MEASUREMENT OF MOLECULAR WEIGHT DISTRIBUTION OF POLYACRYLAMIDE BY TURBIDIMETRIC TITRATION

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by

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Dedicated to my Parents

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ABSTRACT

This thesis reports on a method for measuring the molecular weight distributions of polyacrylamide - a water-soluble polymer. The method which is turbidimetric titration involves the incremental addition of non-solvent or precipitant to a solution of polymer and encourages aggregation. At each point of the titration, optimum condition was obtained. The optimum condition was defined by proper application of Mie theory of light scattering functions. These scattering coefficients and scattering functions were further investigated over a broad range of particle size. Broad polymers were investigated, as this polymer-polyacrylamide can only be made via free-radical polymerization. The conditions necessary to satisfy the inherent assumptions were specified and justified by the experimental technique. A very high molecular weight polymer was polymerized by free radical polymerization in the presence of an electrolyte. The influence of electrolyte, and the method of mixing were studied.

The quality of the distributions and averages obtained by the method was assessed by GPC measurements and viscosity measurements. The method is capable of giving accurately the molecular weight distributions of any polymer in principle, especially when the weight average molecular weight is greater than five million.

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TABLE OF CONTENTS

PAGE

FIGURE INDEX

TABLE INDEX

CHAPTER 1

INTRODUCTION

1.1 Polymer Characterization

With the increasing use of high polymers, it has become evident that the molecular sizes in heterogeneous polymers are not sufficiently characterized by average values only. Choice between rival mechanisms may be made by examination of chain length distribution.(1),(2) For a good appreciation of some thermodynamic parameters of polymer species,(3) swelling, mechanical properties,(4) knowledge of the molecular weight distribution is indeed essential. Virial coefficients are also related to molecular weight distributions.(5) The standard procedure of determining such a distribution function is to effect by physical means a separation of molecules according to molecular sizes in solution,(6),(7) which if achieved using porous packing materials is the principle behind gel permeation chromatography (GPC) or fractionation of the polymer into relatively homogeneous parts and obtain both the average molecular weight and the weight fraction in each of these fractions. Apart from the standard procedure of separation, the distribution function can also be obtained by observing single molecules of the polymer under an electron microscope, a method which was first reported by Quayle.(8)

The difficulties and the time required when the last two methods are applicable are so great that it is not often carried out especially when the number of polymers under investigation is large. GPC method is quite a superior method when applicable. The only difficulty with the GPC seems to be that, at the high molecular weight tail of a high molecular weight polymer, there is usually a poor resolution limit. The search for a simpler or more rapid method of obtaining the chain-length distribution function of polymers of any size has stimulated research in this direction.

Synthetic water-soluble polymers are making increasing inroads into the more than 10,000 million pounds per year world-wide water-soluble polymer market. These inroads have been made primarily in the industrilized countries of the world, especially in the United States, Japan, West Germany, the United Kingdom, France, The Netherlands and Italy. Accurate figures on production in Eastern European countries, the Soviet Union and Mainland China are not readily available, but it is known that the Eastern European countries and the Soviet Union have substantial production facilities and also are involved in further expansion of their output. Mainland China has a need for much of the required know-how. In the trade, water-soluble polymers are also known as "water-soluble resins","hydrocolloids" and "gums".

Some of the applications of water-soluble polymers are in adhesives, construction, cosmetics, detergents, explosives, food, oil-well drilling, paints, paper, pharmaceuticals and textiles. For individual countries and individual water-soluble polymers, the breakdown often varies widely. Yet in all these applications, the molecular weight distributions are not accurately known. One very basic characteristic of water-soluble polymers is the viscosity of solutions. The viscosity of aqueous solutions of water soluble polymers is temperature dependent with the relationship exponential. Water-soluble polymer solutions are non-Newtonian, with few exceptions. Polyacrylamide is an important member of water-soluble polymers, from a commercial point of view. Until recently, polyacrylamide was considered a laboratory curiosity. The rapid growth and attention to polyacrylamide is attributed to the following applications:

(1) High molecular polyacrylamide has been shown to be an excellent flocculant for several decades.

(2) As an excellent thickener in explosives for the aqueous slurry type with improved low temperature flow properties.

(3) As an extremely effective combined lubricant-coolant when used in aqueous solutions in metal working operations.

(4) For reducing frictional losses in the flow of aqueous fluids containing alkaline-earth metal ions, such as the brines commonly used in fracturing oil and water well formations.

(5) For paper coating purposes.

(6) For reducing energy loss during flow of oil through a pipe preferably in the presence of a dispersing agent.

(7) As chromatographic adsorbents.

(8) As extruded catalysts and catalyst supports, for obtaining improved crush strength of extrudate and extruding an inorganic oxide support.

All these are important industrial processes. The flocculation of colloidal suspensions is an important industrial process, used of recent years in water clarification and mineral processing. In flocculation studies, it is understood that the larger molecules play a dominant role in increasing settling rates. Thus a complete knowledge of molecular weight distribution is an important step to provide a precise evaluation of the influence of molecular weights. Most commercial polyelectrolytes have weight average molecular weights which often exceed ten million.

In the application of turbidimetric titration (TT), to provide chain-length distribution, polyacrylamide has been chosen to test the method. This particular method makes use of the light scattered from particles or aggregates of the polymer precipitated out of solution by the addition of non-solvent. Scattered light in this method is a means of "weighing" the precipitate without the actual physical steps of filtration, washing, drying and weighing. The turbidity (with some corrections) is a measure of the increment of polymer which precipitates out for each increment of non-solvent added. The main disadvantages of the turbidimetric method as used in the past have been summarized by Hall(9) and these have been discussed in various sections. Of all these methods, turbidimetric titration seems to be one of the quickest to carry out and this is probably another reason why considerable interest is shown in this method.

1.2 Application and Scope of Turbidimetric Titration

Until recently, Turbidimetric Titration (TT) has been used almost exclusively as a qualitative method of polymer characterization.(10),(11),(12),(13) Unimodal or bimodal distributions could be distinguished at a glance, provided the average molecular weights are sufficiently different.(1) Examination of products from block and graft copolymer synthesis by TT clearly show the presence of homopolymer as well as the copolymer where this occurred.(14),(15) Elias and Grubber(16) have demonstrated its simplicity for identifying the existence of extraneous polymer species in a product.

TT has long been recognized as a useful tool in selection of solvent-precipitant systems for conventional fractional precipitation. Apart from the application of TT to the quantitative determination of molecular weight distribution, the interesting departure from the accepted role to the determination of theta conditions-compositions and temperatures has long been recognized. Cornet and Ballegooijen,(17) Elias,(18) have demonstrated this role.

The determination of polymer solubility parameters using TT have been demonstrated by Suh and Clark.(19) Although no work has been reported, TT could also be applied to determining critical micelle concentrations of emulsifiers where applicable.

CHAPTER 2

LITERATURE REVIEW

2.1 Properties of Polyacrylamide

The polymer is insoluble in most organic solvents and is usually a linear polymer with head to tail arrangement.(20) Polymers with significant amounts of chain branching are usually obtained under special reaction conditions.(21) Solutions of polyacrylamide in water are very viscous. Some of the equations relating intrinsic viscosity to average molecular weights of the polymer have been found to be:

$$[\eta] = 6.31 \times 10^{-5} (\bar{M}_w)^{0.80} \text{ 25°C in } H_2O^{(22)} \qquad 2.1.1$$

$$[\eta] = 3.73 \times 10^{-4} (\bar{M}_w)^{0.66} \text{ 30°C in 1N NaOH}^{(23)} \qquad 2.1.2$$

$$[\eta] = 6.80 \times 10^{-4} (\bar{M}_w)^{0.66} \text{ 25°C in } H_2O^{(24)} \qquad 2.1.3$$

$$[\eta] = 3.02 \times 10^{-3} (\bar{M}_w)^{0.82} \text{ 25°C in 1\% NaCl}^{(25)} \qquad 2.1.4$$

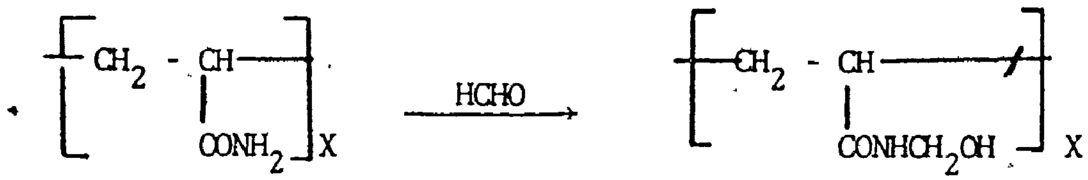
Of the above equations, Eq. 2.1.3 seems to be the most reliable in predicting number-average molecular weight.(59)

Water solutions of polyacrylamides are stabilised against thermal or oxidative degradation by addition of 0.1 - 7% by weight of an alkali metal, alkaline earth or ammoniums thiocyanate. Aqueous polymerization of acrylamide is an example of homogeneous polymerization, and the process is by free radical initiation as opposed to ionic initiation. An ionic polymerization involving a vinyl monomer is not sustainable in water as rapid chain transfer produces H^+ or OH^- ions which are incapable of initiating vinyl polymerization.$^{(23)}$ Of all the solvents, water is unique in having a chain transfer constant of practically zero in free radical processes.$^{(26)}$ This partly accounts for the high molecular weight polymers obtainable in aqueous polymerization. The ratio of the rate constants K_p/K_t exceeds that reported for any other monomer polymerization indicating formation of very high molecular weight polymer.$^{(27)}$

High molecular weight polyacrylamides, have been manufactured commercially under different trade names such as Superfloc, Cyanamer A370, Cyanamer P26, Cyanamer P250, Polyhall 402, etc. Although polyacrylamide is essentially non-ionic in character, several interesting ionic derivatives have been prepared.$^{(28)}$

Some of the chemical reactions of polyacrylamide include

(1) Methylolation

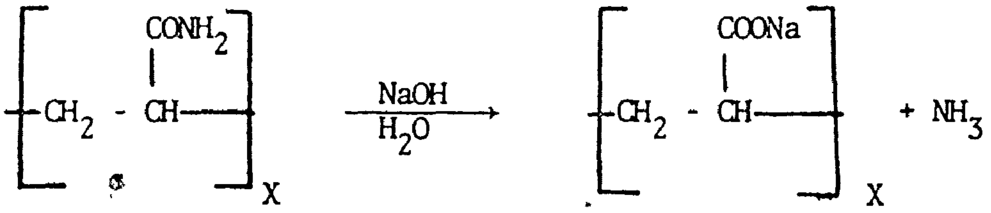


$$\left[CH_2 - \underset{\displaystyle CONH_2}{CH} \right]_X \xrightarrow{HCHO} \left[CH_2 - \underset{\displaystyle CONHCH_2OH}{CH} \right]_X$$

The reaction of formaldehyde in aqueous media with polyacrylamide is an equilibrium reaction and is limited to partial methylolation of the amide groups present in the polymer.

(2) Hydrolysis

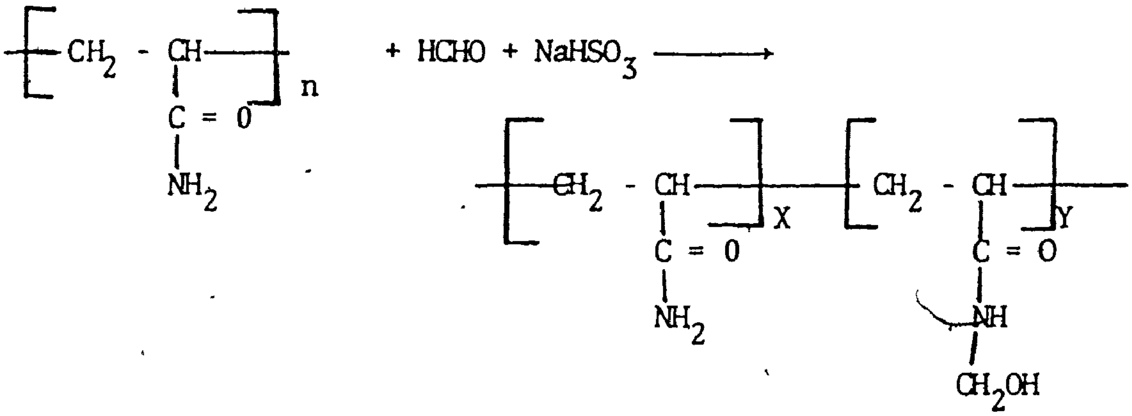
Through the use of this reaction about 70% of the amide groups in an acrylamide polymer may be converted to carboxyl groups. Attempts to obtain complete hydrolysis of polyacrylamide to a polyacrylate by the use of drastic reaction conditions have resulted in degradation of the polymer.



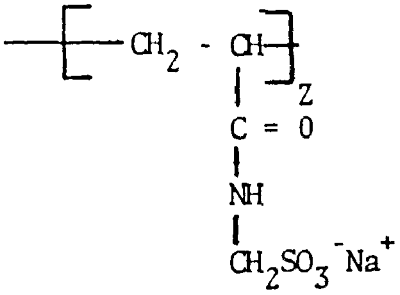
$$\left[-CH_2-\overset{CONH_2}{CH}-\right]_X \xrightarrow[H_2O]{NaOH} \left[-CH_2-\overset{COONa}{CH}-\right]_X + NH_3$$

(3) Ionic Derivatives

An anionic derivative has been prepared through the reaction of polyacrylamide with formaldehyde and sodium bisulfite, sodium sulfite, or sodium sulfonate.



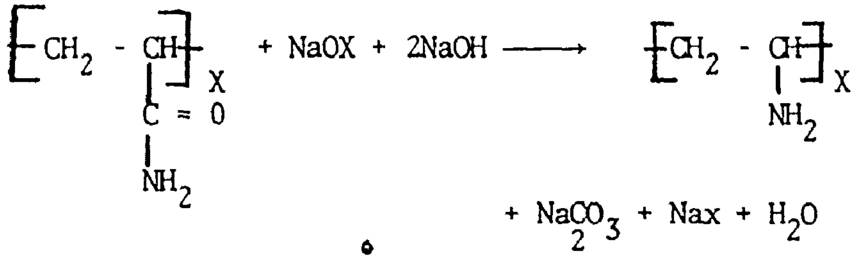
$$\left[-CH_2-\underset{\underset{NH_2}{C=O}}{CH}-\right]_n + HCHO + NaHSO_3 \longrightarrow \left[-CH_2-\underset{\underset{NH_2}{C=O}}{CH}-\right]_X\left[-CH_2-\underset{\underset{\underset{CH_2OH}{NH}}{C=O}}{CH}-\right]_Y$$



$$-\!\!\left[CH_2 - \underset{\underset{\underset{\underset{\underset{CH_2SO_3^-Na^+}{|}}{NH}}{|}}{C = 0}}{|}}{CH}\right]_Z$$

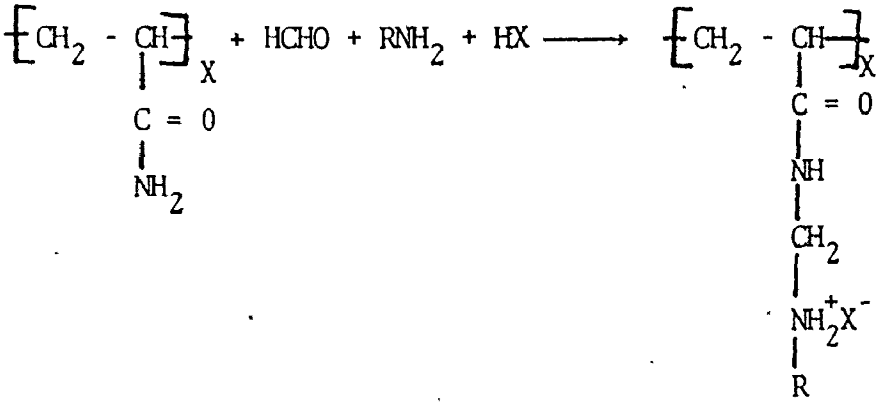
It is important to use conditions of high pH when maximum sulfomethylolation is desired.

A cationic derivative has been prepared through the Hoffman degradation of polyacrylamide by alkali and hypochlorite.



$$\left[CH_2 - \underset{\underset{\underset{NH_2}{|}}{C = 0}}{|}}{CH}\right]_X + NaOX + 2NaOH \longrightarrow \left[CH_2 - \underset{\underset{NH_2}{|}}{CH}\right]_X + Na_2CO_3 + Nax + H_2O$$

Another cationic derivative has been made through the Mannich reaction in which polyacrylamide is reacted with formaldehyde and an amine.



$$\left[CH_2 - \underset{\underset{\underset{NH_2}{|}}{C = 0}}{|}}{CH}\right]_X + HCHO + RNH_2 + HX \longrightarrow \left[CH_2 - \underset{\underset{\underset{\underset{\underset{\underset{\underset{\underset{R}{|}}{NH_2^+X^-}}{|}}{CH_2}}{|}}{NH}}{|}}{C = 0}}{|}}{CH}\right]_X$$

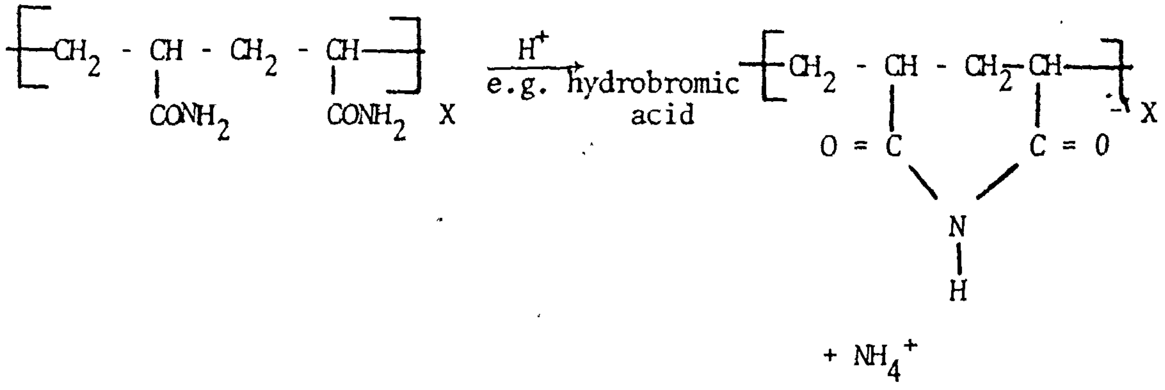
(4) Reaction with Alkylene Oxides

Polymers of acrylamide can be made alcohol-soluble through reaction of the polymer with an alkylene oxide.

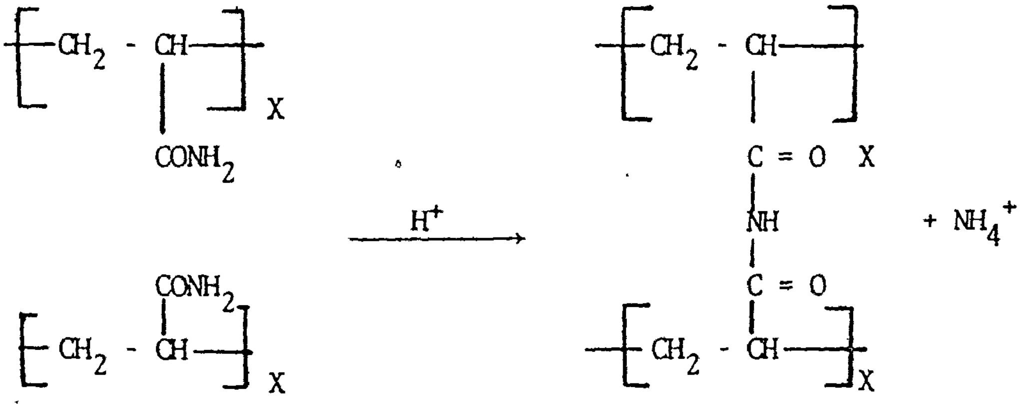
(5) Imidization

Treatment of polyacrylamide with acids having dissociation constants greater than 1 x 10^{-3} converts some of the amide groups to imides.

Imide formation may be intramolecular



or intermolecular



Intramolecular imidization does not change the linear nature of the polymer, but does decrease its water solubility. Intermolecular imidization produces cross linking and greatly reduces the water solubility of the product. Increasing time of heating temperature of reaction and acid concentration increases the degree of cross linking.

(6) Chlorination

Polyacrylamide is included in a list of polymers which, it is claimed, may be chlorinated in the presence of accelerators such as light, metals and metallic salts. The products are said to possess increased hardness, higher softening points and reduced flammability.

(7) Hydrogenolysis

Hydrogenolysis of polyacrylamide has resulted in cleavage of carbon-to-nitrogen linkages.

2.2 Historical Background and Definition of Method

Turbidimetric titration, as the name implies is a titration process in which the end points of the titration are marked by changes in level of turbidity. In principle, it is an analytical fractional precipitation procedure which involves the incremental addition of non-solvent or precipitant to a solution of polymer. The lack of proper theoretical basis, has hindered the development of the method in the past. With more attention being paid to the principles of light scattering theory of large spherical particles and size distribution in polydisperse systems, the method has been gaining renewed popularity.

The origin of turbidimetric titration dates back to 1938, when Bronsted(29) devised the method, and 1945 when Morey and Tamblyn(30) made a first detailed application to measurement of molecular weight distribution of cellulose acetate-butyrate in acetone precipitated by ethanol-water mixture, without the necessity of the usual procedure of evaporating and weighing the dried samples of polymer. In their application, they established the general conditions under which the suspended polymer-rich phase is stable enough for optical transmission to remain constant. It was assumed that as the solution of non-solvent is added, a narrow range of molecular weight, beginning with the higher molecular weight species would separate out, being insoluble in the solvent. This causes a small amount of turbidity leaving all molecules of lower molecular weight in solution. As the addition continues, increasing amounts of polymer are precipitated out according to their molecular weights. Finally, a point is reached at which even the lowest molecular weight species become insoluble in the solution. At this point, the turbidity is greatest, and ideally all the polymer is precipitated out, but remains in suspension as very fine particles.(30) It was further assumed that the increase in turbidity caused by increasing precipitation of these molecules was related in a simple fashion to mass of polymer precipitating. Thus a plot of turbidity against the volume of precipitant added would yield a curve closely related to a cumulative weight precent versus molecular weight. The increase in turbidity is related to the cumulative weight per cent and molecular weight is related to the increase in non-solvent.(30) Though the assumptions seem quite reasonable, one can see that the first assumption is not in good agreement with the theory of phase relationships and the second assumption does not take into consideration the following:

(1) due to the change in size of precipitated particles, the scattering patterns are bound to be affected.

(2) due to the different amounts of non-solvent added to the system, the precipitated particles in the polymer-rich phase are bound to swell to different volumes.

(3) aging, agglomeration or coagulation of precipitate and even settling can alter the turbidity of the system without the quantity of precipitate changing.

(4) there will be change in the refractive index of the solvent precipitant medium unless the two components are closely identical.

(5) the similarity between the refractive index of polymer and that of solvent/non-solvent.

These main disadvantages of the turbidimetric titration method as used in the past have already been summarized by Hall.(9) This measurement was used without taking into account the above considerations by Campbell et al.,(31) Morey et al.,(32) Oth and Desreux,(33) Harns and Miller,(34) and Morey and Tamblyn.(30) The best results they could obtain were only qualitative changes in molecular weight distribution and presence of different species in a mixture. As a result, an exact measurement of the amount of polymer present has been a very difficult task, despite the successful application of the complicated Mie theory to the scattering of light from colloidal spheres and polydisperse system by a number of workers including Heller and Pangonis(35) Tabibian(36) Maron Pierce and Ulevitch.(37)

The first early attempt to examine the nature of the particulate phase formed from the slow addition of a non-solvent to the solution of polymer under isothermal conditions was made by Hasting and Peaker,(38) who examined the system polystyrene in benzene, the non-solvent being methanol. They observed large linear aggregates as well as spherical particles. These results suggested that turbidimetric titration could not be put on a quantitative basis. This conclusion was later questioned by Beattie(39) on the basis of the fact that the observed aggregation might have been formed during the preparation of the specimen.

Before proceeding, however, to discuss further steps of the development of turbidimetric titration (TT) over the years it should be mentioned that certain assumptions are inherent in the method. These are that:

(a) Fractionation is according to polymer solubility, which at every stage of titration, approaches equilibrium under certain conditions.

(b) The particulate phase is in the form of lowest energy surface requirement, the spherical shape.

(c) Particle size distributions should remain fairly constant during the titration unless aggregation is purposely encouraged.

(d) Provided the solvent and non-solvent are identical in refractive index, the refractive index of the particles is proportional to the volume fraction of polymer. Implicit in this are

(e) The refractive index of the particles is independent of the molecular weight of the polymer.

(f) The refractive index of the precipitated particles is also independent of concentration of the polymer.

(g) The weight of polymer precipitating at each step of the titration is directly calculable, absolutely or empirically.

During the last few years, a new approach which seems to place TT measurements on a quantitative basis has been proposed. Howard(40) was the first to devise a sequential method of addition, instead of the continuous or incremental titration methods. From his application, at best, only the approximate form of the distribution of molecular weight could be obtained, because his analysis did not include at least the major assumptions above. The first attempt taken to eliminate the major difficulties plaguing the development of TT method are the work of Beattie and Meehan,(41) Beattie and Jung(42) and Beattie.(39) Most enlightning in the course of development is the work of Beattie,(39) in which with the application of the Mie theory, aggregation of particles to a particular particle size was encouraged. These workers applied the Howard method of addition, and placed the TT method on the best quantitative basis so far attained. These methods are summarized in Table 1. This table contains published relevant studies to date, and shows the method employed, both practically and in displaying the molecular weight distribution. From the table, it can be seen that the number of polymers investigated is quite small, although a number of polymers of widely different characteristics has been examined and, in the case of polystyrene, several different solvent-precipitant systems have been employed in these investigations. No published data on polyacrylamide is available.

In passing, however, it should be borne in mind that, because the principle behind turbidimetric titration is fractionation, there are basically two old known methods of fractional precipitation in TT and these include

(i) addition of non-solvent slowly to a solution of the polymer under isothermal conditions called isothermal precipitation (IP).

(ii) a solution in a poor solvent, just above the precipitation threshold is allowed to cool over a convenient temperature change, called Thermal Gradient Precipitation (TGP) as shown in Table 1. The most widely used technique in TT is the isothermal precipitation method (IP).

The method of Beattie and co-workers, the "absolute" method as it is called, because it does not require an empirical calibration, is an important contribution to the evolution of the turbidimetric titration technique. It is based on some understanding and application of light-scattering principles and theory to the real problem. However, since aggregation to a particular particle size, the point of maximum turbidity, is encouraged, its application to polymer particles less than a particular particle size (small particles) is hindered since they may never grow to this particular particle size.

2.3 Other Solvent and Non-solvent Systems

The choice of solvent/non-solvent systems has been reported to be one of the most important experimental precautions in turbidimetric titrations. One of the main disadvantages of turbidimetric methods as used in the past is the choice of solvent and non-solvent whose refractive index are very different. Most TT methods make use of light scattered from the particles of the polymer precipitated out of solution by the

Table 1

Molecular wt Distributions by Turbidimetric Titrations

Method Representing Data	Polymer	Solvent/Non-solvent System	Type	Authors
Graphical nomograms D.W.D.	Cellulose Acetobutyrate	Acetone/EtOH and water	IP	Morey & Tamblyn (30) (1945)
M.T. D.W.D. Exponential Functions	Polymethylmethacrylate	Acetone/water	IP	Harris & Miller (34) (1951)
M.T. D.W.D.	Polyvinyl acetate	Acetone/water	IP	Morey et al. (32) (1951)
M.T. D.W.D.	Polyvinyl pyrrolidone	Water/Na$_2$SO$_4$	IP	Campbell et al. (31) (1954)
M.T. D.W.D.	Polystyrene	Butanone/Acetone	IP	Hengstenburg (43) (1956)
M.T. Claesson Grid Wesslau Function	Polyvinyl pyrrolidone	Water/Na$_2$SO$_4$	IP	Scholtan (44) (1957)
Claesson Grid modified D.W.D.	Polystyrene	Benzene/Methanol	IP	Gooberman (45) (1959)
Claesson Grid D.W.D.	Polystyrene	Toluene/Methanol	IP	Mathieson (46) (1960)
Method of Slopes Width of distribution Wesslau function	Polyethylene	Chloronaphthalene and 30% dimethyphthalate	TGP	Taylor & Tung (47) (1962)
Curve fitting Tung Exponential function	Nylon 66	m-Cresol/cyclohexane	IP	Howard (40) (1963)
Graphical differentiation D.W.D.	Polystyrene	Butanone/isopropanol	IP	Urwin et al. (48) (1964)
X Absolute Method Cumulative sol. dist.	Polystyrene	Butanone/isopropanol	IP	Beattie (39) (1965)
Probability graph Log-normal dist.	Polypropylene	Tetralin/Butylcellosolve	IP	Tanaka et al. (49) (1965)

.....continued

Table 1 (continued)

Molecular wt Distributions by Turbidimetric Titrations

Method Representing Data	Polymer	Solvent/Non-solvent System	Type	Authors
Method of Slope Width of Dist.	Ethylene-co-propylene	Heptane/n-propanol	TGP	Gamble et al. (50) (1965)
X Absolute Method Cumulative sol. Dist.	Polystyrene	Butanone/iso-propanol	IP	Beattie & Jung (42) (1968)

MT - based on the method of Morey & Tamblyn

IP - Isothermal Precipitation

DWD - Differential weight distribution curves

TGP - Thermal Gradient Precipitation

addition of non-solvent. If the solvent/non-solvent are not iso refractive, instead of having the precipitated polymer suspended in a medium, we have it suspended in multiple media, and this makes the light-scattering principle more complex and almost inapplicable in theory. At the same time, the refractive index of the solvent/non-solvent should be different from that of the polymer under investigation.

By choosing a solvent and precipitant of nearly the same refractive index, first there is little or no change of index of the solution as precipitation proceeds and the need to apply corrections is eliminated. Secondly, the refractive index of the particles in the polymer-rich phase is proportional to the volume fraction of the polymer. As a result, the refractive index of the particles is independent of the molecular weight of the polymer, independent of the concentration of the polymer. This makes the weight of polymer precipitated directly calculatable. By proper application of light scattering theory, this condition may not be of importance as will be noted in recurring sections in the present study. Marked heat of mixing, in cases of rapid stirring, may lead to spurious results and this is another point to keep in mind in choosing solvent/non-solvent systems. Still another very important precaution is the choice of solvent/non-solvent which will result in good separations on the basis of molecular weight. Systems exist which produce precipitates with practically no dependence of the precipitation point upon polymer molecular weight.(51)

Polyacrylamide is insoluble in most organic solvents. The only two known organic solvents in which polyacrylamide is soluble are morpholine and formamide. Non-solvents found for the polymer include glycols, ether, tetra-hydrofuran (THF) esters, Dimethyl-formamide (DMF), nitrobenzene, hydrocarbons, alcohols and acetone, etc. Besides water and methanol which have identical refractive indices, formamide and acetone are another good choice. In cases where the TT method is TGP, the choice of solvent is also important in order to avoid the effect of thermal degradation of the solvent on the measured turbidity.

It has also been customary to assume that the turbidity of the solution containing suspended polymer aggregates after correction for dilution by the precipitant is directly proportional to the mass of polymer in the precipitate. Since the scattering power of an aggregate is a function of the refractive index difference between it and the surrounding medium, this assumption is plausible only if the solvent and precipitant have refractive indices which are almost identical or aggregation to large particles is to be encouraged. Solvent and non-solvent for polyacrylamide have been summarized in Table 2.

Table 2

Solvents and Non-solvents

Solvents	Non-solvents
Water	Alcohols
Morpholine	Glycols
Formamide	Acetone
Dioxane	Ether
	Tetra hydrofuran (THF)
	Esters
	Dimethylformamide (DMF)
	Nitrobenzene
	Hydrocarbons

Apart from choosing an isorefractive solvent/non-solvent pair, it is important that the selected pair be such as to give precipitates of reasonable mobility. Precipitates which settle out as coagulants make equilibrium more difficult to achieve and affect the turbidimetric measurements. It is important too that the amount of non-solvent needed to cover the whole range of polymer molecular weights be large, as this considerably reduces original polymer concentration, thereby increasing separation efficiency and eliminating the possibility of multiple scattering during time of turbidimetric measurements.

CHAPTER 3

PHASE SEPARATION

3.1 Theory and Method of Separation

The generally accepted concept of molecular weight analysis by turbidimetric titration is the separation of polymer species according to their chain length.(52) In the proper sense, it is the separation into two liquid phases, the one rich in polymer being referred to as the precipitate. At the beginning, as the non-solvent is added, the high molecular weight species become insoluble in solvent and separate out to form the polymer-rich phase, causing a small amount of turbidity. As the addition of non-solvent continues, new phases are formed. These new phases represent increasing amounts of polymer in decreasing order of molecular sizes. As addition continues, a point is finally reached at which the lowest molecular weight species become insoluble in solution. At this point, the turbidity is greatest and ideally all of the polymer is precipitated. An ideally sharp separation is one in which all polymer below a certain molecular weight is in the polymer rich phase and all the rest in the polymer-poor phase. Phase relationships show just how far an actual separation by two phase equilibrium is from the ideal one.

The relationship between the concentration of the polymer of size S in two phases is given by the well known basic equation of fractionation theory

$$\phi_i'/\phi_i = \exp\{A_p S_i\} \qquad 3.1.1$$

where A_p on the basis of simple energetics represents the gain in energy when polymer is transferred from the polymer-rich phase to the polymer-poor phase and is given by

$$A_p = 2\psi(\phi_o - \phi_o') - \ln(\phi_o/\phi_o') \qquad 3.1.2$$

with the prime representing the polymer phase, ϕ_o and ϕ_i representing the volume fractions of solvent mixture and polymer of size S_i, and ψ representing the polymer-solvent interaction parameter given by

$$\psi = \chi_{13} + \psi_2(\chi_{23} - \chi_{13} - \chi_{12}) + \chi_{12}\psi_2^2 \qquad 3.1.3$$

where

$$\psi_2 = \phi_2/(\phi_1 + \phi_2) \qquad 3.1.4$$

$$\chi_{12} = V_o \frac{(\delta_1 - \delta_2)^2}{RT} \qquad 3.1.5$$

$$\chi_{i3} = 0.34 + V_o \frac{(\delta_i - \delta_3)^2}{RT} \qquad 3.1.6$$

$$i = 1,2$$

$$V_o = V_1V_2/(\psi_1V_2 + \psi_2V_1) \qquad 3.1.7$$

with the subscripts 1,2 and 3 representing the solvent, non-solvent and polymer respectively, V the molar volume and δ the solubility parameter. The above equations are based on the single-liquid model proposed by Scott.(53) As shown by Eq. (3.1.1), every species of the polymer is more soluble in the polymer rich phase and the ratio (ϕ_i'/ϕ_i) increases exponentially with S_i. In order to have an efficient separation, the dilute phase must be made large relative to the polymer-rich phase.

Two methods of separation employed in TT have been mentioned and again these include isothermal precipitation and thermal gradient methods. In the latter case, where mostly single solvents are employed, the phase relationships are relatively simple. When mixed solvents are the case, as is usually employed in isothermal precipitation procedure, a triangular phase diagram is needed to describe the behaviour of the system. The most widely used technique in TT is isothermal precipitation. The rate of addition of non-solvent is an extremely important variable for obtaining good phase separation, especially when the polymer concerned is of high molecular weight.

To achieve equilibrium at every point of titration implies good phase separation. If addition of non-solvent is very fast, the condition under which phase separation takes place will be too far from equilibrium, so that the entire method of separation is erroneous.

3.2 Aggregation and Swelling

Aggregation has never been encouraged in TT methods until recently.(39) When non-solvent is added to a polymer solution, the precipitated polymer in most cases aggregates in a non-random manner as usually indicated by the non-reproducible and changing turbidities with time. In the past, sometimes adequate stirring was employed to keep the polymer particles suspended and aggregation has always been observed in normal fractionation procedures. Generally, it has always been necessary to establish that aggregation of particles has been negligible during time of measurement, (54) and time of use of fresh solutions and this has been difficult to achieve.(48)(38) Therefore, it is not surprising that turbidity has often been regarded as a method of doubtful accuracy.

The "absolute" method which is the more recent method, encourages aggregation of polymer particles to a particular particle size. This condition can only be attained by growth of particles or adjustment of wavelength or both, which may not be experimentally possible with some polymers. It is important at this point to introduce and define a particle size parameter ρ. It is given by

$$\rho = \frac{4\pi r}{\lambda_m}(m - 1)$$

where λ_m is the wavelength of light in suspending medium

r is the radius of the polymer particle

m is the relative refractive index defined by

$$m = \frac{\mu'}{\mu_o}$$

with μ' and μ_o representing the refractive indices of the polymer particles in the polymer-rich phase and suspending medium respectively. The growth of particles to $\rho \approx 3$ is a kind of aggregation limited to a class of polymers. In principle, as precipitant is mixed with the dilute polymer solution, at a point slightly past the equilibrium precipitation point, growth of particles begins, by nucleation. The nuclei are particles of new phase which contain one or more polymer molecules. Sometimes the particles may collide with each other resulting in coalescence. With the continued growth of particles, the turbidity increases in almost the same fashion, until a maximum is obtained.

One should expect then that for monodisperse polymer, the maximum turbidity is instantaneous with very little or no aggregation. For narrowly distributed molecular size, once the maximum turbidity is attained by aggregation to this particular particle size , the maximum which is almost constant will extend over a short period of time, while for the broad polymer over a longer period of time. Broad polyacrylamide polymers which have been used for the present investigations show that the maximum turbidities obtained as a result of particle growth is constant over a period of more than 3 days. Solutions which have been re-examined for turbidity measurements after a lapse of 3 days to 2 weeks have demonstrated that the aggregates obtained are indeed very stable for all the points of titration. This was sufficient evidence that, the best criterion of equilibrium in phase separation, which is that the volume of the precipitated phase be allowed to reach a constant value, was established.

While for polymers with monodisperse molecular size or narrow size distributions, encouragement of aggregation to a particular particle size ($\rho \approx 3$) may be possible when applicable. This may not seem the case with broad polymers. Present investigations seem to indicate that different broad polymers of one kind, aggregate to different constant value at the point of maximum turbidity. In general, the particles grow in size until the condition, $\rho >> 3$ is attained. In this region, the turbidity is maximum and the scattering coefficient is constant. Polymers of the same kind investigated under neutral conditions showed aggregation of the same kind while polymers investigated in the presence of an electrolyte showed aggregation of different kinds. The most important observation is that the aggregates seem to be in exact multiples and particularly independent of concentration and molecular weight distribution. The inclusion of acid or presence of an electrolyte may be significant in understanding the phenomenon of aggregation in such systems, as it aids it.

Effect of swelling can profoundly alter the assumed direct relation between turbidity and amount of polymer precipitated. Swelling may be influenced by variations in the solvent/precipitant composition. It must be remembered that the particulate phase is a swollen polymer and during the course of titration, there will be a change in degree of swelling as the non-solvent/solvent ratio is changed. The relative refractive index is determined by the degree of swelling and increases with increase in solvent/non-solvent ratio. But when optimum condition is imposed by prolonged stirring, during the course of which the turbidity increases, until a maximum is reached, the particles grow to a constant value. Then the maximum turbidities obtained at the same constant ρ's are independent of the relative refractive index of the swollen polymer particles, which are of stable sizes.

3.3 Criteria for Effective Separation

Criteria for effective separation have been discussed extensively in different sections of the present thesis. For convenience and clearer understanding, they are being summarized in this section.

(1) The condition that the solution be dilute is very important, in order to apply any of the light scattering theories, and obtain physically a true efficient separation. While a concentration could be said to be dilute for one kind of polymer, it could be at the other extreme for another kind of polymer. The choice of a concentration range could rely on the sensitivity of the spectrophotometric instrument whose design for this purpose is based upon the fact that absorbance of an absorbing material is dependent upon its concentration.

While Schulz(55) and other workers who agreed with him,(56)(57) believed that a significantly better separation may be obtained by the use of quite low (less than 1 per cent) starting concentrations, the work of Morey and Tamblyn(51) and others thereafter have concluded that the effect of initial concentration on the efficiency of fractionation by precipitation is minor. The use of very dilute solutions brings no advantages but some added difficulties in time and labour. The present study is in agreement with the work of Morey and Tamblyn. Concentration range covered was quite broad. While for one broad polymer, it was not possible to work at lower concentrations than 0.1 wt %, for another kind of polyacrylamide polymer of almost the same polydispersity, it was not possible to work at concentrations higher than 0.1 wt %.

(2) The choice of solvent/non-solvent is also important in order to obtain an efficient separation. The solvent and precipitant may have identical refractive indices from theoretical considerations, and these should be very different from the refractive index of the polymer. When

the proper choice of solvent/non-solvent has been made, the method of addition of non-solvent should be properly controlled initially, because in this region, the highest molecular weight part of the distribution is almost insoluble in the solvent and very sensitive to the presence of non-solvent. In this region non-equilibrium precipitation can occur, also due to high local concentration of non-solvent, if adequate stirring is absent.

(3) It seems as if the reason why turbidimetric titration has not gained any popularity in the past is because optimum experimental conditions have never been attained in any of the previous experimental work prior to the work of Beattie and co-workers, especially when the polymer MWD is very broad.

(4) The purity of solvent and non-solvent is quite important if an efficient separation according to molecular sizes is to be obtained. Previous workers(39) have shown that the purification and drying of both the solvent and the precipitant have a large effect upon the fraction of material precipitated. Present analysis has lent support in this direction, as will be indicated later.

(5) In order to have an efficient separation, the dilute phase must be made large relative to the polymer-rich phase.

CHAPTER 4

LIGHT SCATTERING THEORY

4.1 Choice of Theory

In general, there are three relevant theories applicable to the light scattering of polydisperse systems.(35) These theories are

(a) Rayleigh Scattering Theory(35)

(b) Rayleigh-Gans Scattering Theory(35)(58)

(c) Mie Theory(58)

Any of the following theories can be applied to the analysis of turbidimetric data depending on the nature of the system under investigation. The nature of the system usually is characterized by two relevant parameters -

(i) the size parameter α_s defined by

$$\alpha_s = \frac{2\pi r}{\lambda_m} \qquad 4.1.1$$

where r is the radius of the particle and λ_m is the wavelength of light in the suspending medium.

(ii) the relative refractive index defined by

$$m = \mu' / \mu_o \qquad 4.1.2$$

where μ' is the refractive index of particle in the precipitating polymer-rich phase and μ_o is the refractive index of the medium suspending the polymer particles. The magnitude of α_s and m clearly defines the region of applicability of the theories (a) and (b), which were the theories first developed. While the first theory is applicable to cases where $\alpha_s \leq 0.4$ (i.e., for particles which can be considered small compared to the wavelength),(35) the second theory is limited by the following conditions - $m \bar{<} 1.05$ and $\alpha_s \leq 10$. However, these restrictions are not affected by the application of Mie theory which makes it more general for any system of varying order of size parameter and any value of m. Nevertheless for the Mie theory to be applicable, two conditions have to be satisfied and these are

(1) no secondary scattering and (2) no mutual interactions between particles. As a general rule, the theories are only applicable to the particular case of isotropic non-absorbing spheres in discussions of turbidity and scattering theory. Thus in view of the fact that the Mie theory is one of the most recent and most general and since the validity of the theory for systems containing polydisperse particles has been ascertained,(37) the choice of the Mie theory will form the basis of our present analysis of large particles of the order of 5 microns.in which the refractive index of the particle differs significantly from that of the suspending medium.

4.2 Theory of Turbidity for Spherical Particles

In the analysis, the following assumptions have been made: (a) The precipitated particles are spherical. Evidence to support this assumption has been shown in the work of Ishige and Hamielec.(59) In short, the procedure involves adding a non-solvent, n-propanol, to a dilute aqueous solution of polyacrylamide (40 wppm) to give a theta solvent (20% water and 80% n-propanol). The solution was then sprayed onto a copper substrate, shadowed with gold-palladium, and protected with carbon. Electron micrographs show individual polyacrylamide molecules as discrete spheres. (b) The solvent and precipitant have almost identical refractive indices which differ from the refractive index of the polymer. (c) The refractive index of the precipitated particles is independent of the molecular weight of the polymer. (d) the refractive index of the precipitated particles is independent of the concentration of the polymer in the range of concentrations used. (e) Application of Mie theory is valid under the conditions used subject to slight modifications representative of the system under investigation.

In the process of turbidimetric titration, a non-solvent is added to a polymer solution until a phase separation occurs, as shown by the turbid medium. From the onset of turbidity, the system consists of small particles of polymer rich phase suspended in a medium of polymer poor phase. The particles tend to assume the shape of lowest surface energy, the spherical shape, since they are fluids. The turbidity, τ, of a solution or dispersion is given by

$$\tau = \frac{2.303}{\ell} \log\left(\frac{I_o}{I}\right) \qquad 4.2.1$$

where I_o and I are the intensities of the incident and transmitted light respectively, and ℓ is the path length of the transmission cell. Equation 4.2.1 is obtained by integration of an expression equivalent to Lambert's law, i.e.,

$$-\frac{dI}{d\ell} = \tau I \qquad 4.2.2$$

τ is related to apparent absorbance A due to scattering by

$$\tau = 2.303 \frac{A}{\ell} \qquad 4.2.3$$

where

$$A = \log(I_o/I) \qquad 4.2.4$$

Turbidity and particle size are related by the Mie equations.(58) For a monodisperse suspension of spherical particles of radius r at infinite dilution, the turbidity τ is given by

$$\tau = n\pi r^2 K \qquad 4.2.5$$

in which

n = number of particles per milliliter

K = scattering coefficient, the ratio of the scattering cross section of the particle to its geometric cross section

K is a function of m, and α_s; it can be calculated for any size (α_s) and refractive index ratio (m). For the Mie theory requirements to be met, the concentrations used in turbidimetric titrations should be sufficiently dilute, otherwise the need to extrapolate to infinite dilution is highly necessary to apply Eq. 4.2.5 any further.

For a polydisperse system, like the present one, Eq. 4.2.5 is given by

$$\tau = \sum n_i \pi r_i^2 K_i \qquad 4.2.6$$

and the concentration of the precipitated phase in grams per milliliter of solution is given by

$$c_p = \sum n_i \left(\frac{4}{3}\right)\pi r_i^3 \rho_p' \qquad 4.2.7$$

where ρ_p' is the density of particles of the polymer-rich phase. Dividing Eq. 4.2.6 by Eq. 4.2.7, we obtain what is usually called the specific turbidity given by

$$\frac{\tau}{c_p} = \left(\frac{3}{4\rho_p'}\right) \frac{\sum n_i r_i^2 K_i(\alpha_s,m)}{\sum n_i r_i^3} \qquad 4.2.8$$

in units of cm^2 per gram.

For practical purposes, sums are replaced usually by integrals. The particle size distribution is defined by

$$dn = f(r)dr \qquad 4.2.9$$

where dn is the number of particles per milliliter of radius between r and r + dr. Then Eq. 4.2.8 in integral form is given by

$$\frac{\tau}{c_p} = \frac{3}{4\rho_p'} \frac{\int_0^\infty f(r) r^2 K(\alpha_s,m) dr}{\int_0^\infty f(r) r^3 dr} \qquad 4.2.10$$

noting that c_p in the integral form is defined by

$$c_p = N_p \frac{4\pi\rho_p'}{3} \int_0^\infty f(r) r^3 dr \qquad 4.2.11$$

where N_p = total number of particles.

Therefore the specific turbidity can be calculated for any wavelength, and for any distribution $f(r)$, given the values of K. With the nature of the system used, it is more in line to replace α_s by a normalized size parameter ρ,(58) given by

$$\begin{aligned} \rho &= 2\alpha_s(m - 1) \\ &= \frac{4\pi\mu_o r(m - 1)}{\lambda} \end{aligned} \qquad 4.2.12$$

Then introduction of ρ for r from Eq. 4.2.12 into Eq. 4.2.10 or 4.2.8 yields

$$\begin{aligned} \frac{\tau}{c_p} &= \frac{\frac{\pi}{4} N_p \int_o^\infty K(m,\rho) D^2 f(D)\, dD}{\rho_p \frac{\pi}{6} N_p \int_o^\infty D^3 f(D)\, dD} \\ &= \frac{3}{2\rho_p} \frac{(m - 1) 2\pi\mu_o}{\lambda} \frac{\int_o^\infty K(m,\rho) f(\rho) . \rho^2 d\rho}{\int_o^\infty \rho^3 f(\rho)\, d\rho} \\ &= \frac{3}{\rho_p} \frac{\pi(m - 1)\mu_o}{\lambda} \frac{\int_o^\infty K(m,\rho) f(\rho) . \rho^2 d\rho}{\int_o^\infty \rho^3 f(\rho)\, d\rho} \\ &= \frac{3}{\rho_p} \frac{\pi(m - 1)\mu_o}{\lambda} \frac{\int_o^\infty \frac{K}{\rho}(m,\rho) \rho^3 f(\rho)\, d\rho}{\int_o^\infty \rho^3 f(\rho)\, d\rho} \end{aligned}$$

$$\frac{\tau}{c_p} = \frac{3}{\rho_p \lambda} \pi\mu_o(m - 1) \left(\frac{K}{\rho}\right)_w \qquad 4.2.13$$

where

$$(\frac{K}{\rho})_w = \sum(\frac{K}{\rho})_i w_i = \int_0^{\infty}(K/\rho)d_w = \frac{\int_0^{\infty}K(\rho,m)\rho^2 f(\rho)d\rho}{\int_0^{\infty}\rho^3 f(\rho)d\rho} \qquad 4.2.14$$

and

w_i = weight fraction of species i

$(\frac{K}{\rho})_w$ is the average weight of $\frac{K}{\rho}$. The value of K/ρ is influenced by m and ρ. In general, as ρ increases, K/ρ increases from zero at $\rho = 0$ to a maximum, then oscillates between a series of successive maxima and minima.(35) The first maximum is the largest. The first maximum occurs at $\rho \approx 3$, then oscillates slowly about a decreasing value. The higher the relative refractive index, the higher the value of $(\frac{K}{\rho})_{max}$. For a polydisperse suspension as in the present system, the behaviour of $(\frac{K}{\rho})_w$ relative to ρ is similar to that for a monodisperse suspension, except that the maximum $\overline{(K/\rho)}_w$ occurs at a ρ-range far broader than the range for norrowly distributed polymers and the first maximum $(\frac{K}{\rho})$ is far less. This behaviour is clearly shown in Figures 1 - 9 for a log-normal particle size distribution for polymers.

4.3 The Basic Equation and Corrected Turbidities

In Eq. 4.2.13, the c_p which represents the concentration of the precipitated phase is not the concentration, c, of the polymer which is precipitated (in grams per unit volume, i.e., milliliter of original solutions). For analytical purposes, we have the reverse problem, to determine c from experimental transmission measurements. It is important to note that for a particular system, the turbidity τ depends on m, which also depends upon the fraction of polymer in the polymer-rich phase, which is not generally known. Thus Eq. 4.2.13 is not suitable to use in its present form.

Therefore, in order to reduce the complexity of having the polymer particles suspended in multiple media rather than a single medium, a precipitant is usually chosen which has the same refractive index as the solvent. This way μ_o, the refractive index of the supporting medium is either the refractive index of the solvent and precipitant (or the average of the two refractive indices if they are very close). Also, in this way, the refractive index of the precipitated droplet depends only upon the concentration of the polymer in the droplet. Hence, the necessity of assumption (b) above in section 4.2 (strictly speaking, this assumption is not a stringent one as will be noted in subsequent sessions to follow, from a complete understanding and application of light scattering theory). Furthermore, the relative refractive index of this droplet m, may be related to the volume fraction of polymer in that phase by a mixing rule such as that of Gladstone and Dale empirical mixing rule which has been proved to be accurate with a wide range of compounds(60) and is assumed to be valid for the polymer-rich phase. Mathematically, it is expressed as follows:

$$\mu' - 1 = (\mu - 1)\phi + (\mu_o - 1)(1 - \phi) \qquad 4.3.1$$

where

ϕ = volume fraction of polymer in polymer-rich phase

μ' = refractive index of polymer-rich phase

μ = refractive index of polymer

μ_o = refractive index of supporting medium as previously defined

= average of refractive indices of solvent and non-solvent

Equation 4.3.1 could be rearranged into a simpler form as

$$(m - 1)\mu_o = \Delta\mu\phi \qquad 4.3.2$$

where $\Delta\mu = \mu - \mu_o$

Substituting Eq. 4.3.2 into the now-so called fundamental equation, Eq. 4.2.13, we have

$$\frac{\tau}{c_p} = \frac{3\pi\Delta\mu\phi}{\lambda\rho_p} \left(\frac{\overline{K}}{\rho}\right)_w \qquad 4.3.3$$

From the theoretical considerations and discussions so far, it has been desirable

(i) to eliminate the difficult measurement of m as a function of per cent precipitant, which places the method on a less laborious basis from a practical point of view. It is interesting to note further from the works of Patat and Taxler(61) on the solution fractionation of poly (vinyl alcohol) and Beattie on solubility distribution of polymers,(39) that the composition of the precipitated phase at a given solvent/precipitant ratio is independent of the starting concentrations and the original molecular weight of the polymer. Also added to this is that at solvent/precipitant ratio exceeding 50%, m seems to be independent of solvent/precipitant ratio.

(ii) to eliminate c_p in the fundamental Eq. 4.2.13 for c, the concentration of the precipitated polymer in grams, per milliliter of original solution. Already the steps from Eq. 4.2.13 to Eq. 4.3.3 has eliminated the presence of m except for the inclusion of $(\frac{\overline{K}}{\rho})_w$ which for a particular polymer-solvent-non-solvent system is dependent on m and ρ. On an empirical basis, $(\frac{\overline{K}}{\rho})_w$ can be obtained less rigorously instead of via the exact Mie theory which involves the prior knowledge of m, and more rigorous computation. To eliminate c_p, it is easy to note that

$$\frac{c}{\rho_p} = \frac{c_p}{\rho_p} \qquad 4.3.4$$

where

ρ_p = density of pure polymer

Substituting Eq. 4.3.4 into Eq. 4.3.3, we have

$$\frac{\tau}{c} = \frac{3\pi\Delta\mu}{\rho_p\lambda} (\frac{\overline{K}}{\rho})_w \qquad 4.3.5a$$

or

$$c = \rho_p\lambda\tau[3\pi(\overline{K}/\rho)_w\Delta\mu] \qquad 4.3.5b$$

Equation 4.3.5a is the basic equation for the method. All factors on the right-hand side of the equation, except $(\frac{\overline{K}}{\rho})_w$ are directly measurable. τ on the left-hand side is also measurable. If $(\overline{K}/\rho)_w$ can be obtained, then c can be related to the turbidity on an absolute basis. However, the evaluation of $(\overline{K}/\rho)_w$ for monodisperse particles, narrow particle size distributions and broad distributions has been shown in a more recent work of Beattie(39) and there seems to be some doubt in the principle for polydisperse systems (broad distribution). This is usually possible only if the particle size distribution is known. On an empirical basis, the particle size distribution need not be known beforehand and the difficult prior evaluation of $(\frac{K}{\rho})_w$ is not necessary to completely express a relationship between turbidity and concentration c. Equation 4.3.5a can be further rearranged as follows:

$$\frac{\tau\lambda}{\Delta\mu} = \frac{3\pi}{\rho_p}(\frac{K}{\rho})_w c$$

$$= k_\lambda c \qquad 4.3.6$$

where

$$k_\lambda = \frac{3\pi}{\rho_p}(\frac{K}{\rho})_w = \text{constant} \qquad 4.3.7$$

The subscript λ on k implies that the constant at maximum turbidity is only a function of wavelength. This proportionality constant k_λ can only be obtained from the system at 100% precipitation. This places turbidimetric analysis in particular for water soluble-polymers (with polyacrylamide where it is possible to obtain 100% precipitation) on a very simple empirical basis. Once the constant is obtained, $(\frac{K}{\rho})_w$ on the right-hand side of Eq. 4.3.7 can be easily obtained without having to go through the complicated method imposed on an absolute basis. The knowledge of $(\frac{K}{\rho})_w$ on an empirical basis, is only to test the experimental technique and assumptions involved, otherwise once the plot of maximum $\tau\lambda/\Delta\mu$ versus concentration c at 100% precipitation has been obtained, the concentration c of polymer precipitated for any % non-solvent can be easily obtained from the basic equation.

Nevertheless, it should be borne in mind that, the evaluation of $(K/\rho)_w$ from K_λ in Eq. 4.3.6 or 4.3.7 is only valid if

(1) in the region of maximum turbidity, the $(K/\rho)_w$ is dependent on particle size distribution and independent of the relative refractive index.

(2) the specific turbidity in the region of maximum turbidity is independent of starting concentration c of polymer.

If condition (1) is satisfied, then the requirements imposed by making the assumptions (c) and (d) above are met. With the present method, after addition of non-solvent, the solution is allowed to reach maximum turbidity by growth of particles. As shown in Tables 11, 12, 13, the maximum turbidities obtained as a result of particle growth is constant over a period of more than 3 days. In fact, solutions which have been re-examined for turbidity measurements after a lapse of 3 days to 2 weeks have demonstrated that the aggregates obtained are indeed very stable for all the different points of titration. Implied in this is that the precipitated phase has reached a constant size, and the scattering coefficient has also reached a constant value, which according to Figures 1 and 2 is a value of ≈ 2 at large ρ or α_s values. In this region, $\rho >> 3$, the maximum turbidities obtained can then be said to be independent of the relative refractive index. When this condition is attained, condition (2) is equally satisfied. If this is not the case, then Eq. 4.3.5a is rearranged as follows

$$(\frac{\tau}{c})_o = \frac{3\pi\Delta\mu}{\rho_p\lambda} (\frac{K}{\rho})_w \qquad 4.3.8$$

The zero subscript on (τ/c) implies that this ratio has to be extrapolated to $c = 0$ in the plot of τ/c versus c, and the Mie theory requirements of no mutual interactions among the particles and no secondary scattering are met.

Substituting Eq. 4.2.14 into Eq. 4.3.6, we have

$$\frac{\tau}{c} = \frac{3\pi\Delta\mu}{\lambda\rho_p} \frac{\int_0^\infty K(\rho,m)\rho^2 f(\rho)d\rho}{\int_0^\infty \rho^3 f(\rho)d\rho} \qquad 4.3.9$$

Since K is independent of ρ at the point of maximum turbidity and also of m, then Eq. 4.3.9 becomes

$$\text{Max}\ \frac{\tau}{c} = \frac{3\pi\Delta\mu K}{\lambda\rho_p} \frac{\int_0^\infty \rho^2 f(\rho)d\rho}{\int_0^\infty \rho^3 f(\rho)d\rho}$$

$$= \frac{3\pi\Delta\mu K}{\lambda\rho_p} \frac{\int_0^\infty \frac{4\pi^2\mu_o^2(m-1)^2D^2f(D)dD}{\lambda^2}}{\int_0^\infty \frac{8\pi^3\mu_o^3(m-1)^3D^3f(D)dD}{\lambda^3}}$$

$$= \frac{3\pi\Delta\mu K}{\lambda\rho_p} \frac{\lambda}{2\pi\mu_o(m-1)} \frac{\int_0^\infty D^2f(D)dD}{\int_0^\infty D^3f(D)dD}$$

$$= \frac{3\Delta\mu K}{2\mu_o(m-1)\rho_p} \frac{\int_0^\infty D^2f(D)dD}{\int_0^\infty D^3f(D)dD} \qquad 4.3.10$$

By definition, area average diameter $\bar{D}_A$ is given by

$$\bar{D}_A = \frac{\int_0^\infty D.D^2 f(D)dD}{\int_0^\infty D^2 f(D)dD} \qquad 4.3.11$$

Introduction of Eq. 4.3.11 into 4.3.10 yields

$$\text{Max } \frac{\tau}{c} = \frac{3}{2} \frac{\Delta\mu K}{\mu_o(m - 1)\bar{D}_A \rho_p} \qquad 4.3.12$$

Equation 4.3.12 is a very simplied form which if m is known, $\bar{D}_A$ can be obtained.

Corrected Turbidities

The concentration calculated from the basic equation using the measured turbidities refer to the final volume (solution plus precipitant). In order to calculate the concentration of original solution before precipitant was added, the turbidity τ must first be corrected by multiplying it by

$$\frac{v + V_o}{V_o} \qquad 4.3.13$$

where

v = volume of precipitant added

V_o = volume of solution

4.4 The Scattering Coefficient K and the Ratio $(\overline{K/\rho})_w$

It is very important at this juncture to discuss in detail the scattering coefficient and the ratio $(\overline{K/\rho})_w$ in the basic Eq. 4.3.5a, because with more attention and better understanding of light scattering functions, determination of latex particle sizes,(37) solubility distributions of polymer(39) are becoming possibilities. The scattering coefficient, K, reflects the oscillatory character of the scattering cross section of a sphere; in other words, it exhibits a series of successive maxima and minima. ρ, a particle size parameter has been defined as

$$\begin{aligned} \rho &= 2\alpha_s(m - 1) \\ &= \frac{4\pi\mu_o\gamma_s(m - 1)}{\lambda} \end{aligned} \qquad 4.2.12$$

where α_s is also a size parameter.

The strong effect of m upon K at small and intermediate α values has been shown.(35) The numerical value of K at the first maximum is larger and the maximum occurs at a lower α value the larger m. These differences become increasingly smaller for the higher maxima until, at a sufficiently large α, m has practically no longer any effect upon K. Scattering is then no longer dependent on m, in agreement with the theory of diffraction from objects very large compared to the wavelength used. This is particularly the case when K is plotted against ρ as shown in Figures 1 and 2. At very large values of ρ or α, K damps out to the value of 2.0, meaning that the scattering cross section is twice as large as the geometric cross section.

The value of K/ρ depends only on m and ρ. With increasing ρ, K/ρ increases from zero (at $\rho = 0$) to a maximum at $\rho \approx 3$, then oscillates about a series of slowly decreasing minima and maxima. The value of K/α_s depends also on m and α_s, and shows the same oscillatory nature as in a plot of K/ρ versus ρ. It is more of an advantage to use plots of K/ρ versus ρ instead of K/α_s versus α_s because in the region of the first maximum, the former curves show a small dependence upon m and in the region $\rho >> 3$, no dependence on m. It should be noted that specific turbidity and $(\overline{K/\rho})_w$ change in the same way with change in particle size or change in ρ. According to the basic equation, Eq. 4.3.5a, it is clear that all other factors besides turbidity τ and $(\overline{K/\rho})_w$ are independent of particle size. Thus, if the particle size can increase, say by stirring, while keeping concentration and other parameters constant, the turbidity must increase as the particles grow until a maximum value is reached, a point at which the particles can grow no more.

At the approximate ρ value ($\rho \approx 3$), a first turbidity maximum is attained. The direct significance of this maximum is that the radius exponent, z, defined by

$$\frac{d}{dr_s} \log\left(\frac{\tau}{c}\right)_0 = \frac{z}{r_s} \qquad 4.4.1$$

has reached the value of 0 at the particular wavelength considered. If r_s approaches zero, the limiting value of 3 is obtained.$^{(35)}$ Thus maximum turbidity is attainable when

$$r_s \frac{d}{dr_s} \log R(r_s) = 3.0 \qquad 4.4.2$$

and this compares with the limiting value

$$r_s \frac{d}{dr_s} \log R(r_s) = 6.0(r_s \longrightarrow 0) \qquad 4.4.3$$

where R is the scattering cross-section of the sphere or total radiations in the α range of Rayleigh scattering.

This first maximum turbidity has recently deserved some attention in TT.(39) It is particularly important because it defines the particle size at a given wavelength for which the specific scattering power of a material of a given relative refractive index reaches its absolute maximal value. In this region, the specific turbidity is comparatively insensitive to particle size and this disadvantage (if particle size distribution is the question) is in part, balanced by the advantage that it is increasingly insensitive to m.

Evaluation of $(\overline{K/\rho})_w$ for any kind of distribution (monodisperse, narrow, moderately broad and very broad) has always been possible only if the distribution is known, either from the exact Mie theory or by means of approximations.(39) For monodisperse particles, according to Beattie

$$\text{Average } (\overline{K/\rho})_w = \max K/\rho \qquad 4.4.4$$

For narrowly distributed particle size distribution,

$$\text{Average } (\overline{K/\rho})_w \approx \max K/\rho \qquad 4.4.5$$

For over a narrow range of ρ values, K/ρ is almost constant, which means that K/ρ varies only slowly with ρ. Evaluation of the average can be done only in the region of the maximum. Thus if it is possible to adjust particle size until $\rho = 3$, K/ρ for monodisperse particles and also $(\overline{K/\rho})_w$ for narrow distributions of particle size can be easily obtained. The calculation of $(\overline{K/\rho})_w$ for broad distributions is more difficult, because for this case, it depends also on the distribution width and the knowledge of the relative refractive index. An approximation by Beattie is given thus by:

$$(\frac{\overline{K}}{\rho})_{w_{broad}} = \frac{\max(K/\rho)_{m=m}}{\max(K/_\rho)_{m=1.0}} \times \max(\frac{\overline{K}}{\rho})_{w,m=1.0} \qquad 4.4.6$$

To use Eq. 4.4.6, the distribution width must be known. This could be obtained by curve fitting procedure.$^{(62)}$ It is important to note that as the distribution width is increased from monodisperse ($\beta = 0$) to broad ($\beta = 1.4$), the value of the maximum of $(\overline{K/\rho})_w$ is decreased and the curves are broadened. $\text{Max}(\overline{K/\rho})_{w,m=1.0}$ is the value of $\max(\overline{K/\rho})$ for $m = 1.0$ and the distribution width β. The ratio $\max(K/\rho)_{m=m}/\max(K/\rho)_{m=1.0}$ is obtained for monodisperse particles. When the particle size distribution is unknown, the methods above are not applicable.

In view of the very low values of $(\overline{K/\rho})_w$(shown in Table 66) obtained in the present studies, using broad polymers, and the optimum conditions imposed in the experimental technique, it was necessary to further investigate the light scattering functions, as Beattie's explanation could not explain the experimental observations. Also since, broad polymers were used in the present investigation, log-normal distribution was assumed for the particle size distribution as this is the broadest distribution at present known. In Figure 3, $(\overline{K/\rho})_w$ values are shown plotted against

ρ_o for log-normal weight distribution for different β's and m = 1.137. Also in Figure 4 are the same plot for $\beta = 1.0$ and two different almost extreme values of m. The calculations of $\overline{(K/\rho)}_w$ are shown in Appendix V. It is obvious from the plots that at $\rho_o >> 3$, the $\overline{(K/\rho)}_w$ values are independent of m and ρ_o where ρ_o in this case, is the weight geometric mean. The same plot is shown in Figure 5, but for different values of β. The broader the distribution, the lower the $\overline{(K/\rho)}_w$ value. At the point of maximum turbidity which is in the region $\rho >> 3$, the $\overline{(K/\rho)}_w$ values which is representative of the limit of particle growth for a particular polymer, are by far lower than the values used with Beattie's explanation. Nevertheless, an alternative explanation to the method of maximum turbidity for polymers in general is presented in Appendix II.

In Figures 6, 7 and 8 are plots of $\overline{(K/\rho)}_w$ versus β for different weight geometric mean ρ_o and at four values of m representative of the range to be anticipated in systems under the present studies. In Figure 8 is the same plot of m = 1.137 on a very large scale for $\rho_o > 30$. The region $\rho_o \approx 3$, the region of first maximum has been included in the above plots. It is important to note that, as ρ_o becomes larger, $\overline{(K/\rho)}_w$ becomes almost increasingly independent of the breadth of the distribution, until at very large ρ's, the independence is extended down to very broad distributions. $\overline{(K/\rho)}_w$ progressively decreases as the region of independence broadens for different increasing values of ρ_o. Implicit in this observation is that in principle as the non-solvent is added to the polymer solution, the precipitated swollen polymer is allowed to grow until a constant size is attained. If this optimum condition is imposed throughout the points

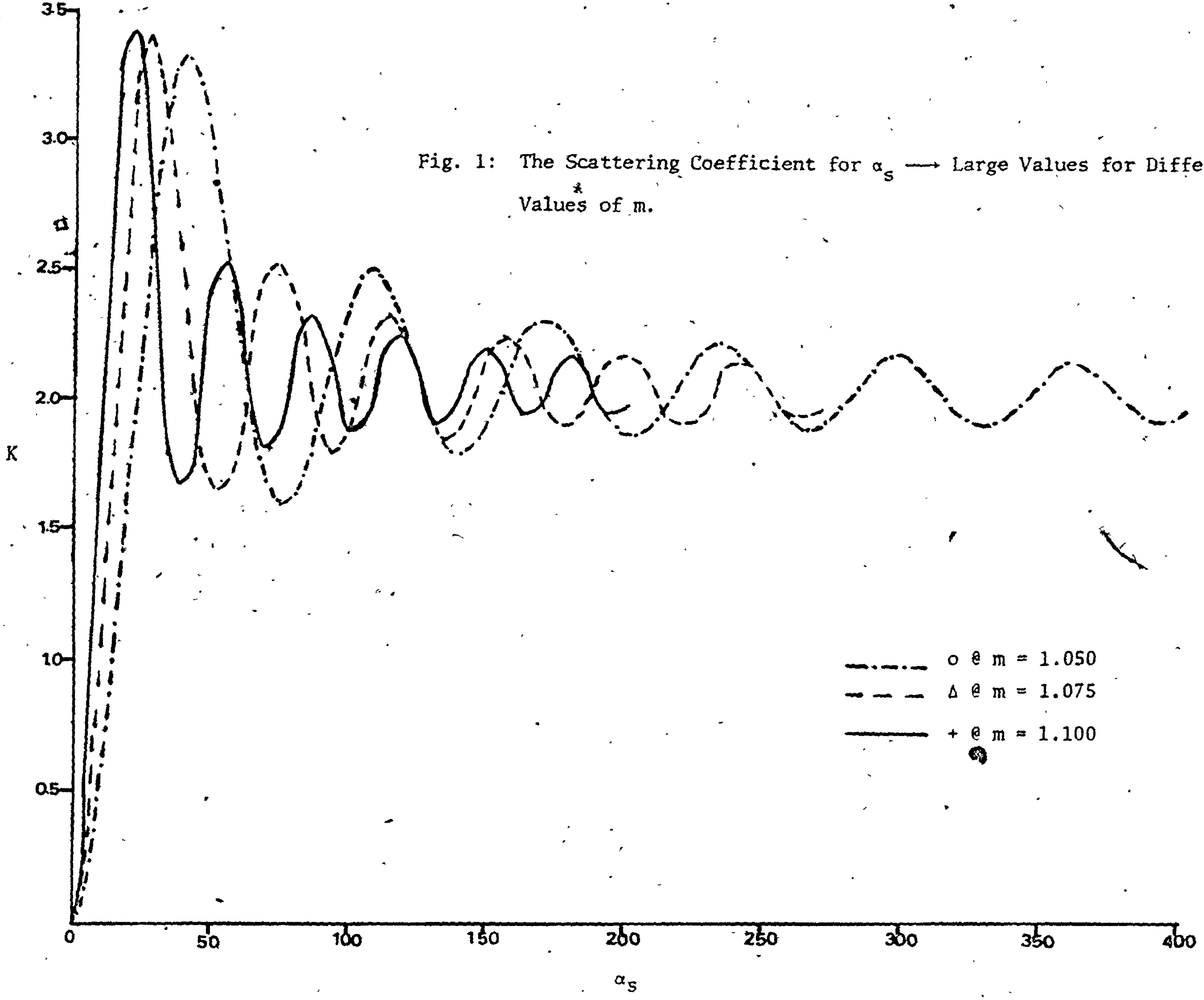


Fig. 1: The Scattering Coefficient for $\alpha_s \longrightarrow$ Large Values for Different Values of m.

Fig. 2: The Scattering Coefficient for ρ ⟶ large values for Different Values of m.

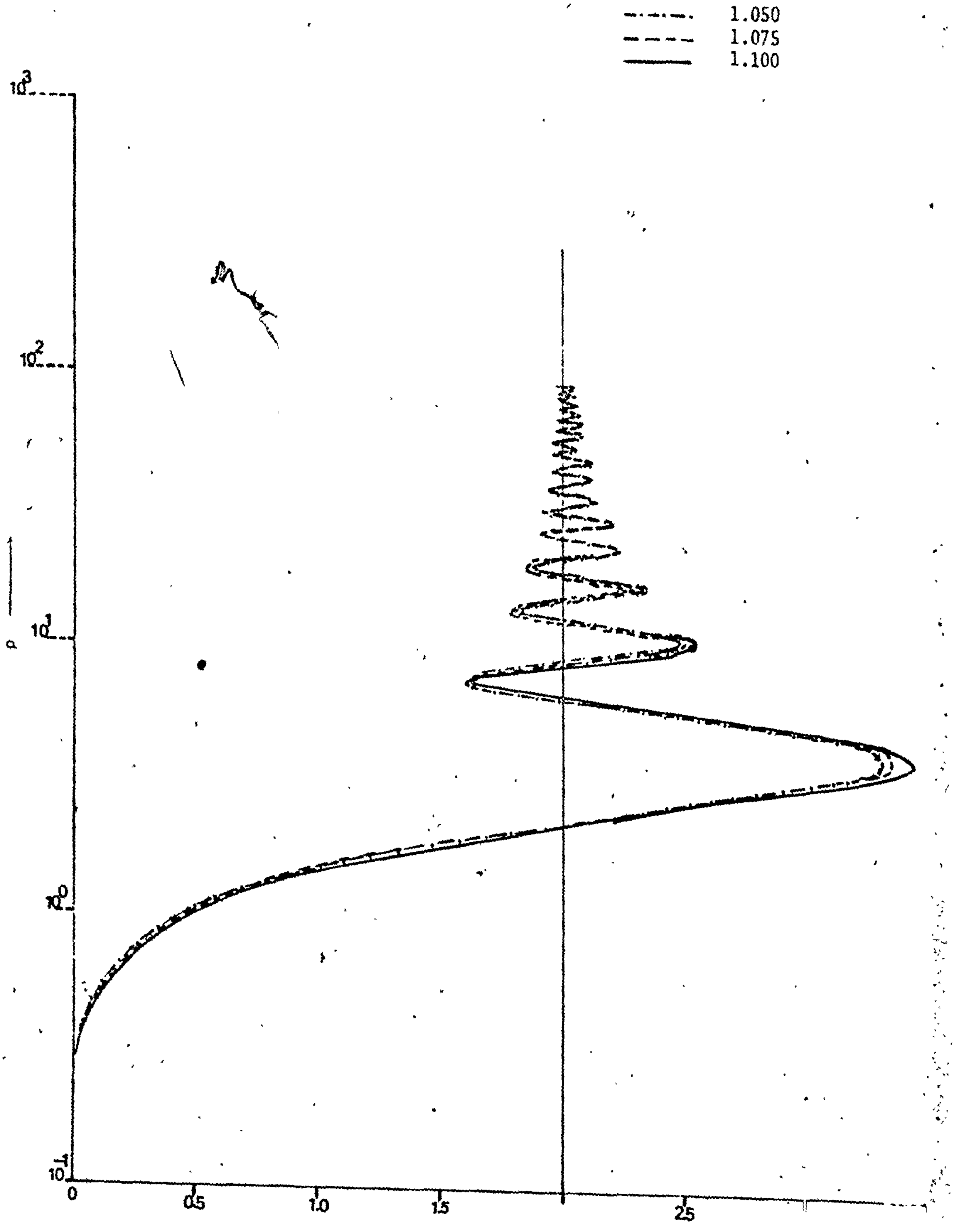


Fig. 3: $(\frac{K}{\rho})_W$ for Log-normal Weight Distributions. Width or Variance Parameters (β) are indicated for m = 1.137

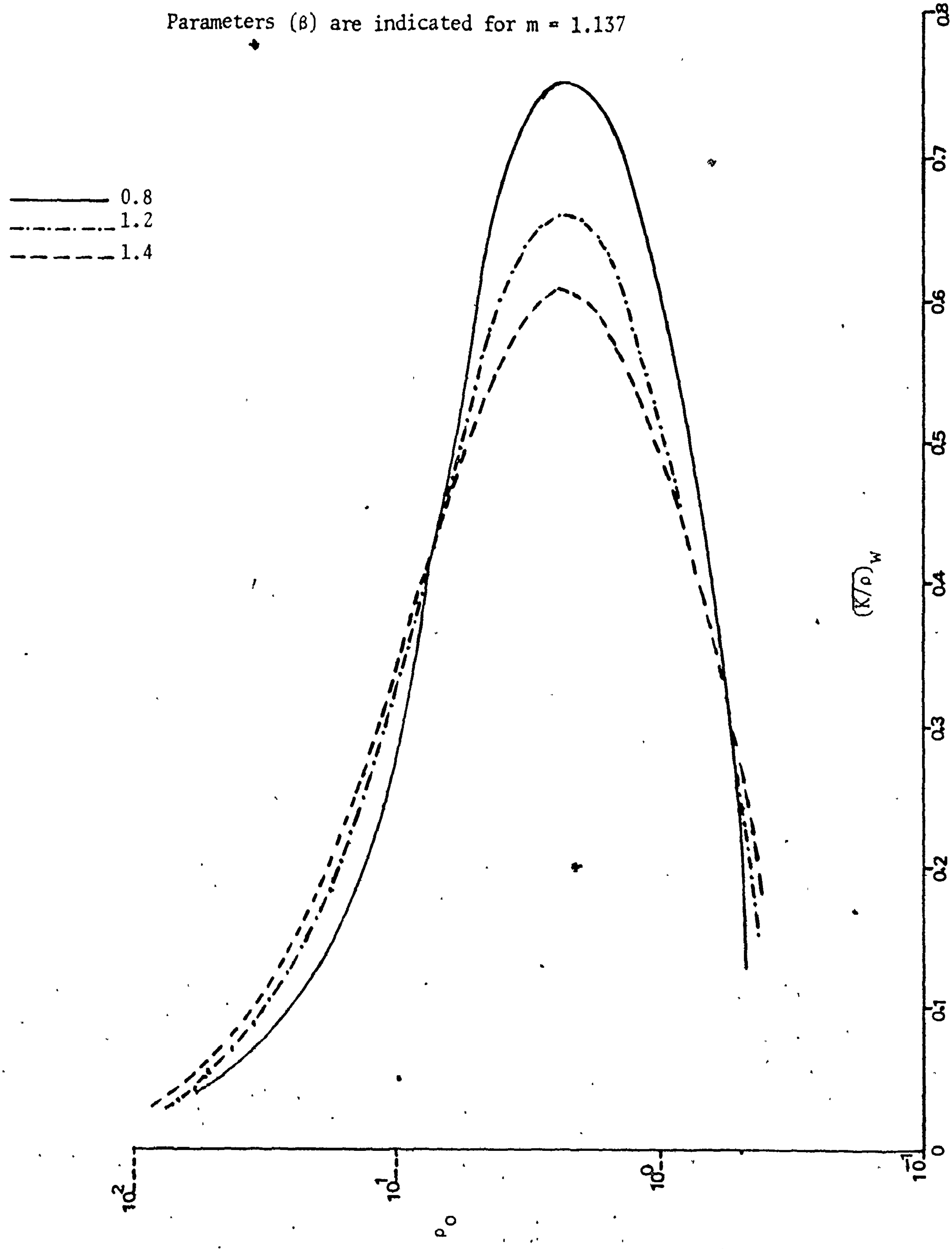


Fig. 4: $(\overline{K}/\rho)_w$ for Log-normal Weight Distribution for $\beta = 1.0$.

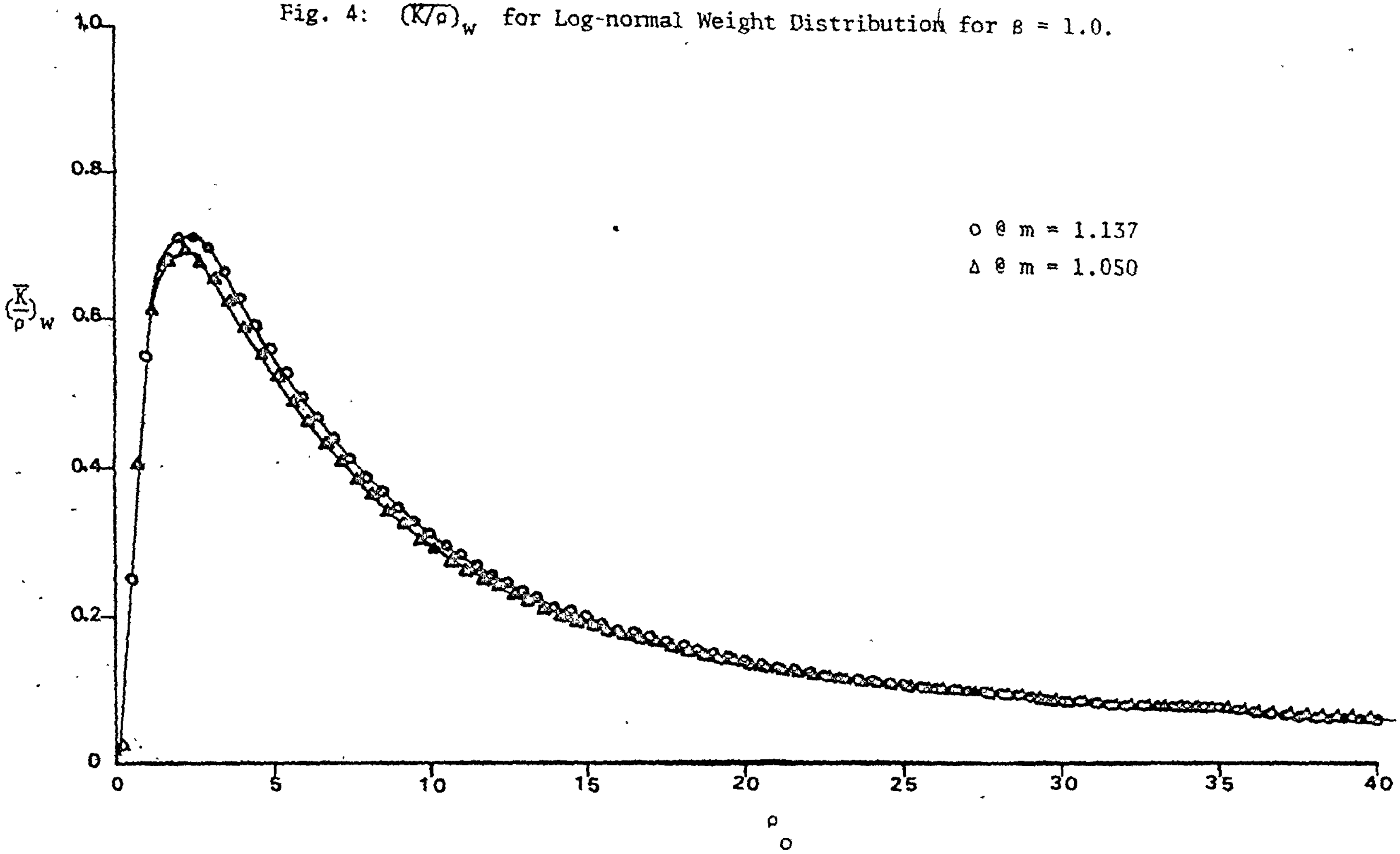
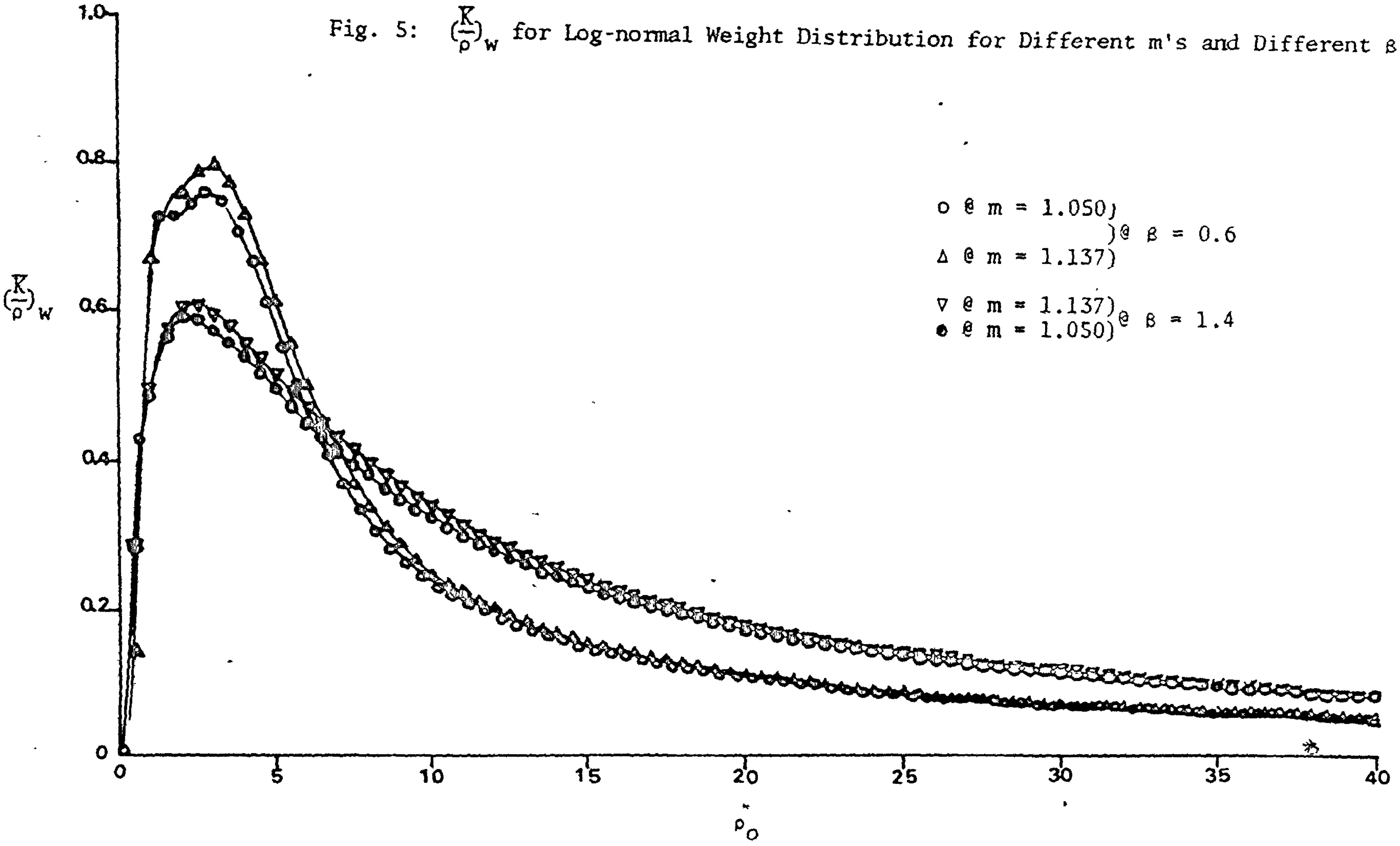


Fig. 5: $(\frac{K}{\rho})_w$ for Log-normal Weight Distribution for Different m's and Different β.



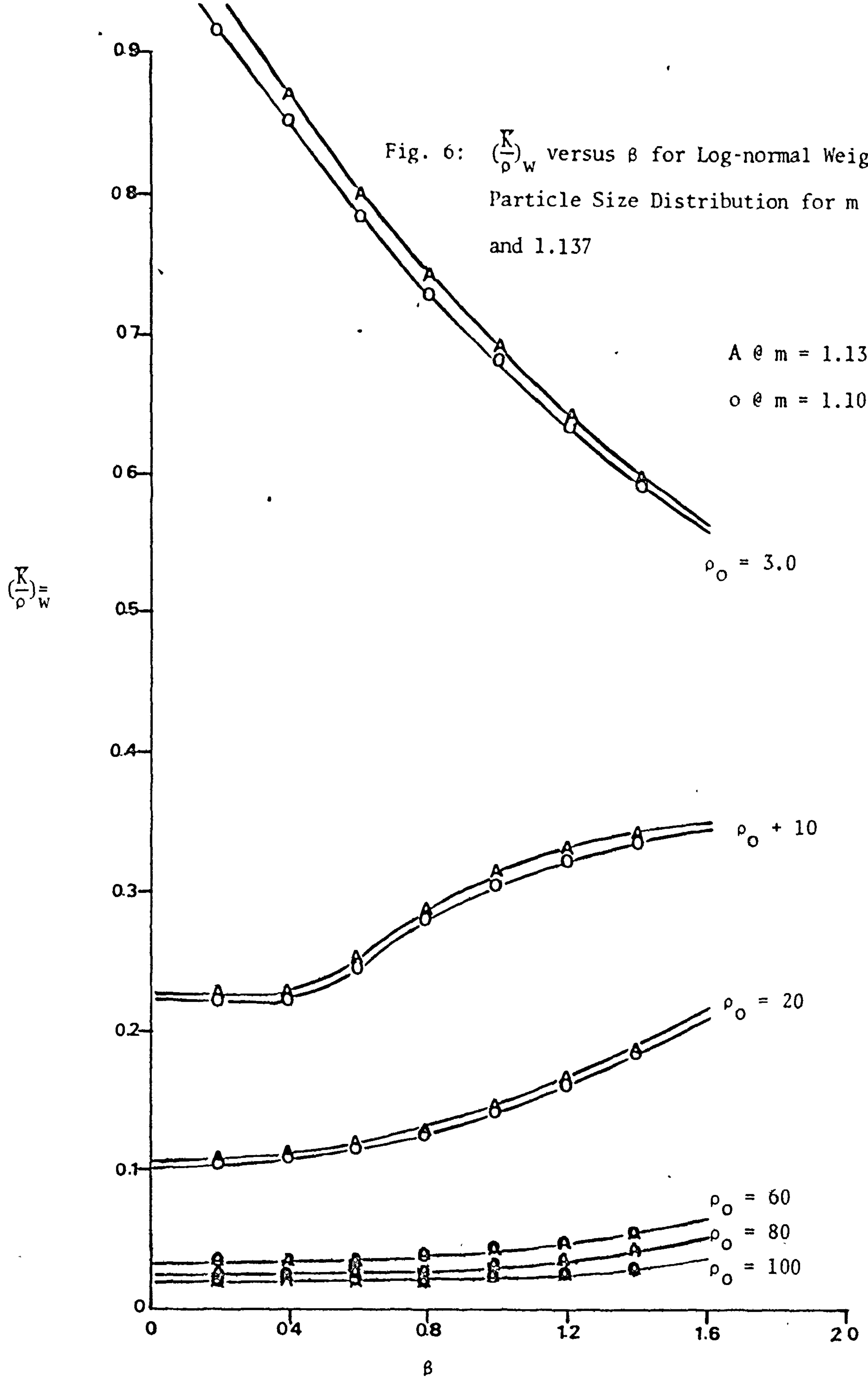


Fig. 6: $(\frac{K}{\rho})_W$ versus β for Log-normal Weight Particle Size Distribution for m = 1.100 and 1.137

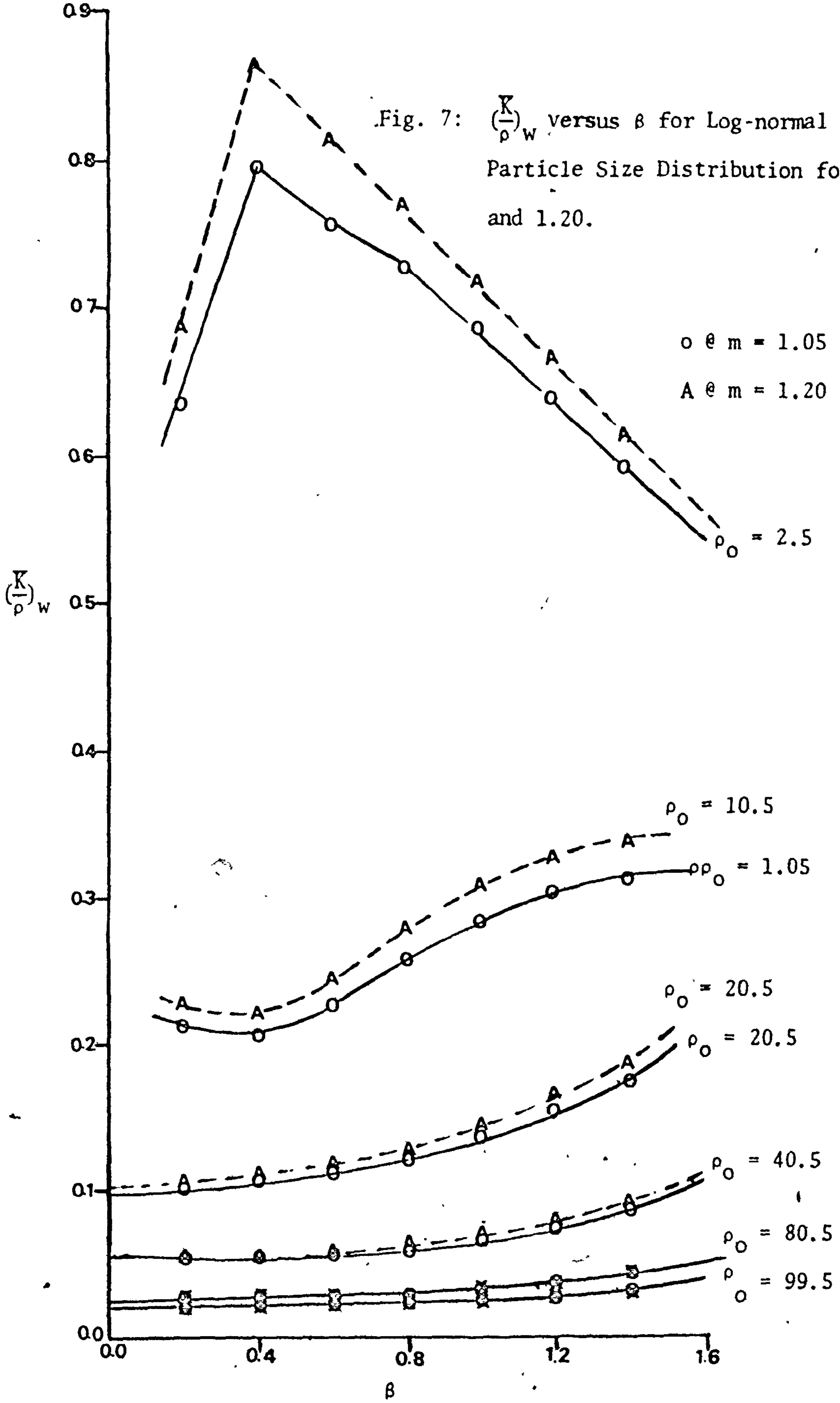


Fig. 7: $(\frac{K}{\rho})_W$ versus β for Log-normal Weight Particle Size Distribution for m = 1.05 and 1.20.

Fig. 8: $(\frac{K}{\rho})_w$ versus β for a Log-normal Weight Particle Size Distribution for m = 1.137 .

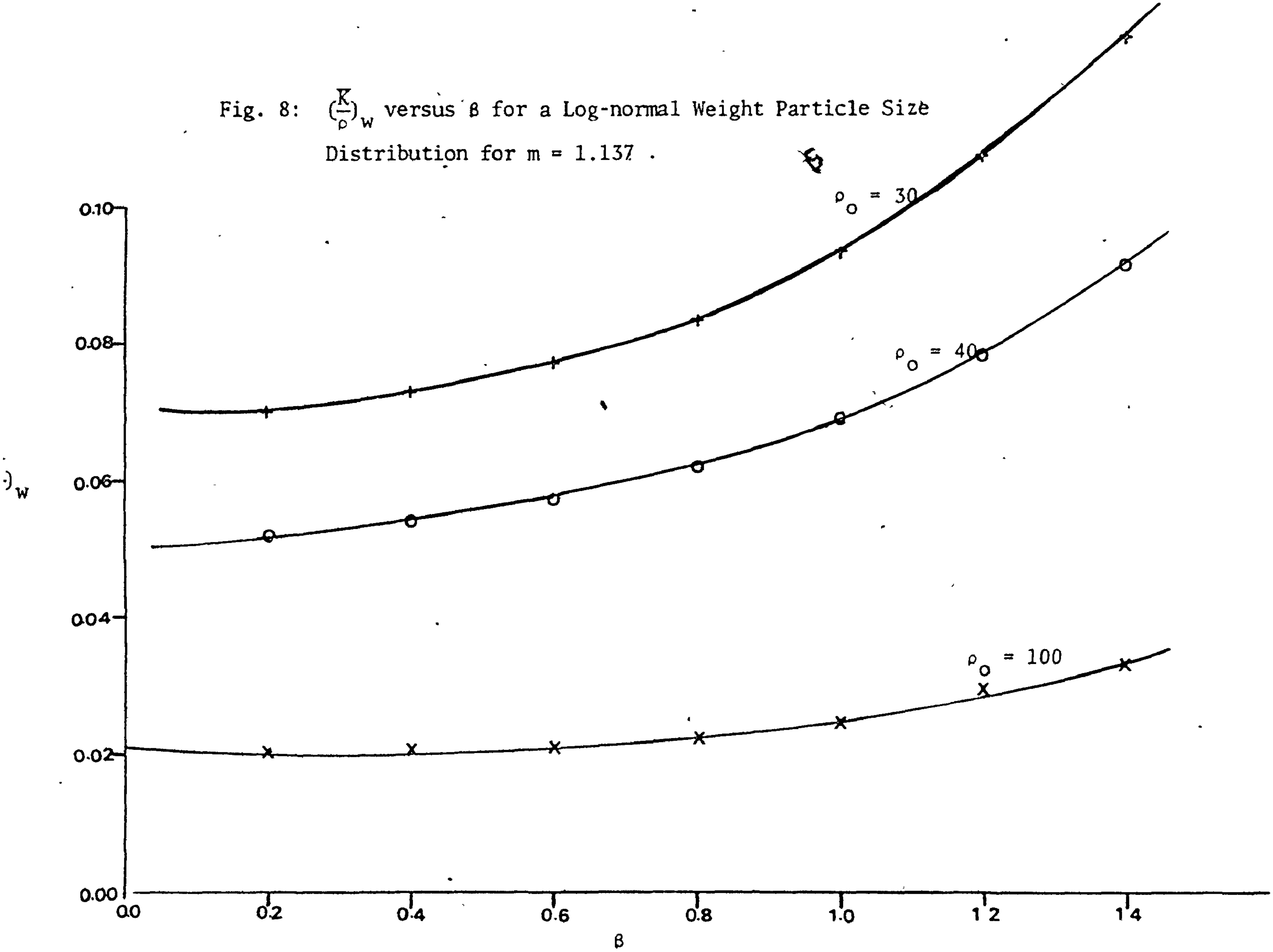
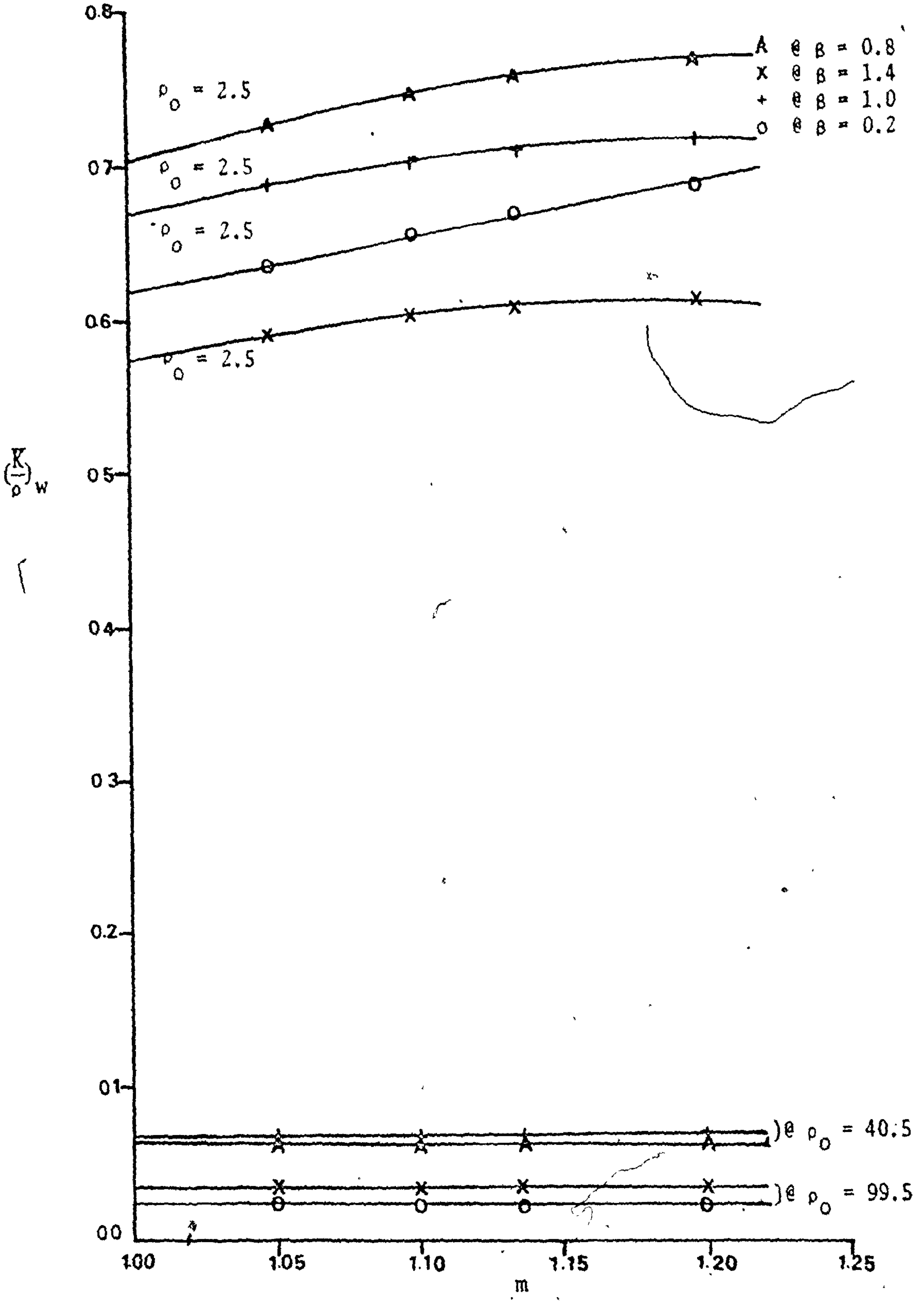


Fig. 9: $(\overline{K/\rho})_W$ versus m for a Log-normal Weight Particle Size Distribution for Different Variances.



of titration, then the particle size distribution of the pure polymer becomes narrow in the swollen state. While the percentage difference in $(\overline{K/\rho})_w$ at very large ρ_0, is very small, it is very significant at intermediate values of ρ_0. The independence of $(\overline{K/\rho})_w$ on m at a particular large ρ_0 is obvious in Figure 9, which contains plots at different ρ_0 and breadth of distribution.

These plots are very significant in order to explain the behaviour of light scattering functions at different regions of ρ_0 and thereby define the region of applicability of turbidimetric titration and meet the necessary requirements of the major assumptions made in the method as used in the past and in the present. Since, however, $(\overline{K/\rho})_w$ is independent of m at large ρ_0, then the need to choose a pair of iso-refractive solvent/non-solvent systems is not important.

4.5 Effect of Swelling on Particle Size Distribution

One of the bases of TT technique is the assumption that the degree of swelling in a given solvent/non-solvent mixture is independent of the molecular weight. This assumption has always been difficult to prove valid in the past. Up to this point in the present study, we are aware that the best criterion of equilibrium in phase separation (Chapter 3) is that the volume of the precipitated phase be allowed to grow until a constant size is reached. Secondly, we realize that the relative refractive index, m, is determined by the degree of swelling (see Eq. 4.3.1). Different states of swelling mean a different particle size and refractive index-two variables which influence the scatter. Also different degrees to which a precipitate is swollen with liquid is according to the polymer chain. Then in order to satisfy the above assumption, turbidimetric measurements representative of the molecular weight distribution of the polymer in question should be independent of m.

From the present analysis of the scattering coefficients and functions, this is possible at increasingly large values of ρ_o. Eventhough the variation in m is unimportant it is yet necessary to consider the effect of swelling on log-normal weight particle size distribution.

For the present purpose, it has been assumed that the volume fraction, ϕ, of the polymer particles in the polymer rich phase is constant. Considering a particle size distribution of the original polymer as given by f(D). Let $\psi(D')$ be the particle size distribution of the swollen polymer. Then

$$\begin{aligned} dn &= f(D)dD \\ &= \psi(D')dD' \qquad 4.5.1 \end{aligned}$$

where dn is the fraction of particles per milliter of diameter between D and D + dD in the original polymer or D' and D' + dD' in the swollen polymer as shown in Figure 10.

$$V' = \alpha V \qquad \alpha > 1 \qquad 4.5.2$$

where

$$\alpha = 1/\phi$$

V' is the volume of swollen polymer having diameter between D' and D + dD' and V is the volume of original polymer having diameter between D and D + dD.

Now

$$\frac{\pi}{6} D'^3 = \alpha \frac{\pi}{6} D^3$$

whence

$$D' = \alpha^{1/3} D \qquad 4.5.3$$

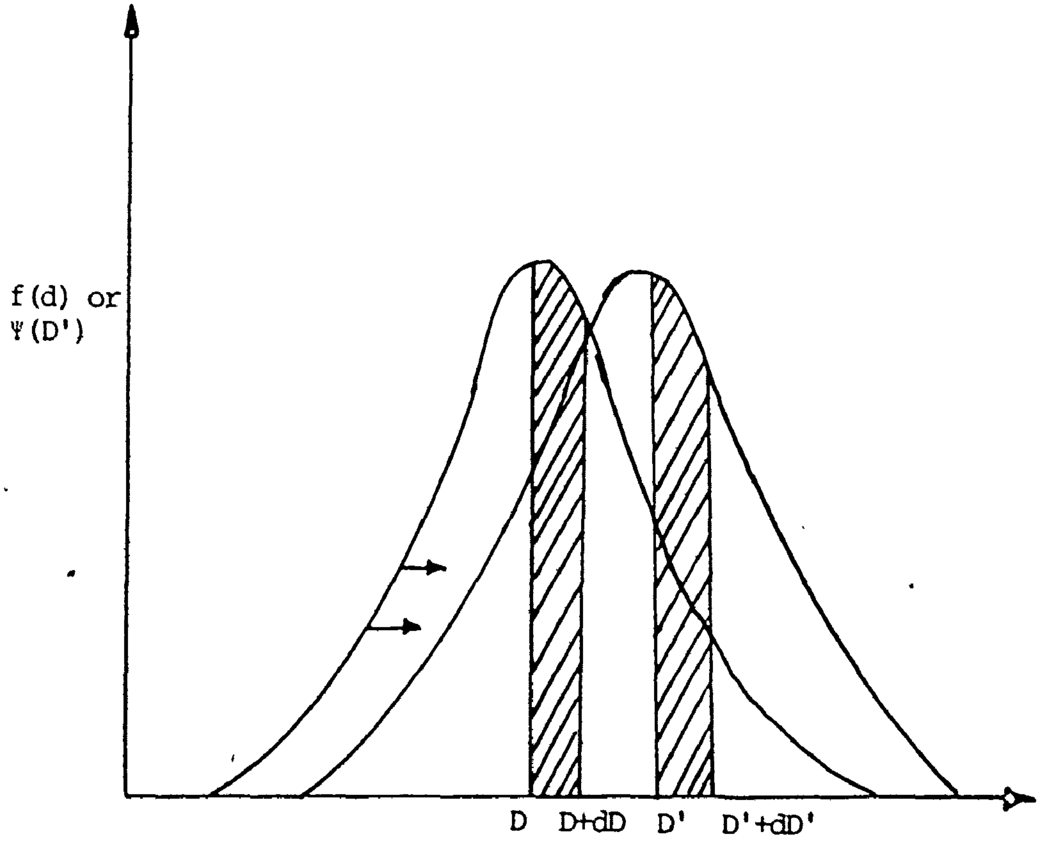


Fig. 10: Particle Size Distribution of Pure Polymer and Swollen Polymer at Constant Values of ϕ.

From Eq. 4.5.1,

$$\psi(D') = f(D) \frac{dD}{dD'} \qquad 4.5.4$$

Differentiation of Eq. 4.5.3 yields

$$\frac{dD'}{dD} = \alpha^{1/3} \qquad 4.5.5$$

Substitution of Eq. 4.5.5 into Eq. 4.5.4 yields

$$\psi(D') = \frac{f(D)}{\alpha^{1/3}} \qquad 4.5.6$$

Thus, under the condition where the particles are allowed to grow to a constant size, Eq. 4.5.6 expresses the particle size distribution of the swollen polymer in terms of that for the unswollen polymer. Since broad standards were used in the present studies, log-normal distribution was assumed for the particle size distribution. Two cases of mean particle size diameter and variances were considered, one for fairly large particles and the other in the region of very large ρ_o. Table 4 shows the values obtained in going from the pure polymer to the swollen state for $\beta = 1.0$ and $\bar{D} = 4200$ Å. Table 3 also shows the kind of values obtained in going from a known swollen state to the pure original polymer for $\beta = 0.4$ and $\rho_o = 100$. In both cases, a value of 0.5 in agreement with values reported in the literature$^{(42)}$ was used for ϕ. In Figures 11 and 12 are shown the plots obtained from the Tables in normalized forms. It is obvious that, after precipitation at the point of maximum turbidity, the breadth of the distribution becomes narrower and this lends support to the observation made of the scattering function behaviour as discussed in the previous section.

Table 3

Particle Size Distribution of Pure and Swollen Polymer for

$\alpha = 2,\ \rho_o = 100$

D' x 10^{-6}(A)	ψ(D')	D x 10^{-6}(A)	f(D)
0.2000	-	-	-
0.5000	0.0057	0.3970	0.0045
0.7000	0.1452	0.5560	0.1153
0.8000	0.3554	0.6350	0.2821
0.9000	0.6507	0.7140	0.5165
1.0000	0.9649	0.7940	0.7660
1.1000	1.2228	0.8730	0.9710
1.2759(ρ_o=100)	1.4105	1.0155	1.1195(ρ_o=79.4)
1.4000	1.3409	1.1111	1.0643
1.5000	1.2044	1.1906	0.9559
1.7000	0.6932	1.3490	0.5502
1.9000	0.5309	1.5080	0.4214
2.0000	0.4053	1.5870	0.3217
2.2000	0.2249	1.7460	0.1785
2.4000	0.1190	1.9050	0.0945
2.6000	0.0609	2.0636	0.0483
2.8000	0.0305	2.2224	0.0242
β = 0.400		β = 0.504	

Table 4

Particle Size Distribution of Pure and Swollen Polymer for Small ρ_o ($\alpha = 2$)

D $\times 10^{-3}$(A)	f(D)	V $\times 10^{-10}$(A^3)	D' $\times 10^{-3}$(A)	ψ(D')
1.000	0.0720	0.0524	1.2599	0.0907
1.500	0.1954	0.1767	1.8899	0.2462
2.000	0.3254	0.4189	2.5198	0.4100
3.000	0.5036	1.4137	3.7798	0.6345
3.200	0.5240	1.7157	4.0318	0.6602
3.400	0.5396	2.0580	4.2837	0.6798
3.600	0.5508	2.4429	4.5357	0.6940
3.800	0.5586	2.8731	4.7877	0.7038
4.000	0.5629	3.3510	5.0397	0.7092
4.200	0.5642	3.8724	5.2917	0.7109
4.400	0.5629	4.4602	5.5437	0.7092
4.600	0.5596	5.0965	5.7956	0.7051
4.800	0.5542	5.7906	6.0476	0.6983
5.000	0.5473	6.5450	6.2996	0.6896
6.000	0.4968	11.3097	7.5595	0.6259
7.000	0.4346	17.9594	8.8195	0.5476
8.000	0.3725	26.8083	10.0794	0.4693
9.000	0.3156	38.1704	11.3393	0.3976
10.000	0.2658	52.3599	12.5992	0.3349
15.000	0.116	176.7150	18.8988	0.1406
20.000	0.0494	418.8790	25.1984	0.0624
$\beta = 1.000$			$\beta = 0.794$	

Fig. 11: Effect of Swelling on Log-normal Weight Particle Size Distribution (normalized).

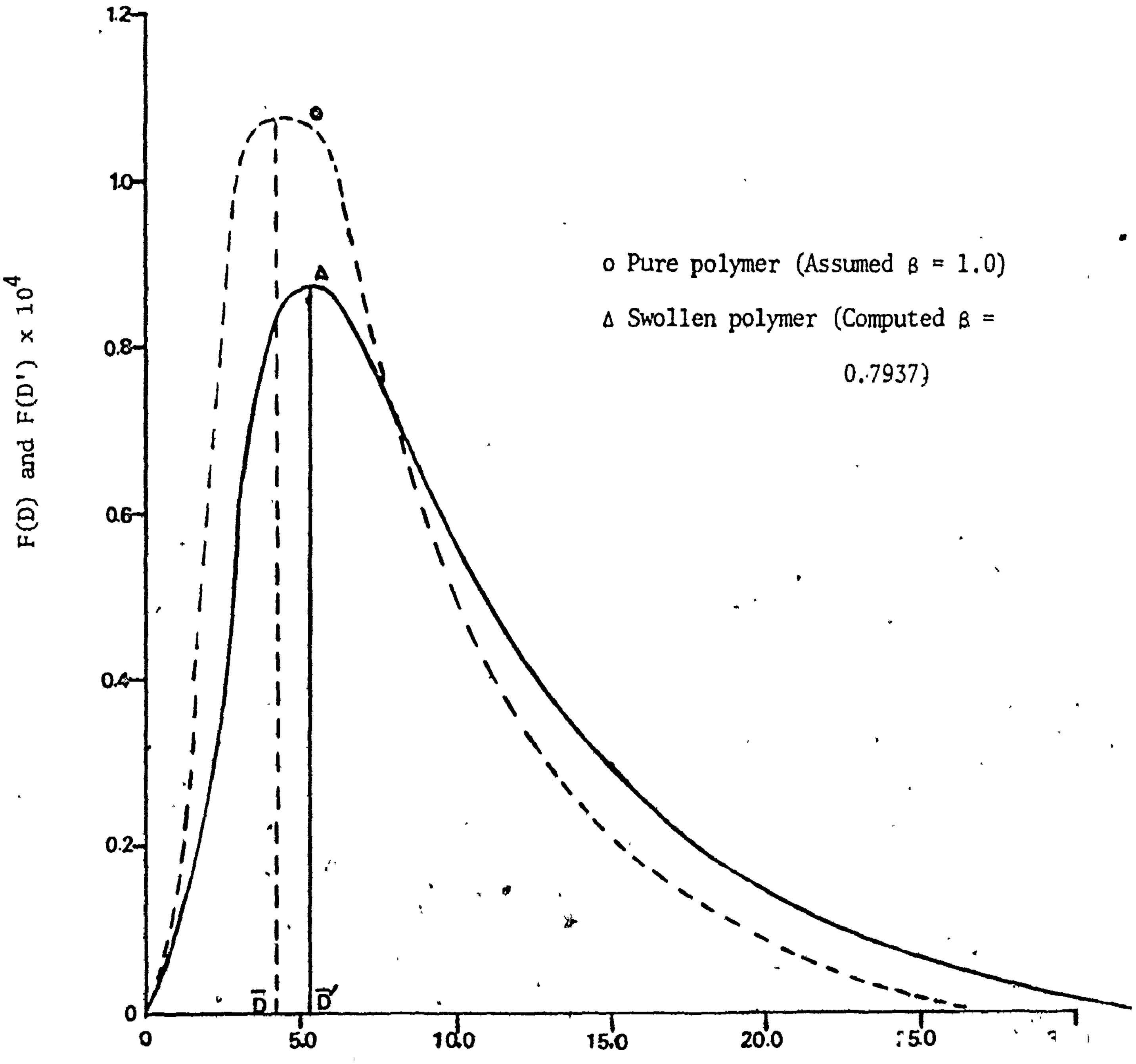
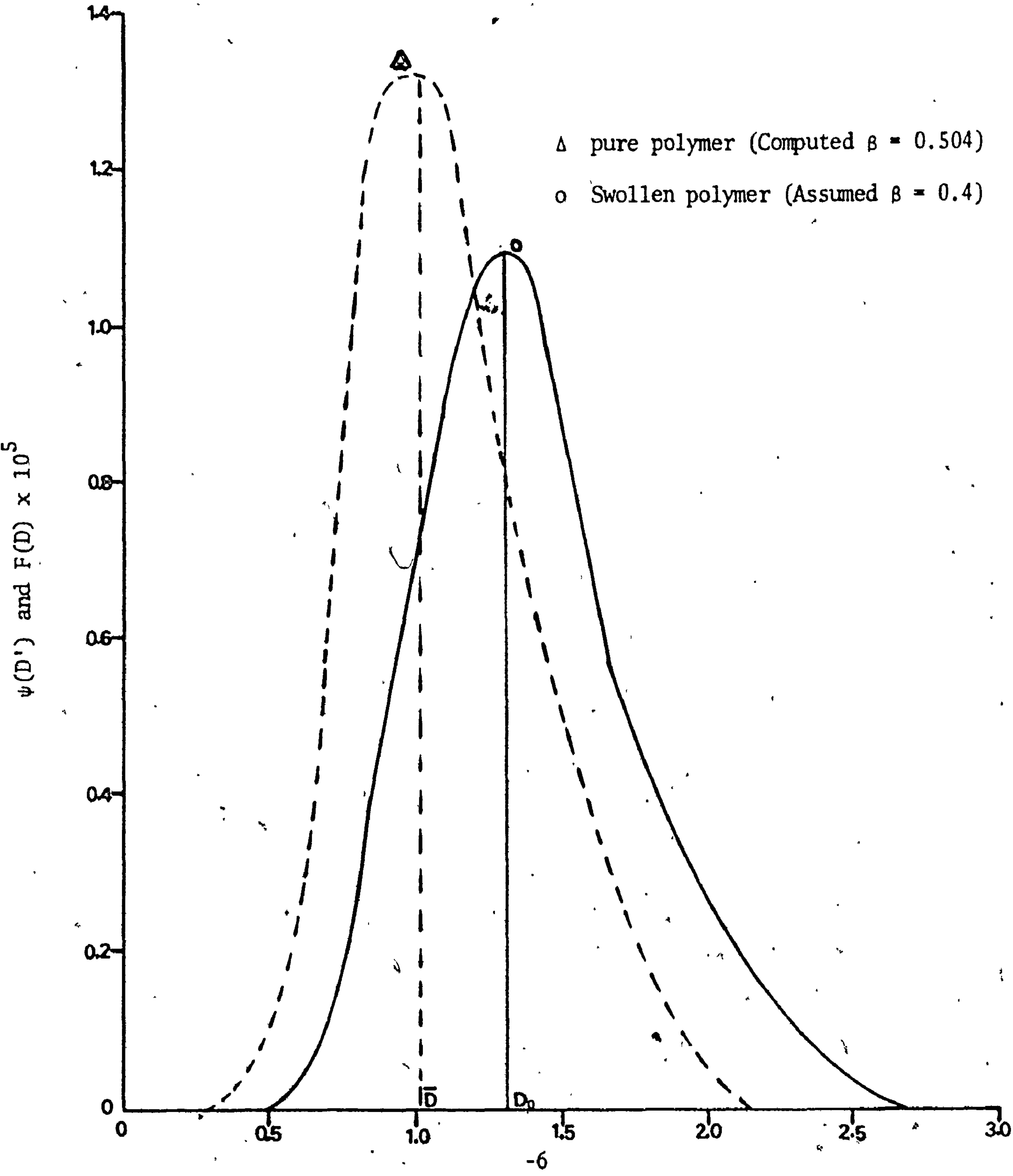


Fig. 12: Effect of Swelling on Log-normal Weight Particle Size Distribution (normalized).



4.6 Concentration Dependence of Turbidity

According to Eq. 4.3.5a, the turbidity developed will be a function of

(1) the concentration of the precipitated polymer

(2) the average (weight) scattering function

(3) the refractive indices of both the particles and the suspending medium.

The refractive index of the particles at various stages of titration changes and is uncertain. A system of suitable non-solvent/solvent must be chosen and the refractive indices should be very different from that of the polymer particles. Thus the conditions imposed on the dependence of turbidity on the refractive indices of both the particles and the suspending medium will be considerably relaxed provided the particles after precipitation are allowed to grow to their desired size with stirring. At the point of maximum turbidity, the maximum turbidity is dependent on the exact unknown particle size distribution, and the scattering coefficient according to light scattering theory is almost constant with respect to large ρ's. In the region of maximum turbidity, $\overline{(K/\rho)}$ for most kinds of polymers is almost independent of the relative refractive index of the polymer. In Table 66 are displayed values of $\overline{(K/\rho)}_w$ at different wavelengths at 100% precipitation for the different polymers investigated. The values are independent of concentration of polymer solutions.

As a consequence of the above requirements and experimental optimum conditions, the turbidity which is maximum, becomes directly proportional to concentration. In view of the fact that the polyacrylamide polymers investigated are broad, each of the polymers showed a different dependence of turbidity on concentration. Figures 13, 15 and 16 show the linear relationship between concentration and absorbances of solution after correction for dilution. Over the range of concentrations investigated, the Beckmann Spectrophotometer gives a value of τ/c or A/c which is almost independent of concentration for wavelength in the visible ranges up to 4000 Å as shown in Figures 14, 58 and 60. It removes any necessity for extrapolation of specific turbidities to infinite dilution. It can then be concluded that Beer's Law is not contradicted, which in general for any system, is a necessary check for quantitative spectrophotometry.

It is interesting to note that the maximum condition imposed on turbidity, by letting particles grow, is the determining factor for the linear relationship between turbidity and concentration. Aggregation to a particular particle size is encouraged. Different polymers aggregate to different particle sizes in the region $\rho >> 3$. When polymer particles aggregate to some particular size, at different stages of titration, the linear relationship between maximum turbidities and concentration is obtained. When aggregation obtained in the region of maximum turbidity is not uniform along the stages of titration, non-linear relationships are obtained. Comparison of Tables 34, 35, 36 with Tables 35, 36 show systems in which turbidities obtained are twice, thrice or multiples of the expected maximum turbidities for the respective stages of titration. Detailed preliminary investigations have shown that this behaviour results when the beginning of titration is not properly controlled. The reader is referred to the experimental analysis section where the conditions required to

Fig. 13: Relationship of Maximum Corrected Absorbances and Concentration for Standard C.

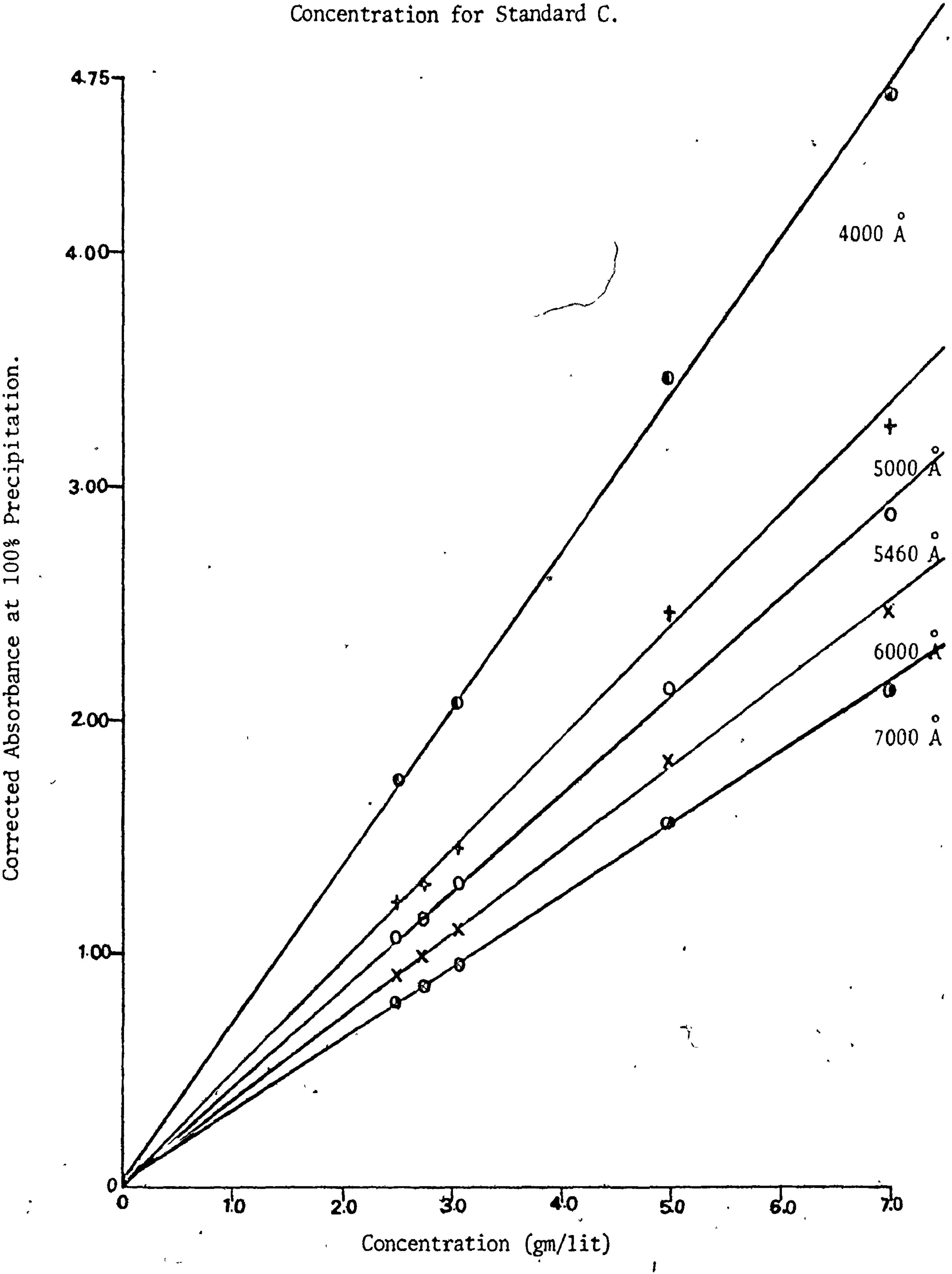


Fig. 14: Independence of Specific Absorbance on Starting Polymer Concentration for Standard C.

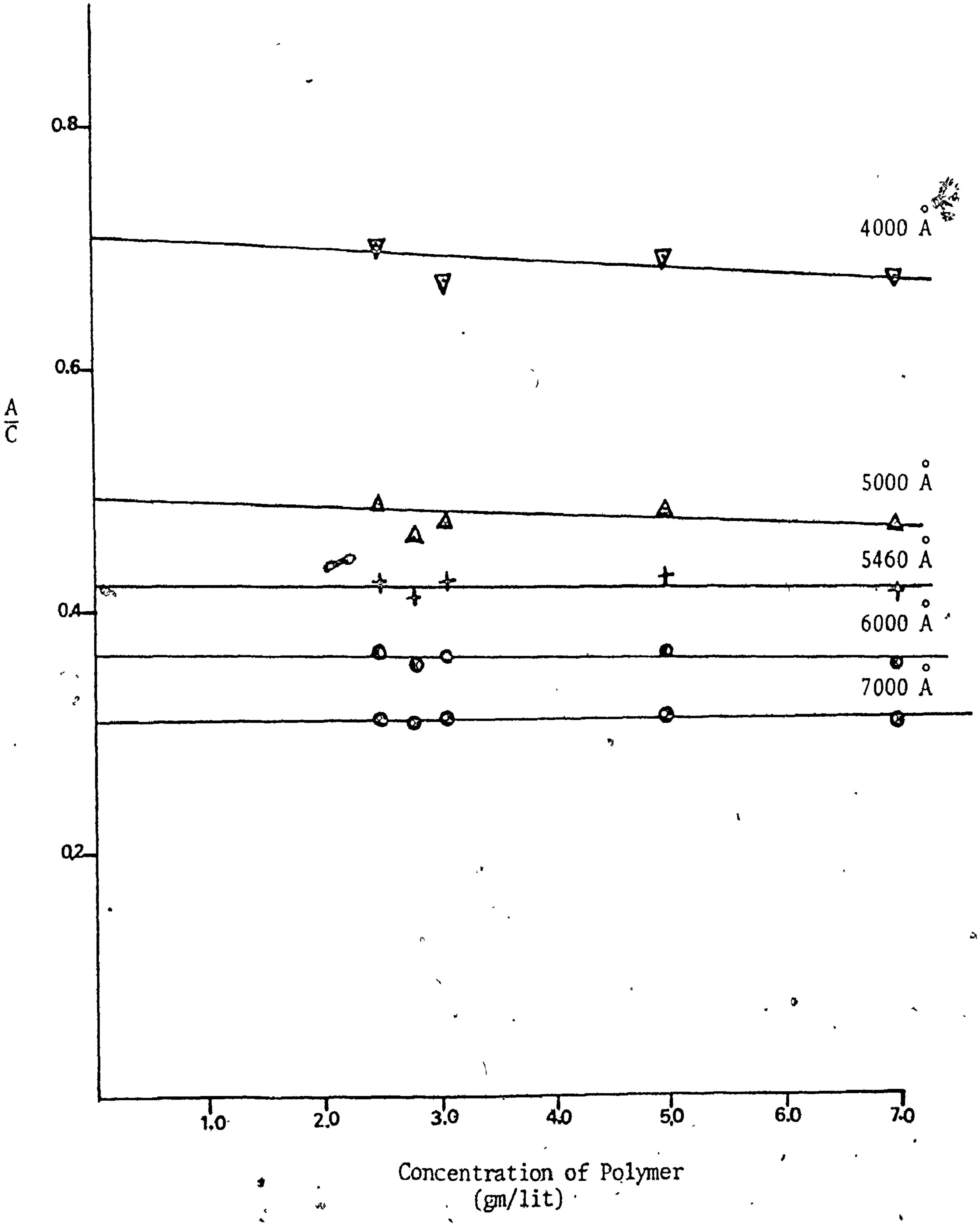


Fig. 15: Relationship Between Max. Corrected Absorbances and Concentration for Standard B.

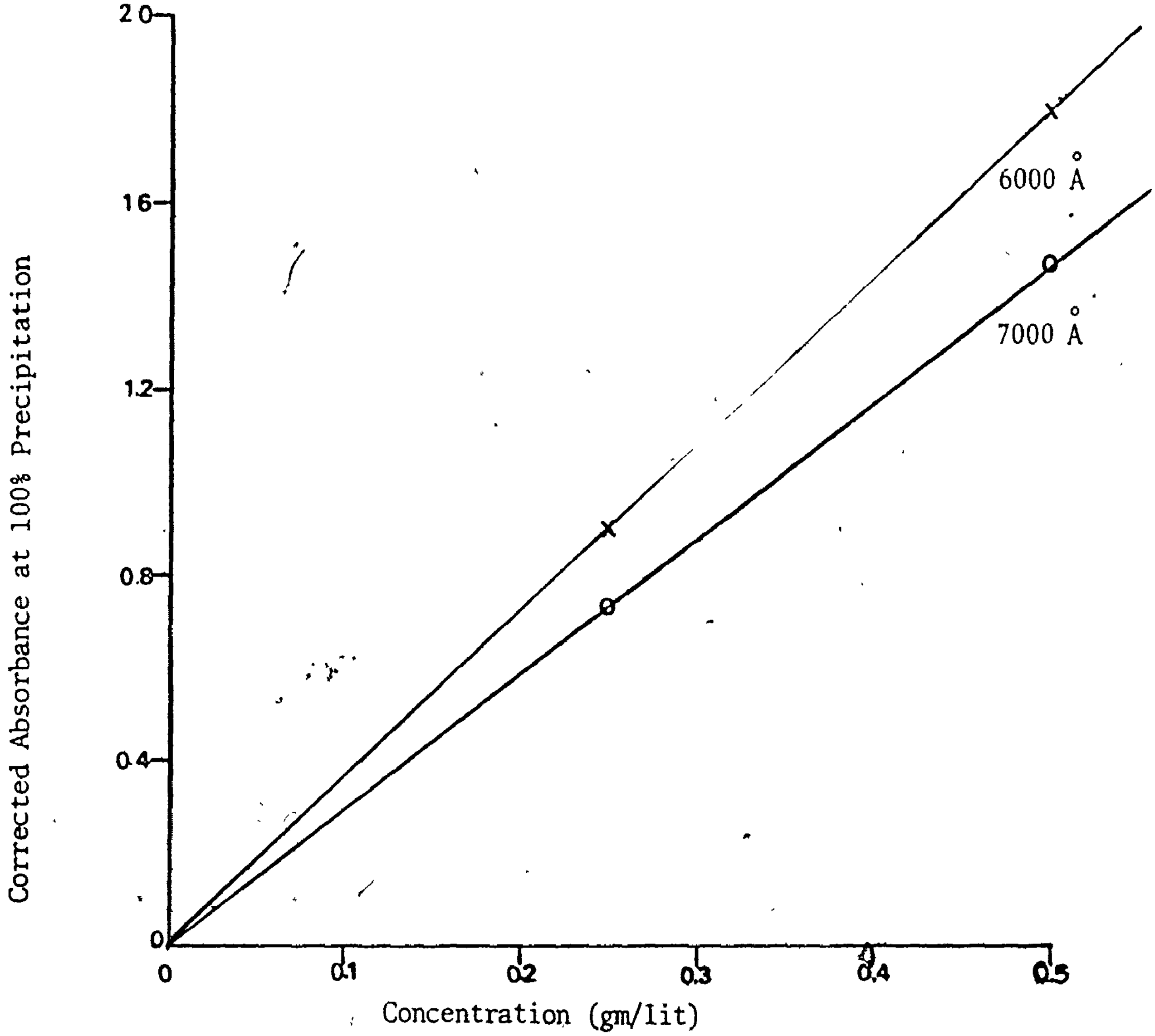
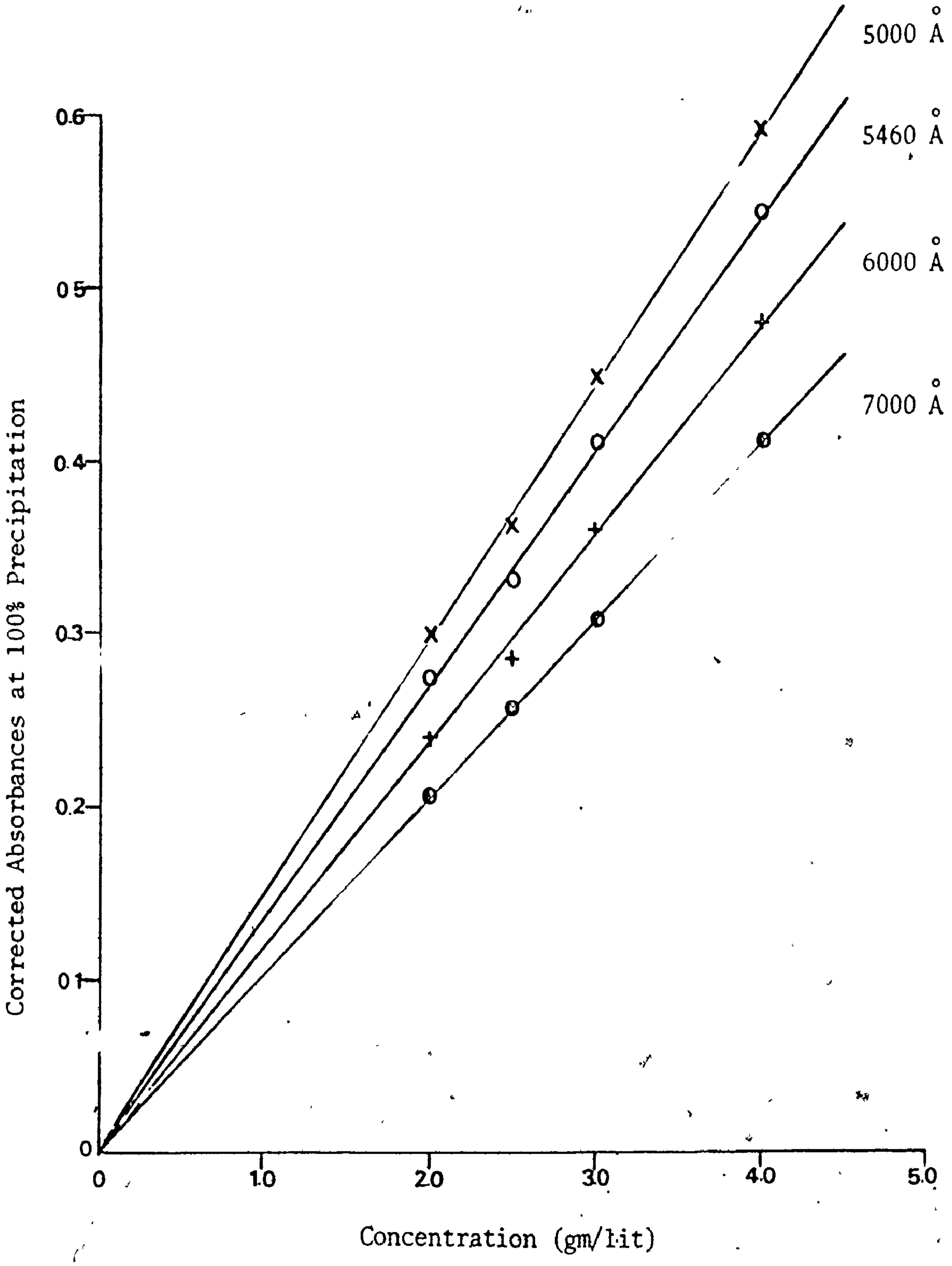


Fig. 16: Relationship Between Maximum Corrected Absorbances and Concentration of Polymer for Standard A.



eliminate this so called"crossing of the point" at the initial stage of titration has been discussed. The initial stage of a titration is a very important stage. When the non-solvent is initially added to the polymer solution, the very high molecular weight part of the distribution precipitates first. These particles are largest in size. With stirring, the particles will grow in size until the point of maximum turbidity is reached. At this point, the corresponding particle size distribution is more a function of the molecular weight of the polymer precipitated. This dependence prevails at each stage of the titration, so that the initial stage of the titration must be properly controlled. As shown in Tables 57 and 58, a standard, the acidified polymer is more prone to this kind of aggregation where to obtain a linear relationship between turbidity and concentration is sometimes difficult.

Apart from the beginning of titration which should be properly controlled, method of stirring has been found to influence the size of aggregates obtained. The rate of particle growth as shown for a case in Table 5 and plotted in Figure 17 is dependent on the rate of stirring. When the method of stirring is by hand shaking,(46) even when the point of precipitation has not been crossed, the polymer particles aggregate in multiples which is inconsistent along the points of titration. As a result the molecular weight averages obtained are larger than expected as indicated in Table 65. This is particularly the case when the molecular weight of the polymer investigated is limited by a low high molecular weight tail. When the method of shaking is by hand, the agitation of the polymer particles is not uniform throughout the solution.

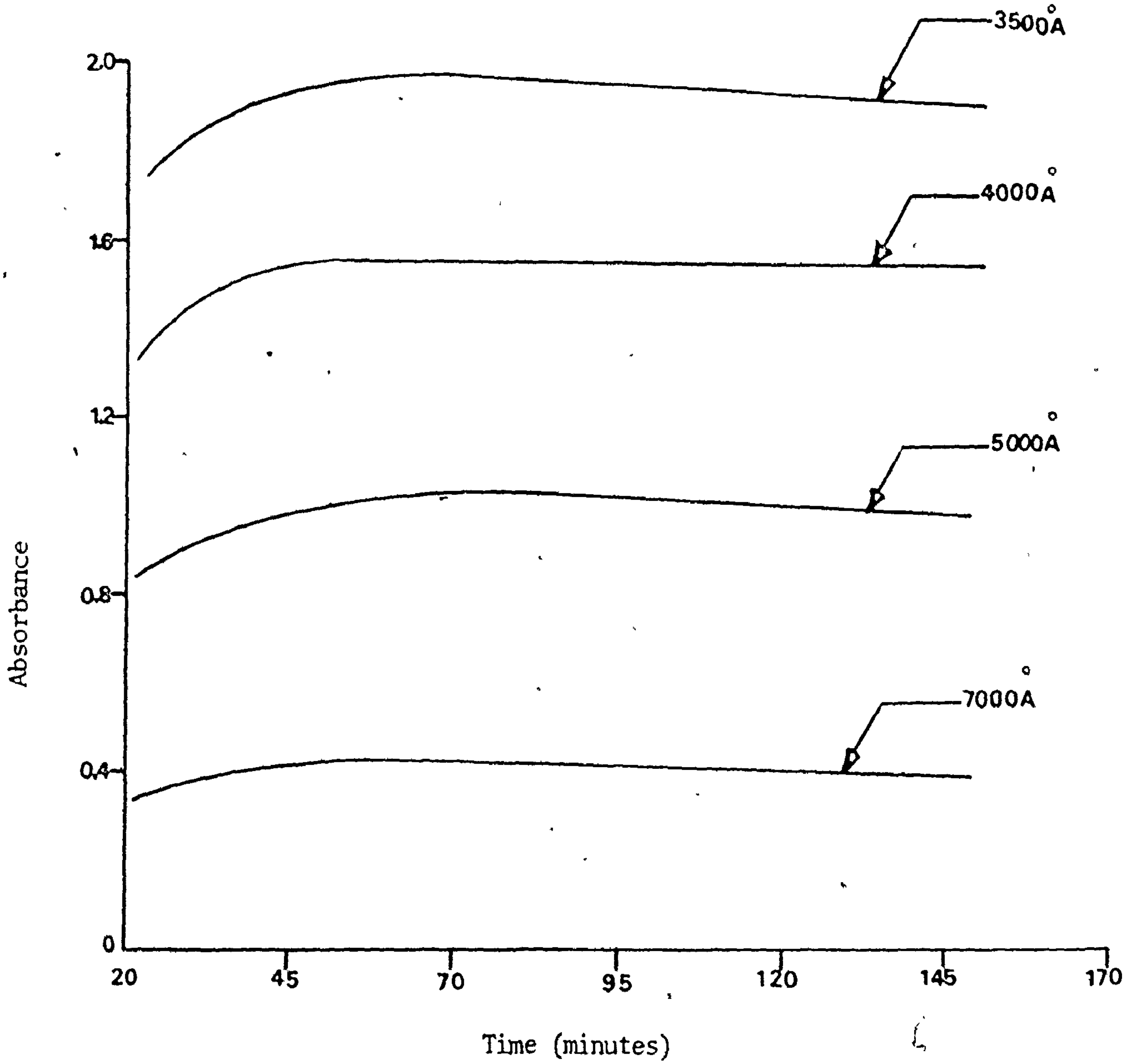
Table 5

Change of Turbidity with Time Using Water Labelled B_W

Starting Solution: 10 ml of 0.5 gm Standard C/100 ml B_W
1.25×10^{-6} < Conductivity of Water < 3.72×10^{-6}
% CH_3OH : 85.7
Near the point of maximum turbidity

Wavelengths	7000 Å		5000 Å		4000 Å		3500 Å
Time(min)	Abs	Time(min)	Abs	Time(min)	Abs	Time(min)	Abs
23.50	0.356	25.50	0.864	26.50	1.388	27.00	1.788
29.32	0.370	31.32	0.934	32.32	1.516	32.82	1.908
35.50	0.390	37.50	0.934	38.50	1.516	39.00	1.908
42.00	0.408	44.00	0.984	45.00	1.548	45.50	1.918
48.20	0.420	50.20	0.994	51.20	1.588	51.70	1.968
52.60	0.424	54.60	1.004	55.60	1.588	56.10	1.968
60.40	0.424	62.40	1.024	63.40	1.588	63.80	1.968
65.90	0.424	67.90	1.024	68.90	1.588	69.40	1.968
71.90	0.424	73.90	1.024	74.90	1.588	75.40	1.968
79.60	0.424	81.60	1.024	82.60	1.580	83.10	1.948
97.50	0.424	99.50	1.008	100.50	1.568	110.00	1.948
106.90	0.424	108.90	1.004	109.90	1.568	110.40	1.928
116.80	0.400	118.80	0.994	119.80	1.508	120.30	1.928
126.60	0.396	128.60	0.964	129.60	1.508	130.10	1.908
136.20	0.388	138.20	0.964	139.20	1.498	139.70	1.908
145.45	0.382	147.45	0.934	147.45	1.468	147.95	1.888

Fig. 17: Change of Turbidity with Time During Stirring Near the Point of Maximum Turbidity.



It is important to note that, the decrease in turbidity after the maximum is reached, is not due to settling of polymer particles, but due to the oscillatory nature of the scattering coefficient. The decrease obtained usually is not at all sharp. In the present studies, solutions which have been investigated under well controlled experimental conditions using well distilled solvent have been found to remain at maximum turbidity for more than 3 days, before any minor decrease was observed.

CHAPTER 5

EXPERIMENTAL

5.1 Materials and Equipment

The basic equipment required for turbidimetric titration (TT) measurements is either a light scattering instrument or a good spectrophotometer. Regardless of which equipment is used, some modifications to the instrument are sometimes necessary to adapt it for turbidimetric titrations. Generally, the most suitable equipment for TT measurements under isothermal conditions is a modified recording light scattering instrument or spectrophotometer with a well designed optical cell which can be thermostated and stirred continuously and also has sufficient room to allow for addition of precipitant. This makes it possible to carry out the experiments and measurements in one vessel. Although most scattering spectrophotometers are not strictly designed for this purpose, some can be more easily converted than others. However, generally any well designed spectrophotometer may be used. For the present investigations, a Beckmann, Model 25 spectrophotometer has been used to measure the absorbances of the turbid suspensions. The specifications of the instrument are presented in Appendix III. The optical cells used were obtained from Canlab. They are 10 mm path length, gold labelled cells manufactured of highest quality optical glass for use in the range 310 to 1000 nm. They have a guaranteed transmission of the dry cell better than 80% at 365 nm, with a matching tolerance in sets of ± 0.5% at 360 nm.

For the purpose of application of turbidimetric titration to obtain the molecular weight distribution of fairly high molecular weight-water-soluble polymers, Polyhall 402, a commercially available linear polyacrylamide manufactured by Stein-Hall Ltd. was used to obtain a molecular weight-solubility calibration curve. No molecular weight information of any kind was supplied by Stein-Hall Ltd., but previous workers(63) who have characterized this polymer have shown that it is a standard, non-ionic intermediate molecular weight polymer with the molecular weight averages via GPC given by

$\overline{M}_n = 2.40 \times 10^6$ Polydisersity = 2.43

and

$\overline{M}_w = 5.83 \times 10^6$

Two broad MWD polyacrylamides, Standards A and B which were synthesized by previous workers in aqueous solution using a free radical initiator, 4,4' azobis-4-cyanovaleric acid (ACV) and isothermal polymerization(59) under the following synthesis conditions were used to test the method.

Standard A

T = 40°C, monomer concentration = 0.281 moles/liter

ACV concentration = 7.14×10^{-4} moles/liter

Standard B

T = 50°C, monomer concentration = 0.563 moles/liter

ACV concentration = 1.43×10^{-3} moles/liter

Standards A and B previously characterized by GPC measurement with theoretical differential MWD,

$$W(M) = \frac{M}{\overline{M}_n^2} \exp(-\frac{M}{\overline{M}_n}) \qquad 5.1.1$$

where M is molecular weight and W(M) is weight fraction have the averages given by

Standard A

$\overline{M}_n = 2.52 \times 10^{+6}$

$\overline{M}_w = 5.04 \times 10^6$

Standard B

$\overline{M}_n = 1.60 \times 10^6$

$\overline{M}_w = 3.35 \times 10^6$

One very broad MWD polyacrylamide called Standard O, was synthesized in acidified aqueous solution in the conditions and manner specified in section 5.5. Its molecular weight averages as obtained via GPC measurements are

$\overline{M}_n = 2.50 \times 10^6$

$\overline{M}_w = 7.16 \times 10^6$

Because this polymer is of higher molecular weight, the molecular weight averages were also obtained by viscosity measurements as shown in Appendix IV.

The solvent and precipitant used in the experiments were water and anhydrous methyl alcohol, respectively. Initially, formamide was tried as a solvent with a corresponding almost isorefractive acetone non-solvent.

The idea of using this combination was discarded since the method is to be applicable to water-soluble polymers in general and the precipitated polymers obtained were in thread-like forms. While n-propanol was found to be a suitable non-solvent when the solvent is water, the idea of using it was discarded since the refractive index is not identical to or close to the refractive index of water. In view of the fact that TT method is a separation process whose efficiency is greatly influenced by the degree of purification of solvent and non-solvent, two different levels of water A_W and B_W in terms of purity were used. The conductivity of the water used measured to be less than 1.25×10^{-6} mho and 3.72×10^{-6} mho, respectively. The methanol is a reagent grade quality used as received (Fisher, certified).

Standard 250 ml conical flasks provided with standard stoppers were used for the titrations. Stirring was done mechanically and when a different suitable method was desirable, it was done by hand shaking. Solutions were transferred into the cells by suction provided disposable pipettes.

As regards to temperature control, no bath was used and the titrations were done at laboratory room temperature. A thermometer was placed somewhere in the room to check the temperature variations at intervals. Fluctuation in temperature between 21-25°C did not affect the resulting maximum turbidities obtained.

5.2 A Review of Previous Experimental Methods

The most widely used technique in TT is the isothermal addition of a non-solvent to a well stirred and very dilute solution of polymer. Most of the TT methods described in the literature,(30)(48)(45)(47) involve measurement of turbidity either after incremental additions of precipitant or simultaneously with continuous addition of precipitant. If the rate of addition of precipitant is too fast, the conditions under which phase separation takes place will be far from equilibrium, with deleterious effects on the fractionation process. In all cases, after addition and a sufficient lapse of time, the particulate phase aggregate to form a uniform whole or mass. Presence of aggregates which has been fully established in normal fractionation procedures, has never been encouraged in TT. With adequate stirring, the particulate phase can be adequately suspended thereby discouraging aggregation. Very rapid stirring could enhance aggregation considerably also. Generally in all the methods, it has usually been assumed that aggregation of particles during the time of turbidity measurement is negligible, even when its presence has been confirmed.(54)

Another method, which takes into account, the non-equilibrium precipitation conditions associated with the single-stage cumulative precipitation procedure above is the method of Howard.(40) This method is non-continuous in the sense that the system is brought to a predetermined solvent/non-solvent content and the turbidity produced by the stable suspension allowed to reach a steady value. In his application, once equilibrium was reached, the turbidity remained constant for several hours before slowly decreasing. The time taken for the turbidity of the system to attain the equilibrium value depended upon the concentration of precipitated polymer and varied from about ten minutes at the lowest concentrations to about 80 minutes at concentrations of 2.0 mg/100 ml and above. This method was used to obtain the molecular weight distribution of nylon 66 polymer and from the results, only an approximate distribution could be obtained. The stable suspensions were obtained by stirring at a slow and constant speed for only 40 seconds. Whether, his inability to accurately deduce the absolute molecular weight distribution of nylon 66, is due to his method, or lack of improper correlation between turbidity and polymer precipitated to all stages of precipitation will be a subject of further discussions.

During the last few years, a new experimental technique which has its origin in a proper understanding and application of light scattering theory, has been proposed by Beattie and co-workers.(39)(41)(42) This method has been able to place TT on a more quantitive basis. This method uses the technique that eliminates the continuous or incremental titrations and replaces it with a sequential method similar to that used by Howard. In this method, aggregation to a uniform whole (which has never been encouraged) is used as an advantage. There are different kinds of aggregations. The kind of aggregation specified by Beattie is a reflection of the nature of changes of the light scattering function with particle size.(39) In other words, the particulate phase are allowed to aggregate to a particular particle size. A series of precipitations containing progressively greater amounts of precipitant is allowed to reach maximum turbidity by stirring at which point, the turbidity is readily calculated in principle. At the maximum, the weight of polymer precipitated is obtained for a known solvent-precipitant ratio. To let the particulate phase grow to a particular particle size requires prolonged stirring. According to Beattie(39) none of the above methods could be used (particularly if the solution is stirred) for the following reasons. At the beginning of such single-stage cumulative precipitations, the precipitating particles are highly swollen, causing m, the relative refractive index to be low. Therefore to attain the condition of maximum turbidity given approximately by $\rho \approx 3$, the particles must be large (see Eq. 4.2.12). At the end of the titration, the opposite is true, that is, m is high and the particles must be small to attain the condition $\rho \approx 3$. Clearly it is impossible to begin with big particles and end with small particles. Therefore each point of the titration must be done with a new solution, so that the particles can grow to the desired size. Since, however, the basis of turbidimetric technique is the assumption that the degree of swelling in a given solvent/non-solvent mixture is independent of the starting concentration and molecular weight of the polymer, the question of using new polymer solutions at each point of the titration will be a subject of further investigation.

However, the method of maximum turbidity seems to have many advantages.

(1) If $\max(\frac{K}{\rho})_W$ at the condition $\rho \hat{=} 3$, can be easily obtained, then the solubility distribution is readily obtained and if the relationship between molecular weight and solubility is also known, the molecular weight distribution can be obtained without resort to empirical methods. This places the method on an absolute basis.

(2) The scattering cross-section per unit volume of scattering

material is at a maximum when $\rho \hat{=} 3$. Therefore, the sensitivity is the highest attainable by a turbidimetric method so far.

(3) The particle size distribution does not affect the result if the distribution is narrow. As a result, little variations in experimental technique which will cause the particle size distribution to be non-reproducible will have little or no affect upon the turbidity. This eliminates the disadvantages that "Aging, agglomeration, or coagulation of precipitate will alter the turbidity without the quantity of precipitate varying".

(4) The wavelength may be selected to correspond to the particle size.

Nevertheless, there are certain limitations to the method of maximum turbidity -

(a) The condition of $\rho \hat{=} 3$ can only be attained either by particle growth or adjustment of wavelength or both, which may not be experimentally possible for some types of polymers.

(b) Particles must be approximately spherical.

(c) The solvent and precipitant must be approximately isorefractive and these must be distinctly different from the refractive index of the polymer.

(d) If the particle size distribution is broad and is unknown, the method is not applicable.

It seems then as if, in general, the development and choice of a general method relies in part on the judicious choice of solvent and precipitant rather than the kind of polymer under investigation. The proper

7

choice of solvent/non-solvent system must be made; this system must be sufficiently selective, particularly near the end point, so as to effect a good separation of the polymer species.

5.3.1 Present Method

A series of preliminary experiments were carried out with the aim of investigating:

(1) the influence of rate of stirring
(2) the influence of rate of addition of non-solvent
(3) the variation of absorbance with time
(4) influence of temperature control
(5) method of addition of non-solvent
(6) influence of coagulation and wavelength on the turbidity of the solution
(7) checking if the proper choice of non-solvent/solvent system is satisfactory from the standpoint of separation and theoretical requirements for different kinds of polyacrylamide

Exact definition of experimental variables and conditions is necessary to obtain reproducibility. The different methods used by previous workers were tested and varied. From the preliminary runs, the following observations and results were obtained:

(a) Variations of rate of stirring have very little or no influence upon the maximum turbidity which resulted after a considerable length of time. Titrations were done using 10 ml and 20 ml of original polymer solutions. Whether the original polymer solution was 10 ml or 20 ml, the maximum turbidity obtained for an equivalent non-solvent/solvent ratio was proportional and reproducible. Under well-controlled conditions, from the onset of precipitation, the turbidity of the solution increases with stirring. The higher the rate of stirring, the less time it takes for the solution to reach maximum turbidity. The solution remains at the maximum turbidity for a considerable length of time before it begins to fall very slowly. In Table 6 are displayed results for two polymer solutions of the same concentration, but different rates of stirring.

(b) The time required for a solution to attain maximum turbidity depends upon the concentration of the original polymer solution. The lower the concentration, the less time it takes to reach maximum turbidity. Table 6 also compares the time for a 0.1 gm/100 ml polymer solution and 0.3 gm/100 ml polymer solution to reach maximum turbidity for the same per cent non-solvent. In all cases, a supposedly distilled water with high conductivity, B_W was used.

(c) The initial rate of addition of non-solvent is found to be indeed the most important experimental variable to control. If the initial rate of addition of non-solvent is not well controlled, the conditions under which phase separation takes place will be far removed from equilibrium, with either co-precipitation in the fractionation process as noticed by the marked increase in turbidity in Tables 34, 35 and 36 or no precipitation at all, regardless of the length of time of stirring, rate of stirring and amount of non-solvent added. The marked increase in turbidity which when allowed to reach a maximum value is usually non-reproducible and meaningless. The co-precipitation which results is an effect of different kind of aggrega-

Table 6

Influence of Rate of Stirring and Time on Starting Concentration

Starting solution: 10 ml of 0.303 gm Standard C/100 ml B_W

Conductivity of water less than 3.72×10^{-6} B_W

*Minimum degree of stirring

% CH_3OH added	Time to Reach Max Turbidity (hrs)	Maximum Turbidities			
		7000	6000	5000	4000
83.30	∿6.0	0.014	0.024	0.043	0.082
85.70	∿3.0	0.106	0.144	0.211	0.345
87.50	∿4.0	0.101	0.137	0.200	0.328
88.90	∿4.0	0.075	0.110	0.184	0.328
90.00	∿2.0	0.069	0.101	0.174	0.304
90.90	∿2.0	0.058	0.088	0.145	0.260
*Maximum degree of stirring					
83.30	∿4.0	0.026	0.046	0.080	0.165
85.70	∿2.5	0.108	0.148	0.210	0.350
87.50	∿2.5	0.103	0.142	0.205	0.342
88.90	∿2.5	0.080	0.112	0.185	0.332
90.00	∿2.	0.070	0.100	0.173	0.302
90.90	∿1.	0.060	0.090	0.148	0.265
Starting Solution: 10 ml of 0.1 gm Standard C/100 ml B_W Maximum degree of stirring					
83.30	∿2.0	0.0060	0.0150	0.0260	0.054
85.70	∿1.0	0.0350	0.0490	0.0700	0.115
87.50	∿1.0	0.0325	0.0460	0.0670	0.110
88.90	∿1.0	0.0260	0.0370	0.0620	0.107
90.00	∿1.0	0.0230	0.0350	0.0580	0.100
90.90	∿0.8	0.0180	0.030	0.0480	0.089

tion clearly visible to the eye or coagulation, and the entire process of co-precipitation, the author classifies as "crossing of the point". Polymers with a high, high molecular weight tail are more prone to this behaviour, whereas polymer Standard C, the polymer which has been used to obtain the molecular weight-solubility distribution does not show this behaviour. The higher the concentration of the original polymer solution, the more difficult it is to control the rate of addition of non-solvent, even when the rate of addition was reduced to 0.025 ml per minute using special syringes. Despite several attempts made to eliminate "crossing of the point", by reducing the concentration of original polymer solution to as low as possible, and regulating the rate of stirring, and reducing the rate of addition to as low as possible, the maximum turbidity obtained at the initial stage of a single-stage cumulative titration was usually non-reproducible and meaningless. The amount of non-solvent added initially and the method of addition, added to good control of rate of addition, low original polymer concentration, rate of stirring, have been found to eliminate the problem of "crossing of the point" which is characteristic of polymers with high-high molecular weight tail end, not necessarily broad polymers. However, small differences in the above mentioned experimental variables, which will cause the particle size distribution to be non-reproducible at the initial stage of the titration, usually has little or no effect upon the maximum turbidity in the latter part of the titration, provided "crossing of the point" has not been crossed too far.

(d) Titrations were done at ambient conditions. To 10 ml of the polymer solutions in a standard 250 ml conical flask which has been allowed to stay for a while at ambient condition, are added slowly the non-solvent from a calibrated pipette or burette. After addition of non-solvent, the flask is well stoppered to prevent evaporation of non-solvent, which if allowed, produces a decrease in turbidity. The well-stoppered flask is placed at least one and half inches above the mechanical stirrer, allowed to reach ambient conditions and stirred. A thermometer placed within the vicinity of titration bench, recorded temperatures which varied from 21°C to 25°C. No attempts were made to use thermostats, since the maximum turbidities obtained were very reproducible to within 0.05% at the beginning of titration and 0.1% at the latter part of the titration, provided the flask is placed at least one inch from the mechanical stirrer. When the flask is placed directly on top of the mechanical stirrer, we have forced precipitation as indicated by an increase in the maximum turbidities obtained.

(e) Whether the titrations were carried out by the single-stage cumulative precipitation procedure or by using different polymer solutions for each point of the titration, that is, for each percent non-solvent added, as according to Beattie, it was found that the maximum turbidities obtained for each percent precipitant were exactly the same and reproducible. The only difference is that, at each point of the titration for a single-stage process which involves using the same original polymer solution for each point of the titration, the system must be given considerable length of time for the solution to reach maximum turbidity. This at least eliminates the problem of having to use a considerably large amount of polymer, in order to obtain its molecular weight distribution. Table 8 shows titrations carried out using different polymer solutions for each point of the titration. This is compared with Table 7 for the same concentration of original polymer but using the single-stage cumulative precipitation procedure. Tables 14 and 16 show likewise. If, then the same separation is obtained, the use of a different aliquot for each point of the titration just because it is clearly impossible to begin with big particles and end with small particles(39) is not necessary. Clearly it seems to contradict the entire separation process, since it is a well known fact that, at the beginning of any titration, the higher molecular weight species separate out first. With increasing amounts of non-solvent on incremental or sequential basis, increasing amounts of polymer are precipitated out according to their molecular weight. Finally at the end of the titrations, the lowest molecular weight species become insoluble. At this point, the turbidity is greatest and ideally all of the polymer is precipitated, but remains in suspension as very fine particles, especially when the solution is stirred. An alternative explanation to the method of maximum turbidity is presented in Appendix II.

Although, in general addition of non-solvent was done in series of 10 cc, not at the beginning of the titration could this be done, because of the problem of "crossing of the point". To overcome this problem, initially the non-solvent is added in aliquots of less than 1 cc, very slowly until the desired amount of non-solvent is in the flask. The rate of stirring should be reasonably slow and addition of non-solvent is along the sides of the flask, rather than dropwise. Dropwise addition seems to contribute most to the system's non-equilibrium conditions, resulting in co-precipitation and undesired kind of aggregation owing also probably to high local concentration of precipitant. The volume of non-solvent added at each step depended upon the molecular weight distribution of the sample. If this was very broad, then smaller steps were necessary than if it was not very broad. Also if the high molecular weight tail was very high, then very small steps were necessary than if it was moderately high.

(f) The maximum turbidities of the solution were measured in the wavelength range covering 3000 Å to 7000 Å. These values increase from 7000 Å to approximately 3000 Å. From about 3200 Å upwards, there seems to be some absorption of light by the particles due to the turbid suspension. At the beginning of the titration, when the rate of addition is not properly controlled, the suspension is bluish and there seems to be considerable absorption even at higher wavelengths up to 4000 Å. Under a well controlled condition, the maximum turbidity obtained at any point of a titration remains constant for a considerable length of time, even for as long as 3 days as shown in Table 11 or 13, so that the need to choose the wavelength to fit the growth rate of the particles, in order to obtain a convenient time to reach maximum turbidity is not necessary. The particles are allowed to grow with stirring, until they have reached their desired size. At this point, the turbidity is maximum. The length of time required to reach maximum turbidity depends on the point of the titration and the kind of polymer in terms of broadness and limit of the high molecular weight tail. The length of time is found to increase as the titration progresses up to about 20% above the mid-point of titration.

Table 7

Single-Stage Cumulative Titration Procedure

Starting solutions: 10 ml of 0.9765 gm/250 ml B_W

Single-Stage Cumulative Precipitation Technique

Non-solvent (ml)	Maximum Corrected Absorbances			
	Wavelengths (A)			
	7000	6000	5000	4000
45	0.0800	0.0900	0.1050	0.1430
50	-	-	-	-
60	0.2000	0.2800	0.4300	0.7130
65	0.2250	0.3000	0.4400	0.7200
70	0.2800	0.3850	0.5600	0.8530

Table 8

Non-continuous Titration Procedure

Independent Titrations Technique

Non-solvent (ml)	Maximum Corrected Absorbances			
	Wavelengths (A)			
	7000	6000	5000	4000
45	0.0820	0.0890	0.1030	0.1420
50	0.1060	0.1300	0.1970	0.2570
60	0.2050	0.2800	0.4150	0.7100
65	0.2270	0.3010	0.4370	0.7180
70	0.2820	0.3900	0.5580	0.8600

(g) Sometimes settling of the polymer particles on the walls of the flask due to stirring, created some problems as noticed by a sharp decrease in turbidity, long before the condition of maximum turbidity is reached. It should be borne in mind that the decrease in turbidity after the maximum turbidity is obtained is not sharp and is not due to settling of the kind or sedimentation, but rather due to particle size effect. The beginning of titration is more sensitive to this kind of settling than the middle and thereafter. This was a common problem when the original polymer solution was high. Among two of the steps taken to remove this problem was the use of greased flasks and occasional shaking by hand. Table 9 shows one kind of separation obtained using greased flasks for one kind of polyacrylamide. The important fact is that even though the separation is not representative of the molecular weight distribution of the polymer concerned, the maximum turbidities are quite reproducible. Instead of the polymer particles settling on the walls of the flask, they form a coagulant which is not desired as noticed by the increase in maximum turbidities.

From the above considerations evolved the standard general procedure which was finally applied to all the different kinds of polyacrylamide and form the basis of turbidimetric titration technique.

5.3.2 Standard Procedure

A known volume usually 10 cc of the polymer solution having a concentration in the range 0.025% to .7% wt is placed in a 250 ml standard concical flask at ambient condition. Apart from the fact that the limit of concentration was set by taking into account the above mentioned considera-

Table 9

Turbidimetirc Data for one Particular Case of a Greased Vessel

Polyacrylamide wt-%	CH_3OH		Maximum Absorbances			
	cc	%	Wavelengths (Å)			
			7000	6000	5460	5000
I 2.5A	15		0.149	0.208	0.264	0.308
	30		0.084	0.120	0.152	0.182
	40		0.051	0.096	0.132	0.156
	50		0.065	0.084	0.105	0.123
	60		0.065	0.083	0.101	0.112
	70		0.076	0.094	0.106	0.123
	80		0.070	0.084	0.098	0.112
	90		0.067	0.082	0.094	0.105
	100		0.064	0.076	0.089	0.102
	110		0.060	0.070	0.081	0.092
	120		0.054	0.065	0.076	0.086
	130		0.050	0.058	0.071	0.077
	140		0.049	0.056	0.068	0.077
	150		0.047	0.055	0.065	0.074
	160		0.047	0.055	0.065	0.073
	180		0.041	0.048	0.056	0.064
	200		0.037	0.044	0.054	0.059
II 2.5A	15		0.144	0.196	0.236	0.284
	30		0.085	0.120	0.152	0.184
	40		0.051	0.098	0.132	0.158
	50		0.065	0.085	0.104	0.125
	60		0.061	0.078	0.100	0.113

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*High degree of settling of Polymer Particles in Masses (Coagulation) tions, the limit was also set by the limitations of the instrument.

After addition of non-solvent as already specified, the solution is stirred. Right from the point when the solution becomes turbid, the spectral turbidity is measured using a recorder. The spectral turbidity measurement is continued at intervals until the turbidity reaches a maximum value. The measurement of the spectral turbidity at intervals is done, by turning off the stirrer, transfering with a suction-provided pipette a part of the turbid suspension into a 1 cm optical cell which in turn is put into the cell compartment of the instrument. The absorbances are then displayed on a recorder at a range of wavelength covering 3000 Å - 7000 Å. The solution is then transferred back into the flask and stirrer turned on. The flask is well stoppered to prevent evaporation of non-solvent. As the measurement at interval proceeds, the increasing absorbance finally reaches a maximum value before beginning to decrease. At this point, a new known volume of non-solvent is added to the solution and the same fashion of spectral turbidity measurement is continued until the maximum is reached. Addition of non-solvent is continued until precipitation of the whole polymer chain is completed. Before every spectral turbidity measurement, the instrument is always standardized against the suspending medium, which is a mixture of methanol and water. Since, however no difference could be distinguished from using a mixture of methanol and water, or methanol only or water only, water was used as the reference standard.

The volume of methanol added at the initial stage of the titration depends upon the molecular weigth distribution of the sample in the high molecular weight region. For cases in which the limit of the high molecular region is very high, the non-solvent was added until precipitation was detected. The process was repeated again, this time, however, the addition of precipitant stopped before precipitation was due to occur. The precipitation point was then approached in series of less than 1cc very slowly, with at least one to two minutes wait between steps. Once precipitation was fully underway, variation in the size of the steps did not modify the results, but there was a marked difference in the results if the onset of precipitation was crossed with too large a step.

While preliminary investigations showed that the separation obtained was dependent on the purity of the water, the polymer solutions for subsequent analysis were prepared using water A_W. All measurements were made at ambient conditions, and since the reproducibility obtained was excellent, no subsequent strigent temperature control was needed.

Reproducibilities were obtained by working at various starting polymer concentrations and using duplicates, triplicates, etc., where necessary when initial precipitation condition was difficult to control. In the Tables, numbers after alphabets, A, B, C, O, represent gms per liter of polymer solution except when specified.

5.4 GPC Measurements

A Waters ALC/GPC model 301 with five four-foot columns of the following specifications was used:

Bio-Glass	2500 Å
CPG-10	2000 Å

Porasil DX	400-800 Å
Porasil CX	200-400 Å
CPG	125-240-370 Å

Carrier solvent - water and room temperature

Sample concentration - 0.025 wt %

Flowrate - 3 ml/min

This column combination has been reported to give good resolution. Standard C or broad MWD standard was used to determine the GPC molecular weight calibration over a fairly broad range of molecular weights. Mark-Houwink constants are available for polyacrylamide in water(59) and have already been used to construct a universal calibration curve for GPC. The universal calibration curve may then be used when necessary to construct a molecular weight calibration curve. The calibration curve is then used to determine the MWD and molecular weight averages of other water soluble polyacrylamides.(63)

5.5 A Polyacrylamide Prepared in the Presences of $FeCl_3$/HCl in ACV Initiated Polymerization

5.5.1 Reagents

The supplied acrylamide monomer is a technical grade monomer which contains an appreciable amount of impurities which do not dissolve in chloroform as well as some visible dust particles. The monomer was twice recrystalized from chloroform,(64) first dissolving the monomer at 50°C and removing undissolved impurities by filtration. The filtrate was then cooled in an ice-bath with the precipitated solids washed with benzene and dried under vacuum at room temperature. Then the large flakes of crystalline acrylamide obtained were crushed into powder in a porcelain mortar and once more dried under vacuum for 24 hrs to further remove the remaining solvents. The purified acrylamide had a melting point of 84.5 ± 0.5°C; then stored in a desiccator over $CaSO_4$.

Water used for preparing aqueous solutions of reagents and final rinsing of the vials was simply distilled water. The initiator, 4,4' azobis-4-cyanovaleric acid

$$HOOC\text{-}CH_2\text{-}CH_2\text{-}C(CH_3)(CN)\text{-}N{=}N\text{-}C(CH_3)(CN)\text{-}CH_2\text{-}CH_2\text{-}COOH \quad (ACV)$$

was purchased from Aldrich Chemical Company Inc. Montreal, Quebec and had already been purified.(50)

The following reagents were used as received; chloroform (Maline-Kroft, Analytical Reagent), benzene, methanol, hydrochloric acid and hydroquinone (Eastern Chemical), and ferric chloride.

5.5.2 Analytical Techniques

Conversion of monomer to polymer was measured gravimetrically. The total reaction mixture in an ampoule was first diluted 20 times by addition of water together with a few drops of aqueous solution of hydroquinone(65) (∿ 0.1 gm/l). Then the solution was poured into methanol of least a ten-fold excess while stirring. The precipitated polymer was filtered on a sintered glass filter and dried under vacuum at 50°C for over 24 hrs. Conversion was calculated as the weight fraction of the recovered polymer to the weight of monomer initially present. Later the conversion was measured by injecting the diluted (0.025 wt %) polymer solution into a GPC, and measuring the area fraction of the polymer peak.

The number average and weight average molecular weights of the precipitated polymers were calculated from the chromatograms and measured intrinsic viscosities using Eq. 2.1.3, known to be most reliable. Viscosity measurements are reported in Appendix IV.

5.5.3 Apparatus and Procedure

Polymerization reactions were carried out in Pyrex glass ampoules shown in Figure 18, without the need of deaerating since kinetic studies were not the purpose. The monomer, initiator and $FeCl_3$/hydrochloric acid of known concentrations were charged into the ampoules, and put into a water bath maintained at 25°C. After a considerable length of time, the ampoules (all) were removed and reactions quenched by thrusting the ampoules into liquid nitrogen.

5.5.4 Experimental Conditions and Results

Polymerizations were carried out at a temperature of 25°C, monomer concentration, 2.252 (mole/liter) and initiator concentration, 7.14×10^{-4} (mol/l), concentration of $FeCl_3$, 1×10^{-5} (mole/l) and hydrochloric acid concentration, 0.05 mol/l.

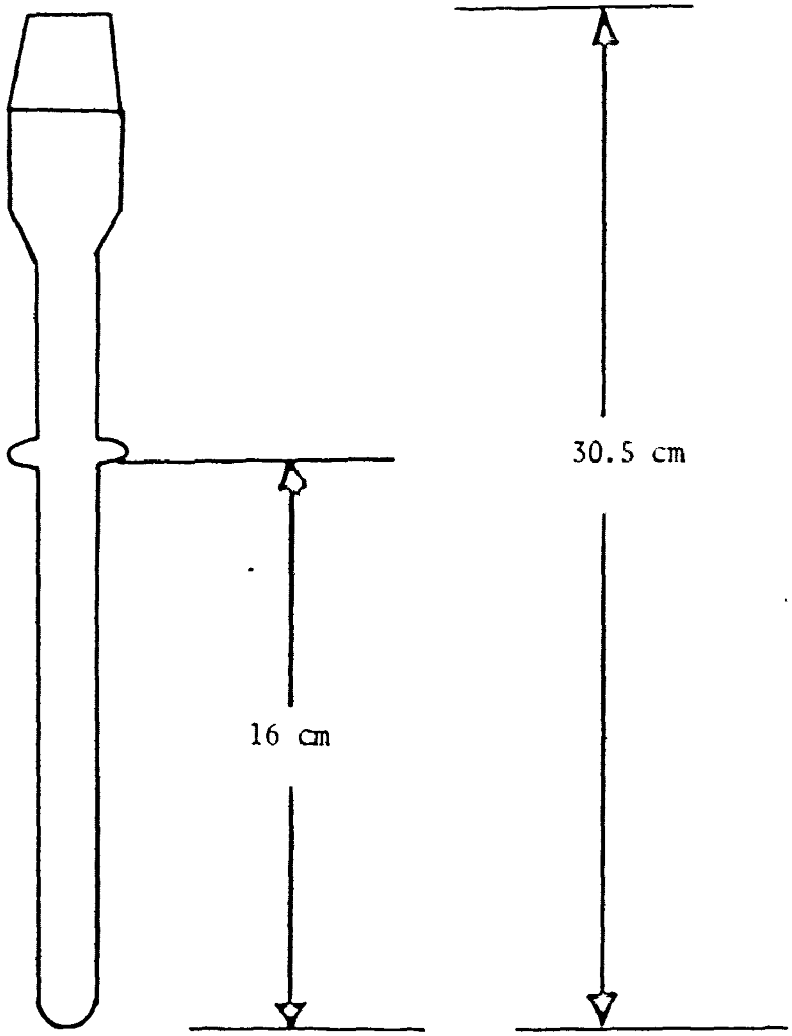
Table 10 lists the measured conversions for three such runs.

Table 10

Summary of Runs

Reaction Time (hrs)	Measured Conversion
96	1.000
96	0.98
96	0.99

Fig. 18: Dimension of Pyrex Ampoules Used.



I.D. = 5.5 mm

CHAPTER 6

PRESENTATION OF DATA

6.1 Molecular Weight Distribution Analysis

The sequence of steps involved for obtaining the molecular weight distribution of any polymer has been displayed in Figure 20. In this method, one broad polymer Standard C, whose molecular weight distributions, has been determined via GPC was used for obtaining the solubility-molecular weight distribution curve. This molecular weight-solubility distribution is a calibration curve from which molecular weight distribution of any polyacrylamide can be easily obtained for the particular solvent/non-solvent system. In principle, the method is capable of giving the molecular weight distribution of any polymer, provided a polymer sample of well characterized molecular weight called polymer standard is available to construct a calibration curve of molecular weight vs. per cent non-solvent.

6.2 Solubility-Molecular Weight Relationships

Molecular weight of any polymer precipitating at any moment has been assumed to depend on(48)

(i) The saturation composition of the solution appropriate to that molecular weight.

(ii) The particular stage of the titration.

Effect of concentrations on the saturation limit has been studied using different starting concentrations and noting the per cent of precipitant at which precipitation starts. Figures 19 shows the plots of concentration of polymer remaining unprecipitated versus volume fraction of precipitant and plots or initial concentration of polymer solution versus per cent non-solvent required to precipitate 50 per cent of polymer or begin precipitation. In all cases, there seems to be an independent relationship. This interesting observation is not surprising in view of the fact that the molecular weight of the polymers concerned are of the order of millions.(45)(48) Hence the molecular weight of any polymer precipitating at any moment is found to depend on the particular stage of the titration.

This particular stage may be represented by the volume fraction of non-solvent in the mixture, ψ_2 given by

$$\psi_2 = \frac{V}{V_o + V} \qquad 6.2.1$$

where V is the volume of non-solvent and V_o is the volume of solvent. We then have

$$M = M(\psi_2) \qquad 6.2.2$$

where M is the molecular weight of polymer precipitated for a volume fraction of non-solvent ψ_2. Equation 6.2.2 is the solubility-molecular weight relationship. Standard C, with theoretical differential MWD,

$$W(M) = \frac{M}{\bar{M}_n^{\,2}} \exp\left(-\frac{M}{\bar{M}_n}\right) \qquad 6.2.3$$

Fig. 19: Independence of Starting Polymer Concentration on the % Precipitant Required to Precipitate 50% of Polymer.

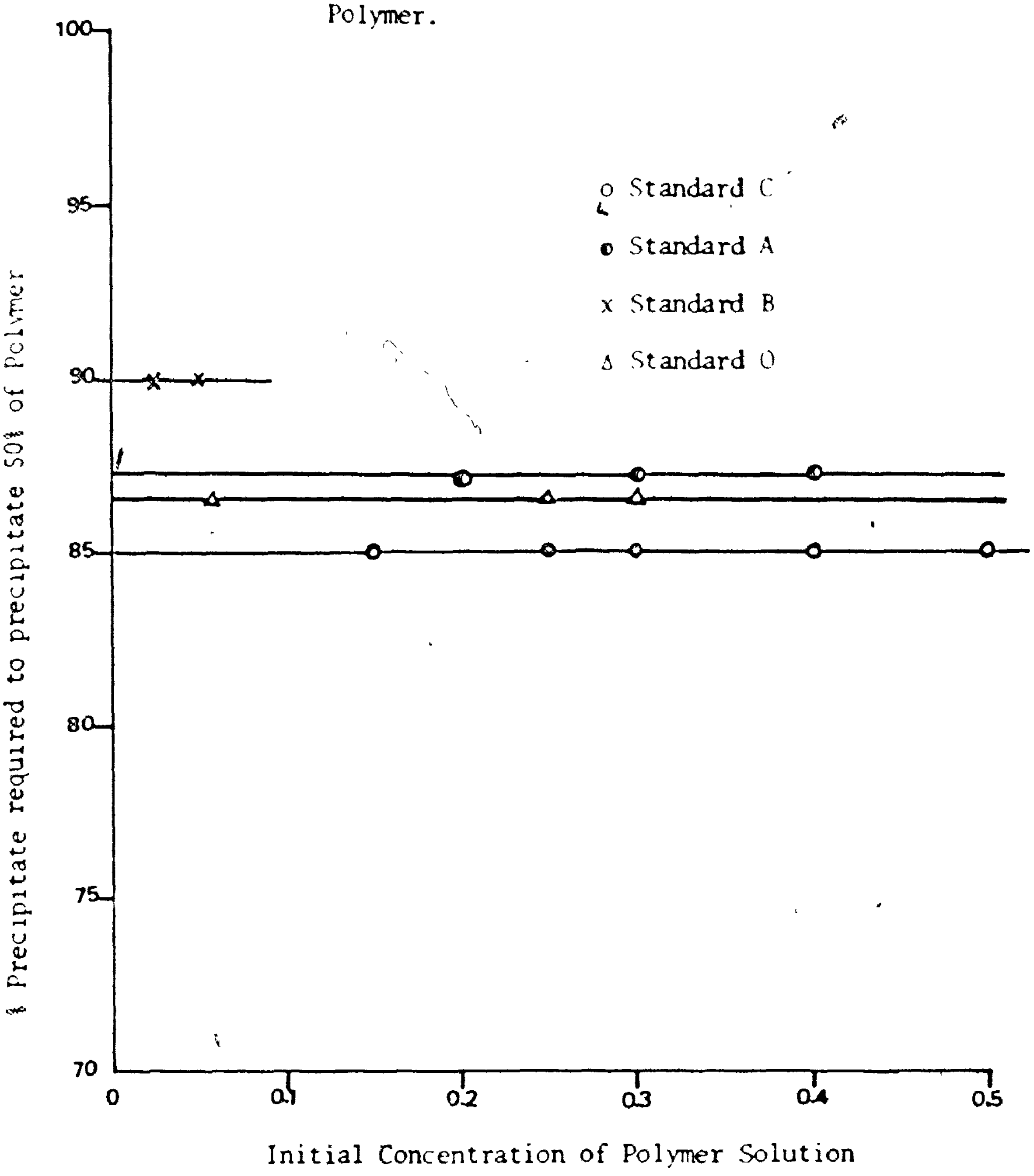
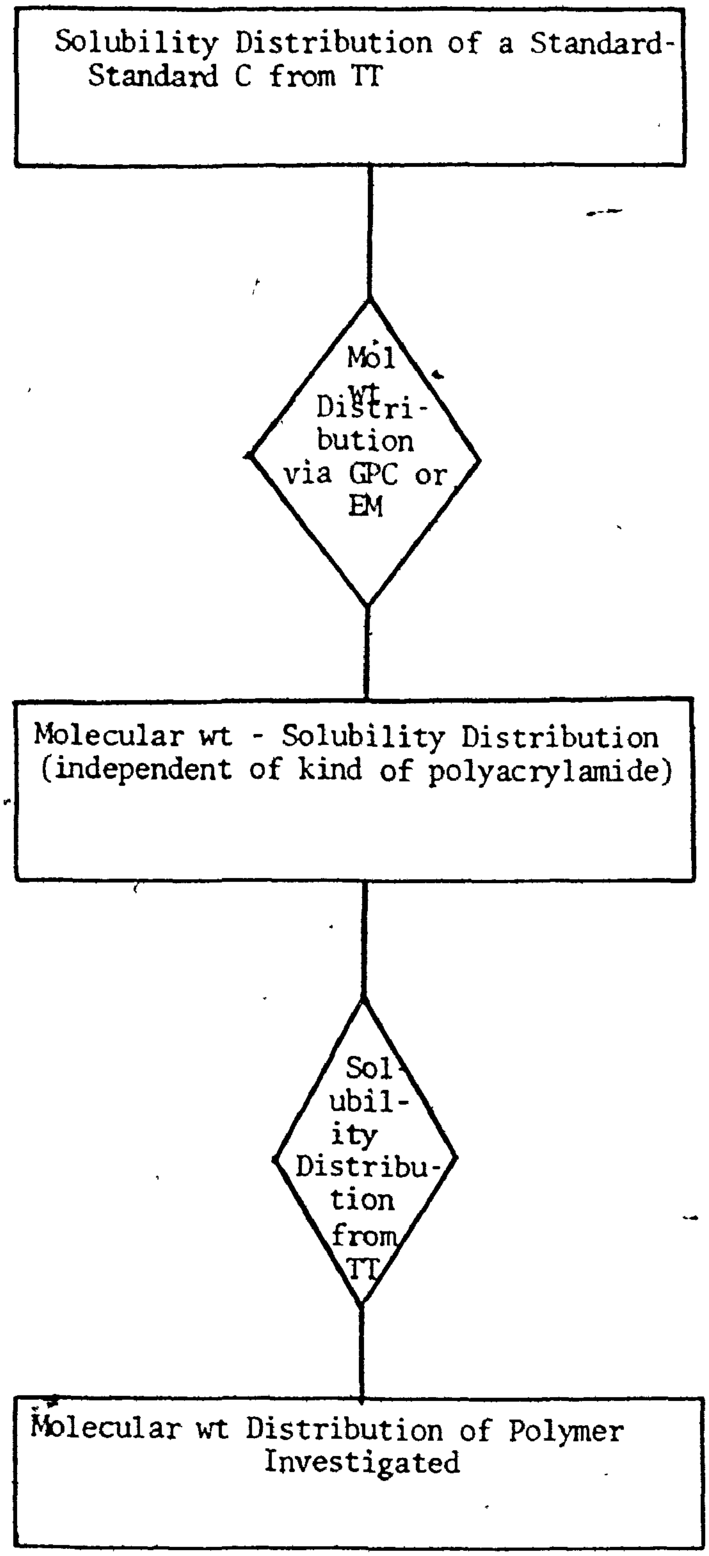


Fig. 20: The Sequence of Steps Involved.



EM = Electron Microscope

where W(M) is weight fraction and

$$\bar{M}_n = 2.4 \times 10^6, \ \bar{M}_w = 5.83 \times 10^6$$

was used to find the general molecular weight-solubility calibration curve as follows:

(1) Different concentrations of Standard C ranging from 0.25 - 0.7 wt % were prepared and used for TT. In Tables 11 - 16 are displayed the corrected maximum absorbances for dilution by the precipitant to 100 per cent precipitation and beyond.

(2) These values are plotted in Figures 21 - 27 against per cent non-solvent added. At 100 per cent precipitation, the amount of polymer precipitated is equivalent to the original concentration of polymer solutions. The corresponding maximum absorbances obtained as shown in the Figures were used to obtain the calibration constants in accordance with Eq. 4.3.6.

(3) The calibration constants were then used to obtain the solubility distributions shown in Figures 28 - 34 and Tables 17 - 21. The reproducibilities obtained at different wavelengths are extremely remarkable. This depends very much on the specific turbidities obtained at 100% precipitation as shown in Table 22. The specific turbidities at 100% precipitation obtained graphically were compared with the values obtained by averaging from 160 ml non-solvent added as shown in Tables 23 to 28 for the different concentrations used.

(4) Standard C was then injected into the GPC, in order to obtain the molecular weight-cumulative distribution. Standard C was injected

Table 11

Maximum Absorbances in a Single-Stage Cumulative Precipitation for C-0.7 wt %

Polyacrylamide wt %	CH_3OH added cc		Maximum and Corrected Absorbances				
			Wavelength Å				
			7000	6000	5460	5000	4000
0.700	50	A_m	0.067	0.075	0.088	0.101	0.140
		A_c	0.402	0.450	0.528	0.606	0.840
	60	A_m	0.089	0.110	0.125	0.143	0.201
		A_c	0.623	0.770	0.875	1.001	1.404
	70	A_m	0.120	0.147	0.179	0.212	0.300
		A_c	0.960	1.176	1.432	1.695	2.400
	80	A_m	0.115	0.134	0.164	0.192	0.280
		A_c	1.035	1.206	1.476	1.728	2.520
	90	A_m	0.122	0.145	0.170	0.194	0.277
		A_c	1.220	1.450	1.700	1.940	2.770
	100	A_m	0.121	0.138	0.164	0.184	0.265
		A_c	1.331	1.518	1.804	2.024	2.915
	110	A_m	0.124	0.144	0.172	0.194	0.280
		A_c	0.148	1.728	2.064	2.328	3.360
	120	A_m	0.130	0.149	0.176	0.210	0.296
		A_c	1.690	1.937	2.288	2.940	3.842
	130	A_m	0.140	0.162	0.185	0.202	0.301
		A_c	1.960	2.268	2.590	3.030	4.214
	140	A_m	0.134	0.154	0.180	0.201	0.296
		A_c	2.010	2.310	2.700	3.216	4.440
	150	A_m	0.132	0.155	0.178	0.191	0.285
		A_c	2.112	2.480	2.848	3.247	4.560

......continued

Table 11 (continued)

Maximum Absorbances in a Single-Stage Cumulative Precipitation for C-0.7 wt%

Poly-acrylamide wt %	CH_3OH added cc		Maximum and Corrected Absorbances				
			Wavelenghts Å				
			7000	6000	5460	5000	4000
0.700	160	A_m	0.125	0.146	0.162	0.191	0.268
		A_c	2.125	2.482	2.890	3.247	4.548
after 2 weeks	170	A_m	0.117	0.135	0.156	0.178	0.250
		A_c	2.106	2.430	2.808	3.204	4.536
	180	A_m	0.110	0.131	0.152	0.174	0.250
		A_c	2.090	2.489	2.888	3.306	4.750
	190	A_m	0.106	0.124	0.144	0.164	0.242
		A_c	2.120	2.480	2.880	3.280	4.840
	200	A_m	0.104	0.120	0.140	0.160	0.231
		A_c	2.184	2.520	2.940	3.360	4.841
	210	A_m	0.098	0.112	0.132	0.152	0.220
		A_c	2.156	2.464	2.904	3.344	4.840
	220	A_m	0.095	0.108	0.128	0.148	0.202
		A_c	2.185	2.484	2.944	3.404	4.646
	230	A_m	0.088	0.104	0.122	0.132	0.200
		A_c	2.112	2.496	2.928	3.360	4.800
	240	A_m	0.085	0.097	0.116	0.119	0.188
		A_c	2.100	2.425	2.900	3.175	4.700
	250	A_m	0.083	0.093	0.108	0.124	0.183
		A_c	2.158	2.418	2.808	3.224	4.758
	260	A_m	0.080	0.090	0.104	0.117	0.173
		A_c	2.160	2.430	2.808	3.159	4.671
	280	A_m	0.070	0.084	0.097	0.109	0.151
		A_c	2.030	2.349	2.813	3.161	4.553
	300	A_m	0.065	0.076	0.091	0.103	0.148
		A_c	2.015	2.356	2.821	3.193	4.588

Table 12

Maximum Absorbances in a Single-State Cumulative Precipitation for IIC-0.5 wt %

Poly-acry-lamide wt %	CH_3OH added cc		Maximum and Corrected Absorbances				
			Wavelength Å				
			7000	6000	5460	5000	4000
0.511	50	A_m	0.048	0.057	0.0625	0.073	0.105
		A_c	0.288	0.342	0.375	0.438	0.630
	60	A_m	0.065	0.063	0.078	0.090	0.110
		A_c	0.455	0.441	0.546	0.630	0.770
	70	A_m	0.093	0.120	0.134	0.160	0.218
		A_c	0.744	0.960	1.072	1.280	1.744
	80	A_m	0.089	0.110	0.127	0.145	0.200
		A_c	0.801	0.990	1.143	1.305	1.800
	90	A_m	0.093	0.110	0.127	0.145	0.213
		A_c	0.930	1.100	1.270	1.450	2.125
	100	A_m	0.088	0.107	0.120	0.137	0.196
		A_c	0.968	1.133	1.320	1.507	2.151
	110	A_m	0.092	0.108	0.125	0.141	0.216
		A_c	1.104	1.296	1.500	1.692	2.586
	120	A_m	0.095	0.111	0.131	0.148	0.218
		A_c	1.235	1.443	1.703	1.924	2.828
	130	A_m	0.100	0.120	0.140	0.156	0.225
		A_c	1.400	1.680	1.960	2.184	3.150
	140	A_m	0.103	0.120	0.141	0.163	0.228
		A_c	1.550	1.800	2.115	2.445	3.413

......continued

Table 12 (continued)

Maximum Absorbances in a Single-State Cumulative Precipitation for IIC-0.5 wt %

wt %	cc		7000	6000	5460	5000	4000
0.50II	150	A_m	0.098	0.116	0.132	0.151	0.214
		A_c	1.568	1.856	2.112	2.416	3.424
	160	A_m	0.094	0.108	0.126	0.144	0.210
		A_c	1.598	1.836	2.142	2.448	3.562
	170	A_m	0.088	0.102	0.117	0.130	0.192
		A_c	1.584	1.836	2.106	2.340	3.447
	180	A_m	0.082	0.096	0.112	0.123	0.183
		A_c	1.558	1.824	2.128	2.337	3.449
	190	A_m	0.078	0.092	0.106	0.116	0.177
		A_c	1.560	1.840	2.120	2.320	3.530
	200	A_m	0.075	0.087	0.102	0.117	0.166
		A_c	1.575	1.827	2.142	2.457	3.476
	210	A_m	0.071	0.082	0.096	0.110	0.157
		A_c	1.562	1.804	2.112	2.420	3.454
	220	A_m	0.068	0.080	0.095	0.108	0.155
		A_c	1.564	1.840	2.185	2.484	3.554
	230	A_m	0.065	0.077	0.090	0.101	0.141
		A_c	1.560	1.848	2.160	2.424	3.384
	240	A_m	0.062	0.074	0.087	0.101	0.138
		A_c	1.550	1.850	2.125	2.525	3.450
	250	A_m	0.058	0.070	0.084	0.090	0.132
		A_c	1.508	1.820	2.184	2.340	3.419
	300	A_m	0.047	0.056	0.065	0.075	0.112
		A_c	1.457	1.736	2.015	2.325	3.457
After 3 days	250		0.058	0.070	0.083	0.091	0.132
After 2 wks	250		0.058	0.072	0.083	0.093	0.140

Table 13

Maximum Absorbances in a Single-Stage Cumulative Precipitation for IC-0.5 wt %

Poly-acrylamide wt %	CH_3OH added cc		Maximum and Corrected Absorbances				
			Wavelengths Å				
			7000	6000	5460	5000	4000
0.5I	50	A_m	-	-	-	-	-
		A_c	-	-	-	-	-
	60	A_m	-	-	-	-	-
		A_c	-	-	-	-	-
	70	A_m	0.094	0.118	0.134	0.162	0.218
		A_c	0.752	0.944	1.072	1.296	1.744
	80	A_m	0.089	0.108	0.127	0.145	0.200
		A_c	0.801	0.972	1.143	1.305	1.800
	90	A_m	0.925	0.110	0.131	0.149	0.213
		A_c	0.925	1.100	1.310	1.490	2.125
	100	A_m	0.087	0.103	0.122	0.140	0.196
		A_c	0.957	1.133	1.342	1.540	2.151
	110	A_m	0.091	0.107	0.126	0.145	0.205
		A_c	1.092	1.284	1.512	1.740	2.460
	120	A_m	0.094	0.110	0.128	0.149	0.219
		A_c	1.222	1.430	1.664	1.937	2.841
	130	A_m	0.100	0.118	0.130	0.160	0.225
		A_c	1.400	1.652	1.820	2.240	3.150
	140	A_m	0.104	0.116	0.135	0.156	0.228
		A_c	1.560	1.740	2.025	2.340	3.420
0.50I	150	A_m	0.098	0.115	0.134	0.152	0.215
		A_c	1.568	1.840	2.144	2.432	3.440
	160	A_m	0.093	0.108	0.124	0.143	0.197
		A_c	1.581	1.836	2.108	2.431	3.349

......continued

Table 13 (continued)

Maximum Absorbances in a Single-Stage Cumulative Precipitation for IC-0.5 wt %

wt %	cc		7000	6000	5460	5000	4000
	170	A_m	0.086	0.100	0.119	0.134	0.188
		A_c	1.548	1.800	2.142	2.412	3.384
	180	A_m	0.082	0.096	0.114	0.130	0.182
		A_c	1.558	1.824	2.166	2.470	3.458
	190	A_m	0.077	0.092	0.108	0.126	0.172
		A_c	1.540	1.840	2.160	2.520	3.440
	200	A_m	0.073	0.087	0.102	0.116	0.162
		A_c	1.533	1.827	2.142	2.436	3.402
	210	A_m	0.070	0.083	0.096	0.113	0.157
		A_c	1.540	1.826	2.112	2.486	3.454
	220	A_m	0.068	0.080	0.091	0.106	0.150
		A_c	1.564	1.840	2.093	2.438	3.450
	230	A_m	0.064	0.076	0.090	0.105	0.147
		A_c	1.536	1.824	2.160	2.520	3.528
	240	A_m	0.062	0.073	0.084	0.099	0.140
		A_c	1.550	1.825	2.100	2.475	3.500
	250	A_m	0.061	0.070	0.082	0.097	0.136
		A_c	1.585	1.820	2.132	2.522	3.536
	260	A_m	0.058	0.068	0.080	0.092	0.131
		A_c	1.566	1.836	2.160	2.484	3.537
	300	A_m	0.047	0.056	0.065	0.075	0.112
		A_c	1.457	1.736	2.015	2.325	3.457
After 3 days	300		0.047	0.057	0.065	0.075	0.112

Table 14

Maximum Absorbances in a Single-Stage Cumulative Precipitation for C-0.28

Poly-acry-lamide wt %	CH_3OH added cc		Maximum and Corrected Absorbances				
			Wavelengths Å				
			7000	6000	5460	5000	4000
0.280	50	A'_m	-	-	-	-	-
		A_c	-	-	-	-	-
	60	A_m	0.033	0.044	0.050	0.055	0.098
		A_c	0.231	0.308	0.350	0.385	0.683
	70	A_m	0.051	0.059	0.066	0.074	0.104
		A_c	0.408	0.472	0.528	0.592	0.832
	80	A_m	0.048	0.057	0.064	0.0745	0.119
		A_c	0.432	0.513	0.576	0.6705	1.071
	90	A_m	0.051	0.060	0.070	0.077	0.112
		A_c	0.510	0.600	0.700	0.770	1.120
	100	A_m	0.048	0.055	0.065	0.072	0.117
		A_c	0.528	0.605	0.715	0.792	1.282
	110	A_m	0.050	0.060	0.068	0.076	0.108
		A_c	0.600	0.720	0.816	0.912	1.290
	120	A_m	0.052	0.061	0.069	0.079	
		A_c	0.676	0.793	0.897	1.027	
	130	A_m	0.056	0.067	0.075	0.085	
		A_c	0.784	0.938	1.050	1.190	
	140	A_m	0.056	0.063	0.072	0.082	
		A_c	0.840	0.945	1.080	1.230	
	150	A_m	0.054	0.062	0.072	0.080	
		A_c	0.864	0.992	1.152	1.280	
0.28	160	A_m	0.051	0.058	0.067	0.075	
		A_c	0.867	0.986	1.139	1.275	

......continued

Table 14 (continued)

Maximum Absorbances in a Single-Stage Cumulative Precipitation for C-0.28

wt %	cc		7000	6000	5460	5000	4000
	170	A_m	0.048	0.055	0.064	0.073	
		A_c	0.864	0.990	1.152	1.314	
	180	A_m	0.045	0.052	0.061	0.069	
		A_c	0.855	0.988	1.159	1.311	
	190	A_m	0.043	0.050	0.057	0.065	
		A_c	0.860	1.000	1.140	1.300	
	200	A_m	0.040	0.047	0.055	0.062	
		A_c	0.840	0.987	1.155	1.302	
	210	A_m	-	-	-	-	
		A_c	-	-	-	-	
	220	A_m	0.037	0.043	0.051	0.056	
		A_c	0.851	0.989	1.173	1.288	
	230	A_m	-	-	-	-	
		A_c	-	-	-	-	
	240	A_m	0.034	0.040	0.045	0.050	
		A_c	0.850	1.000	1.125	1.250	
	250	A_m	0.033	0.038	0.044	0.048	
		A_c	0.858	0.988	1.144	1.248	
	270	A_m	0.030	0.035	0.040	0.045	
		A_c	0.840	0.980	1.120	1.260	
	300	A_m	0.027	0.031	0.037	0.040	
		A_c	0.837	0.961	1.147	1.240	

Table 15

Maximum Absorbances in a Single-Stage Cumulative Precipitation for C-0.307 wt %(IV3)

Polyacrylamide wt %	CH_3OH added cc		Maximum and Corrected Absorbances				
			Wavelengths Å				
			7000	6000	5460	5000	4000
0.307	50	A_m	-	-	-	-	-
		A_c	-	-	-	-	-
	60	A_m	0.036	0.048	0.051	0.054	0.079
		A_c	0.252	0.336	0.357	0.378	0.553
	70	A_m	0.059	0.069	0.08	0.092	0.130
		A_c	0.472	0.552	0.640	0.736	1.040
	80	A_m	0.054	0.063	0.075	0.085	0.123
		A_c	0.486	0.567	0.675	0.765	1.107
	90	A_m	0.055	0.068	0.076	0.088	0.125
		A_c	0.550	0.680	0.760	0.880	1.250
	100	A_m	0.054	0.063	0.074	0.082	0.117
		A_c	0.594	0.693	0.814	0.902	1.287
	110	A_m	0.056	0.066	0.078	0.085	0.122
		A_c	0.672	0.792	0.936	1.020	1.464
	120	A_m	0.058	0.068	0.080	0.090	0.130
		A_c	0.754	0.884	1.040	1.170	1.690
	130	A_m	0.063	0.072	0.085	0.097	0.143
		A_c	0.882	1.008	1.190	1.358	1.995
	140	A_m	0.061	0.070	0.081	0.094	0.134
		A_c	0.915	1.050	1.215	1.400	2.010
	150	A_m	0.060	0.070	0.080	0.090	0.130
0.307		A_c	0.960	1.120	1.280	1.440	2.080

......continued

Table 15 (continued)

Maximum Absorbances in a Single-Stage Cumulative Precipitation for C-0.307 wt% (IV3)

wt %	cc		7000	6000	5460	5000	4000
	160	A_m	0.056	0.065	0.077	0.083	0.118
		A_c	0.952	1.020	1.309	1.411	2.006
	170	A_m	0.053	0.061	0.074	0.080	0.112
		A_c	0.954	1.098	1.332	1.440	2.016
	180	A_m	0.050	0.059	0.070	0.078	0.110
		A_c	0.950	1.121	1.330	1.482	2.090
	190	A_m	0.048	0.056	0.066	0.073	0.103
		A_c	0.960	1.120	1.320	1.460	2.060
	200	A_m	0.046	0.052	0.061	0.070	0.098
		A_c	0.966	1.092	1.281	1.470	2.058
	210	A_m	0.042	0.050	0.060	0.068	0.093
		A_c	0.946	1.100	1.320	1.496	2.046
	220	A_m	0.042	0.048	0.057	0.065	0.089
		A_c	0.966	1.104	1.311	1.495	2.047
	230	A_m	0.040	0.047	0.055	0.060	0.085
		A_c	0.960	1.128	1.320	1.440	2.040
	240	A_m	0.038	0.045	0.052	0.059	0.085
		A_c	0.950	1.125	1.300	1.475	2.113
	250	A_m	0.037	0.042	0.050	0.056	0.082
		A_c	0.962	1.092	1.300	1.456	2.119
	270	A_m	0.034	0.038	0.045	0.050	0.075
		A_c	0.952	1.064	1.260	1.400	2.100
	300	A_m	0.030	0.034	0.041	0.046	0.062
		A_c	0.930	1.054	1.271	1.426	2.093

Table 16

Data for Turbidimetric Titrations of HC 2.5 Polyall 402

Polyacrylamide wt %	CH_3OH added cc		Maximum and Corrected Absorbances				
			Wavlengths (Å)				
			7000	6000	5460	5000	4000
0.25	50	A_m	0.024	0.028	0.032	0.037	-
		A_c	0.144	0.168	0.192	0.222	-
	60	A_m	-	-	-	-	-
		A_c	-	-	-	-	-
	70	A_m	0.046	0.055	0.063	0.075	0.104
		A_c	0.368	0.440	0.504	0.600	0.832
	80	A_m	0.043	0.052	0.060	0.072	0.105
		A_c	0.387	0.468	0.540	0.648	0.945
	90	A_m	0.045	0.056	0.062	0.074	0.105
		A_c	0.450	0.560	0.620	0.740	1.050
	100	A_m	0.043	0.052	0.059	0.068	0.100
		A_c	0.473	0.572	0.649	0.748	1.100
	110	A_m	0.046	0.054	0.064	0.072	0.105
		A_c	0.552	0.648	0.768	0.864	1.260
	120	A_m	0.047	0.055	0.065	0.076	0.108
		A_c	0.611	0.715	0.845	0.988	1.404
	130	A_m	0.051	0.056	0.072	0.080	0.113
		A_c	0.714	0.784	1.008	1.120	1.582
	140	A_m	0.052	0.062	0.072	0.083	0.120
		A_c	0.780	0.930	1.080	1.245	1.800
	150	A_m	0.049	0.057	0.066	0.076	0.108
		A_c	0.784	0.912	1.056	1.216	1.728
	160	A_m	0.047	0.054	0.061	0.071	0.105
		A_c	0.799	0.918	1.037	1.207	1.777

......continued

Table 16 (continued)

Data for Turbidimetric Titrations of HC 2.5 Polyall 402

wt %	cc		7000	6000	5460	5000	4000
0.25	170	A_m	0.044	0.051	0.061	0.072	0.099
		A_c	0.792	0.918	1.098	1.296	1.782
	180	A_m	0.041	0.048	0.055	0.066	0.094
		A_c	0.779	0.912	1.045	1.254	1.786
	190	A_m	0.039	0.046	0.052	0.067	0.088
		A_c	0.780	0.920	1.040	1.240	1.750
	200	A_m	0.037	0.044	0.051	0.058	0.083
		A_c	0.777	0.924	1.071	1.218	1.733
	210	A_m	0.035	0.041	0.049	0.056	0.081
		A_c	0.770	0.902	1.078	1.232	1.771
	220	A_m	0.034	0.040	0.047	0.051	0.077
		A_c	0.784	0.920	1.081	1.173	1.771
	230	A_m	0.032	0.038	0.044	0.051	0.070
		A_c	0.768	0.912	1.056	1.224	1.680
	240	A_m	0.031	0.037	0.042	0.050	0.070
		A_c	0.775	0.925	1.050	1.250	1.750
	250	A_m	0.030	0.035	0.041	0.048	0.067
		A_c	0.780	0.910	1.066	1.248	1.742
	280	A_m	0.027	0.031	0.036	0.041	0.062
		A_c	0.783	0.899	1.044	1.189	1.769
	300	A_m	0.024	0.029	0.033	0.036	0.058
		A_c	0.744	0.899	1.023	1.115	1.793

Fig. 21: Absorbances Corrected for Dilution Versus % Precipitant at 5000 Å. For Standard C.

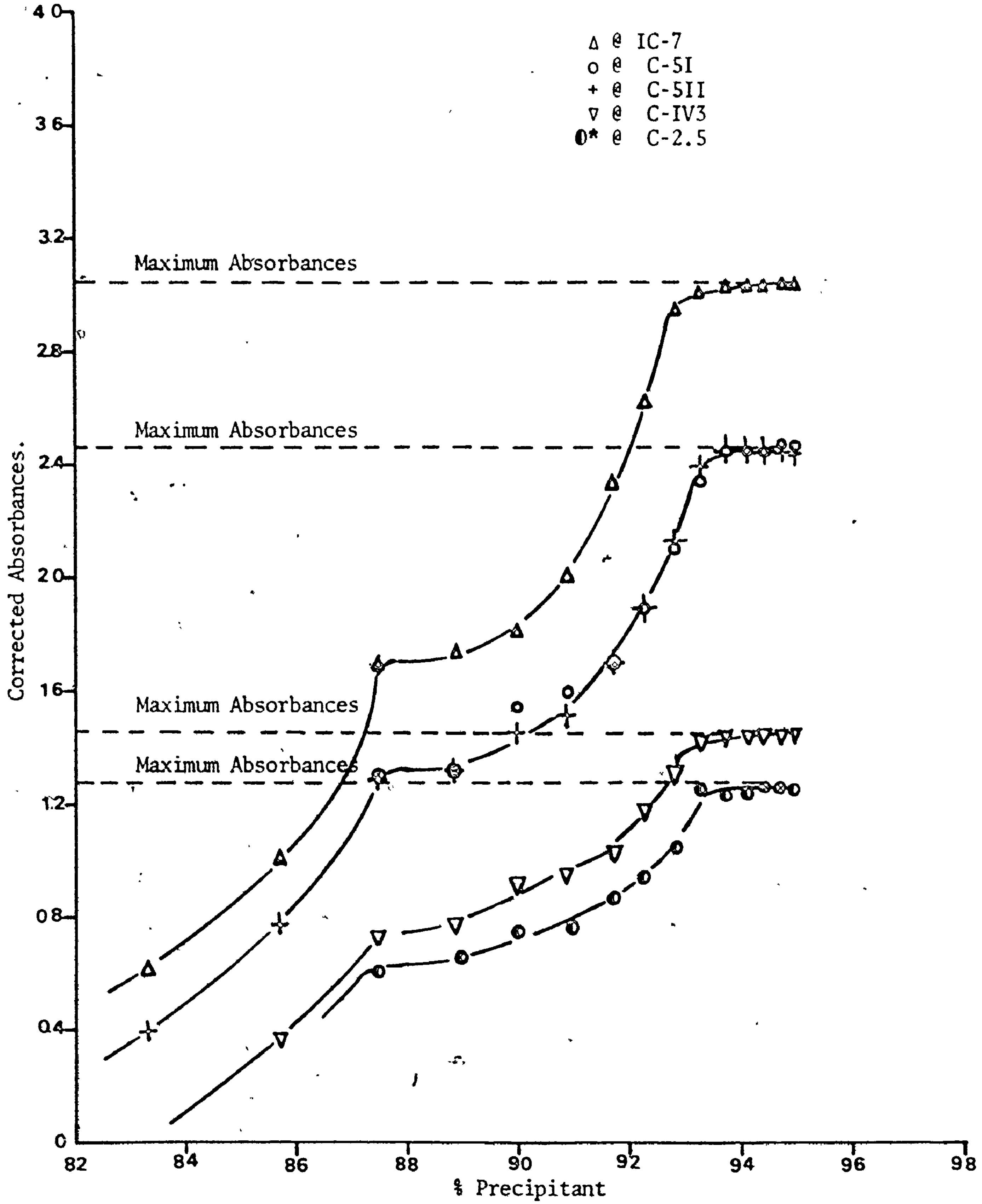


Fig. 22: Corrected Absorbances versus % Precipitant Added at 6000 Å.

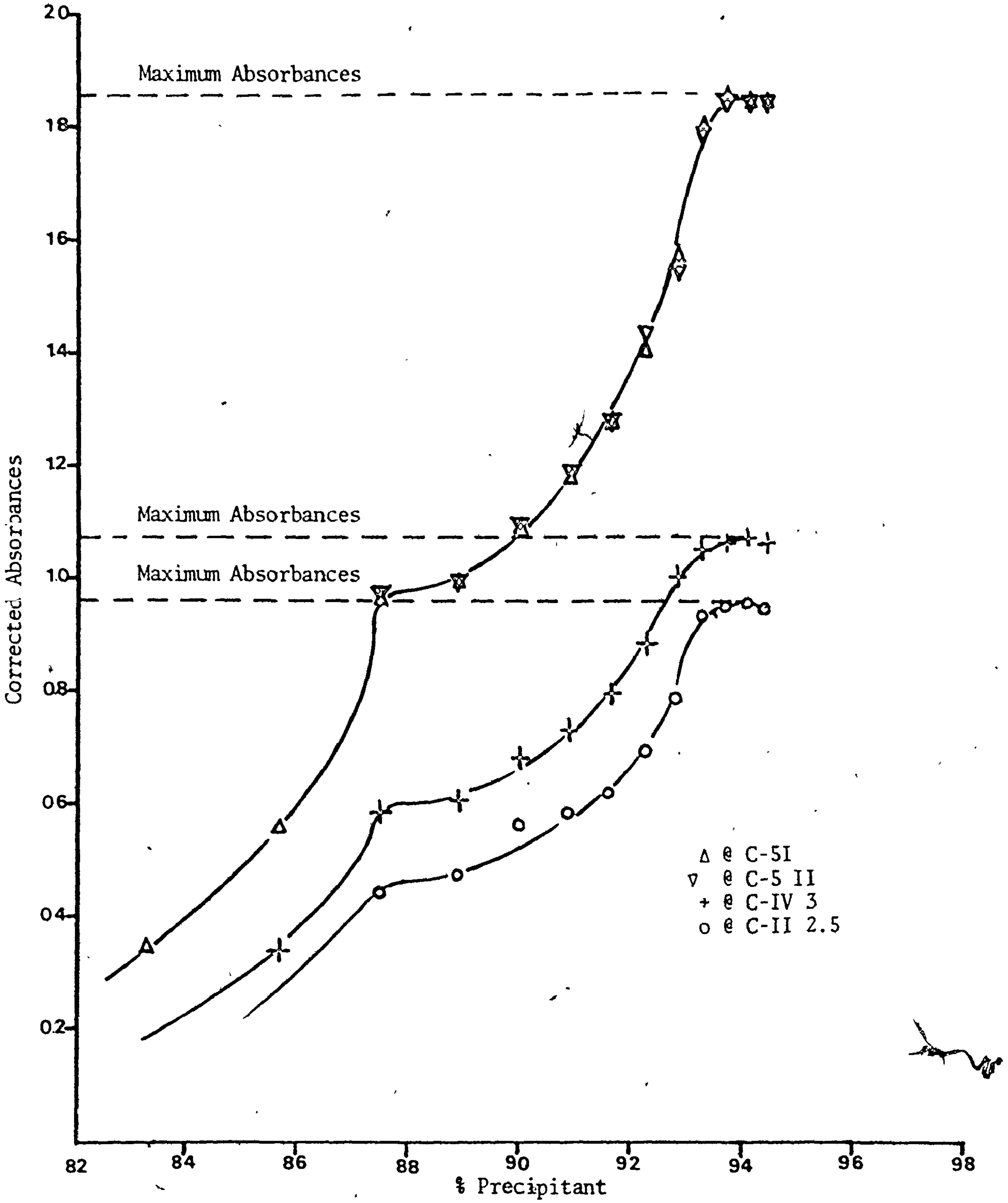


Fig. 23: Corrected Absorbances Due to Dilution Versus % Precipitant For C-2.8

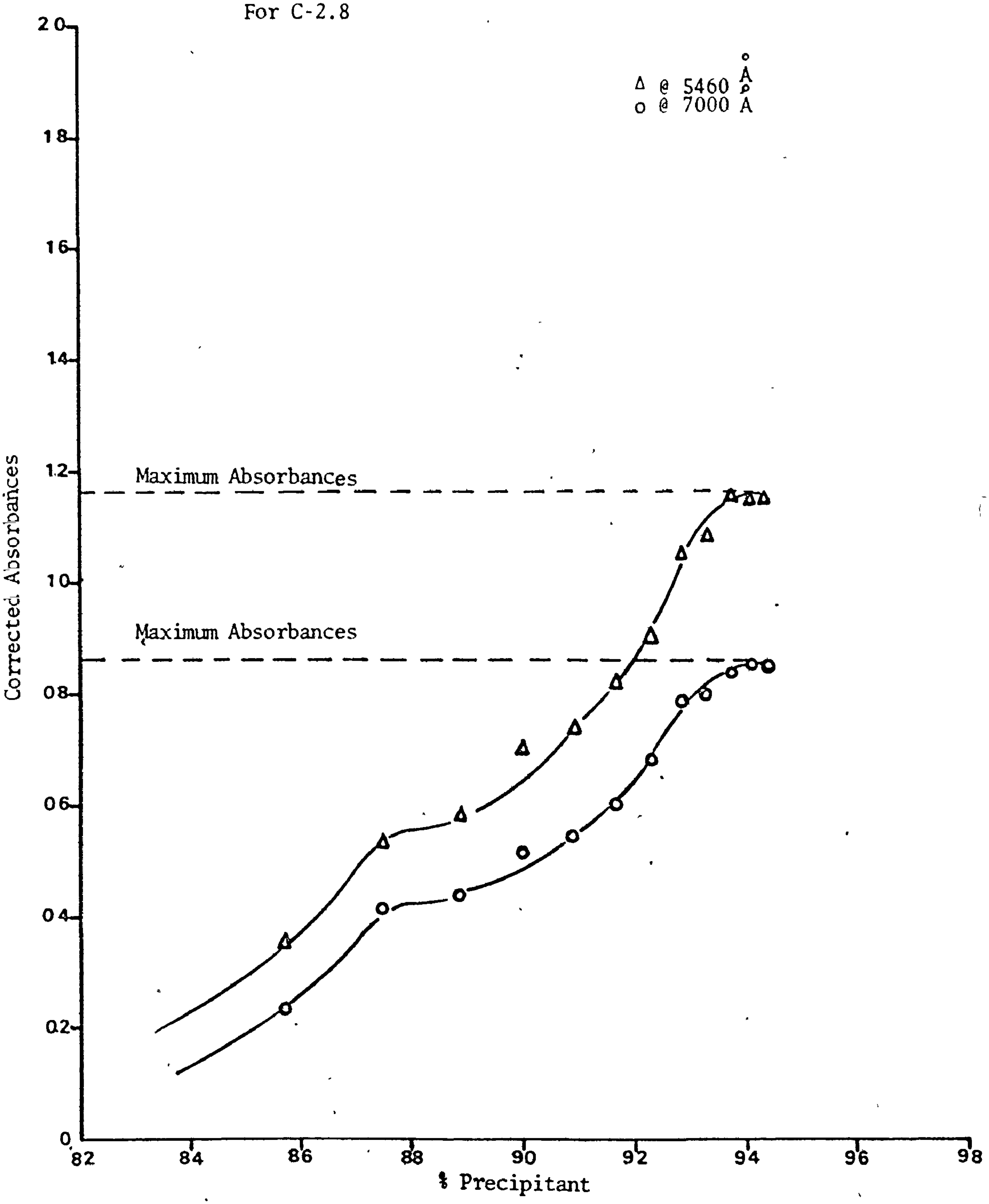
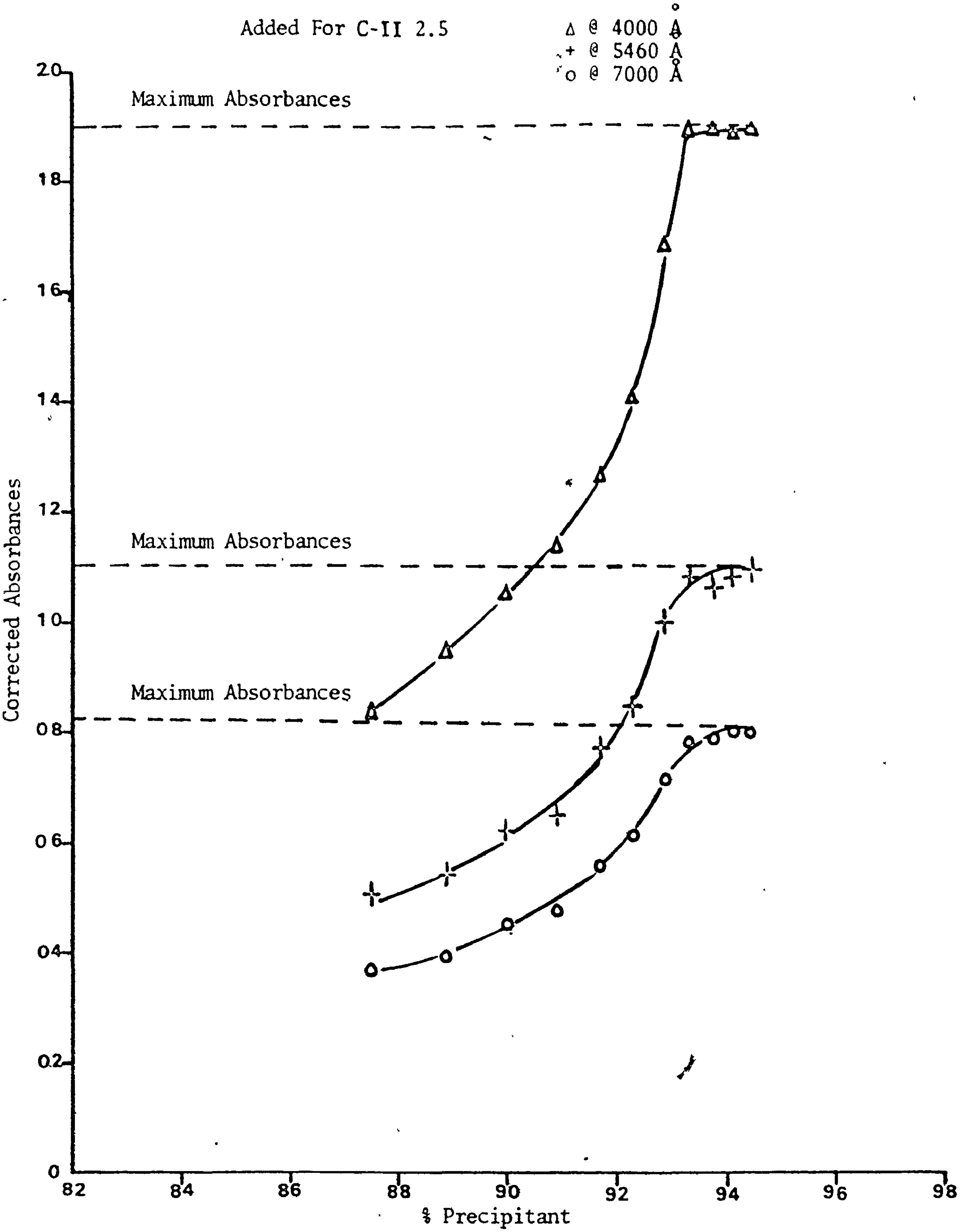


Fig. 24: Corrected Absorbances Due to Dilution Versus % Precipitant Added For C-II 2.5



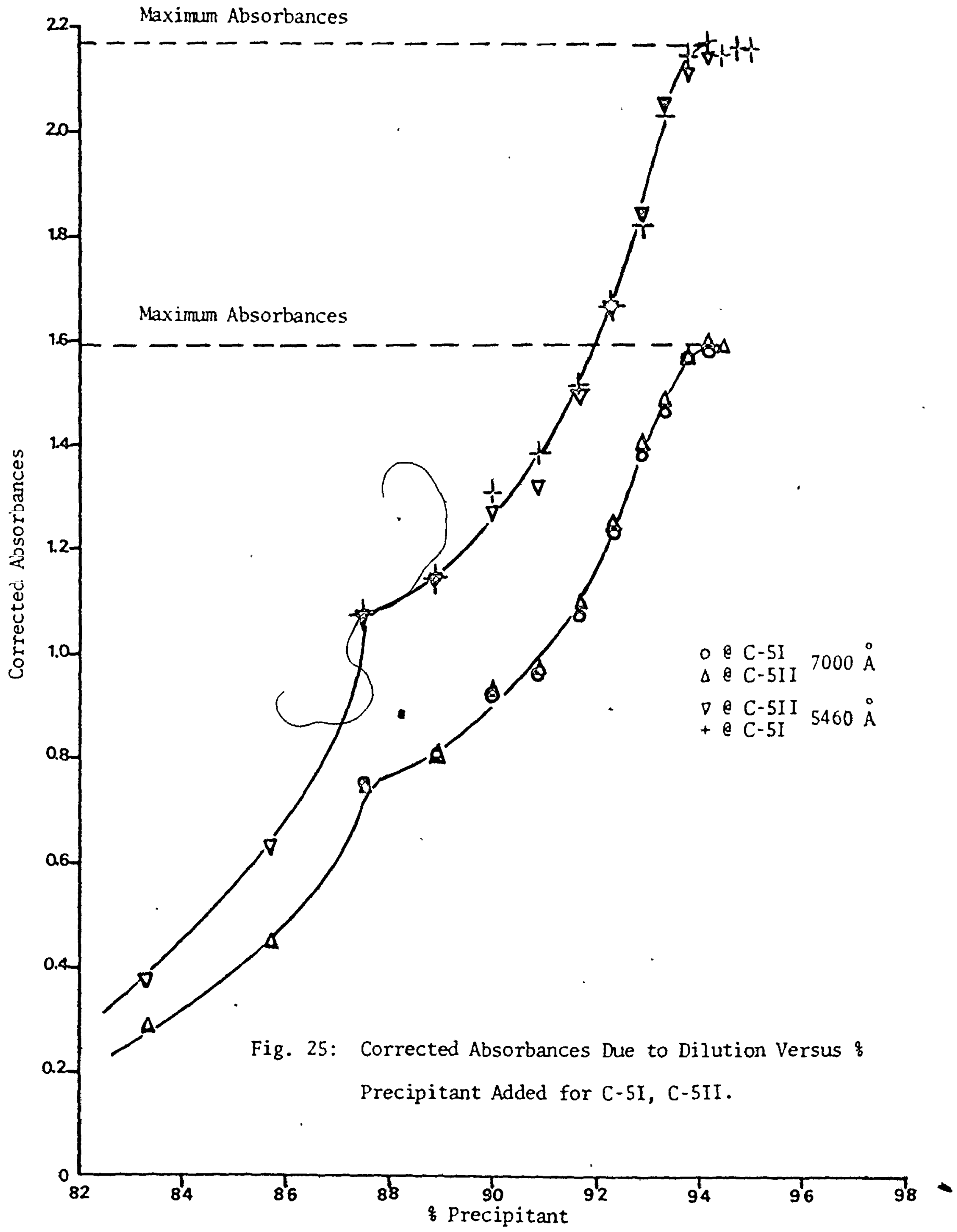
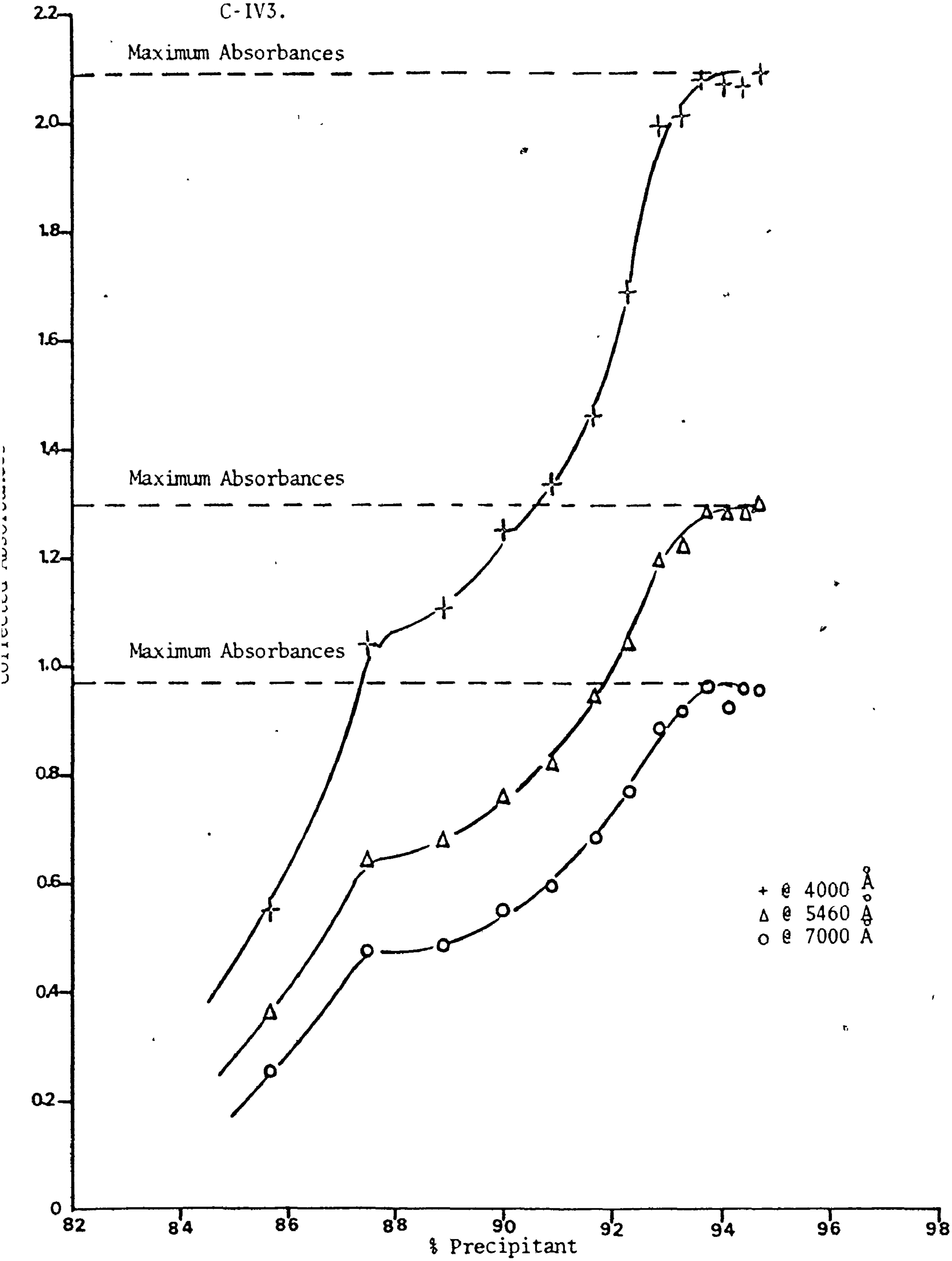


Fig. 25: Corrected Absorbances Due to Dilution Versus % Precipitant Added for C-5I, C-5II.

Fig. 26: Corrected Absorbances Due to Dilution Versus % Precipitant for C-IV3.



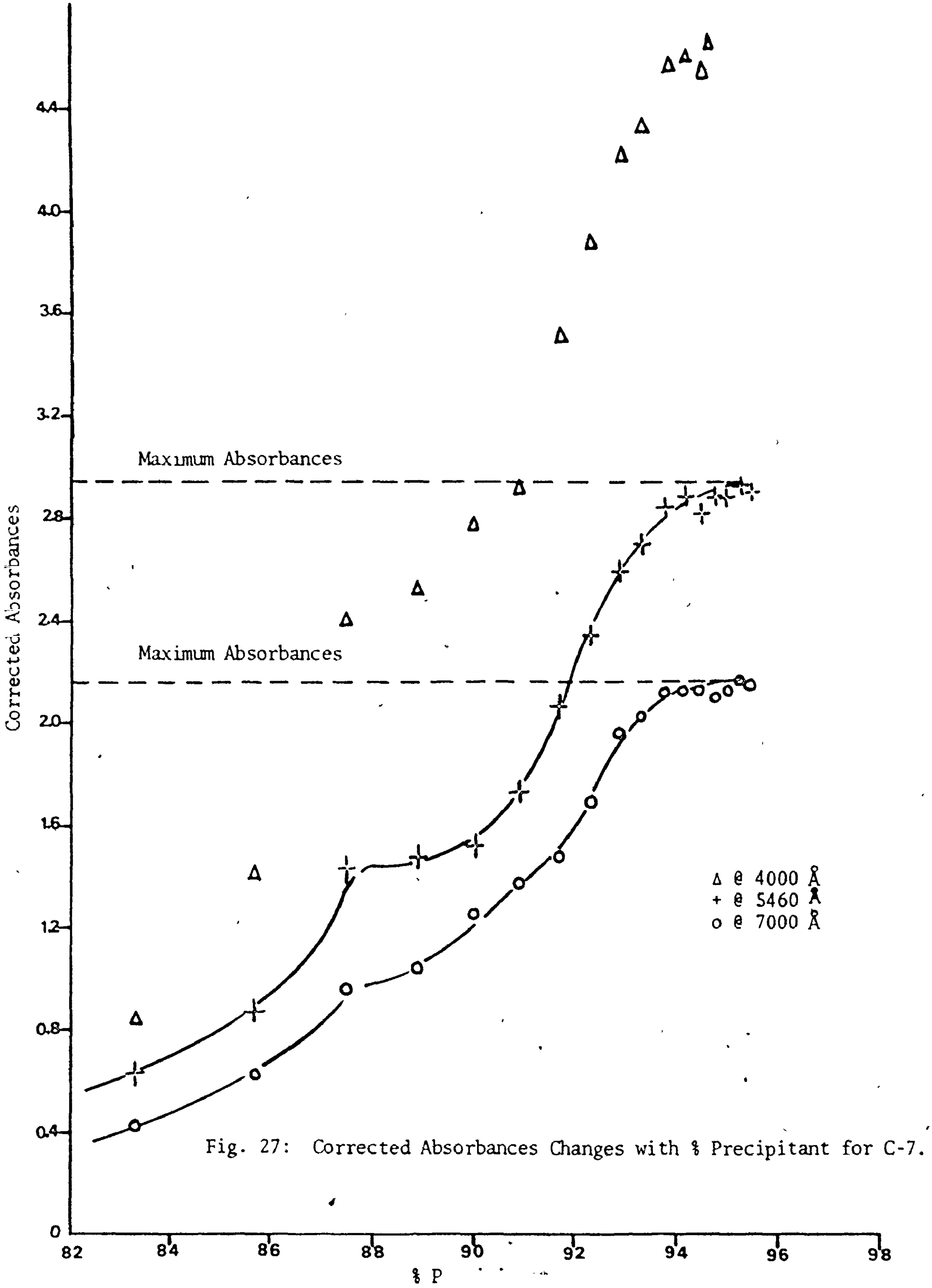


Fig. 27: Corrected Absorbances Changes with % Precipitant for C-7.

Table 17

Solubility Distribution for Standard C at 7000 Å

Sample no. Precipitant	C-2.5		C-2.8		C-3.07		C-5I	
	$cx10^{-4}$ (gm/ml)	wt %	$cx10^{-4}$	wt %	$cx10^{-4}$	wt %	$cx10^{-4}$	wt %
50	4.609	18.437	-	-	-	-	-	-
60	-	-	7.566	27.021	8.106	26.403	-	-
70	11.779	47.116	13.363	47.725	15.182	49.452	24.169	48.337
80	12.387	49.548	14.149	50.532	15.632	50.919	25.743	51.487
90	14.738	58.954	16.704	59.655	17.691	57.625	29.729	59.457
100	15.492	61.967	17.293	61.761	19.106	62.235	30.757	61.514
110	17.668	70.674	19.651	70.183	21.615	70.407	35.006	70.192
120	19.557	78.228	22.140	79.073	24.252	78.998	39.274	78.548
130	22.854	91.415	25.678	91.706	28.370	92.409	44.995	89.989
140	24.966	99.865	26.529	94.747	29.431	95.866	47.244	94.489
150	-	100.000	27.774	99.192	– -	100.000	-	100.000
65	-	-	-	-	-	-	-	-
75	-	-	-	-	-	-	-	-

......continued

Table 17 (Continued)

Solubility Distribution for Standard C at 7000 Å

Sample no. Precipitant	C-5II		C-7I		C-7II		C-7III	
	$cx10^{-4}$	wt %	$cx10^{-4}$	wt %	$cx10^{-4}$	wt %	$cx10^{-4}$	wt %
50	.216	18.433	13.236	18.910	-	-	-	-
60	14.560	29.121	20.513	29.304	20.282	28.975	21.204	30.292
70	23.809	47.617	31.609	45.156	31.872	45.532	32.926	47.037
80	25.633	51.266	34.078	48.683	-	-	34.967	49.953
90	29.761	59.522	41.158	58.795	-	-	-	-
100	30.977	61.954	43.825	62.606	-	-	-	-
110	35.329	70.658	48.994	69.991	-	-	-	-
120	39.521	79.042	55.645	79.493	-	-	-	-
130	44.801	89.603	64.535	92.193	-	-	-	-
140	47.521	95.043	66.181	94.545	-	-	-	-
150	-	100.000	69.540	99.342	-	-	-	-
65	-	-	-	-	-	-	31.115	44.450
75	-	-	-	-	-	-	33.585	47.978

Table 18

Solubility Distribution for Standard C at 6000 Å

	C-2.5		C-2.8		C-3.07		C-SAI	
50	4.600	18.399	-	-	-	-	-	-
60	-	-	8.711	31.111	9.297	30.283	-	-
65	-	-	-	-	-	-	-	-
70	12.047	48.187	13.350	47.677	15.273	49.750	25.783	51.567
75	-	-	-	-	-	-	-	-
80	12.813	51.253	14.509	51.818	15.688	51.102	26.548	53.096
90	15.332	62.329	16.970	60.606	18.815	61.286	30.044	60.089
100	15.661	62.643	17.111	61.111	19.175	62.458	30.946	61.891
110	17.742	70.966	20.364	72.728	21.914	71.381	35.070	70.140
120	19.576	78.304	22.428	80.101	24.459	79.672	39.058	78.115
130	23.382	93.527	26.529	94.748	27.890	90.847	45.121	90.242
140	-	100.000	26.727	95.455	29.052	94.639	48.754	97.507
150	-	-	-	100.000	-	100.000	-	100.000
160	-	-	-	-	-	-	-	-

......continued

Table 18 (continued)

Solubility Distribution for Standard C at 6000 Å

	C-5BII		C-7I		C-7II(Replicate)		C-7III(Triplicate)	
50	9.288	18.576	12.771	18.244	-	-	-	-
60	14.828	29.657	21.853	31.218	21.059	30.089	21.059	30.089
65	-	-	-	-	-	-	32.353	46.219
70	26.072	52.143	33.375	47.678	34.056	48.651	34.056	48.651
75	-	-	-	-	-	-	-	-
80	26.886	53.773	34.226	48.895	-	-	-	-
90	29.874	59.748	41.151	58.787	-	-	-	-
100	30.770	61.540	43.081	61.544	-	-	-	-
110	35.197	70.394	49.041	70.058	-	-	-	-
120	39.189	78.378	54.972	78.532	-	-	-	-
130	45.625	91.251	64.366	91.951	-	-	-	-
140	48.884	97.769	65.558	93.654	-	-	-	-
150	-	100.000	-	100.000	-	-	-	-
160	-	-	-	-	-	-	-	-

Table 19

Solubility Distribution for Standard C for 5460 Å

	C-2.5		C-2.8		C-3.07		C-SAI	
50	-	-	-	-	-	-	-	-
60	-	-	8.552	30.541	8.4138	27.406	-	-
65	-	-	-	-	-	-	-	-
70	11.917	47.668	12.901	46.074	15.084	49.132	25.133	50.266
75	-	-	-	-	-	-	-	-
80	12.768	51.073	14.073	50.262	15.908	51.819	26.798	53.595
90	14.660	58.640	17.103	16.083	17.912	58.344	30.713	61.426
100	15.346	61.382	17.470	62.391	19.184	62.490	31.463	62.926
110	18.159	72.637	19.937	71.205	22.060	71.856	35.449	70.898
120	19.980	79.920	21.916	78.279	24.511	79.839	39.012	78.025
130	23.834	95.337	25.655	91.624	28.046	91.355	45.952	91.904
140	-	100.000	26.388	94.242	28.635	93.274	49.235	98.469
150	-	-	-	100.000	-	100.000	-	100.000

Table 19 (continued)

Solubility Distribution for Standard C at 5460 Å

	C-5BII		C-7I		C-7II		C-7III	
50	8.944	17.888	12.878	18.397	-		12.732	18.188
60	14.751	29.502	21.341	30.488	21.341	30.488	21.171	30.244
65	-	-	-	-	-	-	32.927	47.038
70	25.100	50.200	34.926	49.895	34.731	49.616	35.512	50.731
75	-	-	-	-	-	-	-	-
80	26.762	53.524	36.000	51.428	-	-	-	-
90	29.736	59.472	41.463	59.233	-	-	-	-
100	30.906	61.813	44.000	62.857	-	-	-	-
110	35.121	70.242	50.341	71.916	-	-	-	-
120	39.874	79.749	55.804	79.720	-	-	-	-
130	45.891	91.783	63.170	90.243	-	-	-	-
140	49.521	99.041	65.853	94.076	-	-	-	-
150	-	100.000	-	100.000	-	-	-	-

Table 20

Solubility Distribution for Standard C at 5000 Å

	C-2.5		C-2.8		C.307		C-5AI	
50	4.549	18.194	-	-	-	-	-	-
60	-	-	8.403	30.012	7.9856	26.012	-	-
65	-	-	-	-	-	-	-	-
70	12.293	49.174	12.922	46.149	15.549	50.647	26.366	52.732
75	-	-	-	-	-	-	-	-
80	13.277	53.107	14.635	52.269	16.161	52.643	26.549	53.098
90	15.162	60.647	16.807	60.024	18.591	60.557	30.313	60.616
100	15.326	61.303	17.287	61.739	19.056	62.071	31.330	62.660
110	17.702	70.810	19.906	71.094	21.549	70.191	35.399	70.797
120	20.243	80.879	22.416	80.058	24.717	80.513	39.406	78.813
130	22.948	91.791	25.974	92.765	28.689	93.450	45.571	91.141
140	-	100.000	26.847	95.883	29.788	97.028	47.605	95.210
150	-	-	-	100.000	-	100.000	-	100.000

......continued

Table 20 (continued)

Solubility Distribution for Standard C at 5000 Å

	C-5 II		C-7I		C-7II		C-7III	
50	9.062	18.124	13.025	18.607	-	-	12.896	18.423
60	15.931	31.863	21.514	30.735	21.364	30.520	12.364	30.520
65		-	-	-	-	-	34.174	48.820
70	26.483	52.966	36.431	52.044	37.140	53.057	36.108	51.583
75	-	-	-	-	-	-	-	-
80	27.000	54.000	37.140	53.057	-	-	-	-
90	30.001	60.002	41.696	59.566	-	-	-	-
100	31.180	62.360	43.502	62.145	-	-	-	-
110	35.007	70.015	50.036	71.480	-	-	-	-
120	39.808	79.615	56.161	80.230	-	-	-	-
130	45.187	90.374	63.189	90.271	-	-	-	-
140	-	100.000	65.124	93.034	-	-	-	-
150	-	-	-	100.000				

Table 21

Solibility Distribution for Standard C at 4000 Å

	C-2.5		C-2.8		C-3.07		C-5 I	
50	4.5383	18.1530	-	-			-	-
60	-	-	-	-	8.2330	26.8176	-	-
65	-	-	-	-	-	-	-	-
70	11.8737	47.4950	-	-	15.4834	50.4346	25.2270	50.4540
75	-	-	-	-	-	-	-	-
80	13.4864	53.9455	-	-	16.4809	53.6837	26.0370	52.0740
90	14.9850	59.9395	-	-	18.6099	60.6185	30.7380	61.4760
100	15.6980	62.7937	-	-	19.1607	62.4128	31.1142	62.2284
110	17.9818	71.9274	-	-	21.7960	70.9964	35.5840	71.1680
120	20.0369	80.1476	-	-	25.1606	81.9562	41.0950	82.1900
130	22.5772	90.3088	-	-	29.7014	96.7471	45.5650	91.1300
140	-	100.0000	-	-	29.9247	97.4745	49.4700	98.9410
150	-	-	-	-	-	100.0000	-	100.0000

......continued

Table 21 (continued

Solubility Distribution for Standard C at 4000 Å

	C-5 II		C-7I		C-7II		C-7III	
50	9.086	18.171	12.564	17.948	-	-	12.564	17.948
60	15.143	30.286	21.000	29.999	21.000	30.000	21.987	31.410
65	-	-	-	-	-	-	34.775	49.679
70	25.151	50.303	35.987	51.281	-	-	35.897	51.281
75	-	-	-	-	-	-	-	-
80	25.959	51.918	37.692	53.845	-	-	-	-
90	30.646	61.292	41.057	58.653	-	-	-	-
100	31.021	62.042	43.600	62.285	-	-	-	-
110	35.477	70.955	50.256	71.794	-	-	-	-
120	40.785	81.569	57.465	82.093	-	-	-	-
130	45.428	90.857	63.029	90.041	-	-	-	-
140	49.221	98.443	66.409	94.870	-	-	-	-
150	-	100.000	-	100.000	-	-	-	-

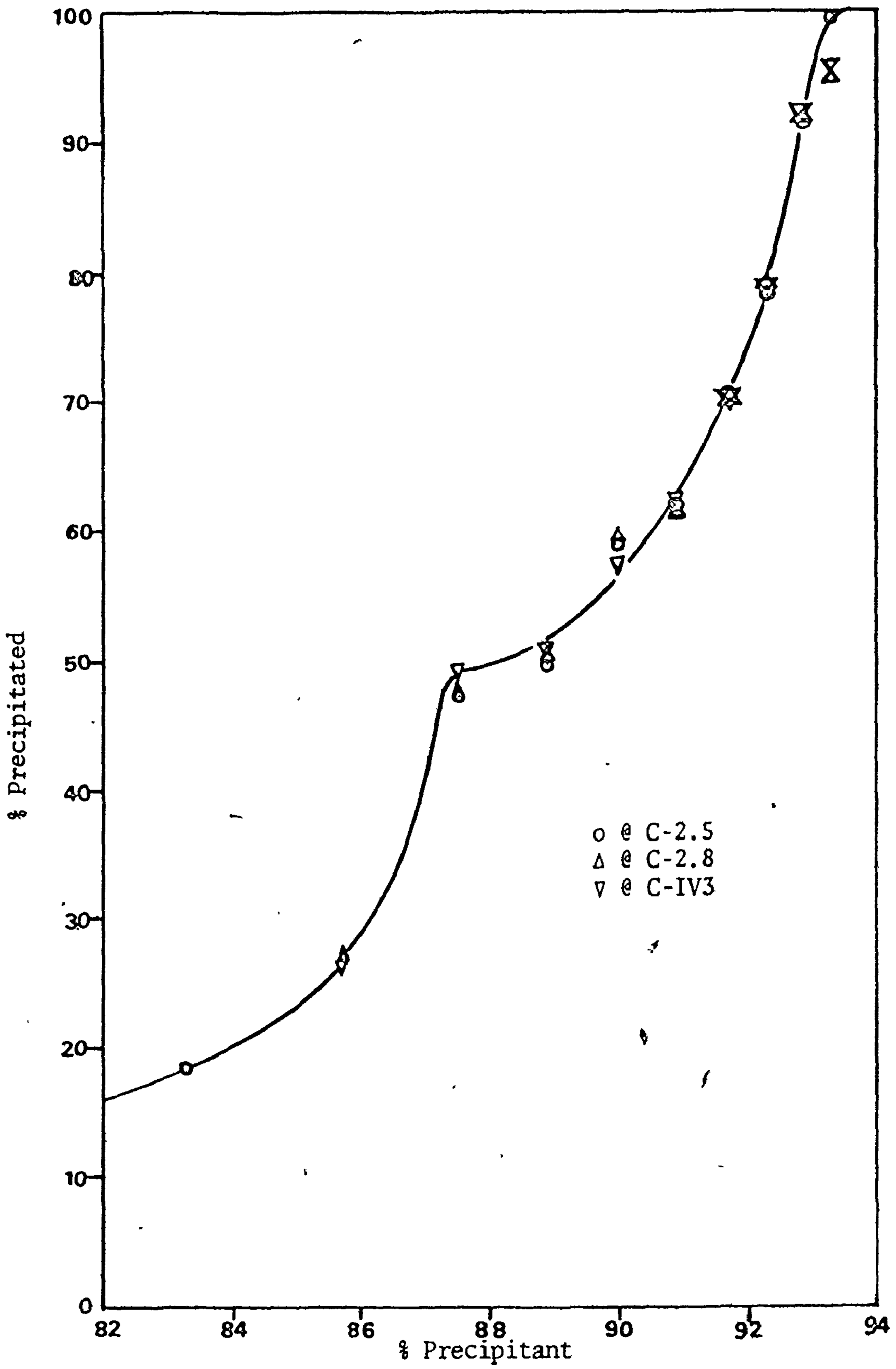


Fig. 28: Turbidimetric Precipitation Curve of Polyall 402 at 7000 Å.

Fig. 29: Turbidimetirc Precipitation Curve of Polyall 402 at 6000 Å.

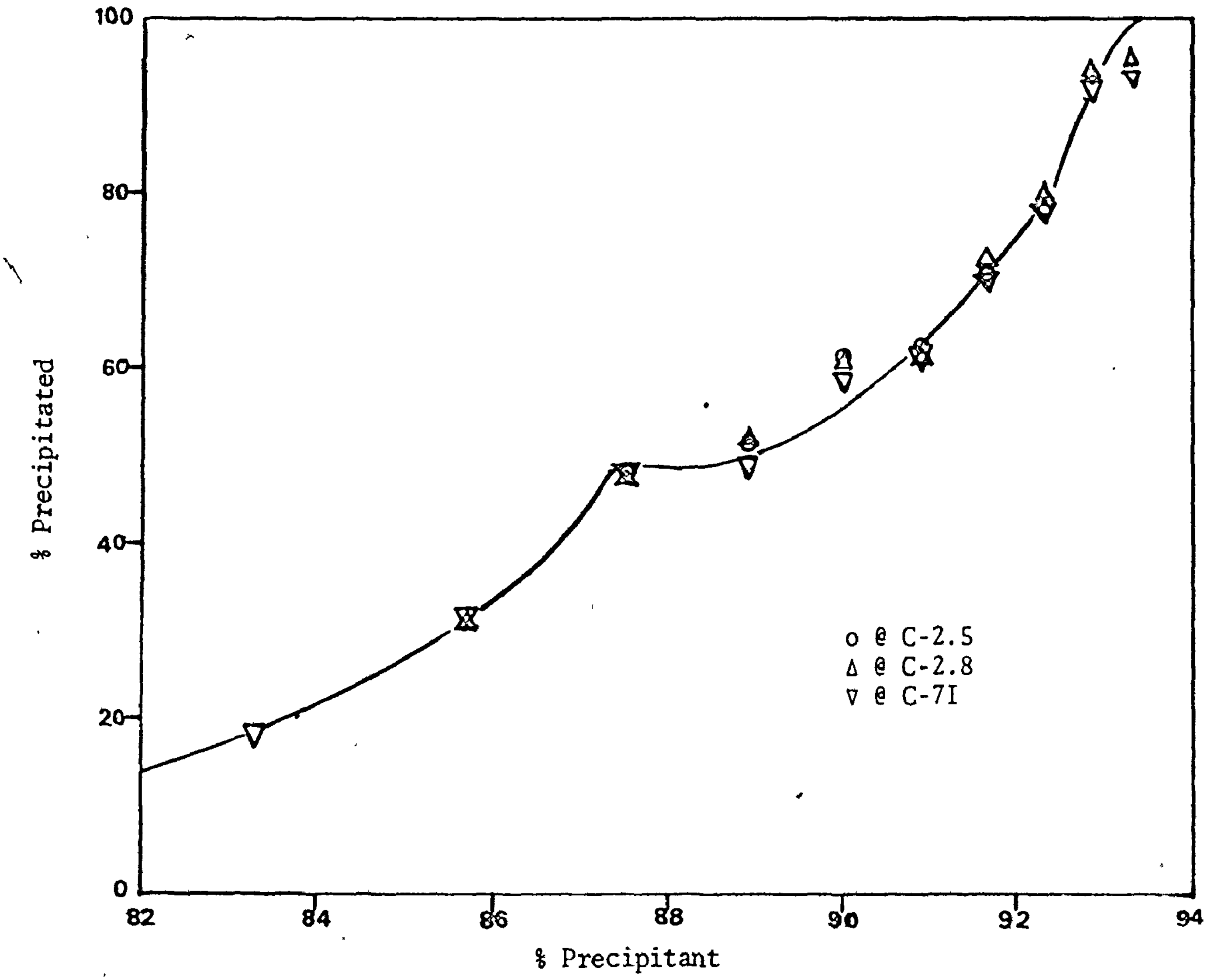


Fig. 30: Turbidimetric Precipitation Curve of Polyall 402 at 5460 Å.

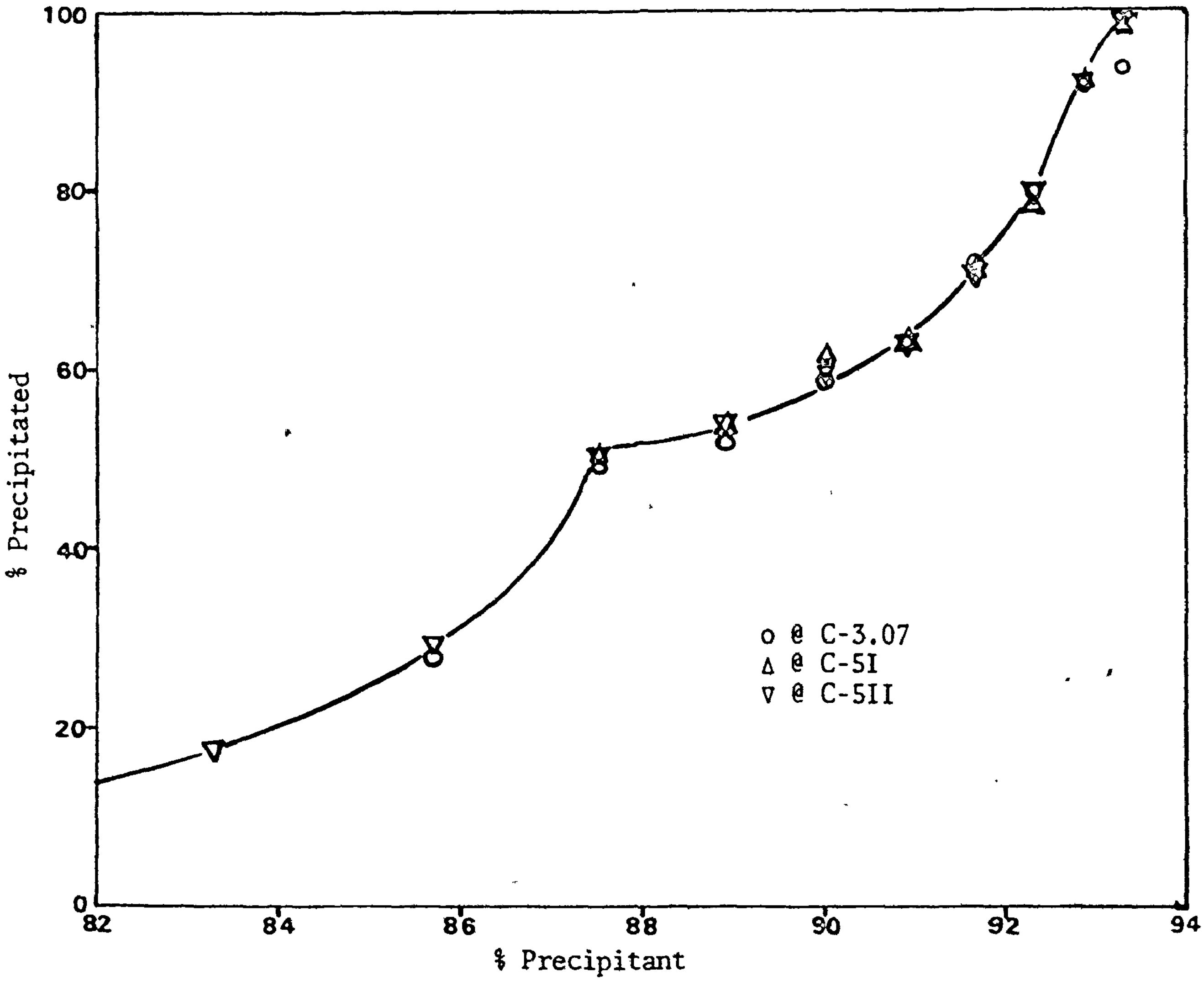


Fig. 31: Turbidimetric Precipitation Curve of Polyall 402 at 5460 Å.

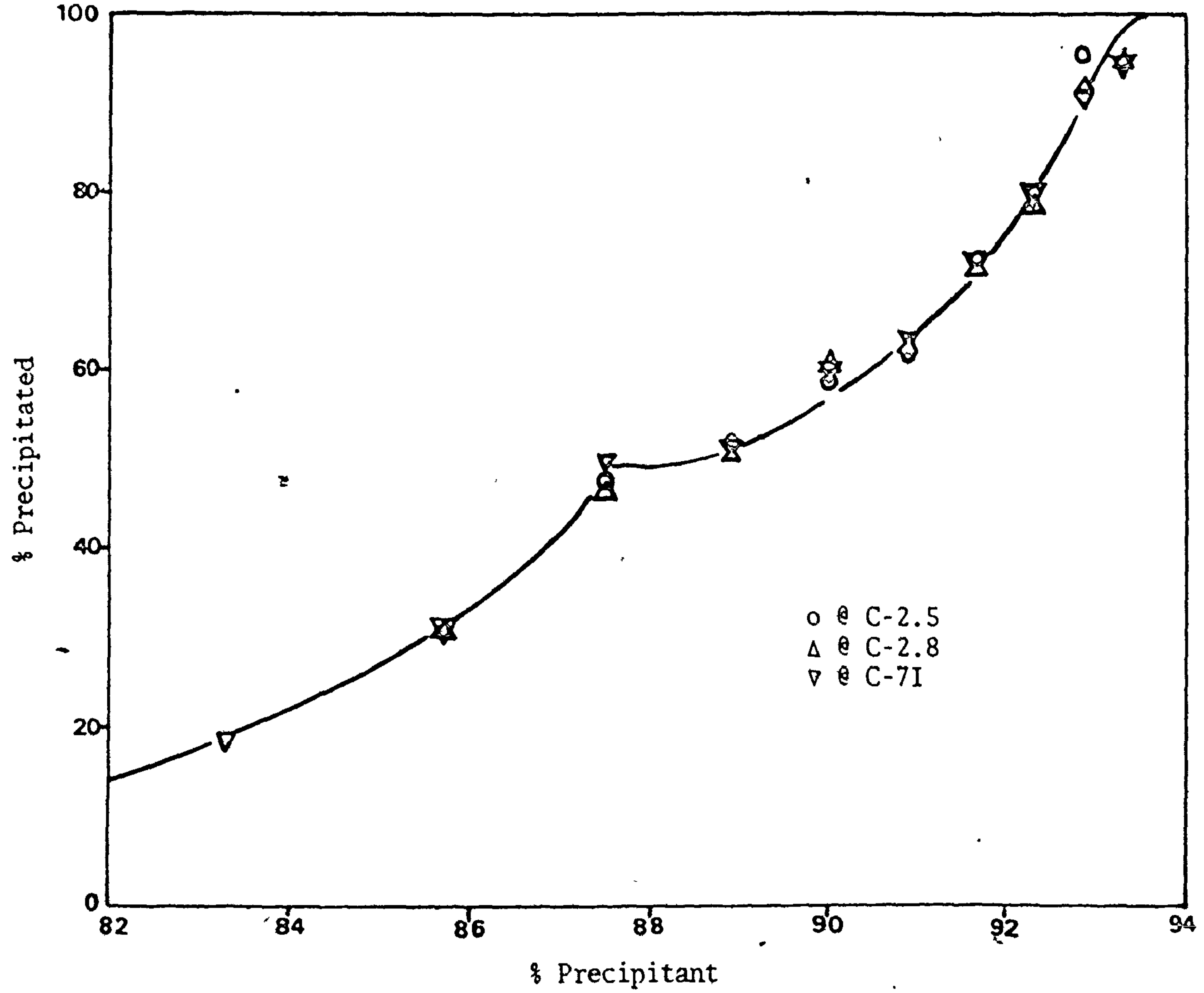


Fig. 32: Turbidimetric Precipitation Curve for Polyall 402 at 5000 Å.

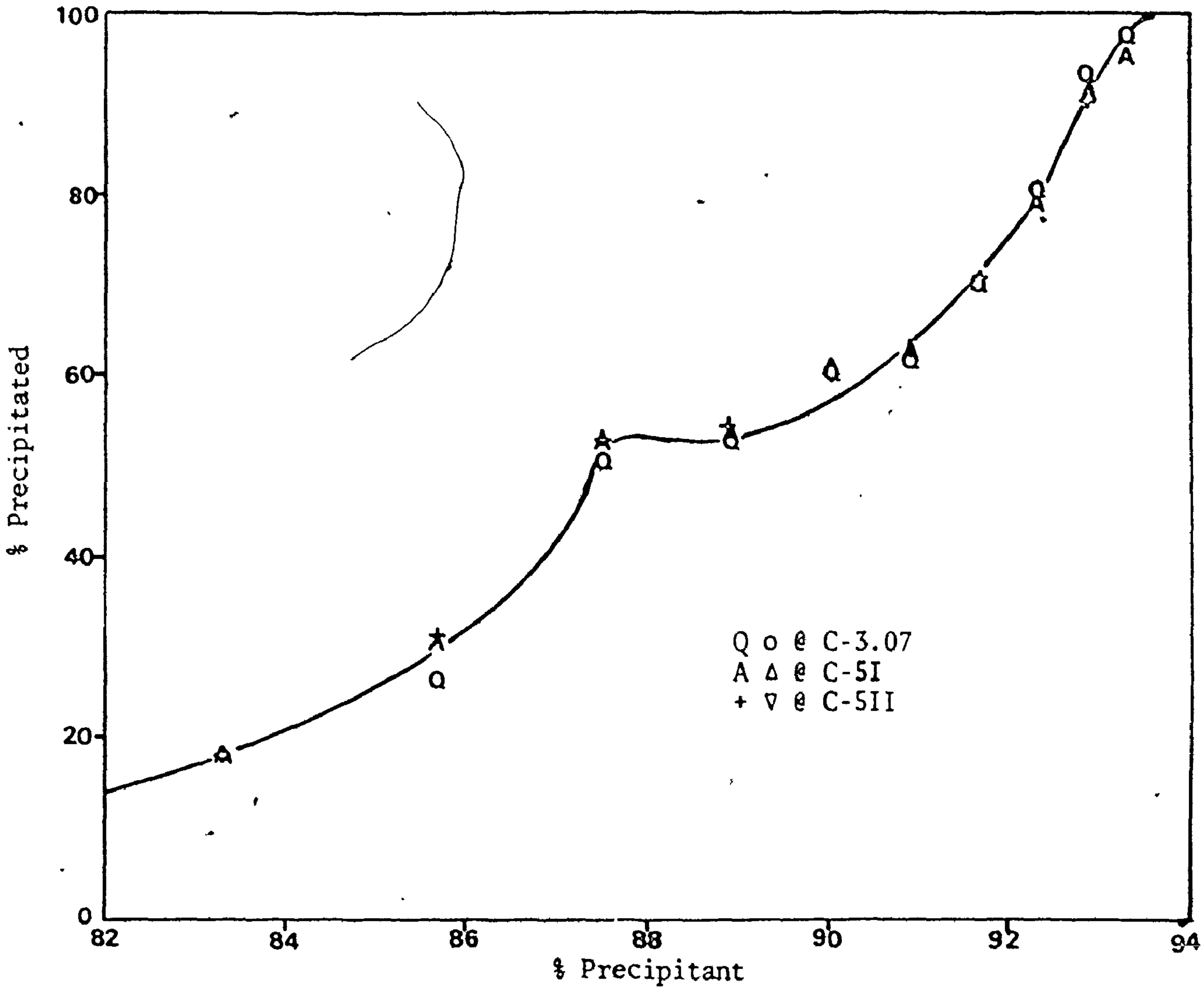


Fig. 33: Turbidimetric Precipitation Curve of Polyall 402 at 4000 Å.

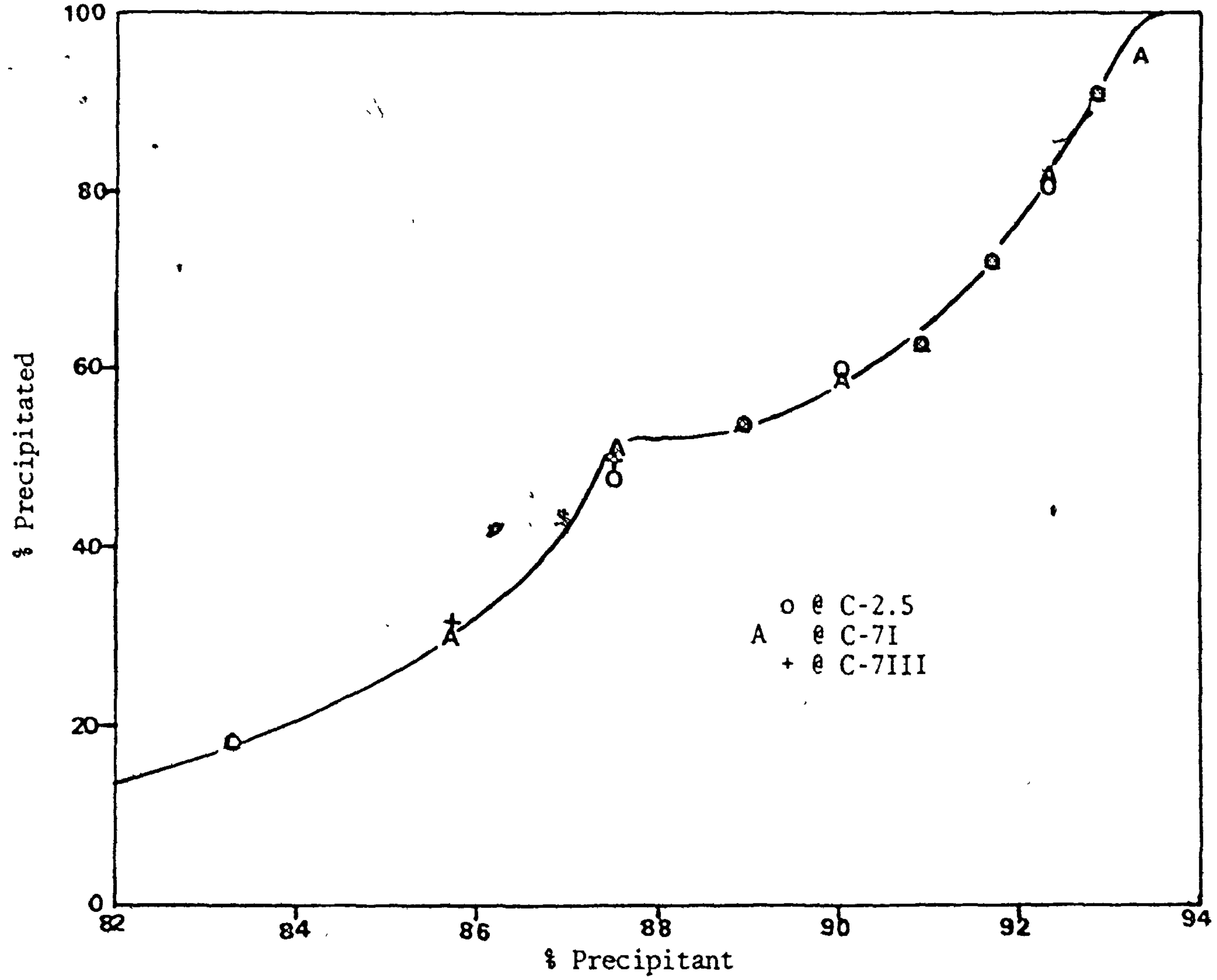
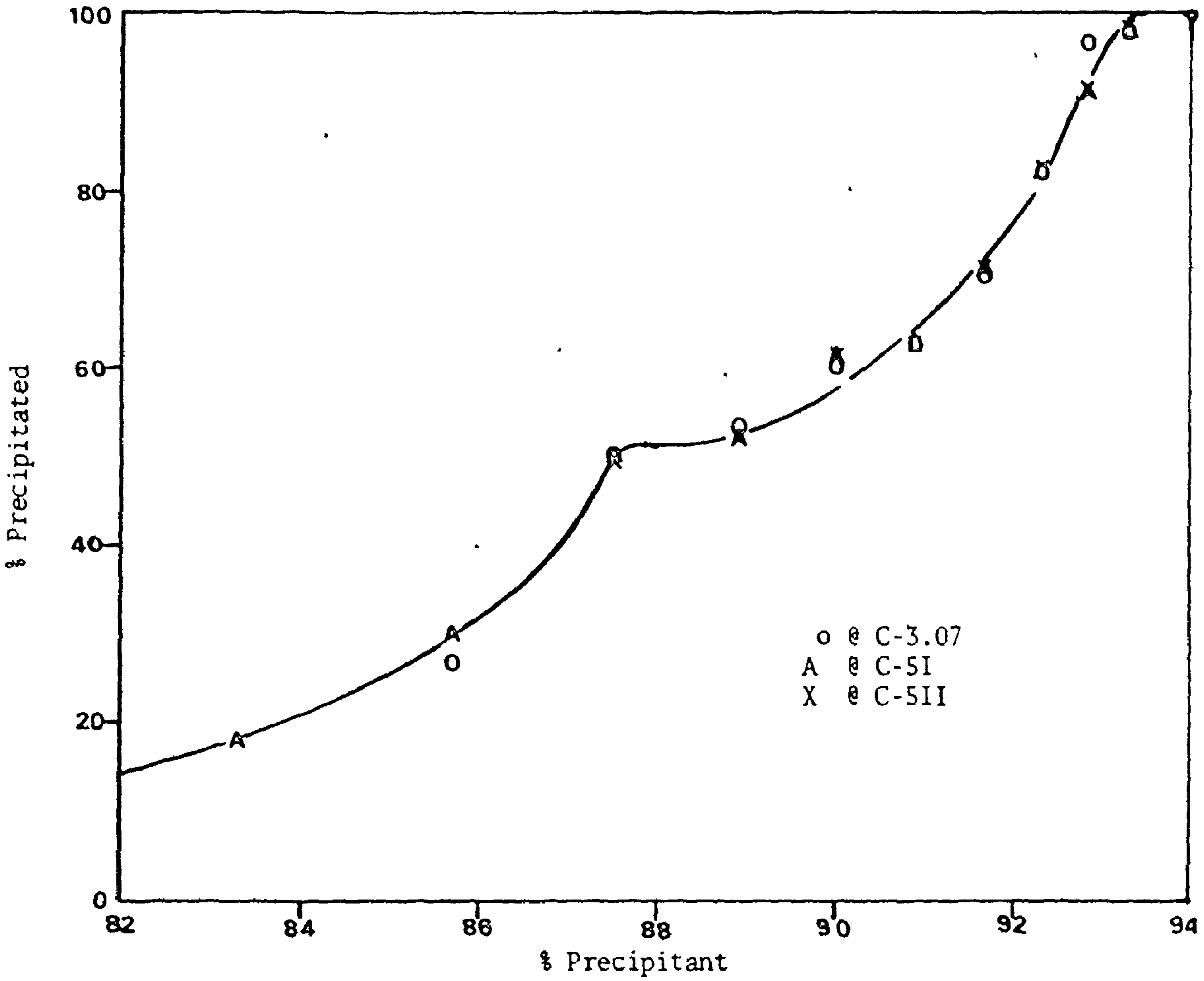


Fig. 34: Turbidimetric Precipitation Curve of Polyall 402 at 4000 Å.



three times over a period of six months. The distributions obtained are shown in Tables 30 - 32. The MWD by GPC for Standard C as obtained by previous workers,(63) tabulated in Table 29, was obtained for the purpose of comparison. Figures 35 - 39 show the cumulative most probable distribution and solubility distributions of the standard. The use of these curves as shown provided the molecular weight-solubility distribution in Table 33 and Figure 40. The calibration curve was then used to obtain the MWD and molecular weight averages of other polymers.

As shown in Figure 40, the need of finding the best linear fit for the log-normal calibration curve was not necessary. After 92% non-solvent, the curve seems to drop off, probably due to poor resolution of the low molecular weight chains. For precipitation using non-solvent up to 92%, the calibration equation was found to be

$$\log_e M = - 18.239\psi_2 + 31.239 \qquad 6.2.4$$

or

$$M = D_3 C^{-D_1\psi_2} \qquad 6.2.5$$

where

$D_1 = 18.239$

$D_3 = 3.6891 \times 10^{13}$

Equation 6.2.5 expresses the molecular weight-solublility distribution up to 92% non-solvent used.

Table 22

Specific Turbidities for Standard C at Different Wavelengths Obtained Graphically

A/C x 10^2 (Aml/gm)

Sample No.	Poly-acrylamide wt %	7000 Å		6000 Å		5460 Å		5000 Å		4000 Å	
		A_c	A/C	A_c	A/C	A_c	A/C	A_c	A/C	A_c	A/C
C-7I	0.7000	2.1260	3.0371	2.4665	3.5236	2.8700	4.1000	3.2569	4.6527	4.6801	6.6858
C-5I	0.5000	1.5558	3.115[illegible]	1.8306	3.6612	2.1327	4.2653	2.4578	4.9135	3.4565	6.9130
C-5II	0.5000	1.5625	3.1249	1.8411	3.6822	2.1355	4.2709	2.4167	4.8333	3.4670	6.9340
C-IV3	0.3070	0.9545	3.1090	1.1096	3.6142	1.3026	4.2431	1.4532	4.7335	2.0621	6.7169
C-III3	0.2800	0.8549	3.0532	0.9900	3.5357	1.1460	4.0928	1.2828	4.5814	-	-
C-2.5	0.2500	0.7811	3.1242	0.9131	3.6525	1.0573	4.2292	1.2201	4.8805	1.7518	7.0071

Table 23

Specific Absorbances for C-7

Volume of Precipitant cc	Specific Absorbance A/C $\times 10^{+2}$ (Absorbance unit ml/gm)				
	7000	6000	5460	5000	4000
50	0.5743	0.6429	0.7543	0.8657	1.2000
60	0.8900	1.1000	1.2500	1.4300	2.0050
70	1.3714	1.6800	2.0457	2.4214	3.4286
80	1.4786	1.7229	2.1086	2.4686	3.6000
90	1.7429	2.0714	2.4286	2.7714	3.9571
100	1.9014	2.1685	2.5771	2.8914	4.1643
110	2.1257	2.4686	2.9486	3.3257	4.8000
120	2.4143	2.7671	3.2685	4.2000	5.4886
130	2.8000	3.2400	3.7000	4.3286	6.0200
140	2.8700	3.3000	3.8571	4.5943	6.3429
150	3.0171	3.5429	4.0686	4.6386	6.5143
160	3.0336	3.5457	4.1286	4.6386	6.5571
170	3.0086	3.4714	4.0114	4.5771	6.4800
180	2.9857	3.5557	4.1257	4.7229	6.7857
190	3.0286	3.5429	4.1143	4.6857	6.8429
200	3.1200	3.6000	4.2000	4.8000	6.9150
210	3.0800	3.5200	4.1486	4.7771	6.8357
220	3.1214	3.5486	4.2057	4.8628	6.6371
230	3.0171	3.5657	4.1829	4.8000	6.8571
240	3.0000	3.4643	4.1429	4.5357	6.7143
250	3.0829	3.4543	4.0114	4.6057	6.7971
260	3.0857	3.4714	4.0114	4.5129	6.6729
270	-	-	-	-	-
280	2.9000	3.3557	4.0186	4.5129	6.5043
290	-	-	-	-	-
300	2.8787	3.3657	4.0300	4.5127	6.5543

C = original concentration of polymer solution
= 0.7 wt %.

Table 24

Specific Absorbances for IC-5

Volume of Precipitant (cc)	% Precipitant	Specific Turbidity A/C x 10^{+2} (Absorbance unit ml/gm)				
		7000 Å	6000 Å	5460 Å	5000 Å	4000 Å
50	83.33	-	-	-	-	-
60	85.71	-	-	-	-	-
70	87.50	1.504	1.888	2.144	2.592	3.488
80	88.89	1.602	1.944	2.286	2.610	3.600
90	90.00	1.850	2.200	2.620	2.980	4.250
100	90.91	1.914	2.266	2.684	3.080	4.302
110	91.67	2.184	2.568	3.024	3.480	4.920
120	92.31	2.444	2.860	3.328	3.874	5.682
130	92.86	2.800	3.080	3.640	4.480	6.300
140	93.33	3.120	3.570	4.050	4.680	6.840
150	93.75	3.136	3.680	4.288	4.864	6.880
160	94.12	3.162	3.672	4.216	4.862	6.698
170	94.44	3.096	3.600	4.284	4.824	6.768
180	94.74	3.116	3.648	4.332	4.940	6.916
190	95.00	3.080	3.680	4.320	5.040	6.880
200	95.24	3.066	3.654	4.284	4.872	6.804
210	95.46	3.080	3.652	4.224	4.972	6.908
220	95.65	3.128	3.680	4.186	4.876	6.900
230	95.83	3.072	3.648	4.320	5.040	7.056
240	96.00	3.100	3.650	4.200	4.950	7.000
250	96.15	3.170	3.640	4.264	5.044	7.072
260	96.30	3.132	3.672	4.266	4.968	7.074
270	96.43	-	-	-	-	-
280	96.55	-	-	-	-	-
290	96.67	-	-	-	-	-
300	96.77	2.914	3.472	4.030	4.650	6.913

C = original concentration of polymer solution
= 0.5 wt %.

Table 25
Specific Absorbances for IIC-5

Volume of Precipitant cc	Specific Absorbance A/C x 10^2 (Absorbance unit ml/gm)				
	7000	6000	5460	5000	4000
50	0.5760	0.6840	0.7500	0.8760	1.2600
60	0.9100	0.8820	1.0920	1.2600	1.5400
70	1.4880	1.9200	2.1440	2.5600	3.4880
80	1.6020	1.9800	2.2860	2.6100	3.6000
90	1.8600	2.2000	2.5400	2.9000	4.2500
100	1.9360	2.2660	2.6400	3.0140	4.3020
110	2.2080	2.5920	3.0000	3.3840	5.1720
120	2.4700	2.8860	3.4060	3.8480	5.6560
130	2.8000	3.1360	3.6960	4.3680	6.3000
140	3.1000	3.6000	4.2300	4.8900	6.8260
150	3.1360	3.7120	4.2240	4.8640	6.8480
160	3.1960	3.6720	4.2840	4.8280	7.1240
170	3.1680	3.6720	4.2120	4.6800	6.8940
180	3.1160	3.6480	4.2560	4.6740	6.8970
190	3.1200	3.6800	4.2400	4.6400	7.0600
200	3.1500	3.6540	4.2840	4.9140	6.9510
210	3.1240	3.6080	4.2240	4.8400	6.9080
220	3.1280	3.6800	4.3700	4.9680	7.1070
230	3.1200	3.6960	4.3200	4.8480	6.7680
240	3.1000	3.7000	4.2500	5.0500	6.9000
250	3.0160	3.7440	4.3160	5.0440	6.8380
260	-	-	-	-	-
270	-	-	-	-	-
280	-	-	-	-	-
290	-	-	-	-	-
300	2.9140	3.4720	4.0300	4.6500	6.9130

C = original concentration of original polymer solution
= 0.5 wt %.

Table 26

Specific Absorbances for IVC-3

Volume of Precipitant cc	Specific Absorbance A/C x 10^2 (Absorbance unit ml/gm)				
	7000	6000	5460	5000	4000
50	-	-	-	-	-
60	0.8209	1.0945	1.1629	1.2313	1.8013
70	1.5375	1.7980	2.0847	2.3974	3.3876
80	1.5831	1.8469	2.1987	2.4919	3.6059
90	1.7915	2.2150	2.4756	2.8664	4.0717
100	1.9349	2.2573	2.6515	2.9381	4.1922
110	2.1883	2.5798	3.0489	3.3225	4.7687
120	2.4560	2.8795	3.3875	3.8111	5.5049
130	2.8730	3.2834	3.8762	4.4235	6.4984
140	2.9700	3.4202	3.9577	4.5603	6.5472
150	3.1270	3.6482	4.1694	4.6906	6.7752
160	3.1010	3.5993	4.2638	4.5961	6.5342
170	3.1075	3.5765	4.3388	4.6906	6.5668
180	3.0945	3.6515	4.3322	4.8274	6.8078
190	3.1270	3.6482	4.2997	4.7557	6.7101
200	3.1466	3.5570	4.1726	4.7883	6.7036
210	3.0814	3.5831	4.2997	4.8730	6.6645
220	3.1466	3.5961	4.2707	4.8697	6.6678
230	3.1270	3.6743	4.2997	4.6006	6.6450
240	3.0945	3.6645	4.2345	4.8060	6.6450
250	3.1336	3.5570	4.2345	4.7427	6.8811
260	-	-	-	-	-
270	3.1010	3.4961	4.1042	4.5603	6.9023
280	-	-	-	-	-
290	-	-	-	-	-
300	3.0293	3.4332	4.1401	4.6450	6.8160

C = original concentration of original polymer solution
= 0.3 wt %.

Table 27

Specific Absorbances for IIIC-3 (2.8)

Volume of Non-solvent cc	Specific Absorbance A/C x 10^2 (Absorbance unit ml/gm)			
	7000	6000	5460	5000
50	-	-	-	-
60	0.8250	1.1000	1.2500	1.3750
70	1.4571	1.6857	1.8857	2.1143
80	1.5429	1.8321	2.0571	2.3946
90	1.8214	2.1429	2.5000	2.7500
100	1.8857	2.1607	2.5536	2.8286
110	2.1428	2.5714	2.9143	3.2571
120	2.4143	2.8321	3.2036	3.6679
130	2.8000	3.3500	3.7500	4.2500
140	3.0000	3.3750	3.8571	4.3929
150	3.0857	3.5429	4.1143	4.5714
160	3.0964	3.5214	4.0678	4.5536
170	3.0857	3.5357	4.1143	4.6929
180	3.0536	3.5286	4.1390	4.6821
190	3.0714	3.5714	4.0714	4.6429
200	3.0000	3.5250	4.125	4.6500
210	-	-	-	-
220	3.0393	3.5321	4.1893	4.6000
230	-	-	-	-
240	3.0357	3.5714	4.0179	4.4643
250	3.0643	3.5286	4.0857	4.4571
260	-	-	-	-
270	3.0000	3.5000	4.0000	4.5000
280	-	-	-	-
290	-	-	-	-
300	2.9893	3.4321	4.0964	4.4286

C = original concentration of polymer solution
= 0.28 wt %.

Table 28

Specific Absorbances for C 2.5

Vol. of Precipitantant (cc)	% Precipitant	Specific Turbidity A/C $\times 10^2$ (Absorbance unit ml/gm)				
		7000	6000	5460	5000	4000
50	83.33	0.5760	0.6720	0.7680	0.8880	-
60	85.71	-	-	-	-	-
70	87.50	1.4720	1.7600	2.0160	2.4000	3.3280
80	88.89	1.5480	1.8720	2.1600	2.5920	3.7800
90	90.00	1.8000	2.2400	2.4800	2.9600	4.2000
100	90.91	1.8920	2.2880	2.5960	2.9920	4.4000
110	91.67	2.2080	2.5920	3.0720	3.4560	5.0400
120	92.31	2.4440	2.8600	3.3800	3.9520	5.6160
130	92.86	2.8560	3.1360	4.0320	4.4800	6.3280
140	93.33	3.1200	3.7200	4.3200	4.9800	7.2000
150	93.75	3.1360	3.6480	4.2240	4.8640	6.9120
160	94.12	3.1960	3.6720	4.1480	4.8280	7.1060
170	94.44	3.1680	3.6720	4.3920	5.1840	7.1280
180	94.74	3.1160	3.6480	4.1800	5.0160	7.1440
190	95.00	3.1260	3.6800	4.1600	4.9600	7.0000
200	95.24	3.1080	3.6960	4.2840	4.8720	6.9300
210	95.46	3.0800	3.6080	4.3120	4.9280	7.0840
220	95.65	3.1360	3.6800	4.3240	4.6920	6.8540
230	95.83	3.0720	3.6480	4.2240	4.8960	6.7200
240	96.00	3.1000	3.7000	4.2000	5.0000	7.0000
250	96.15	3.1200	3.6400	4.2640	4.9920	6.9680
260	96.30	-	-	-	-	-
270	96.43	-	-	-	-	-
280	96.55	3.1320	3.5950	4.1760	4.7560	7.0760
290	96.67	-	-	-	-	-
300	96.77	2.9760	3.5950	4.0920	4.4600	7.1700

C ≡ Original Concentration of Polymer Solution
≑ 0.25 wt %

Table 29

Molecular Weight Distribution and Averages for Standard C Measured by GPC

Molecular Wt $M \times 10^{-4}$	Differential MWD $W(M) \times 10^{8}$	Cumulative MWD	
47.35	6.065	-	-
68.24	14.200	(0.9951)	0.0049
98.35	21.630	(0.9412)	0.0588
141.70	24.060	(0.8420)	0.1580
204.30	19.070	(0.7072)	0.2928
294.40	13.110	(0.5622)	0.4378
424.30	8.122	(0.4243)	0.5757
611.60	4.828	(0.3031)	0.6969
881.40	2.627	(0.2025)	0.7975
1270.00	1.371	(0.1248)	0.8752
1831.00	0.637	(0.0685)	0.9315
2639.00	0.333	(0.0293)	0.9707
3803.00	0.170	(0.0000)	1.0000

Effective Calibration Curve

$$M = D_1 \exp(- D_2 . V)$$

where V = elution volume

$$D_1 = 0.6118 \times 10^{17}$$

$$D_2 = 0.7310$$

$$\bar{M}_n = 2.40 \times 10^{6}$$

$$\bar{M}_w = 5.83 \times 10^{6}$$

Table 30

Molecular Weight Distribution and Effective Calibration Constants for Standard C Measured by GPC

Molecular Weight $M \times 10^{-4}$	Differential MWD $W(M) \times 10^{8}$	Cumulative MWD	
28.26	-	-	-
41.69	-	-	-
61.52	9.874	-	-
90.77	22.750	(0.9669)	0.0331
133.90	24.490	(0.8650)	0.1350
197.60	19.670	(0.7243)	0.2757
291.60	13.500	(0.5685)	0.4315
430.30	8.188	(0.4181)	0.5819
634.90	4.593	(0.2874)	0.7126
936.70	2.334	(0.1828)	0.8172
1382.00	1.055	(0.1074)	0.8926
2039.00	0.477	(0.0570)	0.9430
3009.00	0.202	(0.0241)	0.9759
4440.00	0.055	(0.0058)	0.9942
6551.00	0.	(0.0000)	1.0000

Effective Calibration Curve

$$M = D_1 \exp(- D_2 . V)$$

where V = elution volume

$D_1 = 0.1893 \times 10^{18}$

$D_2 = 0.7780$

Table 31

Molecular Weight Distribution and Effective Calibration Constants for Standard C Measured by GPC

Molecular Weight $M \times 10^{-4}$	Differential MWD $W(M) \times 10^{8}$	Cumulative MWD	
36.06	2.551	-	-
54.56	5.901	-	-
82.55	14.490	0.0154	(0.9846)
124.90	25.410	0.0999	(0.9001)
189.00	21.900	0.2515	(0.7485)
285.90	14.960	0.4302	(0.5698)
432.70	8.398	0.6015	(0.3985)
654.60	4.075	0.7399	(0.2601)
990.50	1.811	0.8388	(0.1612)
1499.00	0.829	0.9059	(0.0941)
2268.00	0.345	0.9510	(0.0490)
3431.00	0.161	0.9804	(0.0196)
5191.00	0.062	1.0000	(0.0000)

Effective Calibration Curve

$$M = D_1 \exp(-D_2 . V)$$

where V is the elution volume

$D_1 = 0.1403 \times 10^{19}$

$D_2 = 0.8283$

Table 32

Molecular Weight Distribution and Averages for Standard C Measured by GPC (by previous workers)(63)

Molecular Wt. $M \times 10^{-4}$	Differential MWD $W(M) \times 10^{8}$	Cumulative MWD	
10	2.220	-	-
20	4.190	0.0032	(0.9968)
40	7.430	0.0149	(0.9851)
60	9.900	0.0323	(0.9677)
80	11.730	0.0541	(0.9459)
90	12.450	0.0662	(0.9338)
100	13.050	0.0789	(0.9211)
150	14.680	0.1490	(0.8510)
200	14.770	0.2231	(0.7769)
250	14.050	0.2954	(0.7046)
300	12.930	0.3629	(0.6371)
400	10.440	0.4797	(0.5203)
500	8.250	0.5728	(0.4272)
600	6.540	0.6464	(0.3536)
700	5.260	0.7050	(0.2950)
800	4.290	0.7526	(0.2474)
1000	2.980	0.8243	(0.1757)
1500	1.301	0.9254	(0.0746)
2000	0.549	0.9692	(0.0308)
2500	0.220	0.9873	(0.0127)

$$\overline{M}_n = 2.40 \times 10^{6}$$

$$\overline{M}_w = 5.83 \times 10^{+6}$$

$$\frac{\overline{M}_w}{\overline{M}_n} = 2.43$$

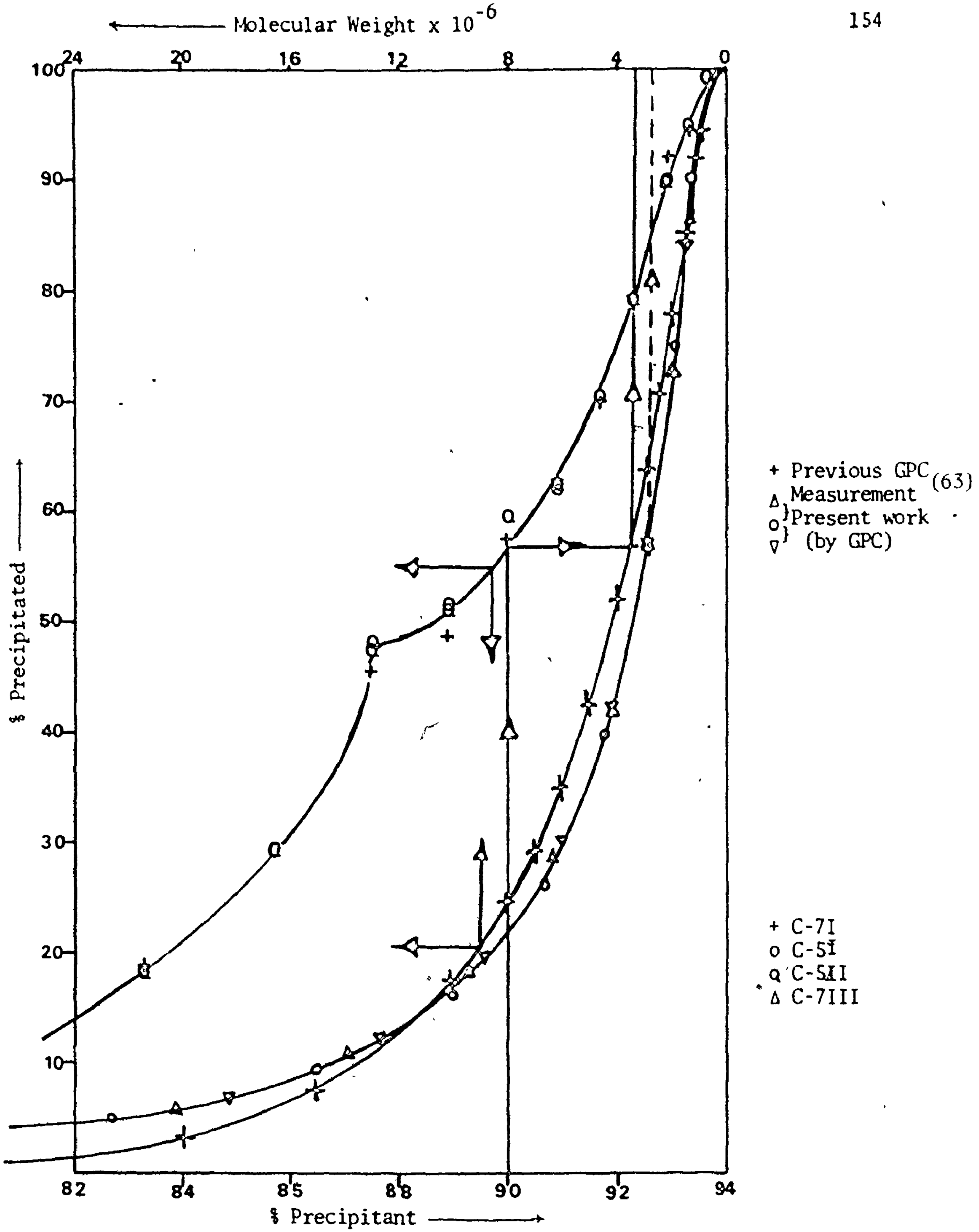


Fig. 35: Turbidimetric Precipitation Curve of Polyall 402 at 7000 Å and Cumulative Most Probable Distributions.

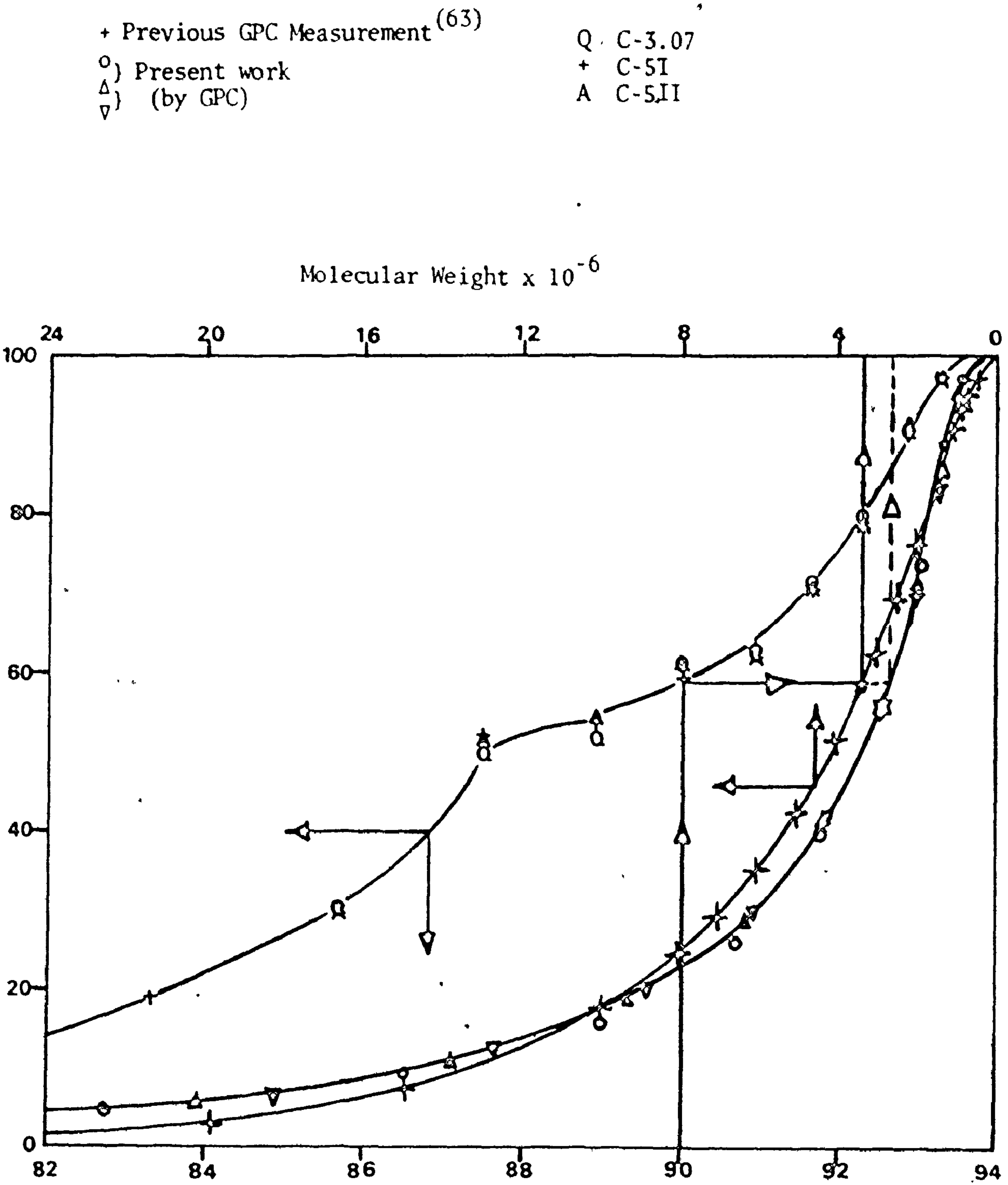


Fig. 36:. Turbidimetric Precipitation Curve of Polyall 402 at 6000 Å and Cumulative most Probable Distribution.

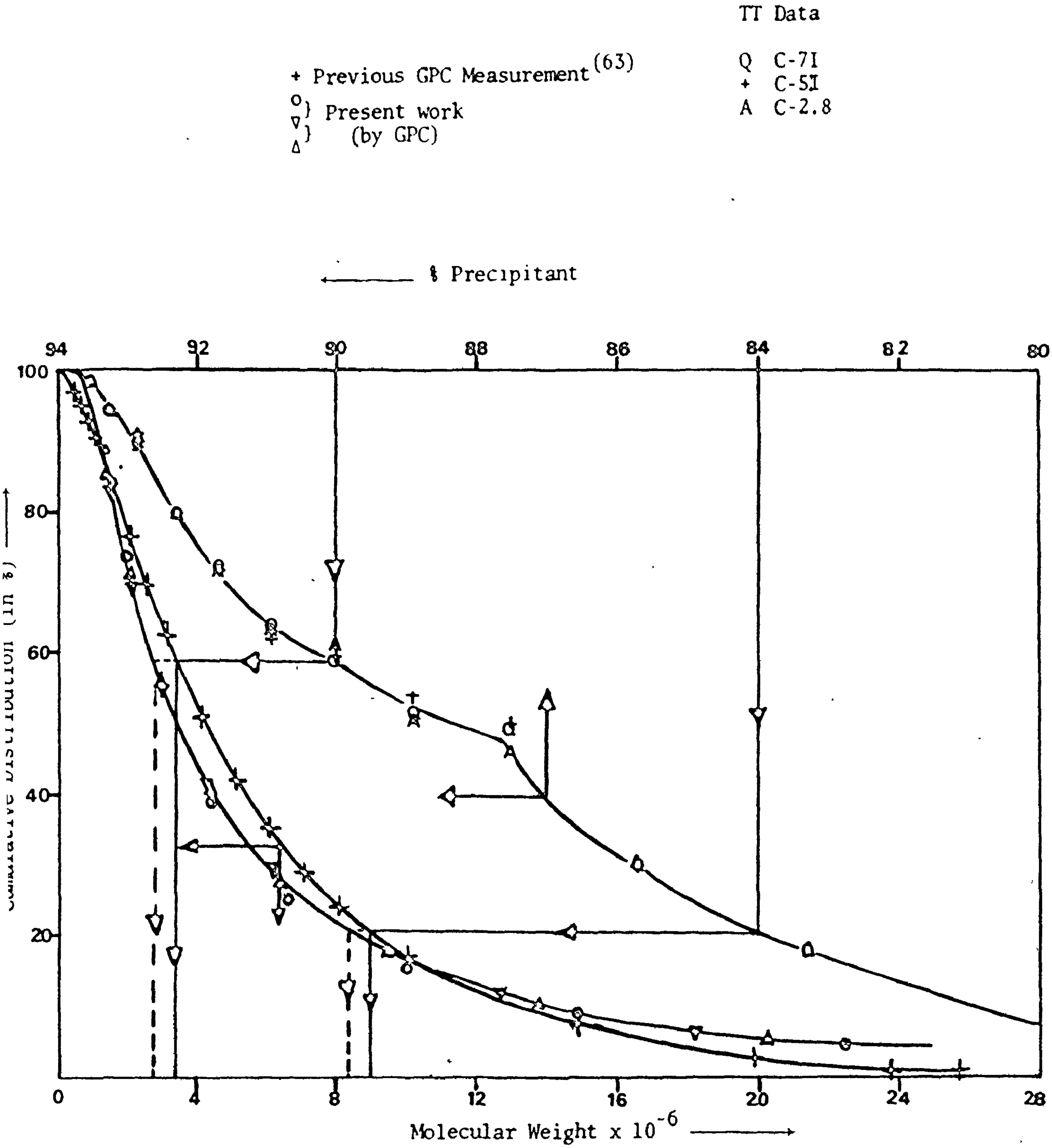


Fig. 37: Cumulative Most Probable Distribution and Cumulative Turbidimetric Precipitation Curve for Standard C (5460 Å).

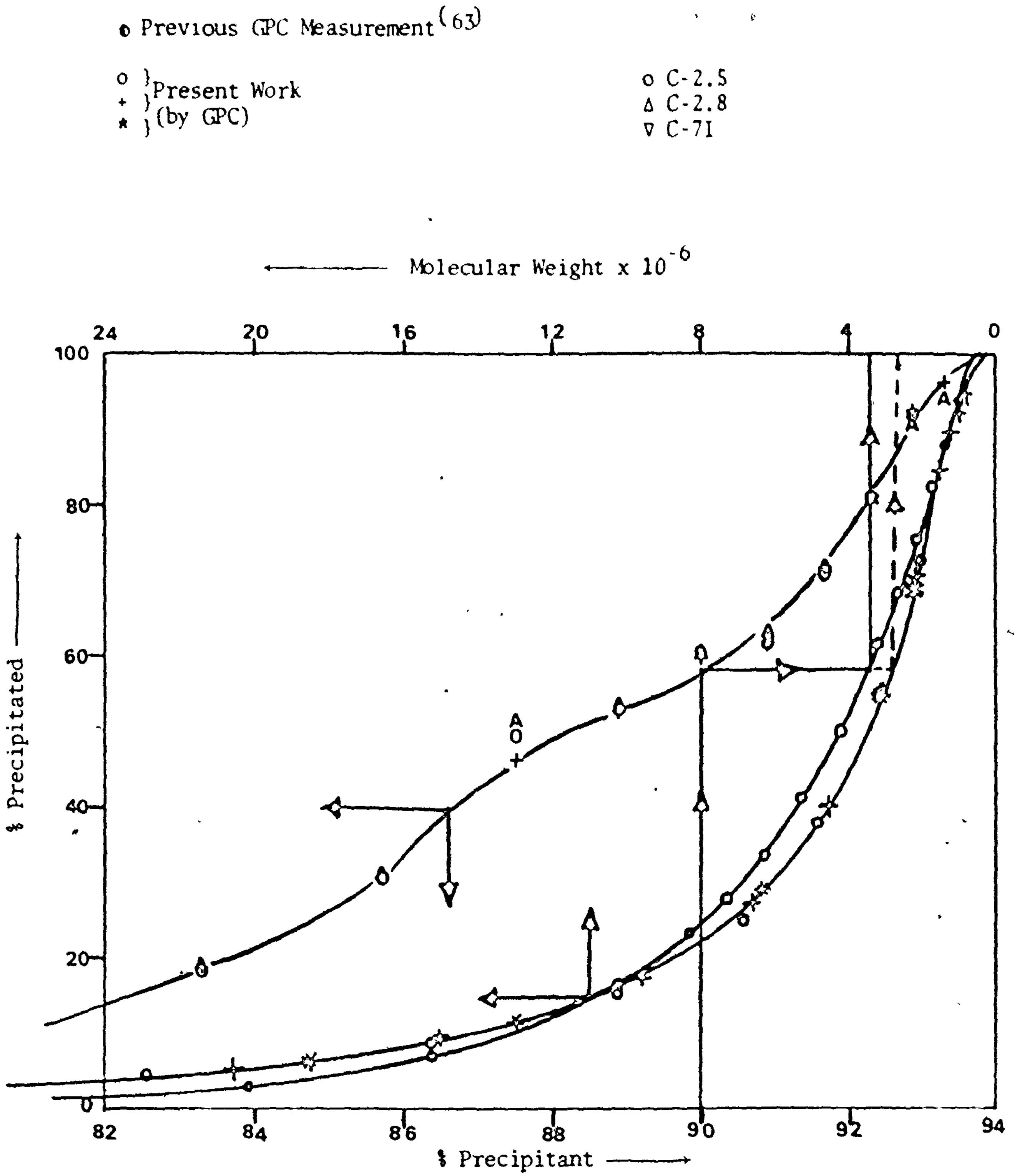


Fig. 38: Turbidimetric Precipitation Curve of Polyall 402 at 5000 Å and Cumulative Most Probable Distribution.

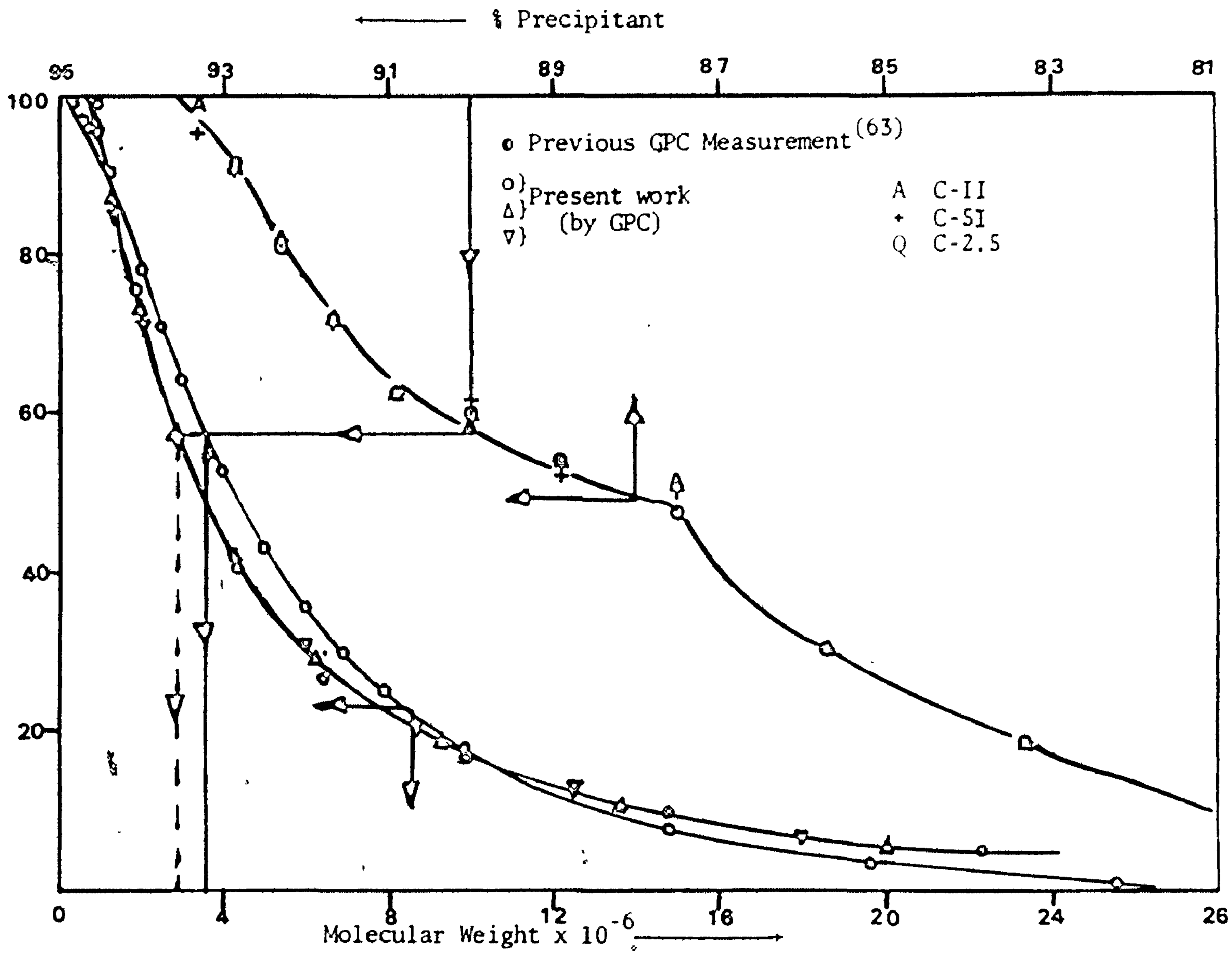


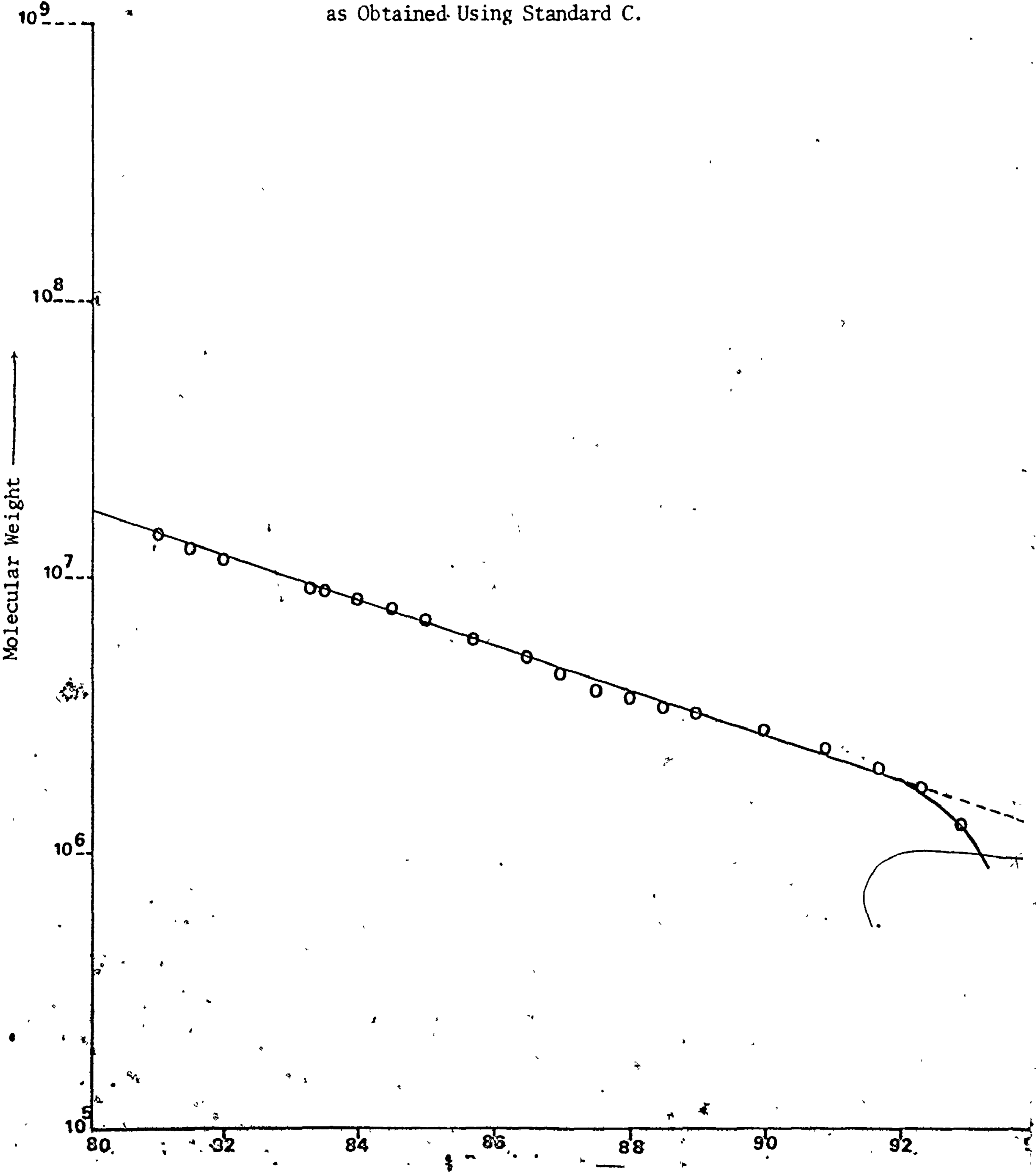
Fig. 39: Cumulative most probable distribution and cumulative turbidimetric precipitation curve for Standard C (4000 Å).

Table 33

Solubility Molecular Weight Relationship for Standard C

% Precipitant	Molecular Weight $M \times 10^{-6}$					
	7000 Å	6000 Å	5460 Å	5000 Å	4000 Å	Averages
81.00	14.20	14.20	14.00	14.10	14.20	14.14
81.50	12.80	13.00	12.95	13.00	13.00	12.95
82.00	11.80	11.85	11.80	11.75	11.80	11.80
83.30	9.30	9.30	9.40	9.35	9.40	9.35
83.50	9.00	9.00	9.20	9.00	9.00	9.04
84.00	8.30	8.30	8.40	8.50	8.30	8.36
84.50	7.60	7.70	7.80	7.75	7.60	7.69
85.00	6.90	6.90	7.00	6.95	6.95	6.94
85.70	6.00	6.00	6.00	6.00	6.00	6.00
86.50	5.30	5.15	5.10	5.00	5.15	5.14
87.00	4.60	4.40	4.60	4.45	4.60	4.53
87.50	4.00	3.60	3.90	4.00	3.90	3.88
88.00	3.60	3.40	3.60	3.60	3.60	3.56
88.50	3.50	3.20	3.45	3.45	3.50	3.42
89.00	3.30	3.10	3.30	3.30	3.30	3.26
90.00	2.80	2.70	2.80	2.75	2.90	2.79
90.91	2.40	2.40	2.40	2.30	2.50	2.40
91.70	2.00	2.00	2.00	2.00	2.00	2.00
92.30	1.70	1.65	1.65	1.78	1.60	1.68
92.86	1.25	1.20	1.25	1.30	1.20	1.24

Fig. 40: Molecular Weight-Solubility Calibration Curve as Obtained Using Standard C.



6.3 Application of Calibration Curve to Obtaining the Molecular Weight Distribution of other Water Soluble Polymers

Maximum turbidity values were measured for the different points of the titration up to 100% precipitation by the standard procedure, for all the polyacrylamides investigated. In Tables 46 - 51 are displayed these values for Standard A, Tables 39 - 41 for Standard B and in Tables 57 - 59 for Standard O. These values have been plotted as shown in Figures 46 and 47 for A, Figures 43 for B and Figures 51 for O. From the point of 100% precipitation, the amount of polymer precipitated at different points of the titration were obtained. These, as displayed in Tables 44, 45, 52, 53, 63 and 64 were used to obtain the solubility distribution curves shown in Figures 44, 45, 48 and 52. Finally, using the calibration curve in Figure 40 or the equation up to 92.0% non-solvent, the cumulative-molecular weight distributions were obtained as shown in Figures 49, 53, 55, 56 and 57.

Included with the final turbidimetric data are those obtained during the preliminary investigations and shaking by hand for some of the polymers. While the maximum absorbances at different points of titration for Standards A and C were not vulnerable to shaking by hand, polymers standards B and O were vulnerable to hand-shaking. GPC measurements of standards using the calibration constants of Standard C were obtained during GPC analysis, by injection of Standard C, followed by the standard.

6.4 Evaluation of Molecular Weight Averages

The weight mean molecular weight is defined by

$$\bar{M}_w = \int WMdM \qquad 6.4.1$$

Table 34

Preliminary Turbidimetric Titrations Data on IB 0.5

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths A			
		7000	6000	5460	5000
		0.0050	0.0080	0.0110	0.0140
IB 0.05	10	0.0100	0.0160	0.0220	0.0280
		0.0090	0.0150	0.0180	0.0250
	20	0.0270	0.0450	0.0540	0.0750
		0.0320	0.0340	0.0400	0.0440
	30	0.1280	0.1360	0.1600	0.1760
		0.0600	0.0660	0.0780	0.0860
	40	0.3000	0.3300	0.3900	0.4300
		0.0720	0.0770	0.0820	0.0870
	50	0.4320	0.4620	0.4920	0.5220
		0.0750	0.0820	0.0870	0.0890
	60	0.5250	0.5740	0.6090	0.6230
		0.1560	0.1770	0.1870	0.1970
	70	1.2480	1.4160	1.4960	1.5760
		0.1420	0.1560	0.1670	0.1760
	80	1.2780	1.4040	1.5030	1.5840
		0.1370	0.1520	0.1620	0.1710
	90	1.3700	1.5200	1.6200	1.7100
		0.1250	0.1420	0.1540	0.1630
	100	1.3750	1.5620	1.6940	1.7930
		0.1140	0.1340	0.1440	0.1520
	110	1.3680	1.6080	1.7280	1.8240
		0.1080	0.1260	0.1350	0.1410
	120	1.4040	1.6380	1.7550	1.8330
		0.1020	0.1200	0.1290	0.1360
	130	1.4280	1.6800	1.8060	1.9040
		0.0980	0.1180	0.1260	0.1340
	140	1.4700	1.7700	1.8900	2.0100
		-	-	-	-
	150	-	-	-	-

Table 35

Preliminary Turbidimetric Titration Data on IB 0.25

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
		7000	6000	5460	5000
		0.0270	0.0400	0.0500	0.0600
IB 0.025	10	0.0540	0.0800	0.1000	0.1200
		0.0090	0.0150	0.0205	0.0260
	20	0.0270	0.0450	0.0615	0.0780
		0.0065	0.0080	0.0110	0.0140
	30	0.0260	0.0320	0.0440	0.0560
		0.0090	0.0120	0.0150	0.0180
	40	0.0450	0.0600	0.0750	0.0900
		0.0120	0.0150	0.0180	0.0200
	50	0.0720	0.0900	0.1080	0.1200
		0.0270	0.0290	0.0310	0.0330
	60	0.1820	0.2030	0.2170	0.2310
		0.0300	0.0320	0.0340	0.0360
	70	0.2400	0.2560	0.2720	0.2880
		0.0280	0.0300	0.0320	0.0340
	80	0.2520	0.2700	0.2880	0.3060
		0.0290	0.0310	0.0330	0.0350
	90	0.2900	0.3100	0.3300	0.3500
		0.0280	0.0300	0.0325	0.0355
	100	0.3080	0.3300	0.3575	0.3905
		0.0290	0.0310	0.0365	0.0395
	110	0.3480	0.3720	0.4380	0.4740
		0.0300	0.0325	0.0345	0.0355
	120	0.3900	0.4225	0.4485	0.4615
		0.0280	0.0305	0.0360	0.0405
	130	0.3920	0.4270	0.5040	0.5670
		0.0330	0.0350	0.0410	0.0450
	140	0.4950	0.5250	0.6150	0.6750
		0.0305	0.0360	0.0380	0.0420
	150	0.4880	0.5760	0.6080	0.6720

Table 36

Preliminary Turbidimetric Titration Data for IB 0.25 (with usual mechanical stirring and occasional shaking by hand)

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
		7000	6000	5460	5000
		0.0020	0.0035	0.0045	0.0055
IO .025B	20	0.0060	0.0105	0.0135	0.0165
		0.0040	0.0050	0.0060	0.0070
	30	0.0160	0.0200	0.0240	0.0280
		0.0050	0.0060	0.0070	0.0080
	40	0.0250	0.0300	0.0350	0.0400
		0.0120	0.0160	0.0180	0.0195
	50	0.0720	0.0960	0.1080	0.1170
		0.0425	0.0495	0.0560	0.0625
	60	0.2975	0.3465	0.3920	0.4375
		0.0480	0.0580	0.0665	0.0740
	70	0.3840	0.4640	0.5320	0.5920
		0.0630	0.0750	0.0860	0.0970
	80	0.5670	0.6750	0.7740	0.8730
		0.0610	0.0740	0.0845	0.0965
	90	0.6100	0.7400	0.8450	0.9650
		0.0600	0.0740	0.0865	0.0975
	100	0.6600	0.8140	0.9515	1.0725
		0.0565	0.0695	0.0815	0.0915
	110	0.6780	0.8340	0.9780	1.0980
		0.0545	0.0670	0.0765	0.0855
	120	0.7085	0.8710	0.9945	1.1115
		0.0510	0.0630	0.0720	0.0810
	130	0.7140	0.8820	1.0080	1.1340
		0.0485	0.0600	0.0695	0.0765
	140	0.7275	0.9000	1.0425	1.1475
		0.0450	0.0550	0.0645	0.0705
	150	0.7200	0.8800	1.0320	1.1280
	40				

Table 37

Turbidimetric Titration Data for IIB 0.25 (with usual mechanical stirring and occasional shaking by hand)

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
		7000	6000	5460	5000
		0.0030	0.0035	0.0045	0.0054
II 0.025B	20	0.0090	0.0105	0.0135	0.0162
		0.0040	0.0050	0.0060	0.0070
	30	0.0160	0.0200	0.0240	0.0280
		0.0050	0.0060	0.0070	0.0080
	40	0.0250	0.0300	0.0350	0.0400
		0.0120	0.0150	0.0180	0.0200
	50	0.0720	0.0900	0.1080	0.1200
		0.0430	0.0520	0.0572	0.0650
	60	0.3010	0.3640	0.4004	0.4550
		0.0480	0.0590	0.0680	0.0755
	70	0.3840	0.4720	0.5440	0.6040
		0.0630	0.0770	0.0875	0.0975
	80	0.5670	0.6930	0.7875	0.8775
		0.0610	0.0750	0.0850	0.0965
	90	0.6100	0.7500	0.8500	0.9650
		0.0600	0.0740	0.0860	0.0960
	100	0.6600	0.8140	0.9460	1.0560
		0.0565	0.0705	0.0815	0.0915
	110	0.6780	0.8460	0.9780	1.0980
		0.0540	0.0670	0.0760	0.0855
	120	0.7020	0.8710	0.9880	1.1115
		0.0510	0.0630	0.0730	0.0810
	130	0.7140	0.8820	1.0220	1.1340
		0.0485	0.0600	0.0695	0.0765
	140	0.7275	0.9000	1.0425	1.1475
		0.0450	0.0550	0.0645	0.0705
	150	0.7200	0.8800	1.0320	1.1280
	*	0.0090	0.0120	0.0150	0.0170
	40	0.0450	0.0600	0.0750	0.0850

Table 38

Turbidimetric Titration Data for B 0.5 (with shaking by hand and mechanical stirring)

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
		7000	6000	5460	5000
		0.0050	0.0075	0.0095	0.0115
0.05 B	20	0.0150	0.0225	0.0285	0.0345
		0.0080	0.0100	0.0120	0.0140
	30	0.0320	0.0400	0.0480	0.0560
		0.0100	0.0120	0.0140	0.0160
	40	0.0500	0.0600	0.0700	0.0800
		0.0260	0.0330	0.0385	0.0405
	50	0.1560	0.1980	0.2310	0.2430
		0.0860	0.1060	0.1205	0.1330
	60	0.6020	0.7420	0.8435	0.9310
		0.0960	0.1180	0.1355	0.1520
	70	0.7680	0.9440	1.0840	1.2160
		0.1250	0.1510	0.1750	0.1942
	80	1.1250	1.3590	1.5750	1.7478
		0.1215	0.1492	0.1705	0.1930
	90	1.2150	1.4920	1.7050	1.9300
		0.1200	0.1485	0.1698	0.1930
	100	1.3200	1.6335	1.8678	2.1230
		0.1140	0.1380	0.1640	0.1840
	110	1.3680	1.6560	1.9680	2.2080
		0.1085	0.1340	0.1560	0.1705
	120	1.4105	1.7420	2.0280	2.2165
		0.1020	0.1270	0.1460	0.1620
	130	1.4280	1.7780	2.0440	2.2680
		0.0970	0.1200	0.1390	0.1530
	140	1.4550	1.8000	2.0850	2.2950
		0.0900	0.1100	0.1300	0.1415
	150	1.4400	1.7600	2.0800	2.2640

Table 39

Turbidimetric Titration Data for IB 0.25 (with mechanical stirring)

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
		7000	6000	5460	5000
I 0.025B	40				
		0.0120	0.0150	0.0175	0.0195
	50	0.0720	0.0900	0.1050	0.1170
		0.0215	0.0260	0.0300	0.0340
	60	0.1505	0.1820	0.2100	0.2380
		0.0300	0.0365	0.0420	0.0470
	70	0.2400	0.2920	0.3360	0.3760
		0.0350	0.0430	0.0500	0.0550
	80	0.3150	0.3870	0.4500	0.4950
		0.0350	0.0435	0.0500	0.0550
	90	0.3500	0.4350	0.5000	0.5500
		0.0350	0.0430	0.0500	0.0550
	100	0.3850	0.4730	0.5500	0.6050
		0.0350	0.0430	0.0500	0.0550
	110	0.4200	0.5160	0.6000	0.6600
		0.0350	0.0430	0.0500	0.0550
	120	0.4550	0.5590	0.6500	0.7150
		0.0350	0.0435	0.0500	0.0550
	130	0.4900	0.6090	0.7000	0.7700
		0.0485	0.0600	0.0695	0.0765
	140	0.7275	0.9000	1.0425	1.1475
		0.0450	-	-	-
	150	-	-	-	-
		-	-	-	-
	160	-	-	-	-

Table 40

Turbidimetric Titration Data for II 0.25B (with mechanical stirring)

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
		7000	6000	5460	5000
IIB 0.025	40				
		0.0120	0.0150	0.0180	0.0195
	50	0.0720	0.0900	0.1080	0.1170
		0.0210	0.0260	0.0300	0.0340
	60	0.1470	0.1820	0.2100	0.2380
		0.0300	0.0365	0.0420	0.0465
	70	0.2400	0.2920	0.3360	0.3720
		0.0350	0.0435	0.0500	0.0550
	80	0.3150	0.3915	0.4500	0.4950
		0.0350	0.0435	0.0505	0.0555
	90	0.3500	0.4350	0.5050	0.5550
		0.0350	0.0430	0.0500	0.0550
	100	0.3850	0.4730	0.5500	0.6050
		0.0345	0.0430	0.0500	0.0550
	110	0.4140	0.5160	0.6000	0.6600
		0.0345	0.0430	0.0500	0.0550
	120	0.4485	0.5590	0.6500	0.7150
		0.0350	0.0430	0.0500	0.0550
	130	0.4900	0.6020	0.7000	0.7700
		0.0485	0.0600	0.0695	0.0765
	140	0.7275	0.9000	1.0425	1.1475
		-	-	-	-
	150	-	-	-	-

Table 41

Single-Stage Cumulative Turbidimetric Data for B - 0.05

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
		7000	6000	5460	5000
I 0.05B	40				
		0.0230	0.0290	0.0360	0.0390
	50	0.1380	0.1740	0.2160	0.2340
		0.0430	0.0520	0.0600	0.0660
	60	0.3010	0.3640	0.4200	0.4620
		0.0600	0.0730	0.0850	0.0940
	70	0.4800	0.5840	0.6800	0.7520
		0.0700	0.0860	0.1000	0.1100
	80	0.6300	0.7740	0.9000	0.9900
		0.0700	0.0860	0.1000	0.1100
	90	0.7000	0.8600	1.0000	1.1000
		0.0700	0.0860	0.1000	0.1100
	100	0.7700	0.9460	1.1000	0.1210
		0.0700	0.0860	0.1000	0.1100
	110	0.8400	0.1032	1.2000	0.1320
		0.0700	0.0860	0.1000	0.1100
	120	0.9100	0.1118	1.3000	0.1430
		0.0700	0.0860	0.1000	0.1100
	130	0.9800	0.1204	1.4000	0.1540
		0.0970	0.1200	0.1390	0.1530
	140	1.4550	1.8000	2.0850	2.2950
		0.0900	0.1100	0.1300	0.1425
	150	1.4400	1.7600	2.0800	2.2800

Fig. 41: Maximum Corrected Absorbances versus % Precipitant Added for B-0.25.

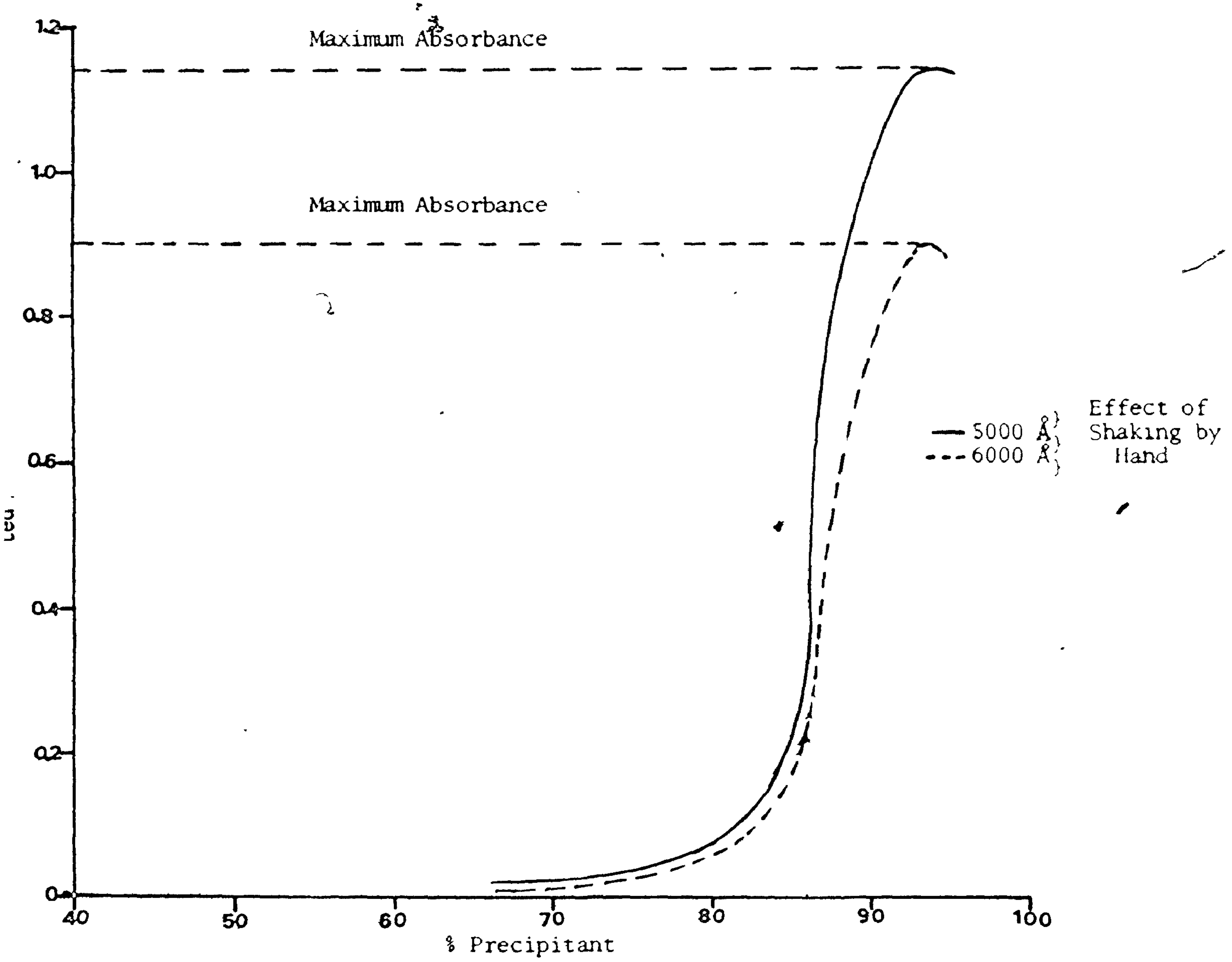


Fig. 42: Maximum Corrected Absorbances versus % Precipitant added for B - 0.25.

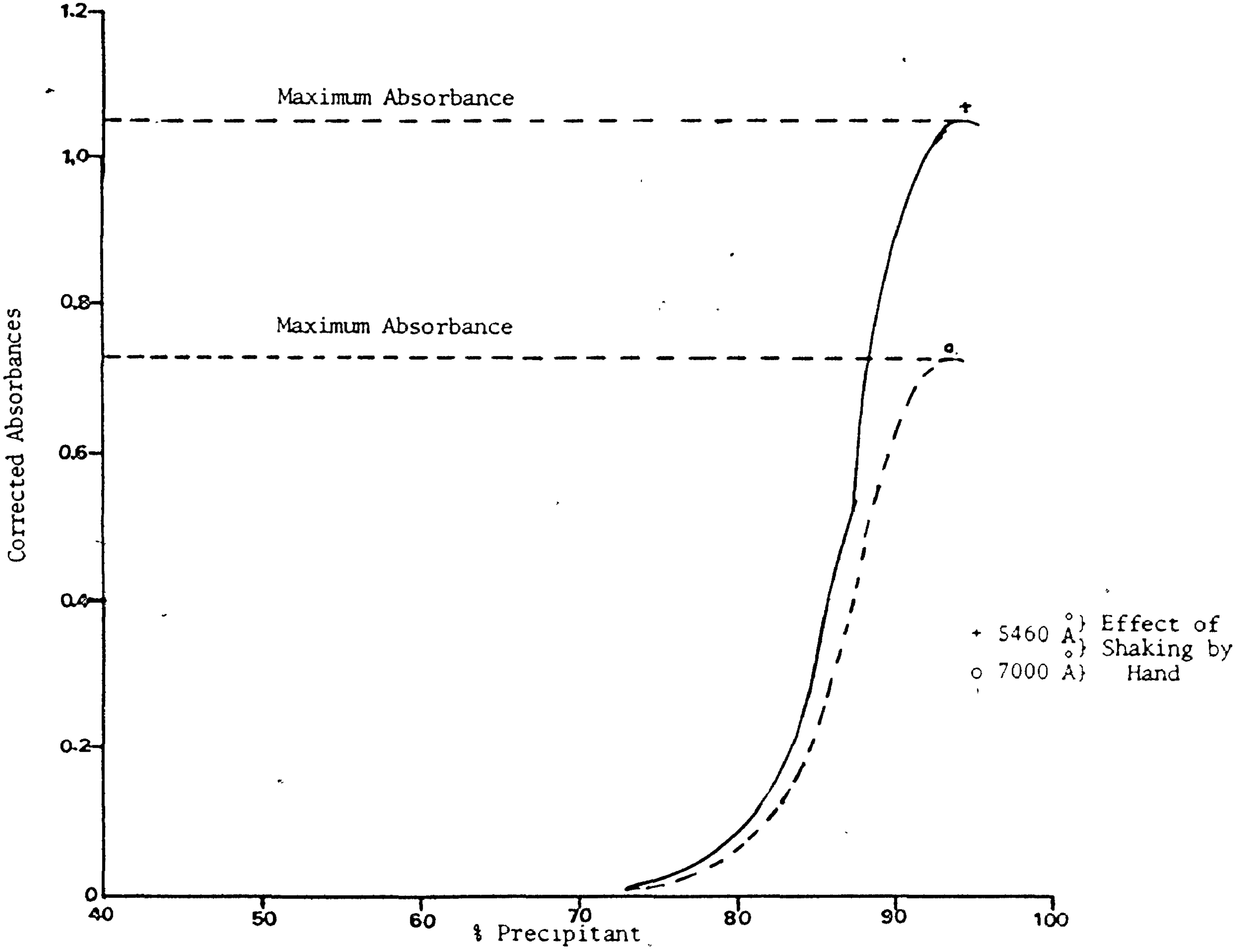


Fig. 43: Maximum Corrected Absorbances versus Per cent Precipitant for B - 0.25.

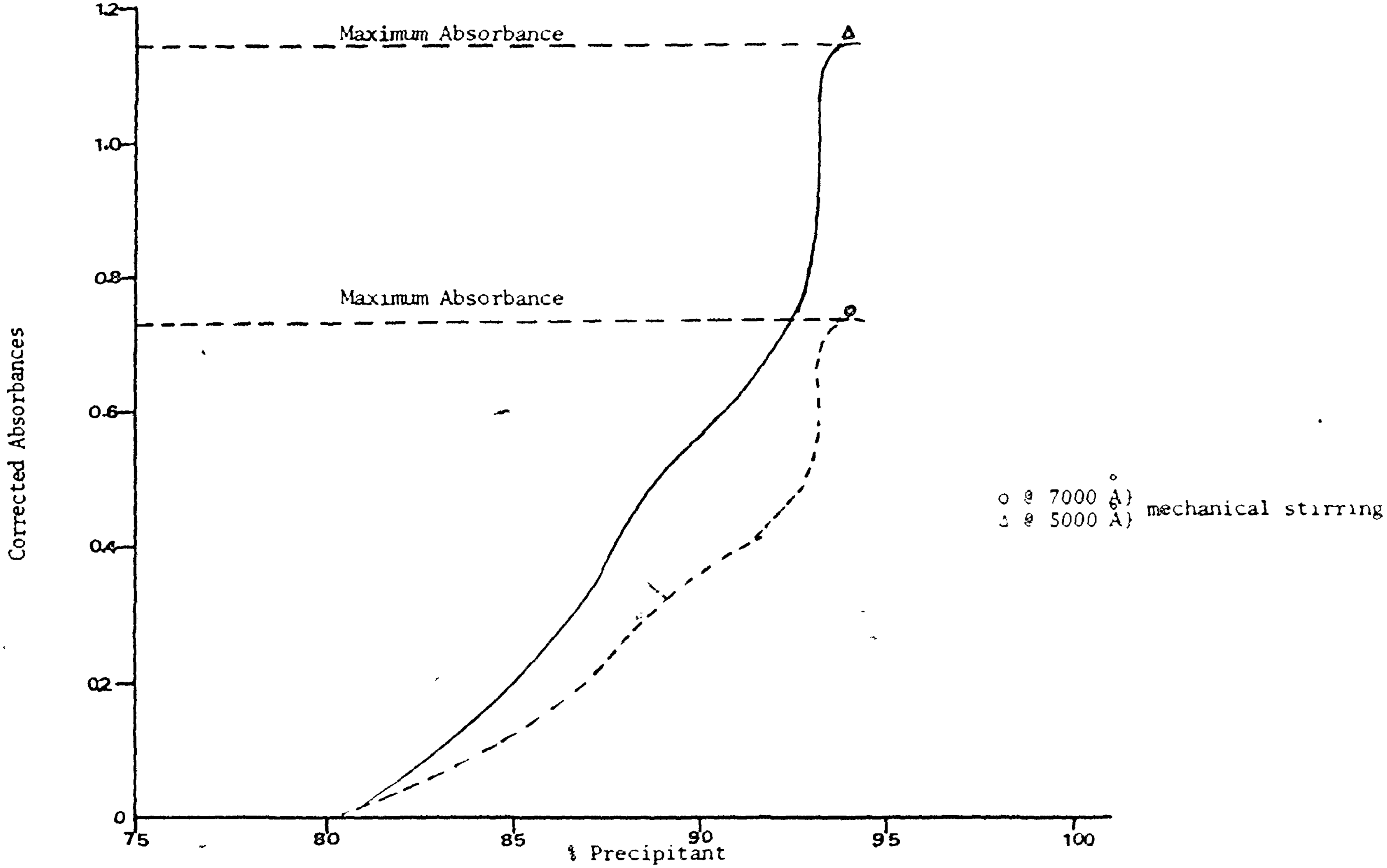


Table 42

Turbidimetric Precipitation of Standard B (with shaking by hand)

I Polyacrylamide, wt % 0.025

% CH$_3$OH	Wavelengths Å							
	7000		6000		5460		5000	
	c x 10^{-5} g/ml	% Precipitated	c x 10^{-5} g/ml	% Precipitated	c x 10^{-5} g/ml	% Precipitated	c x 10^{-5} g/ml	% Precipitated
50.00	-	-	-	-	-	-	-	-
66.70	0.3104	1.2414	0.2917	1.1667	0.3237	1.2950	0.3595	1.4379
75.00	0.5517	2.2069	0.5556	2.2222	0.5755	2.3022	0.6100	2.4401
80.00	0.8621	3.4483	0.8333	3.3333	0.8454	3.3816	0.8715	3.4858
83.30	2.4828	9.9310	2.6667	10.6667	2.5899	10.3597	2.5490	10.1961
85.70	10.2586	41.0300	9.6250	38.5000	9.4005	37.6019	9.5316	38.1264
87.50	13.2414	52.9660	12.8889	51.5560	12.7578	51.0311	12.8976	51.5904
88.90	19.5517	78.2070	18.7500	75.0001	18.5611	74.2446	19.0196	76.0784
90.00	21.0345	84.1370	20.5556	82.2223	20.2638	81.0551	21.0240	84.0959
90.90	22.7586	91.0346	22.6111	90.4445	22.8177	91.2709	23.3660	93.4641
91.70	23.3793	93.5170	23.1667	92.6667	23.4352	93.8129	23.9216	95.6863
92.30	24.4310	97.7240	24.1945	96.7779	23.8489	95.3956	24.2157	96.8627
92.86	24.6207	98.4828	24.5000	98.0001	24.0000	96.0000	24.7059	98.8235
93.33	-	100.0000	-	100.0000	-	100.0000	-	100.0000
* 80.00	1.5517	6.2070	1.6667	6.6667	1.7989	7.1942	1.8519	7.4074

......continued

Table 42 (continued)

Turbidimetric Precipitation of Standard B (with shaking by hand)

II Polyacrylamide, wt % 0.025

% CH_3OH	Wavelengths Å 7000 c x 10^{-5} g/ml	 7000 % Precipitated	 6000 c x 10^{-5} g/ml	 6000 % Precipitated	 5460 c x 10^{-5} g/ml	 5460 % Precipitated	 5000 c x 10^{-5}	 5000 % Precipitated
50.00	-	-	-	-	-	-	-	-
66.70	0.3103	1.2414	0.2917	1.1667	0.3237	1.2950	0.3529	1.4118
75.00	0.5517	2.2069	0.5556	2.2222	0.5755	2.3022	0.6100	2.4401
80.00	0.8621	3.4483	0.8333	3.3334	0.8393	3.3573	0.8715	3.4858
83.30	2.4828	9.9310	2.5000	10.0000	2.5899	10.3597	2.6144	10.4575
85.70	10.3793	41.5173	10.1111	40.4445	9.6019	38.4076	9.9129	39.6514
87.50	13.2414	52.9660	13.1111	52.4445	13.0456	52.1822	13.1590	52.6362
88.90	19.5517	78.2070	19.2500	77.0001	18.8843	75.5395	19.1177	76.4706
90.00	21.0345	84.1370	20.8334	83.3334	20.3837	81.5347	21.0240	84.0959
90.90	22.7586	91.0346	22.6111	90.4445	22.6858	9017433	23.0065	92.0262
91.70	23.3793	93.5170	23.5000	94.0001	23.4532	93.8129	23.9216	95.6863
92.30	24.2069	96.8277	24.1945	96.7779	23.6930	94.7721	24.2157	96.8628
92.86	24.6207	98.4828	24.5000	98.0001	24.5084	98.0335	24.7059	98.8236
93.33	-	100.0000	-	100.0000	-	100.0000	-	100.0000

Table 43

Turbidimetric Precipitation of Standard B (with shaking by hand)

Polyacrylamide, wt % 0.05

% CH_3OH	Wavelengths Å							
	7000		6000		5460		5000	
	$c \times 10^{-5}$ gm/cc	% Precipitated	$c \times 10^{-5}$ gm/cc	% Precipitated	$c \times 10^{-5}$ gm/cc	% Precipitated	$c \times 10^{-5}$ gm/cc	% Precipitated
50.00	-	-	-	-	-	-	-	-
66.70	0.5172	1.0345	0.6250	1.2500	0.6835	1.3669	0.7516	1.5033
75.00	1.1035	2.2069	1.1111	2.2222	1.1511	2.3022	1.2200	2.4401
80.00	1.7241	3.4483	1.6667	3.3334	1.6787	3.3573	1.7429	3.4858
83.30	5.3793	10.7586	5.5000	11.0000	5.5396	11.0791	5.2941	10.5882
85.70	20.7586	41.5173	20.6111	41.2223	20.2278	40.4556	20.2832	40.5665
87.50	26.4828	52.9656	26.2222	52.4445	25.9952	51.9904	26.4924	52.9848
88.90	38.7932	77.5863	37.7500	75.50000	37.7698	75.5395	38.0784	76.1569
90.00	41.8966	83.7932	41.4445	82.8890	40.8873	81.7745	42.0479	84.0959
90.90	45.5173	91.0346	45.3750	90.7501	44.7913	89.5827	46.2527	92.5055
91.70	47.1725	94.3449	46.0000	92.0001	47.1942	94.3884	48.1046	96.2092
92.30	48.6380	97.2760	48.3889	96.7779	48.6331	97.2661	48.2898	96.5796
92.86	49.2414	98.4829	49.3889	98.7779	49.0168	98.0336	49.4118	98.8236
93.33	-	100.0000	-	100.0000	-	100.0000	-	100.0000

Table 44

I Polyacrylamide, wt % 0.025
(Mechanical stirring)

% CH_3OH	Wavelengths Å							
	7000		6000		5460		5000	
	c x 10^{-5} gm/cc	% Precipitated	c x 10^{-5} gm/cc	% Precipitated	c x 10^{-5} gm/cc	% Precipitated	c x 10^{-5} gm/cc	% Precipitated
80.00	-	-	-	-	-	-	-	-
83.33	0.2474	9.897	0.2500	10.000	0.2518	10.072	0.2549	10.196
85.70	0.5172	20.687	0.5056	20.222	0.5036	20.144	0.5185	20.741
87.50	0.8247	32.990	0.8111	32.444	0.8058	32.230	0.8192	32.767
88.90	1.0825	43.299	1.0750	43.000	1.0791	43.166	1.0784	43.137
90.00	1.2028	48.110	1.2083	48.333	1.1990	47.962	1.1983	47.930
90.90	1.3230	52.921	1.3139	52.556	1.3189	52.758	1.3181	52.723
91.70	1.4433	57.732	1.4333	57.333	1.4389	57.554	1.4379	57.516
92.30	1.5636	62.543	1.5528	62.111	1.5588	62.350	1.5577	62.309
92.86	1.6839	67.354	1.6917	67.667	1.6787	67.146	1.6776	67.102
93.33	-	100.000	-	100.000	-	100.000	-	100.000
II Polyacrylamide, wt % 0.025								
80.00	-	-	-	-	-	-	-	-
83.33	0.2474	9.897	0.2500	10.000	0.2590	10.360	0.2549	10.196
85.70	0.5052	20.206	0.5056	20.222	0.5036	20.144	0.5185	20.741
87.50	0.8247	32.990	0.8111	32.444	0.8058	32.230	0.8105	32.418
88.90	1.0825	43.299	1.0880	43.500	1.0791	43.166	1.0784	43.137
90.00	1.2028	48.110	1.2083	48.333	1.2110	48.441	1.2092	48.366
90.90	1.3230	52.921	1.3139	52.556	1.3189	52.758	1.3181	52.723
91.70	1.4227	56.907	1.4333	57.333	1.4389	57.554	1.4379	57.516
92.30	1.5412	61.650	1.5528	62.111	1.5588	62.350	1.5577	62.309
92.86	1.6839	67.354	1.6722	66.889	1.6787	67.146	1.6776	67.102
93.33	-	100.000	-	100.000	-	100.000	-	100.000

Table 45

Polyacrylamide, wt % 0.050
(Mechanical stirring)

% CH_3OH	Wavelengths Å							
	7000		6000		5460		5000	
	c x 10^{-5} gm/cc	% Precipitated	c x 10^{-5} gm/cc	% Precipitated	c x 10^{-5} gm/cc	% Precipitated	c x 10^{-5} gm/cc	% Precipitated
80.00	-	-	-	-	-	-	-	-
83.33	0.4742	9.485	0.4833	9.667	0.5179	10.360	0.5098	10.196
85.70	1.0344	20.687	1.0111	20.222	1.0072	20.144	1.0065	20.131
87.50	1.6500	33.000	1.6222	32.444	1.6307	32.614	1.6383	32.767
88.90	2.1650	43.299	2.1500	43.000	2.1583	43.166	2.1569	43.137
90.00	2.4055	48.110	2.3889	47.778	2.3981	47.962	2.3965	47.930
90.90	2.6461	52.921	2.6278	52.556	2.6379	52.758	2.6362	52.723
91.70	2.8866	57.732	2.8667	57.333	2.8777	57.554	2.8758	57.516
92.30	3.1272	62.543	3.1056	62.111	3.1175	62.350	3.1155	62.309
92.86	3.3677	67.354	3.3444	66.889	3.3573	67.146	3.3551	67.102
93.33	-	100.000	-	100.000	-	100.000	-	100.000

Fig. 44: Turbidimetric Precipitation Curve of Standard B at Various Wavelengths Specified.

Mechanical stirring and shaking by hand {○ C-0.25B @ 5460 Å
{▽ C-0.25B @ 6000 Å
{△ C-0.25B @ 5000 Å

Mechanical stirring {● C-0.25B

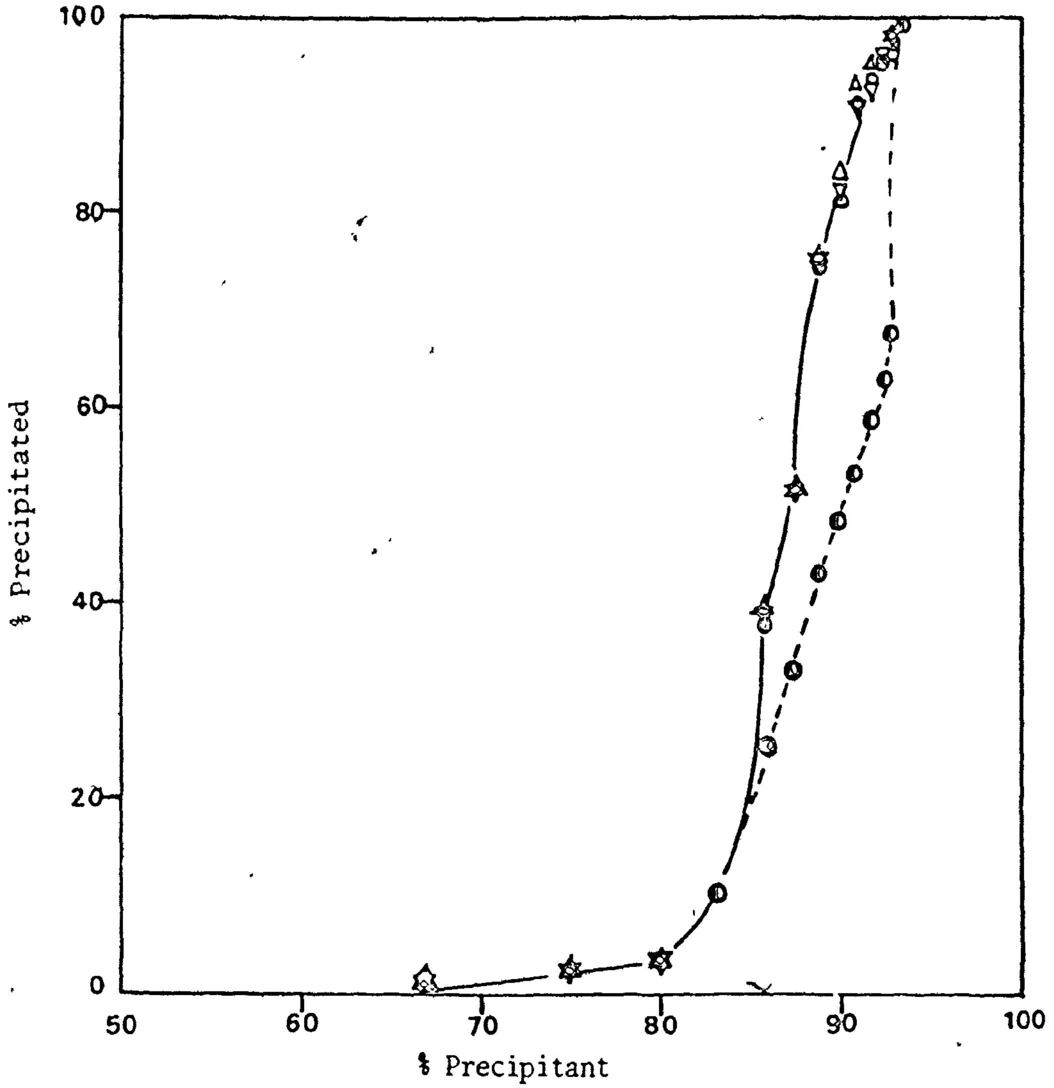


Fig. 45: Turbidimetric Precipitation Curve of Standard C-B at 7000 Å

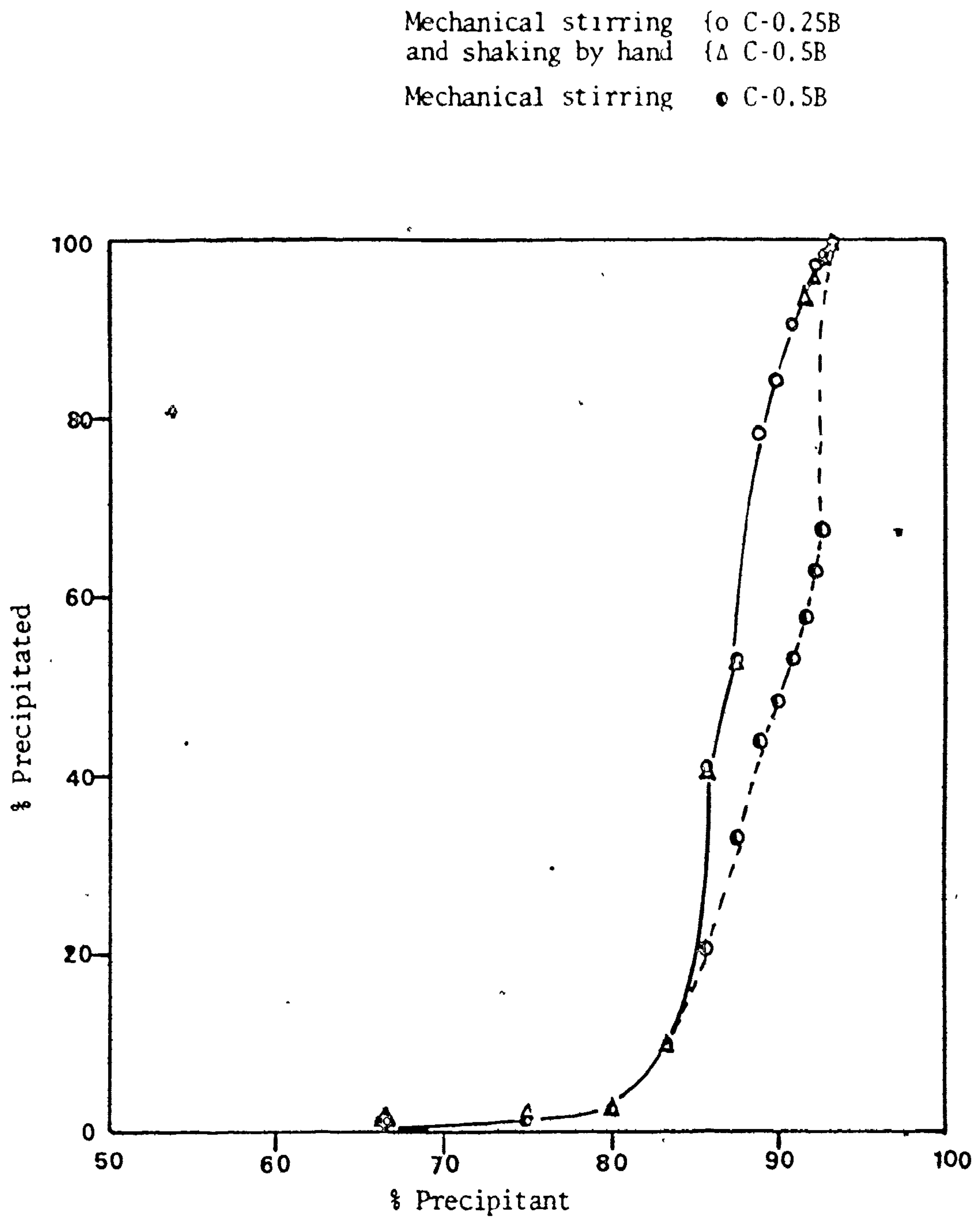


Table 46

Final Turbidimetric Titration[a] Data for IA 2.0

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
	cc	7000	6000	5460	5000
		-	-	-	-
0.20	40	-	-	-	-
		0.0045	0.0050	0.0060	0.0065
	50	0.0270	0.0300	0.0360	0.0390
		0.0105	0.0115	0.0133	0.0150
	60	0.0735	0.0805	0.0931	0.1050
		0.0140	0.0160	0.0180	0.0200
	70	0.1120	0.1280	0.1440	0.1600
		0.0150	0.0170	0.0195	0.0220
	80	0.1350	0.1530	0.1755	0.1980
		0.0145	0.0165	0.0192	0.0210
	90	0.1450	0.1650	0.1920	0.2100
		0.0140	0.0165	0.0185	0.0195
	100	0.1540	0.1815	0.2035	0.2145
		0.0145	0.0160	0.0185	0.0195
	110	0.1740	0.1920	0.2220	0.2340
		0.0140	0.0155	0.0175	0.0185
	120	0.1820	0.2015	0.2275	0.2405
		0.0133	0.0150	0.0170	0.0190
	130	0.1863	0.2100	0.2380	0.2660
		0.0140	0.0160	0.0180	0.0200
	140	0.2100	0.2400	0.2700	0.3000
		0.0130	0.0150	0.0165	0.0185
	150	0.2080	0.2400	0.2640	0.2960

Table 47

Final Turbidimetric Titration Data for IIA 2.0

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
	cc	7000	6000	5460	5000
		-	-	-	-
0.2	40	-	-	-	-
		0.0043	0.0050	0.0057	0.0065
	50	0.0258	0.0300	0.3420	0.0390
		0.0103	0.0115	0.0135	0.0140
	60	0.0721	0.0805	0.0945	0.0980
		0.0140	0.0160	0.0180	0.0200
	70	0.1120	0.1280	0.1440	0.1600
		0.0145	0.0165	0.0195	0.0220
	80	0.1305	0.1485	0.1755	0.1980
		0.0145	0.0165	0.0195	0.0210
	90	0.1450	0.1650	0.1950	0.2100
		0.0140	0.0165	0.0190	0.0200
	100	0.1540	0.1815	0.2090	0.2200
		0.0145	0.0165	0.0185	0.0195
	110	0.1740	0.1980	0.2220	0.2340
		0.0140	0.0160	0.0180	0.0195
	120	0.1820	0.2080	0.2340	0.2535
		0.0135	0.0150	0.0175	0.0190
	130	0.1890	0.2100	0.2450	0.2660
		0.0140	0.0160	0.0182	0.0202
	140	0.2100	0.2400	0.2730	0.3030
		0.0130	0.0150	0.0165	0.0185
	150	0.2080	0.2400	0.2640	0.2960

Table 48

Final Turbidimetric Titrations Data for A 2.5

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
	cc	7000	6000	5460	5000
		0.0007	0.0008	0.0010	0.0012
0.25	40	0.0035	0.0040	0.0050	0.0060
		0.0060	0.0070	0.0080	0.0090
	50	0.0360	0.0420	0.0480	0.0540
		0.0130	0.0143	0.0165	0.0183
	60	0.0910	0.1001	0.1155	0.1281
		0.0175	0.0200	0.0225	0.0250
	70	0.1400	0.1600	0.1800	0.2000
		0.0180	0.0200	0.0230	0.0255
	80	0.1620	0.1800	0.2070	0.2295
		0.0175	0.0195	0.0230	0.0260
	90	0.1750	0.1950	0.2300	0.2600
		0.0170	0.0190	0.0220	0.0240
	100	0.1870	0.2090	0.2420	0.2640
		0.0180	0.0200	0.0230	0.0250
	110	0.2160	0.2400	0.2760	0.3000
		0.0170	0.0190	0.0220	0.0140
	120	0.2210	0.2470	0.2860	0.3120
		0.0165	0.0185	0.0213	0.0240
	130	0.2310	0.2590	0.2982	0.3360
		0.0170	0.0190	0.0220	0.0240
	140	0.2550	0.2850	0.3300	0.3600
		0.0150	0.0170	0.0200	0.0220
	150	0.2400	0.2720	0.3200	0.3520

Table 49

Final Data for Turbidimetric Titrations of IA 3.0

Polyacrylamide wt %	CH_3OH added cc	Maximum and Corrected Absorbances, Wavelengths Å 7000	6000	5460	5000
		0.0010	0.0011	0.0012	0.0015
0.30	40	0.0050	0.0055	0.0060	0.0075
		0.0065	0.0075	0.0090	0.0105
	50	0.0390	0.0450	0.0540	0.0630
		0.0155	0.0170	0.0200	0.0220
	60	0.1085	0.1190	0.1400	0.1540
		0.0210	0.0240	0.0270	0.0300
	70	0.1680	0.1920	0.2160	0.2400
		0.0220	0.0255	0.0290	0.0320
	80	0.1980	0.2295	0.2610	0.2880
		0.0220	0.0250	0.0290	0.0315
	90	0.2200	0.2500	0.2900	0.3150
		0.0210	0.0240	0.0275	0.0300
	100	0.0231	0.2640	0.3025	0.3300
		0.0215	0.0240	0.0280	0.0300
	110	0.2580	0.2880	0.3360	0.3600
		0.0210	0.0235	0.0275	0.0300
	120	0.2730	0.3055	0.3575	0.3900
		0.0200	0.0230	0.0265	0.0290
	130	0.2800	0.3200	0.3710	0.4060
	140	0.0210	0.0240	0.0275	0.0300
		0.3150	0.3600	0.4125	0.4500
		0.0195	0.0220	0.0260	0.0270
	150	0.3120	0.3520	0.4160	0.4320

Table 50

Final Data for Turbidimetric Titrations of IIA 3.0

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
	cc	7000	6000	5460	5000
		0.0009	0.0011	0.0012	0.0014
0.30	40	0.0045	0.0055	0.0060	0.0070
		0.0065	0.0075	0.0085	0.0100
	50	0.0390	0.0450	0.0510	0.0600
		0.0160	0.0170	0.0190	0.0210
	60	0.1120	0.1190	0.1330	0.1470
		0.0210	0.0240	0.0270	0.0300
	70	0.1680	0.9120	0.2160	0.2400
		0.0220	0.0255	0.0290	0.0320
	80	0.1980	0.2295	0.2610	0.2880
		0.0220	0.0250	0.0285	0.0315
	90	0.2200	0.2500	0.2850	0.3150
		0.0210	0.0240	0.0275	0.0300
	100	0.2310	0.2640	0.3025	0.3300
		0.0215	0.0235	0.0285	0.0305
	110	0.2580	0.2820	0.3420	0.3660
		0.0215	0.0235	0.0275	0.0300
	120	0.2795	0.3055	0.3575	0.3900
		0.0205	0.0230	0.0270	0.0290
	130	0.2870	0.3220	0.3710	0.4060
		0.0210	0.0240	0.0275	0.0300
	140	0.3150	0.3600	0.4125	0.4500
		0.0195	0.0225	0.0260	0.0275
	150	0.3120	0.3600	0.4160	0.4400

Table 51

Final Turbidimetric Titration Data for A 4.0

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
	cc	7000	5000	5460	5000
		0.0010	0.0012	0.0015	0.0018
0.4	40	0.0050	0.0060	0.0075	0.0090
		0.0090	0.0100	0.0120	0.0133
	50	0.0540	0.6000	0.0720	0.0798
		0.0207	0.0235	0.0265	0.0280
	60	0.1447	0.1645	0.1855	0.1960
		0.0280	0.0320	0.0360	0.0400
	70	0.2240	0.2560	0.2880	0.3200
		0.0295	0.0340	0.0385	0.0430
	80	0.2655	0.3060	0.3465	0.3870
		0.0290	0.0330	0.0385	0.0420
	90	0.2900	0.3300	0.3850	0.4200
		0.0280	0.0320	0.0370	0.0410
	100	0.3080	0.3520	0.4070	0.4510
		0.0285	0.0325	0.0370	0.0390
	110	0.3420	0.3900	0.4440	0.4680
		0.0280	0.0320	0.0365	0.0390
	120	0.3650	0.4160	0.4745	0.5070
		0.0267	0.0307	0.0350	0.0400
	130	0.3738	0.4298	0.4900	0.5600
		0.0280	0.0320	0.0365	0.0400
	140	0.4200	0.4800	0.5475	0.6000
		0.0260	0.0300	0.0340	0.0370
	150	0.4160	0.4800	0.5440	0.5920
		0.0245	0.0280	0.0315	0.0350
	160	0.4165	0.4760	0.5355	0.5950

Table 52

Turbidimetric Precipitation Data of Standard A

I Polyacrylamide, wt % 0.3

% CH_3OH	7000		6000		5460		5000	
80.00	0.4762	1.5873	0.4583	1.5278	0.4364	1.4545	0.5000	1.6668
83.30	3.7143	12.3810	3.7499	12.5000	3.9273	13.0910	4.2002	14.0001
85.70	10.3333	34.4440	9.91663	33.0554	10.1817	33.9390	10.2667	34.2224
87.50	16.0000	53.3333	15.9999	53.3333	15.7091	52.3636	16.0000	53.3333
88.90	18.8571	62.8571	19.1249	63.7497	18.9818	63.2727	18.8000	64.0003
90.00	20.9520	69.8410	20.8333	69.4442	21.0909	70.3030	21.0000	70.0000
90.90	22.0000	73.3333	22.0000	73.3333	22.0000	73.3333	22.0010	73.3337
91.70	24.5714	81.9047	24.0000	80.0000	24.4364	81.4545	24.0000	80.0000
92.30	26.0000	86.6667	26.0000	86.6667	26.0000	86.6667	26.0000	86.6667
92.86	26.6670	88.9000	26.8333	89.4400	26.9818	89.9394	27.0667	90.2220
93.33	-	100.0000	-	100.0000	-	100.0000	-	100.0000
II Polyacrylamide, wt % 0.3								
80.00	0.4286	1.4286	0.4583	1.5278	0.4364	1.4545	0.4667	1.5556
83.30	3.7143	12.3810	3.7499	12.5000	3.7091	12.3636	4.0000	13.3334
85.70	10.6667	35.5555	9.1663	33.0554	9.6727	32.2424	9.8001	32.6668
87.50	16.0000	53.3333	16.0000	53.3333	15.7091	52.3636	16.0000	53.3333
88.90	18.8571	62.8571	19.1249	63.7497	18.9818	63.2727	19.8000	64.0003
90.00	20.9520	69.8410	20.8333	69.4442	20.7273	69.0903	21.0000	70.0000
90.90	22.0000	73.3333	22.0000	73.3333	22.0000	73.3333	22.0010	73.3337
91.70	24.5714	81.9047	23.4999	78.3330	24.8727	82.9091	24.0001	80.0004
92.30	26.6190	88.7301	26.0000	86.6667	26.0000	86.6667	26.0000	86.6667
92.86	27.3333	91.1111	26.8333	89.4400	26.9818	89.9394	27.0667	90.2220
93.33	-	100.0000	-	100.0000	-	100.0000	-	100.0000

Table 53

Turbidimetric Precipitation Data of Standard A

Polyacrylamide, wt % 0.40

% CH_3OH	7000		6000		5460		5000	
	c x 10^{-4} g/cc	% Precipitated	c x 10^{-5} g/cc	% Precipitated	c x 10^{-4} g/cc	% Precipitated	c x 10^{-4} g/cc	% Precipitated
50.00	-	-	-	-	-	-	-	-
66.70	-	-	-	-	-	-	-	-
75.00	-	-	-	-	-	-	-	-
80.00	0.4762	1.1905	0.4999	1.2500	0.5480	1.3699	0.6000	1.5001
83.30	5.1428	12.8571	5.0000	12.5000	5.2603	13.1510	5.3200	13.3001
85.70	13.7810	34.4524	13.7083	34.2708	13.5525	33.8813	13.0667	32.6668
87.50	21.3330	53.3330	21.3333	53.3333	21.0411	52.6027	21.3334	53.3334
88.90	25.2857	63.2143	25.5000	63.7500	25.3151	63.2877	25.8001	64.5003
90.00	27.6190	69.0476	27.5000	68.7500	28.1279	70.3196	28.0001	70.0000
90.90	29.3333	73.3333	29.3333	73.3333	29.7352	74.3379	30.0669	75.1760
91.70	32.5714	81.4286	32.5000	81.2500	32.4384	81.0959	31.2002	78.0004
92.30	34.6667	86.6667	34.6667	86.6667	34.6667	86.6667	33.8802	84.5004
92.86	35.6000	89.0000	35.8167	89.5417	35.7991	89.4977	37.3335	93.3338
93.33	-	100.0000	-	100.0000	-	100.0000	-	100.0000

Table 53 (continued)

Turbidimetric Precipitation Data of Standard A

Polyacrylamide, wt % 0.25

% CH_3OH	7000		6000		5460		5000	
	$c \times 10^{-4}$ g/cc	% Precipitated	$c \times 10^{-5}$ g/cc	% Precipitated	$c \times 10^{-4}$ g/cc	% Precipitated	$c \times 10^{-4}$ g/cc	% Precipitated
80.00	0.3431	1.3726	0.3509	1.4035	0.3977	1.5909	0.3333	1.3333
83.30	3.5294	14.1176	3.6842	14.7368	4.0909	16.3636	3.7500	15.0000
85.70	8.9216	35.6863	8.7807	35.1228	8.7500	35.0000	8.8958	35.5833
87.50	13.7255	54.9020	14.0351	56.1404	13.6364	54.5455	13.8889	55.5556
88.90	15.8824	63.5294	15.7895	63.1579	15.6818	62.7273	15.9375	63.7500
90.00	17.1569	68.6274	17.1053	68.4211	17.4242	69.6970	18.0556	72.2222
90.90	18.3330	73.3333	18.3333	73.3333	18.3333	73.3333	18.3333	73.3333
91.70	21.1765	84.7059	21.0526	84.2105	20.9091	83.6364	20.8333	83.3333
92.30	21.6667	86.6667	21.6667	86.6667	21.6667	86.6667	21.6667	86.6667
92.86	22.6471	90.6882	22.7199	90.8772	22.5909	90.3637	23.3333	93.3333
93.33	-	100.0000	-	100.0000	-	100.0000	-	100.0000

Fig. 46: Maximum Corrected Absorbances versus % Precipitant for A - 0.4 and A - 0.2 wt %.

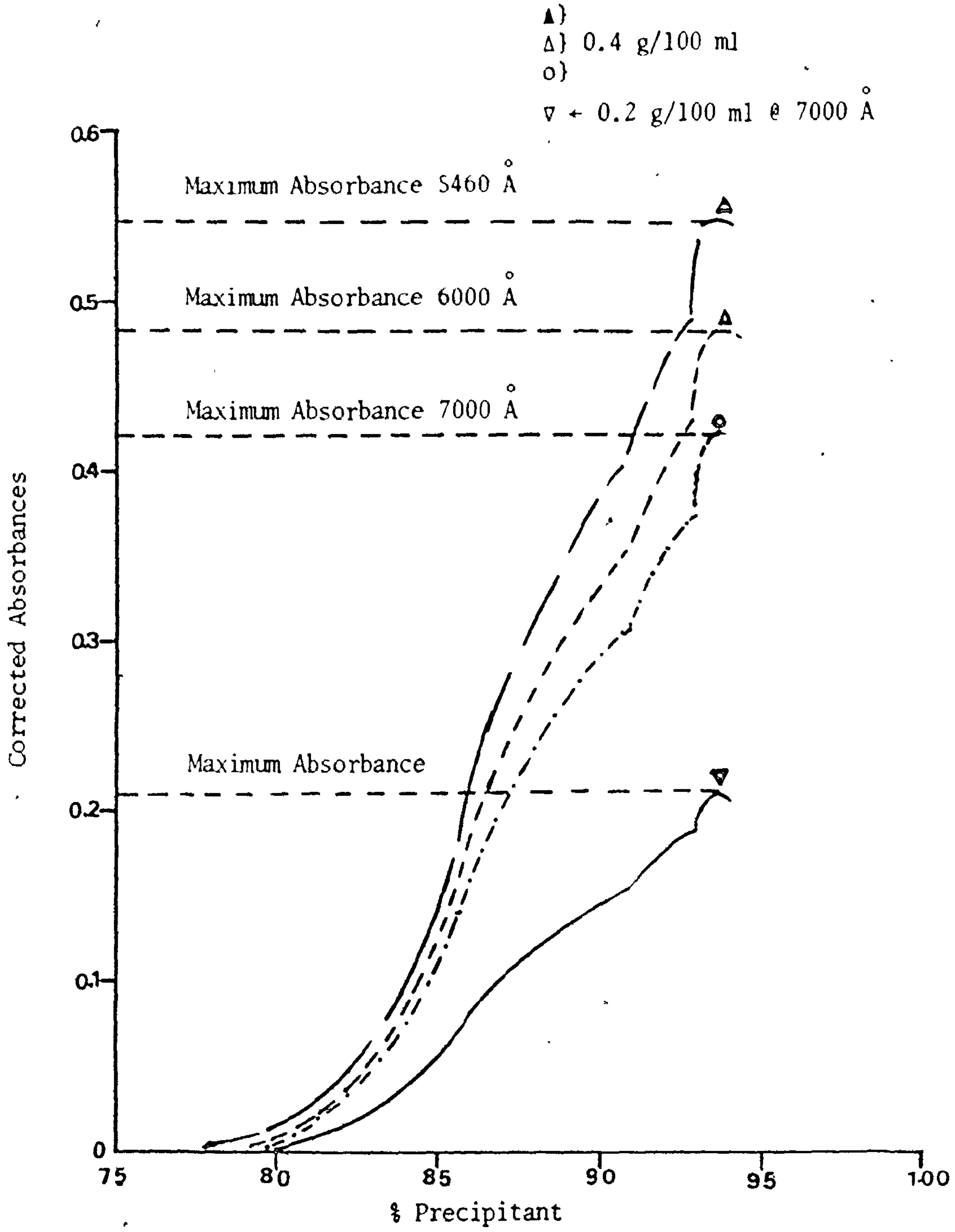


Fig. 47: Maximum Correction Absorbances versus % Precipitant for A - 3.

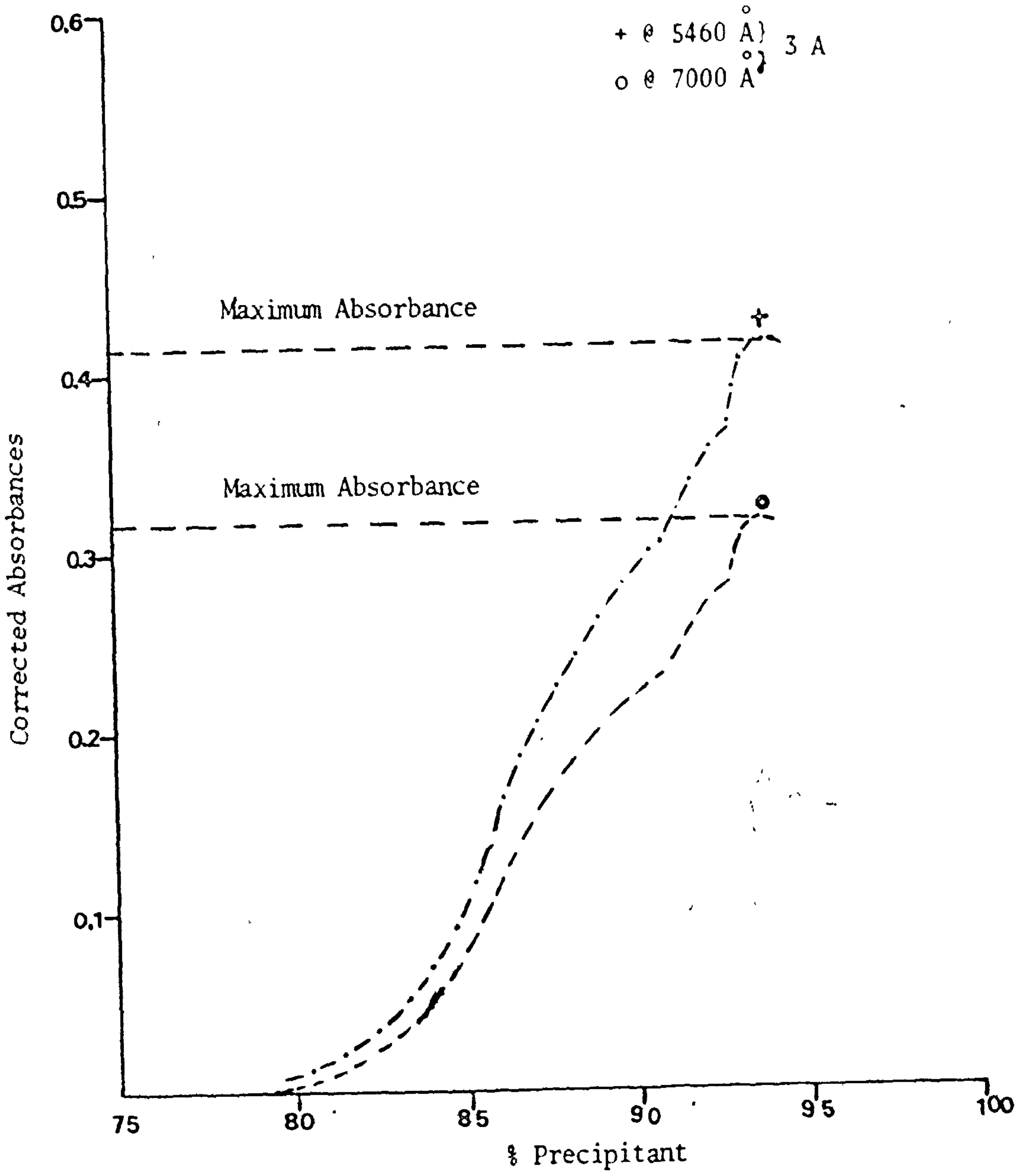


Fig. 48: Solubility Distribution of Standard A.

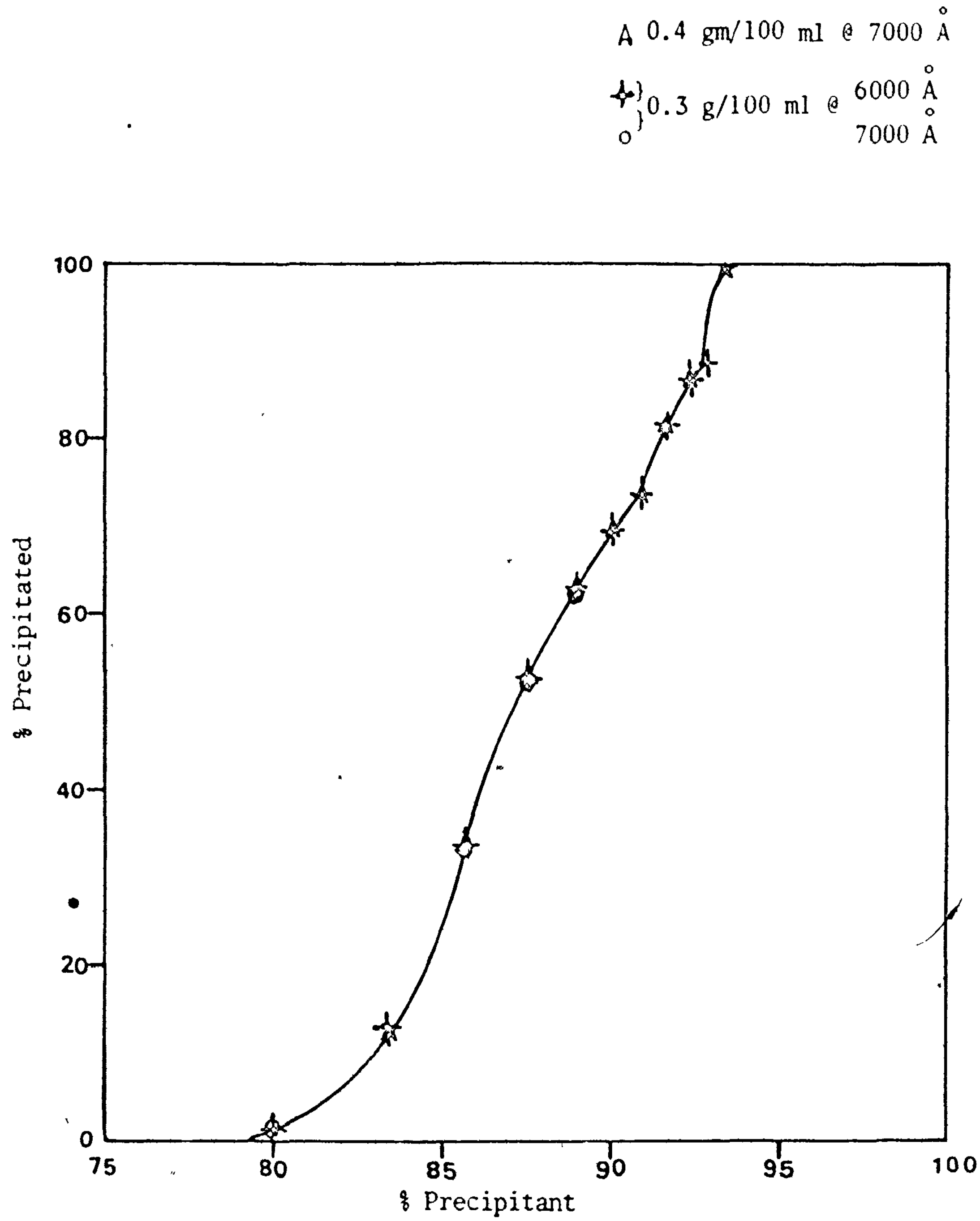


Fig. 49: Cumulative Most Probable Distribution for Standard A and Solubility Distribution.

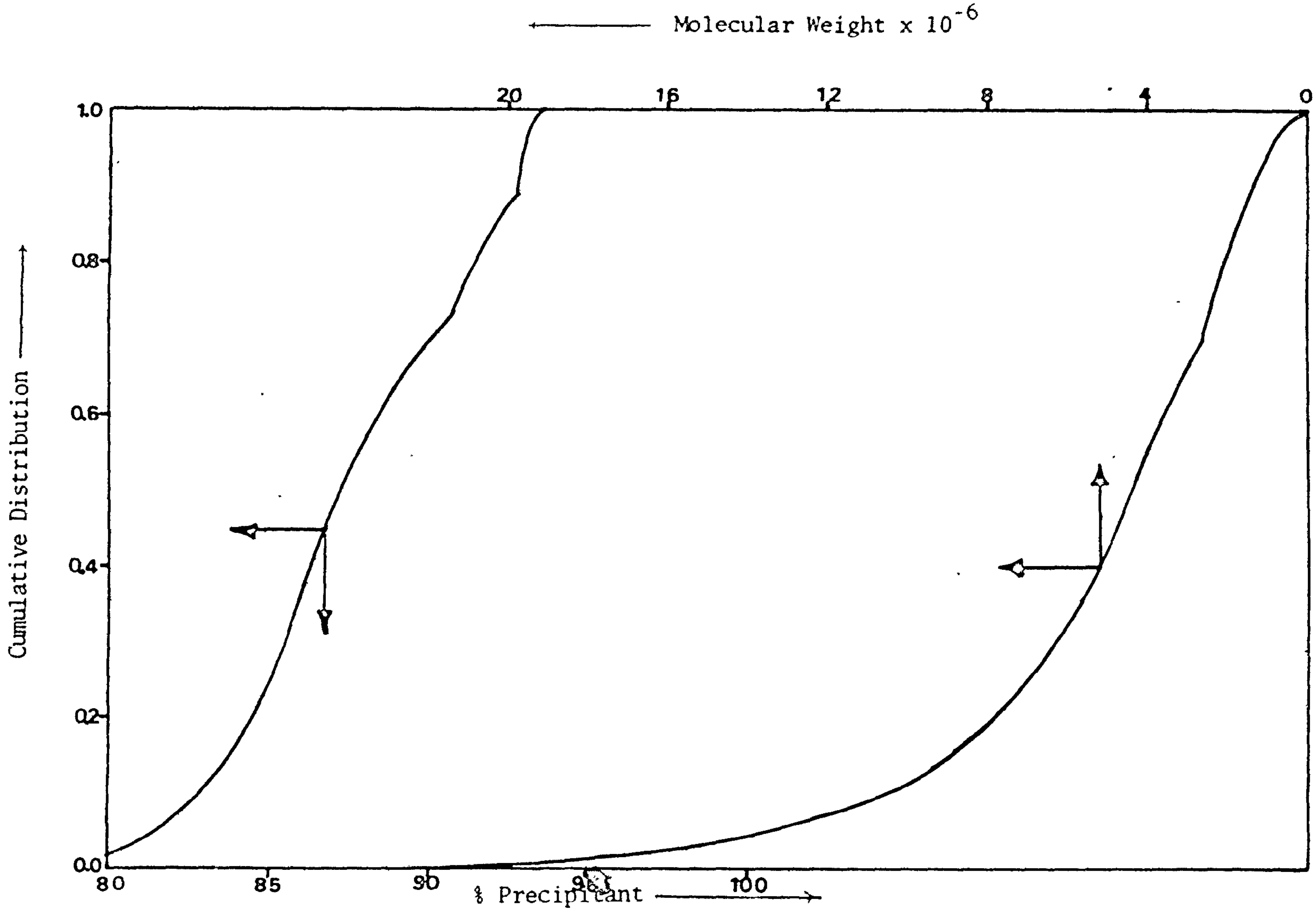


Table 54

Turbidimetric Titration Data for Standard O (Obtained with mechanical stirring and occasional shaking by hand)

Polyacrylamide wt %		CH_3OH added	Maximum and Corrected Absorbances			
			Wavelengths Å			
	cc	%	7000	6000	5460	5000
IO 0.25	20	66.70	-	-	-	-
	30	75.00	-	-	-	-
			0.0150	0.0165	0.0180	0.0180
	40	80.00	0.0750	0.0825	0.0900	0.0900
			0.0130	0.0150	0.0170	0.0170
	50	83.30	0.0780	0.0900	0.1020	0.1020
			0.0130	0.0160	0.0180	0.0180
	60	85.70	0.0910	0.1120	0.1260	0.1260
			0.0190	0.0230	0.0250	0.0260
	70	87.50	0.1520	0.1840	0.2000	0.2080
			0.0180	0.0220	0.0240	0.0245
	80	88.90	0.1620	0.1980	0.2160	0.2205
			0.0205	0.0240	0.0260	0.0270
	90	90.00	0.2050	0.2400	0.2600	0.2700
			0.0205	0.0240	0.0260	0.0270
	100	90.90	0.2255	0.2640	0.2860	0.2970
			0.0250	0.0280	0.0300	0.0310
	110	91.70	0.3000	0.3360	0.3600	0.3720
			0.0260	0.0290	0.0310	0.0320
	120	92.30	0.3380	0.3770	0.4030	0.4160
			0.0260	0.0290	0.0310	0.0320
	130	92.86	0.3640	0.4060	0.4340	0.4480
			0.0260	0.0290	0.0310	0.0320
	140	93.33	0.3900	0.4350	0.4650	0.4800
			0.0270	0.0300	0.0326	0.0330
	150	93.75	0.4320	0.4800	0.5120	0.5280

Table 55

Turbidimetric Titration Data for Standard O
(Obtained with mechanical stirring and occasional shaking by hand)

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
	cc	7000	6000	5460	5000
		0.0050	0.0060	0.0070	0.0080
IO 0.06	20	0.0150	0.0180	0.0210	0.0240
		0.0090	0.0100	0.0140	0.0155
	30	0.0360	1.0400	0.0560	0.6200
		0.0110	0.0130	0.0160	0.0180
	40	0.0550	0.0650	0.0800	0.0900
		0.0100	0.0120	0.0150	0.0180
	50	0.0600	0.0720	0.0900	0.1080
		0.0100	0.0120	0.0150	0.0180
	60	0.0700	0.0840	0.1050	0.1260
		0.0130	0.0165	0.0210	0.0250
	70	0.1040	0.1320	0.1680	0.2000
		0.0140	0.0165	0.0210	0.0250
	80	0.1260	0.1485	0.1890	0.2250
		0.0150	0.0180	0.0230	0.0270
	90	0.1500	0.1800	0.2300	0.2700
		0.0150	0.0180	0.0230	0.0280
	100	0.1650	0.1980	0.2530	0.3080
		0.0180	0.2250	0.0270	0.0310
	110	0.2160	0.2700	0.3240	0.3720
		0.0190	0.0230	0.0290	0.0330
	120	0.2470	0.2990	0.3770	0.4290
		0.0190	0.0225	0.0295	0.0330
	130	0.2660	0.3150	0.4130	0.4620
		0.0190	0.0225	0.0290	0.0330
	140	0.2850	0.3375	0.4350	0.4950

Table 56

Turbidimetric Titration Data for Standard O (While stirring mechanically and occasionally stirring by hand)

Polyacrylamide wt %	CH$_3$OH added cc	Maximum and Corrected Absorbances			
		Wavelengths Å			
		7000	6000	5460	5000
		0.0080	0.0120	0.0120	0.0130
IO 0.30	20	0.0240	0.0360	0.0360	0.0390
		0.0150	0.0180	0.0190	0.0220
	30	0.0600	0.0720	0.0760	0.0880
		0.0180	0.0200	0.0210	0.0240
	40	0.0900	0.1000	0.1050	0.1200
		0.0160	0.0180	0.0190	0.0220
	50	0.0960	0.1080	0.1140	0.1320
		0.0160	0.0180	0.0200	0.0220
	60	0.1120	0.1260	0.1400	0.1540
		0.0240	0.0260	0.0280	0.0310
	70	0.1920	0.2080	0.2240	0.2480
		0.0230	0.0250	0.0270	0.0300
	80	0.2070	0.2250	0.2430	0.2700
		0.0260	0.0280	0.0310	0.0340
	90	0.2600	0.2800	0.3100	0.3400
		0.0260	0.0280	0.0320	0.0350
	100	0.2860	0.3080	0.3520	0.3850
		0.0320	0.0340	0.0390	0.0420
	110	0.3840	0.4080	0.4680	0.5040
		0.0330	0.0350	0.0370	0.0410
	120	0.4290	0.4550	0.4810	0.5330
		0.0330	0.0350	0.0390	0.0420
	130	0.4620	0.4900	0.5460	0.5880

......continued

Table 57

Turbidimetric Titration Data of Standard 0
(Obtained with mechanical stirring only for 0.06 wt % starting polymer concentration)

Polyacrylamide wt %	CH_3OH added	Maximum and Corrected Absorbances			
		Wavelengths Å			
	cc	7000	6000	5460	5000
		-	-	-	-
0 0.06	30	-	-	-	-
		0.0080	0.0090	0.0120	0.0140
	40	0.0400	0.0450	0.0600	0.0700
		0.0160	0.0200	0.0250	0.0280
	50	0.0960	0.1200	0.1620	0.1680
		0.0200	0.0240	0.0320	0.0350
	60	0.1400	0.1680	0.2240	0.2450
		0.0240	0.0285	0.0360	0.0410
	70	0.1920	0.2280	0.2880	0.3280
		0.0230	0.0275	0.0350	0.0400
	80	0.2070	0.2475	0.3150	0.3600
		0.0240	0.0280	0.0360	0.0410
	90	0.2400	0.2800	0.3600	0.4100
		0.0225	0.0265	0.0345	0.0385
	100	0.2475	0.2915	0.3795	0.4235
		0.0220	0.0260	0.0330	0.0380
	110	0.2640	0.3120	0.3960	0.4560
		0.0210	0.0245	0.0320	0.0360
	120	0.2730	0.3185	0.4160	0.4680
		0.0200	0.0235	0.0305	0.0345
	130	0.2800	0.3290	0.4270	0.4830
		0.0200	0.0235	0.0305	0.0345
	140	0.3000	0.3525	0.4575	0.5175
		0.0200	0.0235	0.0300	0.0345
	150	0.3200	0.3760	0.4800	0.5520
		0.0190	0.0225	0.0290	0.0330
	160	0.3230	0.3825	0.4930	0.5610

Fig. 50: Maximum Corrected Absorbances versus % Precipitant Added for Standard 0 (mechanical stirring and shaking by hand).

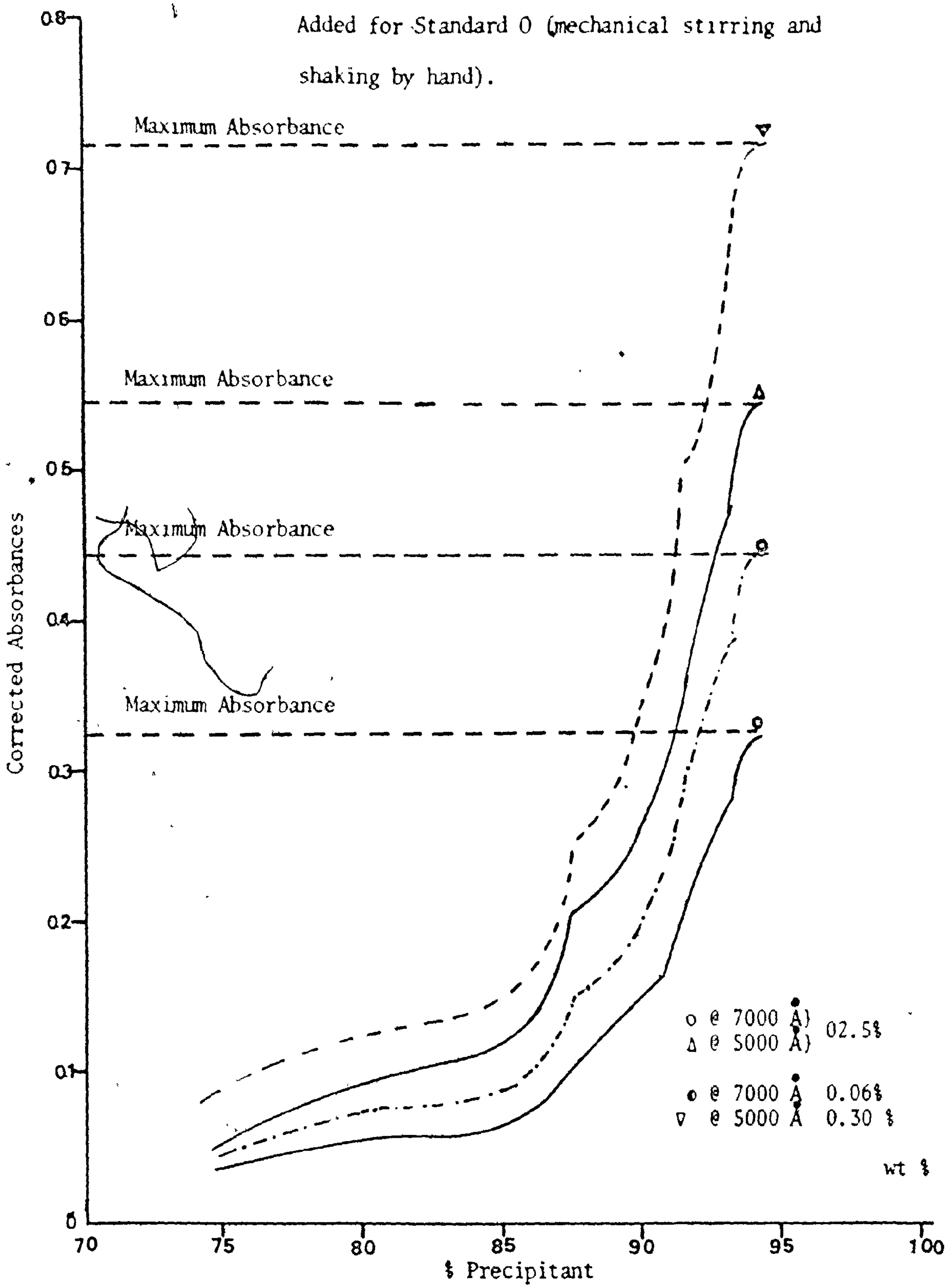


Table 58

Turbidimetric Titration Data of Standard O (with mechanical stirring only for 0.25 wt % polymer starting concentration)

Polyacrylamide wt %	CH_3OH added ml	Maximum and Corrected Absorbances			
		Wavelengths Å			
		7000	6000	5460	5000
		0.0105	0.0115	0.0120	0.0130
0.25 0	40	0.0525	0.0575	0.0600	0.0650
		0.0205	0.0240	0.0250	0.0270
	50	0.1230	0.1440	0.1500	0.1620
		0.0265	0.0300	0.0320	0.0340
	60	0.1855	0.2100	0.2240	0.2380
		0.0325	0.0360	0.0385	0.0400
	70	0.2600	0.2880	0.3080	0.3200
		0.0315	0.0350	0.0375	0.0390
	80	0.2835	0.3150	0.3375	0.3510
		0.0325	0.0365	0.0390	0.0405
	90	0.3250	0.3650	0.3900	0.4050
		0.0310	0.0340	0.0365	0.0380
	100	0.3410	0.3740	0.4015	0.4180
		0.0300	0.0335	0.0360	0.0370
	110	0.3600	0.4020	0.4320	0.4440
		0.0285	0.0315	0.0340	0.0350
	120	0.3705	0.4095	0.4420	0.4550
		0.0275	0.0305	0.0325	0.0335
	130	0.3850	0.4270	0.4550	0.4690
		0.0275	0.0305	0.0325	0.0335
	140	0.4125	0.4575	0.4875	0.5025
		0.0270	0.0300	0.0320	0.0330
	150	0.4320	0.4800	0.5120	0.5280
		0.0260	0.0290	0.0310	0.0320
	160	0.4420	0.4930	0.5270	0.5440

Table 59

Turbidimetric Titration Data of Standard O (during mechanical stirring only for 0.3 wt % polymer starting concentration)

Polyacrylamide wt %	CH_3OH added ml	Maximum and Corrected Absorbances Wavelengths Å 7000	6000	5460	5000
		0.0135	0.0145	0.0160	0.0180
030.0	40	0.6750	0.7250	0.0800	0.0900
		0.0275	0.0280	0.0330	0.0380
	50	0.1650	0.1680	0.1980	0.2280
		0.0360	0.0360	0.0410	0.0460
	60	0.2520	0.2520	0.2870	0.3220
		0.0410	0.0425	0.0470	0.0520
	70	0.3280	0.3400	0.3760	0.4160
		0.0400	0.0415	0.0460	0.0510
	80	0.3600	0.3735	0.4140	0.4590
		0.0410	0.0425	0.0470	0.0520
	90	0.4100	0.4250	0.4700	0.5200
		0:0390	0.0410	0.0450	0.0500
	100	0.4290	0.4510	0.4950	0.5500
		0.0380	0.0400	0.0435	0.0480
	110	0.4560	0.4800	0.5220	0.5760
		0.0365	0.0385	0.0415	0.0455
	120	0.4745	0.5005	0.5395	0.5915
		0.0345	0.0360	0.0400	0.0440
	130	0.4830	0.5040	0.5600	0.6160
		0.0345	0.0360	0.0400	0.0440
	140	0.5175	0.5400	0.6000	0.6600
		0.0340	0.0360	0.0400	0.0440
	150	0.5440	0.5760	0.6400	0.7040
		0.0330	0.0345	0.0380	0.0420
	160	0.5610	0.5865	0.6460	0.7140

Fig. 51: Maximum Corrected Absorbances versus % Non-solvent Added for Standard 0.

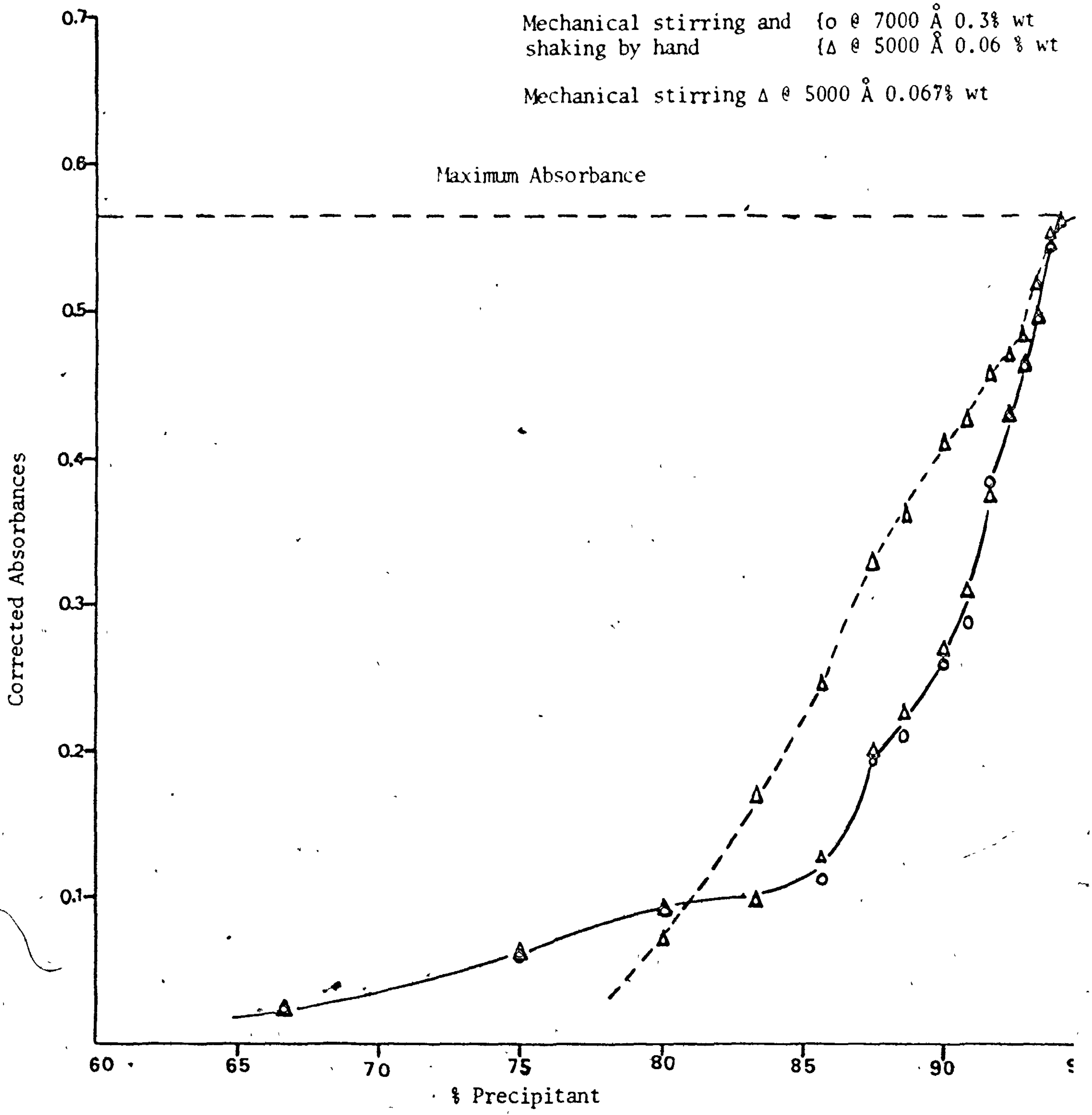


Table 60

Turbidimetric Precipitation Data of Standard O (Mechanical stirring and shaking by hand)

Polyacrylamide, wt % 0.3

% CH_3OH	Wavelengths Å							
	7000		6000		5460		5000	
	c x 10^{-4} gm/ml	% Precipitated	c	%	c	%	c	%
66.70	1.2834	4.28	1.8414	6.14	1.6718	5.57	1.6837	5.46
75.00	3.2086	10.70	3.6829	12.28	3.5294	11.77	3.6975	12.33
80.00	4.8128	16.04	5.1151	17.05	4.8762	16.25	5.0420	16.81
83.30	5.1337	17.11	5.5243	18.41	5.2941	17.65	5.5462	18.49
85.70	6.3636	21.21	6.4450	21.48	6.5016	21.67	6.4706	21.57
87.50	10.2674	34.23	10.6394	35.47	10.4025	34.68	10.4202	34.73
88.90	11.0695	36.90	11.5090	38.36	11.2848	37.62	11.3445	37.82
90.00	13.9037	46.35	14.3223	47.74	14.3963	47.99	14.2857	47.62
90.90	15.2941	50.98	15.7546	52.52	16.3467	54.49	16.1765	53.92
91.70	20.5348	68.45	20.8696	69.57	21.7337	72.45	21.1765	70.59
92.30	22.9412	76.47	23.2737	77.58	22.3375	74.46	22.3950	74.65
92.86	24.7059	82.35	25.0639	83.55	25.3560	84.52	24.7059	82.35
93.33	26.4706	88.24	26,8542	89.51	26.4706	88.24	26.4706	88.24
93.75	29.0909	96.97	29.4629	98.21	29.7204	99.07	29.5798	98.60
94.12	-	100.00	-	100.00	-	100.00	-	100.00

Table 61

Turbidimetric Titration Data of Standard O (Mechanical stirring and shaking by hand)

Polyacrylamide, wt % 0.25

% CH_3OH	Wavelengths Å							
	7000		6000		5460		5000	
	c x 10^{-5} gm/ml	%	c	%	c	%	c	%
66.70								
75.00								
80.00	4.2421	16.97	4.1836	16.73	4.2695	17.08	4.1360	16.54
83.30	4.4118	17.65	4.5639	18.26	4.8387	19.36	4.6875	18.75
85.70	5.1470	20.59	5.6795	22.72	5.9772	23.91	5.7904	23.16
87.50	8.5973	34.39	9.3306	37.32	9.4877	37.95	9.5588	38.24
88.90	9.1629	36.65	10.0406	40.16	10.2467	40.99	10.1333	40.53
90.00	11.5950	46.38	12.1704	48.68	12.3340	49.34	12.4081	49.63
90.90	12.7545	51.02	13.3874	53.55	13.5674	54.27	13.6489	54.60
91.70	16.9700	67.87	17.0385	68.15	17.0778	68.31	17.0956	68.38
92.30	19.1200	76.47	19.1176	76.47	19.1176	76.47	19.1177	76.47
92.86	20.5900	82.35	20.5882	82.35	20.5882	82.35	20.5882	82.35
93.33	22.0600	88.24	22.0588	88.24	22.0588	88.24	22.0588	88.24
93.75	24.4300	97.74	24.3408	97.36	24.2884	97.15	24.2647	97.06
94.12	-	100.00	-	100.00	-	100.00	-	100.00

Table 62

Turbidimetric Titration Data of Standard O
(Mechanical stirring and occasional shaking by hand)

Polyacrylamide, wt % 0.06

% CH_3OH	Wavelengths Å							
	7000		6000		5460		5000	
	c x 10^{-5} gm/ml	%	c	%	c	%	c	%
66.70	0.2786	4.64	0.2824	4.71	0.2556	4.26	0.2567	4.27
75.00	0.6687	11.15	0.6275	10.46	0.6815	11.36	0.6631	11.05
80.00	1.0217	17.03	1.0196	16.99	0.9736	16.23	0.9626	16.04
83.30	1.1146	18.58	1.1294	18.82	1.0953	18.26	1.1551	19.25
85.70	1.3003	21.67	1.3177	21.96	1.2779	21.30	1.3476	22.46
87.50	1.9319	32.20	2.0706	34.51	2.0446	34.08	2.1390	35.65
88.90	2.3406	39.00	2.3294	38.82	2.3002	38.34	2.4064	40.11
90.00	2.7864	46.44	2.8235	47.06	2.7992	46.64	2.8877	48.13
90.90	3.0650	51.08	3.1059	51.77	3.0791	51.32	3.2941	54.90
91.70	4.0124	66.87	4.2353	70.59	4.1136	68.56	3.9786	66.31
92.30	4.5883	76.47	4.6902	78.17	4.5882	76.47	4.5882	76.47
92.86	4.9412	82.35	4.9412	82.35	5.0264	83.77	4.9412	82.35
93.33	5.2941	88.24	5.2941	88.24	5.2941	88.24	5.2941	88.24
93.75	5.9443	99.07	5.7726	96.21	5.8418	97.36	5.8182	96.97
94.12	-	100.00	-	100.00	-	100.00	-	100.00

Table 63

Turbidimetric Titration Data of Standard 0
(Mechanical Stirring Only)

Polyacrylamide, wt % 0.06

% CH_3OH	Wavelengths Å							
	7000		6000		5460		5000	
	c x 10^{-5} gm/ml	%	c	%	c	%	c	%
75.00								
80.00	0.7430	12.384	0.7059	11.765	0.7302	12.170	0.7487	12.478
83.30	1.7833	29.721	1.8824	31.373	1.8256	30.426	1.7968	29.947
85.70	2.6006	43.344	2.6353	43.922	2.7262	45.436	2.6203	43.672
87.50	3.5666	59.443	3.5765	59.608	3.5051	58.418	3.5080	58.467
88.90	3.8452	64.087	3.8824	64.706	3.8337	63.895	3.8503	64.171
90.00	4.4582	74.303	4.3922	73.203	4.3813	73.022	4.3850	73.084
90.90	4.5975	76.625	4.5726	76.209	4.6187	76.978	4.5294	75.490
91.70	4.9040	81.734	4.8941	81.569	4.8195	80.325	4.8770	81.283
92.30	5.0712	84.520	4.9961	83.268	5.0629	84.381	5.005	83.423
92.86	5.2012	86.687	5.1608	86.013	5.1968	86.613	5.1658	86.096
93.33	5.5728	92.879	5.5294	92.157	5.5680	92.799	5.5348	92.246
93.75	5.9443	99.071	5.8980	98.301	5.8418	97.363	5.9037	98.396
94.12		100.000	-	100.000	-	100.000	-	100.000

......continued

Table 63 (continued)

Turbidimetric Titration Data of Standard O (Mechanical Stirring Only)

Polyacrylamide, wt % 0.25

% CH_3OH	Wavelengths Å							
	7000		6000		5460		5000	
	$c \times 10^{-5}$ gm/ml	%	c	%	c	%	c	%
75.00								
80.00	0.2970	11.878	0.2916	11.663	0.2846	11.385	0.2987	11.949
83.30	0.6957	27.828	0.7302	29.209	0.7116	28.463	0.7445	29.779
85.70	1.0492	41.968	1.0649	42.596	1.0626	42.505	1.0938	43.750
87.50	1.4706	58.824	1.4605	58.418	1.4611	58.445	1.4706	58.824
88.90	1.6035	64.140	1.5974	63.895	1.6010	64.042	1.6131	64.522
90.00	1.8382	73.529	1.8509	74.037	1.8501	74.004	1.8612	74.449
90.90	1.9287	77.149	1.8966	75.862	1.9047	76.186	1.9210	76.838
91.70	2.0362	81.448	2.0385	81.542	2.0493	81.973	2.0404	81.617
92.30	2.0956	83.824	2.0766	83.063	2.0968	83.871	2.0910	83.640
92.86	2.1776	87.104	2.1653	86.613	2.1584	86.338	2.1553	86.213
93.33	2.3331	93.326	2.3200	92.799	2.3126	92.505	2.3093	92.371
93.75	2.4434	97.738	2.4341	97.363	2.4288	97.154	2.4265	97.059
94.12	-	100.000	-	100.000	-	100.000	-	100.000

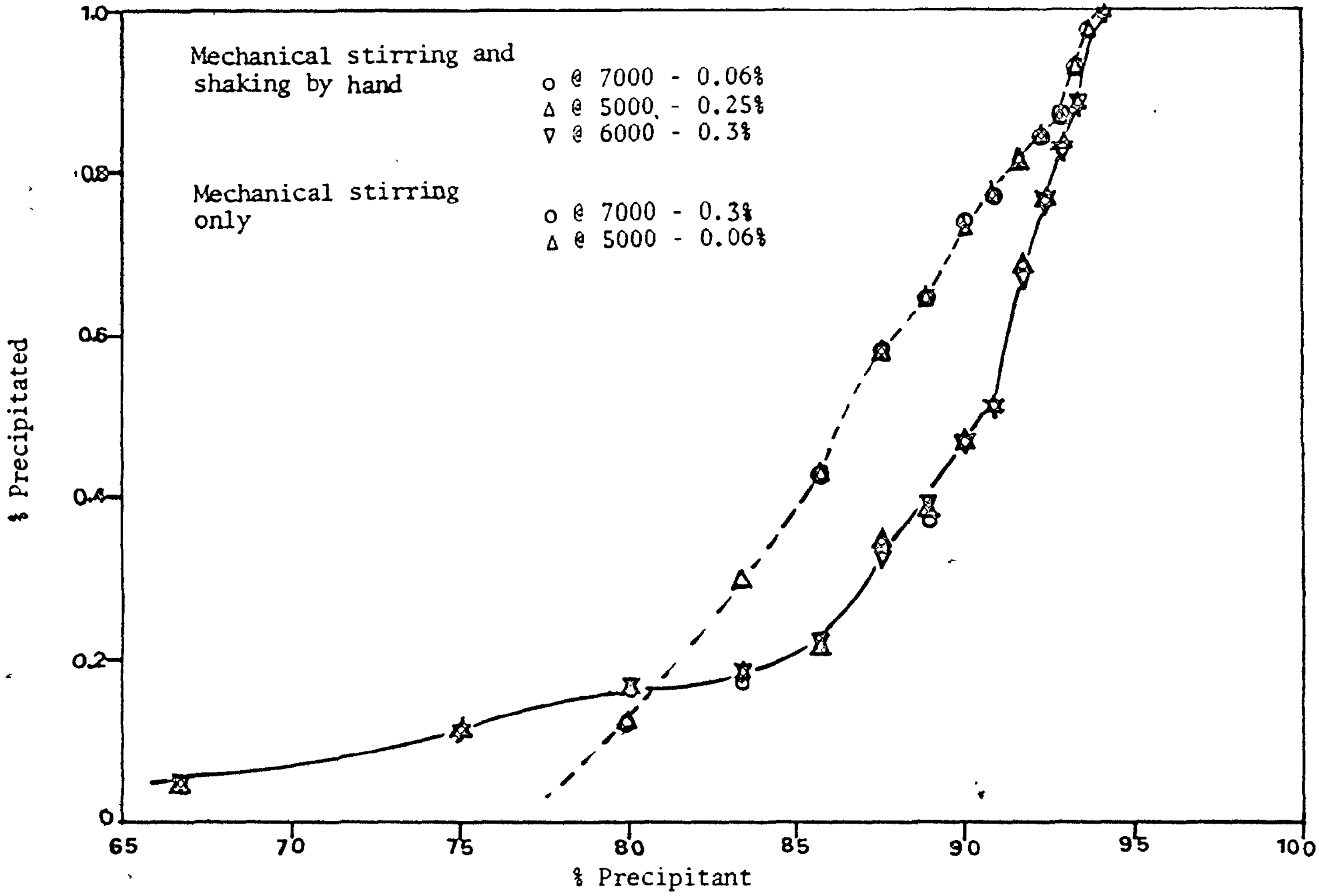
Table 64

Turbidimetric Titration Data of Standard O (Mechanical stirring only)

Polyacrylamide, wt % 0.30

	Wavelengths Å							
	7000		6000		5460		5000	
	c	%	c	%	c	%	c	%
76.00	-	-	-	-	-	-	-	-
80.00	0.3610	12.032	0.3708	12.362	0.3715	12.384	0.3782	12.605
83.30	0.8824	29.412	0.8593	28.645	0.9195	30.650	0.9580	31.933
85.70	1.3476	44.920	1.2890	42.967	1.3328	44.427	1.3529	45.098
87.50	1.7540	58.467	1.7392	57.971	1.7461	58.204	1.7479	58.263
88.90	1.9251	64.171	1.9105	63.683	1.9226	64.087	1.9286	64.286
90.00	2.1925	73.084	2.1739	74.264	2.1827	72.755	2.1849	72.829
90.90	2.2941	76.471	2.3069	76.897	2.2988	76.625	2.3109	77.031
91.70	2.4385	81.283	2.4552	81.841	2.4242	80.805	2.4202	80.672
92.30	2.5374	84.581	2.5601	85.337	2.5054	83.514	2.4853	82.843
92.86	2.5829	86.096	2.5780	85.934	2.6006	86.687	2.5882	86.275
93.33	2.7674	92.246	2.7622	92.072	2.7864	92.879	2.7731	92.437
93.75	2.9091	96.970	2.9463	98.210	2.9721	99.071	2.9580	98.600
94.12	-	100.000		100.000	-	100.000	-	100.000

Fig. 52: Solubility Distribution of Standard O.



for a continuous distribution, where $W = W(M)$ is the differential weight molecular weight distribution function, such that the weight fraction w_{12} of polymer having a molecular weight between M_1 and M_2 (for all M_1 and M_2) is given by

$$w_{12} = \int_{M_1}^{M_2} W(M)dM \qquad 6.4.2$$

However, in this work, W was measured in arbitrary units and therefore the area under the distribution curve is no longer unity. Introducing the scale factor $\int_0^\infty WdM$, we have

$$\bar{M}_W = \frac{\int_0^\infty WMdM}{\int_0^\infty WdM} \qquad 6.4.3$$

Number average molecular weight was evaluated from the relation

$$\bar{M}_n = \frac{\int_0^\infty NMdM}{\int_0^\infty NdM} \qquad 6.4.4$$

where $N = N(M)$

$= W(M)/M$

Polydispersity is given by

$$P = \bar{M}_W/\bar{M}_N \qquad 6.4.5$$

Equations 6.4.2, 6.4.3 and 6.4.5 were used as shown to obtain the weight- and number-average molecular weights and polydisperisty.

CHAPTER 7

RESULTS

The shape of the absorbance or turbidity versus per cent precipitant plots are almost that of an S. There is a marked resemblance to the integral molecular weight distribution expected from a cumulative distribution. Accordingly, plots of integral molecular weight distributions were obtained. Since, however, changes in the distribution are best visualized by plotting differential distribution curves, these were also obtained.

The quality of the distributions derived from the present method was assessed by a qualitative visual comparison between them and those derived by the known conventional GPC technique which is assumed to give correct results; and by a quantitative comparison between the number- and weight-average molecular weights computed from the turbidimetric distributions with those found from GPC distribution - a method attributed to Ishige and Hamielec.(59) Where it was feared spurious results are to be expected from GPC measurements due to poor high molecular weight resolution limit, viscosity measurements of the averages were obtained. Viscosity measurements are presented in Appendix IV.

Standard C, a standard intermediate non-ionic polyacrylamide was used to obtain the general molecular weight-solubility relationship. Figure 40 shows the curve on a log-normal plot. There is also a marked resemblance between this calibration curve and the GPC calibration curve of molecular weight versus elution volume. Accordingly, an attempt was made to check if the curvature at the low-molecular weight end of the curve was due to poor resolution limit resulting from low molecular weight material. The calibration curve when corrected beyond 92% of non-solvent is found to be represented by

$$M = D_3 e^{-D_1 \psi_2}$$

where D_1 was found to be 18.239

D_3 also found to be 3.6891×10^{13}

Results of averages obtained using this equation and the curve without any corrections were obtained.

Scattering functions $\overline{(K/\rho)}_W$ were obtained, in order to study this principle, conditions and regions in which the size of aggregates occur. It must be borne in mind that in this method, aggregation to a uniform whole was encouraged throughout the titration. These values are tabulated in Table 66. Included in this table are proportionality constants expressing variation of turbidity with concentration of polymer precipitated and specific turbidities. The dependence of these relationships on the polymer starting concentrations have been shown in Figures 58 - 61. High rate of stirring, when possible, is known to enhance aggregation. Presence of electrolytes in polymer solutions is also known to encourage aggregation and settling. Results, when vigorous hand-shaking was applied to increase aggregation were obtained in addition to the conventional method of uniform mechanical stirring. Polymer Standard O, polymerized in the presence of an electrolyte, hydrochloric acid, was used to study the influence of the presence of an electrolyte during turbidimetric titrations.

In Table 65 are shown the molecular weight averages obtained as a result of all the above considerations. The polydispersities obtained from the present method and GPC have been included in Table 65 and these are in parentheses. The integral molecular weight distributions for Standard B, obtained by varying the methods of mixing and by GPC are shown in Figure 53. Figure 54 shows the integral molecular weight distributions for Standard C, obtained by the present method and GPC. Important in the plot, is the comparison between GPC distribution and TT distribution obtained using the calibration equation and uncorrected at the low molecular weight end of the distribution.

The validity of Eq. 6.2.3 was confirmed. The resolution of the method with respect to wide broad range of polydispersity is quite evident in Figure 56 which compares Standard 0 with Standard A. The integral molecular weight distribution of the Standard A has also been compared with that of the GPC in Figure 55. The molecular weight distributions of all the polymers have also been presented in differential forms in Figures 62 - 64.

Table 65

Comparison between GPC (and or viscosity measurement) and Computed Values for $\bar{M}_w$ and $\bar{M}_n$ and P (in bracket)

		$\bar{M}_w \times 10^{-6}$			$\bar{M}_n \times 10^{-6}$		
Sample	Viscosity	GPC Value	Computed Value (TT)		GPC Value	Computed Value (TT)	
			Present Method	Shaking by Hand		Present Method	Due to Shaking by Hand
Standard 0	$\bar{M}_n = 3.14$	7.16(2.866)	7.97(2.536)	7.68(3.906)	2.50	3.14	1.97
Standard A	-	5.04(2.000)	5.19(2.002)	-	2.52	2.59	-
Standard B	-	3.35(2.0938)	3.54(2.314)	4.86(2.010)	1.60	1.53	2.41
Standard C	-	5.83(2.429)	6.19(2.282)	-	2.40	2.71	-
Standard A*	-	-	5.88(1.414)	-	-	4.16	-
Standard B*	-	-	3.56(1.991)	-	-	1.79	-
Standard C*	-	-	6.39(2.175)	-	-	2.94	-
Standard 0*	-	-	7.83(2.224)	-	-	3.52	-

*Obtained using Eq. 6.2.3 beyond 92% non-solvent.

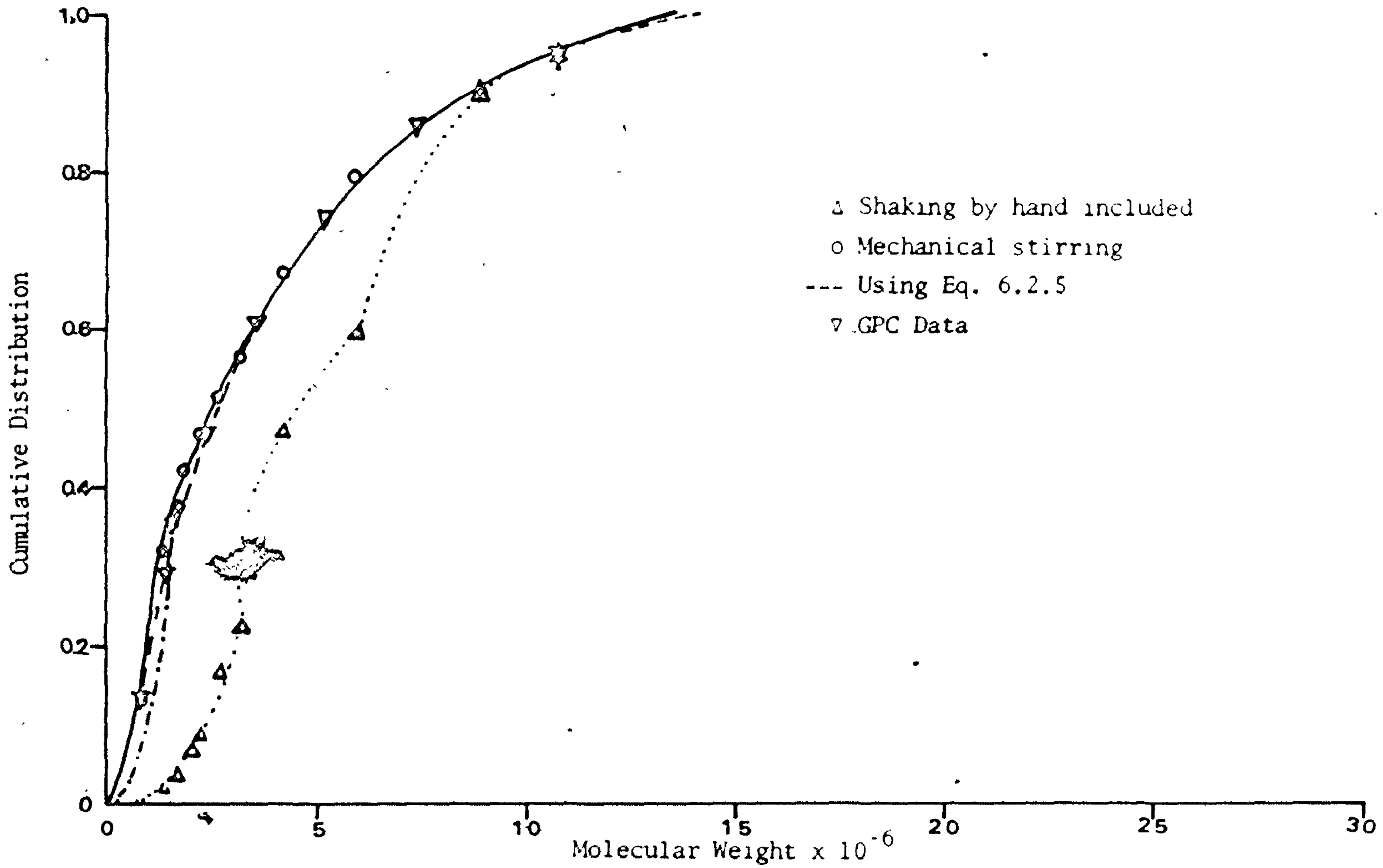


Fig. 53: Integral Molecular Weight Distribution for Standard B from TT.

Fig. 54: Cumulative Most Probable Distribution for TT and Cumulative Most Probable Distribution for GPC for Standard C. (on % Precipitated vs. Molecular Weight Scales).

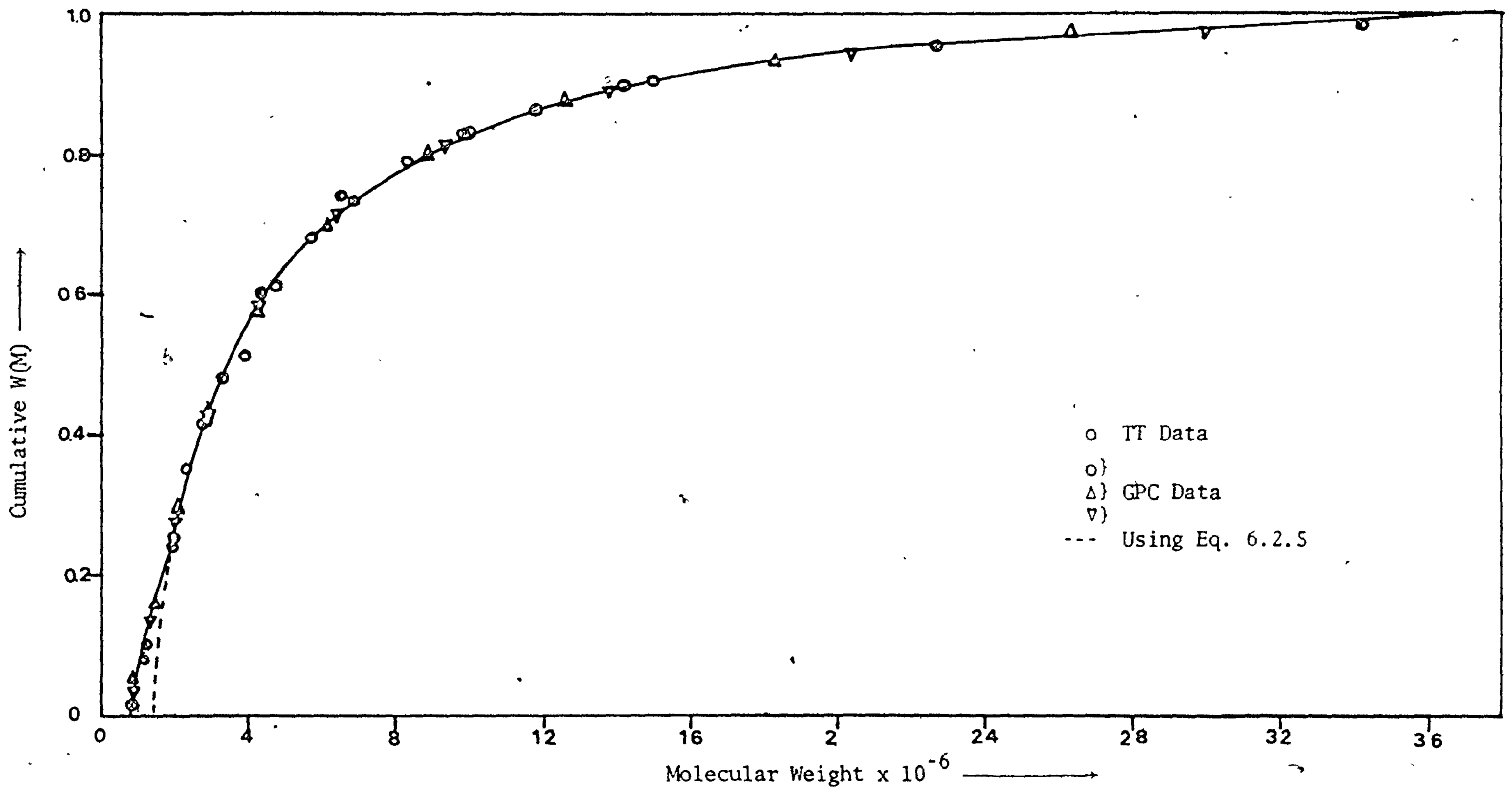


Fig. 55: Cumulative Most Probable Distribution of Standard A.

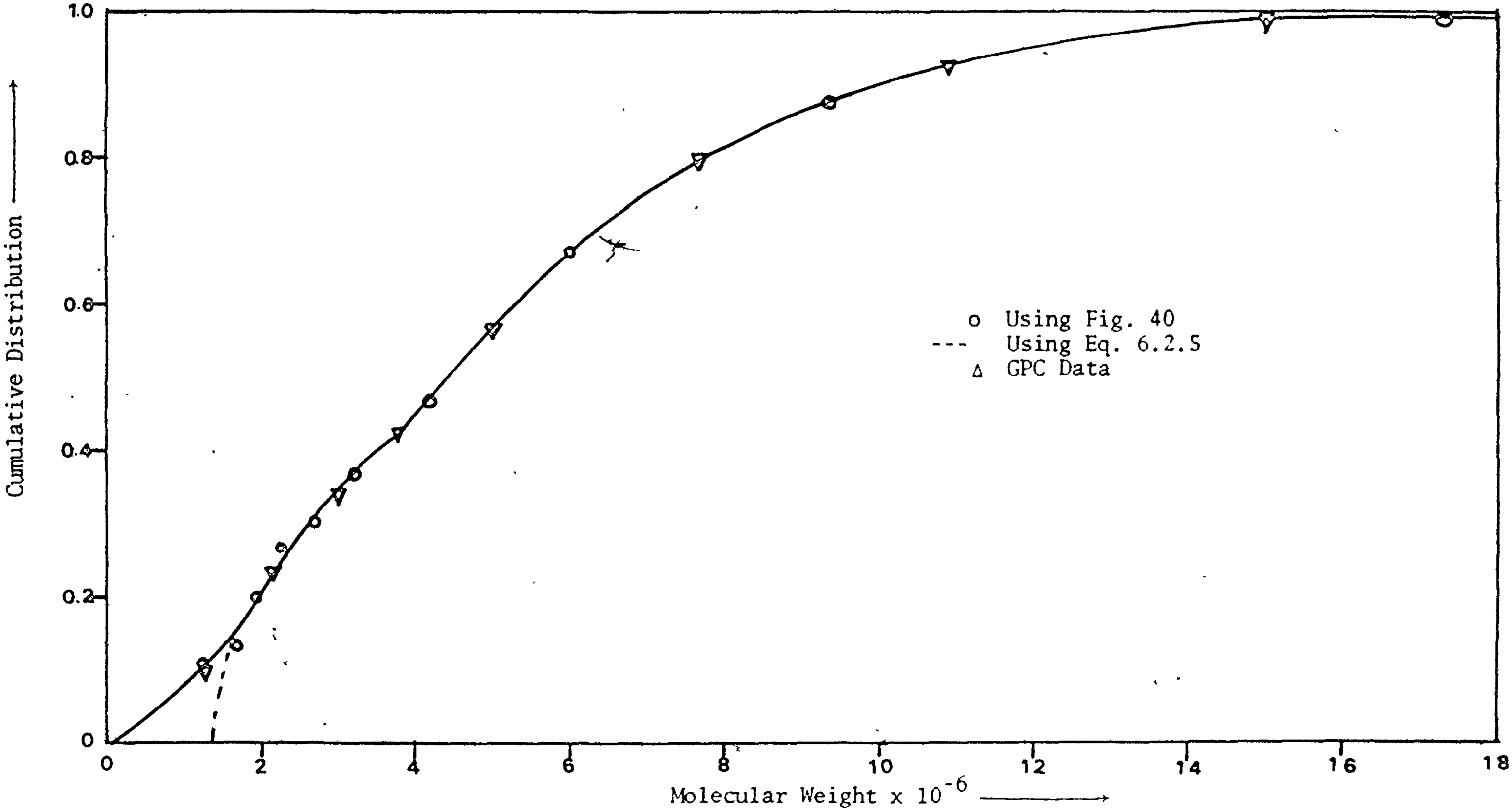


Fig. 56: Cumulative Molecular Weight Distribution of Standard O and A with the Most Probable Distribution.

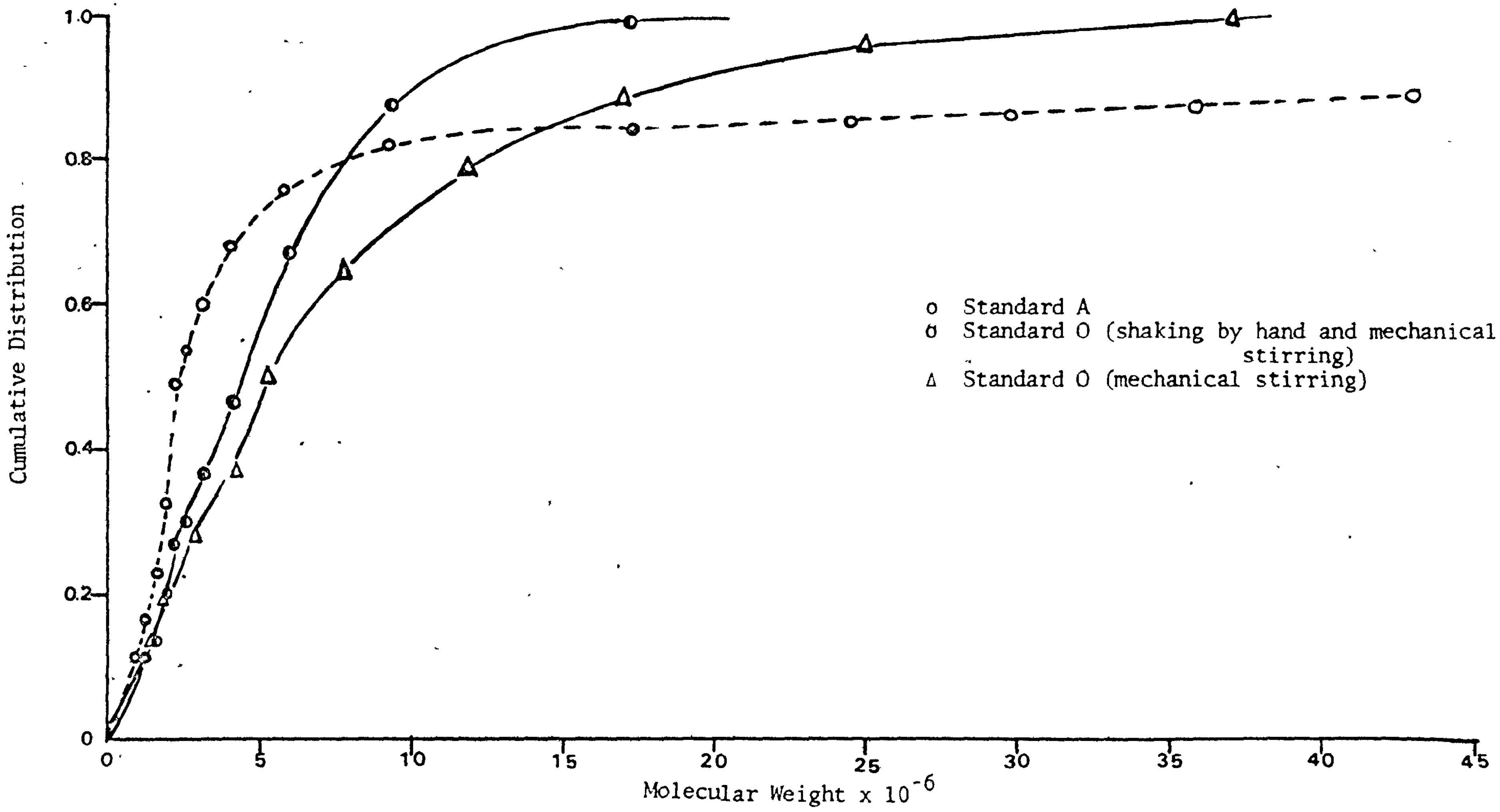


Fig. 57: Integral Molecular Weight Distribution of Standard O.

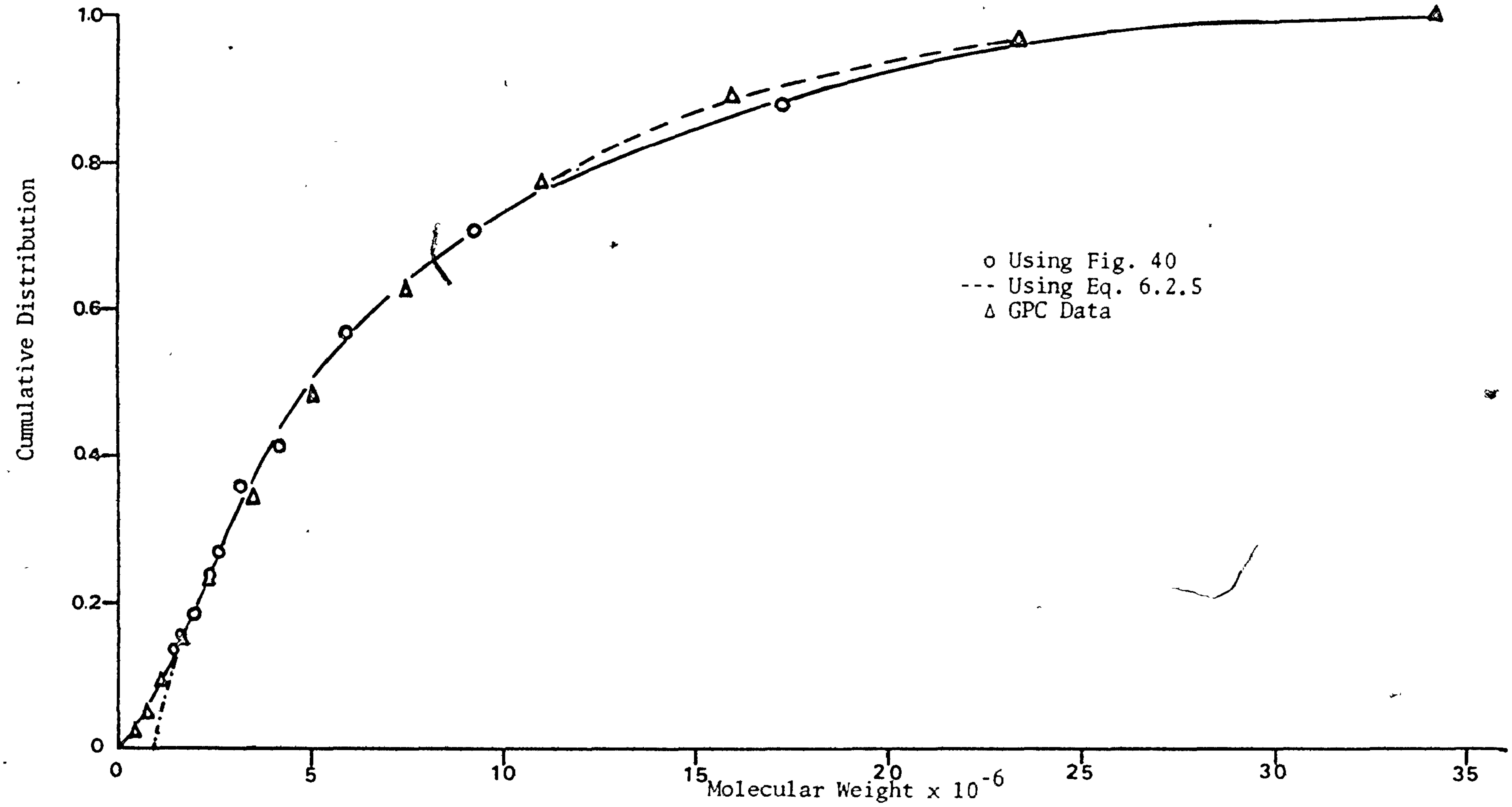


Table 66

Computed Values of the Maximum Specific Absorbance, Scattering Function$(K/\rho)_w$ and Max Turbidity-Concentration Proportionality Constants K_λ.

Polymer Conc.		7000 Å	6000 Å	5460 Å	5000 Å
0.4 wt % A	$A/C\times10^{-2}$	1.0500	1.2000	1.369	1.5000
	K_λ	0.0972	0.0946	0.0978	0.0976
	$(\bar{K}/\rho)_w$	0.0110	0.0107	0.0111	0.0111
0.25 wt % A	$A/C\times10^{-2}$	1.0200	1.1400	1.3200	1.4400
	K_λ	0.0944	0.0897	0.0943	0.0937
	$(\bar{K}/\rho)_w$	0.0107	0.0102	0.0107	0.0106
0.3 wt % A	$A/C\times10^{-2}$	1.0500	1.2000	1.3750	1.5000
	K_λ	0.0972	0.0946	0.0982	0.0976
	$(\bar{K}/\rho)_w$	0.0110	0.0107	0.0112	0.0111
0.025 wt % B	$A/C\times10^{-3}$	2.9000	3.6000	4.1400	4.5900
	K_λ	2.6838	2.8390	2.9578	2.9878
	$(\bar{K}/\rho)_w$	0.3047	0.3223	0.3358	0.3392
0.05 wt % B	$A/C\times10^{-3}$	2.9100	3.6000	4.1700	4.5900
	K_λ	2.6930	2.8390	2.9793	2.9878
	$(\bar{K}/\rho)_w$	0.3057	0.3223	0.3382	0.3392

......continued

Table 66 (continued)

Computed Values of the Maximum Specific Absorbance, Scattering Function $(\bar{K}/\rho)_w$ and Max Turbidity-Concentration Proportionality Constants K_λ.

Polymer Conc.		7000 Å	6000 Å	5460 Å	5000 Å
0.7 wt % C	$A/C\mathrm{x}10^{-2}$	3.0371	3.5236	4.1000	4.6527
	K_λ	0.2811	0.2779	0.2929	0.3029
	$(\bar{K}/\rho)_w$	0.0319	0.0316	0.0333	0.0344
I 0.5 wt % C	$A/C\mathrm{x}10^{-2}$	3.1115	3.6612	4.2653	4.9155
	K_λ	0.2880	0.2888	0.3047	0.3100
	$(\bar{K}/\rho)_w$	0.0327	0.0328	0.0346	0.0363
II 0.5 wt % C	$A/C\mathrm{x}10^{-2}$	3.1249	3.6822	4.2709	4.8333
	K_λ	0.2892	0.2904	0.3051	0.3146
	$(\bar{K}/\rho)_w$	0.0328	0.0330	0.0346	0.0357
0.307 wt % C	$A/C\mathrm{x}10^{-2}$	3.1090	3.6142	4.2431	4.7335
	K_λ	0.2877	0.2851	0.3032	0.3081
	$(\bar{K}/\rho)_w$	0.0327	0.0324	0.0344	0.0350
0.25 wt % C	$A/C\mathrm{x}10^{-2}$	3.1242	3.6525	4.2292	4.8805
	K_λ	0.2891	0.2889	0.3022	0.3177
	$(\bar{K}/\rho)_w$	0.0328	0.0328	0.0343	0.0361
0.06 wt % O	$A/C\mathrm{x}10^{-2}$	5.3833	6.3750	8.2170	9.3500
	K_λ	0.4982	0.5028	0.5870	0.6086
	$(\bar{K}/\rho)_w$	0.0566	0.0571	0.0666	0.0691

......continued

Table 66 (continued)

Computed Values of the Maximum Specific Absorbance, Scattering Function $(\bar{K}/\rho)_w$ and Max Turbidity-Concentration Proportionality Constants K_λ.

Polymer Conc.		7000 Å	6000 Å	5460 Å	5000 Å
0.25 wt % O	$A/C\times10^{-2}$	1.7680	1.9720	2.1080	2.1760
	K_λ	0.1636	0.1555	0.1506	0.1406
	$(\bar{K}/\rho)_w$	0.0186	0.0177	0.0171	0.0161
0.30 wt % O	$A/C\times10^{-2}$	1.8700	1.9550	2.1533	2.3800
	K_λ	0.1731	0.1542	0.1539	0.1549
	$(\bar{K}/\rho)_w$	0.0197	0.0175	0.0175	0.0176

Table 67

ρ_o Values

Using K = 2.0

	ρ_o			
Polymer Type	7000 Å	6000 Å	5460 Å	5000 Å
A	182	182	179	180
B	7	6	6	6
C	61	60	58	56
O(0.06)	35	35	30	29
O(0.25)	108	113	117	124
O(0.30)	102	114	114	114

Fig. 58: Turbidity/concentration Proportionality Constant versus Starting Concentration of Polymer Standard B.

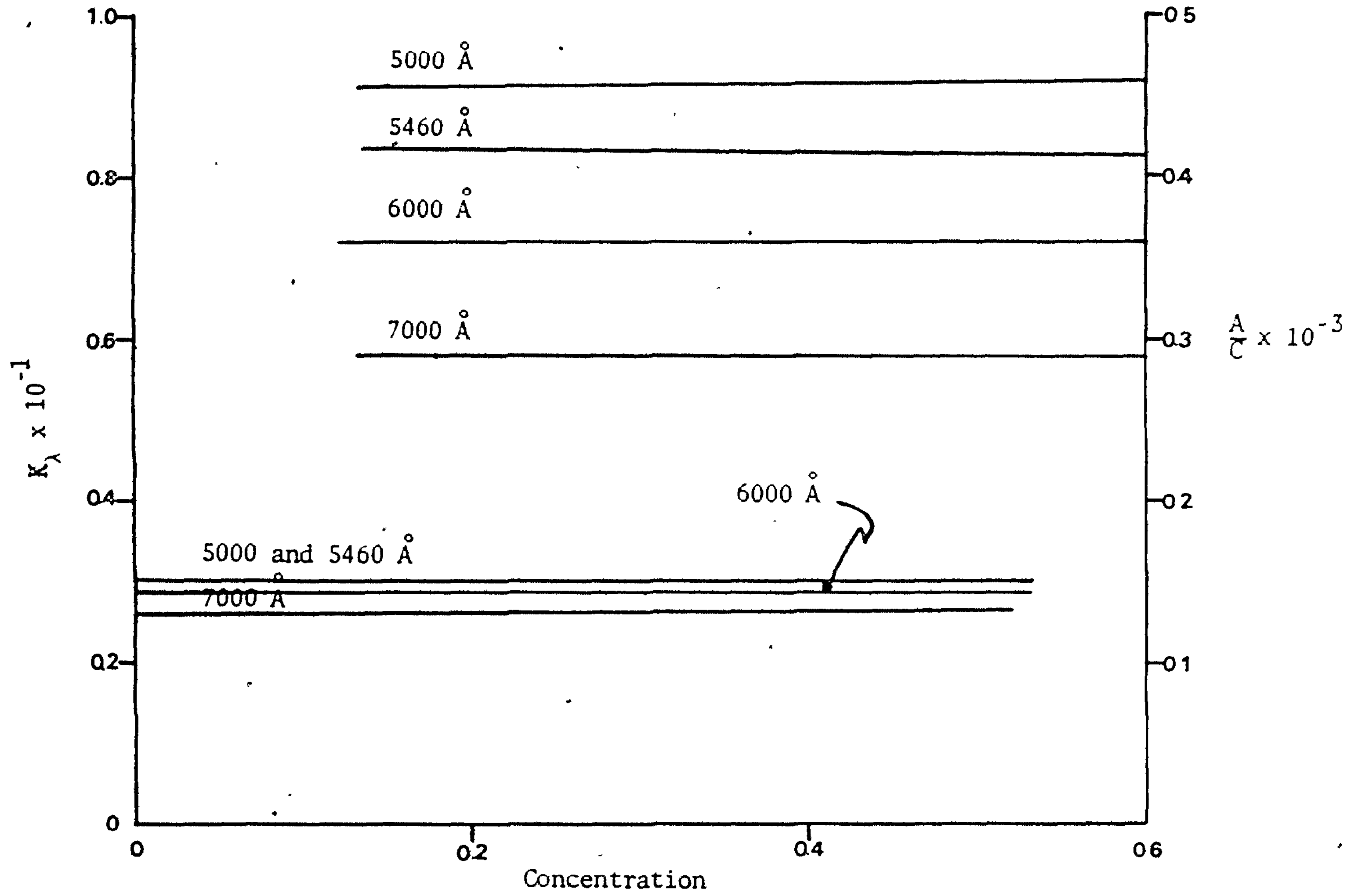


Fig. 59: Turbidity/concentration Proportionality Constant versus Starting Concentration of Standard O.

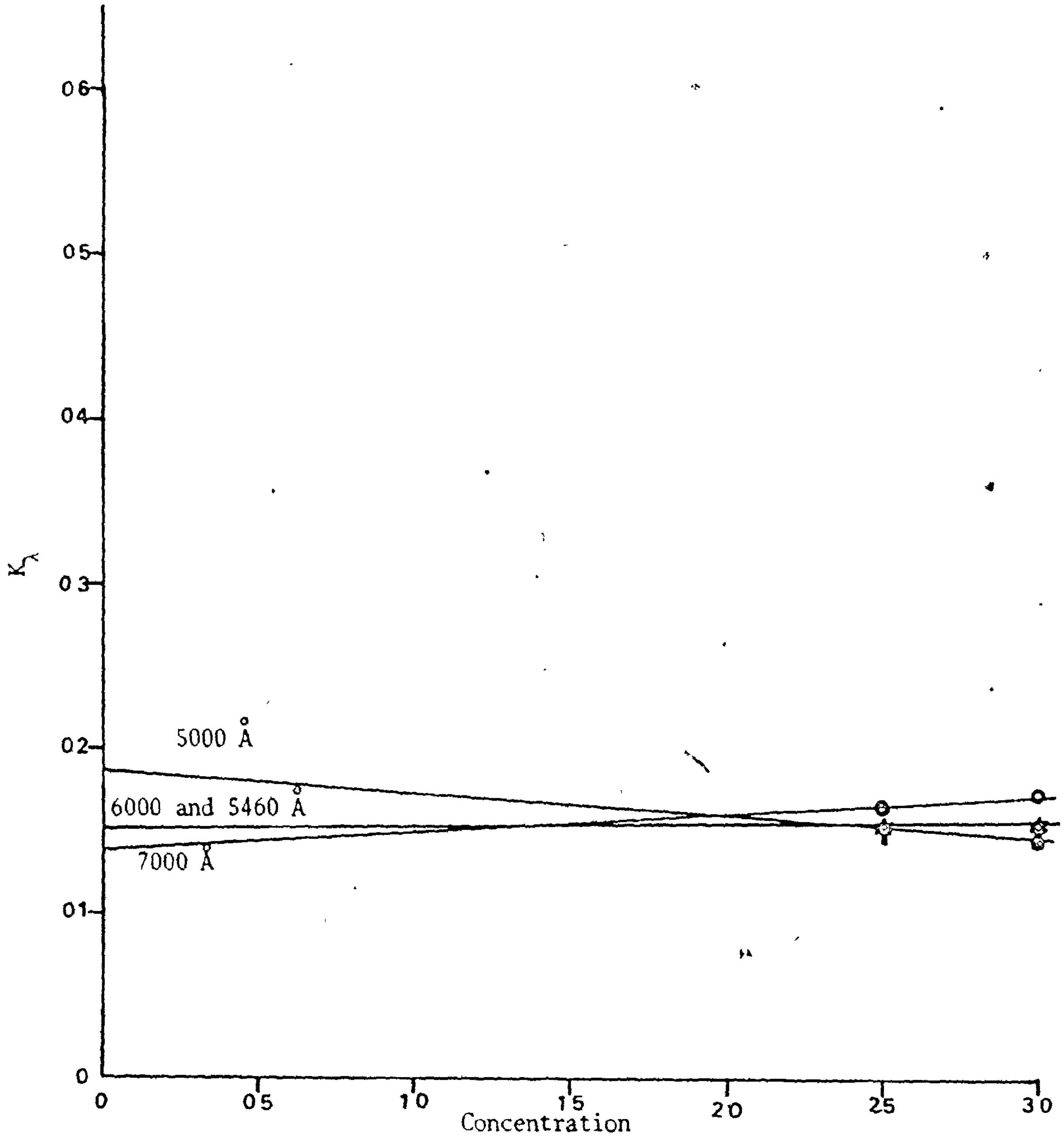


Fig. 60: Turbidity/concentration Proportionality Constant versus Starting Concentration of Standard A.

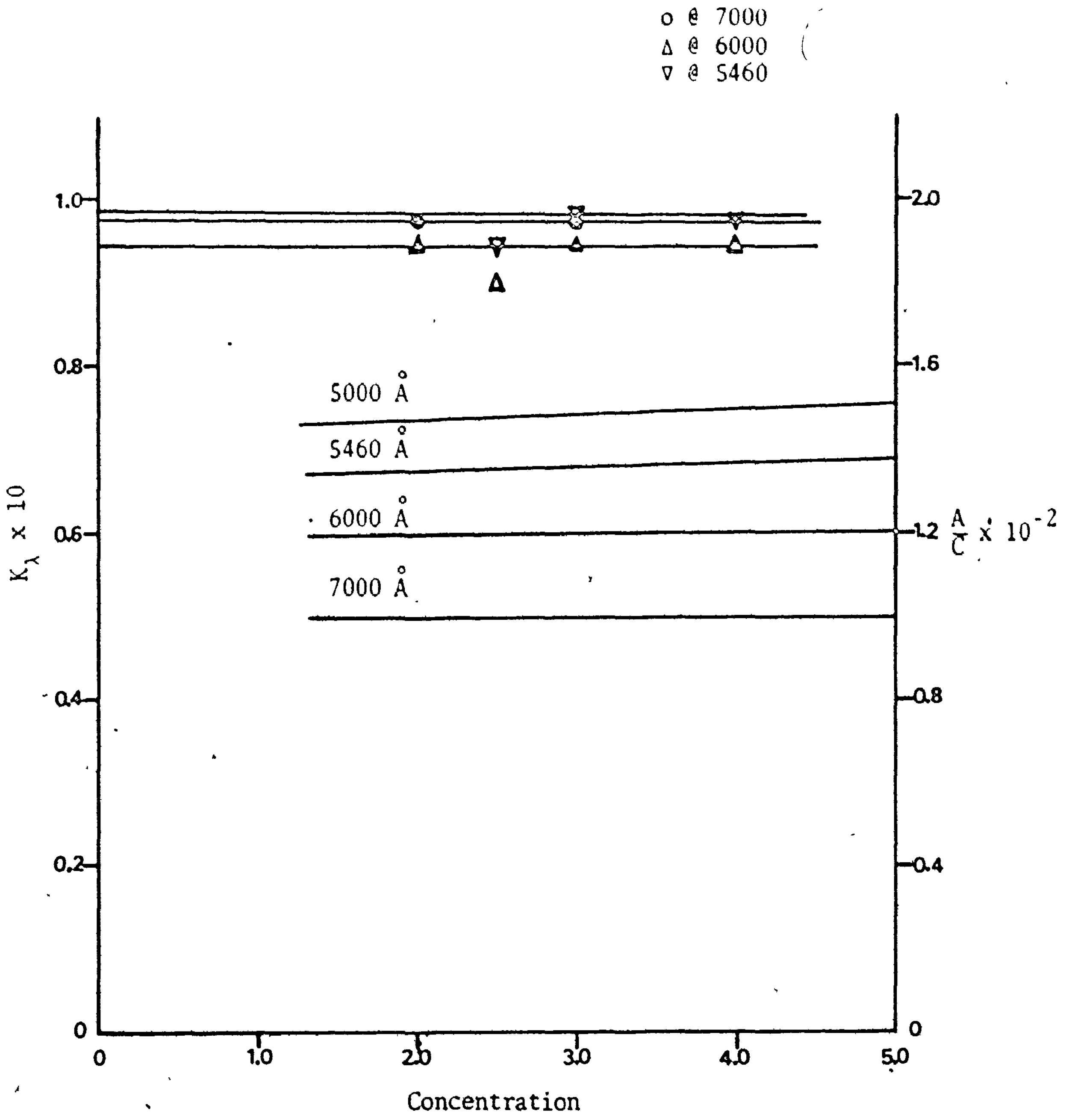


Fig. 61: Turbidity/concentration Proportionality Constant versus Starting Concentration of Standard C.

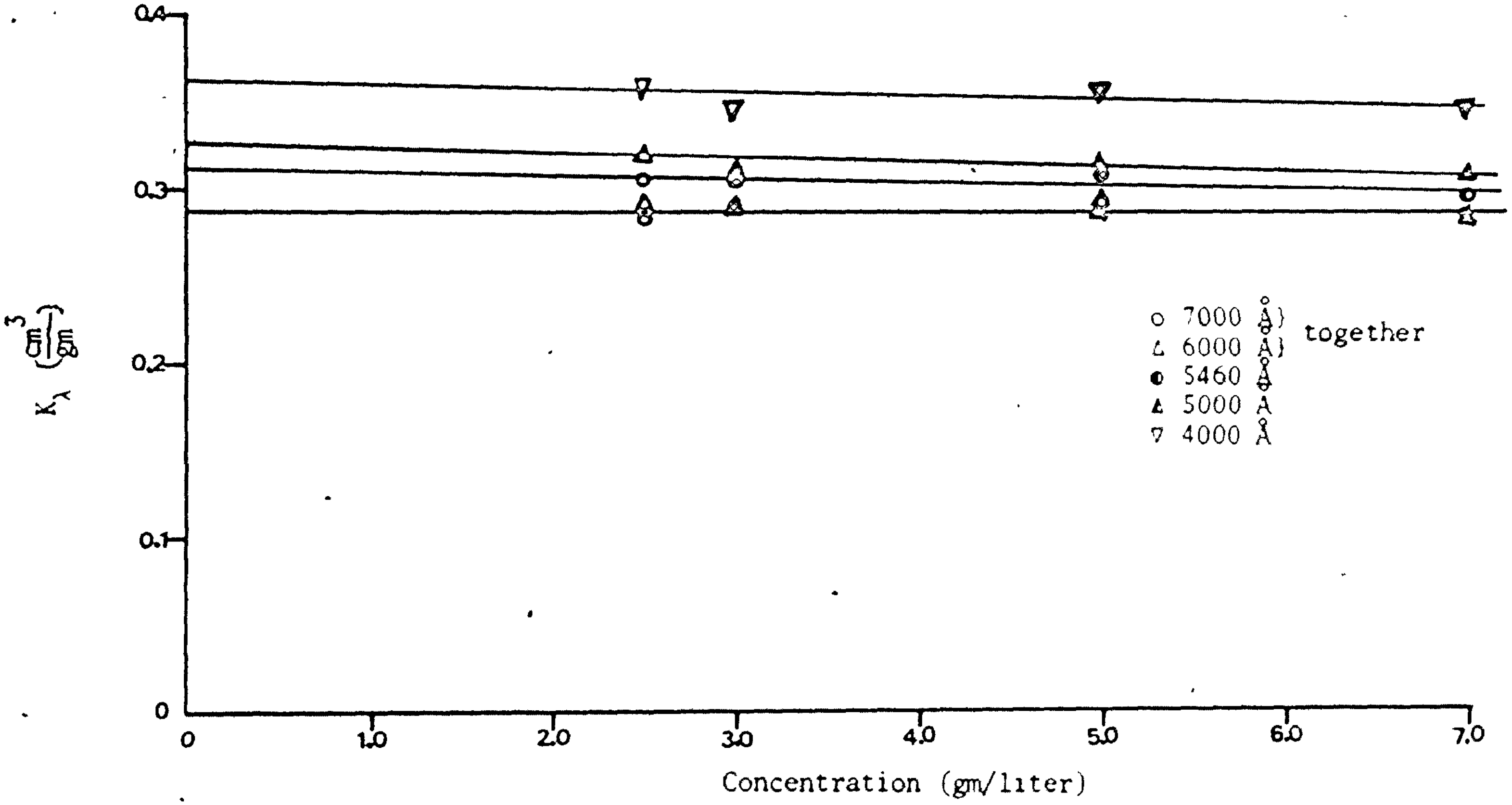
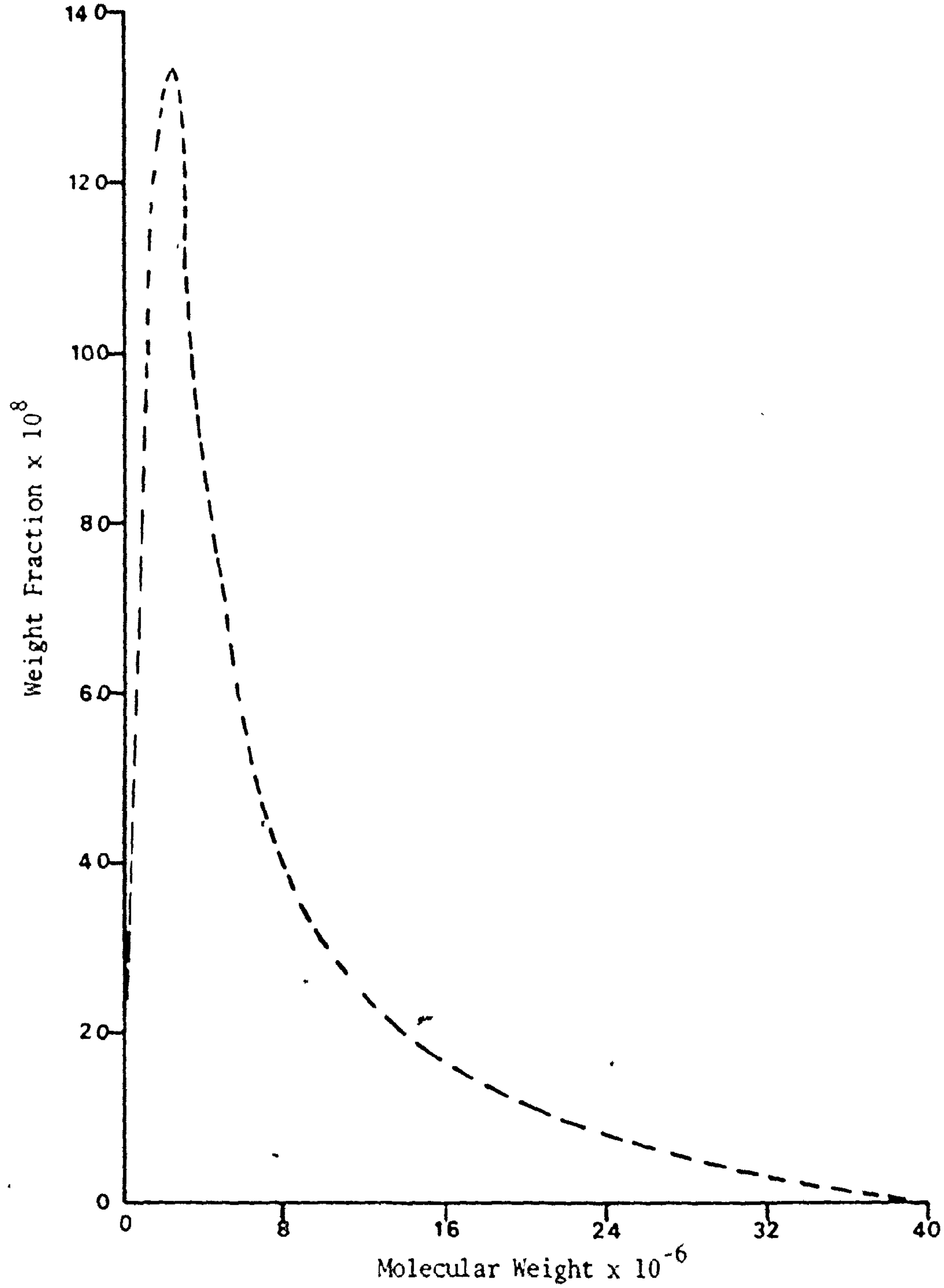


Fig. 62: Differential Molecular Weight Distribution of Standard O.



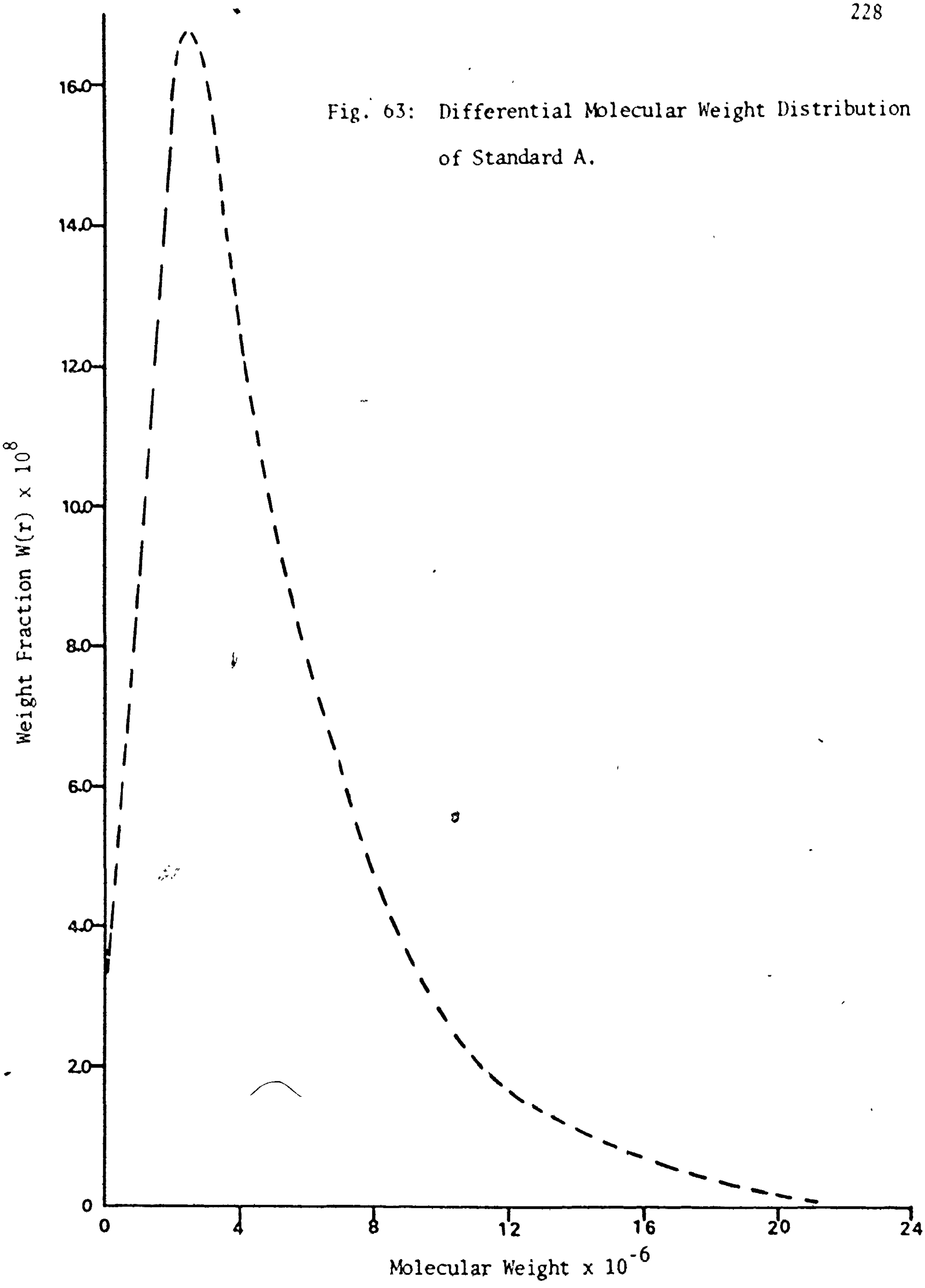


Fig. 63: Differential Molecular Weight Distribution of Standard A.

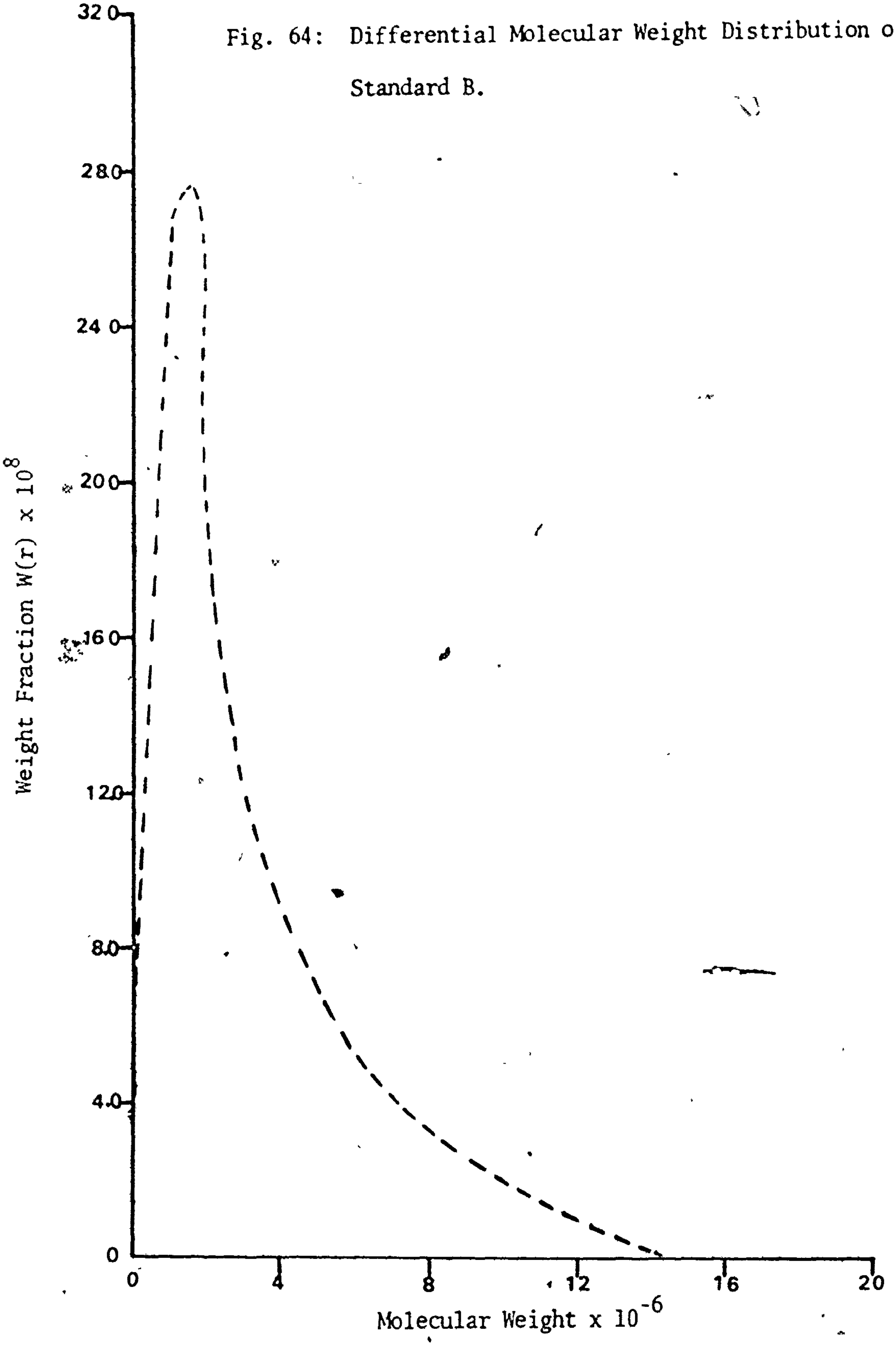


Fig. 64: Differential Molecular Weight Distribution of Standard B.

CHAPTER 8

DISCUSSION OF RESULTS

Morey and Tamblyn(30) and later Claesson(66) have discussed procedures by which experimental turbidity data are converted to molecular weight distribution data. One of the assumptions involved in both cases is that the turbidity developed is proportional to the weight of the polymer precipitated out of solution. All other subsequent methods of approach later developed with the exception of a few as shown in Table 1, were modifications of the Morey and Tamblyn and Claesson Grid methods. All of the methods require an empirical calibration curve, which was usually obtained only when a number of previously well characterized fractions were available. Hence, in general, the method has been limited to polymers made anionically, or via condensation, or emulsion or a catalyst-type polymerization. While Taylor and Tung(47) employed the change in slope of the turbidity against temperature curve with molecular weight distribution to evaluate the breadth of the distribution (β)occurring in the Wesslau distribution from a calibration curve of the slope parameter with β, Urwin et al.(48) employed the classical method of graphical differentiation. In general, when the methods were extended to a broad range of polymers, the results obtained were usually unreliable quantitatively.

An absolute method, not requiring calibration was next proposed by Beattie.(39) It is based on the observation that the scattering function $\acute{K}/\rho$ is found to be almost constant with respect to ρ over a small range of m at the turbidity first maximum which occurs at $\rho \doteq 3.0$.(41) Thus a direct amount of the polymer precipitating can only be known when the size of the particle, or more correctly, the size distribution is known at each stage of the titration so that the parameter m can be determined reliably. In principle, the condition $\rho \doteq 3$ may be attained by particle growth and or adjustment of the wavelength, although this may not always be experimentally possible. The corresponding $(\overline{K}/\rho)_w$ in Eq. 4.3.5a depends on both m, the relative refractive index, and the width of the particle distribution. Narrow distributions will have little effect on the value obtained and in this case, variations in particle size are not important. In the case of broader distributions, a log-normal distribution may be assumed and by a curve fitting procedure, the breadth of the distribution β may be obtained, the maximum in $(\overline{K}/\rho)_w$ is then found corrected to the m of the particles. For broader distributions which do not conform to log-normal behaviour, the method fails.

In the present study, broad polymers were investigated. It was assumed that the particle size distribution is unknown. No attempt was made to evaluate the kind of distribution by the curve fitting procedure described by Beattie. Analysis indicated that the particle size distribution does conform to the assumed log-normal behaviour. Values of the maximum turbidities at complete precipitation when the concentration of the precipitated polymer is known, were obtained at several initial concentrations. These values were used to obtain the proportionality constant K_λ. The different values of K_λ obtained for all the polyacrylamides under the experimental conditions, as shown in Table 66, indicate that there is not a general optical density-concentration relationship valid for all polyacrylamides. This is to be anticipated since aggregation to a uniform whole was encouraged. A given polyacrylamide has its own maximum turbidity-concentration dependence relationship which is independent of other polyacrylamides. Under neutral experimental conditions, for one kind of broad polyacrylamide, a given maximum turbidity always corresponds to the same concentration of precipitated polymer c_p irrespective of the initial concentration and independent of the molecular weight of the polymer fraction. In the presence of an electrolyte, this is not the case as indicated by the different values of K_λ for different initial starting concentrations in Table 66 for Standard O. There is no doubt that the presence of an electrolyte aids aggregations and probably this is the major reason why this behaviour is to be expected.

Thus a general empirical calibration curve relating optical density with concentration for a whole family of broad polyacrylamide polymers cannot be obtained by the present method, since aggregation which has always hindered the development of turbidimetric titration was used as an advantage. Solubility distribution of the polymers were obtained. Standard C, the polymer whose molecular weight distribution is correctly known,(63) was used to obtain the relationship between solubility and molecular weight as shown in Figure 40. As already shown in Figure 54, the use of Eq. 6.2.5 is valid up to 92% of non-solvent. Using this equation beyond this point, tends to reduce the polydispersity obtained. As shown in Table 65, the weight average molecular weight obtained is higher than when the correction for the low molecular weight end of Figure 40 is not taken into consideration.

The stability of the polymer aggregates obtained was studied, by varying the method of mixing. This is important because it is required only that the scattering properties be constant during the time to obtain the spectrum. The two methods of mixing used were mechanical stirring alone and mechanical stirring with shaking by hand. As indicated by the integral molecular weight distributions obtained under the varied experimental conditions in Figures 53 and 56, and molecular weight averages in Table 65, it is obvious that the stability of the polymer aggregates at the point of maximum turbidity is important. Shaking by hand, a method where uniform mixing is difficult to achieve, has been found to considerably affect the size and numbers of the polymer aggregates to different levels at different points of the titration. This is very obvious by comparing Tables 36 to 38 with Table 39 to 41 for Standard B or Tables 54 to 56 with Tables 57 to 59 for Standard O. Close observations show that the aggregates obtained when the polymer fraction precipitating is narrow are usually in multiples of the expected values of the maximum turbidities.

It is important to note that the maximum turbidities of Standards C and A with weight-average molecular weight greater than five million were not affected by hand-shaking. Standard O has a weight average molecular weight greater than five million. It is to be expected that the smaller the particle sizes, the more vulnerable it is to hand-shaking and probably this is the reason why distributions of molecular weight for Standard C and A were independent of method of mixing except when the starting concentrations are very high. At such high concentrations, preliminary investigations showed that there is a high degree of settling of polymer particles. For the same reasons, the molecular weight distribution of Standard B is dependent on the method of mixing. The weight average molecular weight of Standard B under hand-shaking condition inclusive, is very high compared to the actual value (Table 65). With hand-shaking, there is an increase in size of the aggregates at some points of the titration. This increase in size was not observed for Standard O. It seems therefore, that the presence of an electrolyte plays a very significant role in systems where aggregation is important. The difference in maximum turbidities for Standard O, under the varying experimental variables above, is in fact due to the presence of an electrolyte. Its weight-average molecular weight is high and shaking by hand should not affect the distribution obtained. Despite the different states of aggregation obtained for Standard O, the agreement between the number average molecular weights obtained from viscosity measurements shown in Appendix IV and that from the present method is extremely remarkable and excellent.

Validity of Eq. 6.2.3, by this method is confirmed by examination of Table 65, where the polydispersities obtained for Standards A, B show that they have the most probable distribution. Standard O, with a much higher polydispersity supports the evidence that the breadth of the molecular-weight distribution increases with decreasing polymerization temperature. From Figures 53 - 57, it is seen that there is an excellent agreement between the measured MWD's, using the present method and the measured MWD,s using GPC, thus proving the validity of the solubility-molecular weight calibration curve. In all the samples investigated, the weight-average molecular weights derived from the present method are less than 5% greater than the corresponding GPC value. This difference is probably due to the fact that the method is more capable of detecting the high molecular weight tail of a distribution. From the differences in values obtained for the different standards, there is no doubt that the method is capable of giving the molecular weight distribution of a polydisperse polymer with sufficient accuracy.

The scattering functions $(\overline{K/\rho})_w$ were obtained at 100% precipitation and these are included in Table 66. These were obtained using Eq. 4.3.7. The variation of $(\overline{K/\rho})_w$ with different broad polymers is in the same direction as variation of K . $(\overline{K/\rho})_w$ seems to be constant at higher wavelength in the visible light region, and seems to increase with decrease in wavelength at the lower region. Nevertheless, the values obtained are considerably smaller comparing them with other values of $(\overline{K/\rho})_w$ for a polystyrene system (0.720).(39) This is not surprising since extreme optimum condition in the region where K = 2 has been imposed and also since the broader the polymer, the smaller $(\overline{K/\rho})_w$ value. The maximum $(\overline{K/\rho})_w$ values obtained seem to indicate that the point of maximum turbidity is in the region $\rho >> 3$ for broad polymers (see Chapter 4.4) and Table 67 which contains computed ρ_o assuming a $\overline{K}$ value of 2.0.

Experimental variables which cannot be easily controlled include rate of stirring, rate of addition, time of addition and temperature control. The effect of these variables on the turbidity were tested. Apart from the initial point of precipitation, these variables have very little influence on the resulting maximum turbidities. As can be noticed from the tables of turbidimetric data for Standards B and O during the preliminary investigation, the high molecular weight tail end is very sensitive to the presence of non-solvent, and for this reason, these variables particularly rate of addition, have to be properly controlled. The specified method has been presented in Sections 5.3.1 and 5.3.2. Standard C, the polymer used to obtain the molecular weight-solubility calibration curve did not show this initial point difficulty; instead it was with a considerable length of time of stirring did precipitation begin, and this is probably due to the kind of distribution at the high molecular weight tail, or point of equilibrium phase separation relationship. Provided the initial point of precipitation is not crossed too far, the method is still capable of giving the molecular weight distribution. "Crossing of the point" at the initial point of titration is readily detectable because of the non-reproducibilities obtained each time of titration. As indicated by the turbidimetric data obtained for all samples analysed, the reproducibilities of the maximum turbidities obtained at the different starting concentrations and wavelength ranges covered are extremely remarkable and excellent and the major reason is probably that optimum experimental conditions have been allowed to prevail.

Other preliminary experiments have indicated that purfication of solvent has a large effect upon the fraction of polymer precipitated. Stringent temperature control is not required as long as the titration is carried out at laboratory ambient condition.

CHAPTER 9

SUMMARY AND CONCLUSIONS

A relatively simple experimental technique has been developed for the measurement of molecular weight distribution of polyacrylamide using turbidimetric titration. The simplicity of the method is that solubility and molecular weight distribution can be obtained directly from the turbidimetric data, without knowledge of the scattering function Max $(\overline{K/\rho})_W$. This latter may involve the use of the complicated Mie theory computational analysis, which in turn, involves the prior knowledge of m, the relative refractive index, the experimental measurement of which is difficult. Thus the nature or knowledge of the particle size distribution is of no consequence and important in the result is that there is no strict limitation for an allowable range of ρ, provided $\rho >> 3$, attainable by aggregation.

A single-stage cumulative precipitation technique was developed as opposed to the use of new polymer solutions for the different volume fractions of non-solvent. Solubility distributions were obtained for the four polymer samples investigated. With the use of Standard C, whose molecular weight distribution is correctly known using gel permeation chromatography (GPC),an exponential molecular weight-solubility relationship was obtained which holds up to 92% non-solvent. The calibration curve was used as obtained. With the use of the curve, or Eq. 6.2.3, in part, molecular weight distributions of other polymers were obtained from their solubility distributions. The experimental work with very broad polyacrylamide indicates that under the specified conditions, the reproducibilities of turbidimetric precipitation curves is very good and that the method is accurate. The experimental findings agree with the theory. Additional verification of the theory comes from the fact that

(1) The concentrations of polymer calculated at different wavelengths and at different starting concentrations give identical results.

(2) Exact exponential relationship of the molecular weight-solubility curve is valid for other polymers for the solvent/non-solvent system.

(3) Uniform mixing conditions have very little influence upon the resulting maximum turbidity.

(4) The revealing nature and agreement between the experimentally obtained $\overline{(K/\rho)}_w$ and that predicted by the Mie scattering theory for large ρ_o, in the region of which all of the assumptions are satisfied.

It must be mentioned that many of the usual precautions given for turbidimetric titration are not necessary with this method, except in some cases at the initial point of precipitation shaking by hand as a method of mixing, is not applicable when the weight average molecular weight is below five million and in the presence of an electrolyte. The optimum experimental conditions for obtaining the greatest accuracy in this method is then that the turbidity at each point of the titration is measured at intervals until it reaches a maximum. Since the points of maximum turbidity are independent of m in the region of large ρ, the condition that solvent and precipitant have identical refractive indices is not important.

There is no doubt that the reason why turbidimetric titration has been regarded as a method with doubtful accuracy in the past is because optimum conditions have never been attained. Secondly, light scattering theory has not been properly applied.

CHAPTER 10

RECOMMENDATIONS

(1) It is recommended that irrespective of whether the weight average molecular weight is greater or less than five million, the method of mixing should be such that it provides a uniform state of mixing.

(2) For polymers polymerized in the presence of an electrolyte, it may sometimes be necessary to remove the electrolyte before analysis. This is not a severe recommendation as the amount of electrolyte in the system can be easily controlled.

(3) It is recommended that polymer solutions, to be used for turbidimetric titration be allowed to stand at about 4°C conditions for more than one day before use. This is highly recommended as it removes the problem imposed by the initial point of precipitation.

(4) The effect of presence of an electrolyte on the stability of the aggregates should be further investigated. Some experimental data obtained in the present work at very low concentrations indicates a pattern of aggregate size formation.

CHAPTER 11

NOMENCLATURE

A	absorbance of turbid suspension(in absorbance unite)
A_c	corrected absorbances
A_m	measured absorbances
A_1	constant in dispersion formula in the Abbe Instrument Manual
A_p	gain in energy when polymer is transferred from one phase to another phase
A_w	distilled water with conductivity less than 1.25×10^{-6} mho labelled A_w
B_1	constant in dispersion formula in the Abbe Instrument Manual
B_w	distilled water with conductivity less than 3.72×10^{-6} mho but greater than 1.25×10^{-6} mho labelled B_w
c	concentration of polymer which is precipitated in gm/ml of original solution
c_p	concentration of precipitated phase in gm/milliter of solution
D	diameter of pure polymer particle
D'	diameter of swollen polymer particle
$\bar{D}_A$	area average diameter
d_n	number of particles per milliliter between a small size range
D_1	molecular weight-solubility slope parameter calibration constant
D_3	molecular weight-solubility intercept calibration constant
DWD	differential weight distribution curve

$f(D)$	diameter particle size distribution function
$f(r)$	radius particle size distribution function
$f(\rho)$	normalized particle size parameter-particle size distribution function
I_o	intensity of incident light
I	intensity of transmitted light
IP	isothermal precipitation
K	scattering coefficient
K_1	scattering coefficient of i^{th} particle
K_λ	turbidity-concentration calibration constant
ℓ	path length of the transmission cell
m	relative refractive index of the system
M	molecular weight of polymer
$\overline{M}_N$	number average molecular weight of polymer
MT	method based on Morey and Tamblyn
$\overline{M}_W$	weight average molecular weight of polymer
n	number of particles per milliliter
n_i	number of particles per milliliter of size i
N	normal solution-e.g., IN represents the strength of a solution in which the equivalent weight of a compound is dissolved in 1 liter of solution
N_C	refractive index at α-hydrogen spectral line
N_D	refractive index at sodium spectral line
N_F	refractive index at β-hydrogen spectral line
$N(M)$	number of polymer chains having a molecular weight M
N_P	total number of particles

P	polydispersity
R	universal gas constant
r	radius of polymer particle (A)
r_i	radius of polymer particle of size i
R_1, R_2	constants in Gladstone and Dale formula-independent of temperature and state of aggregation
R(x)	total radiation or scattering cross-section of sphere
S	size of polymer particle
T	temperature (°C)
t	time of stirring
TGP	thermal gradient precipitation technique
TT	turbidimetric titration
v	volume of precipitant added (cc)
V_o,V_1, V_2,V_3	volume of solvent mixture, solvent, non-solvent and polymer respectively (cc)
w_{12}	wt fraction of polymer having molecular weight between M_1 and M_2
W(M)	wt fraction of polymer having molecular weight M
Z	value measured from the dispersion scale during refractive index measurements

Greek Symbols

ϕ_i',ϕ_i	volume fraction of polymer in polymer-rich phase and polymer-poor phase respectively of size S_i
ϕ_o,ϕ_o'	volume fraction of solvent mixture in polymer-poor phase and polymer-rich phase respectively.

ψ_1, ψ_2	volume fraction of solvent and non-solvent respectively in solvent mixture
$\delta_1, \delta_2, \delta_3$	solubility parameter of solvent, non-solvent and polymer respectively
ψ	polymer-solvent interaction parameter
$\chi_{12}, \chi_{23}, \chi_{13}$	Flory-Huggins interaction parameters between solvent-non-solvent, non-solvent-polymer, solvent-polymer respectively
ξ_1, ξ_2	Couchy constants
ρ	normalized particle size parameter
ρ_o	weight geometric mean
α_s	particle size parameter
α_1	Abbe instrumental constants dependent on Z
$\psi(D')$	particle size distribution of swollen polymer
ρ_p', ρ_p	density of particles in polymer-rich phase and pure polymer respectively
μ	mean of log-normal particle size distribution
β	variance or breadth of log-normal particle size distribution
σ_g	geometric standard deviation
λ, λ_m	wavelength of light in vacuo and suspending medium respectively (A)
α	reciprocal of volume fraction of polymer in polymer-rich phase
τ	turbidity of suspension
μ_o, μ, μ'	refractive indices of solvent mixture, polymer particles in polymer-rich phase and of pure polymer respectively

$\Delta\mu$	difference between refractive indices of pure polymer and solvent mixture $(\mu - \mu_o)$
$\rho_{solvent}$	density of solvent
η_{sp}, η_r	specific viscosity and relative viscosity
η	intrinsic viscosity
$\frac{\delta\mu}{\delta c}$	refractive index increment with increase in concentration
$\frac{\tau}{c}$	specific turbidity
$(\frac{\overline{K}}{\rho})_w$	average weight of scattering function

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APPENDIX I

MEASUREMENT OF REFRACTIVE INDICES OF POLYACRYLAMIDE

Since no literature values could be obtained for the refractive index of polyacrylamide μ, the rule of Gladstone and Dale,(67) may be converted into the form:

$$\frac{\partial\mu}{\partial c} = R_2 - \frac{\rho_1}{\rho_2} R_1 \qquad \text{A1-1}$$

with

$$R_2 = \frac{\mu - 1}{\rho_p} (\rho_2 = \rho_p) \qquad \text{A1-2}$$

$$R_1 = \frac{\mu_{solvent} - 1}{\rho_{solvent}} \qquad \text{A1-3}$$

where the subscripts 1 and 2 refer to solvent and polymer respectively. The ρ_p is the density, and R_1 and R_2 are supposed to be constants independent of temperature or state of aggregation. c is the concentration of polymer solution.

The refractive index increment of polymer solutions in water was obtained approximately with the improved type of Abbe Refractometer. Polymer solutions of three different concentrations were prepared in the same manner as for turbidimetry. Their refractive indices were measured. The refractive index of water used for preparing the solutions was also measured. These measurements could only be made at 589.3 nm.

Using the method stipulated in the manual for the Abbe instrument and Couchy formula,(68) the refractive index at 5460 A or any other wavelength can be obtained. The results are given in Table A1-1. A plot of refractive index difference vs. concentration is shown in Fig. A1-1. The value $d\mu/dc$ obtained from the slope of the line was 0.162 (cc/gm). This compares to the reported values of 0.161,(59) 0.163(69) and 0.186.(23)

The density of polyacrylamide used in Eq. A1-2 was $\rho_p = 1.070$ gm/cm^3.(20) For water, the values of 0.997 gm/cc and 1.334 were used for the density and refractive index respectively. Using these values, $R_1 = 0.335$. Using the value of 0.162 for $d\mu/dc$, in Eq. A1-1, R_2 was found to be 0.4741. Using Eq. A1-2, the refractive index of polyacrylamide at 5460 A was found to be 1.5073.

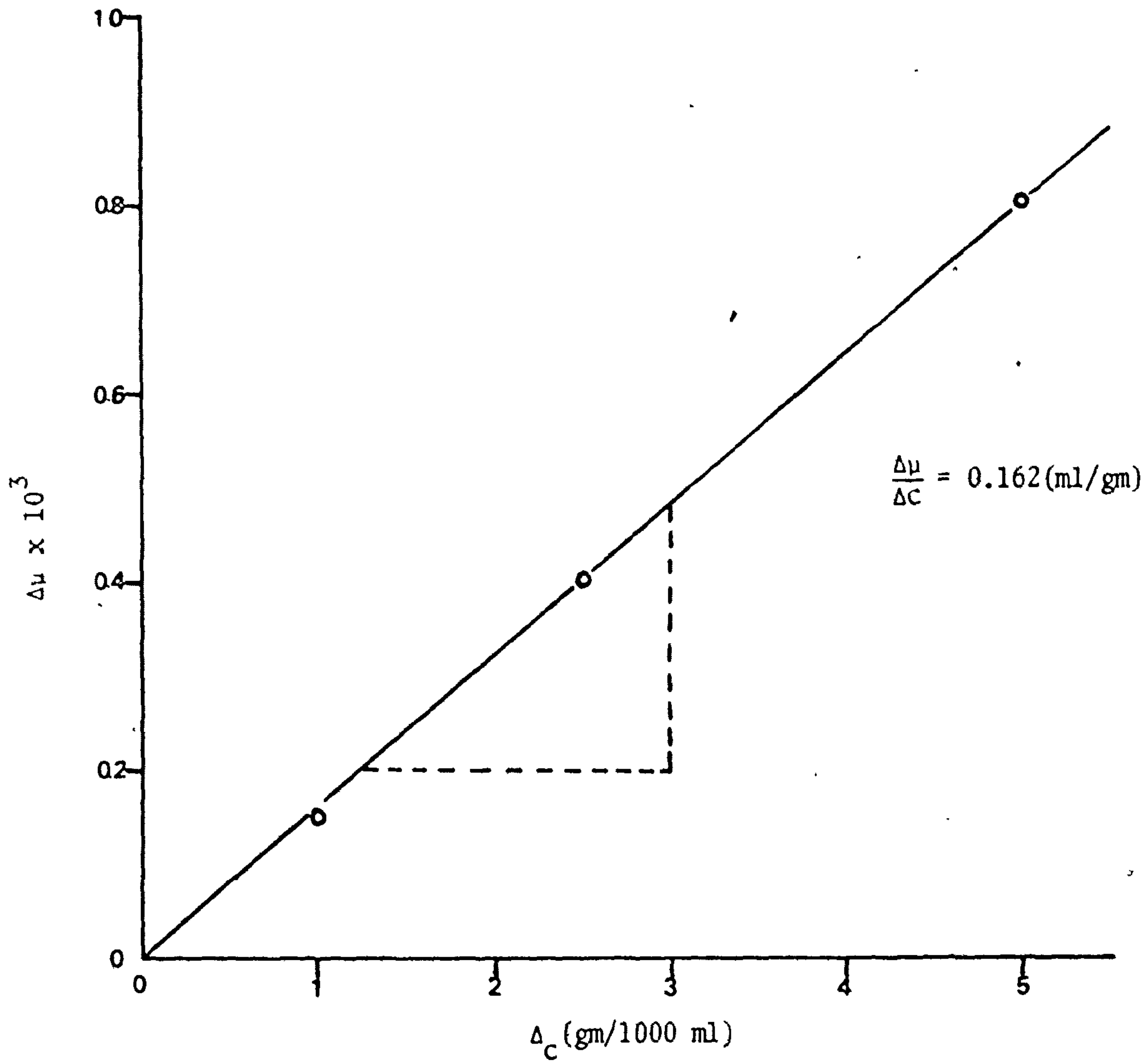
Table A1-1

Refractive Index Difference Measurements

Concentration (gm/1)	$\Delta\mu \times 10^3$ (5460 mμ)
1.0	0.15
2.5	0.40
5.0	0.80

The refractive index at 5893 A was also measured according to the method specified in the Manual for the Improved Type of Abbe Refractometer. Polyacrylamide is a powdered substance. Two kinds of liquid which have different refractive indices and a fairly wide range of refractive indices

Fig. A1.1: Refractive Index Differences vs. Polymer Concentration.



were selected for mixing the powdered polyacrylamide. These liquids should not dissolve or react chemically with the powdered specimen. The two liquids used were methyl alcohol with $N_D = 1.331$ and alpha-monobromonaphthalein ($N_D = 1.6582$) where N_D is the refractive index obtained using the Abbe instrument directly. The two liquids were mixed at various different mixing ratios in order to obtain various different refractive indices. Then the powdered specimen was put into these mixed liquid in various different mixing ratios. In the case in which the refractive index of the mixed liquid coincides with the refractive index of the powdered polymer, the powdered polymer can hardly be noticed by visual observation. When this is the case, the refractive index of the powdered polymer is the refractive index of the mixed liquid which can be measured directly from the instrument. For the particular mixed liquid which was obtained by mixing 3 to 4 drops of methanol with 7 to 6 drops of α-monombromonaphthalein, N_D was obtained to be

$$N_D = 1.5063$$

where D is the symbol to represent sodium spectral line with wavelength = 589.3 nm.

A dispersion value ($N_F - N_C$) is obtained by the following formula.(70),

$$N_F - N_C = A_1 + B_1\alpha_1 \qquad \text{A1-4}$$

where N_F and N_C are refractive indices at β-hydrogen spectral line and α-hydrogen spectral line respectively with λ_o of 486.1 nm and 656.3 nm respectively.

For the values of A and B in the above formula, these values were obtained from the attached Table in the instruction sheet according to the read value of the refractive index of the mixed liquid N_D. At the same time, the refractive index of the mixed liquid was measured. The dispersion scale was also read from the dispersion scale knob. This was repeated several times from the left and right scales by turning the dispersion scale knob and the values are displayed in Table A1-2.

Table A1-2

Z-Values

Refractive Index N_D = 1.5063	
Read Values from the Dispersion Scale	
Left	Right
41.8	41.7
41.7	41.6
41.7	41.8
41.7	41.7
41.7	41.7
Mean value of the Z = 41.7 left and right	

Measurements were done at 25°C

$Z = 41.7$ $B_1 = 0.02662$ $\alpha_1 B_1 = -0.0153065$

$A_1 = 0.02333237$ $\alpha_1 = -0.575$

Equation A1-4 becomes

$$N_F - N_C = A_1 + B_1\alpha_1$$
$$= 0.00802$$

The region of normal dispersion is approximately described by the Couchy formula(68)

$$\bar{n}_o = \xi_1 + \xi_2/\lambda_o^2 + \xi/\lambda_o^4$$

where ξ_1, ξ_2 and ξ are empirical constants.

For graphical interpolation, it is used in the simplied form

$$\bar{n}_o = \xi_1 + \xi_2/\lambda_o^2 \qquad \text{A1-5}$$

Using A1-5 equation,

$$N_F - N_C = \xi_2\left(\frac{1}{(486.1)^2} - \frac{1}{(656.3)^2}\right)$$
$$= \xi_2(0.0000019)$$
$$= 0.00802$$
$$\xi_2 = 4226.2$$

Using Eq. A1-5, we have

$$1.5063 = \frac{4226.2}{(589.3)^2} + \xi_1$$

Therefore

$$\xi_1 = 1.4931$$

Hence the Couchy equation becomes

$$\bar{n}_o = 1.4931 + \frac{4226.2}{\lambda_o^2} \qquad \text{A1-6}$$

Using Eq. AI-6, at 546 nm

$$\bar{n}_o = 1.5072$$

and this compares with the value of 1.5073 obtained using the Gladstone and Dale formula above. Using Eq. A1-6, Table A1-3 was obtained

Table A1-3

Refractive Index of Polymer at Various Wavelengths

$\lambda(\mathring{A})$	μ
3000	1.5400
3200	1.5343
4000	1.5194
5000	1.5099
5460	1.5072
6000	1.5047
7000	1.5015

Measurement of Refractive Indices of Water and Methanol at Wavelength of Interest

The refractive index of the supporting medium μ_o was obtained by using the averages of the refractive indices of water and methanol. Values obtained for the refractive indices of water and methanol at 5461 nm and 25°C (68) are $\mu_{H_2O} = 1.3340$ and $\mu_{CH_3OH} = 1.3284$. Average of both gives

$$\mu_o = 13312$$

The refractive indices for water and methanol at other wavelengths were obtained using the Abbe refractometer and Couchy formula, in a manner similar to that used for the polymer. The refractive index measured for water at 589.3 nm was 1.3325 and the Couchy constants in Eq. A1-5 were found to be

$$\xi_1 = 1.3243$$

$$\xi_2 = 2904.21$$

Similarly for methanol, at 589.3 nm

$$\mu_{CH_3OH} = 1.3269$$

and the Couchy constants were obtained to be

$$\xi_1 = 1.3179$$

$$\xi_2 = 3125.0$$

Table A1-3 shows the refractive indices obtained at the various wavelengths of interest.

Table A1-4

Refractive Index of Mixed Solvent

λ(Å)	μ_{H_2O}	μ_{CH_3OH}	μ_o
3000	1.3566	1.3526	1.3546
3200	1.3527	1.3484	1.3506
4000	1.3425	1.3374	1.3400
5000	1.3359	1.3300	1.3330
5460	1.3340	1.3284	1.3312
6000	1.3324	1.3266	1.3295
7000	1.3302	1.3243	1.3273

$$\mu_o = \frac{\mu_{H_2O} + \mu_{CH_3OH}}{2}$$

The values in Table A1-3 and Table A1-4, have been represented graphically in Figure A1.2 while the refractive indices and differences for polyacrylamide in Water and Methanol at 25°C are displayed in Table A1-5.

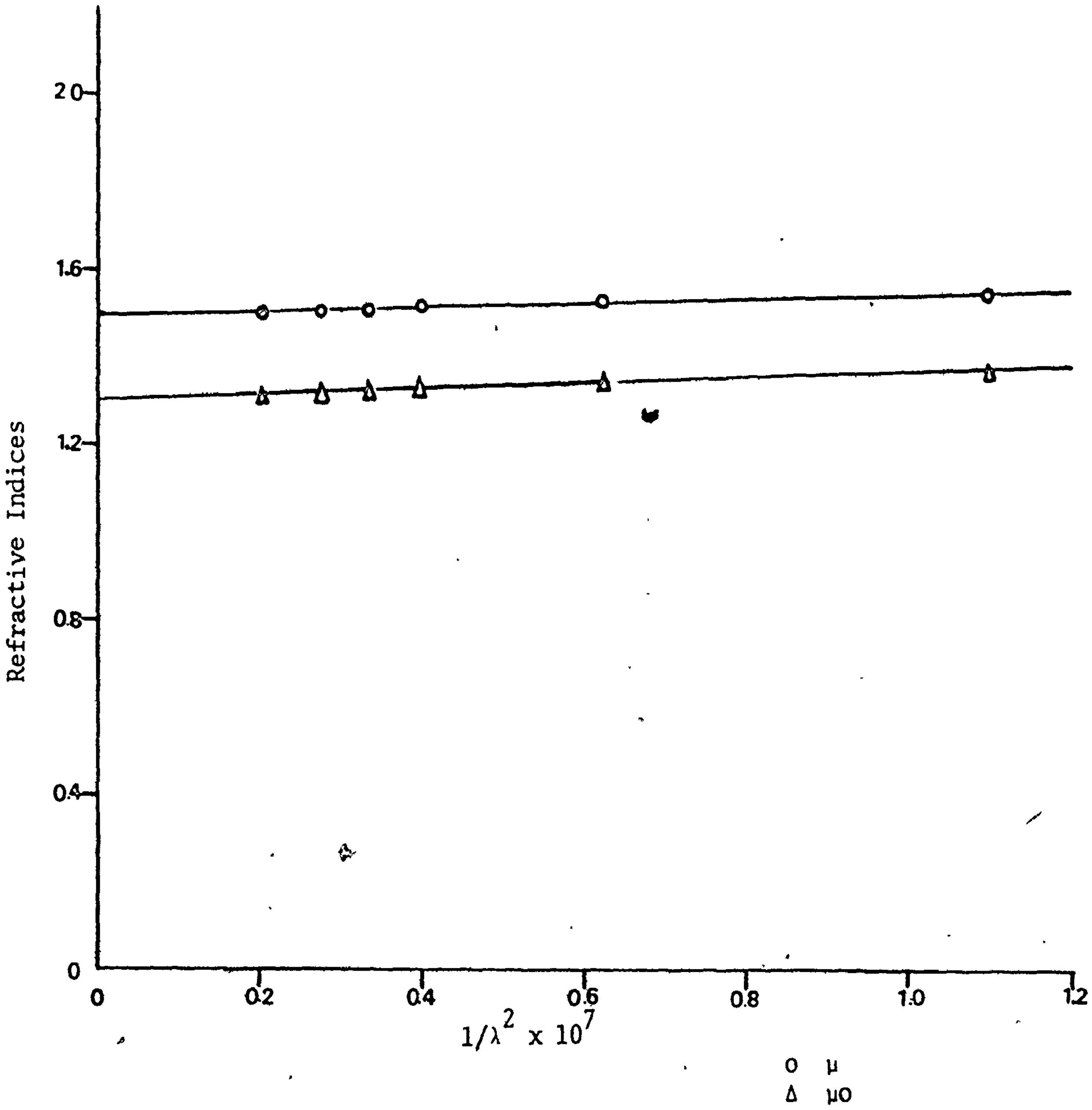
Table A1-5

Refractive Indices and Differences for Polyacrylamide in Water and Methanol at 25°C

λ(A)	μ_o	μ	$\Delta\mu$	$\mu_o/\lambda \times 10^4$	$1/\lambda^2 \times 10^7$
3000	1.3546	1.5400	0.1854	4.5150	1.1000
3200	1.3506	1.5343	0.1837	4.2210	0.6250
4000	1.3400	1.5194	0.1794	3.3500	0.4000
5000	1.3330	1.5099	0.1769	2.6660	0.3350
5460	1.3312	1.5072	0.1760	2.4380	0.2870
6000	1.3295	1.5047	0.1752	2.2160	0.2770
7000	1.3273	1.5015	0.1742	0.1890	0.2040

$$\Delta\mu = \mu - \mu_o$$

Fig. A1.2: Refractive Index vs. $1/\lambda^2$.



APPENDIX II

An Alternative Explanation to the Method of Maximum Turbidity

According to the method of maximum turbidity first developed by Beattie and co-workers,(39)(41) aggregation of particles to a particular particle size ($\rho \simeq 3$) was encouraged. Concentration of polymer which was precipitated was calculated from the maximum turbidity on an absolute basis. Most of other turbidimetric titrations methods described in the literature involve measurement of turbidity either after incremental additions of non-solvent or simultaneously with continuous addition of precipitant. In the method of maximum turbidity, each point of the titrations is made using new polymer solutions, so that the particles can grow to the desired size. None of the incremental or continuous methods could be used because at the beginning of titration, the precipitating particles are highly swollen, causing m to be low. Therefore to attain the condition of maximum turbidity given by $\rho \cong 3.0$, the particles must be small and m is high. It is impossible to begin with big particles and end with small particles, hence the need to use different solutions for each point of titration, so that particles are allowed to grow to the desired size. This seems to be a severe restriction, especially when the polymer is broad, because

(1) considerable length of time is required for the system to reach maximum turbidity with the use of new polymer solutions.

(2) In principle, a turbidimetric separation process begins with big particles and ends with the smallest particles. It does not matter whether addition of non-solvent is done on incremental or continuous basis or with the use of new polymer solutions, since for each amount of non-solvent, new phases are formed according to order of their sizes.

(3) This would require the use of a large amount of polymer and materials in order to obtain a molecular weight distribution of a polymer. Under such conditions, the method cannot be applied to conversion analysis in polymerization reactions, or to very expensive polymers.

In the present method, addition of non-solvent was on incremental basis and at each point of the titration, the solutions were allowed to reach maximum turbidity. At the beginning of the titration, large groups of particles are present, according to the order of the size separation. With stirring, the particles are allowed to grow. The time for the solution to reach maximum turbidity increases as the titration progresses, until almost complete precipitation. At each point of the titration, new polymer phase is formed, and with mixing, nucleation will be expected to occur at a point just past the equilibrium precipitation point. The nuclei are particles of new phase which contain one or more polymer molecules. When particles collide, some of them may be expected to break. Hence, shaking by hand was found to be undesirable since the rate of particle growth is closely related to the method and rate of stirring. This was confirmed in preliminary experiments.

With well-controlled initial rate of initial point of titration, and uniform stirring, once precipitation has reached equilibrium precipitation point, the particles grow to the size corresponding to the maximum $\tau\lambda/\Delta\mu$. It must be borne in mind that turbidity changes in the same way with change in particle size or change in ρ. Maximum turbidity could be at any point in $(\overline{K/\rho})_w$ versus ρ_0 plots not necessarily at the maximum of the curve. The $(\overline{K/\rho})_w$ values which have been displayed in Table 66 indicate that, for broad polymers, the point of maximum turbidity is in the region $\rho \gg 3$. In other words, the condition of maximum turbidity can be attained in the region $\rho \gg 3$, not necessarily in the region $\rho \cong 3$. While the region $\rho \approx 3$ may be possible for narrolwy distributed and monodispersed particles and lower molecular weight polymer or latex solutions, this region may not be true for polymers with the most probable distribution, broader and high molecular weight polymers and/or when aggregation is encouraged.

APPENDIX III

SPECIFICATIONS FOR THE BECKMAN MODEL 25 SPECTROPHOMETER

(1) Monochromator

Single monochromator, filter-grating, 1200 lines/mm and blazed at 250 mm.

(2) Optical Principle

Double-beam and single beam.

(3) Wavelength Range

190 to 700 nm.

(4) Wavelength Presentation

Linear, digital counter.

(5) Wavelength Accuracy

± 0.5 nm.

(6) Wavelength Repeatability

Better than 0.25 nm.

(7) Stray Light

Less than 0.1% at 220 nm.

(8) Resolution

0.2 nm.

(9) Slits

Two programs for double-beam operature, and manually adjustable 0.05 nm to 2.0 mm.

(10) Photometric Readout

(a) Digital Display

4-digit digital display, 0 to 2 A, or 0 to 8000 counts in concentration.

(b) Recorder

100-millivolt per absorbance unit.

(c) Differential

- 0.3 A to + 0.7 A with 1 A pushbutton depressed

(d) BCD Connector

0 to 2 A or 0 to 8000 counts in concentration through 36-pin connector.

(11) Photometric Accuracy

0.5% of reading or 0.001 A which ever is larger.

(12) Photometric Repeatability

0.25% of reading or 0.001 A, which ever is larger.

(13) Recorder Scales

0.1 A, 0.25 A, 0.5 A, 1.0 A, and 2.0. A full scale.

(14) Scanning Speeds

100, 50, 20 and 5 nm/min selectable on accessory recorder unit.

(15) 0 A Line

Maximum deviation ± 0.009 A throughout operating range including noise.

(16) Baseline Stability

Double-beam better than 0.0004 A per hour.

(17) Approximate Weight

Normal: 70 pounds net, Shipping: 85 pounds.

(18) Overall Dimensions

24 inches long x 16 inches deep x 14 inches high.

(19) Power Requirements

120/240 volts (± 10%). 50/60 Hz, 2 amperes.

APPENDIX IV

VISCOSITY MEASUREMENTS

The viscometer used was Cannon-Ubbelhode viscometer 57-L181. This was set in constant temperature bath operating at 25 ± 0.1°C as shown in Figure AIV-1. This was vertically aligned by using a string with a sinker. The viscosity range covered during the analysis of a sample Standard 0, corresponds to a flow time of 5 mins to 12 mins. This satisfies a pre-requisite for the use of an empirical number-average molecular weight vs. intrinsic viscosity raltionship equation.

$$[\eta] = 6.8 \times 10^{-4} \bar{M}_n^{0.66}$$

obtained with flow times greater than 1.6 min.(24)

The procedure for viscosity measurements are as follows:

(1) Charged 5 ml of sample solution into A and allowed 30 min for the sample to come to bath temperature.

(2) Suck the solution above the etch mark E_1 by application of vacuum to B while sealing C by a finger.

(3) Allowed sample to flow down freely.

(4) Measured the flow time between the two etch marks E_1 and E_2 by a second stop-watch to the order of 0.1 sec.

(5) Viscosity at several other concentrations were obtained by adding the corresponding amount of solvent from D, mixing carefully and

and thoroughly by applying vacuum to C while sealing B by a finger and repeating the above.

Viscosities were obtained from the following formula:

$\eta(cp)$ = Viscometer Constant x Solution Density x Flow Time

Specific viscosities were then calculated by,

$$\eta_{sp} = \frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}} = \eta_r - 1$$

To obtain intrinsic viscosity $[\eta]$, η_{sp}/c is obtained, where c is the sample concentration in gm/100 ml, and plotted against c and extrapolated to c = 0, i.e., zero concentration. Similarly $\ln(\eta/\eta_o)/c$ is obtained and plotted against c and extrapolated to c = 0. The subscript o in η denotes solvent.

In the use of the above formula, the solution density of unity was used since the presence of polyacrylamide in water in the order of 0.1 gm/100 ml has been known to cause no significant change in density.

Viscosity measurements of Standard 0 are summarized in Table AIV-1. The plots of η_{sp}/c vs. c and $\ln \eta/\eta_o/c$ vs. c are shown in Figure AIV-2. Intrinsic viscosity obtained and corresponding $\overline{M}_n$ are as follows:

$[\eta] = 13.2$

$\overline{M}_n = 3.14 \times 10^6$

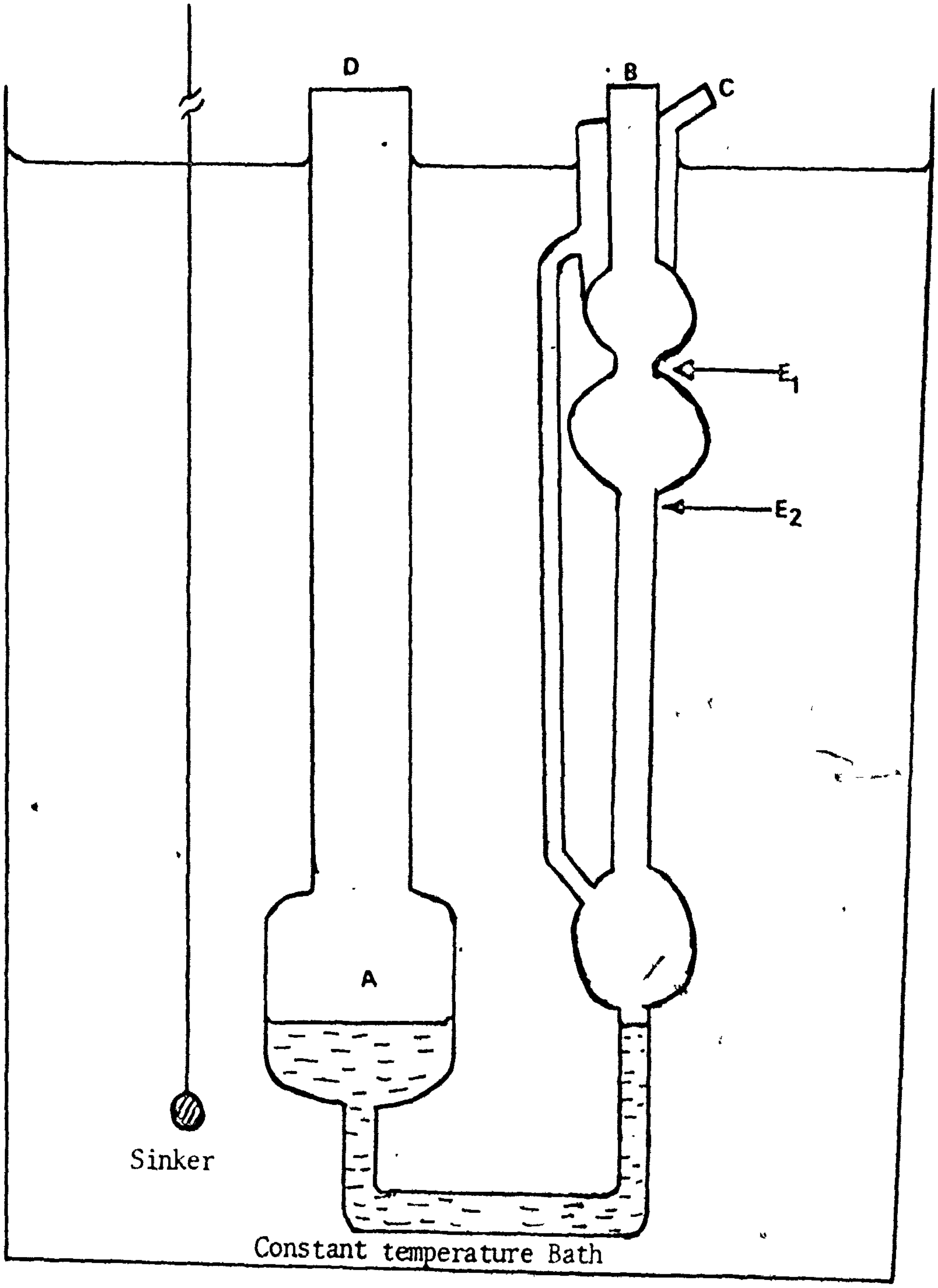


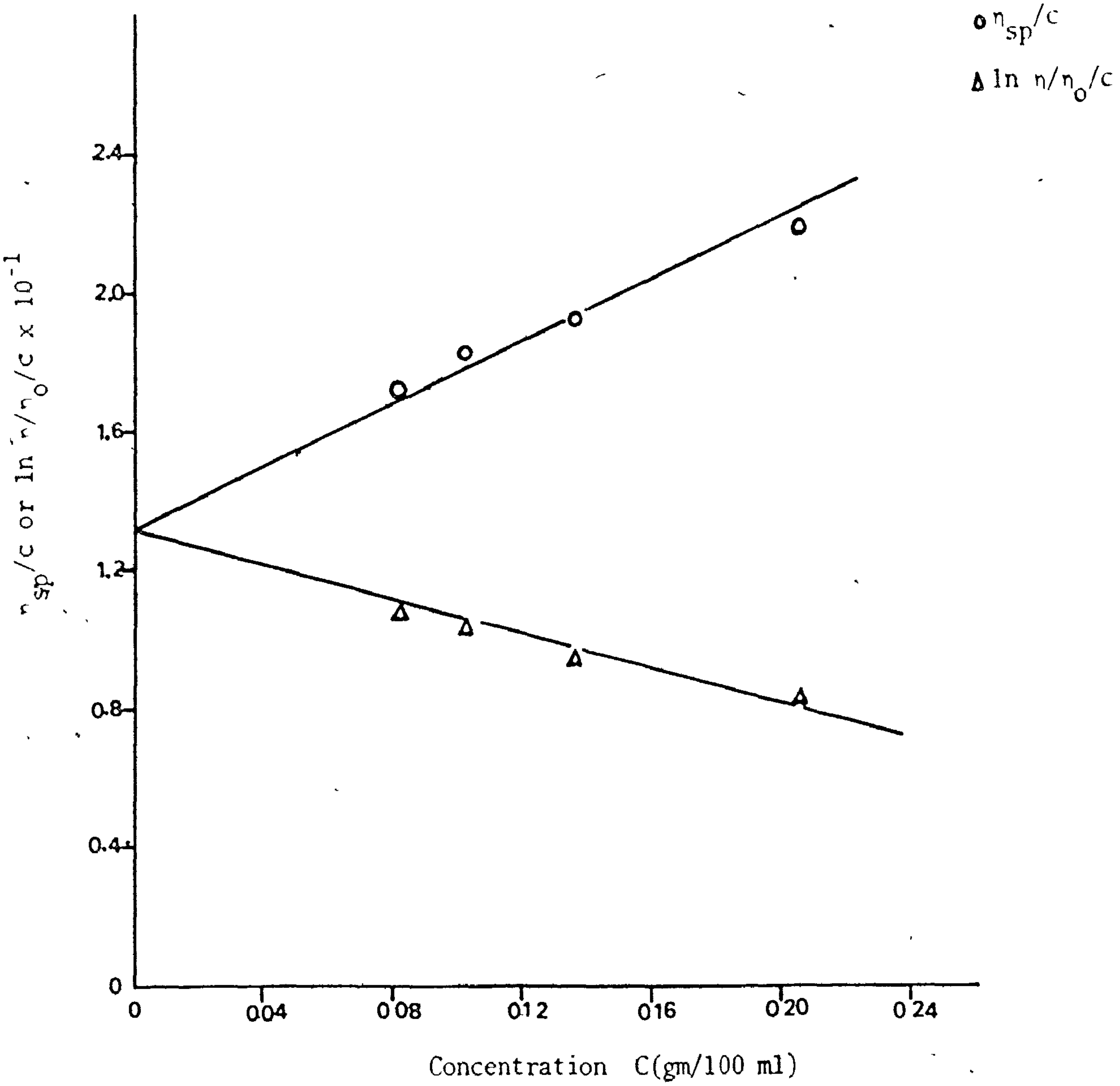
Fig. AIV-1: Viscometer Set-up.

Table AIV-1

Viscosity Measurements

	Concentration of Polymer Solution (Standard O)	Time (secs)	η_{sp}	$\frac{\eta_{sp}}{c}$	η/η_o	$\frac{\ln \eta/\eta_o}{c}$
	Solvent	123.7	-	-	-	-
		123.8	-	-	-	-
		123.6	-	-	-	-
		124.1	-	-	-	-
		123.7	-	-	-	-
Average		123.7	-	-	-	-
	0.206	675.8	-	-	-	-
		678.7	-	-	-	-
		679.2	-	-	-	-
		681.2	-	-	-	-
Average		678.7	4.487	21.780	5.4867	8.2637
	0.137	449.5	-	-	-	-
		449.5	-	-	-	-
		449.6	-	-	-	-
Average		449.5	2.6338	19.230	3.6338	9.418
	0.103	356.4	-	-	-	-
		356.9	-	-	-	-
		356.0	-	-	-	-
Average		356.4	1.8812	18.260	2.8812	10.2737
	0.0824	299.0	-	-	-	-
		300.3	-	-	-	-
		298.0	-	-	-	-
Average		299.1	1.418	17.208	2.4180	10.7150

Fig. AIV-2: Intrinsic Viscosity versus Concentration and ln $\eta/\eta_o/c$ versus Concentration.



APPENDIX V

Calcuation of $(\bar{K}/\rho)_w$ for Log-normal Weight Distributions of Spheres for Different Values of m

Since broad standards were used in the present studies, log-normal weight distributions, the broadest distribution was assumed for the particle size distribution.

The definition of $(\bar{K}/\rho)_w$ from Eq. 4.2.14 is

$$(\frac{\bar{K}}{\rho})_w = \int_0^\infty (K/\rho)dw \qquad \text{AV-1}$$

where w is the weight fraction having a size parameter between ρ and ρ + $d\rho$. The normalized log-normal distribution by weight is given by:(71)

$$d_w = \frac{1}{\rho\sqrt{2\pi}\ \ln\sigma_g} \exp\{-\frac{1}{2}(\frac{\ln\rho - \mu}{\ln\sigma_g})^2\}d\rho \qquad \text{AV-2}$$

Now $\mu = \ln\rho_0$

and $\beta = \sqrt{2}\ \ln\sigma_g$

where σ_g is the geometric standard deviation, ρ_0 is the weight geometric mean.

Substituting Eq. AV-2 into Eq. AV-1, we have

$$(\bar{K}/\rho)_w = \frac{1}{\beta\sqrt{\pi}} \int_0^\infty \frac{K}{\rho^2} \exp\{-(\frac{\ln\rho - \ln\rho_0}{\beta})^2\}d\rho \qquad \text{AV-3}$$

Integration of Eq. AV-3 was carried out using a subroutine which uses the Simpson's rule. All computations were made on a CDC6400. Results are given in Table AV-1 and some of the results have been plotted in Figures 1 - 9. The scattering coefficients were obtained from a subroutine.(72)

Table AV-1

Table of $(\overline{K/\rho})'_w$ for m = 1.05 for log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
0.50	-	0.0437	0.1563	0.2222	0.2566	0.2773	0.2899
1.50	0.1587	0.6416	0.7311	0.7094	0.6628	0.6128	0.5657
2.50	0.6357	0.7966	0.7580	0.7271	0.6857	0.6380	0.5902
3.50	0.9205	0.8167	0.7344	0.6766	0.6350	0.5969	0.5594
4.50	0.7490	0.6879	0.6365	0.5976	0.5683	0.5425	0.5164
5.50	0.4564	0.5155	0.5240	0.5154	0.5028	0.4891	0.4732
10.50	0.2128	0.2061	0.2275	0.2577	0.2832	0.3015	0.3136
15.50	0.1334	0.1406	0.1479	0.1636	0.1852	0.2069	0.2257
20.50	0.1018	0.1051	0.1109	0.1204	0.1358	0.1545	0.1734
25.50	0.0814	0.0840	0.0887	0.0957	0.1070	0.1224	0.1395
30.50	0.0678	0.0700	0.0738	0.0796	0.0884	0.1009	0.1160
35.50	0.0581	0.0600	0.0632	0.0681	0.0753	0.0857	0.0990
40.50	0.0509	0.0525	0.0553	0.0595	0.0656	0.0745	0.0862
45.50	0.0452	0.0466	0.0491	0.0528	0.0581	0.0658	0.0761
50.50	0.0407	0.0420	0.0442	0.0475	0.0521	0.0588	0.0681
55.50	0.0370	0.0381	0.0401	0.0431	0.0472	0.0532	0.0615
60.50	0.0339	0.0349	0.0368	0.0394	0.0431	0.0485	0.0560
65.50	0.0313	0.0322	0.0339	0.0363	0.0397	0.0445	0.0514
70.50	0.0290	0.0299	0.0315	0.0336	0.0367	0.0411	0.0475
75.50	0.0271	0.0279	0.0293	0.0313	0.0341	0.0382	0.0440
80.50	0.0254	0.0262	0.0274	0.0292	0.0318	0.0356	0.0410
85.50	0.0239	0.0246	0.0257	0.0273	0.0297	0.0333	0.0384
90.50	0.0226	0.0233	0.242	0.0257	0.0179	0.0312	0.0360
95.50	0.0214	0.0220	0.0228	0.0242	0.0263	0.0294	0.0339
99.50	0.0205	0.0211	0.0218	0.0230	0.0251	0.0281	0.0324

Table IV-2

Table of $(\overline{K}/\rho)_w$ m = 1.1 for Log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
0.50	-	0.0432	0.1543	0.2198	0.2549	0.2766	0.2903
1.00	0.1738	0.8956	0.6829	0.6011	0.5558	0.5219	0.4921
1.50	0.1621	0.6472	0.7375	0.7169	0.6710	0.6710	0.5470
2.00	1.0710	0.7375	0.7543	0.7462	0.7044	0.6525	0.6013
2.50	0.6571	0.8234	0.7815	0.7466	0.7021	0.6521	0.6026
3.00	0.9190	0.8545	0.7852	0.7290	0.6823	0.6362	0.5911
3.50	0.9558	0.8473	0.7607	0.6987	0.6536	0.6128	0.5731
5.00	0.5745	0.6215	0.6005	0.5752	0.5522	0.5307	0.5081
10.00	0.2238	0.2218	0.2486	0.2815	0.3073	0.3247	0.3353
15.00	0.1402	0.1487	0.1566	0.1741	0.1975	0.2201	0.2393
20.00	0.1064	0.1097	0.1160	0.1264	0.1430	0.1629	0.1825
25.00	0.0843	0.0871	0.0920	0.0996	0.1117	0.1280	0.1460
30.00	0.0698	0.0722	0.0762	0.0823	0.0917	0.1050	0.1210
35.00	0.0597	0.0616	0.0650	0.0701	0.0778	0.0889	0.1030
40.00	0.0520	0.0537	0.0567	0.0611	0.0675	0.0769	0.0892
40.50	0.0514	0.0531	0.0560	0.0603	0.0667	0.0759	0.0881
45.00	0.0462	0.0476	0.0502	0.0541	0.0597	0.0677	0.0786
50.00	0.0415	0.0428	0.0451	0.0485	0.0534	0.0650	0.0707
55.00	0.0376	0.0388	0.0409	0.0440	0.0483	0.0546	0.0633
60.00	0.0345	0.0355	0.0374	0.0402	0.0441	0.0497	0.0576
65.00	0.0318	0.0328	0.0345	0.0367	0.0405	0.0455	0.0528
70.00	0.0295	0.0304	0.0320	0.0342	0.0374	0.0420	0.0486
75.00	0.0275	0.0283	0.0298	0.0318	0.0347	0.0389	0.0451
80.00	0.0257	0.0265	0.0278	0.0296	0.0323	0.0363	0.0420
85.00	0.0242	0.0250	0.0261	0.0277	0.0302	0.0339	0.0392
90.00	0.0228	0.0235	0.0245	0.0260	0.0284	0.0318	0.0368
95.00	0.0216	0.0223	0.0231	0.0245	0.0267	0.0299	0.0346
99.50	0.0206	0.0212	0.0220	0.0232	0.0253	0.0284	0.0328
100.00	0.0205	0.0211	0.0219	0.0231	0.0251	0.0282	0.0327

Table AV-3

Table of $(\overline{K/\rho})_w$ m = 1.137 for Log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
0.50	-	0.0420	0.1503	0.2147	0.2499	0.2724	0.2871
1.00	0.1693	0.8732	0.6694	0.5926	0.5505	0.5188	0.4904
1.50	0.1634	0.6443	0.7347	0.7152	0.6706	0.6216	0.5750
2.00	1.0870	0.7465	0.7617	0.7515	0.7087	0.6562	0.6046
2.50	0.6701	0.8396	0.7948	0.7565	0.7097	0.6581	0.6076
3.00	0.9409	0.8736	0.8013	0.7415	0.6919	0.6438	0.5972
3.50	0.9795	0.8674	0.7774	0.7122	0.6643	0.6213	0.5801
5.00	0.5886	0.6365	0.6145	0.5879	0.5633	0.5400	0.5160
10.00	0.2288	0.2265	0.2541	0.2878	0.3140	0.3315	0.3418
15.00	0.1435	0.1520	0.1600	0.1778	0.2017	0.2248	0.2441
20.00	0.1086	0.1120	0.1182	0.1289	0.1458	0.1662	0.1862
25.00	0.0856	0.0885	0.0936	0.1013	0.1138	0.1305	0.1489
30.00	0.0704	0.0730	0.0773	0.0836	0.0933	0.1070	0.1233
35.00	0.0600	0.0621	0.0658	0.0711	0.0790	0.0904	0.1047
40.00	0.0524	0.0541	0.0572	0.0618	0.0685	0.0782	0.0908
40.50	0.0517	0.0534	0.0565	0.0610	0.0676	0.0771	0.0896
45.00	0.0465	0.0479	0.0506	0.0547	0.0604	0.0688	0.0800
50.00	0.0417	0.0430	0.0454	0.0490	0.0540	0.0613	0.0713
55.00	0.0378	0.0390	0.0412	0.0444	0.0488	0.0553	0.0643
60.00	0.0346	0.0357	0.0377	0.0405	0.0445	0.0503	0.0548
65.00	0.0319	0.0329	0.0347	0.0372	0.0409	0.0461	0.0535
70.00	0.0296	0.0305	0.0321	0.0344	0.0377	0.0425	0.0493
75.00	0.0276	0.0285	0.0299	0.0320	0.0350	0.0394	0.0457
80.00	0.0259	0.0267	0.0280	0.0298	0.0326	0.0366	0.0425
85.00	0.0243	0.0251	0.0262	0.0279	0.0305	0.0342	0.0397
90.00	0.0230	0.0236	0.0247	0.0262	0.0286	0.0321	0.0372
95.00	0.0217	0.0224	0.0232	0.0246	0.0269	0.0302	0.0350
99.50	0.0207	0.0213	0.0221	0.0233	0.0255	0.0286	0.0332
100.00	0.0206	0.0212	0.0219	0.0232	0.0253	0.0285	0.0330

Table AV-4

Table of $(\overline{K/\rho})_w$ m = 1.2 for Log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
0.50	-	0.0396	0.1417	0.2033	0.2386	0.2623	0.2785
1.00	0.1594	0.8243	0.6385	0.5716	0.5360	0.5086	0.4831
1.50	0.1641	0.6329	0.7217	0.7058	0.6642	0.6173	0.5721
2.00	1.1060	0.7593	0.7687	0.7552	0.7108	0.6577	0.6058
2.50	0.6882	0.8624	0.8132	0.7690	0.7180	0.6639	0.6118
3.00	0.9743	0.9026	0.8251	0.7589	0.7042	0.6525	0.6037
3.50	1.0180	0.8994	0.8032	0.7320	0.6788	0.6320	0.5880
4.00	1.0230	0.8468	0.7576	0.6945	0.6475	0.6069	0.5686
4.50	0.8310	0.7596	0.6991	0.6516	0.6135	0.5800	0.5475
5.00	0.6120	0.6607	0.6364	0.6069	0.5790	0.5526	0.5259
5.50	0.5014	0.5670	0.5751	0.5630	0.5452	0.5258	0.5045
6.00	0.4354	0.4866	0.5182	0.5213	0.5129	0.4999	0.4837
6.50	0.3685	0.4214	0.4674	0.4825	0.4823	0.4753	0.4637
7.00	0.3070	0.3704	0.4228	0.4469	0.4538	0.4520	0.4447
7.50	0.2678	0.3310	0.3843	0.4146	0.4274	0.4302	0.4266
8.00	0.2478	0.3007	0.3513	0.3855	0.4029	0.4097	0.4095
8.50	0.2402	0.2772	0.3231	0.3592	0.3803	0.3906	0.3934
9.00	0.2381	0.2587	0.2989	0.3357	0.3595	0.3727	0.3782
9.50	0.2369	0.2437	0.2781	0.3146	0.3404	0.3560	0.3638
10.00	0.2339	0.2312	0.2602	0.2956	0.3228	0.3404	0.3503
10.50	0.2279	0.2203	0.2446	0.2785	0.3077	0.3259	0.3375
11.00	0.2189	0.2106	0.2310	0.2631	0.2917	0.3123	0.3255
11.50	0.2078	0.2018	0.2189	0.2492	0.2779	0.2996	0.3141
12.00	0.1958	0.1936	0.2082	0.2367	0.2652	0.2877	0.3034
12.50	0.1841	0.1859	0.1987	0.2252	0.2535	0.2766	0.2933
13.00	0.1734	0.1787	0.1000	0.2148	0.2426	0.2661	0.2837
13.50	0.1642	0.1719	0.1822	0.2053	0.2325	0.2563	0.2746
14.00	0.1565	0.1655	0.1750	0.1966	0.2232	0.2471	0.2660

......continued

Table AV-4(continued)

Table of $(\overline{K/\rho})_w$ m = 1.2 for Log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
14.50	0.1502	0.1595	0.1684	0.1877	0.2144	0.2385	0.2578
15.00	0.1451	0.1538	0.1624	0.1813	0.2063	0.2303	0.2501
15.50	0.1408	0.1485	0.1567	0.1745	0.1988	0.2277	0.2428
16.00	0.1369	0.1435	0.1515	011682	0.1917	0.2154	0.2358
16.50	0.1334	0.1388	0.1466	0.1624	0.1851	0.2086	0.2291
17.00	0.1298	0.1344	0.1420	0.1569	0.1789	0.2021	0.2228
17.50	0.1263	0.1303	0.1377	0.1518	0.1730	0.1960	0.2168
18.00	0.1228	0.1264	0.1337	0.1471	0.1676	0.1902	0.2110
18.50	0.1193	0.1228	0.1299	0.1426	0.1624	0.1847	0.2056
19.00	0.1158	0.1193	0.1263	0.1384	0.1575	0.1795	0.2003
19.50	0.1125	0.1161	0.1228	0.1345	0.1530	0.1745	0.1953
20.00	0.1093	0.1130	0.1196	0.1308	0.1486	0.1698	0.1905
20.50	0.1064	0.1101	0.1165	0.1273	0.1445	0.1653	0.1859
21.00	0.1036	0.1073	0.1135	0.1240	0.1406	0.1611	0.1815
21.50	0.1010	0.1047	0.1108	0.1208	0.1369	0.1570	0.1773
22.00	0.0985	0.1022	0.1082	0.1178	0.1334	0.1531	0.1733
22.50	0.0963	0.0998	0.1056	0.1150	0.1301	0.1494	0.1694
23.00	0.0941	0.0975	0.1032	0.1123	0.1269	0.1458	0.1657
23.50	0.0921	0.0953	0.1009	0.1097	0.1239	0.1424	0.1621
24.00	0.0901	0.0932	0.0987	0.1077	0.1210	0.1392	0.1586
24.50	0.0882	0.0912	0.0966	0.1049	0.1183	0.1361	0.1553
25.00	0.0864	0.0893	0.0946	0.1026	0.1156	0.1331	0.1521
25.50	0.0847	0.0875	0.0926	0.1005	0.1131	0.1302	0.1490
26.00	0.0830	0.0857	0.0907	0.0984	0.1107	0.1274	0.1461
26.50	0.0813	0.0840	0.0889	0.0964	0.1084	0.1248	0.1432
27.00	0.0797	0.0824	0.0872	0.0945	0.1062	0.1222	0.1405
27.50	0.0782	0.0808	0.0855	0.0927	0.1041	0.1198	0.1378
28.00	0.0768	0.0793	0.0839	0.0910	0.1020	0.1174	0.1352
28.50	0.0753	0.0779	0.0824	0.0893	0.1000	0.1152	0.1327
29.00	0.0740	0.0765	0.0809	0.0876	0.0982	0.1130	0.1303

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Table AV-4(continued)

Table of $\overline{(K/\rho)}_w$ m = 1.2 for Log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
29.50	0.0727	0.0751	0.0795	0.0861	0.0963	0.1109	0.1280
30.00	0.0714	0.0738	0.0781	0.845	0.0946	0.1088	0.1258
30.50	0.0702	0.0726	0.0767	0.0831	0.0929	0.1069	0.1236
31.00	0.0690	0.0713	0.0754	0.0817	0.0913	0.1050	0.1215
31.50	0.0679	0.0702	0.0742	0.0803	0.0897	0.1031	0.1194
32.00	0.0667	0.069	0.0730	0.0790	0.0882	0.1014	0.1174
32.50	0.0657	0.068	0.0718	0.0777	0.0867	0.0997	0.1155
33.00	0.0646	0.0668	0.0707	0.0765	0.0853	0.0980	0.1137
33.50	0.0636	0.0658	0.0696	0.0753	0.0838	0.0964	0.1118
34.00	0.0627	0.0648	0.0685	0.0741	0.0826	0.0948	0.1101
34.50	0.0617	0.0638	0.0675	0.0730	0.0813	0.0933	0.1084
35.00	0.0608	0.0629	0.0665	0.0719	0.0800	0.0918	0.1067
35.50	0.0599	0.0610	0.0655	0.0708	0.0788	0.0904	0.1051
36.00	0.0590	0.0610	0.0645	0.0698	0.0776	0.0089	0.1035
36.50	0.0582	0.0602	0.0636	0.0688	0.0765	0.0877	0.1020
37.00	0.0574	0.0593	0.0627	0.0678	0.0754	0.0864	0.1005
37.50	0.0566	0.0585	0.0618	0.0669	0.0743	0.0851	0.0991
38.00	0.0558	0.0577	0.0610	0.0659	0.0732	0.0839	0.0977
38.50	0.0551	0.0560	0.0602	0.0650	0.0722	0.0827	0.0963
39.00	0.0543	0.0562	0.0549	0.0642	0.0712	0.0815	0.0950
39.50	0.0536	0.0554	0.0586	0.0633	0.0703	0.0804	0.0937
40.00	0.0529	0.0547	0.0578	0.0625	0.0693	0.0793	0.0924
40.50	0.0523	0.0540	0.0571	0.0617	0.0684	0.0782	0.0912
41.00	0.0516	0.0533	0.0564	0.0609	0.0675	0.0772	0.0900
41.50	0.0510	0.0527	0.0557	0.0601	0.0666	0.0762	0.0888
42.00	0.0503	0.0520	0.0550	0.0594	0.0658	0.0752	0.0877
42.50	0.0497	0.0514	0.0543	0.0587	0.0650	0.0742	0.0865
43.00	0.0491	0.0508	0.0536	0.0579	0.0642	0.0733	0.0854

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Table AV-4(continued)

Table of $(\overline{K/\rho})_w$ m = 1.2 for Log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
43.50	0.0485	0.0502	0.0530	0.0572	0.0634	0.0723	0.0844
44.00	0.0480	0.0496	0.0524	0.0566	0.0626	0.0714	0.0833
44.50	0.0474	0.0490	0.0518	0.0559	0.0619	0.0706	0.0823
45.00	0.0469	0.0484	0.0512	0.0553	0.0611	0.0697	0.0813
45.50	0.0463	0.0479	0.0506	0.0546	0.0604	0.0689	0.0803
46.00	0.0458	0.0474	0.0500	0.0540	0.0597	0.0681	0.0794
46.50	0.0453	0.0468	0.0495	0.0534	0.0590	0.0673	0.0785
47.00	0.0448	0.0463	0.0489	0.0528	0.0584	0.0665	0.0775
47.50	0.0443	0.0458	0.0484	0.0522	0.0577	0.0657	0.0767
48.00	0.0439	0.0453	0.0479	0.0517	0.0571	0.0650	0.0758
48.50	0.0434	0.0448	0.0474	0.0511	0.0564	0.0642	0.0749
49.00	0.0429	0.0444	0.0469	0.0505	0.0558	0.0635	0.0741
49.50	0.0425	0.0439	0.0464	0.0500	0.0552	0.0628	0.0733
50.00	0.0421	0.0435	0.0459	0.0495	0.0546	0.0621	0.0725
50.50	0.0416	0.0430	0.0454	0.0490	0.0541	0.0615	0.0717
51.00	0.0412	0.0426	0.0450	0.0485	0.0535	0.0608	0.0709
51.50	0.0408	0.0421	0.0445	0.0480	0.0529	0.0601	0.0702
52.00	0.0404	0.0417	0.0441	0.0475	0.0524	0.0600	0.0694
52.50	0.0400	0.0413	0.0436	0.0470	0.0519	0.0589	0.0687
53.00	0.0396	0.0409	0.0432	0.0466	0.0513	0.0583	0.0680
53.50	0.0392	0.0405	0.0428	0.0461	0.0508	0.0577	0.0673
54.00	0.0389	0.0401	0.0424	0.0457	0.0503	0.0571	0.0666
54.50	0.0385	0.0398	0.0420	0.0452	0.0498	0.0565	0.0659
55.00	0.0381	0.0394	0.0416	0.0448	0.0493	0.0560	0.0653
55.50	0.0378	0.0390	0.0412	0.0444	0.0489	0.0554	0.0646
56.00	0.0374	0.0387	0.0408	0.0440	0.0484	0.0549	0.0640
56.50	0.0371	0.0383	0.0404	0.0435	0.0480	0.0544	0.0634
57.00	0.0368	0.0380	0.0401	0.0431	0.0475	0.0538	0.0627

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Table AV-4(continued)

Table of $(\overline{K/\rho})_w$ m = 1.2 for Log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
57.50	0.0364	0.0376	0.0397	0.0428	0.0471	0.0533	0.0621
58.00	0.0361	0.0373	0.0394	0.0424	0.0466	0.0528	0.0616
58.50	0.0358	0.0370	0.0390	0.0420	0.0462	0.0523	0.0610
59.00	0.0355	0.0367	0.0387	0.0416	0.0458	0.0518	0.0604
59.50	0.0352	0.0363	0.0383	0.0412	0.0454	0.0514	0.0598
60.00	0.0349	0.0360	0.0380	0.0409	0.0450	0.0509	0.0593
60.50	0.0346	0.0357	0.0377	0.0405	0.0446	0.0504	0.0588
61.00	0.0343	0.0354	0.0374	0.0402	0.0442	0.0500	0.0582
61.50	0.0340	0.0351	0.0370	0.0398	0.0438	0.0495	0.0577
62.00	0.0337	0.0348	0.0367	0.0395	0.0434	0.0491	0.0572
62.50	0.0335	0.0346	0.0364	0.0392	0.0430	0.0487	0.0567
63.00	0.0332	0.0343	0.0361	0.0388	0.0427	0.0482	0.0562
63.50	0.0329	0.0340	0.0358	0.0385	0.0423	0.0478	0.0557
64.00	0.0327	0.0337	0.0355	0.0382	0.0419	0.0474	0.0552
64.50	0.0324	0.0335	0.0353	0.0379	0.0416	0.0470	0.0547
65.00	0.0321	0.0332	0.0350	0.0376	0.0413	0.0466	0.0543
65.50	0.0319	0.0329	0.0347	0.0373	0.0409	0.0462	0.0538
66.00	0.0316	0.0327	0.0344	0.0370	0.0406	0.0458	0.0534
66.50	0.0314	0.0324	0.0342	0.0367	0.0402	0.0455	0.0529
67.00	0.0312	0.0322	0.0339	0.0364	0.0399	0.0451	0.0525
67.50	0.0309	0.0319	0.0336	0.0361	0.0396	0.0447	0.0520
68.00	0.0307	0.0317	0.0334	0.0358	0.0393	0.0443	0.0516
68.50	0.0305	0.0315	0.0331	0.0355	0.0390	0.0440	0.0512
69.00	0.0302	0.0312	0.0329	0.0353	0.0387	0.0436	0.0508
69.50	0.0300	0.0310	0.0326	0.0350	0.0384	0.0433	0.0504
70.00	0.0298	0.0308	0.0324	0.0347	0.0381	0.0429	0.0500
70.50	0.0296	0.0305	0.0322	0.0345	0.0378	0.0426	0.0496
71.00	0.0294	0.0303	0.0319	0.0342	0.0375	0.0423	0.0492

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Table AV-4(continued

Table of $(\overline{K/\rho})_w$ m = 1.2 for Log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
71.50	0.0292	0.0301	0.0317	0.0340	0.0372	0.0420	0.0488
72.00	0.0290	0.0299	0.0315	0.0337	0.0369	0.0416	0.0484
72.50	0.0288	0.0297	0.0312	0.0334	0.0366	0.0413	0.0481
73.00	0.0286	0.0295	0.0310	0.0332	0.0364	0.0410	0.0477
73.50	0.0284	0.0293	0.0308	0.0330	0.0361	0.0407	0.0473
74.00	0.0282	0.0291	0.0306	0.0327	0.0358	0.0404	0.0470
74.50	0.0280	0.0289	0.0304	0.0325	0.0356	0.0401	0.0466
75.00	0.0278	0.0287	0.0301	0.0323	0.0353	0.0398	0.0463
75.50	0.0276	0.0285	0.0299	0.0320	0.0351	0.0395	0.0459
76.00	0.0274	0.0283	0.0297	0.0318	0.0348	0.0392	0.0456
76.50	0.0272	0.0281	0.0295	0.0316	0.0345	0.0389	0.0452
77.00	0.0270	0.0279	0.0293	0.0313	0.0343	0.0386	0.0449
77.50	0.0269	0.0277	0.0291	0.0311	0.0341	0.0384	0.0446
78.00	0.0267	0.0275	0.0289	0.0309	0.0338	0.0381	0.0443
78.50	0.0265	0.0274	0.0287	0.0307	0.0336	0.0378	0.0440
79.00	0.0263	0.0272	0.0285	0.0305	0.0333	0.0375	0.0436
79.50	0.0262	0.0270	0.0284	0.0303	0.0331	0.0373	0.0433
80.00	0.0260	0.0268	0.0282	0.0301	0.0329	0.0370	0.0430
80.50	0.0258	0.0267	0.0280	0.0299	0.0327	0.0368	0.0427
81.00	0.0257	0.0265	0.0278	0.0297	0.0324	0.0365	0.0424
81.50	0.0255	0.0263	0.0276	0.0295	0.0322	0.0363	0.0421
82.00	0.0254	0.0262	0.0274	0.0293	0.0320	0.0360	0.0419
82.50	0.0252	0.0260	0.0273	0.0291	0.0318	0.0358	0.0416
83.00	0.0251	0.0258	0.0271	0.0289	0.0316	0.0355	0.0413
83.50	0.0249	0.0257	0.0269	0.0287	0.0313	0.0353	0.0410
84.00	0.0247	0.0255	0.0267	0.0285	0.0311	0.0350	0.0407
84.50	0.0246	0.0254	0.0266	0.0283	0.0309	0.0348	0.0405

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Table AV-4(continued)

Table of $(\overline{K/\rho})_w$ m = 1.2 for Log-normal wt Distribution

ρ_0	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
85.00	0.0245	0.0252	0.0264	0.0281	0.0307	0.0346	0.0402
85.50	0.0243	0.0251	0.0762	0.0279	0.0305	0.0344	0.0399
86.00	0.0242	0.0250	0.0261	0.0278	0.0303	0.0341	0.0397
86.50	0.0240	0.0248	0.0259	0.0276	0.0301	0.0339	0.0394
87.00	0.0239	0.0246	0.0258	0.0274	0.0299	0.0337	0.0391
87.50	0.0237	0.0245	0.0256	0.0272	0.0297	0.0335	0.0389
88.00	0.0236	0.0243	0.0254	0.0271	0.0296	0.0333	0.0386
88.50	0.0235	0.0242	0.0253	0.0269	0.0294	0.0330	0.0384
89.00	0.0233	0.0241	0.0251	0.0267	0.0292	0.0328	0.0381
89.50	0.0232	0.0239	0.0250	0.0266	0.0290	0.0326	0.0349
90.00	0.0231	0.0238	0.0248	0.0264	0.0288	0.0324	0.0377
90.50	0.0229	0.0236	0.0247	0.0262	0.0286	0.0322	0.0374
91.00	0.0228	0.0235	0.0245	0.0261	0.0284	0.0320	0.0372
91.50	0.0227	0.0234	0.0244	0.0259	0.0283	0.0318	0.0370
92.00	0.0226	0.0232	0.0242	0.0257	0.0281	0.0316	0.0367
92.50	0.0224	0.0231	0.0241	0.0256	0.0279	0.0314	0.0365
93.00	0.0223	0.0230	0.0240	0.0254	0.0278	0.0312	0.0363
93.50	0.0222	0.0229	0.0238	0.0253	0.0276	0.0310	0.0361
94.00	0.0221	0.0227	0.0237	0.0251	0.0274	0.0388	0.0358
94.50	0.0220	0.0226	0.0235	0.0250	0.0272	0.0307	0.0356
95.00	0.0218	0.0225	0.0234	0.0248	0.0271	0.0305	0.0354
95.50	0.0217	0.0224	0.0233	0.0247	0.0269	0.0303	0.0352
96.00	0.0216	0.0222	0.0231	0.0245	0.0268	0.0301	0.0350
96.60	0.0215	0.0221	0.0230	0.0244	0.0266	0.0299	0.0348
97.00	0.0214	0.0220	0.0229	0.0242	0.0264	0.0298	0.0346
97.50	0.0213	0.0219	0-0227	0.0241	0.0263	0.0296	0.0344
98.00	0.0212	0.0218	0.0226	0.0239	0.0261	0.0294	0.0342
98.50	0.0210	0.0217	0.0225	0.0238	0.0260	0.0292	0.0340

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Table AV-4 (continued)

Table of $(\overline{K/\rho})_w$ m = 1.2 for Log-normal wt Distribution

ρ_o	β = 0.2	β = 0.4	β = 0.6	β = 0.8	β = 1.0	β = 1.2	β = 1.4
99.00	0.0209	0.0215	0.0223	0.0237	0.0258	0.0291	0.0338
99.50	0.0208	0.0214	0.0222	0.0235	0.0257	0.0289	0.0336
100.00	0.0207	0.0213	0.0221	0.0234	0.0255	0.0287	0.0334