CONTINUOUS INTERFACIAL POLYCONDENSATION OF NYLON 6-10

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ABSTRACT:

Nylon 6-10 has been prepared by continuous interfacial polycondensation from hexamethylenediamine and sebacoyl chloride in a stirred system. The effect of monomer concentration and stirring on the intrinsic viscosity of the polyamide 6-10 solution in m-cresol was measured.

As stirring rate (RPM) and monomer ratio increased the intrinsic viscosity and the polymer yield went through a maximum. Diffusion coefficients (D_{AB}) for hexamethylenediamine were calculated and were used for the calculations of j_D factors and K/D_{AB} ratios. A relationship between Reynolds Number and j_D factor was established by a correlation curve.

APPROVAL OF THESIS

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FOR

DEPARTMENT OF POLYMER ENGINEERING
NEWARK COLLEGE OF ENGINEERING

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FACULTY COMMITTEE

APPROVED: ______________________________

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INTRODUCTION:

Polyamides are also called Nylons. There are different kinds of Nylons, for example, Nylon 6-6,6-10,11, etc. The number designation represents the number of carbon atoms in the diamine and dibasic acid or dibasic acid chloride, respectively from which the polymer is made.

Polyamides can be made by various methods. Condensation reactions usually take place under conditions of high temperature and reduced pressure. A catalyst may be used for increasing the rate of polymer formation. High temperature work requires complicated equipment. The cost of the process is high because of the expensive equipment, purity of compounds used, and long reaction time. Interfacial polycondensation occurs at room temperature and at atmospheric pressure. The process is mainly governed by the diffusion of reactants from one liquid phase to another since the reaction itself is quite rapid. The interfacial polycondensation reaction is very rapid and irreversible. The purity of reactants is not a stringent condition and simple equipment is sufficient.

The interfacial condensation polymers can be made by two different ways. One is an unstirred system in which the rate of production of a specific polymer is dependent upon the choice of solvent, the reactant concentrations, the area of the interface, and the rate at which the film is wound up. The wind-up speed is limited by the toughness of the film. The miscibility of the liquids is low. In this system, film formation can often be started smoothly, but soon afterwards there is accumulation of sludge in one or both phases, weakening the film.

The other way is using a stirred system. This method does not require any coherence or strength in the film. The product may be granular or powdery. The stirring is a critical variable. The shape and size of the blades and vessel and the nature of the reacting mixture are other important factors.

The factors considered above initiated our interest in the interfacial polycondensation reaction. The polyamides are easily prepared by this process; hence, we selected to prepare polyamide 6-10 in our study. A number of studies have been reported on batch and semi-continuous interfacial polymerisation. We considered that the study of the continuous system would be of interest.

BACKGROUND AND THEORY:

Condensation Polymerization:

Polymers can be catergorized in several ways. One method is by their structural configuration. There are, for example, linear, branched, or cross-linked polymers. In linear

(see figures on next page)

polymers the repeating units are joined together head to head to form a long chain or coil. The branched polymers have side chains growing off at various points to give

(see figures on next page)

structure similar to trees. The crosslinked polymers are chains, or collections of chains, which are

(see figures on next page)

linked together by small structural units.

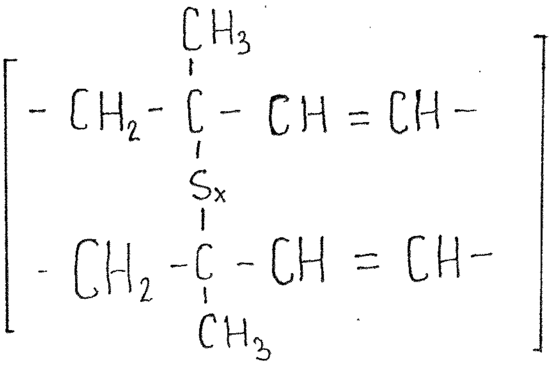
One method of classification is by processing. Here the two categories are thermoplastic and thermosetting. Thermoplastic polymers are those which are fusible; that is, they can be softened or melted by heat. The thermosetting polymers are those which are so heavily cross-linked that they burn before they can be melted or softened.

Another method of characterizing is by the chemical reactions from the polymers themselves. There are two principal groups - condensation and addition polymers.

LINEAR POLYMERS

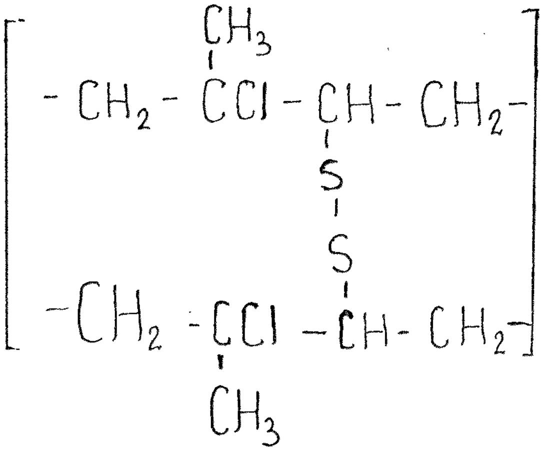
$$\left[-CH_2-CH_2-\right]_n$$

BRANCHED POLYMERS



$$\left[\begin{array}{c} CH_3 \\ | \\ -CH_2-C-CH=CH- \\ | \\ S_x \\ | \\ -CH_2-C-CH=CH- \\ | \\ CH_3 \end{array}\right]$$

CROSSLINKED POLYMERS



$$\left[\begin{array}{c} \overset{CH_3}{\overset{|}{\ }} \\ -CH_2-CCl-CH-CH_2- \\ | \\ S \\ | \\ S \\ | \\ -CH_2-CCl-CH-CH_2- \\ | \\ CH_3 \end{array}\right]$$

Condensation polymers, the molecular formula of the structural units (or units), lack certain atoms present in the monomers from which it is formed or to which it may be degraded by chemical means. Addition polymers, the molecular formula of the structural unit (or units), is identical with that of the monomer from which the polymer is derived. (1,2)

Addition and condensation polymers can be differentiated by their reaction processes. Condensation polymerization proceed by stepwise intermolecular condensation of functional groups. Addition polymerization usually proceed by chain mechanism involving active centers of one sort or another. The structural units of condensation polymers usually are joined by inter-unit functional groups, e.g., ester or amide. Most addition polymers do not possess functional groups within the polymer chain; however, they may be present as lateral substituent. Linear condensation polymers usually conform to the type formula: (-R-X-R-X-R-X-R-) where R is divalent radical and X is functional group (e.g., -OCO- ; -O- ; -NHCO- ; -S-S-) polar in nature and susceptible to cleavage reagent such as water or alcohol. Polar groups are at regularly spaced in the chains of linear condensation polymers; and addition polymers, whose chain skeleton usually consists exclusively of C-atoms, are essentially non-polar. (1,2,3, The average degree of polymerization and the molecular weight of a linear polymer depend on the degree of completion of condensation reaction. To obtain the product of high molecular weight (about 10000 or more), it is necessary that the condensation process be an efficient one and that it must be reasonably free from side reactions, particularly those which consume functional groups without producing intramolecular linkages. (1,2)

The early process of condensation polymerization was carried out at high temperature and high pressure. The reason was that they all are slow. Rates of high temperature polycondensation reaction are increased by increasing temperature, by a change in solvent polarity, and by the presence of catalyst, but even with all these aids few of the rates approach those of the reactions at lower temperature. For polymer growth it is necessary to remove the non-polymerization mixture. Heat, stirring, and reduced pressure help to remove the volatile by products and increase the conversion to high polymer. At high temperature the molecular species are in the stage of mobile interchange or equilibrium by way reaction of end groups with functional groups in polymer chain. In the case of polyamides, exchange between amide groups segment is possible. (4)

The effect of heat at high temperatures on the stability of natural and synthetic polymers has aroused more interest and has been investigated more extensively than that of any other energy transfer agent (such as light, mechanical impact, supersonic waves or infrared ultra violet or gamma radiation). Study of thermal behavior of polymers particularly on their thermal degradation is of prime importance from a scientific point of view. The degradation can be described as an irreversible change in the chemical structure of polymer as a result of exposure to external forces. Such studies throw light on the strength of the various bonds holding together of the polymer molecule, on the effect of time, temperature, pressure, and other variables on the rates and products of degradation. (5)

The general course of degradation of polyamides may be described as follows: (6)

A) Splitting of the polymer chain at the C-N linkage.

B) Changes in the degree of crystallitinity or local order.

C) Loss of di-pole associated plasticizers.

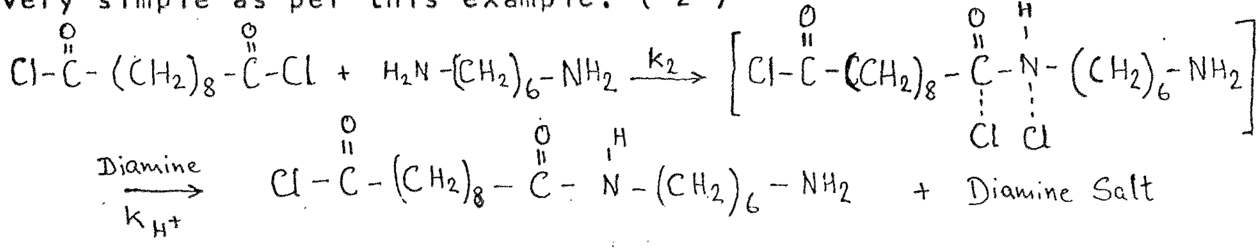
The studies on the thermal degradation of nylons were carried out by Taylor (7). He reported in 1947 that, during the process of polycondensation of nylons, ammonia as well as carbondioxide was yield. He assumed that side reactions are responsible for their production. In 1951

Achhammer and co-workers (6) pyrolyzed a number of homopolymers and mixtures of 6, 6-6, 6-10 nylons to find their relative thermal stability, chemical nature of degradation products, and rates and active energies involved in the degradation process. Generally, in pyrolysis of organic polymers, the rate of degradation approximately doubles for every 10°C rise in temperature. In view of this reaction we expect a rather low activation energy of thermal degradation for the nylons.

INTERFACIAL POLYCONDENSATION:

Over the last 10 years a new low temperature, low pressure method of polycondensation based on the Schotten-Baumann reaction has evolved (8,9,10). It allows rapid preparation of condensation polymers at room temperature. The low temperature procedure possesses great experimental advantages over high temperature processes in terms of speed and simplicity of equipment.

The chemistry of interfacial polycondensation is very simple as per this example. (2)



$$Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-Cl + H_2N-(CH_2)_6-NH_2 \xrightarrow{k_2} \left[Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\underset{Cl}{\overset{O}{\overset{\|}{C}}}-\underset{Cl}{\overset{H}{N}}-(CH_2)_6-NH_2 \right]$$

$$\xrightarrow[K_{H^+}]{\text{Diamine}} Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_6-NH_2 + \text{Diamine Salt}$$

The reactions of this type are believed to react by a molecular displacement mechanism (11, 12) to form a protonated amide from which proton is eliminated rapidly in the; presence of more base. The proton acceptor is presumably an amine group and a diamine molecule or the end of an oligomer chain. Water also acts as the proton carrier.

In the interfacial polycondensation method, the fast reacting intermediates are dissolved in a pair of immiscible liquids, one of which is preferably water. (2). The water phase contains diol or diamine and an added alkali. The other phase contains diacid halide in organic liquid (such as carbon tetrachloride, dichloro methane, xylene, hexane). The evidence cited points to the formation of the most interfacial condensation polymers in the organic phase just below the interface. The primary functions of an aqueous phase are to serve as a solvent medium for the diamine and acid acceptor and to remove by-products (acid) from the polymerization zone. Partition equilibrium is never achieved during polymerization because acylation takes place in the organic phase as rapidly as diamine is transferred. For the fast reactions the mass transfer of the diamine is the rate controlling factor step at all concentrations (2). The diamine has to penetrate more deeply into the acid chloride layer and react. During polycondensation the diamine first meets a high concentration of acid chloride and presumably is acylated to a large extent at both ends. Next, diamine finds a layer of acid chlorideterminated oligomers plus diacid chloride. Thus high polymer forms because of high reaction rate, increasing probability that diamine reacts with an oligomer than with new diacid chloride, and the diffusion of oligomer chain is slow. The reaction is exothermic (9).

VARIABLES AFFECTING INTERFACIAL POLYCONDENSATION:

REACTION RATE:

The absolute reaction rate of unhindered aliphatic acid chloride with primary diamines have reaction rates of the order of 10^2 - 10^6 l/mole-sec., in homogeneous solutions. The reaction rates are frequently faster than the rate of mixing. Bender and Jones (13) have shown that the reaction rate for benzoyl chloride and marpholene in cyclohexane at 25°C is 2.64 X 10^3 l/mole-sec. Hall (14) has found that the reaction of excess aniline with ethylchloroformate in water at 25° l is 0.6 l/mole-sec. The rate would be much lower in nonpolar solvents, such as those which have been used in interfacial polycondensation processes. Interfacial polycondensations can be carried out successfully with reactants for which the rate constants are considerably less than those above. The principal requirements are that the polymerization rate be appreciably faster than that of all side reactions and that the polymerization be complete before the polymer is immobilized in the precipitated state. The reaction rate for benzoyl chloride and ethanol is 6.9 X 10^5 l/mole-sec. (2).

TEMPERATURE:

Most interfacial polycondensations are carried out at ambient temperature, and the mixture is allowed to warm up from the heat of reaction and the heat of stirring. The reactions are already rapid; there is no need for heating; and, in fact, many preparations are improved by cooling and controlling the temperature (8,15,16). Raising the temperature will change the solubility of the intermediates and the polymer and will accelerate side reactions as well as the polymer forming reaction. Korshak and co-workers (17) found increase in temperature to be detrimental, that is, η_{sp} / concentration and yield of 6-6 polyamide in a benzene - water system decreased from 1.1 and 43% at 5°C to 0.64 and 20% at 20°C. There was parallel increase in the hydrolysis of adipoyl chloride measured independently.

REACTANTS FLOW RATE:

R.C. Kispert (18) indicated that eddy diffusion is responsible for an increase in mass transter of diamine in a continuous cascade system. Flow rates of 60, 180, 300 cc/min. of each reactant phase were used. The effect of improved mass transfer can be explained by considering the treatment of uncatalyzed liquid - liquid heterogeneous reaction by Hougen and Watson (19). For the system with stirring, that is, influencing mass transfer, the reaction rate (r_b) in organic phase is as follows:

$$r_b = \left(1/ (1/k_b) + (R_{Bb} x_{Bb} V_b / k_{AL} A_v) \right) (R_{Aa} R_{Bb} x_{Aa} x_{Bb} k_a)$$

k_b = Specific reaction rate in organic phase

$x_{Aa} x_{Bb}$ = Mole fraction of diamine (aqueous phase) and sebacoyl chloride (organic phase) respectively.

k_a = Distribution equilibrium constant of diamine

$R_{Aa} R_{Bb}$ = Activity coefficient of diamine and sebacoyl chloride

V_b = Volume of organic phase

A_{vi}= Interfacial area per unit volume

k_{AL} = Mass transfer coefficient of diamine

E.W. Hudgins (20 used a semi-continuous reactor, and the reactant phase flow rates were varied from 10 to 50 cc/min. He also studied the effect of stirring.

STIRRING AND CONCENTRATION EFFECT:

Stirring is a critical variable in preparation of polymers by low temperature polycondensation process. For convenience of discussion, the systems are divided into three general cases on polymer behavior.

A) Polymer precipitates rapidly relative to the total time for uniform mixing.

B) Polymer is extremely solvent-insensitive and forms non-swollen precipitates.

C) Polymer remains in solution until after polymerization is complete.

A polymer film will tear away, and a fresh interface will result in the formation of new film. This will repeat until the reactants are consumed. Under ideal conditions fast stirring would provide fresh interface so rapidly that there would be little time for formation of low molecular weight polymer. Korshak and co-workers (17) found that the yield and the specific viscosity of 6-6 polyamide were increased by increasing stirring rate from 1000 to 7500 RPMs. To some extent the location of peaks in molecular weight and yield depends upon range of optimum stirrability (2).

The effect of stirring is to increase the availability of the diamine. To keep the reactants balanced at the polymerization site and thus attain the highest viscosity number, the acid chloride must be more concentrated, or the diamine more diluted, as stirring speed increases. A number of researchers confirm the fact that peaks in the viscosity of the polymer arise from variation of the reactant concentrations, but do not confirm the shift in position of the peaks with changes in the solvent phase or the rate of stirring (17,21,22). The latter showed a peak shift even with moderate stirring.

Detergents assist stirring and produce a shift in peak. Whether the detergent assists diamine transport by changes in interfacial tension or merely helps disperse the phases and break-down polymer fragments is not shown. Detergents also help maintain a higher yield over a wide range of conditions.

According to Turetskii and Sokolov (23) dilute acid halide systems which are resistant to hydrolysis or have low solubility in water would be expected to work best. In batch process, rapid addition of diacid chloride to highly stirred diamine solution has given higher yield, than if the diamine solution is added to diacid solution.

Magat (15) worked with batch process of polyamide 6-10 in stirred system. He prepared by taking .022 molar hexamethylene diamine, 0.022 molar sebacoyl chloride, and 0.044 molar sodium hydroxide, optimum conditions with inherent viscosity 1.76 dl/gm. He concluded that 12% excess diacid chloride decreases inherent viscosity 1.5 dl/gm, while 12% excess diamine decreases inherent viscosity 1.28 dl/gm.

The diamine can be used as an acid acceptor in an interfacial polycondensation reaction, but the yield and molecular weight are not as high as when inorganic basesare used. The small excess amount of diamine might work beneficially. Earekson (24) states that if the diamine is increased from 1:1 ratio, the yield and the inherent viscosity of the polymer decreases. Morgan and Kwolek (25) stated that the most useful solvents for interfacial polycondensation have had very little miscibility with water phase. Miscibility can not be increased in the preparation of 6-10 polyamide without producing a decrease in the inherent viscosity and a loss in polymer yield. The high dilution of the reactants and the use of diamine as the acid acceptor probably cause the formation of a polymer with low viscosity.

Because of simplicity of the interfacial polycondensation and the high reaction rate, the simple glass apparatus was suggested by Morgan, Beaman, Koller, Wittbeker, and Magat (9,15,16). Beaman and co-workers (16) also suggested and used a simple glass injection tube to prepare 6-6 polyamids.

The rapid rate of reaction at room temperature and atmospheric pressure, the irreversibility of the reaction, the quantitative yield of the polymer, and the simple apparatus were the main factors which arroused our interest in this type of reaction, and particularly 6-10 polyamide. Over and above all these, there has been much work done on 6-10 polyamide. The present work mainly deals with the study and the effect of continuous interfacial polycondensation of 6-10 polyamide on yield and the intrinsic viscosity using different stirring rates (RPM) and different concentration of the monomers as major variables.

EXPERIMENTAL PROCEDURE:

A flow chart of the experimental apparatus is shown in Fi f. 1. Solutions of hexamethylenediamine in water (aqueous phase) and sebacoyl chloride in carbon tetrachloride (organic phase) were stored in constant head reservoirs (A). Flow rates from tanks with this type of arrangement are not influenced by the fluid level. From the reservoirs the liquids flowed through 1/4" polyvinyl chloride rightangled valves (C), which regulated the flow of liquids into the system. Next, liquids went to a polyvinyl chloride duplex pump, (maximum flow rate 12.4 gal/hour) which metered the flow rates. The flow from the pump was then split through the use of a 1/4" polyvinyl chloride T (D). One stream (the bypass) passed through 1/4" polyvinyl chloride needle valve (E) and returned to reservoirs. The other stream passed through a 1/4" polyvinyl chloride check valve (F) and continued to the 2"X4"X !" Durelin block (G), which was used, support the reactor and to keep it in a horizontal position.

The reactor is shown in Fig. 2. The thick-walled glass reactor (G) was 6" long, 3/4" in diameter, and had conical ends. It was attached to the Durelin block (C) by means of a flange (F) and a gasket arrangement. A stainless steel paddle with a pitch of 45° and a diameter of 3/8" was used as the agitator (E) for the reactor.

The stirrer was attached to a 3/32" diameter shaft and extended 1/2" in to the reacting zone. The agitator was driven by means of a variable speed motor (A) which had shaft extensions on both sides of the motor body. One side was attached to the stirrer through the use of bearing blocks and couplings, the other end to a Smith hand tachometer which measured the RPMs, on the other shaft. The speed varied between 1000 to 10,000 RPM, with approximately 20 RPM error after running for one hour. A 2 1/2" long U-shaped glass over flow tube (H) was attached to the reactor with a flange (F) and gasket arrangement.

To minimize the fluctuations, the pump was primed for an hour before each run. The reactor was first filled with hexamethylenediamine, and the desired RPM was set. The flow rate of solutions was set at 70 cc/min. and was checked before each run. Sebacoyl chloride was then allowed to enter the reactor, where the polymer was formed. After a steady state was achieved, polymer and unreacted materials flowed into a 4-liter beaker containing 1-liter dilute hydrochloric acid solution. The solution in the beaker was stirred with a constant speed to react hydrochloric acid with unreacted hexamethylenediamine. This stirring process was used to stop any further polymerization taking place.

The following procedure was used to separate the polymer from the rest of the mixture.

A) Stir the mixture in the 4-liter beaker for 5 minutes.

B) Filter and wash with distilled water.

C) Dry at 50 to 60°C for 12 hours.

The dried polymer was then used to determine whether intrinsic viscosity of a polymer is related to its molecular weight. A 0.2 gram sample of dried polymer was placed in a 10 cc volumetric flask and was dissolved with m-cresol. The solution was stored for 15-20 hours to dissolve the polymer solution completely. The solution was thus filtered with Buchner funnel using vaccum. The filtered polymer solution (3 cc) was placed in a calibrated Ubbelohde viscometer, size 200. The viscometer was put in a constant temperature water bath, the temperature of which was set at 30°C, and the viscometer was kept in it for three hours to ensure constant temperature of the sample. The efflux time of the samples was then determined.

RESULTS:

Tables 1 to 4 give the data collected for relative viscosities, specific viscosities, reduced specific viscosities, and intrinsic viscosities as a function of different stirring rates and monomer concentrations.

Table 5 gives the data of polymer yield per minute as a function of different stirring rates and monomer concentrations.

Table 6 gives the data of calculated values for Reynold's number as a function of relative viscosity.

Table 7 gives the data of calculated values for mass transfer coefficient (K) and dimensionless J_D factor.

The figures 1 to 30 show the plot of reduced specific viscosity versus concentration of the polymer solutions.

The figures 31 to 34 show the plot of polymer yield per minute versus Reynold's number and different stirring rates (RPM).

The figures 35 and 36 show the plot of intrinsic viscosities versus Reynold s number and different stirring rates (RPM) having monomer concentrations ratio as parameter.

Figure 37 shows the plot of intrinsic viscosity versus monomer ratios (sebacoyl chloride/hexamethylenediamine) and different stirring rates (RPM) as a parameter.

Figure 38 shows the plot of density of the polymer.

Figure 39 shows the plot of log j_D versus log Re from literature.

Figure 40 and 41 are the plots of log j_D versus log Re.

Figure 42 is the plot of log K/D_A versus log Re.

DISCUSSION :

This section considers and discuses the data presented in the Results Section.

The data of relative viscosity (η_{Re}), specific viscosity (η_{sp}), reduced specific viscosity ($\eta_{Re.sp.}$), and intrinsic viscosity are given in Tables 1 to 4 and Figures 1 to 30.

$$\eta_{Re} = \frac{\text{efflux time of solution}}{\text{efflux time of solvent}}$$

$$\eta_{sp.} = \eta_{Re} - 1.0$$

$$\eta_{Re.sp.} = \eta_{sp.} / \text{Concentration of polymer}$$

As from the figure, excellent linear plots of reduced specific viscosity versus concentration of the polymer solution were generally obtained. The closeness of fit of the data and its reproducibility assured the precision of the relative viscosity data. These data were important because they measured the degree of polymerization of the polymer.

POLYMER YIELD

In Figures 31 to 34 yield (Polymer weight) data are presented as gm/min versus stirrer speed (RPM) and Reynolds number (Re) with the reactant ratio as a parameter. Table 5 presents the data of yield/minute.

The yield was calculated as follows: The two monomers Sebacoyl Chloride (70 ce/min) and hexamethylene diamine 70 (ce/min) were fed in to the reactor, and the stirrer was kept at constant RPM. The polymer formation take place in the reactor. The polymer was then collected in a beaker formed in the reactor for three minutes. The reaction was stopped with hydrochloric acid. The polymer was then washed and dried. The polymer was weighted to determine the yield/min. (gm/cm)

As can be seen, the nylon 6-10 yield first increases at a constant reactant ratio and then decreases or levels off with increasing stirring rate (RPM) or Reynolds number. This fact can be explained as follows: The increase in stirring rate RPM the mass transport of the diamine increases. We know that mass transport is a rate controlling factor in this kind of reaction. For this reason the yield first increases with increasing stirring rate RPM at constant reactant ratio. In the later part the decrease in yield is due to improved mass transport which imbalances the reactants and hence leads us in the decrease in the polymer yield.

The decrease in polymer yield may be due to the choking of the reactor. At high stirring rate RPM the polymer formation is rapid so that reactor fills with polymer and chokes off the further formation of polymer.

The polymer yield increases with increasing reactant ratio (sebacoyl chloride/hexamethylene diamine, i.e., increasing the concentration of sebacoyl chloride and keeping hexamethylene diamine concentration constant) at a constant stirring speed RPM. In the work of Kispert (18), he reported that, as the ratio increased, the yield of the polymer also increased. (His work was with continuous cascade system.) In the work of Morgan (2,9,25) with batch processes, he reported that yield of the polymer increases with increasing reactant ratio. This may be explained as follows:

1. polymerization zone has more molecules of Sebacoyl Chloride than hexamethylene diamine, which reacts in the formation of a small network and more yield.
2. The reactants get little longer time to stay in the reactor which helps in formation of more polymer yield.
3. The diamine molecules are not used by acid (by product) in the presence of more molecules of Sebacoyl Chloride.

In Figures 32 and 34 the plot shows that even the ratio is higher but the yield decreases. The fact can be explained because the diamine concentration is decreased from 0.025 molar to 0.01 molar and the concentration of Sebacoyl Chloride was kept constant 0.055 molar.

Intrinsic Viscosity of a Function of Stirring Rate and Reactants Ratio.

Fig. 35 and 36 plot of intrinsic viscosity versus RPM and Reynolds number, respectively. Reynolds number is a dimensionless group and was calculated by using the formula:

$$Re = (d^2/\nu) \quad N$$

N the stirring rate RPM.

d the Stirrer diameter (cm)

$\nu = \mu/\rho$ Kinamatic viscosity (cm^2/sec)

μ viscosity of slurry (cp)

ρ density of slurry (gm/cc)

The calculations are shown in sample calculations. In calculations the assumption was made that system is heterogeneous. The Reynolds number is

$$Re = \text{inertial forces/viscous forces}$$

and as such is a measure of hydrodynamic conditions.

Both Figures 35 and 36 show the same trend, namely a decrease in intrinsic viscosity at a constant speed or constant Reynolds number with increasing reactant ratio. (sebacoyl chloride/hexamethylenediamine). In the work of Morgan (2,9) with batch processes, he reported that intrinsic viscosity decreases with increasing reactant ratio (unstirred system). At constant stirring rate, he reported that withincreasing reactant ratiothe intrinsic viscosity decreases. The work of Kispert (18) dealt with the continuous cascade system, he reported that as reactant ratio increases, the intrinsic viscosity first increases and then decreases. He used in his system NaOH as an acid acceptor with the ratio 2:1 with diamine. The above kind of behavior may be explained as followed:

1. The diamine concentration is the same and sebacoyl chloride concentration increases in the polymerization zone, so that diamine has more molecules of sebacoyl chloride to react with. As a result we get small polymer chain.
2. The diamine acts as an acid acceptor and neutralizes the acid (byproduct) in the polymerization zone.
3. We know that the more the transport of the diamine molecules, the better the polymer; but when sebacoyl chloride molecules are more in the polymerization zone, the mass transport of the diamine molecules is affected.

As shown in Figures 35 and 36, the intrinsic viscosity first decreases and then increases at constant reactant ratio with increasing RPM or Reynolds number. This kind of work has not been done in literature. The above kind of behavior can be explained as follows:

The intrinsic viscosity decreases between 2000 to 3000 RPM The laminar zone is up to 2000 RPM. Next, between 2000 to 3000 RPM is transition zone; and after 3000 RPM is turbulent zone. The resultant changes in hydrodynamic conditions affect the mass transfer and ultimately the molecular weight of the polymer formed. Because of the above reasons the intrinsic viscosity decreases in the transition zone and then increases in the turbulent zone.

The diamine molecules reacts with oligomer chains and not with new sebacoyl chloride molecule. That means that the long polymer chain formation take place and lead to higher intrinsic viscosity.

MASS TRANFER IN CONTINUOUS POLYMERIZATION

As has been pointed presently (2,9,16,18,25,31) the actual reaction rate in interfacial polycondensation systems is very rapid being of the order of 10^2 to 10^6 1/mole-sec (2,9,25). Consequently the rate controlling step in the process is the transfer of mass (diamine to the organic phase). The importance of mass transfer as rate controlling step has been pointed out by many authers (2,9,16,18,25).

Because mass tranfer is the principal transport process occuring in interfacial polycondensation it behooves us to treat the data from a mass transfer viewpoint. We then computed both mass tranfer coefficient (K)

$$K = (1/6)\ (1/m_{in}c_i)\ (dci/dt) \qquad (28)$$

$$m_{in} = 35 \qquad (28)$$

$$m_{in} = c_{o\ in} / c_{i\ in} \qquad (28)$$

c_i concentration of hexamethylenediamine

and j_D factor (dimensionless group)

$$j_D = (K/cN)\ (\mu/\rho\ D_{AB})^{0.66} \qquad (29)$$

K	mass transfer coefficient
c	concentration of diamine (molar)
N	RPM
μ	viscosity of the slurry (cp)
ρ	density of the slurry (gm/cc)
D_{AB}	diffusion coefficient of diamine

to demonstrate the analogy behavior heat and mass transfer.

In calculating mass transfer coefficient (K), the size of the droplets were assumed constant. The value of m_{in} was taken 35, as given in the literature (28). The calculation for mass transfer coefficient (K) is shown in sample calculations. The units for mass transfer coefficient (K) is cm/hr. The data for mass transfer coefficient (K) are given in Table 7 and Figure 42. The plot of log K/D_{AB} versus log Re is shown in Figure 42. For this present work there is no literature concerning the log K/D_{AB} versus log Re plot. For the first time this kind of work has been done for the chemically reacting system.

In Figure 39 to 41 and Table 7 the data for j_D factor are given. In Figure 40 we plotted the log j_D versus log Re. In Figure 39 literature data (29) for log j_D versus log Re are presented for droplets, in distribution column. The shape and size of the droplets in present work and literature are not the same but close enough to compare the data of present work and literature. There is no work done in literature on j_D factor for chemically reacting system. Figure 40 shows the multiplicity of lines is probably due to our having a chemically reacting system.

In Figure 41 we have modified j_D factor by using unity reactant ratio. For example we have 0.4 reactant ratio; and to make unity reactant ratio, we have to multiply the reactant ratio 0.4 by 2.5; that means the j_D factor for that reactant ratio should be multiplied by 2.5 to make the j_D factor for unity. Note that this brings all the j_D factors data for different reactant ratio close together so that one correlation line can be used.

CONCLUSIONS AND RECOMMENDATION

1) Intrinsic viscosity at constant RPM decreases with increasing reactant ratio (sebacoyl chloride/hexamethylenediamine). It has been stated (18) that a peak intrinsic viscosity will be obtained when there is a balance of reactants. For sebacoyl chloride concentrations below than the balance point, a less compact polymer metwork is formed. For sebacoyl chloride concentration higher the balance point, the formation of the polycondensation zone is restricted, resulting in lower intrinsic viscosity.

2) Intrinsic viscosity at constant reactant ratio first increases with RPM, and then decreases. This can be explained as follows. Stirring cases should have better diamine mass transport than non-stirring cases. The improved diamine mass transfer causes an imbalance of reactants and resulting lower intrinsic viscosity.

3) With increasing RPM the polymer yield (gm/min) increases up to a maximum and then levels off or decreases. This can be explained as due to the improved mass transport of diamine which result in increase in yield in the beginning but the imbalance in the concentration of reactants will ultimately level off or decrease the yield.

4) The plot of log J_D factors versus log Re indicates the same trend as found in literature. A higher the j_D factor,

lower will be the value of Re. Log J_D versus log Re gives one correlator curve at monomer ratio one.

Recommendations:

It is recommended that future work can take the following course:

1) The work can be done with benefit with narrow range of monomer concentration ratio. This will help in elucidating the behavior of intrinsic viscosity with change in RPM.
2) If one monomer concentration is kept constant, the concentration of the other monomer should be varied for a longer range of concentrations. This work may help to understand the behavior of polymer yield and intrinsic viscosity curve.
3) The selection of narrow range of RPM will be useful to predict the actual trend of the intrinsic viscosity and polymer yield curve.
4) The work can be done in presence of an acid acceptor.
5) The equipment for the experimental work can be modified for better results.
    a) Longer reactor tube can be used.
    b) Diameter of the reactor tube can be increased.
    c) The distance of the stirrer in the reactor can be increased.
    d) The number of stirrers can be increased. The material of the stirrer can be changed fruitfully.

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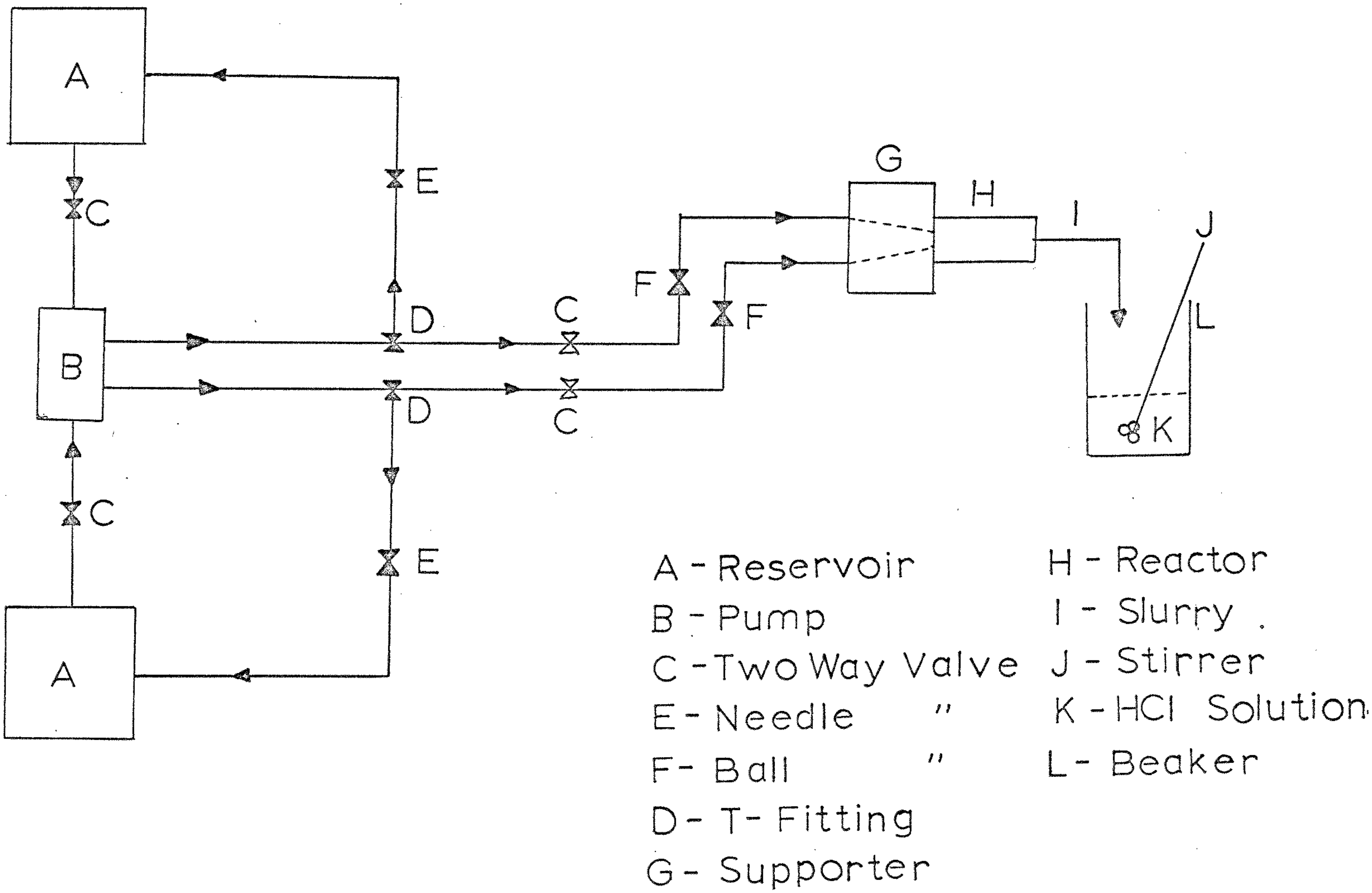
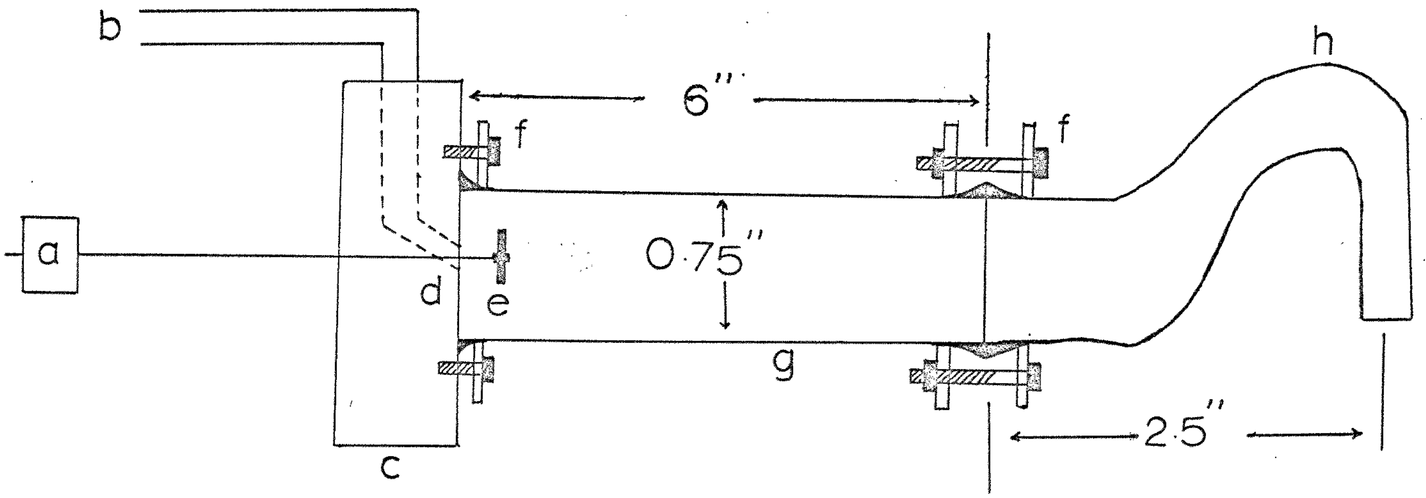
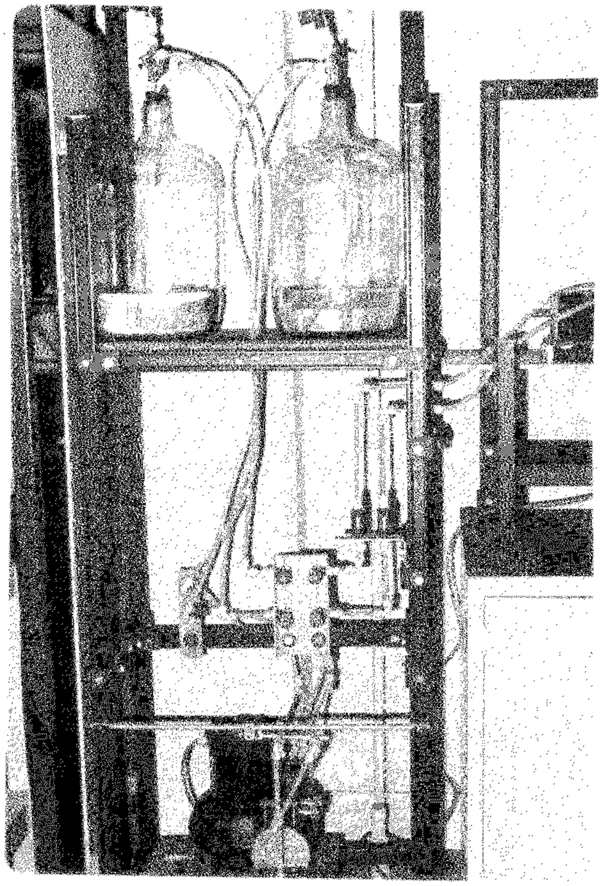
Flow Chart of the Apparatus

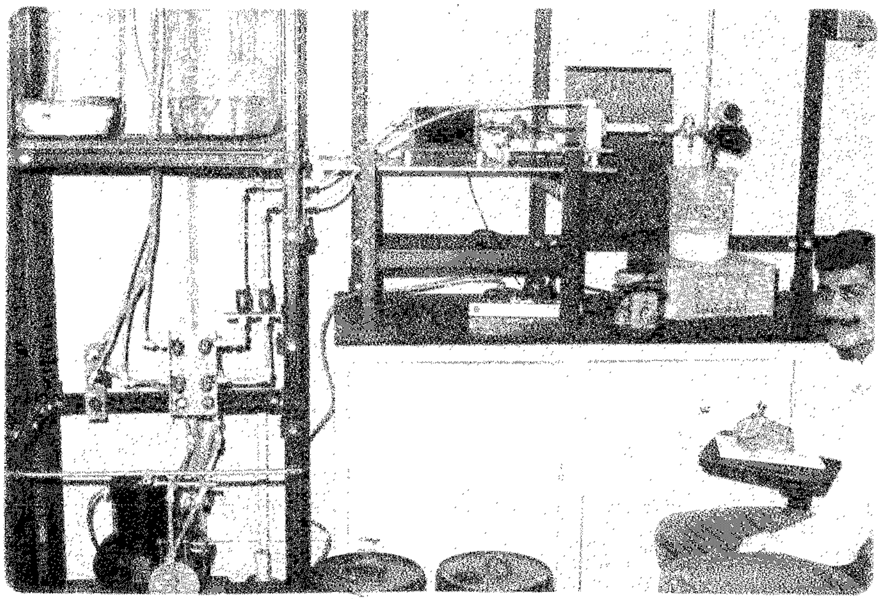


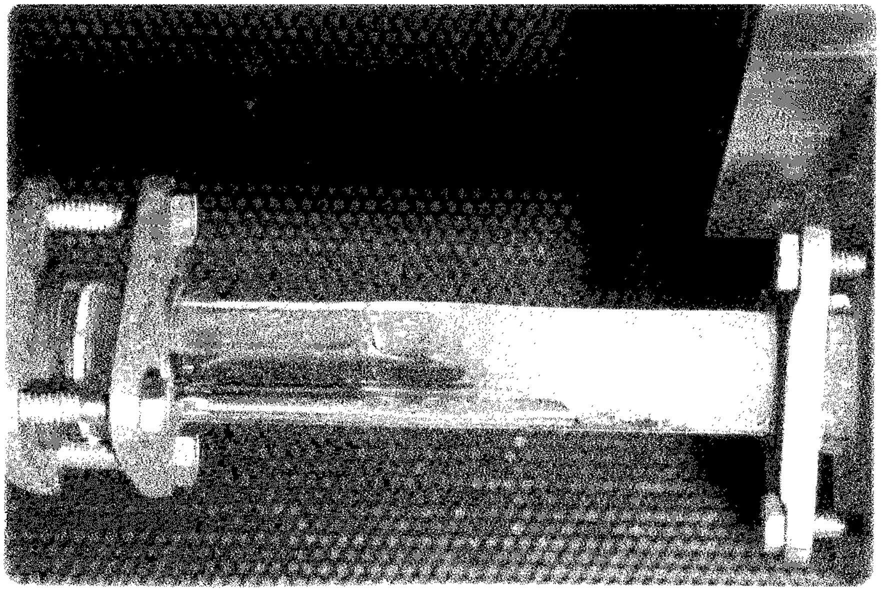
A - Reservoir
B - Pump
C - Two Way Valve
E - Needle "
F - Ball "
D - T- Fitting
G - Supporter

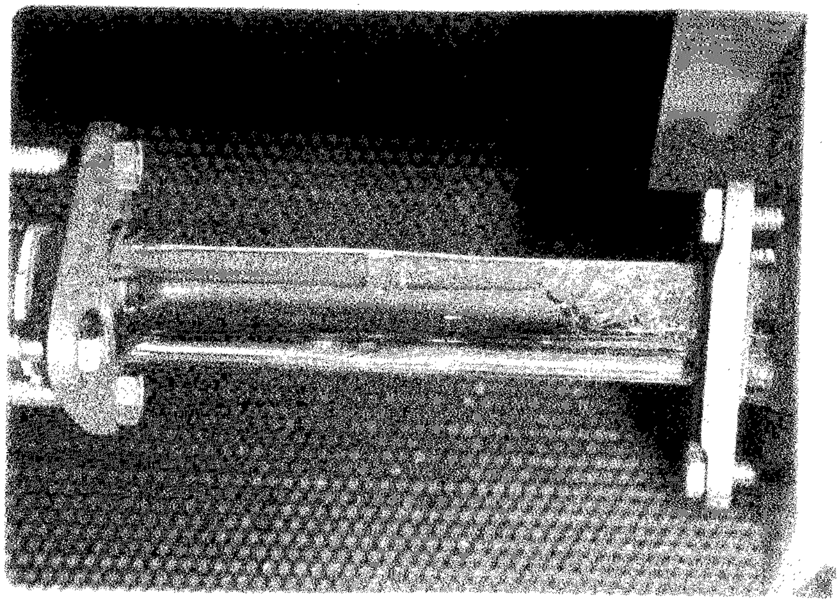
H - Reactor
I - Slurry
J - Stirrer
K - HCl Solution
L - Beaker

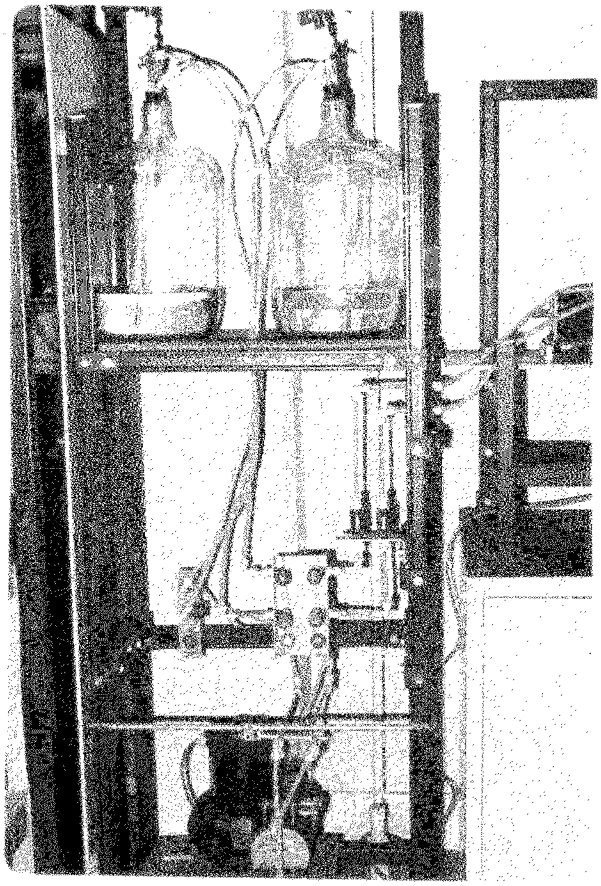

b
h
6''
f
f
a
0.75''
d
e
g
2.5''
c

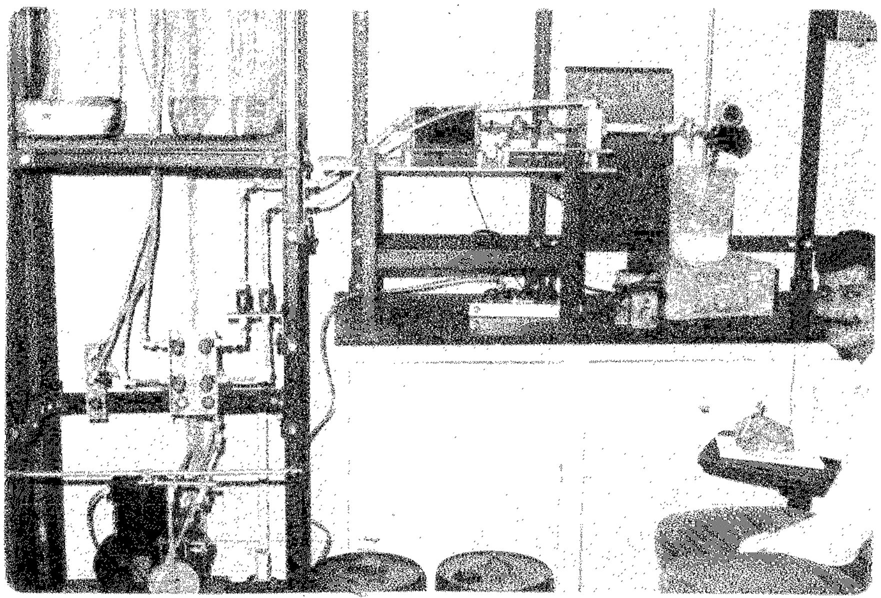












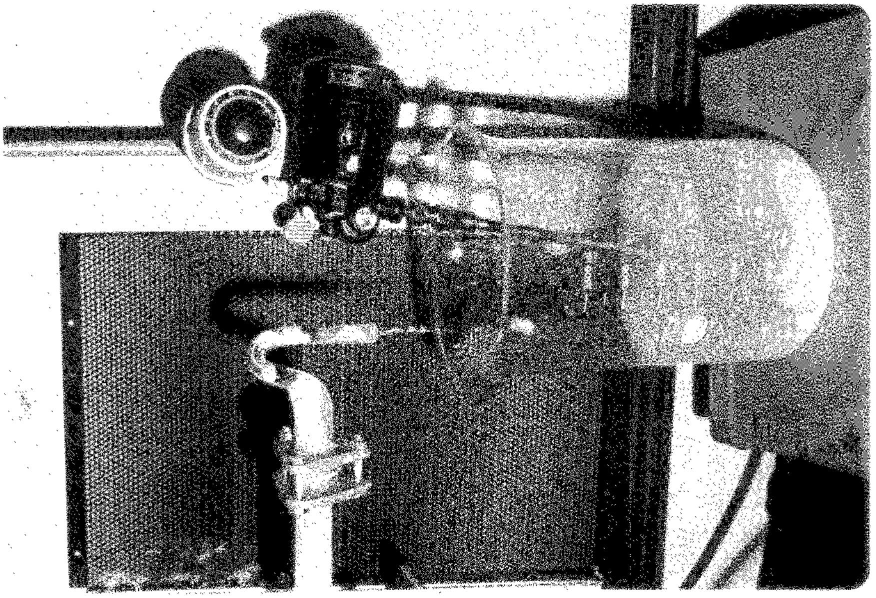


TABLE 1 (CONTINUED)

Serial Number	R.P.M.	Efflux Time of Solvent Sec.	Concentration of Polymer gm/dl	Efflux Time of Solution Sec.	Relative Viscosity	Specific Viscosity	Reduced Specific Viscosity dl/gm	Intrinsic Viscosity dl/gm
5	4000	102.56	2.0	244.7	2.386	1.386	0.693	0.501
			1.5	201.65	1.96616	0.96616	0.6441	
			1.2	178.32	1.7387	0.7387	0.6156	
			1.0	163.77	1.5968	0.5968	0.5968	
			0.75	146.5	1.4284	0.4284	0.5712	
6	5000	90.94	2.00	232.9	2.561	1.561	0.7805	0.563
			1.5	189.82	2.0873	1.0873	0.725	
			1.2	165.65	1.8215	0.8215	0.6929	
			1.0	151.87	1.67	0.67	0.67	
			0.75	134.9	1.483	0.483	0.644	
7	6000	102.56	2.0	240.75	2.3474	1.3474	0.6737	0.495
			1.5	199.65	1.9466	0.9466	0.6311	
			1.2	176.65	1.7223	0.7223	0.602	
			1.0	162.50	1.5844	0.5844	0.5844	
			0.75	145.5	1.4187	0.4187	0.5582	

TABLE 2

Temperature 30^{oc}
Solvent M-Cresol

Hexamethylene Diamine 0.025 molar
Sebacoyl Chloride 0.025 molar

Serial Number	R.P.M.	Efflux Time of Solvent Sec.	Concentration of Polymer gm/dl	Efflux Time of Solution Sec.	Relative Viscosity	Specific Viscosity	Reduced Specific Viscosity dl/gm	Intrinsic Viscosity dl/gm
1	2000	90.94	2.01	129.88	1.417	0.417	0.2074	0.177
			1.723	122.7	1.3492	0.3492	0.2027	
			1.5	118.17	1.30	0.3	0.20	
			1.2	112.05	1.2328	0.2328	0.194	
			1.0	108.55	1.193	0.193	0.193	
2	3000	102.56	2.00	143.8	1.402	0.402	0.201	0.122
			1.7143	136.02	1.3262	0.3262	0.18	
			1.5	130.5	1.2724	0.2724	0.1816	
			1.2	123.36	1.2028	0.2028	0.169	
			1.0	112.0	1.162	0.162	0.162	
3	4000	102.56	2.0	154.0	1.504	0.504	.252	0.154
			1.7143	145.4	1.418	0.418	.238	
			1.5	137.8	1.3435	0.3435	.229	
			1.2	128.8	1.2556	.2556	.213	
			1.0	123.38	1.203	.203	0.203	
4	5000	102.68	2.005	158.94	1.548	0.548	0.274	0.186
			1.7143	148.8	1.4491	0.4491	.262	
			1.5	140.5	1.378	.3780	.252	
			1.2	132.25	1.288	.288	.24	
			1.0	126.3	1.23	0.23	.23	

TABLE 2 (CONTINUED)

Serial Number	R.P.M.	Efflux Time of Solvent Sec.	Concentration of Polymer gm/dl	Efflux Time of Solution Sec.	Relative Viscosity	Specific Viscosity	Reduced Specific Viscosity dl/gm	Intrinsic Viscosity dl/gm
5	6000	90.94	2.005	141.33	1.554	0.554	0.277	0.216
			1.7143	132.19	1.4617	0.4617	0.268	
			1.5	126.5	1.3927	0.39270	0.2618	
			1.2	118.7	1.3048	0.3048	0.254	
			1.0	113.25	1.264	0.264	0.246	
6	8000	102.56	2.005	176.96	1.72	0.720	0.36	0.284
			1.7143	162.61	1.60	0.60	0.349	
			1.5	154.85	1.51	0.510	0.340	
			1.2	143.3	1.396	0.396	0.33	
			1.0	135.6	1.321	0.321	0.321	
7	10000	102.68	2.000	164.5	1.602	0.602	0.301	0.227
			1.7143	154.35	1.50	0.50	0.290	
			1.5	146.1	1.4245	0.4245	0.283	
			1.2	135.87	1.323	0.33	0.27	
			1.0	129.78	1.264	0.264	.264	

TABLE 3

Temperature 30^{oc}
Solvent M-Cresol

Hexamethylene Diamine 0.025 molar
Sebacoyl Chloride 0.055 molar

Serial Number	R.P.M.	Efflux Time of Solvent Sec.	Concentration of Polymer gm/dl	Efflux Time of Solution Sec.	Relative Viscosity	Specific Viscosity	Reduced Specific Viscosity dl/gm	Intrinsic Viscosity dl/gm
1	2000	90.94	2.0	119.0	1.309	0.309	0.1545	0.109
			1.7143	113.97	1.2533	0.2533	.148	
			1.5	110.5	1.21525	0.21525	.1435	
			1.2	105.9	1.1644	0.1644	.137	
			1.0	102.9	1.1315	0.1315	.1315	
2	3000	102.56	2.0	134.42	1.31	0.31	.155	.102
			1.7143	128.4	1.252	.252	.147	
			1.5	124.16	1.2106	0.2106	.13105	
			1.2	119.0	1.1608	0.1608	.1340	
			1.0	115.75	0.1285	0.1285	.1285	
3	4000	90.94	2.0	119.55	1.314	.314	.157	.108
			1.7143	114.39	1.258	.258	0.15	
			1.5	110.65	1.2168	.2168	0.1445	
			1.2	105.9	1.1644	.1644	0.137	
			1.0	103.0	1.132	.132	.132	
4	5000	102.56	2.0	140.75	1.362	.362	.181	.13
			1.7143	133.15	1.2983	.2983	.174	
			1.5	128.58	1.2537	.2537	.169	
			1.2	122.26	1.192	.192	.16	
			1.0	118.58	1.156	.156	.156	

TABLE 3 (CONTINUED)

Number	R.P.M.	Efflux Time of Solvent Sec.	Concentration of Polymer gm/dl	Efflux Time of Solution Sec.	Relative Viscosity	Specific Viscosity	Reduced Specific Viscosity dl/gm	Intrinsic Viscosity dl/gm
5	6000	90.94	2.0	128.0	1.408	.408	.204	.156
			1.7143	123.04	1.3386	.3385	.1975	
			1.5	117.15	1.288	.2880	.192	
			1.2	111.13	1.222	.2220	.185	
			1.0	107.31	1.18	.180	.18	
6	7000	102.56	2.0	150.55	1.468	.468	.234	.174
			1.7143	141.54	1.38	.38	.225	
			1.5	136.2	1.328	.328	.219	
			1.2	128.53	1.253	.2532	.21	
			1.0	123.49	1.204	.204	.204	
7	8000	102.56	2.0	148.12	1.451	.451	.2255	.122
			1.7143	139.55	1.3607	.3607	.2105	
			1.5	136.62	1.3	.30	.20	
			1.2	125.2	1.2208	.2208	.184	
			1.0	120.37	1.1735	.1735	.1735	

TABLE 4

Temperature 30^{oc}
Solvent M-Cresol

Hexamethylene Diamine 0.01 molar
Sebacoyl Chloride 0.055 molar

Serial Number	R.P.M.	Efflux Time of Solvent Sec.	Concentration of Polymer gm/dl	Efflux Time of Solution Sec.	Relative Viscosity	Specific Viscosity	Reduced Specific Viscosity dl/gm	Intrinsic Viscosity dl/gm
1	2000	90.94	2.0	105.23	1.157	0.157	0.7785	.047
			1.7143	102.46	1.1267	0.1267	0.734	
			1.5	100.43	1.10435	0.10435	0.0696	
			1.2	98.1	1.07873	0.07873	0.0656	
			1.0	98.65	1.0628	0.0628	0.0628	
2	2500	90.94	2.0	102.6	1.1282	0.1282	.0641	.032
			1.7143	100.3	1.10286	0.10286	.06	
			1.5	98.6	1.08423	0.08423	0.5615	
			1.2	96.64	1.06268	0.06268	0.0522	
			1.0	95.15	1.0463	0.0463	0.0463	
3	3000	102.56	2.0	117.85	1.14908	0.14908	0.7454	.038
			1.7143	114.8	1.11934	0.11934	.07	
			1.5	112.59	1.0978	0.0978	.0652	
			1.2	109.95	1.072	0.072	0.06	
			1.0	108.55	1.0584	0.0584	0.0584	
4	3500	102.56	2.0	121.6	1.1856	0.1856	0.0928	.046
			1.7146	117.9	1.14947	0.14947	0.0872	
			1.5	114.9	1.1203	0.1203	0.0802	
			1.2	111.7	1.0891	0.0891	0.0743	
			1.0	109.8	1.0706	0.0706	0.0700	

TABLE 4 (CONTINUED)

Serial Number	R.P.M.	Efflux Time of Solvent Sec.	Concentration of Polymer gm/dl	Efflux Time of Solution Sec.	Relative Viscosity	Specific Viscosity	Reduced Specific Viscosity dl/gm	Intrinsic Viscosity dl/gm
5	4000	90.94	2.0	109.2	1.2	0.2	0.1	.055
			1.7143	105.75	1.163	0.163	0.095	
			1.5	103.1	1.134	0.134	0.0893	
			1.2	99.9	1.0985	0.0985	0.0821	
			1.0	98.0	1.07763	0.07763	0.07763	
6	5000	90.94	2.0	111.93	1.2308	.2308	.1154	.065
			1.7143	107.66	1.184	.184	.1073	
			1.5	104.95	1.154	.154	.1027	
			1.2	101.2	1.104	.104	.095	
			1.0	99.14	1.09	.09	.09	
7	6000	102.56	2.0	131.20	1.279	0.2790	.1395	.086
			1.7143	125.8	1.2266	0.2266	.132	
			1.5	121.9	1.1886	0.1886	.126	
			1.2	117.08	1.1416	.1416	.118	
			1.0	114.15	1.113	.113	.113	
8	7000	90.94	2.0	117.22	1.289	.289	.1445	.11
			1.7143	113.57	1.2387	.2387	.1395	
			1.5	109.49	1.204	.204	.136	
			1.2	105.13	1.156	.156	.13	
			1.0	102.5	1.127	.127	.127	

TABLE 5

Serial Number	Concentration of Hexamethylene Diamine Molar	Concentration of Sebacoyl Chloride Molar	Ratio of Monomer Solutions	Flow Rate of Hexamethylene Diamine cc/m	Flow Rate of Sebacoyl Chloride cc/m	R.P.M.	Polymer yield/ min./gms.
1	0.025	0.01	0.4	70.0	70.0	2000	.0473
						2500	0.05214
						3000	0.05364
						3500	0.0576
						4000	0.0584
						5000	0.0777
						6000	0.0658
2	0.025	0.025	1.0	70.0	70.0	2000	0.148
						3000	0.19
						4000	0.2159
						5000	0.226
						6000	0.232
						8000	0.2227
						10000	0.2169
3	0.025	0.055	2.2	70.0	70.0	2000	0.2197
						3000	0.3412
						4000	0.3844
						5000	0.372
						6000	0.3269
						7000	0.3156
						8000	0.292
4	0.01	0.055	5.5	70.0	70.0	2000	0.2195
						2500	0.1975
						3000	0.174
						3500	0.198
						4000	0.2059
						5000	0.1845
						6000	0.175
						7000	0.140

TABLE 6

Viscosity of Solvent - .8418 cp.
Density of Slury - .81886 gm/cc

Diameter of Stirrer - .9525 cm
D^2 - .90725 cm cm

R.P.M.	Concentration of Hexamethylene diamine molar	Concentration of Sebacoyl chloride molar	Relative Viscosity of Polymer 1 % Solution	Viscosity cp.	Kinematic Viscosity cm cm/sec	Intrinsic Viscosity dl/gm	Reynolds Number
2000	0.025	0.010	1.4200	1.1953	0.0146	0.3400	2071.34
	0.025	0.025	1.1930	1.0043	0.0123	0.1770	2465.88
	0.025	0.055	1.1315	0.9525	0.0116	0.1090	2599.87
	0.010	0.055	1.0628	0.8946	0.0109	0.0470	2767.92
2500	0.025	0.010	1.5040	1.2660	0.0154	0.4020	2445.20
	0.025	0.025	------	------	------	------	-------
	0.025	0.055	------	------	------	------	-------
	0.010	0.055	1.0463	0.8800	0.0107	0.0320	3514.75
3000	0.025	0.010	1.5230	1.2820	0.0156	0.4320	2897.33
	0.025	0.025	1.1620	0.9780	0.0119	0.1220	3797.44
	0.025	0.055	1.1285	0.9500	0.0116	0.1020	3910.20
	0.010	0.055	1.0584	0.8910	0.0109	0.0380	4169.34
3500	0.025	0.010	1.5606	1.3137	0.0160	0.4660	3299.15
	0.025	0.025	------	------	------	------	-------
	0.025	0.055	------	------	------	------	-------
	0.010	0.055	1.0706	0.9010	0.0110	0.0460	4809.13
4000	0.025	0.010	1.5968	1.3442	0.0164	0.5010	3684.54
	0.025	0.025	1.2030	1.0127	0.0123	0.1540	4890.70
	0.025	0.055	1.1320	0.9530	0.0116	0.1080	5197.45
	0.010	0.055	1.0770	0.9070	0.0111	0.0550	5459.67

TABLE 6 (CONTINUED)

R.P.M.	Concentration of Hexamethylene diamine molar	Concentration of Sebacoyl chloride molar	Relative Viscosity of Polymer 1 % Solution	Viscosity cp.	Kinematic Viscosity cm cm/sec	Intrinsic Viscosity dl/gm	Reynolds Number
5000	0.025	0.010	1.6700	1.4058	0.0172	0.5630	4404.18
	0.025	0.025	1.2300	1.0354	0.0126	0.1860	5979.64
	0.025	0.055	1.1560	0.9730	0.0119	0.1300	6362.46
	0.010	0.055	1.0900	0.9176	0.0112	0.0650	6747.66
6000	0.025	0.010	1.5844	1.3337	0.0163	0.4950	5570.00
	0.025	0.025	1.2640	1.0640	0.0130	0.2160	6982.00
	0.025	0.055	1.1800	0.9933	0.0121	0.1560	7479.00
	0.010	0.055	1.1130	0.9370	0.0114	0.0860	7929.26
7000	0.025	0.010	-------	-------	------	-------	-------
	0.025	0.025	-------	-------	------	-------	-------
	0.025	0.055	1.2040	1.0135	0.0124	0.1740	8552.58
	0.010	0.055	1.1270	0.9487	0.0116	0.1100	9137.00
8000	0.025	0.010	------	------	------	------	-------
	0.025	0.025	1.3210	1.1120	0.0136	0.2840	8907.48
	0.025	0.055	1.1735	0.9878	0.0121	0.1220	10027.00
	0.010	0.055	------	------	------	------	--------
10000	0.025	0.010	------	------	------	-------	--------
	0.025	0.025	1.2640	1.0640	0.0123	0.2270	11636.20
	0.025	0.055	------	------	------	-------	--------
	0.010	0.055	------	------	------	-------	-------

TABLE 7

RPM	concentration of hexamethylenediamine	concentration of sebacoyl chloride	yield per min.	d_{ci}/dt	K	K/D_{AB}	K/C	Reynolds number	J_D
2000	0.025	0.01	0.0473	.0001214	.000199	10.311	.0685	2071.34	0.00194
	0.025	0.025	0.148	.00038	.000623	30.226	.2144	2465.88	0.006078
	0.025	0.055	0.2197	.000564	.000924	40.789	.3182	2599.87	0.00902
	0.010	0.055	0.2195	.0005634	.00231	119.600	1.9866	2767.92	0.0563
2500	0.025	0.010	0.05214	.0001338	.00022	11.366	.0755	2445.2	0.00171
	0.025	0.025	--------	------	-----	-----	----	-----	------
	0.025	0.055	--------	------	-----	-------	----	-----	------
	0.010	0.055	0.1975	.000507	.00207	107.6	1.7873	3514.75	0.04054
3000	0.025	0.010	0.05364	.0001377	.000226	11.692	.07769	2897.33	0.001468
	0.025	0.025	0.19	.000487	.0008	41.417	.2752	3797.44	0.0052
	0.025	0.055	0.3412	.000876	.00143	74.377	.4942	3910.2	0.00934
	0.010	0.055	0.174	.0004466	.00183	94.8	1.5747	4169.34	0.0297
3500	0.025	0.010	0.0576	.0001478	.000242	12.566	.0834	3299.15	0.00135
	0.025	0.025	-----	------	-----	-----	----	-----	------
	0.025	0.055	-----	------	-----	-----	----	-----	------
	0.010	0.055	0.198	.000508	.00208	107.88	1.792	4809.13	0.029
4000	0.025	0.010	0.0584	.00015	.000245	12.728	.0846	3684.54	0.0012
	0.025	0.025	0.2159	.000554	.000908	47.06	.3127	4890.7	0.00443
	0.025	0.055	0.3844	.000986	.001617	83.77	.5566	5197.45	0.0079
	0.010	0.055	0.2059	.000528	.00216	112.16	1.863	5459.69	0.0264
5000	0.025	0.010	0.0777	.0002	.000327	16.935	.1125	4404.18	0.01276
	0.025	0.025	0.226	.00058	.000951	49.265	.327	5979.64	0.00371
	0.025	0.055	0.372	.000955	.001565	81.075	.5387	6362.46	0.00611
	0.010	0.055	0.1845	.000474	.00194	100.528	1.67	6747.66	0.019

TABLE 7 CONTINUED

RPM	concentration of hexamethylene diamine	concentration of sebacoyl chloride	yield per min.	d_{ci}/dt	K	K/D_{AB}	K/C	Reynolds number	J_D
6000	0.025	0.010	0.0658	.000169	.000277	14.343	.0953	5570.0	0.0009
	0.025	0.025	0.232	.0006	.000976	50.572	.336	6982.0	0.00317
	0.025	0.055	0.3269	.00084	.001375	71.232	.473	7479.0	0.00447
	0.010	0.055	0.175	.00045	.00184	95.322	1.583	7929.26	0.015
7000	0.025	0.010	-----	-----	-----	-----	----	-------	------
	0.025	0.025	-----	-----	-----	-----	----	-------	------
	0.025	0.055	0.3156	.00081	.00133	68.8	.457	8552.58	0.0037
	0.010	0.055	0.14	.00036	.00147	76.26	1.267	9137.0	0.0103
8000	0.025	0.010	-----	------	-----	----	----	------	------
	0.025	0.025	0.2227	.00057	.000937	48,54	.322	8907.48	0.0023
	0.025	0.055	0.292	.00075	.00123	63.65	.423	10027.0	0.003
	0.010	0.055	-----	------	-----	-----	----	------	-------
10000	0.025	0.010	-----	------	-----	-----	----	------	-------
	0.025	0.025	0.2169	.000556	.000913	47.28	.3141	11636.2	0.0018
	0.025	0.055	-----	-------	-------	-----	-----	------	-------
	0.010	0.055	-----	-------	-------	-----	-----	------	-------

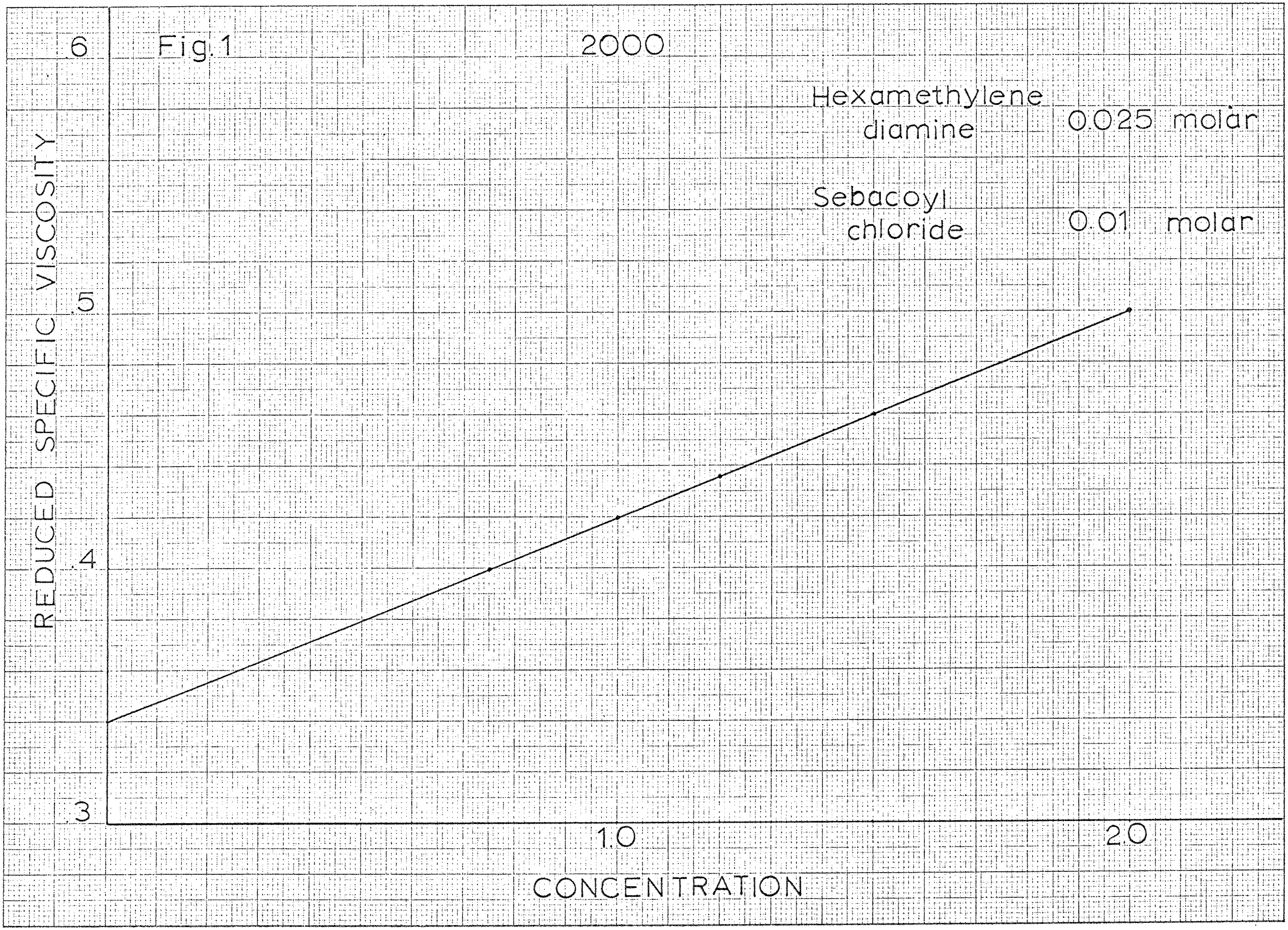


Fig. 1

2000
Hexamethylene diamine 0.025 molar
Sebacoyl chloride 0.01 molar
REDUCED SPECIFIC VISCOSITY
.6
.5
.4
.3
1.0
2.0
CONCENTRATION

Fig. 2

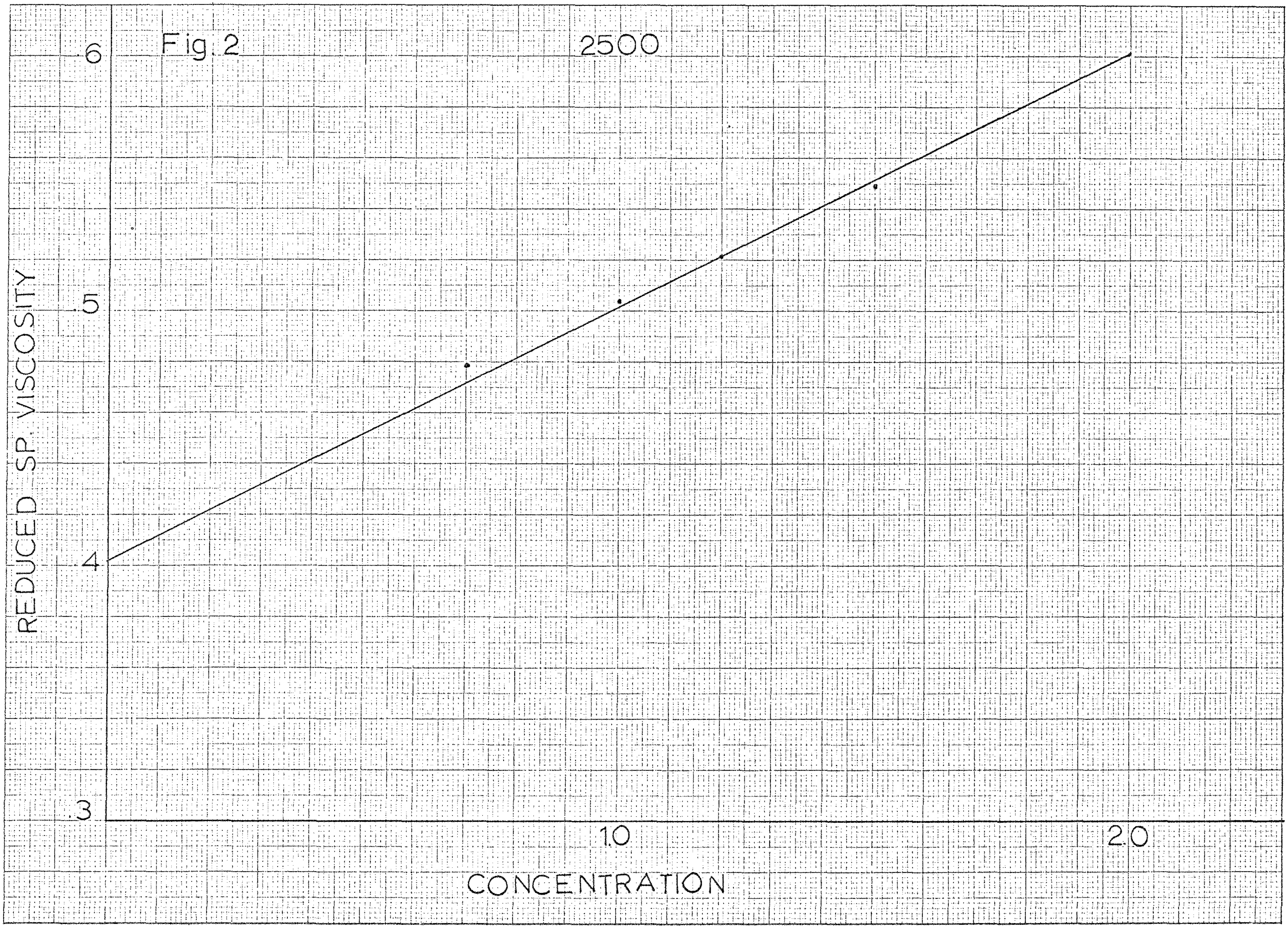


Fig. 3

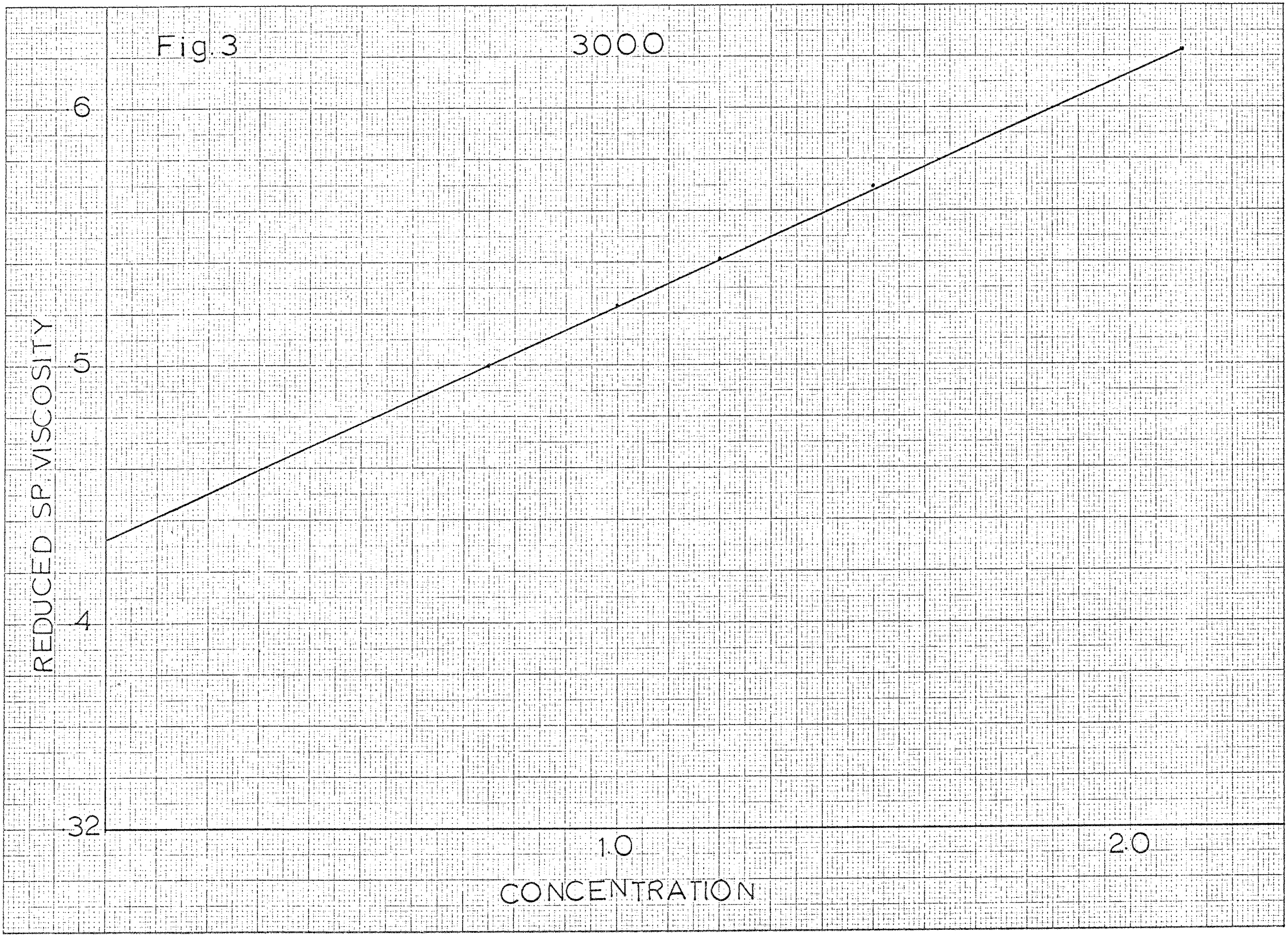
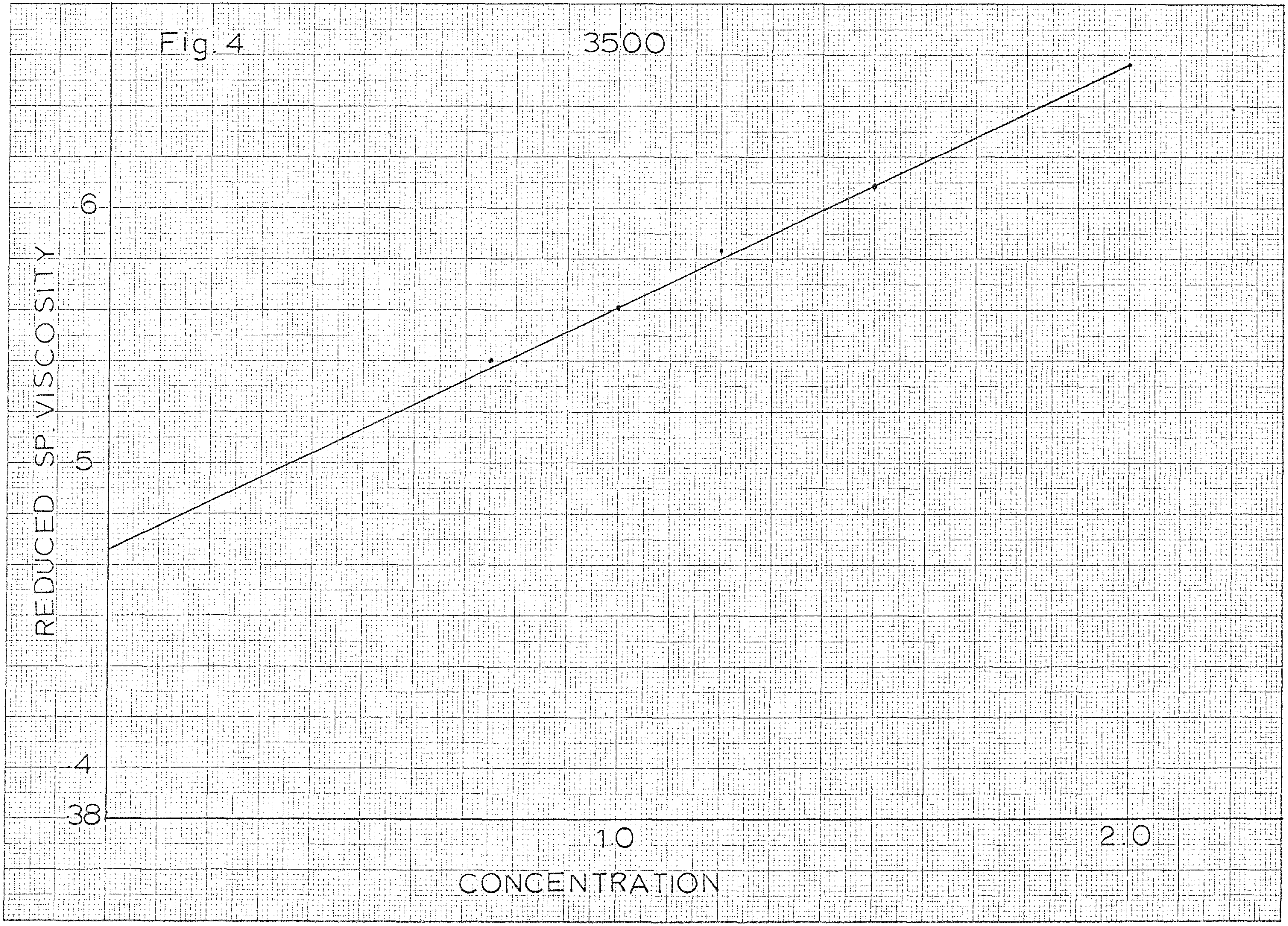


Fig. 4



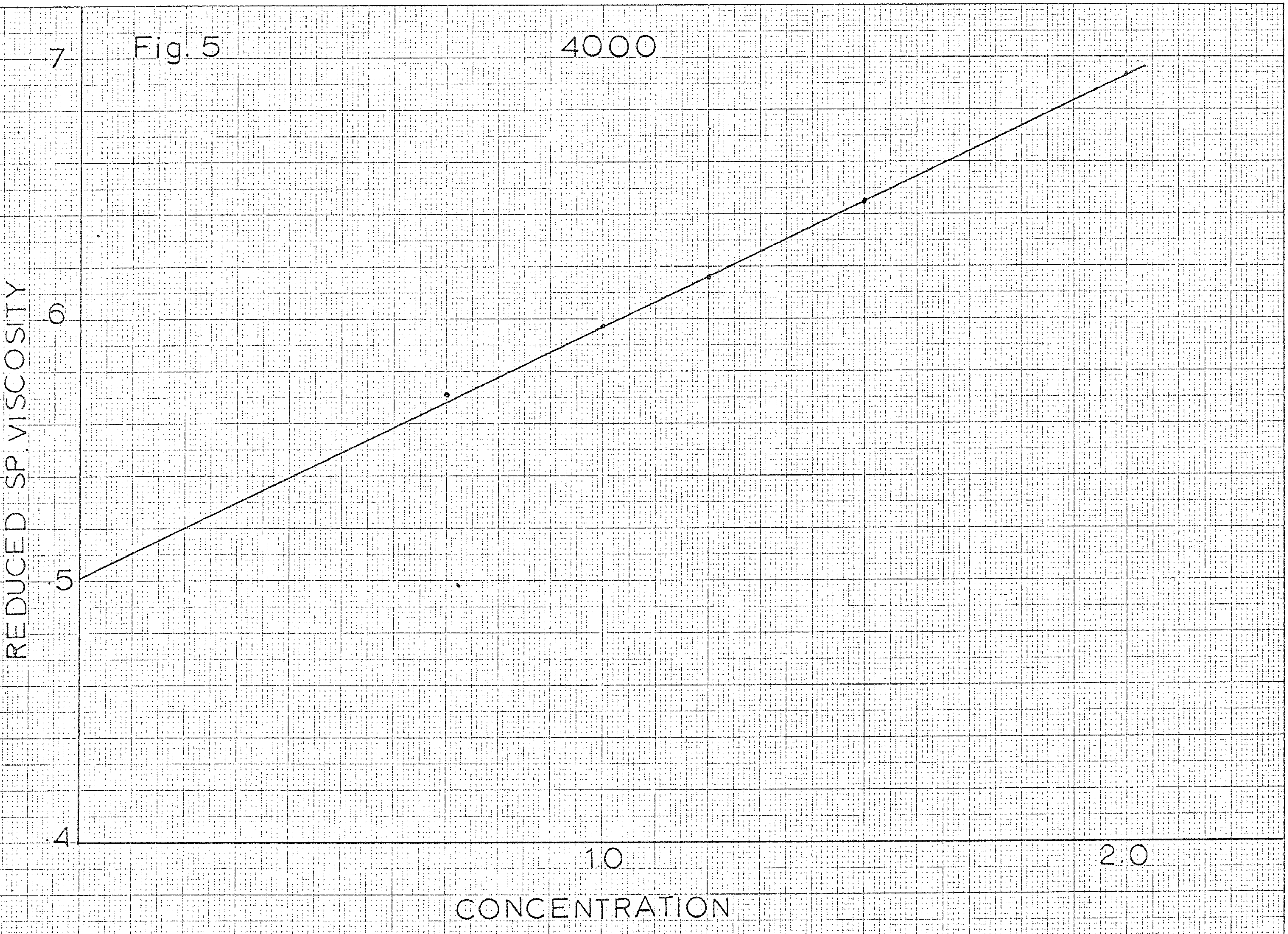


Fig. 5
4000
7
6
5
4
REDUCED SP. VISCOSITY
1.0
2.0
CONCENTRATION

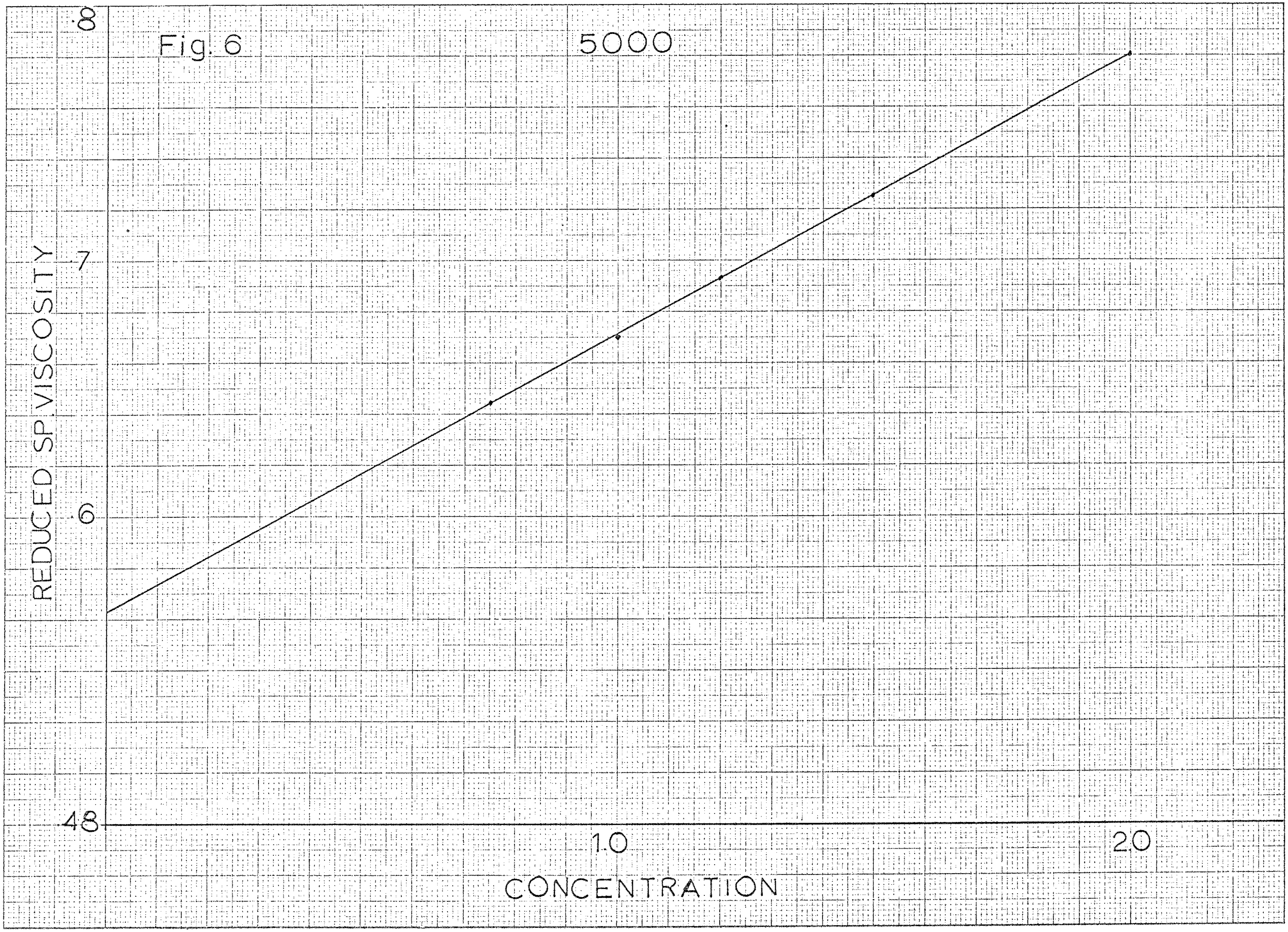


Fig. 6
5000
·8
·7
·6
·48
1.0
2.0
CONCENTRATION
REDUCED SP. VISCOSITY

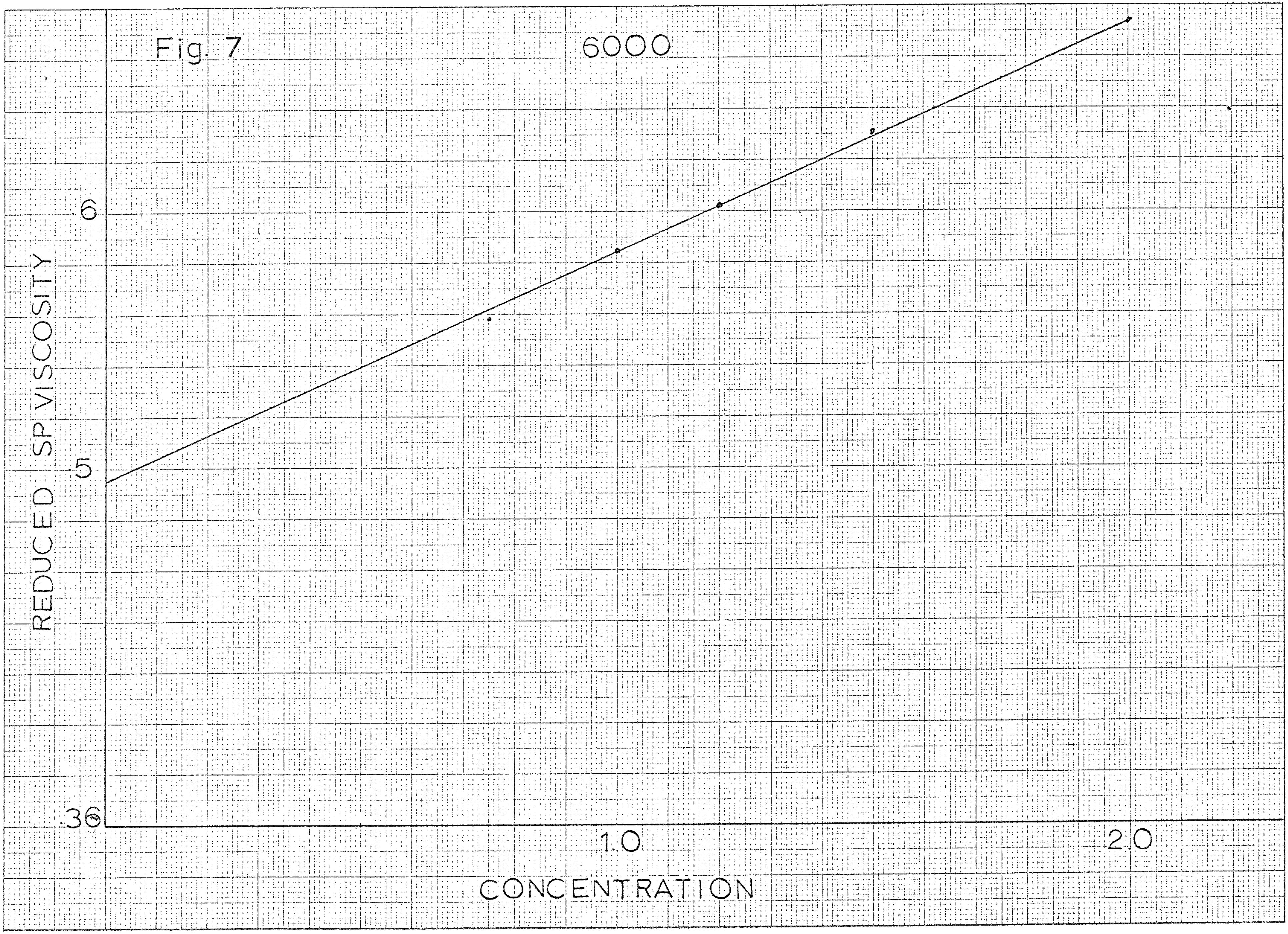


Fig. 7
6000
6
5
.36
1.0
2.0
REDUCED SP. VISCOSITY
CONCENTRATION

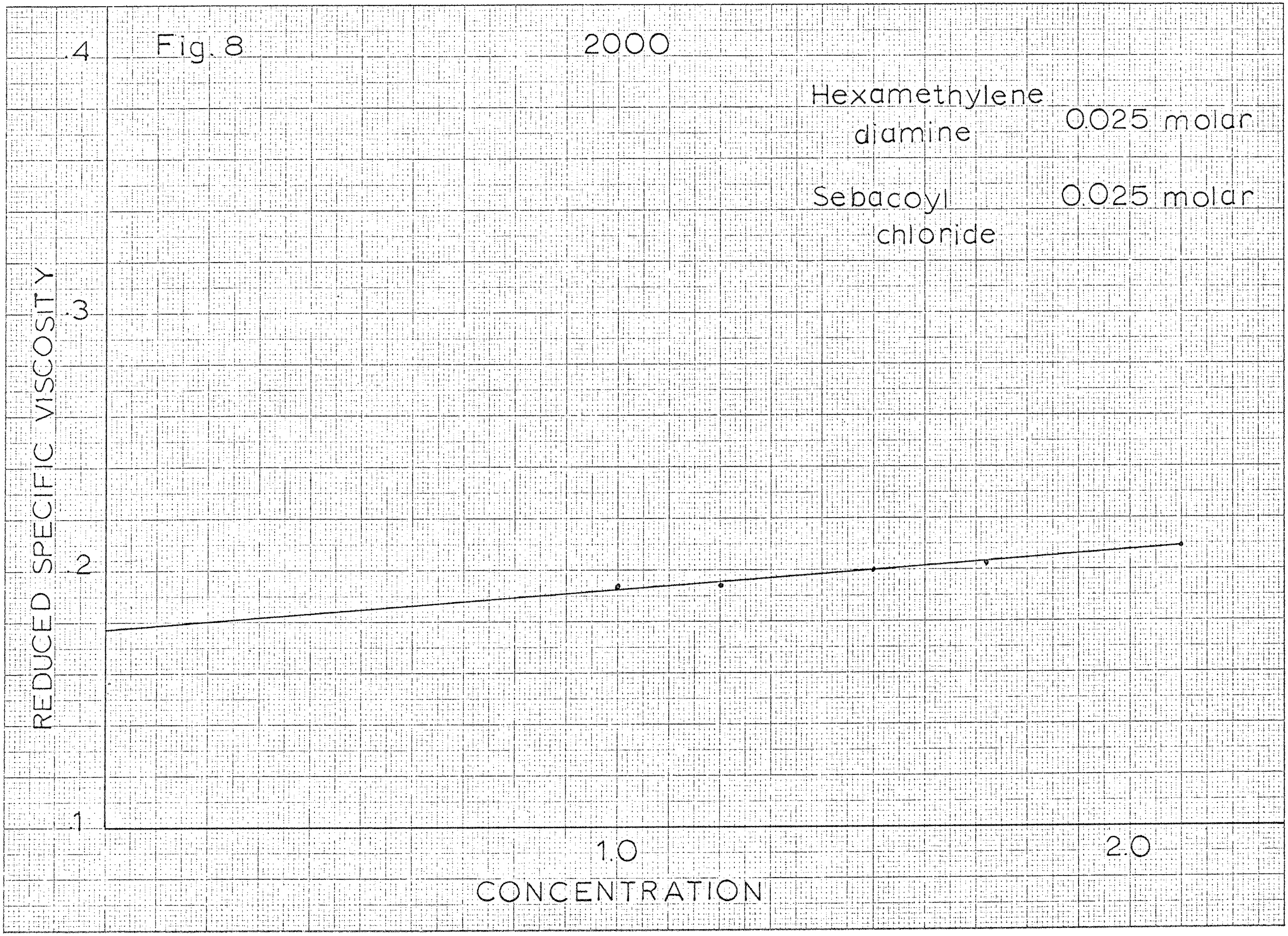


Fig. 8

2000
Hexamethylene diamine 0.025 molar
Sebacoyl chloride 0.025 molar
REDUCED SPECIFIC VISCOSITY
.4
.3
.2
.1
1.0
2.0
CONCENTRATION

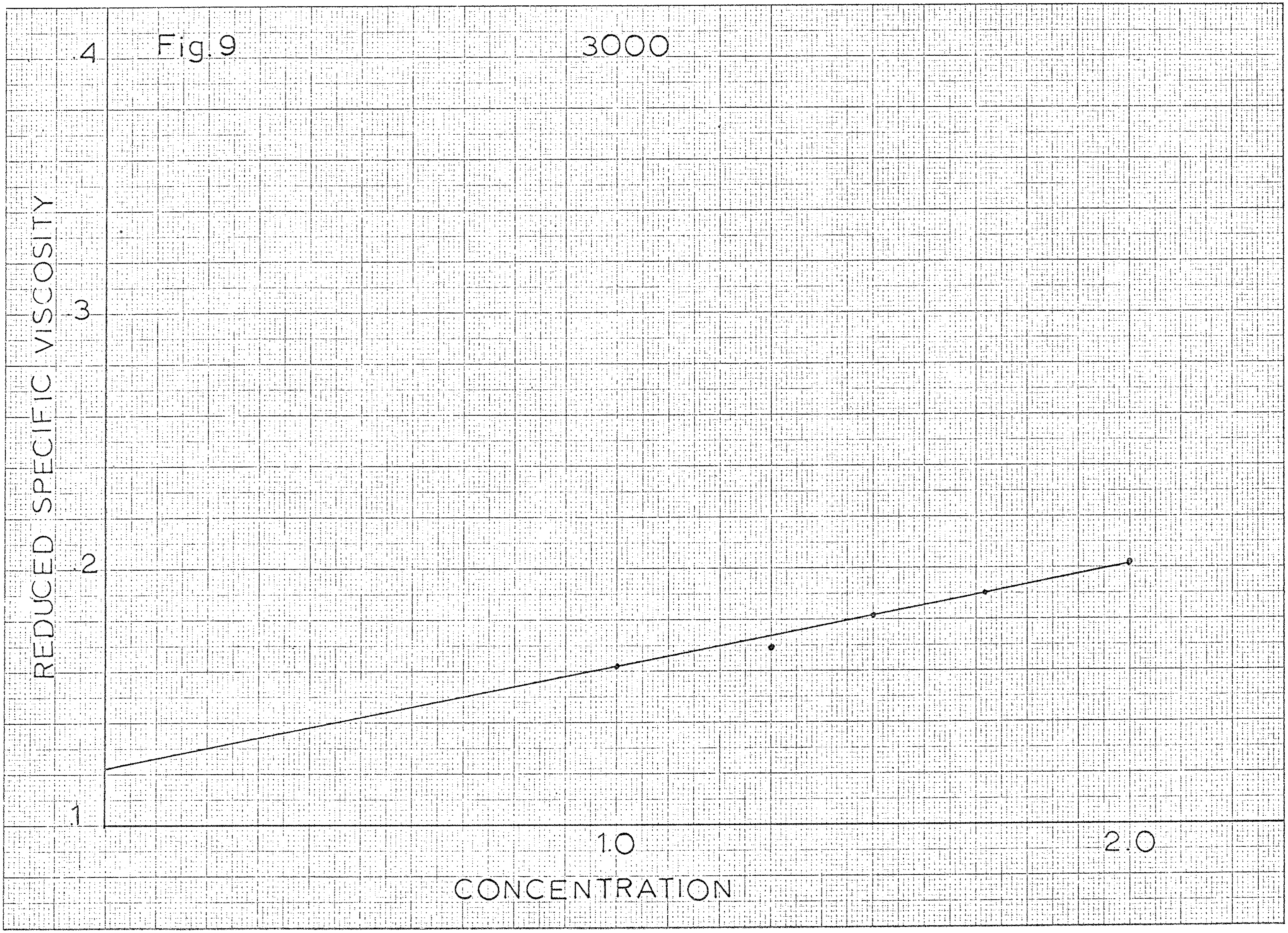
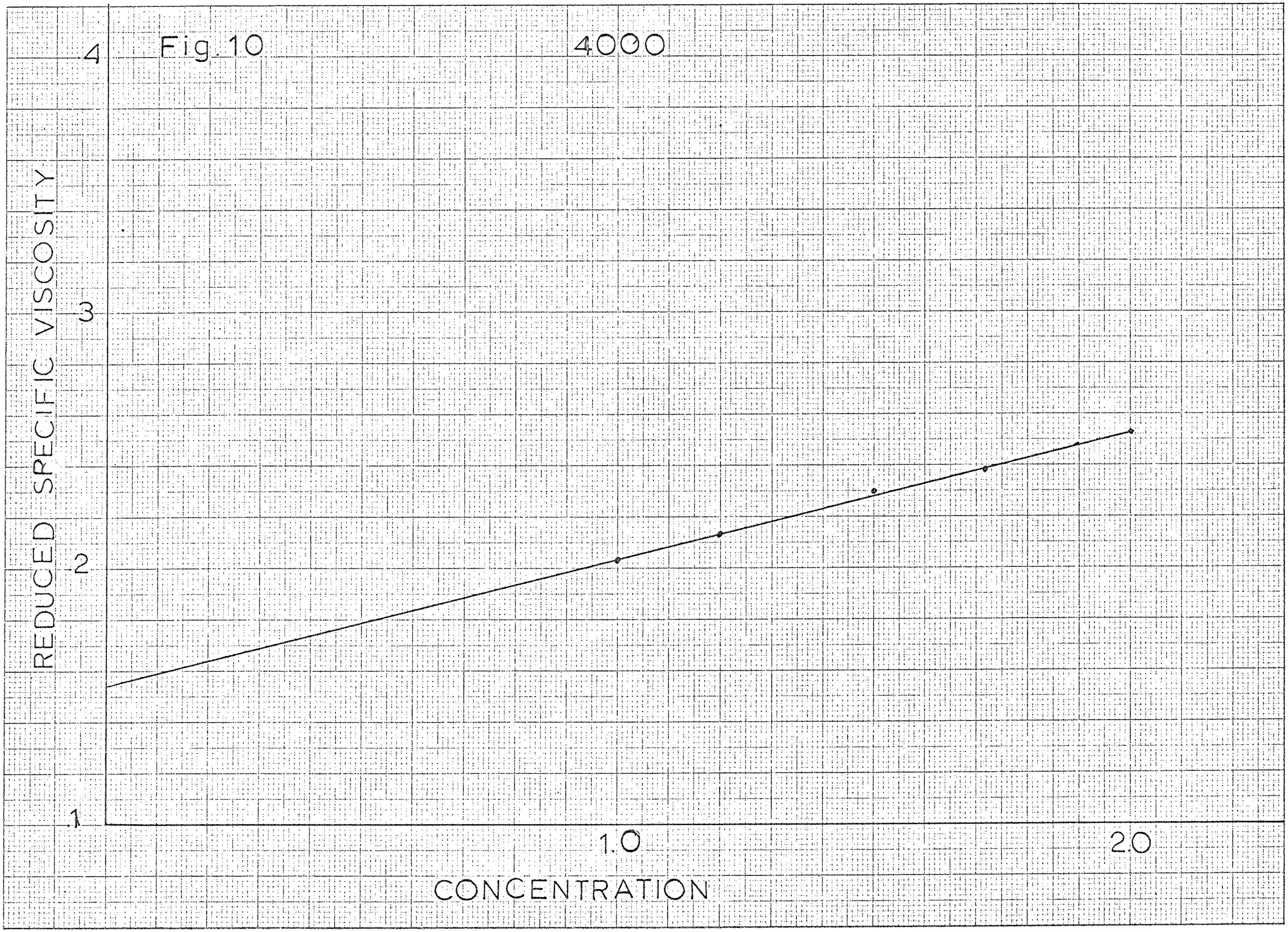


Fig. 9

KEUFFEL & ESSER CO.



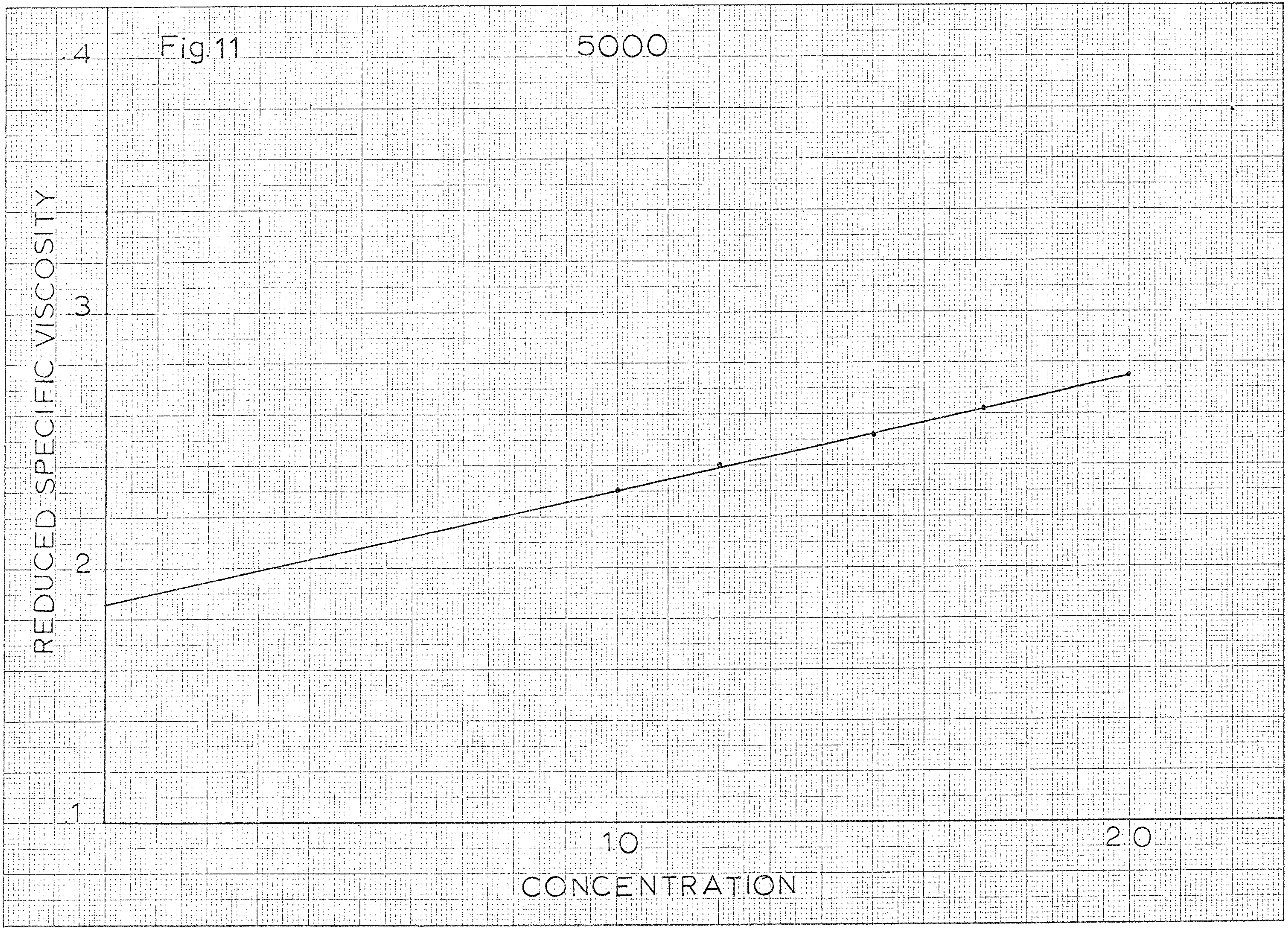
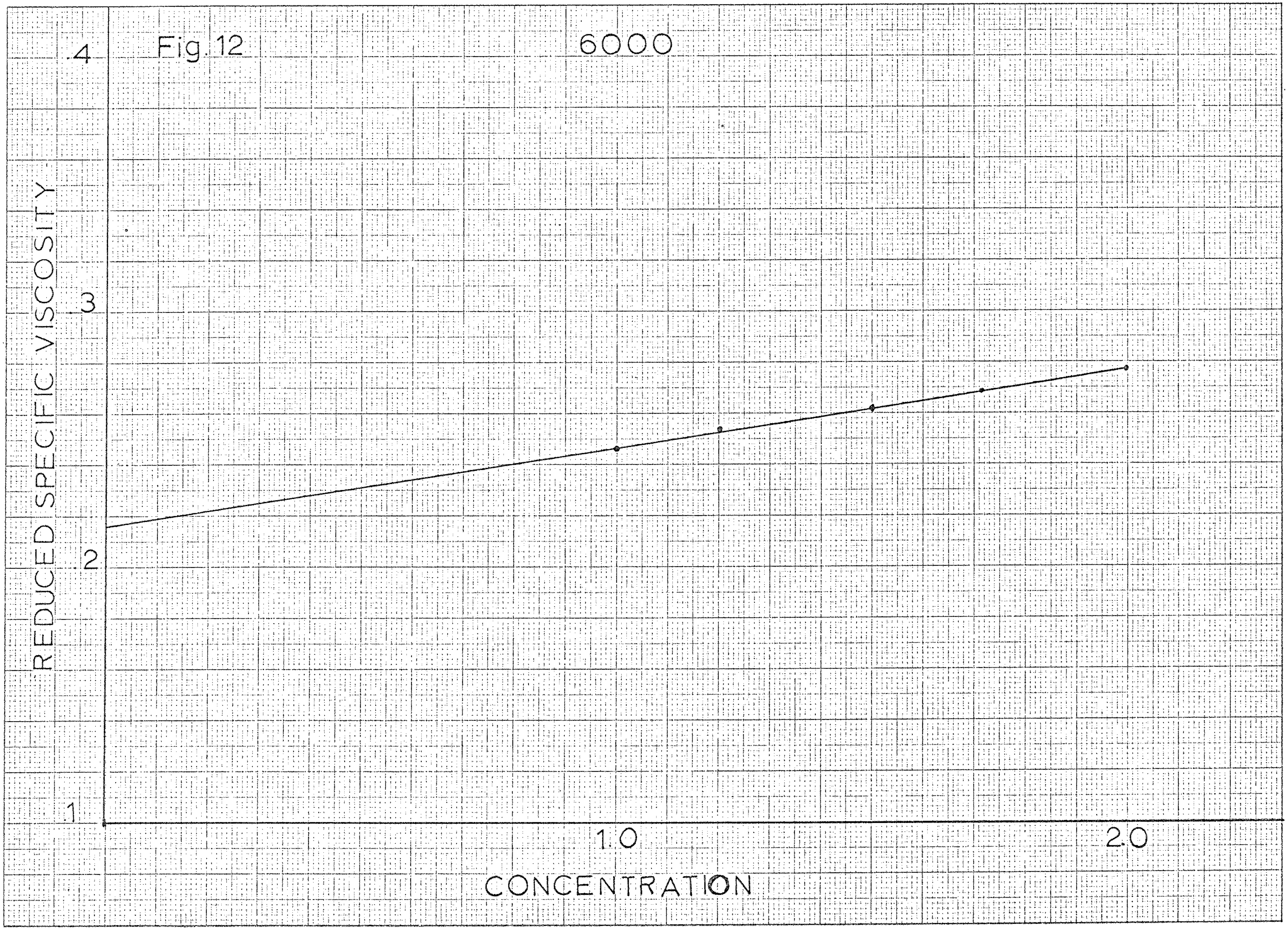


Fig.11

KEUFFEL & ESSER CO.



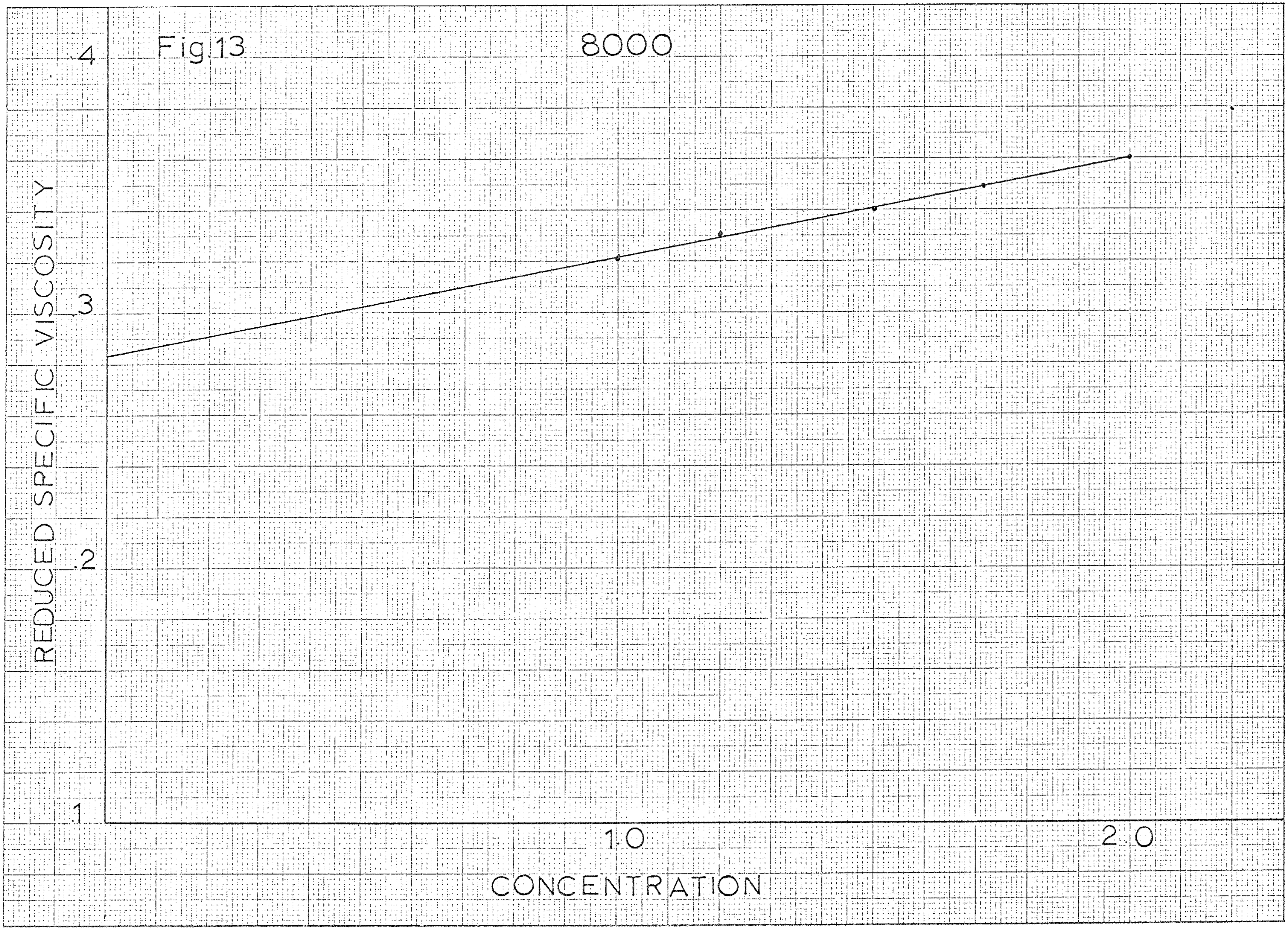
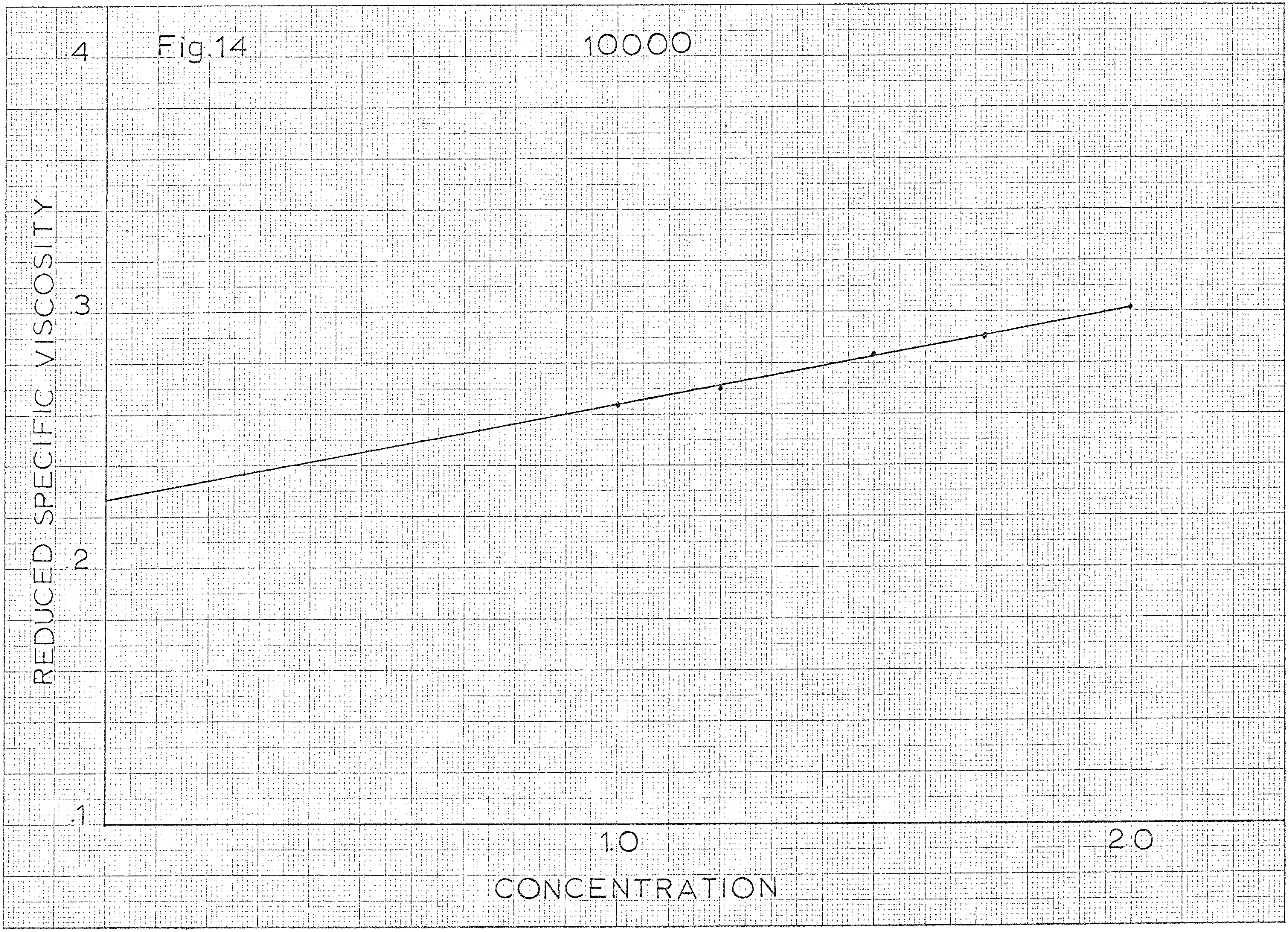


Fig.13
8000
.4
.3
.2
.1
1.0
2.0
REDUCED SPECIFIC VISCOSITY
CONCENTRATION

Fig.14


10000
REDUCED SPECIFIC VISCOSITY
.4
.3
.2
.1
1.0
2.0
CONCENTRATION

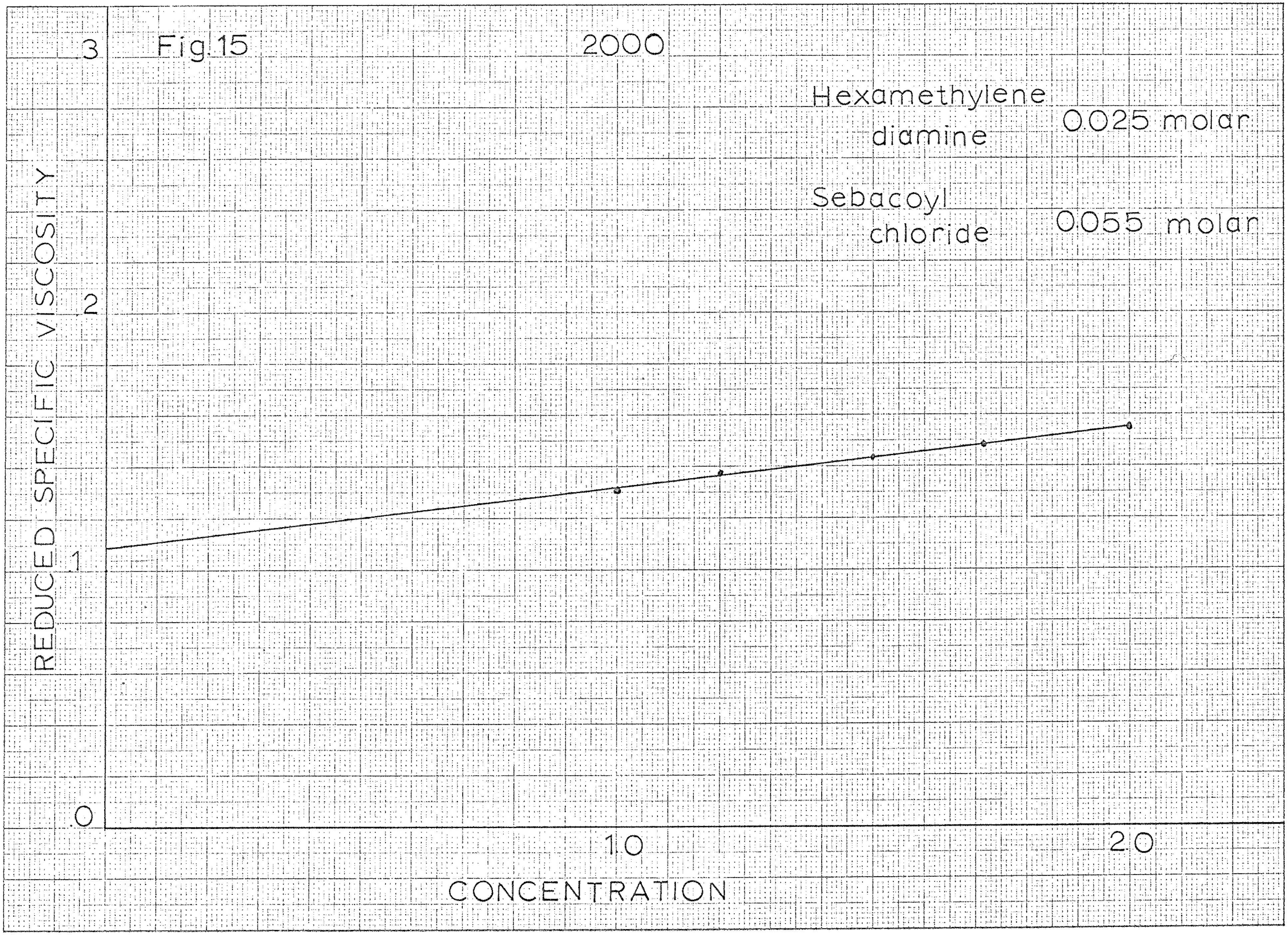


Fig.15

2000
Hexamethylene diamine 0.025 molar
Sebacoyl chloride 0.055 molar
REDUCED SPECIFIC VISCOSITY
3
2
1
0
1.0
2.0
CONCENTRATION

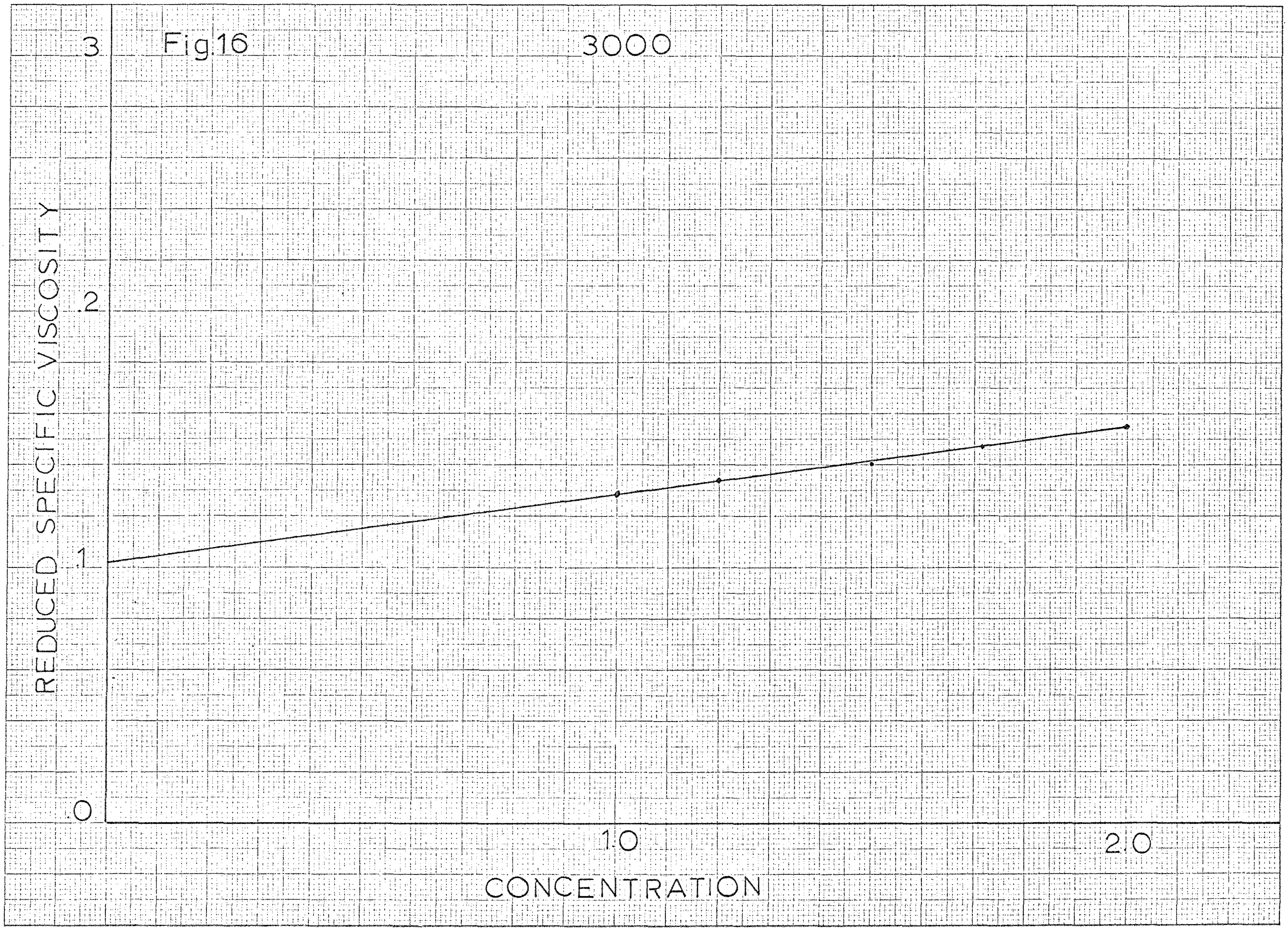


Fig 16

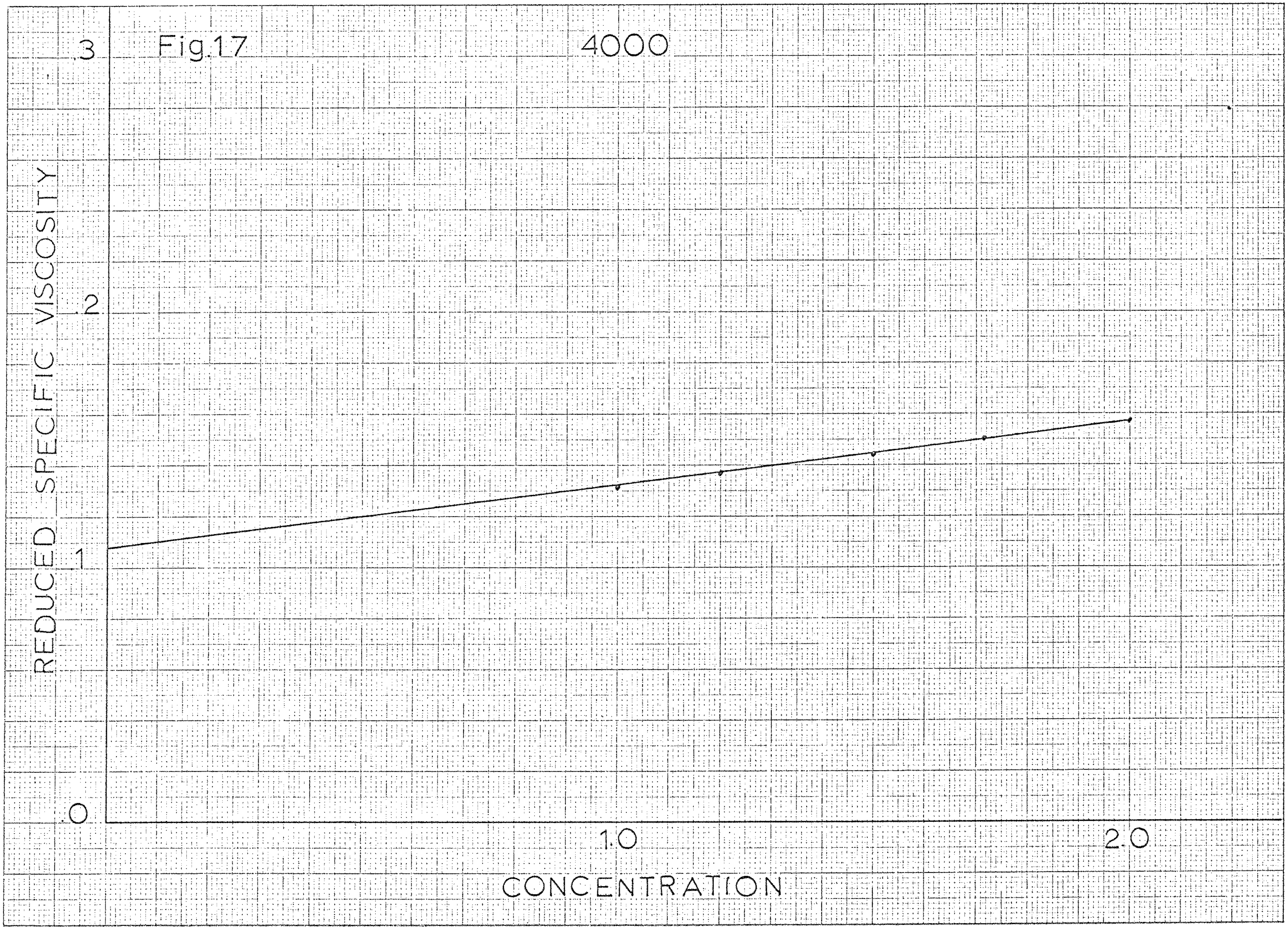


Fig.17

Fig. 18

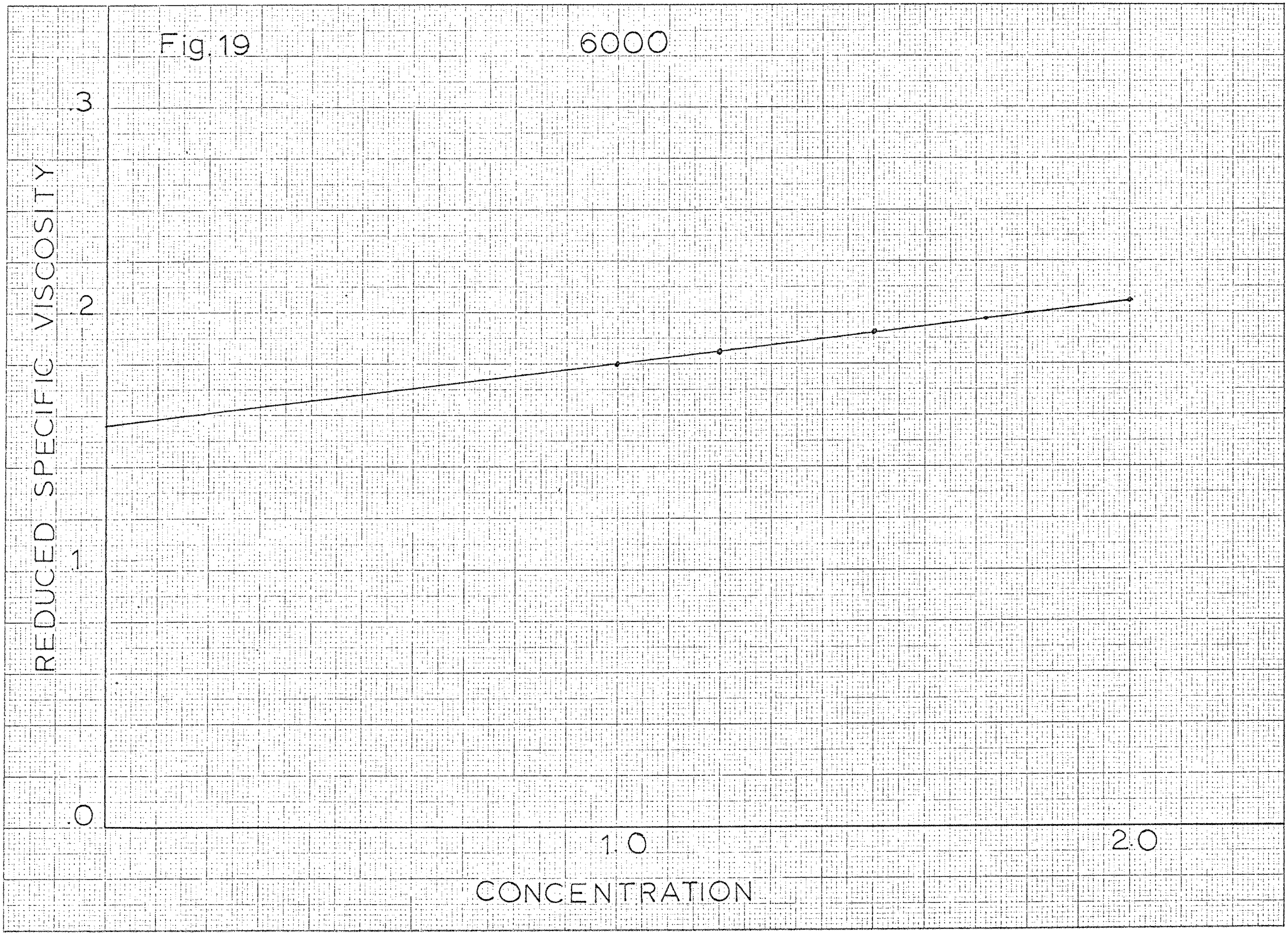


Fig. 19
6000
.3
.2
.1
.0
REDUCED SPECIFIC VISCOSITY
1.0
2.0
CONCENTRATION

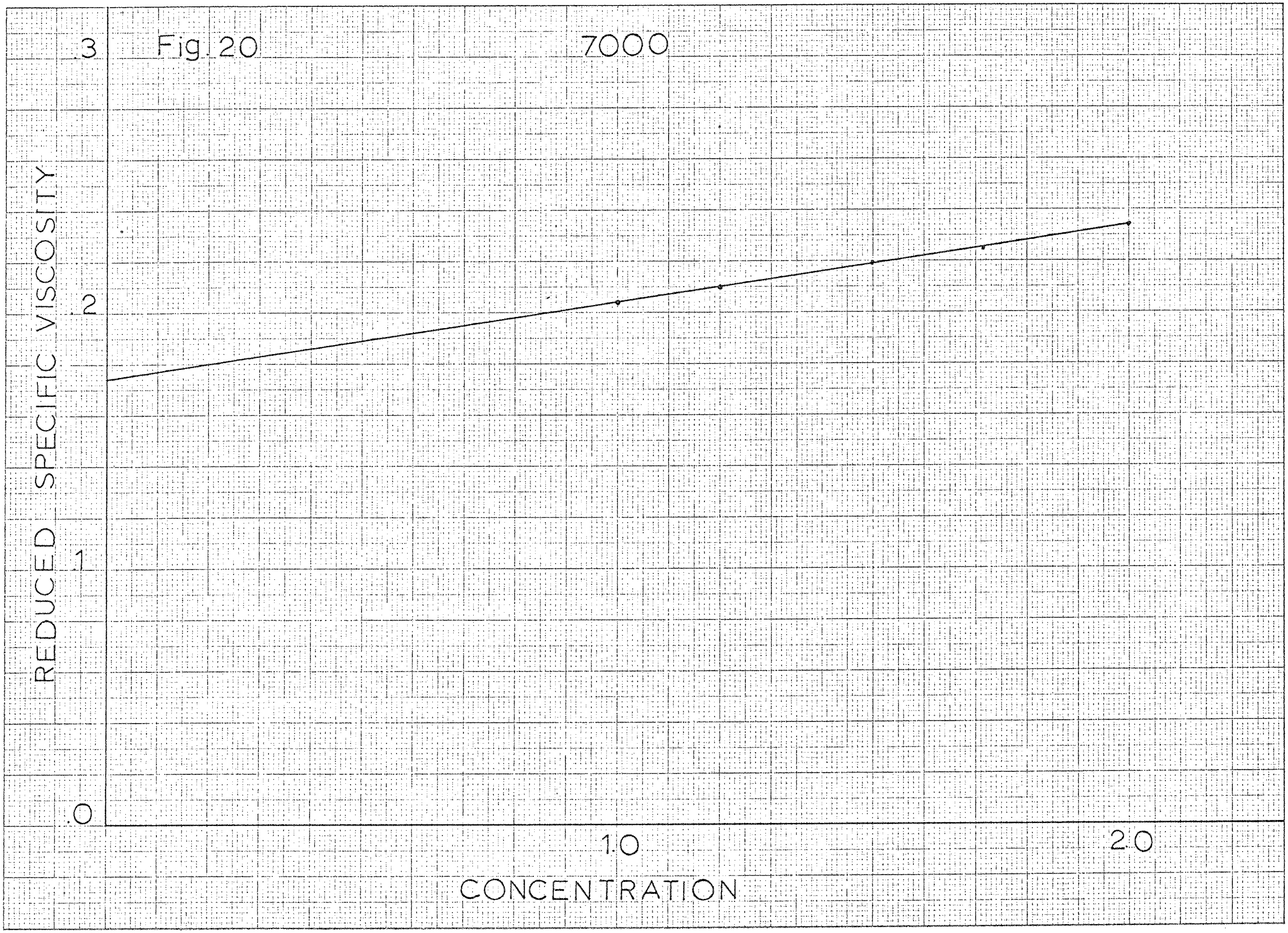


Fig. 20
7000
REDUCED SPECIFIC VISCOSITY
.3
.2
.1
.0
1.0
2.0
CONCENTRATION

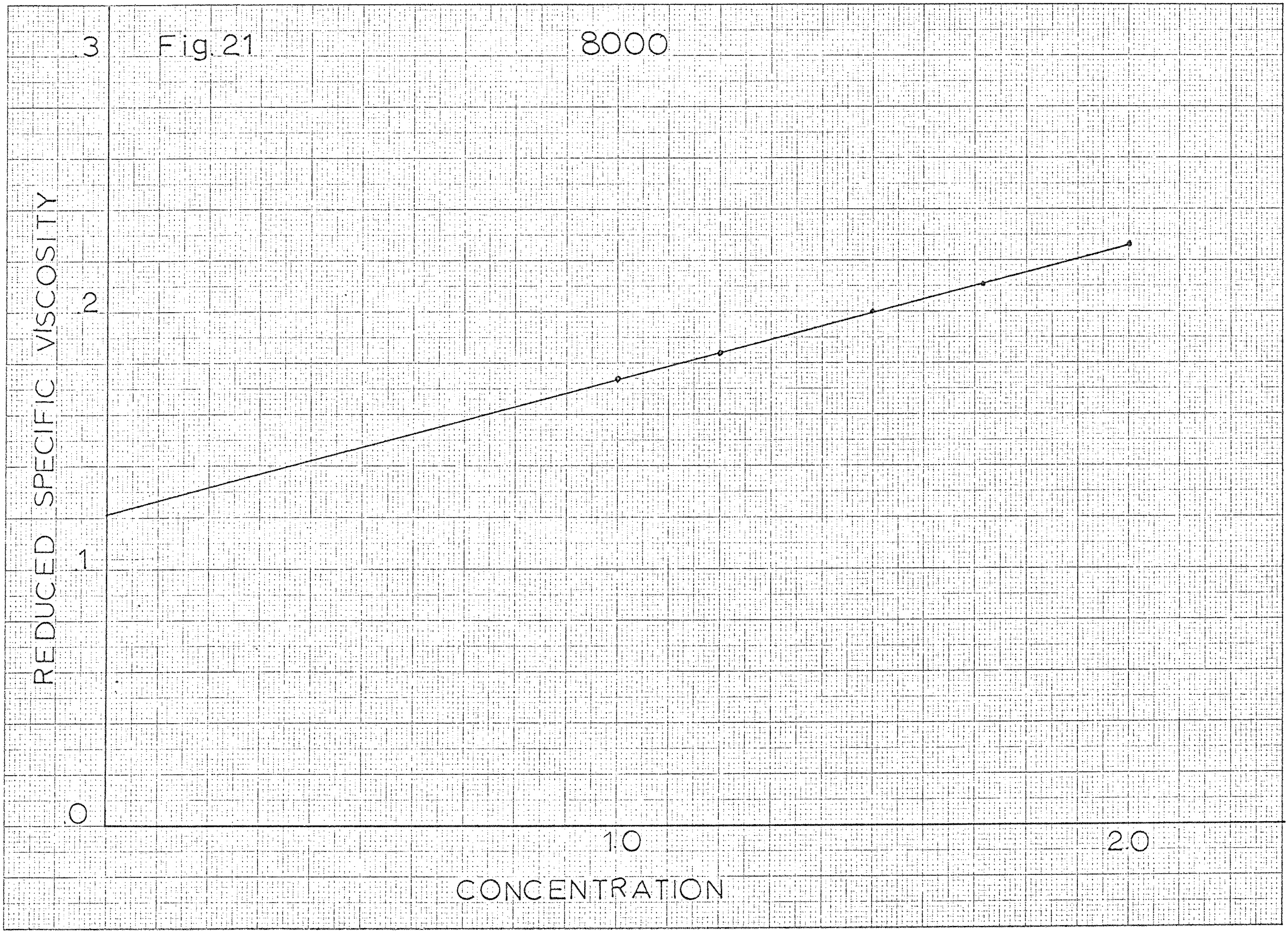


Fig. 21
8000
3
2
1
0
1.0
2.0
REDUCED SPECIFIC VISCOSITY
CONCENTRATION

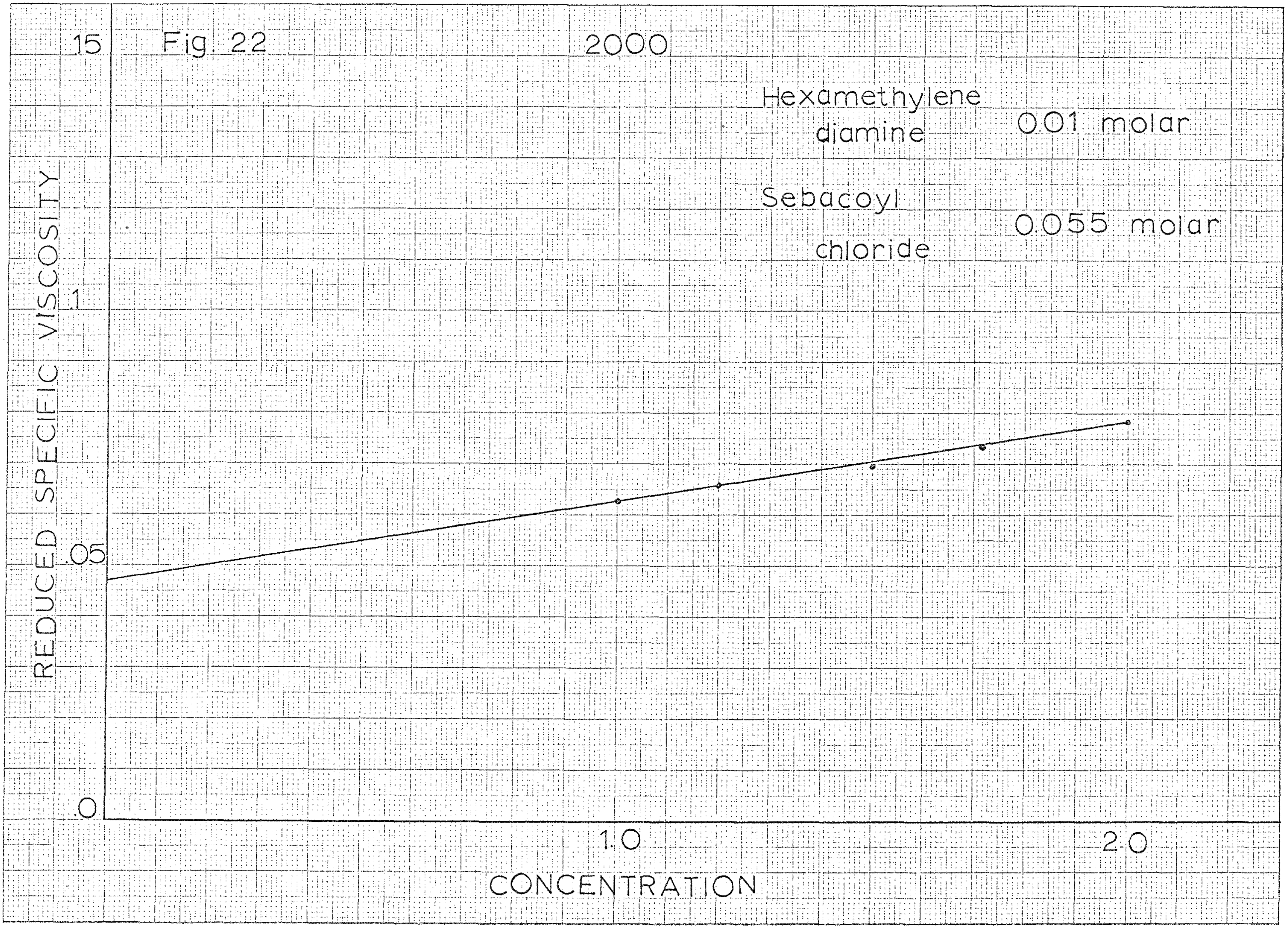


Fig. 22

15
2000
Hexamethylene diamine
0.01 molar
Sebacoyl chloride
0.055 molar
REDUCED SPECIFIC VISCOSITY
.1
.05
.0
1.0
2.0
CONCENTRATION

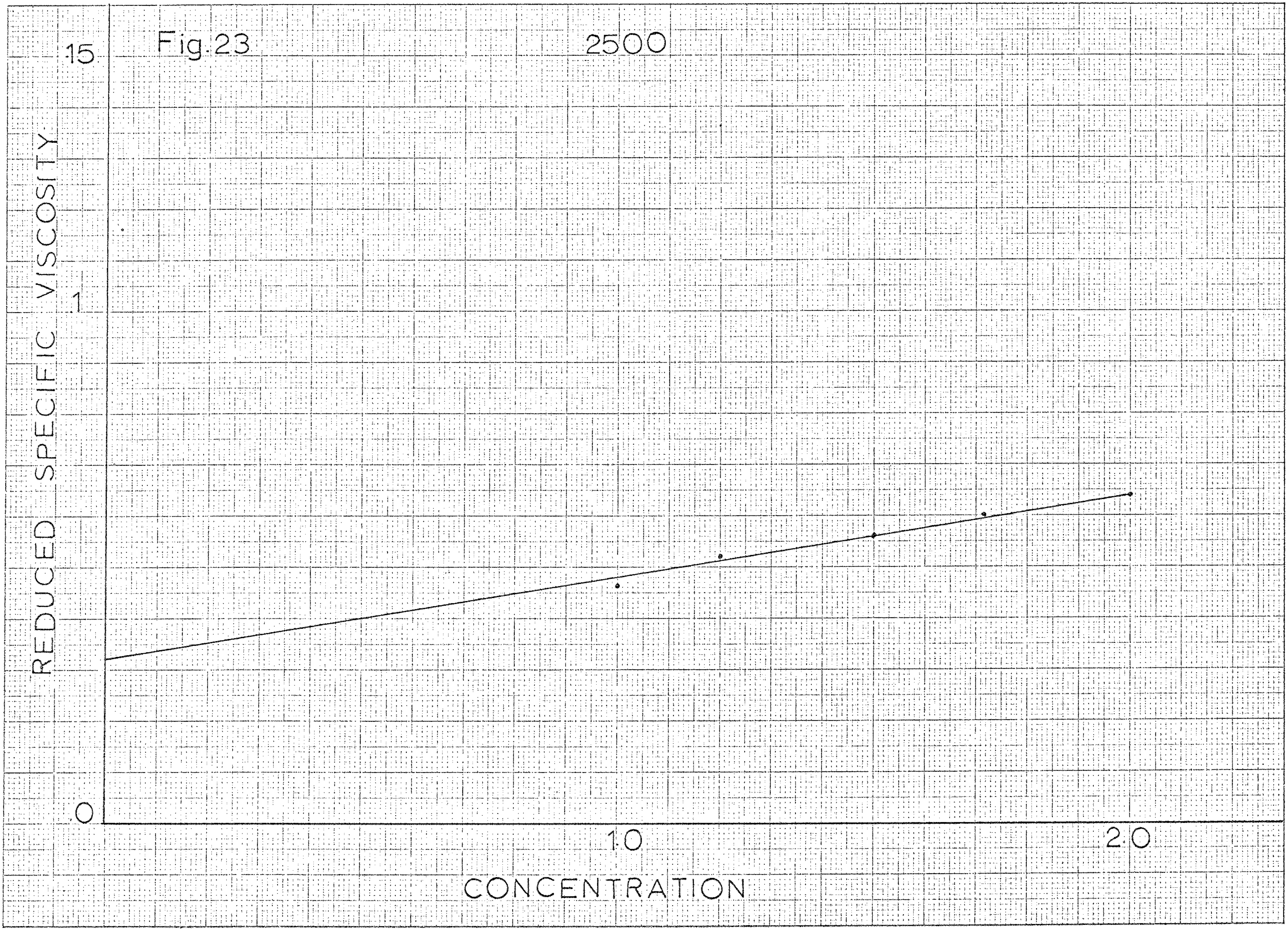


Fig. 23

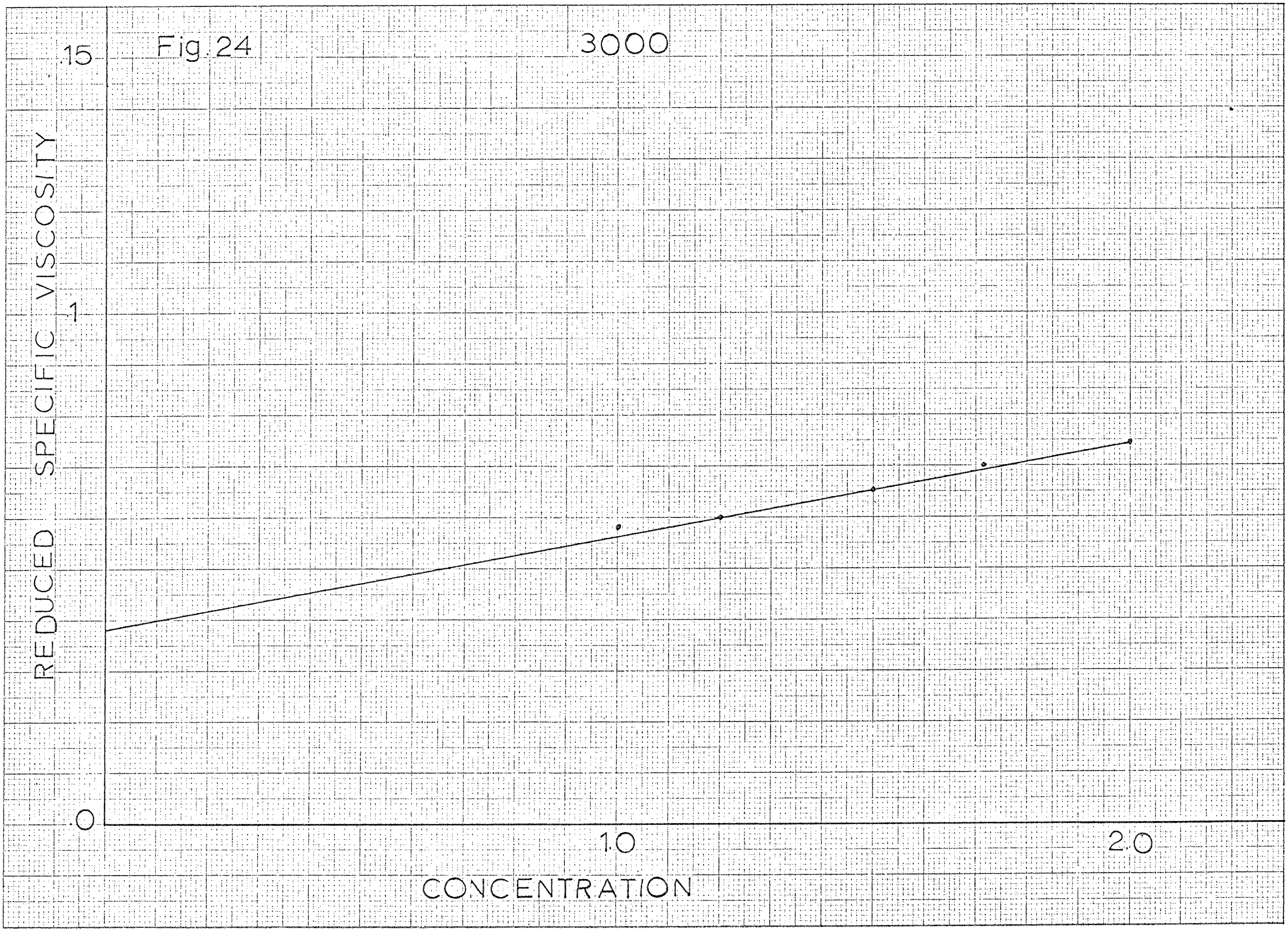


Fig. 24
3000
REDUCED SPECIFIC VISCOSITY
.15
.1
0
1.0
2.0
CONCENTRATION

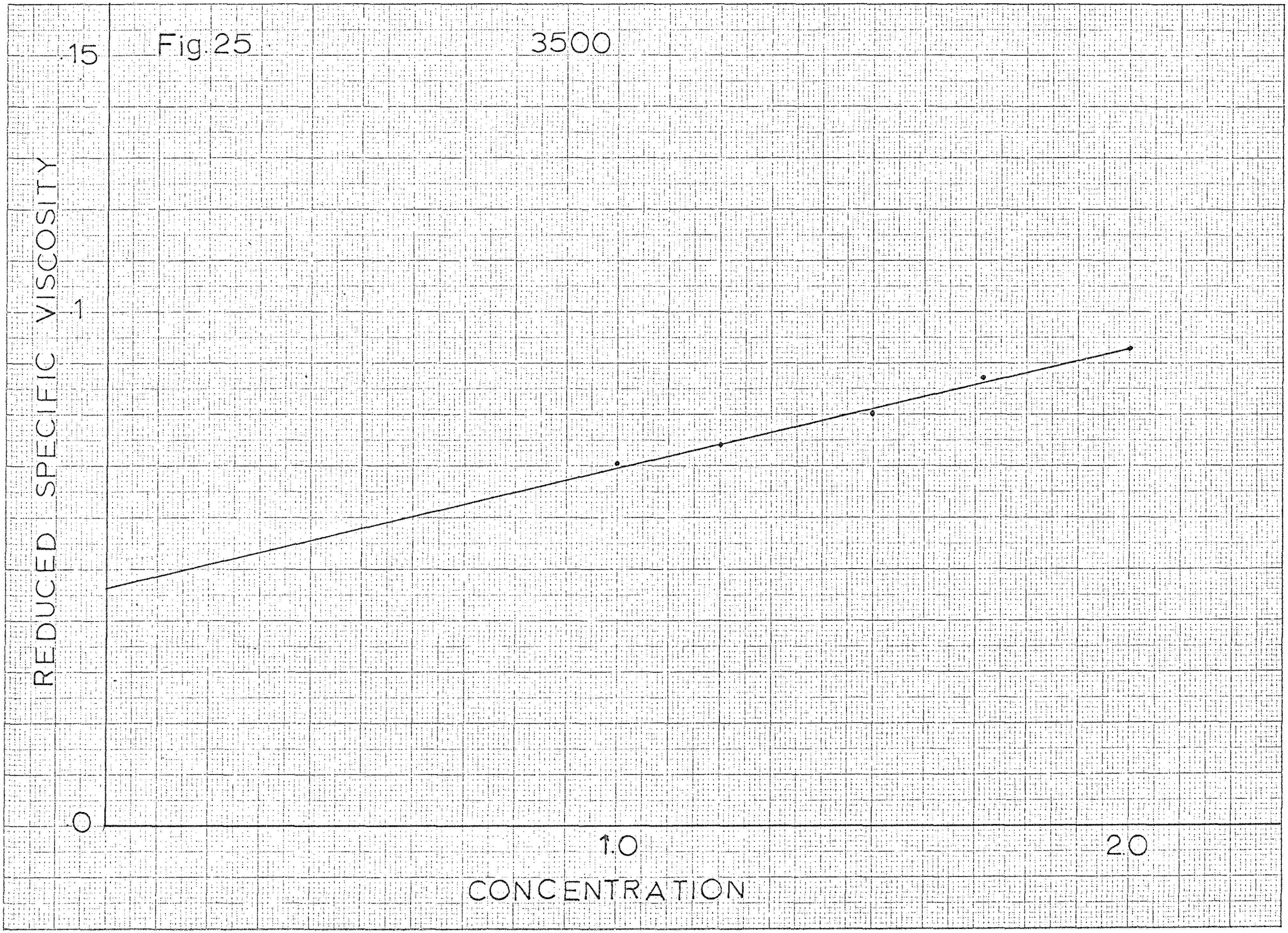
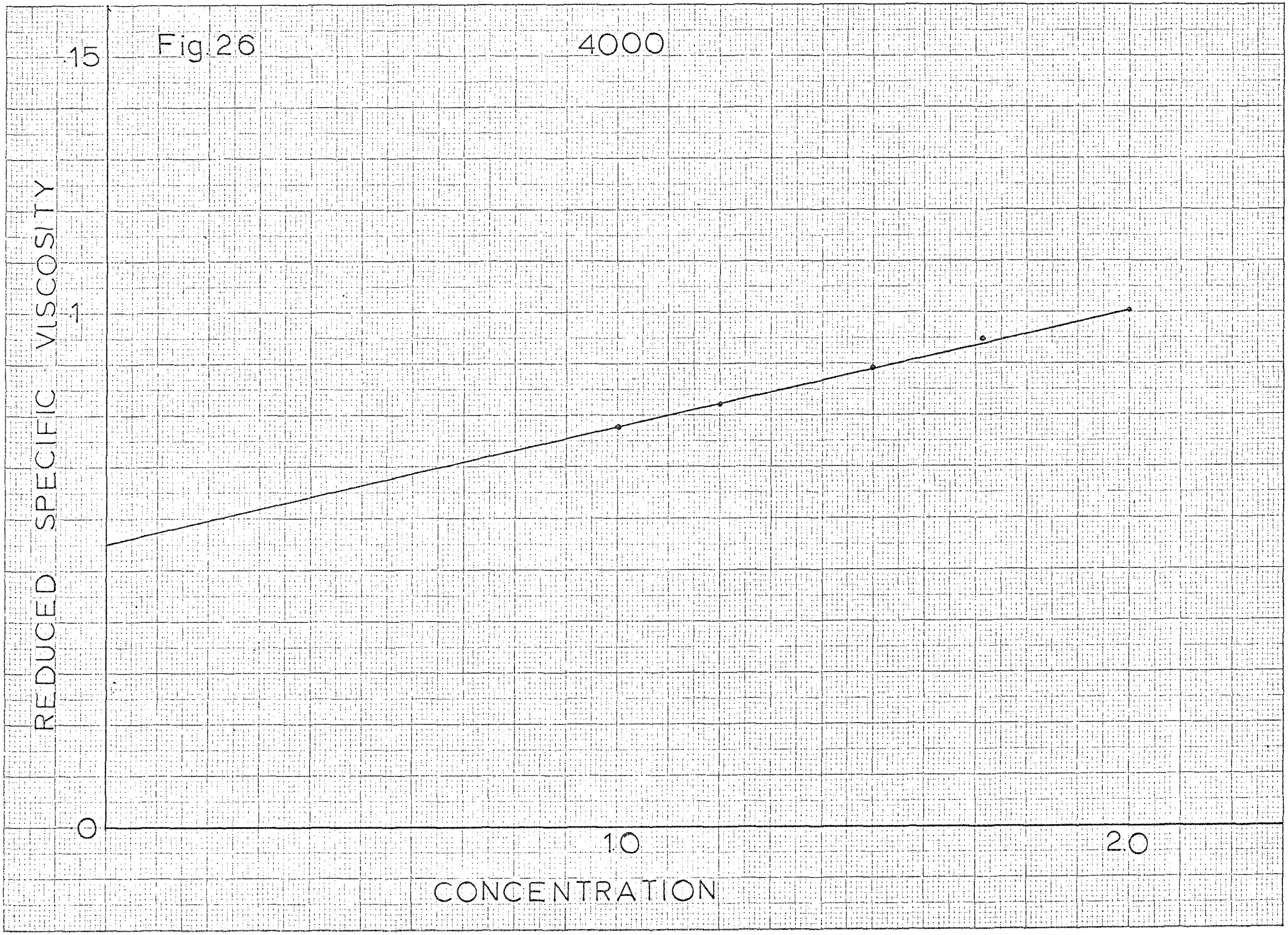


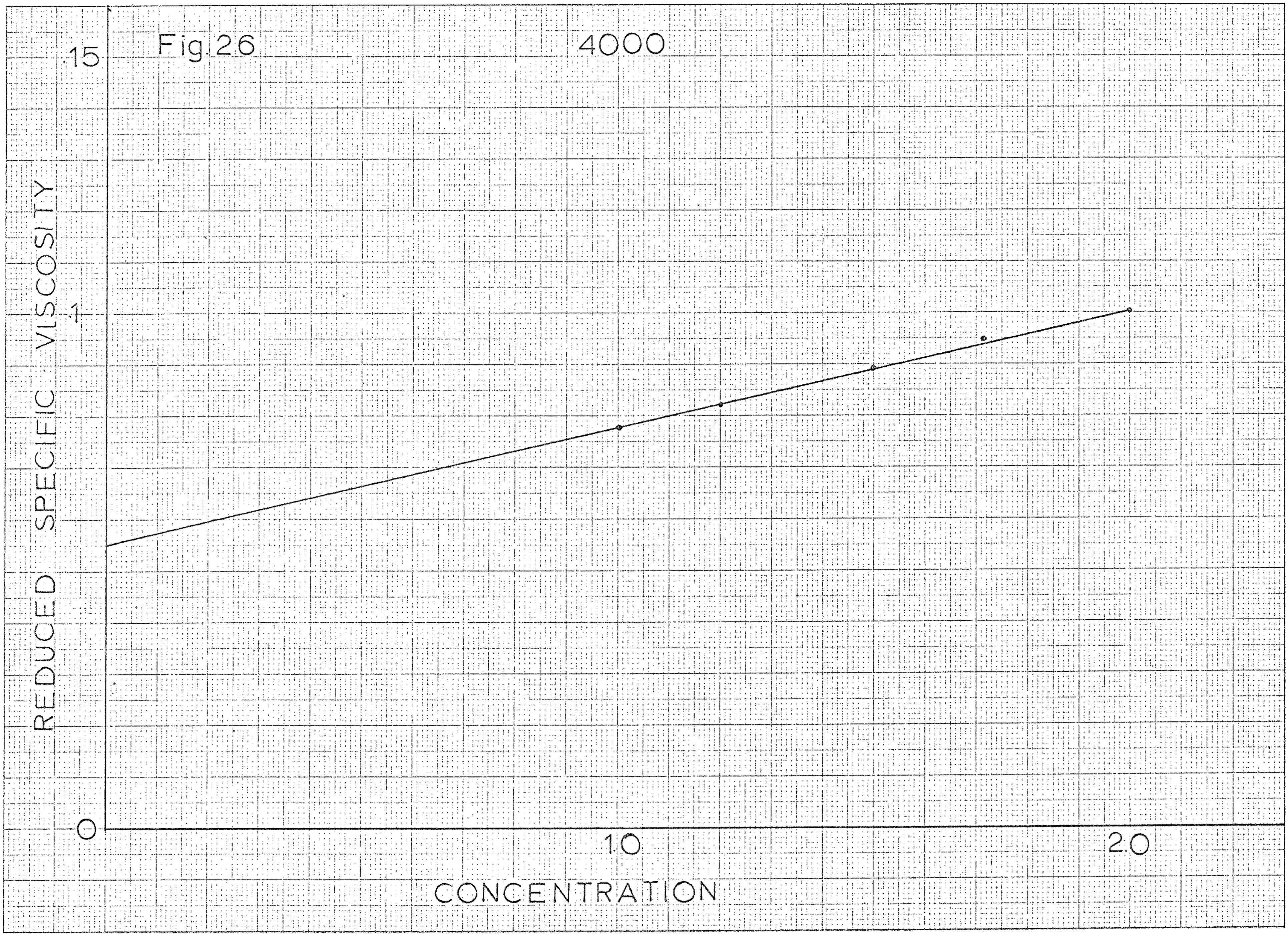
Fig. 25

Fig. 26



46 1474 18 X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 26



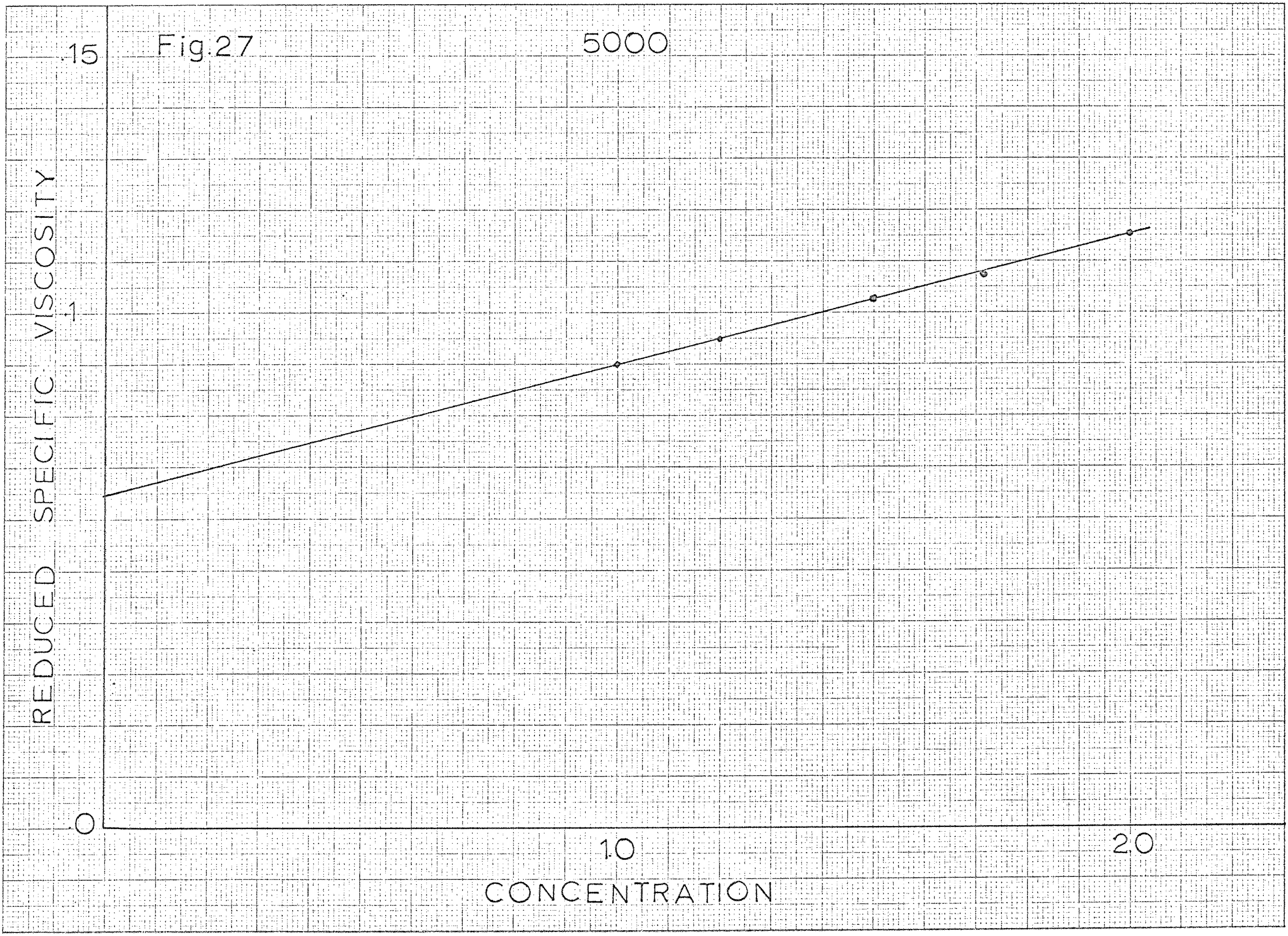


Fig.27

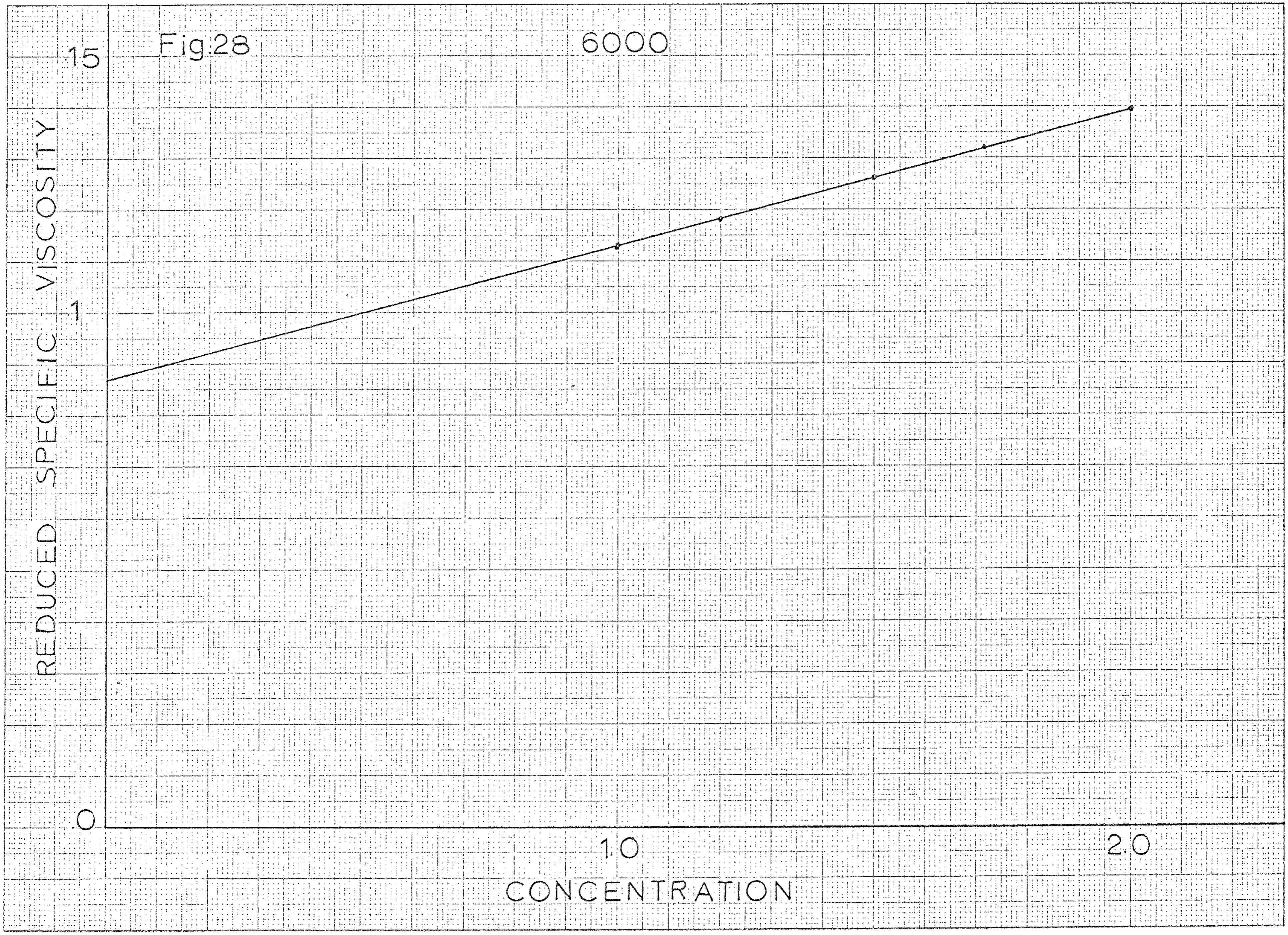


Fig.28

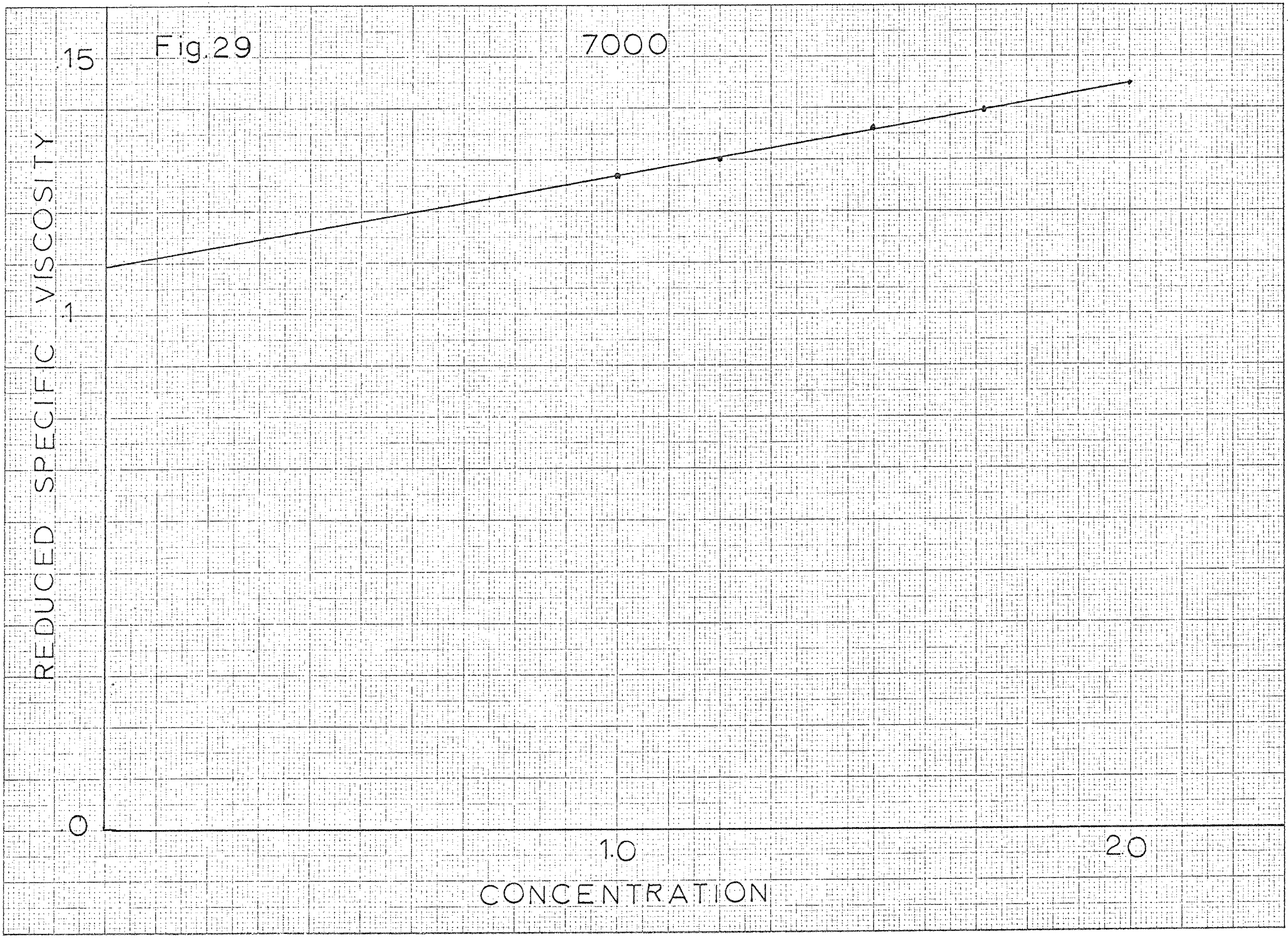
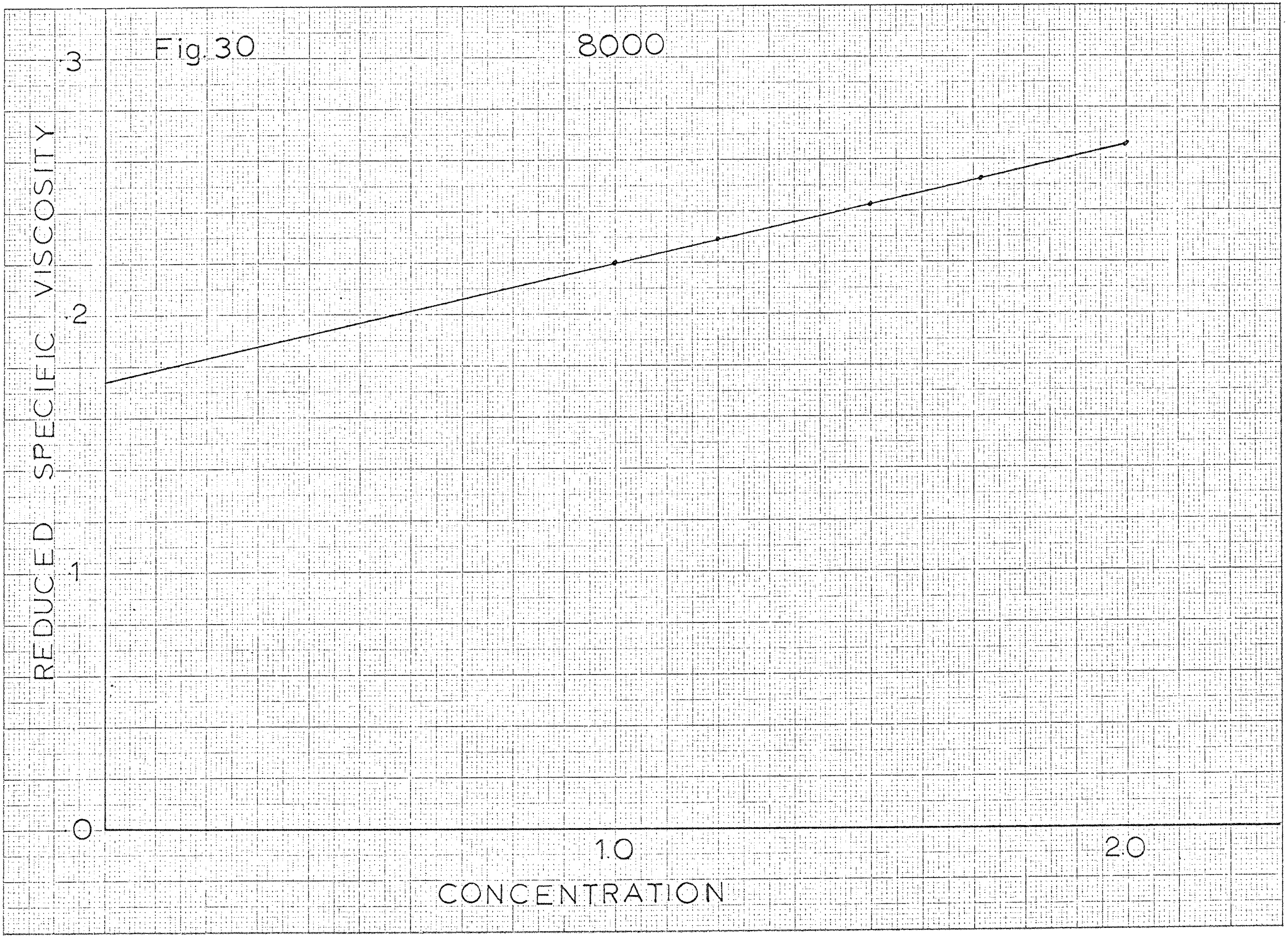


Fig. 29
7000
REDUCED SPECIFIC VISCOSITY
.15
.1
0
1.0
2.0
CONCENTRATION

KEUFFEL & ESSER CO.



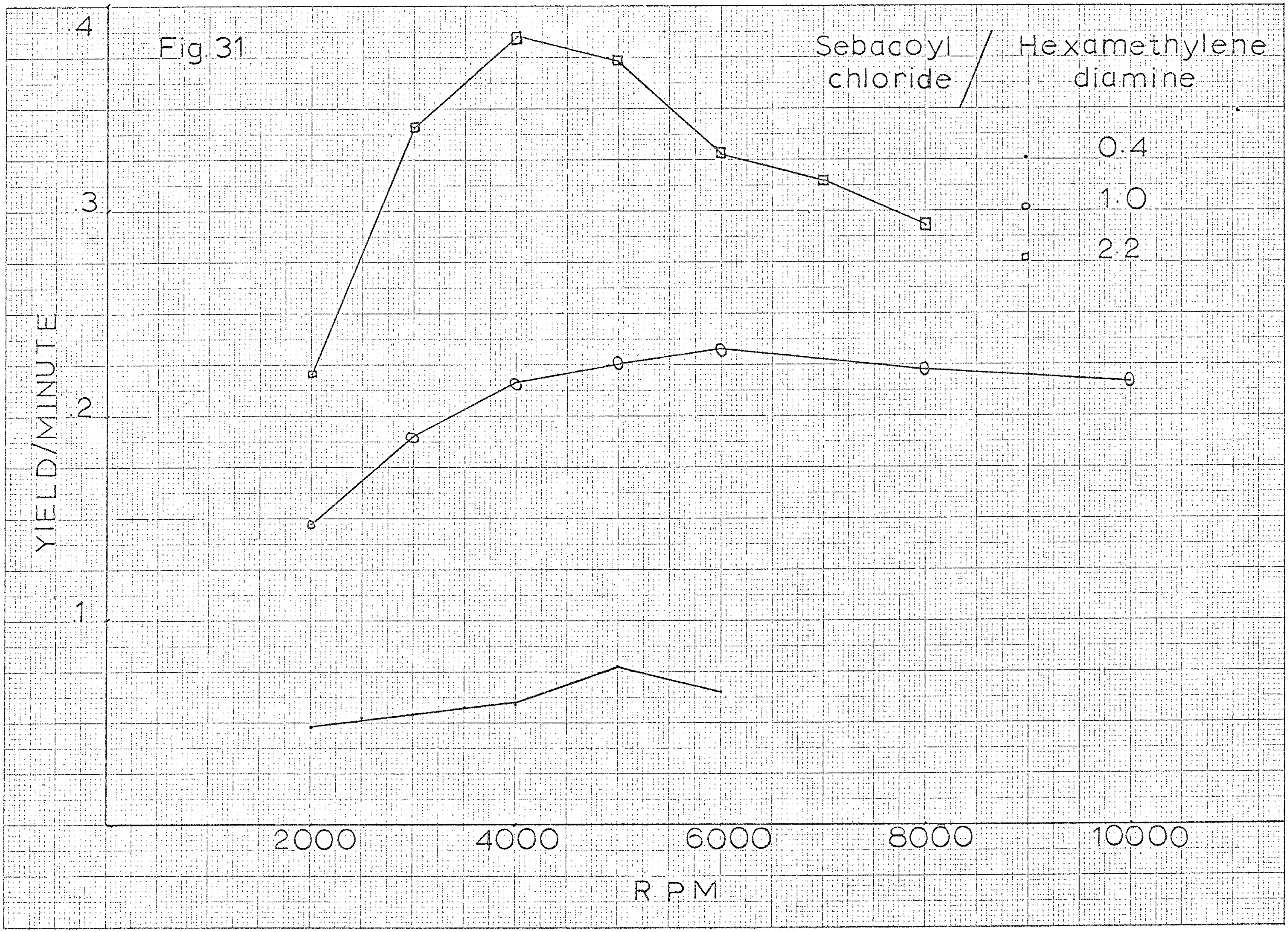


Fig. 31
Sebacoyl chloride / Hexamethylene diamine
0.4
1.0
2.2
YIELD/MINUTE
.4
.3
.2
.1
2000
4000
6000
8000
10000
R P M

Fig. 32

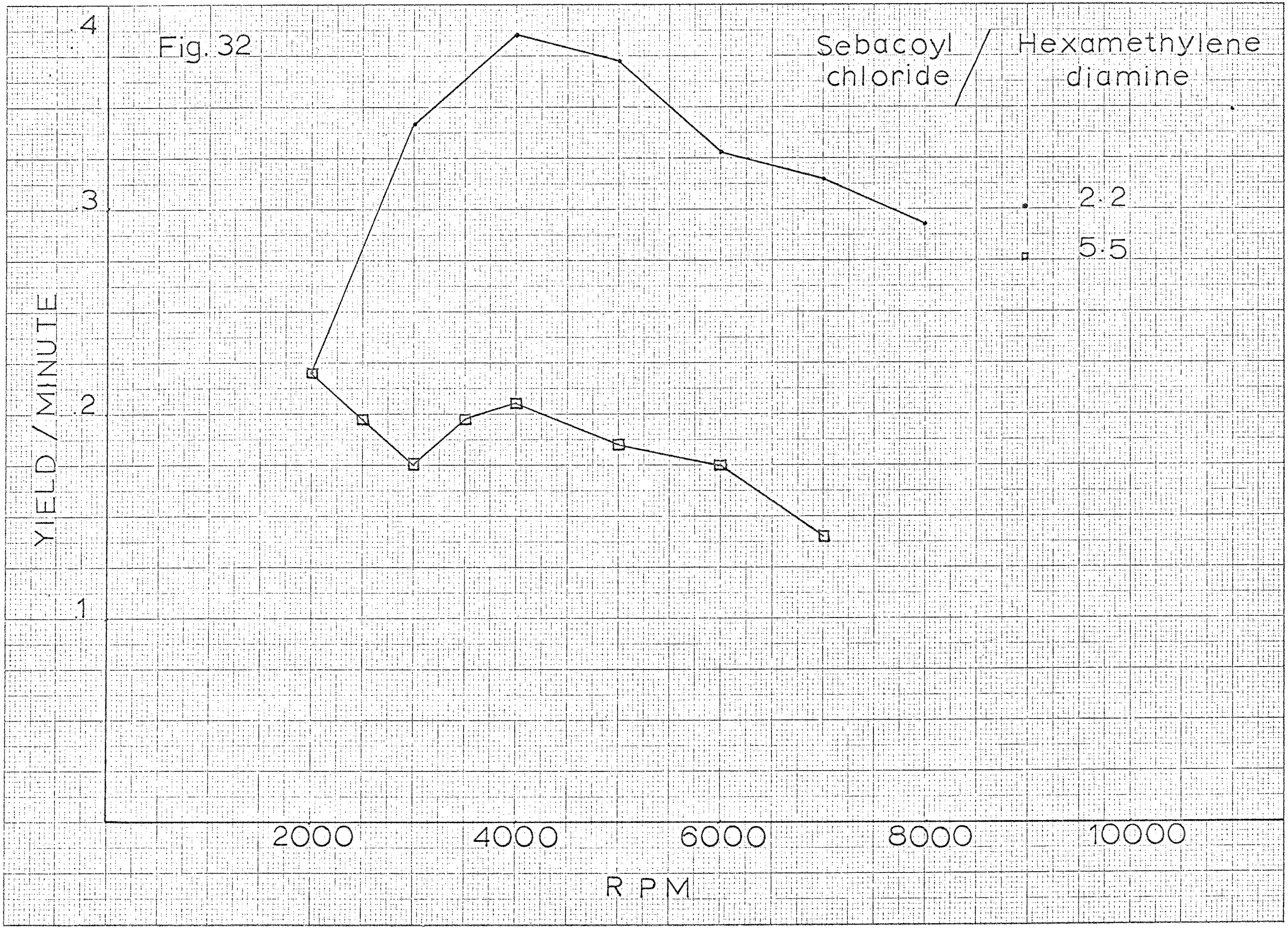

Sebacoyl chloride / Hexamethylene diamine
2·2
5·5
YIELD / MINUTE
.4
.3
.2
.1
2000
4000
6000
8000
10000
R P M


Fig.33
Sebacoyl chloride / Hexamethylene diamine
0.4
1.0
2.2
.4
.3
.2
.1
YIELD / MINUTE
2000
4000
6000
8000
10000
12000
REYNOLDS NUMBER

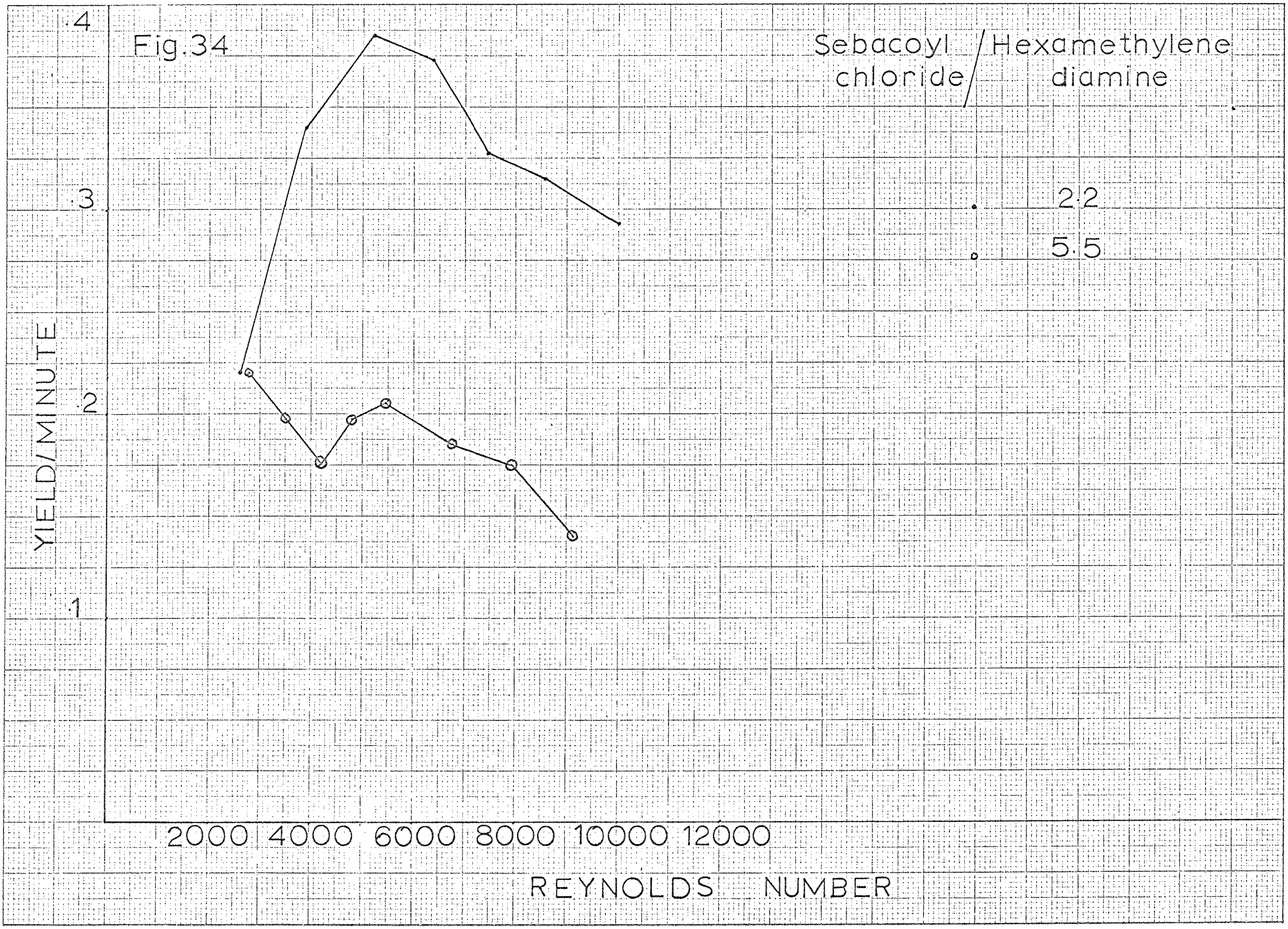
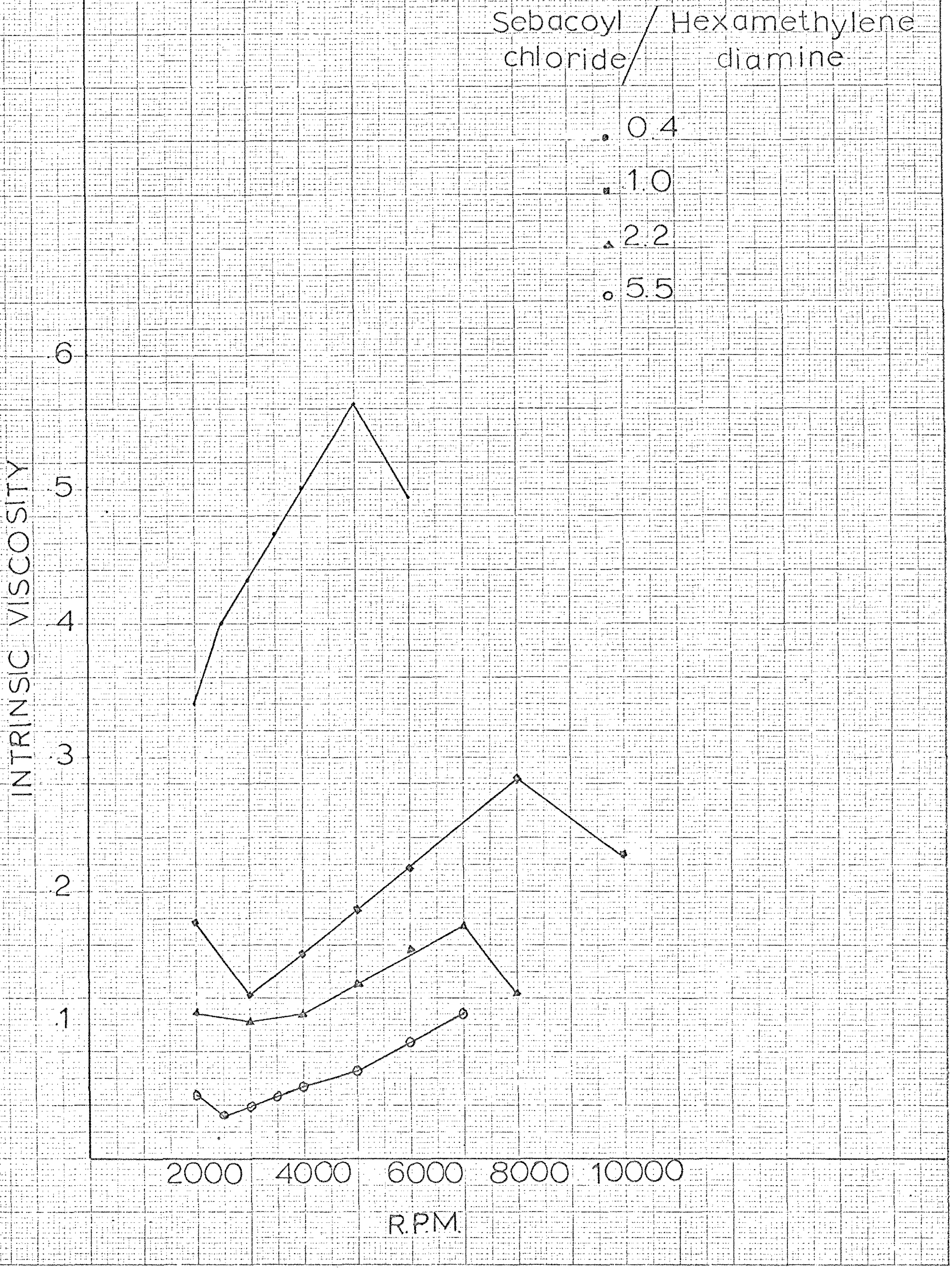


Fig. 34

Sebacoyl chloride / Hexamethylene diamine
• 2.2
○ 5.5
YIELD/MINUTE
.4
.3
.2
.1
2000
4000
6000
8000
10000
12000
REYNOLDS NUMBER

Fig. 35


Sebacoyl chloride / Hexamethylene diamine
● 0.4
■ 1.0
▲ 2.2
○ 5.5
INTRINSIC VISCOSITY
6
5
4
3
2
1
2000
4000
6000
8000
10000
R.P.M.

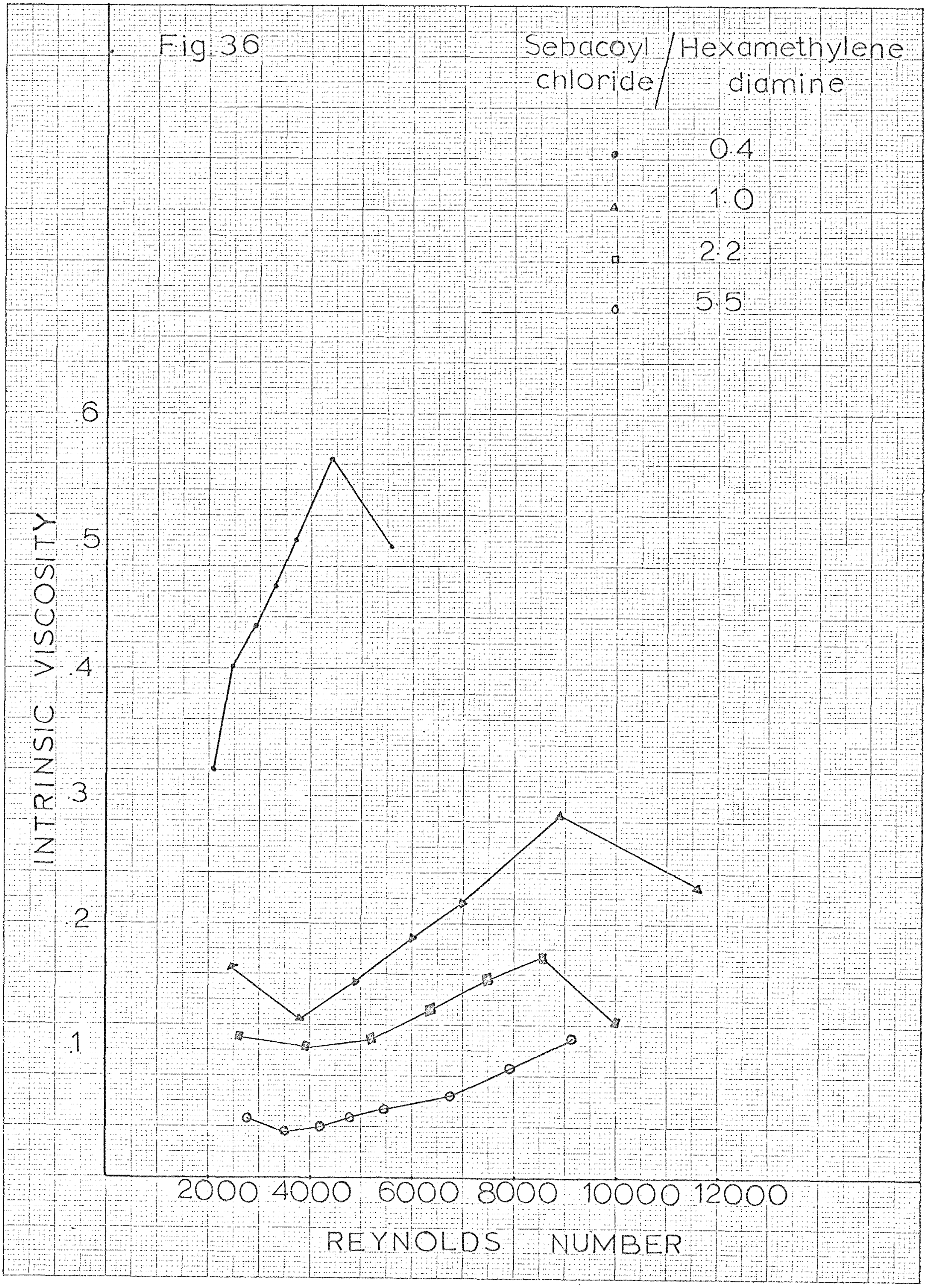


Fig. 36

Sebacoyl chloride / Hexamethylene diamine
0.4
1.0
2.2
5.5
INTRINSIC VISCOSITY
.1
.2
.3
.4
.5
.6
2000
4000
6000
8000
10000
12000
REYNOLDS NUMBER

Fig. 37

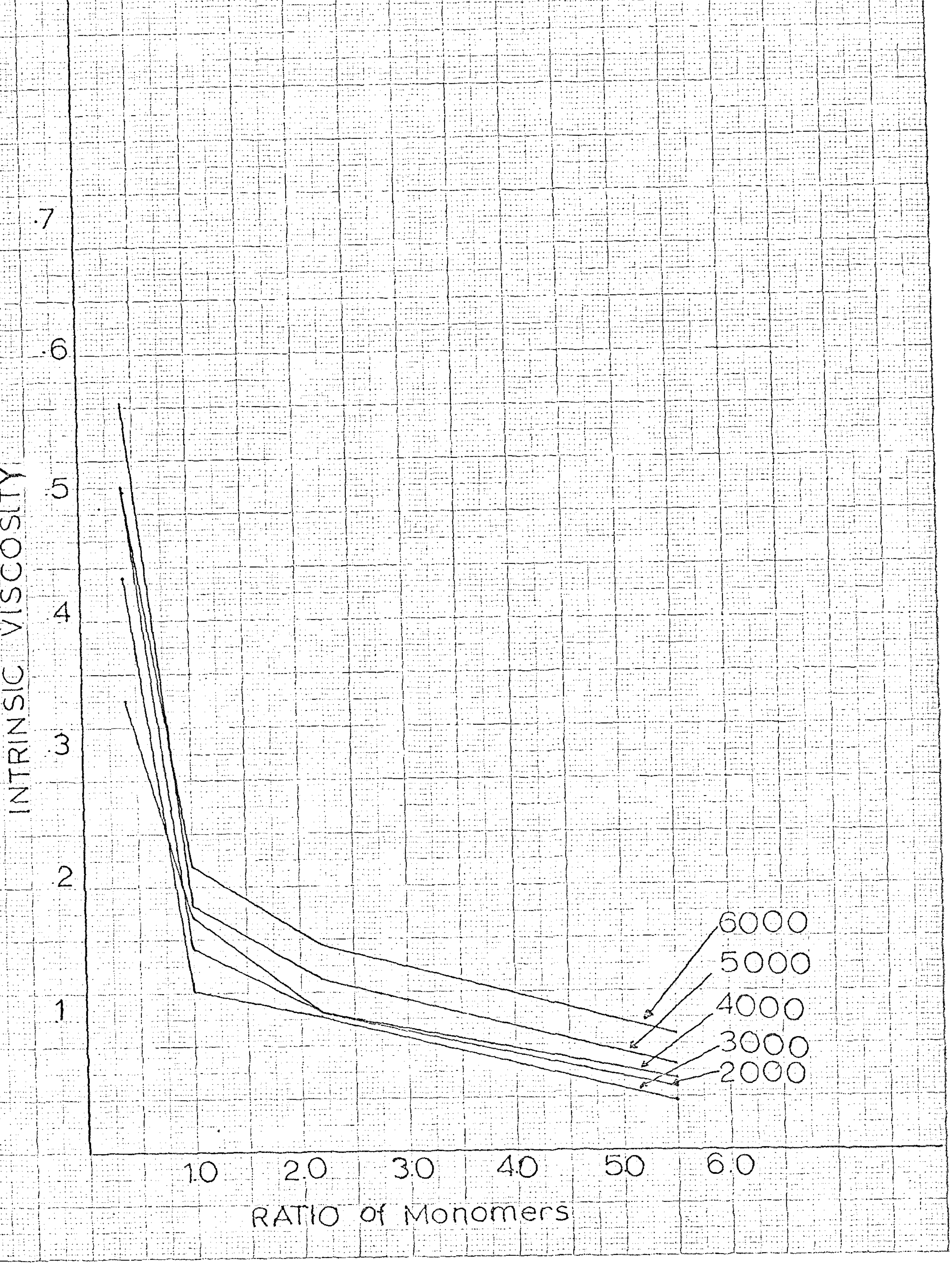
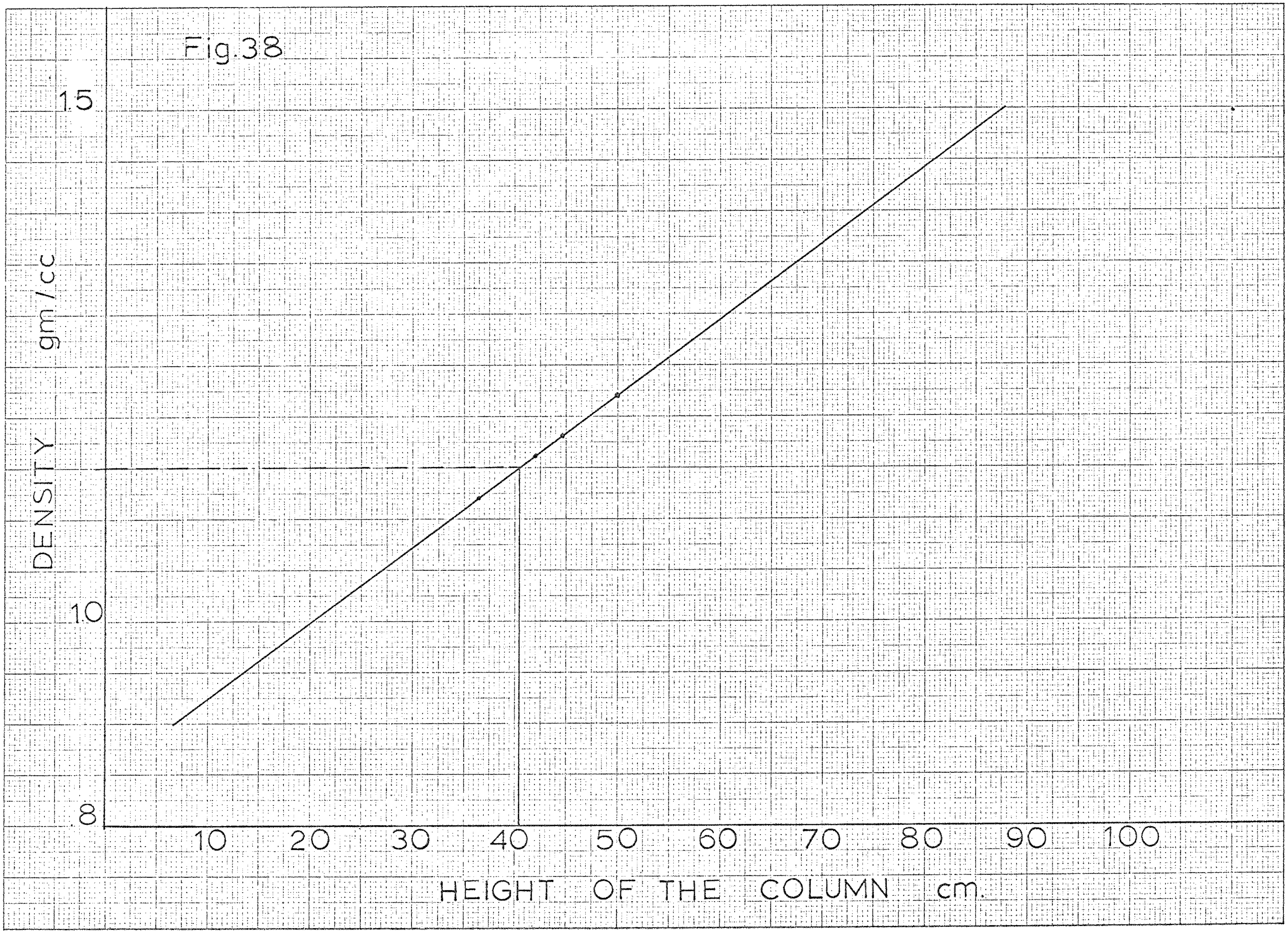
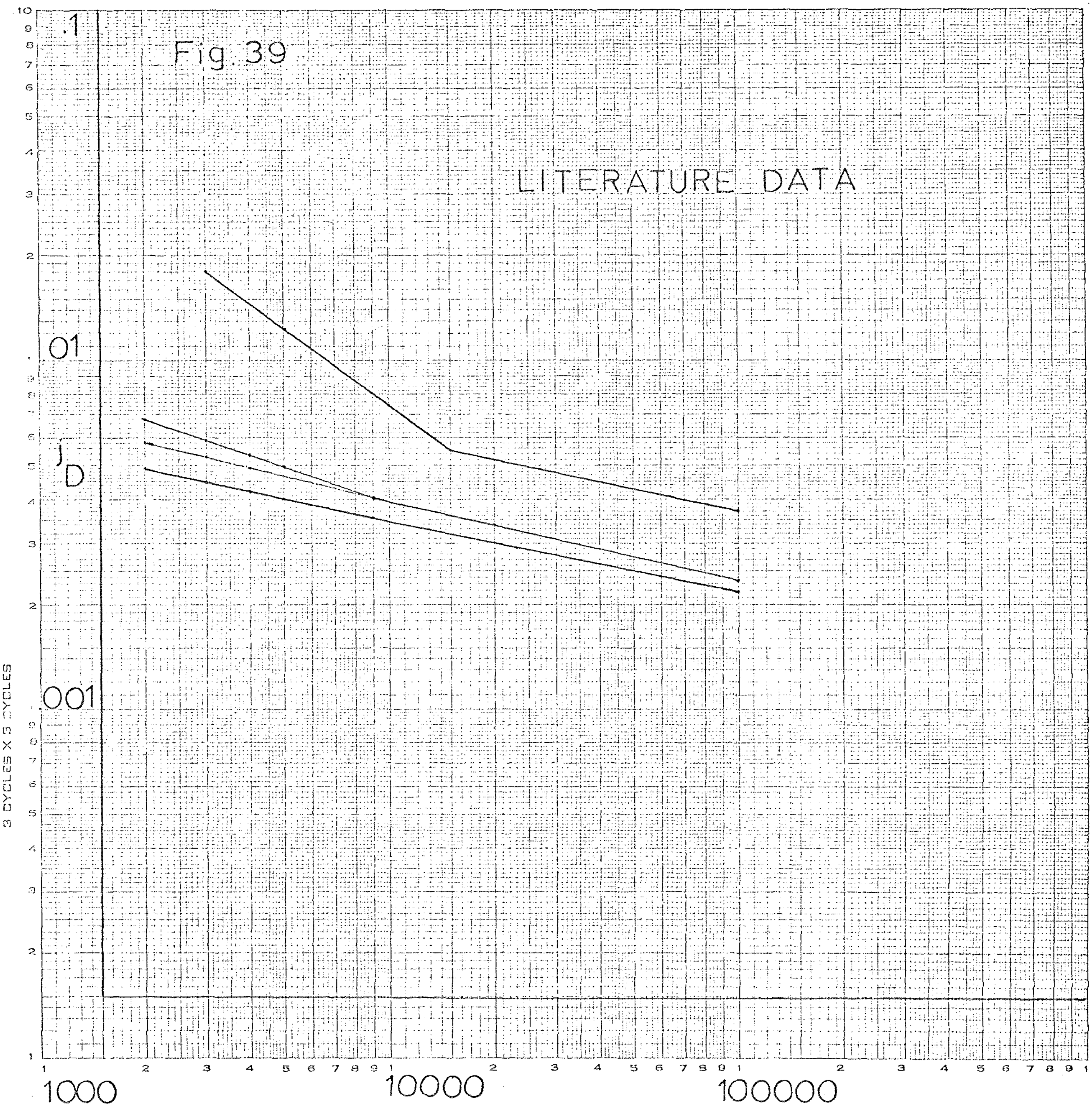
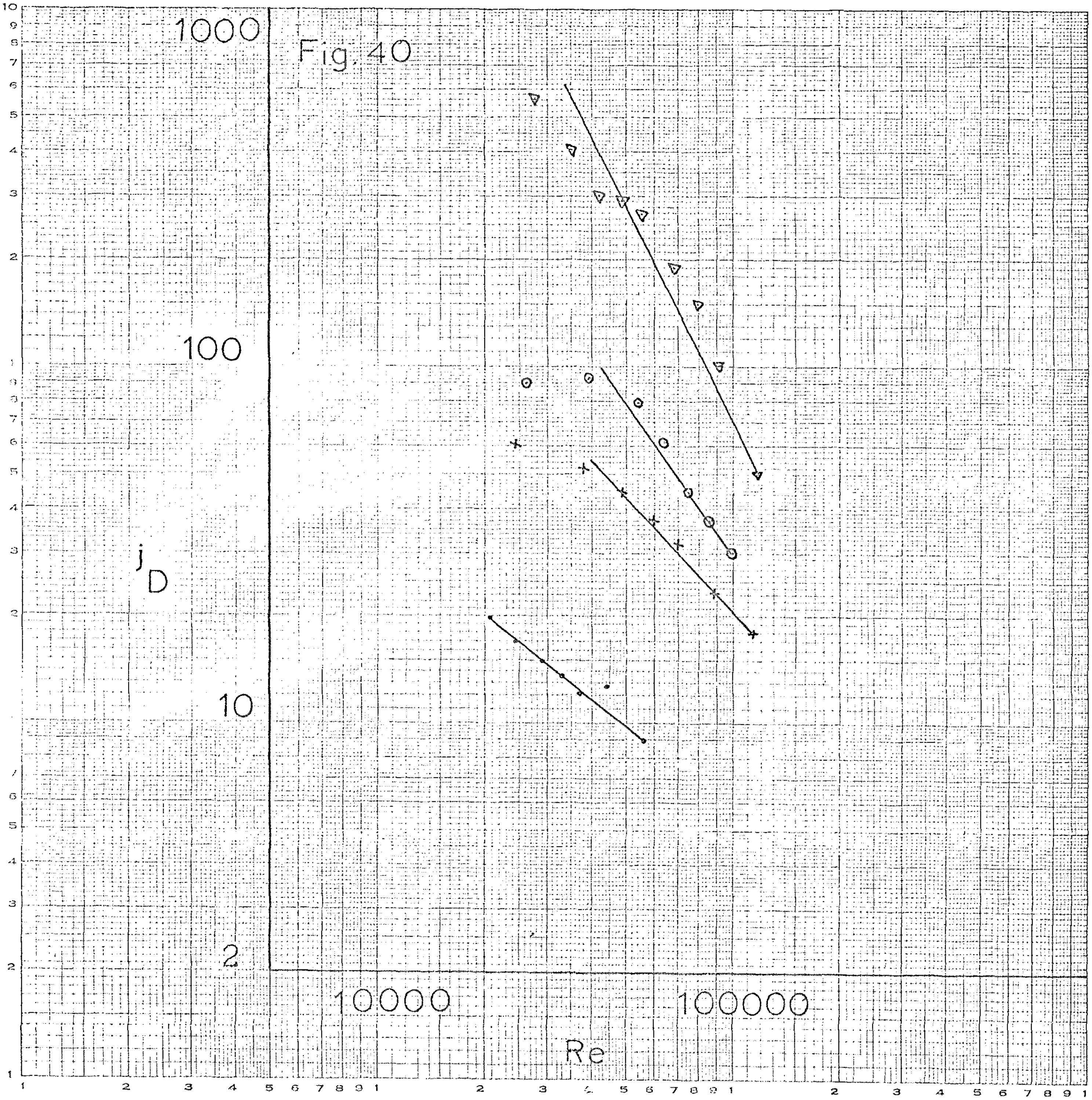

.7
.6
.5
.4
.3
.2
.1
INTRINSIC VISCOSITY
1.0
2.0
3.0
4.0
5.0
6.0
RATIO of Monomers
6000
5000
4000
3000
2000

Fig.38


1.5
1.0
.8
DENSITY gm/cc
10
20
30
40
50
60
70
80
90
100
HEIGHT OF THE COLUMN cm.


.1
Fig. 39
LITERATURE DATA
01
j_D
001
1000
10000
100000
Re
3 CYCLES X 3 CYCLES



1000
Fig. 40
100
j
D
10
2
10000
100000
Re
3 CYCLES X 3 CYCLES

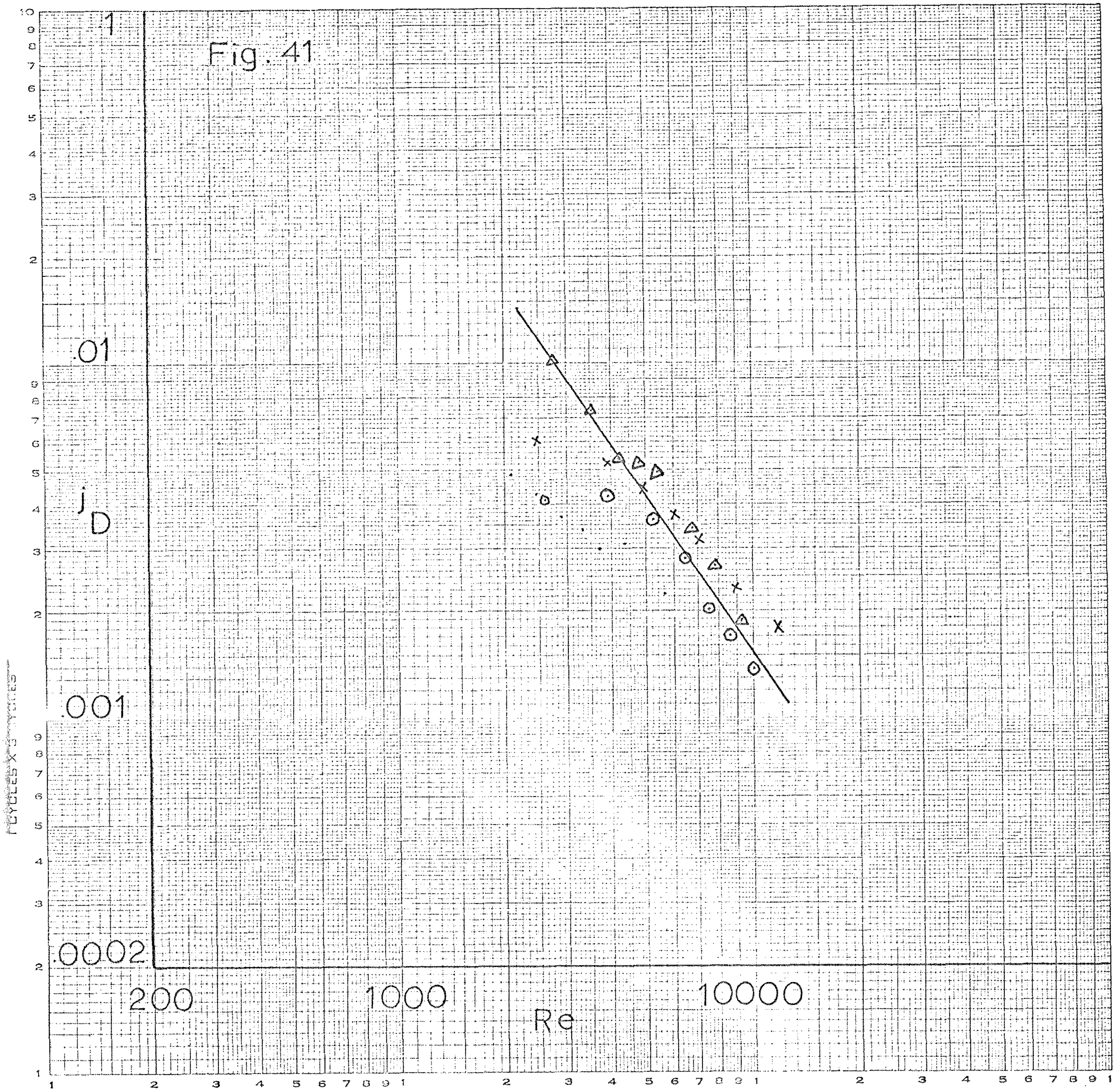


Fig. 41

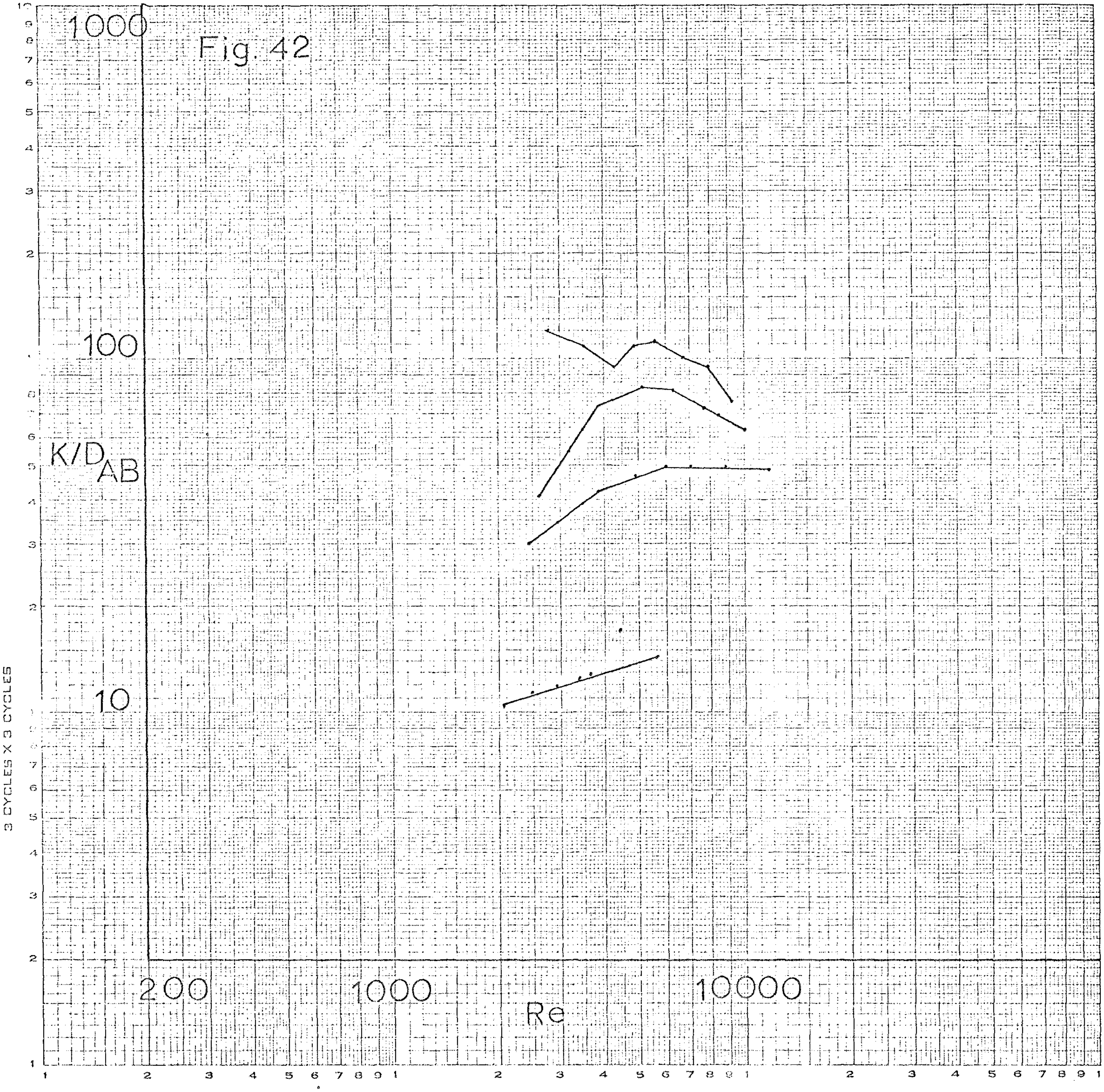


Fig. 42
1000
100
10
K/D$_{AB}$
200
1000
10000
Re
3 CYCLES X 3 CYCLES

SAMPLE CALCULATION:

REYNOLD'S NUMBER:

Temperature 29°C.

Weight of empty sp. gravity bottle:	20.3065	gms.
Weight of water	25.4545	"
Weight of m-cresol	26.1595	"
Weight of carbon tetrachloride	40.3835	"
Weight of hexamethylenediamine	23.5815	"
Weight of sebacoyl chloride	28.3520	"
Weight of hexamethylenediamine mixture	25.0190	"
Weight of sebacoyl chloride mixture	39.7140	"

Density of water at 29°C. 0.996 gm/cc
(Handbook of Chemical Engineering - Perry
4th Edition.)

ρ liquid = (weight of liquid/weight of water)
(density of water)

Density of m-cresol	1.02356	gm/cc
Density of carbon tetrachloride	1.58	"
Density of hexamethylenediamine	0.9231	"
Density of sebacoyl chloride	1.10935	"
Density of hexamethylenediamine mixture (0.025) molar	0.9961	"
Density of sebacoyl chloride mixture (0.01) molar	1.5812	"

Viscosity of water at 29°C is 0.818 cp.

(handbook of Chemical Engineering - Perry)

Efflux time of water is	67.15 sec.
Efflux time of carbon tetrachloride	43.60 "
Efflux time of m-cresol	849.70 "
Efflux time of hexamethylenediamine	712.8 "
Efflux time of sebacoyl chloride	413.2 "
Efflux time of mixture of water and hexamethylenediamine	67.8 "
Efflux time of mixture of sebacoyl chloride and carbon tetrachloride	43.75 "

$$\mu_L = ((t \times \rho_L)/(t \times \rho_W)) \times \mu_W \qquad (26)$$

Viscosity of m-cresol	10.6374 cp.
Viscosity of sebacoyl chloride	5.6064 "
Viscosity of carbon tetrachloride	0.845 "
Viscosity of hexamethylenediamine and water mixture (0.025)	0.8257 "
Viscosity of hexamethylenediamine	8.0476 "
Viscosity of sebacoyl chloride and carbon tetrachloride (0.01 molar)	0.846 "

Volume of sebacoyl chloride (0.01 molar) =
5.975/1.10935
5.386

Volume fraction of sebacoyl chloride =
5.386/1000 = 0.005386

Volume fraction of carbon tetrachloride = 0.994614

Total volume = 1000.00

Weight of sebacoyl chloride = 5.975 gm.

Weight of carbon tetrachloride = 629.5025 gm.

Moles of sebacoyl chloride	0.01
Moles of carbon tetrachloride	4.09193
Total moles	4.10193
Mole fraction of sebacoyl chloride	0.002438
Mole fraction of carbon tetrachloride	0.997562

$$\mu_{mix} = X_1Y_1\mu_1 + X_2Y_2\mu_2 + 2(X_1Y_1X_2Y_2)^{1/2}\mu_{12} \qquad (27)$$

X_1 X_2 mole fraction of componets

Y_1 Y_2 Volume fraction of componets

μ_1 μ_2 Viscosity of components

μ_{12} Viscosity of interacting substances

$$0.846 = ((0.002438)(0.005386)(5.6068) + (0.997562)(0.994614)(0.842)) + 2((0.002438)(0.997562)(0.005386)(0.994614))^{1/2}\mu_{12}$$

μ_{12} = 1.45496

Volume of sebacoyl chloride (0.055) = 13.145/1.10935
11.85

Volume fraction of sebacoyl chloride = 0.01185

Volume fraction of carbon tetrachloride = 0.98815

Volume of carbon tetrachloride = 988.15

Weight of carbon tetrachloride = 625.45

Moles of sebacoyl chloride = 0.055

Moles of carbon tetrachloride = 4.0653

Total moles = 4.1203

Moles fraction of sebacoyl chloride = 0.0133485

Moles fraction of carbon tetrachloride = 98665

μ_{mix} = 0.858 cp.

Average viscosity of the solvent mixture = (0.858+0.8257)/2 = 0.8418 cp.

maximum weight of polymer was collected (0.025 hexa. and 0.055 molar seba.)	0.38 gm
Density of polymer (from graph 38)	1.15 gm/cc
Volume of polymer	0.3304 cc
Total volume	140.0 cc
Volume of carbon tetrachloride and water	139.6696 cc
Volume of hexamethylenediamine solution (0.025 molar)	69.8348 cc
Weight of hexamethylenediamine solution (0.025 molar)	70.09 gms
Volume of sebacoyl chloride solution (0.055 molar)	69.8348 cc
Weight of sebacoyl chloride solution (0.055 molar)	44.17 cc

Total weight 44.17 + 70.09 + 0.38 = 114.64 gms

Density of slurry 114.64/140 = 0.81886 gm/cc

$$Re = (d^2 / \nu) N$$

d diameter of stirrer 0.9525 cm

ν kinematic viscosity = μ/ρ

μ Relative viscosity of polymer X viscosity of solvent (0.8418)

ρ density of slurry (0.81886)

N RPM

Calculations for j_D factor:

Molecular weight of hexamethylenediamine	116.21
Molecular weight of sebacoyl chloride	207.14

$dci / dt = (\text{MW of HMD} / \text{MW of HMD} + \text{MW of SC})$
$(\text{yield} / 140) = 0.002567\ (Y)$ yield gm/cc-min

When aqueous phase is dispersed phase

$m_{in} = Co_{in} / Ci_{in}$ ------(19a)

$(a/6)(dci/dt) = - K_D\ (Co - m_{in}\ Ci$ ----- (9a)

$K_D / d = - (1/6)\ (1/(Co - m_{in}\ Ci)\ (dci/dt)$

$K = (1/6)\ (1/m_{in}\ Ci)\ (dci / dt)$

$m_{in} = 35.0$

$Ci = 0.025$ molar

$= 0.002905$ gm/cc

$Ci = 0.01$ molar

$= 0.0011621$ gm/cc

$K = (1/6)\ (1/m_{in}\ Ci)\ (dci/dt)$

$= 0.0042078\ Y$ 1/min when Ci is 0.025

$= 0.010518\ Y$ " when Ci is 0.010

$D_{AB} = (7.4\text{X}10^{-8}\ (Y_B M_B)^{1/2}\ T) / (\mu\ V_A^{.6})$

$V_A = 116.21/0.9961 = 116.655$ cc/gm-mole

μ 0.826 cp

Y_B 1.0

M_B 153.823 gm/gm-mole

T 302°K

D_{AB} = 1.9303×10^{-5} cm^2/sec

$$j_D = (K/C\ N)\ (\mu/\rho\ D_{AB})^{0.66} \qquad (29)$$

K mass transfer coefficient cm/hr

C concentration of hexamethylenediamine
(0.002905 and 0.0011621)

N RPM

μ viscosity 0.826 cp

ρ density 0.9961 gm/cc

j_D = (0.9961/N) (56.933) K/C