.2	3.65
14	852.0	3.78
15	852.8	3.90
16	853.8	4.05
17	855.0	4.21
18	856.0	4.40
19	856.7	4.67
20	857.8	5.18
21	859.2	9.50
22	862.3	10.32
23	865.2	10.56
24	868.3	10.72
25	871.0	10.83
26	873.4	10.92
27	875.6	11.00

TABLE LIII

(Data Plotted in Figure 38)

Ml. HCl	Dial Reading	pH
0	852.2	10.05
1	852.5	6.54
2	852.8	5.97
3	852.8	5.71
4	853.3	5.52
5	853.5	5.40
6	853.5	5.28
7	854.0	5.18
8	854.5	5.12
9	854.5	5.04
10	855.0	4.97
11	855.2	4.88
12	855.5	4.83
13	855.9	4.77
14	855.9	4.71
15	856.4	4.67
16	856.6	4.61
17	856.8	4.56
18	857.4	4.48
19	857.4	4.43
20	857.8	4.37
21	858.0	4.29
22	858.8	4.24
23	858.8	4.17
24	859.0	4.09
25	859.3	4.03
26	859.3	3.92
27	859.7	3.83
28	860.2	3.72
29	860.7	3.58
30	861.7	3.42
31	862.6	3.23
32	863.6	3.02
33	865.4	2.84
34	867.0	2.70
35	868.3	2.58

TABLE LIV

STABILITY TO HYDROLYSIS OF THE MONOETHYL ESTER OF POLY 63:37 (ITACONIC ANHYDRIDE CO STYRENE)

Time in Minutes	Resistance in Ohms
0	48.6
5	48.6
10	48.6
15	48.6
20	48.6
33	48.6
48	48.6
63	48.6
78	48.6
93	48.5
108	48.5
123	48.5
138	48.4
153	48.4
183	48.4
333	48.4
393	48.4
453	48.4
1083	48.4
1203	48.2
1503	48.2

TABLE LV

STABILITY TO HYDROLYSIS OF THE DIMETHYL ESTER OF POLY 63:37
(ITACONIC ANHYDRIDE CO STYRENE)

Time in Minutes	Resistance
0	32.2
2	32.2
4	32.2
7	32.2
10	32.2
15	32.2
22	32.2
27	32.2
42	32.2
57	32.1
72	32.1
87	32.1
127	32.1
297	32.1
357	32.0
417	32.0
1467	31.9
1850	31.9