ABSTRACT.

A commercial sample of poly(vinyl chloride) was fractionated by a fractional precipitation method and the fractions characterized by light scattering, osmometry, viscometry and Gel-Permeation Chromatography (G.P.C.). The precipitation points of a number of polymer - solvent - poor-solvent systems were investigated to determine the effect of solvent power and molecular weight on these points. These were used to determine the compositions of solutions, the properties of which approximated "theta-solutions". The number average molecular weight ($\bar{M}n$) was determined in both T.H.F. and these specially prepared "theta-solutions", the results in both cases showing excellent agreement.

Light scattering and viscometry measurements were used to measure the weight average molecular weights ($\bar{M}w$) and from these measurements, Mark-Houwink type constants were calculated for the molecular weight range covered. The G.P.C. peak elution volumes were related to both light scattering and viscometry. The polystyrene "calibration" curve was shown to have some shortcomings, these being the constants used to translate it to an equivalent P.V.C. curve, and the dissimilarity of the shapes of polystyrene and P.V.C. There was some evidence of anomalous behaviour of the first (highest molecular weight) fraction previously

reported by other authors.

The normal distributions for eight fractions was calculated and from these, the normal and weight distributions for the composite sample.

ACKNOWLEDGEMENT.

The author wishes to express his gratitude to Dr. W. Hayduk for his kind assistance and guidance throughout.

Many thanks are also extended to Mr. G. Gasperetti and his staff for their assistance in the construction of experimental equipment.

Finally the author wishes to thank his wife for the many ways in which she assisted in the completion of this work.

TABLE OF CONTENTS.

THEORY AND LITERATURE SURVEY

APPARATUS AND PROCEDURE

ANALYTICAL EQUIPMENT AND OPERATION

RESULTS AND DISCUSSION

APPENDICES

LIST OF FIGURES.

LIST OF TABLES.

NOMENCLATURE.

Å	Angstrom, 10^{-8} cms.
a	Mark-Houwink exponent. Relating molecular weight to intrinsic viscosity.
B	second virial coefficient, cms. - $\text{litres}^2/\text{gm.}^2$ (osmotic pressure).
b	constant for light scattering photometer, working standard.
C	concentration in grams/litre, unless otherwise specified.
G	Gibbs free energy.
Gs	intensity of light scattered at 90°.
Gw	intensity of light transmitted.
H	light scattering constant.
h	hydraulic head across osmometer membrane, cms. solvent.
K	Staudinger constant relating molecular weight to intrinsic viscosity.
M	molecular weight gms./gram-mole.
M_i	molecular weight of species i, g./g.mole.
Mn	number average molecular weight, g./g.mole.
Mv	viscosity average molecular weight, g./g.mole.
Mw	weight average molecular weight, g./g.mole.
M_z	z - coverage molecular weight, g./g. mole.
M_{z+1}	(z+1)-average molecular weight, g./g.mole.
m	moment of molar-molecualr weight distribution curve.
N_A	Avogadro's number.
N_O	Avogadro's number.
N	refractive index.

n	number of species in a system.
n_i	number of gram moles of species i.
R	universal gas constant, 82.06 cm.^{3} atm./g.mole ^{o}K.
R_h	hydrodynamic radius.
$\langle S^2 \rangle$	mean square radius of gyration in good solvent.
$\langle So^2 \rangle$	mean square radius of gyration of unperturbed molecule.
T	absolute temperature ^{o}K.
V_c	eluted volume.
V_o	void volume
V_i	total internal volume.
V_{iacc}	internal volume accessible to a particular species.
X	relative size
$\bar{X}n$	ratio of number average partial molar volume of polymer to that of solvent.
α	expansion factor for molecule in good solvent.
ϕ	volume fraction of polymer in solution.
Φ	constant relating intrinsic viscosity, molecular weight and $S2$.
π	osmotic pressure.
(η)	intrinsic viscosity.
η_o	pure solvent viscosity, cp.
η	solution viscosity, cp.
η_{sp}	specific viscosity, dimensionless.
η_r	reduced viscosity, decilitres/gram.
δ	solubility parameter (cals/cc.)$^{\frac{1}{2}}$
σ_{ni}	standard deviation, gms./gm. mole.
λ	wave length of light, mμ

τ	turbidity of liquid.
μ	chemical potential.
χ	interaction coefficient.

INTRODUCTION

A homopolymer such as poly(vinyl chloride) has several different average molecular weights resulting from its molecular weight distribution. Usually the polymerization process cannot be controlled accurately enough to produce the same number of repeating monomer units for each polymer molecule in any one sample.

To accurately characterize a polymer it is necessary to determine its molecular weight distribution and, until recently, this could only be done by a time consuming process of fractionation. To assist the partial characterization, various molecular weight averages have been defined for a particular molecular weight distribution.

These different statistical averages, with one exception, are the first, second and higher moments of the molecular weight distribution function about the axis of zero molecular weight. These averages are defined generally as:

$$\overline{M}_m = \frac{\Sigma n_i \; M_i^m}{\Sigma n_i \; M_i^{m-1}} \qquad .....(1)$$

where:

$m = 1$ The first moment; known as the number average molecular weight, $\overline{M}_n$

$m = 2$ The second moment; known as the weight average molecular weight, $\overline{M}_w$

m = 3 The third moment; known as the z-average molecular weight, $\overline{M}_z$

m = 4 The fourth moment; known as the z + 1-average molecular weight, M_{z+1}

The other frequently used average molecular weight is the viscosity average molecular weight defined as:

$$\overline{M}_v = \left(\frac{\Sigma_{ni} M_i^{1+a}}{\Sigma_{ni} M_i} \right)^{1/a} \qquad .....(2)$$

This variation in the molecular weights of a polymer is known as the polydispersity and is a measure of the breadth of the molecular weight distribution. The ratio $\overline{M}_w/\overline{M}_n$ is frequently used to measure the broadness of the distribution and is referred to as the polydispersity index.

The molecular weight distribution curve for a polydisperse polymer is usually asymmetrical about the peak. This is shown in Figure 1. Also indicated are the four most frequently used types of molecular weight averages and their relative positions.

Fractionation is the process in which a polydisperse polymer is broken down into a series of fractions, each with reduced polydispersity. These fractions will provide information about the molecular weight distribution of the parent polymer. Because a polymer is usually polydisperse with respect to

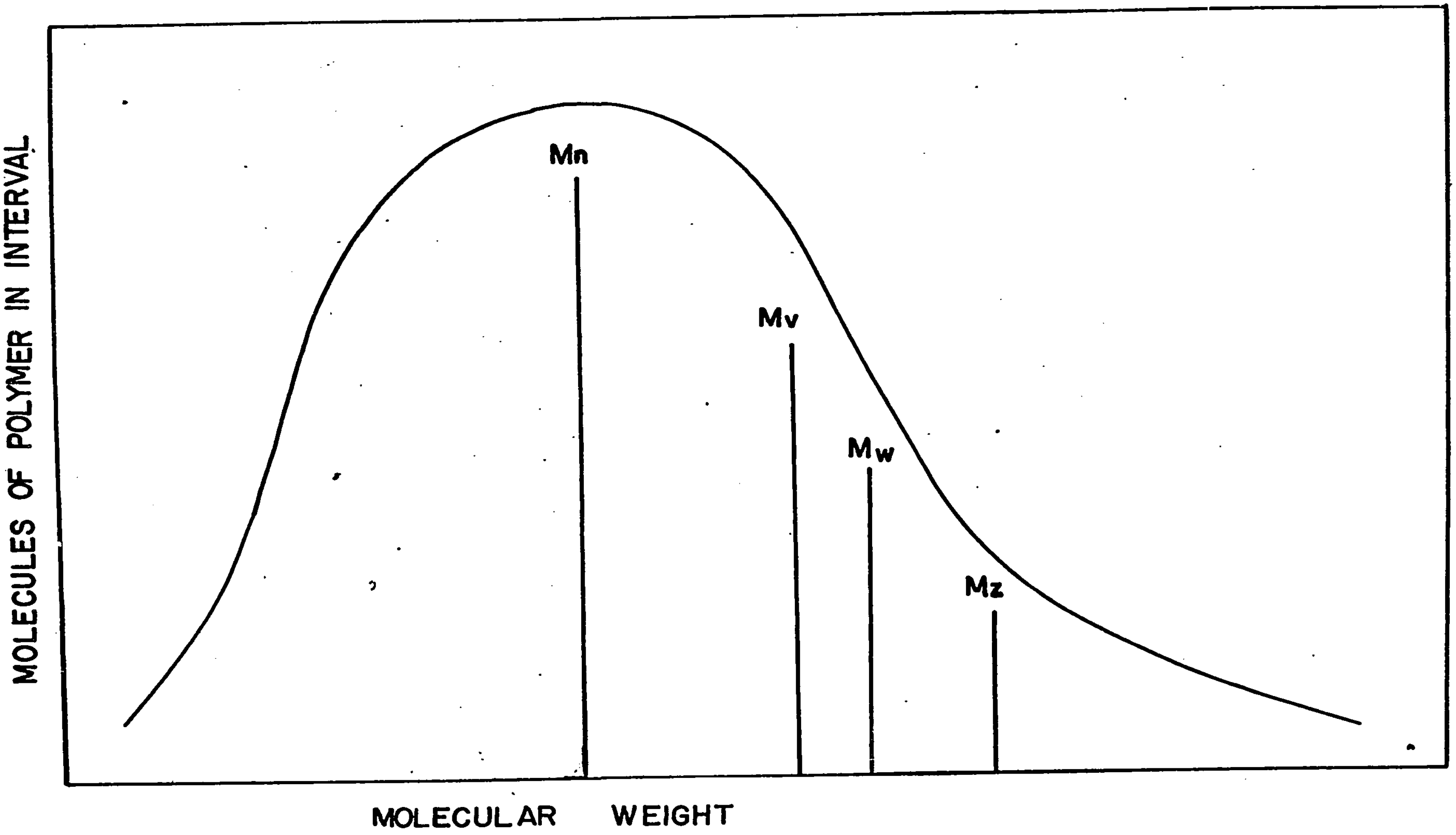


Figure 1 - Distribution of various molecular weight averages about the mean.

both molecular weight and structure, the process of fractionation can be carried out to isolate fractions of similar molecular weight or similar molecular structure; for example, frequency of branching. In this work only the former was done, no attempt being made to determine the branching index of either the parent polymer or any of its fractions.

Most methods of fractionation utilize the fact that some polymer species are less soluble in a solvent than other polymer species. The method of fractionation used in this work utilized this fact and the actual fractionation was accomplished by the addition of a non-solvent to a solution of a polymer in a good solvent.

A very useful method of fractionation has been developed recently and can be used either preparatively or analytically. Known as Gel-Permeation Chromatography (G.P.C.), it is used mainly as an analytical tool to determine the molecular weight distribution of polymers. Fractionation takes place in columns of highly cross-linked gels. The separation occurs on a basis of size, the chemical nature of the solvent and solute being relatively unimportant.

The gels, formed as spherical pellets, are made so as to provide a range of pore sizes which are accessible to molecules of particular sizes. The smallest molecules will diffuse into the pores and so will be retarded compard with the largest molecules which cannot enter the pores and so must pass in the interstitial spaces of the packing and are eluted first.

The chromatogram is a trace of refractive index difference versus volume, and since the refractive index difference varies linearly with concentration, it is a measure of the concentration versus the molecular weight since molecular weight and volume are also linearly related. The chromatographic columns are calibrated directly to measure the weight-average molecular weight using narrowly distributed fractions of the polymer under investigation.

The scope of this work included the fractionation of a commercial polymer of relatively narrow distribution (a polydispersity index of approximately 1.5) into fractions of even narrower distribution. These fractions were carefully characterized by osmometry, viscometry, light-scattering and gel-permeation chromatography.

The purpose was to correlate the viscometry and G.P.C. analyses with the average molecular weights as measured by osmometry and light-scattering. While the latter two types of measurements yield the most useful information, they are also the most time consuming to perform.

A faster method of determining the number average molecular weight by osmometry using a mixed solvent/ non-solvent was also investigated. Such a solvent has the property of a theta-solvent since the reduced osmotic pressure-concentration plot can be considered to be independent of concentration at very low concentrations.

THEORY

Fractionation

With the exception of G.P.C. all methods of fractionation are based on the fact that a given polymer becomes less soluble in a given solvent as its degree of polymerizarion increases. The basis for all two-liquid-phase fractionation processes is that, at thermodynamic equilibrium, the distribution in the two phases is different in that one contains lower molecular weight polymer that the other. This equilibrium can be expressed in terms of the chemical potential of mixing for a solution composed of (n+1) components.[1]

At equilibrium in a two phase system, the chemical potential of mixing of a species in one phase must be the same as the chemical potential of mixing in the other phase. It should be realized that, though closely approached, equilibrium is never fully attained in most real cases. Gibbs[2] has proposed that for a system of n+1 components at constant pressure, the independent variables are the concentrations of the n components and the temperature. Additional conditions are that the internal energy of mixing and volume of mixing must be zero and the concentration of the polymer components in the solution must be proportional to their amounts in the original polymer. As a result there are no remaining degrees of freedom for the independent variables and the critical phase is represented by a single point for a single solvent/polydisperse polymer system.

However if there is another solvent present (such as a poor-solvent) there could then be one degree of freedom and therefore either a "critical concentration" or a "critical temperature" can be specified for a fixed ratio of the two solvents. Conversely for a fixed concentration or temperature there would be a critical ratio of the two solvents.

Flory-Huggins Theory

The most useful and simplest explanation of the solubility of polymers has been put forward by Flory and Huggins.[3] Use is made of interaction parameters and these have been shown to depend only on temperature, solvent and solute.

The Theory states that the partial molal Gibbs Free Energy of mixing of the solvent, $\Delta\bar{G}$, in a solution of linear polydisperse polymer of a single type and a single solvent is given by:

$$\Delta\bar{G}_1 = \mu_1 - \mu_1^o = RT(\ \ln(1-\phi)+(1-\bar{X}_n^{-1})\phi+\chi^o\phi^2+\chi'\phi^3+--) \quad ..3$$

At equilibrium, equating the chemical potentials of the species of relative size in the two phases, the following expression is derived:

$$\frac{C_1}{C_2} = \text{Exp}\ (\sigma_s{}^o\chi) \qquad .....4$$

where σ_s^o is a complex function of the volume fractions in both phases, the molar volume ratios, and the interaction coefficient χ^o. σ_s^o is greater than zero, independent of X and has been shown to increase with decreasing solvent power at increasing χ^o.

Equation 4 is the basis for fractionation. It gives the ratio of the concentration of the polymer species which have a size x, in the two phases.

A similar expresssion can be derived for a two-solvent system and a polydisperse polymer, but σ_s^o is replaced by σ_m^o which is a very complex function.

Review of Fractionation Methods.

There are several fractionation methods based on the solubility theory and these will be outlined below:

i. Evaporation of solvent

In the evaporation method the solvent is evaporated until a point is reached where some polymer in solution is at the point of insolubility. Further evaporation results in coacervate (jelly-like solid) formation which will be richer in the higher molecular weight species and a supernatant upper phase which will be richer in the lower molecular weight species. Successsive fractions are produced in a similar manner.

Evaporation can be accomplished by bubbling a stream of nitrogen through a stirred polymer solution.

The advantage of this system is the decrease in volume as the fractionation proceeds.

A variation of this method was attempted in this work using a heated 4ft. long, $\frac{1}{4}$in. I.D. hollow stainless steel tube on which polymer was deposited. Evaporation was effected by passing nitrogen over the polymer solution as it flowed down the tube as well as heating the tube by using water from a heated, temperature-controlled bath. The variables that were investigated included initial polymer solution concentration, solution injection rate, gas flow rate, tube temperature and the rotation speed of the steel tube. Also used were the solvent/non-solvent mixtures in an attempt to fractionate the polymer. This fractionation procedure was not as successful as the fractional precipitation method finally used, as discussed subsequently.

ii. Fractional Solution

This method involves the extraction of successively higher molecular weights by solvent(s) of increasing solvent power. In practice the polymer is first dissolved and deposited on a supporting medium, such as a column packed with glass beads. The deposition is accomplished by lowering the temperature of the column as the solution is passed into it. The successive fractions are then removed either by using several individual solvents of increasing solvent power or by using solvent/non-solvent mixtures to accomplish the same end.

A refinement of this method involves preferential deposition of polymer on the support. By careful control of the deposition conditions, the polymer is deposited in decreasing molecular weights; this in turn facilitates the removal of the fractions.

A modification of this method, known as film extraction, deposits polymer on aluminium foil in a thin (0.001") coating. The foil is then cut into small pieces and extracted as outlined above.

iii. Coacervation Method.

The polymer is first dissolved completely and a precipitant is added to precipitate approximately ninety-percent of the polymer. The supernatant liquid containing the remaining low molecular weight polymer is extracted. Successive fractions are extracted with liquids of increasing solvent power.

Its advantage is that equilibrium is attained quickly because the polymer is a swollen gel. This is outweighed by the large volume of solution required for the extraction.

iv. Fractional Precipitation.

This method involves the addition of a non-solvent or precipitant to produce a precipitate which is richer in the higher molecular weight material. This is done with or without variations in temperature to facilitate the process. This coacervate is allowed time to come to equilibrium, after which it is extracted and the process repeated to obtain the desired number of fractions.

The main disadvantage with this method is the large volume of precipitant that is sometimes necessary. However, by careful selection of the solvent/non-solvent system a suitably powerful non-solvent could be found that would minimise the solvent volume. Another disadvantage, when compared with the fractional solution method, is that it produces relatively more overlapping of the fractions, particularly at the higher molecular weight end of the distribution.

Its advantages are reproduceability, ease of sealing-up or sealing down, and the use of simple, readily available laboratory equipment. This method was used for the fractionation in this work.

Gel-Permeation Chromatography.

The most important aspect of G.P.C. is that it separates only on the basis of size, the chemical nature of the solvent and solute being unimportant. The medium of separation is a column packed with spherical gel beads which have pores of various sizes. A single gel bead consists of heavily cross-linked polymer chains which form pores that are inter-connected openings rather than distinct passages. This heavy cross-linking prevents the gels collapsing under pressure, swelling or being affected by the solvent.

The solvent fills the pores as well as the interstitial spaces. Upon injection of a dissolved polymer, small molecules are able to diffuse through these pores and to permeate the gel, becoming loosely absorbed on the pore surfaces. The largest molecules cannot permeate the gel and must pass in the interstitial spaces unhindered through the column.

The retardation of smaller molecules and the flushing of larger molecules is the basis of G.P.C. Because the elution rate is low and the diffusion rate of the molecules into the gel is comparatively fast, the diffusion rate is not considered to affect the separation in the gel. Many researchers[4,5,6] have investigated the concentration equilibrium of a solute diffusing into a gel and have concluded that the time required for a solute zone to pass by a gel bead is generally much greater than the half equilibrium time for diffusion of the solute molecules into the gel pores.

Thus the separation is based on the volume inside the gel accessible to molecules of a certain size. Each solute species has a volume in the gel which it can occupy and this is the sum of the void volume and that volume of pores which is accessible to it. Thus an amount exactly equal to this volume has to pass through the column for a given solute to be eluted.

$$V_e = V_o \; V_i K_d \qquad \ldots..5$$

The distribution coefficient, K_d, is the ratio of the volume accessible to a particular species V_i acc. and the total internal volume.

$$K_d = \frac{V_i\text{acc.}}{V_i} \qquad .....6$$

$$K_d = \frac{V_c - V_o}{V_i} \qquad .....7$$

Therefore it can be clearly seen for a given solvent-column system, that each molecular species has its own value of K_d. For very large molecules $K_d = 0$ and for the smallest, $K_d = 1$.

Porath[7], Laurent and Killander[8] have suggested two models to explain the relationship between the molecular size and K_d.

Porath suggested that all pores are of equal size and of identical conical shape. A solute molecule could enter a pore only up to a depth where its diameter was equal to the cone diameter. He then related the distribution coefficient to the hydrodynamic volume of the molecule and the cone diameter.

Laurent and Killander proposed a theory based on a model consisting of a network of straight rigid rods which are infinitely long and distributed at random through the gel. The polymer molecules are assumed to be spherical. They then related the distribution coefficient to the diameter of the molecules, and the diameter and concentration of rods.

Neither of these models have proven entirely satisfactory, though the latter has been shown to fit experimental data. In practice, a calibration of the columns is made using narrow distribution linear polystyrene samples and a plot of logarithm of molecular weight ($\overline{M}_w$) vs. elution volume is used to determine the molecular weight.

G.P.C. Size Parameters.

Though researchers are in general agreement that separation is based on the size of the molecule, there is as yet no conclusive evidence to support the use of one particular size parameter. The most frequently mentioned is the hydrodynamic radius which is:

$$R_h = \left(\frac{M(\eta)}{10_{\pi} N_A}\right)^{1/3} \qquad .....8$$

Other size parameters often used in the literature are $\langle S^2 \rangle$, the mean square radius of gyration of a molecule in a good solvent and $\langle S_o^2 \rangle$, the mean square radius of an unperturbed molecule.

Pannell[9] has investigated the use of hydrodynamic volume as the size parameter and has shown that it has serious limitations. Use was made of specially prepared branch-chained polystyrenes, as well as linear polystyrenes. A study of the peak-elution-volumes (P.E.V.) of the straight-chained polystyrenes with increasing degrees of branching shows conclusively that for a given molecular weight, the greater the degree of branching, the greater the P.E.V. Therefore the use of straight-chained polystyrenes to calibrate a set of columns restricts the G.P.C. to analyses of polymers of essentially the same structure as that for the calibrating samples.

The relation between $(\eta)M$ and the mean square radius of gyration in a good solvent and the mean square radius of the unperturbed molecule is given by:

$$(\eta)M = \Phi\langle S^2\rangle^{3/2} = \Phi\alpha^3\langle S_0{}^2\rangle^{3/2} \qquad .....9$$

The constant Φ, is directly proportional to the Mark-Houwink exponent and consequently polymers with markedly different Mark-Houwink exponents in a given solvent will have different values of $\langle S^2\rangle^{3/2}$ and $\langle S_0{}^2\rangle^{3/2}$ for a given value of hydrodynamic volume, and vice-versa. Dawkins et al.[10] have investigated the effect of different Mark-Houwink exponents on G.P.C. results. Linear polystyrene (a=0.70) and linear poly(dimethylsiloxane) (a=0.57) were used and the results showed that the G.P.C. cannot discriminate between the different size parameters in spite of the difference between the Mark-Houwink exponents.

G.P.C. Operating Parameters.

The operating parameters are flow rate, solution concentration and viscosity. The work done in this area will be reviewed below.

The effect of concentration on G.P.C. results, is the most pronounced and has been widely reported in the literature.[11,12,13] The most important effect is the variation of p.e.v. with variation in concentration. It is agreed that, although the hydrodynamic volume is not the correct size parameter for a universal calibration, the log of hydrodynamic volume is related to the p.e.v. The hydrodynamic volume depends on concentration, as well as molecular weight. For a given polymer sample the effect of increased concentration is to decrease the hydrodynamic volume and hence produce a higher p.e.v. resulting in a higher apparent molecular weight.

Rudin[12] has investigated the effects of concentration on p.e.v. and has found that for a given change in sample concentration, p.e.v. shifts are more pronounced the narrower the distribution. These shifts are more severe the higher the mean molecular weight. It was also observed that samples having a wide distribution eluted at a lower p.e.v. than would be expected.

The effect of solvent viscosity in G.P.C. measurements has been investigated by Goetze et al.[14] The viscosity of the sample was changed by using different solvents, hence producing a different viscosity for a given concentration. It was concluded that the change of p.e.v. with change in viscosity was negligible.

The effect of flow rate on p.e.v. has been investigated by Yau[15] and Little.[13] There are two main causes of inaccuracies in the measurement of eluted volume. The first is evaporation of the solvent from the flow-measuring syphon and the second is the continued flow of eluent into the syphon while dumping is taking place. At low flow rates, the former is more pronounced and at higher flow rates the latter is the more important. Little investigated the effect of flow rate on p.e.v. and concluded that changes in flow rate did not affect the p.e.v. However, he found that peak width increased with flow rate and was independent of the concentration at high flow rates, and also that resolution decreased with increased flow rate. The flow rates investigated ranged from 0.1 to 12.5 mls./minute.

Osmometry and Theta-Solvents.

The osmotic pressure of a solution is a colligative property depending only upon the number of molecules in solution and not upon the chemical nature of those molecules. It is related to the number average molecular weight of a polymer by the van't Hoff equation.[16]

$$\Pi = \frac{CRT}{M} \qquad .....10$$

For real solutions the van't Hoff equation is valid only at infinite dilution and for solutions where Raoult's Law applies, and is written:

$$\left(\frac{\Pi}{C}\right)_{C\to 0} = \frac{RT}{M} \qquad .....11$$

At finite concentrations the osmotic pressure is represented by the following power series:

$$\frac{\Pi}{C} \cdot \frac{M}{RT} = 1 + A_2MC + A_3M^2C^2 \quad --. \qquad .....12$$

where A_2 and A_3 are the second and third virial coefficients. At low polymer concentration (less than 1 Wt. %) the terms $A_3M^2C^2$ and greater, can be neglectd and equation 12 becomes:

$$\frac{\Pi}{C} = \frac{RT}{M} + BC \qquad .....13$$

In practice the osmotic pressure is measured by placing pure solvent and solution on opposite sides of a semipermeable membrane. The membrane is carefully selected to pass solvent but not polymer. The osmotic pressure is observed as a hydraulic head, h, across the membrane. This head is used to calculate the osmotic pressure.

The concept of a theta or Flory temperature for a given polymer-solvent system is one at which the polymer is at the point of precipitation, that is, there is no net polymer-solvent interaction. Polymer-solvent systems at the theta-temperature exhibit a unique property: There is no concentration dependence of the (Π/C) versus C plot. Therefore equation 13 is reduced to:

$$\frac{\Pi}{C} = \frac{RT}{M} \qquad .....14$$

Because it is not always convenient to make measurements at the theta-temperature, a theta-solvent is therefore desirable as it can be used to reduce the number of measurements necessary in the determination of molecular weights.

It is possible to produce a theta-solvent/polymer system by the addition of a poor or non-solvent to a solution of a polymer in a good solvent. In practice this is accomplished by the dropwise addition of the non-solvent to the agitated polymer solution until the point is reached where the addition of one more drop will cause permanent cloudiness. This solution can be considered to be a theta-solvent.

Sarkar and Palit[17] have reported the use of binary mixtures of good and poor solvents to determine viscosities, osmotic pressures and light scattering ratios for solutions of polystyrene and poly(methylmethacrylate). However, no apparent attempt was made to reach the "theta-point" with any of the solutions used, and although theta-solvents were produced, the method would not be satisfactory for the rapid determination of M because, even with a solution of low concentration there would be considerable error in the determination of M if the second virial coefficient was non-zero.

Viscometry.

The measurements of viscosities of dilute polymer solutions is a rapid method of determination of polymer molecular weights.

The increase in the viscosity of a solvent by a polymer, the specific viscosity, is defined as:

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} \qquad \ldots\ldots 15$$

The intrinsic viscosity can be defined as the ratio of the specific viscosity η_{sp} to concentration C at infinite dilution:

$$(\eta) = \lim_{C \to o} \frac{\eta - \eta_o}{\eta_o C} = \lim_{C \to o} \frac{\eta_{sp}}{C} = \lim_{C \to o} \eta_v \qquad \ldots\ldots 16$$

The relation between reduced viscosity and concentration has been expressed as:

$$\frac{\eta_{sp}}{C} = (\eta) + k'(\eta)^2 C \qquad \ldots\ldots 17$$

Huggins[18]

in

$$\frac{\eta_r}{C} = (\eta) + k''(\eta)^2 C \qquad \ldots\ldots 18$$

Kraemer[19]

Staudinger[20] proposed that (η), the intrinsic viscosity was proportional to the molecular weight for a given polymer-solvent system and expressed the relationship as:

$$(\eta) = KM \qquad \ldots\ldots 19$$

The molecular weight M is interpreted as the viscosity average molecular weight for a polydisperse polymer. However, for low polydispersity polymers, Kraemer and Lansing[21] interpreted M to be the weight average molecular weight. The Staudinger equation was further modified by Mark and Houwink[22] to include an index term "a":

$$(\eta) = KM^a \qquad .....20$$

Bohnadecky et al[23] have investigated the variation of a and K with polydispersity and molecular weight of poly(vinyl chloride) and came to the following conclusions: If the exponent a is close to 0.77 but the constant K is greater than 1.50×10^{-4} in T.H.F., the polydispersity index is approximately 1.5 - 1.8. If the exponent is larger, this suggests that the polydispersity increases with increasing molecular weight. In plots of (η) versus $\overline{M}w$ a low value of the exponent indicates the presence of microgels in solutions causing increased turbidity in light scattering, resulting in higher molecular weight. The line may also exhibit curvature which can be brought about by branching of the polymer.

Light Scattering Photometry.

The scattering of light by polymer molecules in solution is a well known phenomena. If a polymer is dissolved in a solvent, the light scattered by the polymer molecules exceeds the light scattered by the solvent and allows an absolute method for determining the weight average molecular weight of the polymer.

When light is incident on an electron it becomes an oscillating dipole and radiates light in all directions. If there are two dipoles oscillating sufficiently close to each other, they behave as one. Consequently a polymer molecule with an average root mean square end to end distance of approximately one tenth the wave length of the incident light, behaves as a single polarized dipole in that all of the radiated light will be in phase.

Debye[24,25] showed that the turbidity of the polymer solution is proportional to the intensity of the scattered light. He further showed that the turbidity was proportional to the molecular weight:

$$\frac{H_C}{\tau} = \frac{1}{MP(\theta)} + 2A_2C \qquad .....21$$

$$H = \frac{32\pi^3 N^2 \left(\frac{\delta N}{\delta C}\right)^2}{3N_A \lambda^4} \qquad .....22$$

P(θ) is a molecular shape factor and can be eliminated from equation 21 by plotting $\frac{HC}{\tau}$ versus concentration and extrapolating to zero concentration. The intercept is $\frac{1}{Mw}$. Light scattering measurements are therefore useful in obtaining weight average molecular wights of polymer samples.

APPARATUS AND PROCEDURE

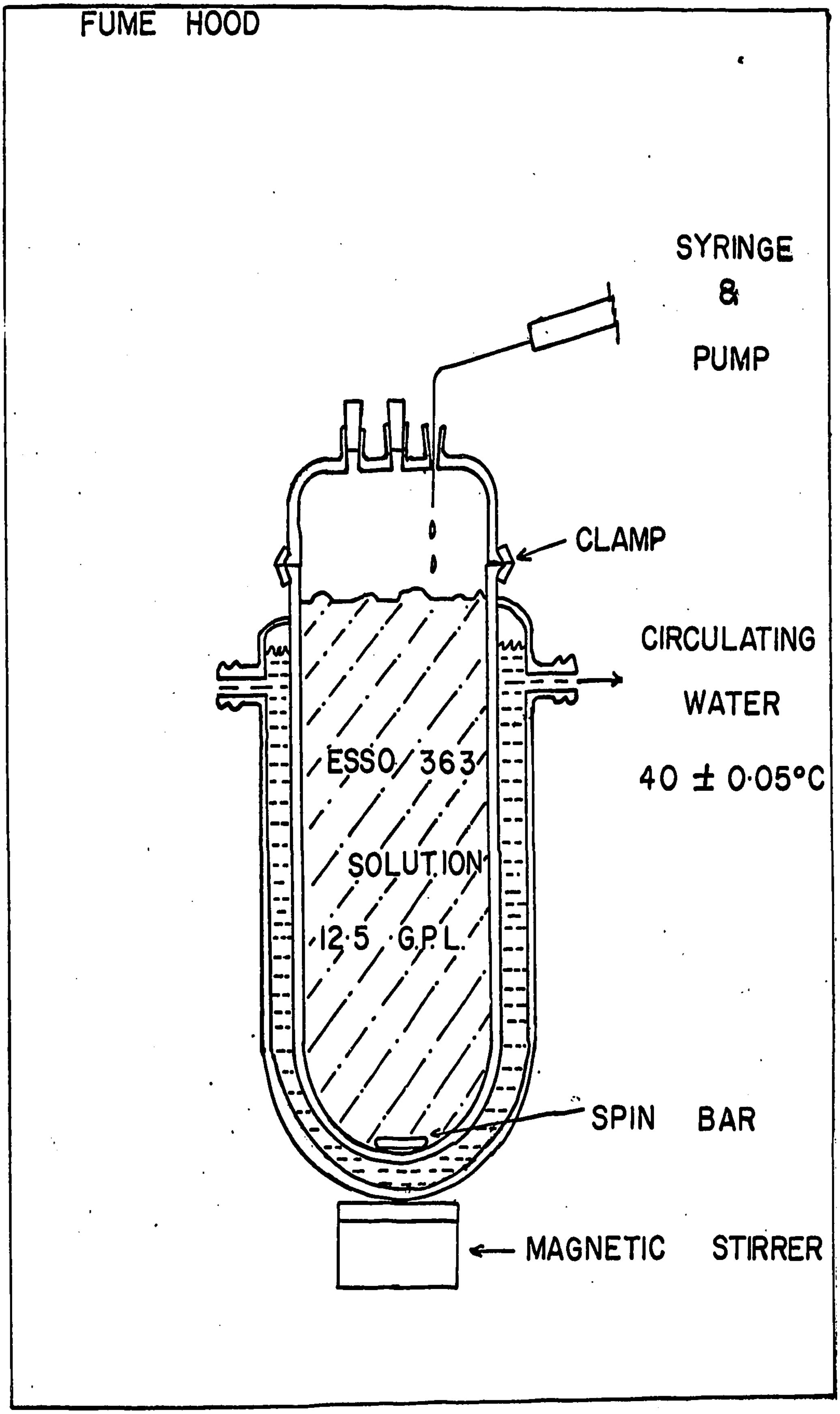
Fractionation.

The apparatus used to carry out the fractionation was a three litre, jacketed glass reaction vessel. Thermostatted circulating water at 40±0.05°C. was passed through the jacket and stirring was by a magnetic stirrer. A poor solvent, water or methanol, was added by means of a Harvard infusion pump using both a $\frac{1}{2}$ r.p.m. and $\frac{1}{4}$ r.p.m. motor to give addition rates of approximately $\frac{1}{2}$ and $\frac{1}{4}$ ml. per minute. Cooling was accomplished by passing tap water at 17°C. through the jacket.

The method outlined by Pezzin et al[26] was adopted. Because tetrahydrofuran(T.H.F.) was used as a solvent, both methanol and water were used as non-solvents with different degrees of success.

The fractionation was carried out in a temperature controlled room at 23°C. (±1°C.) and addtition of non-solvent was made at this temperature. The selection of suitable fractionation conditions was made after preliminary experiments with various concentrations of P.V.C. in T.H.F. and using solvents which included methanol, water and mixtures of both.

Two fractionations were performed, one using a P.V.C. concentration of 40g/l and methanol as precipitant and the other a concentration of 12.5 g/l and



FRACTIONATION APPARATUS

Figure 2 - Fractionation Apparatus for Esso 363.

water as precipitant.

With the solution at room temperature, non-solvent was added at approximately 0.5 ml./min, until polymer precipitation was imminent, as predicted by preliminary turbidity experiments outlined in the following section. Additional non-solvent was then added until there was considerable turbidity. The solution was then heated to 40°C. until the polymer redissolved. It was then allowed to cool very slowly to room temperature without stirring over a period of not less than twenty four hours.

The precipitate and residual solution were separated by completely syphoning the solution and then dissolving the gelatinous mass in T.H.F.

The second and successive fractions were similarly recovered from the supernatant liquid. The relatively long equilibrium period is necessary to allow the coagulation of molecules into the heavier phase containing the relatively larger molecular weight polymer.

The extracted polymer were re-precipitated with a 10:1 excess of methanol, carefully filtered, washed with hot water, distilled water and pure methanol, dried to constant weight in an oven for sixteen hours and cooled under vacuum in a dessicator. The weight of each fraction was determined by filtering through a pre-weighed filter. The weight of polymer being the difference between the weights of paper and polymer and the pre-weighed paper.

Solutions in which solvent behaved as a theta-solvent were investigated for solutions of polymers having different molecular weights, polydispersity indices and concentrations.

Solutions of approximately 20 grams per litre were prepared in T.H.F. and lower concentrations were produced by successive dilutions. Each non-solvent being investigated was very carefully added with constant agitation to each solution to the point where the addition of one more drop produced permanent turbidity.

A graph of concentration versus volume of non-solvent added, showed the composition of "theta-solutions". By choosing a composition represented by a point just below the curve, it was possible to produce essentially "theta-solutions".

For these experiments, Esso grade 363 ($\overline{M}n$ 49,000, $\overline{M}w$ 72,500) was used in conjunction with methanol, ethanol, ethylene glycol, water, normal heptane, N.S. 1 (40% water, 40% ethanol and 20% acetone), N.S. 2 (25% water, 75% ethanol) and N.S. 3 (17% water, 83% ethanol) as poor solvents. Two other grades of polymer were investigated with methanol as the poor solvent; these were Pressure Chemical P.V.-2 ($\overline{M}n$ = 25,300, $\overline{M}w$ = 68,000) and P.V.-4 ($\overline{M}n$ = 54,000, $\overline{M}w$ = 132,000). In every case samples were dissolved in T.H.F. Poor solvents were added at room temperature (23 ± 1°C.) to the point of turbidity.

PROPERTIES AND SOURCES OF CHEMICALS.

The chemicals, their properties and sources are listed below:

LIQUID	S.G.	VISCOSITY C.P.	QUALITY	SOURCE
T.H.F.	0.885	0.469	Certified	Fisher Chemicals
Methanol	0.795	-	"	"
n-Heptane	0.678	-	Chromato-quality	Matheson, Coleman & Bell
Ethanol	-	-	Certified	Fisher Chemicals
Ethylene glycol	-	-	"	"
Acetone	-	-	"	"

POLYMER	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	SOURCE
Esso Grade 363	72.5	49.0	Imperial Oil Enterprises
" " 353	52.4	35.1	"
P.V.-2	68.0	25.3	Pressure Chemical Co. Pittsburgh, Pa.
P.V.-4	132.0	54.0	"
Polystyrene	(a)*	(a)	Waters Associates Farmingham, Ma.

The P.V.C. samples were chosen because of the differences in polydispersity indices of the two different grades, the Pressure Chemical samples having a larger index.

*(a) The molecular weights of these samples are listed in Appendix B-5. These were used for the calibration of the G.P.C. column.

ANALYTICAL EQUIPMENT AND OPERATION.

Sample Preparation.

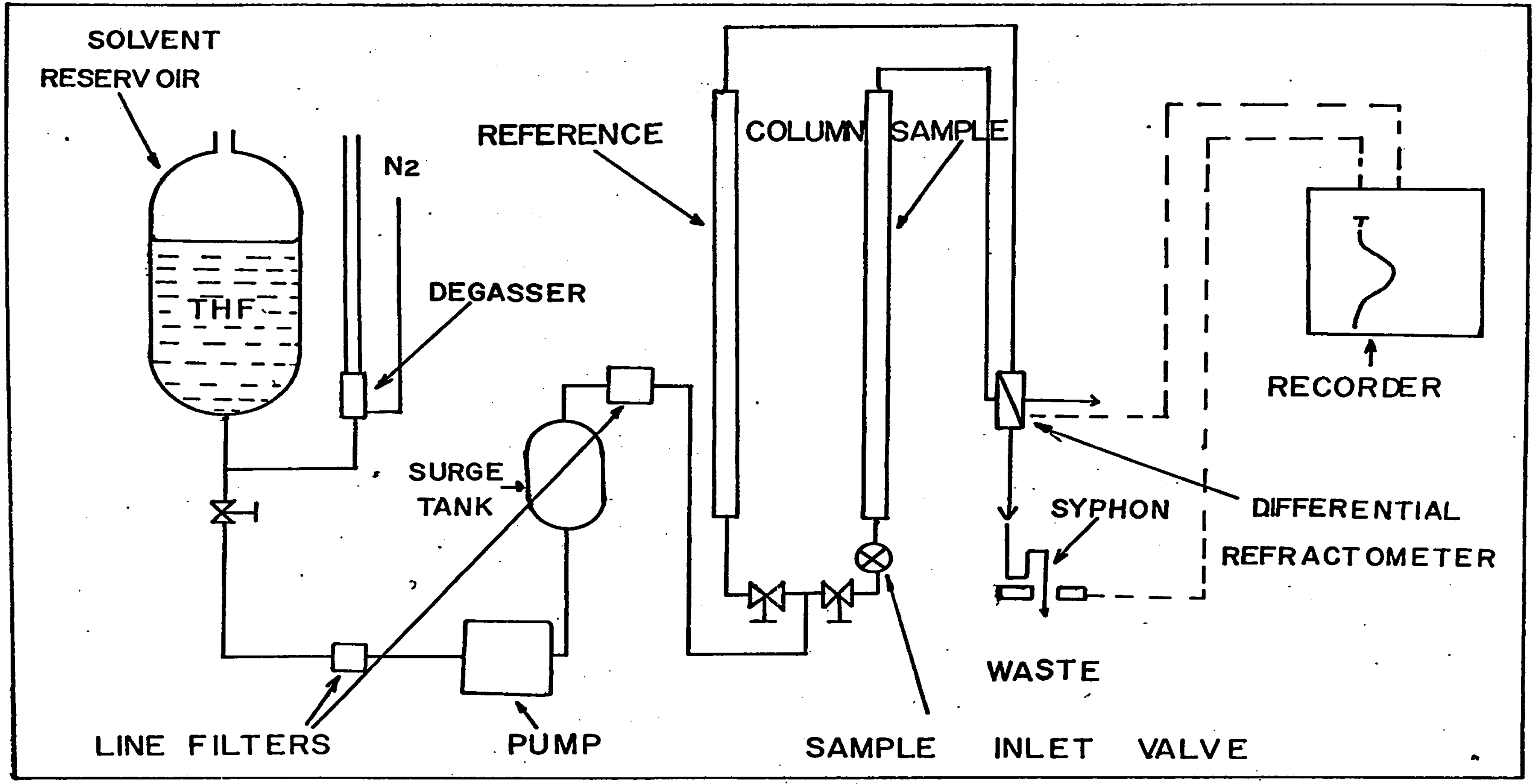
After removing from the filter paper, each fraction was stored in an airtight sample bottle to prevent moisture absorption on the polymer. Solutions of 200 or 250 mls. were prepared by dissolving a carefully weighed sample in T.H.F. with the aid of a magnetic spin bar and magnetic stirrer. Dilution of this large sample provided 4 or 5 different concentrations on which measurements were made.

The solutions were filtered through 10 micron filters and these solutions were used for all light scattering, osmometry and viscometry. For G.P.C., concentrations of 0.5 and 0.1 weight per cent were produced by dilution.

Gel Permeation Chromatography (G.P.C.).

A Waters Associates model G.P.C.-200 was used throughout the experiments. The columns were arranged to provide greater separation in the lower molecular weight range (10,000 to 150,000). This was accomplished by four columns of 4' length and 3/8" O.D. arranged using two columns with an upper permeability limit of 1.5×10^5Å followed by two columns with an upper permeability limit of 1.5×10^4Å.

The columns originally had a relatively high plate count as measured with trichlorobenzene of



GEL PERMEATION CHROMATOGRAPH

Figure 3 - Waters Associates Gel-Permeation Chromatography.

approximately 500 plates per foot, but this deteriorated to approximately 200 plates per foot by the time the calibration and analyses of fractions were carried out. However, over that period there was no observable shift in the p.e.v. of the polystyrene standards or with the commercial P.V.C. samples.

The G.P.C. was operated at a flow rate of 1 ml. per minute and an injection time of 120 seconds. The sample loop consists of a coil of 1/16" stainless steel tubing that has an approximate capacity of 2 mls. The amount of solution is thus regulated by opening this valve for a specific time interval at a specific flow rate. The polystyrene samples were analyzed at a concentration of 0.1% by weight and the P.V.C. fractions at both 0.5% and 0.1% by weight.

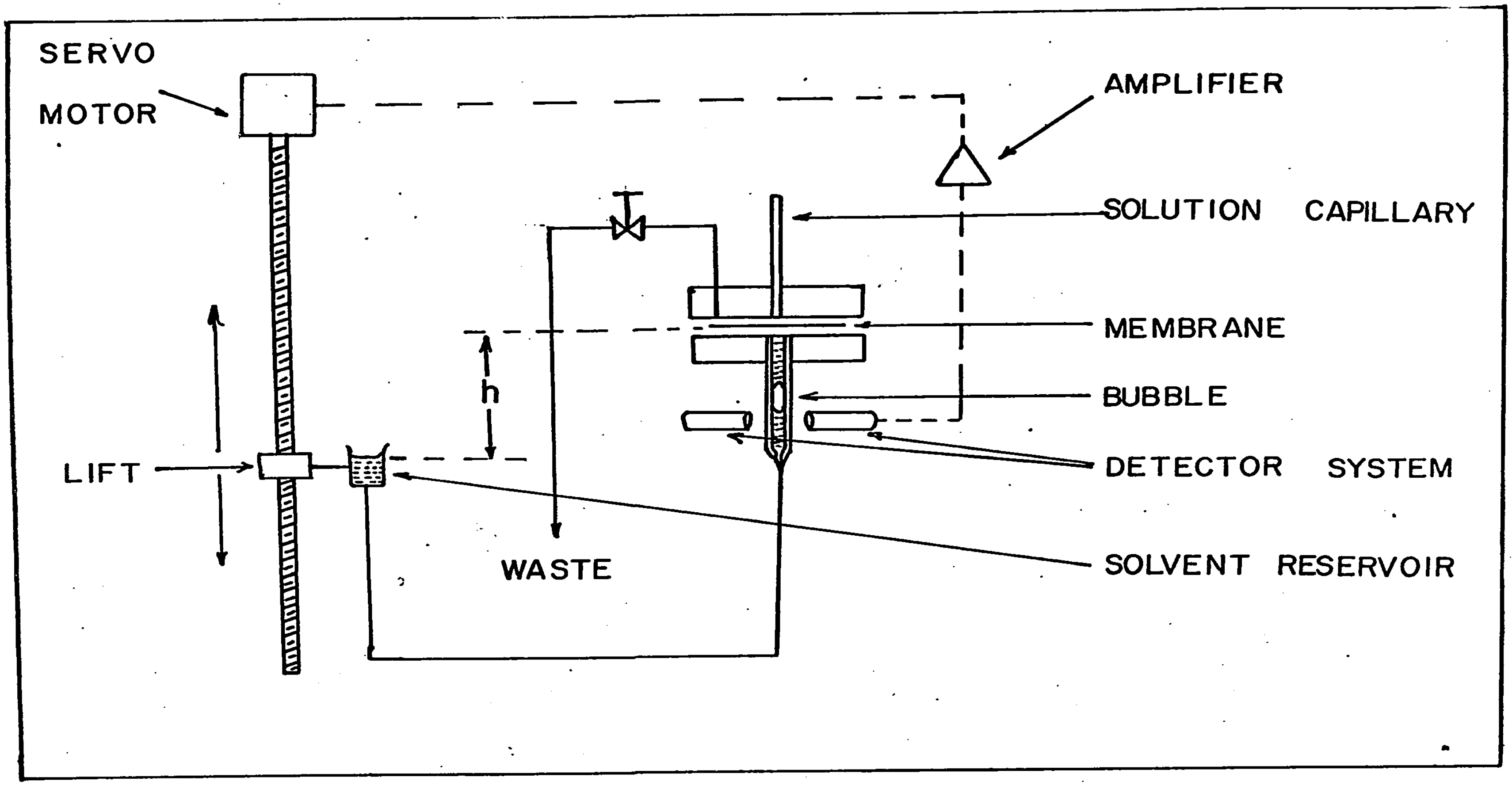
All samples were filtered through 10 micron teflon filters under 10-20 p.s.i.g. nitrogen pressure in the filtering apparatus to prevent particles from entering the columns.

The analytical G.P.C. consisted of a solvent system, a detection device and an electronics system. The solvent system consisted of a solvent reservoir, a pump, a surge tank, relief valve and columns. The entire system was made to withstand pressures of 300 p.s.i.g. at which point the relief valve would discharge into the waste collector. The detector consisted of a very accurate differential refractometer that measures the difference between the refractive indices of the solution and that of the pure solvent. After detection, the sample flowed to a syphon which collected approximately 5mls. of solution before automatically dumping to a syphon collector. Since the syphon was used in conjunction with a photo-electric detector to indicate directly on the chart recorder each time the syphon discharged and was used to determine how much liquid had eluted.

High Speed Membrane Osmometer.

The automatic osmometer used was the Hewlett-Packard model 501, a schematic diagram for which is shown in Figure 4.

The osmometer membrane is mounted in a horizontal position in the osmometer with the solvent chamber below it and the sample chamber above it. The membrane is then clamped rigidly in position. It operates on the principle of preventing a flow of solvent through the membrane by adjusting the vertical position of a small levelling-bottle connected to the solvent chamber. Flow through the membrane is detected by movement of an air bubble in the solvent system positioned in a capillary such that even a minute flow would result in a measurable movement of the air bubble. A flight source and photo sensitive detector are used to activate a servo-mechanism to raise and lower the levelling bottle and hence to maintain the bubble in one position.



HIGH SPEED MEMBRANE OSMOMETER

Figure 4 - Hewlett-Packard High Speed Membrane Osmometer.

The solvent pressure is adjusted by a servo mechanism until a sensor can detect no tendency for the solvent to flow through the membrane in either direction. Equilibrium is reached rapidly, usually in less than three minutes, and so transport of even small polymer molecules through the membrane into the solvent chamber is prevented.

Whenever the osmometer was used with a theta-solvent, care was exercized to ensure that the solvent reservoir, connecting tube, bubble chamber and the solvent chamber contained only the mixed solvent to be used. Since the "theta-solutions" were at the point of incipient precipitation, the solution chamber was very carefully rinsed with the solvent to ensure that there was no residual solution remaining in the chamber from a previous pressure determination.

The membranes used were obtained from the Schleicher and Schuel Company, N.H. The type 08 was used for all measurements. They were supplied in 20% ethanol-water mixture and refrigerated until use. They were conditioned to pure ethanol in a series of solution baths, each with increasing ethanol composition, allowing them to remain for two hours in each bath. Further conditioning to the solvent to be used was done in a similar fashion, with four solutions, of solvent-ethanol in the volume proportions of 25-75, 50-50, 75-25 and 100% solvent. The membranes were then refrigerated until use.

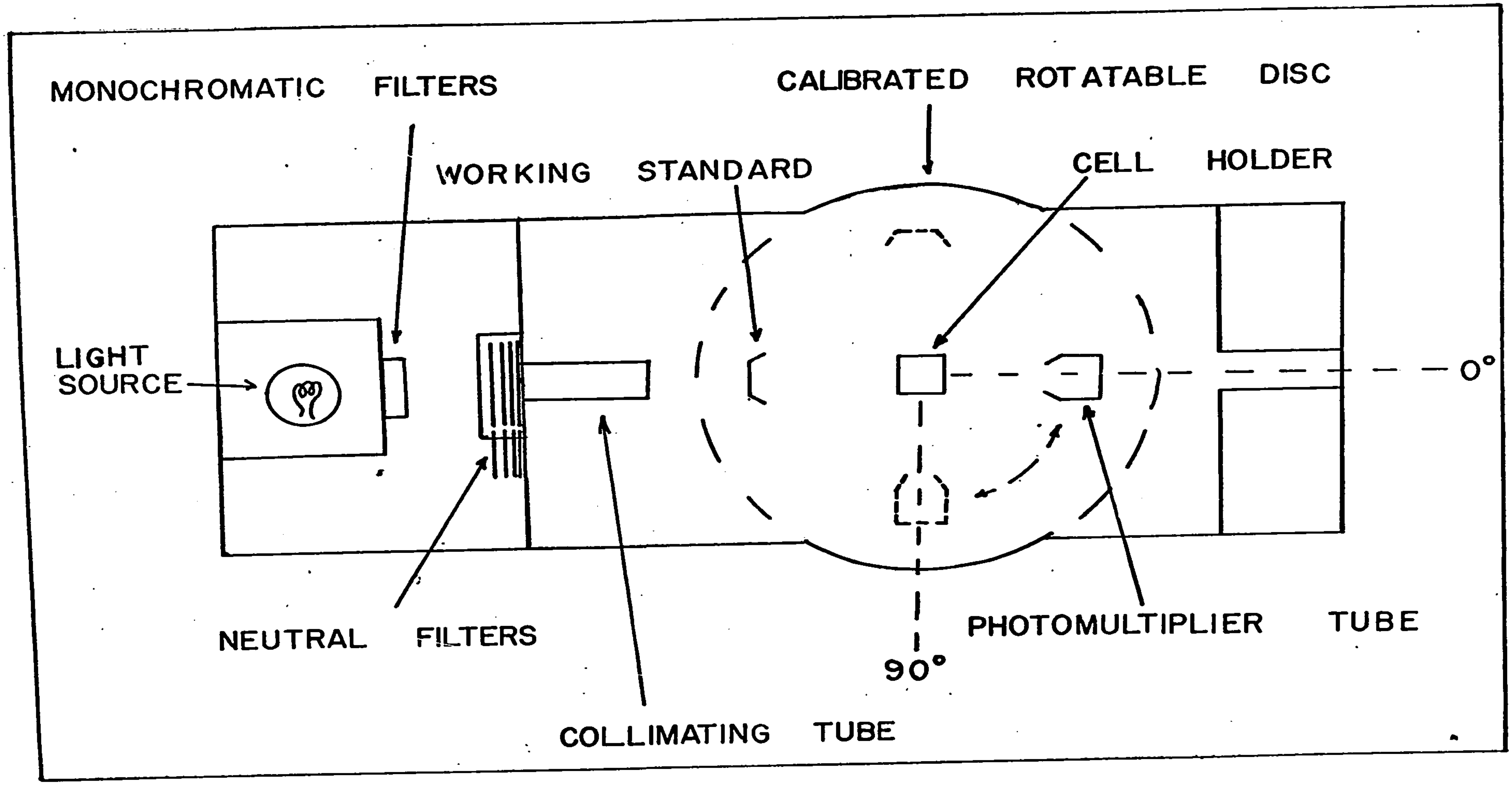
Light Scattering Photometer.

A Brice-Phoenix model 4000 Light Scattering Photometer was used to measure the weight average molecular weights, the schematic diagram of which is shown in Figure 5.

It consists of a source of white light and two monochromatic filters which give either blue (436mμ) or green (546mμ) light. There are four neutral filters of accurately known transmittance which are used to vary the intensity of the light incident upon the solution. A movable photo-sensitive detector is mounted so that the intensity of light emitted from the solution can be measured at various angles from the incident beam.

There is a fixed cell holder at the centre of a graduated rotateable disc, which ensures that the solution cell is correctly placed in the incident light beam. Fixed to this rotating disc is a photomultiplier tube which receives the transmitted and scattered light and transmits an electrical signal that is directly proportional to the intensity of the light received. This transmitted signal goes to a recorder which gives a proportional deflection.

The solution is carefully filtered through a 0.2μ teflon filter directly into a 30 x 30 mm. Light Scattering cell which is then placed into the cell



LIGHT SCATTERING PHOTOMETER

Figure 5 - Brice-Phoenix Light Scattering Photometer.

holder. Molecular weights were calculated from the excess turbidity caused by polymer molecules in solution. The ratio of intensity of the light scattered at 90°(Gs) to that transmitted at 0°(Gw) is proportional to the turbidity. With all filters removed the intensity of the light scattered at 90° is measured and then with the rotating arm and photomultiplier tube set at 0°, the intensities of the transmitted light are measured with various combinations of the four neutral filters in the incident beam. This procedure is repeated with different concentrations of the polymer solution and with the pure solvent as well.

From these readings, using machine constants provided, the excess turbidity of the solutions can be calculated and from these the molecular weight. See Appendix A for the constants and sample calculations.

The refractive index differences were measured by a Brice-Phoenix differential refractometer. This instrument was capable of measuring refractive index differences to an accuracy of $\pm 3 \times 10^{-6}$. It consists of a source of white light, two monochromatic filters, a differential cell, collimator and measuring scale. Accurate refractive index difference readings were required for the calculation of sample molecular weights in conjunction with light scattering measurements.

Viscometry.

Ostwald viscometers were used for all viscosity measurements. A viscometer consits of an upper and lower bulb connected by a capillary tube. The time for liquid flow through the capillary was carefully measured and using constants supplied with each tube, the viscosity is calculated. Before each measurement the viscometer was carefully cleaned with T.H.F., hot chromic acid, acetone and distilled water. This was done to ensure that no polymer particles were stuck to the surface of the capillary. Viscosities were measured at 25 - 0.05°C.

Viscosity measurements were made only for the eight fractions of the second fractionation of Esso grade 363 P.V.C. From these readings the intrinsic viscosities were calculated and, using a Mark-Houwink type relationship, the weight average molecular weights were calculated.

The constants were[28]:

$$a = 0.706$$

$$K = 1.63 \times 10^{-5} \text{ in litres/gram}$$

$$(\eta) = 1.63 \times 10^{-5} (\bar{M}w)^{0.766} \qquad .....23$$

RESULTS AND DISCUSSION.

The results are presented and discussed under several headings, the first dealing with selection of mixed solvents for P.V.C. which would simplify osmotic pressure measurements. Possible suitable mixed solvent compositions were obtained by turbidity experiments and tested by actual osmotic pressure measurements. Fractionation of commercial P.V.C by solvent precipitation yielded eight polymer fractions having a wide range of molecular weights. The results of tests for solution viscosity, osmotic pressure, light scattering, and G.P.C. measurements for these fractions and the original sample, are discussed under separate headings. Finally, some of the shortcomings of the novel fractional deposition method for fractionation originally attempted, are presented.

A. Turbidity Curves.

Plots of polymer concentration in T.H.F. versus amount of non-solvent required to produce turbidity or cloudiness are shown in Figures 6 and 7. The effect of different non-solvents on the turbidity point of Esso 363 is shown in Figure 6. Water as the poorest solvent when added to the solution required the lowest volume to reach the turbidity point and ethanol required the largest volume. The amount of non-solvent was observed to increase with decreasing

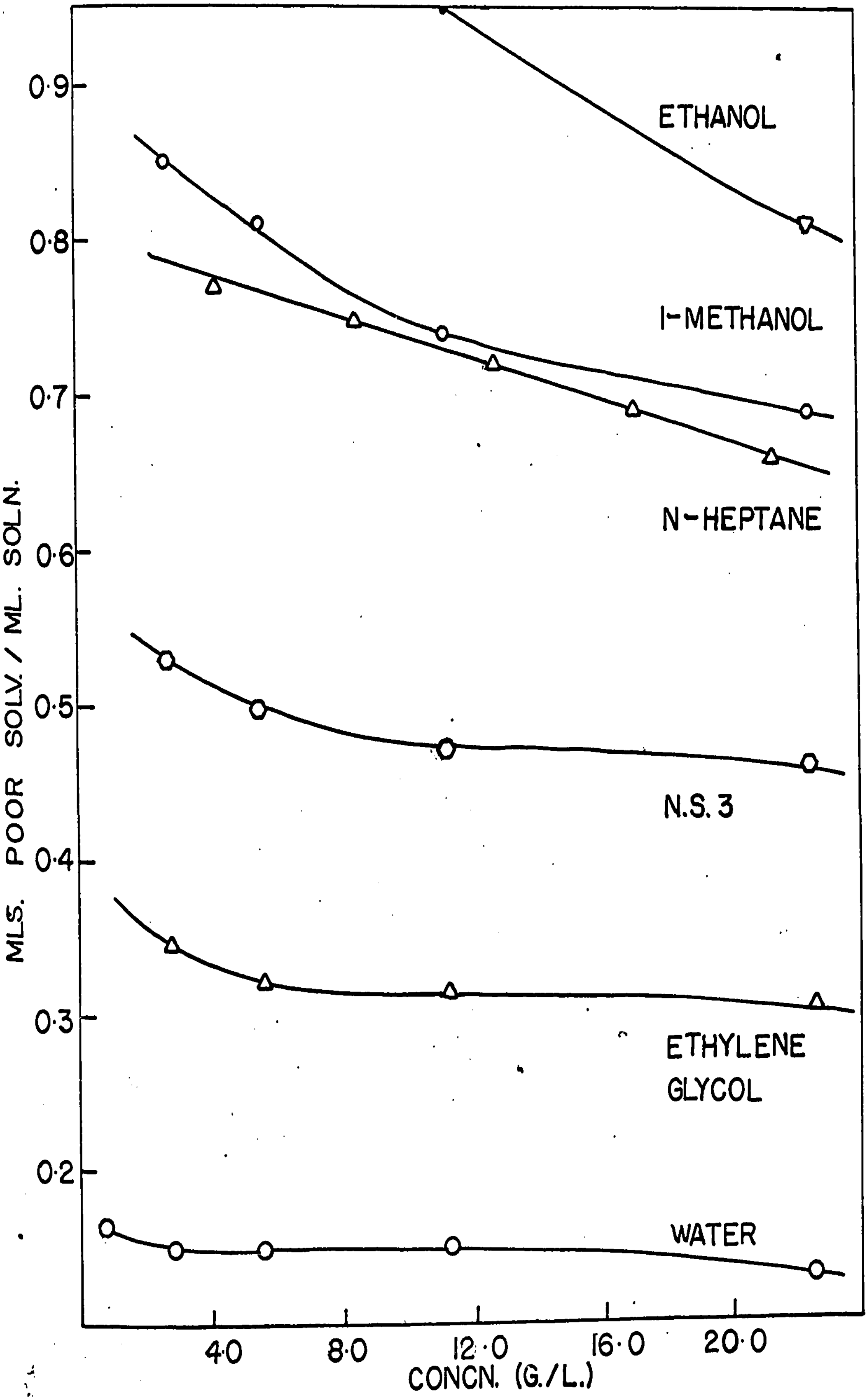


Figure 6 - Turbidity Curves for Esso 363 and several poor solvents.

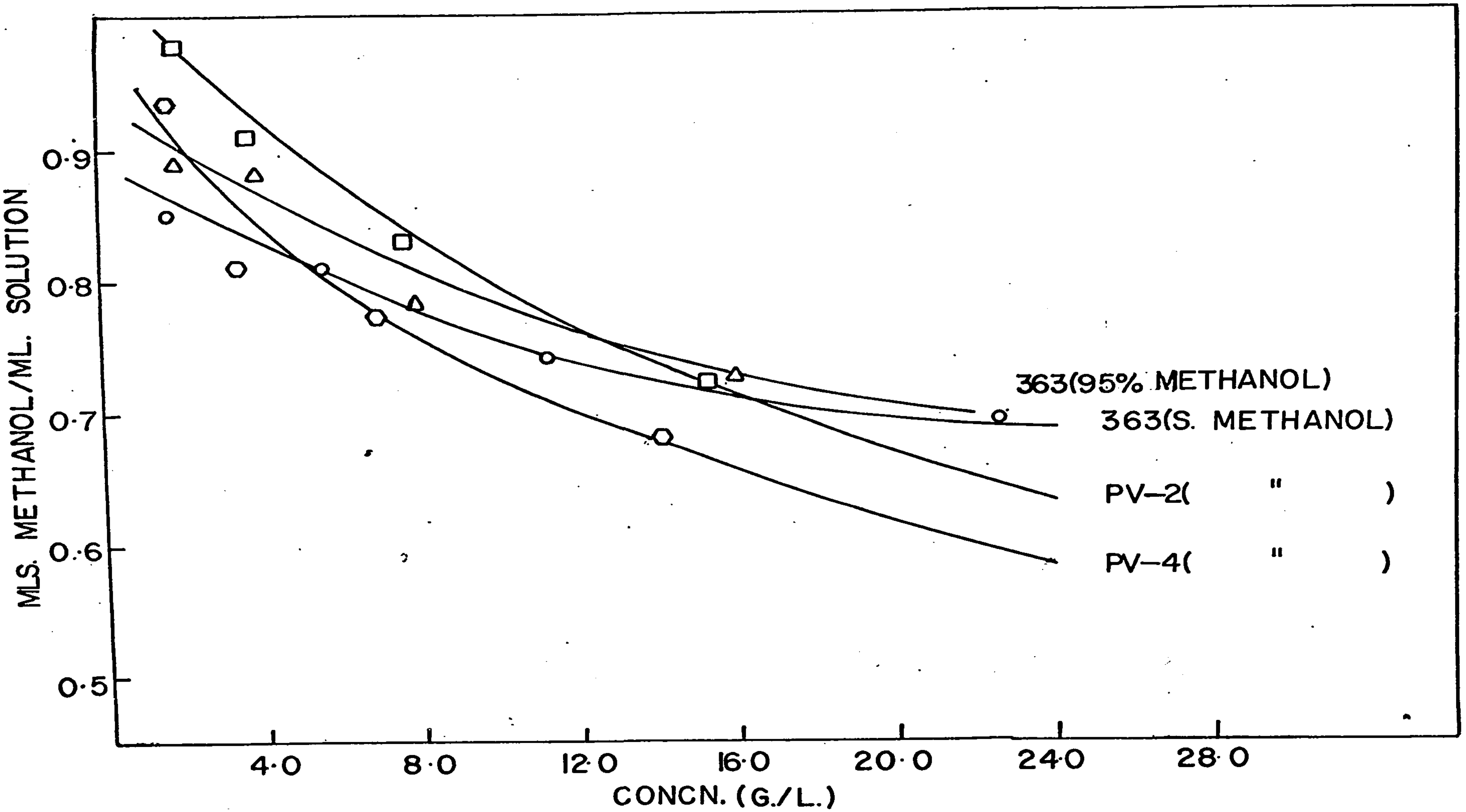


Figure 7 - Turbidity curves - Effect of Molecular Weight.

Fraction	Cumulative Mls. Water	Wt. Gms.	Cum. Wt.%	Mn T.H.F.	Mn x 10^{-3} Meth./T.H.F.	Mw x 10^{-3} L.S.	Mw x 10^{-3} viscos.	Mw/Mn	P.E.V. 1/10%
1	266	1.740	6.96	102.16	109.12	176.70	120.50	1.73	26.00
2	284	1.685	13.70	97.58	98.74	121.24	119.30	1.24	25.92
3	308	1.625	20.20	80.16	-	118.30	114.60	1.48	25.88
4	326(a)	3.449	33.99	76.88	76.20	111.73	100.30	1.45	26.16
5	333	2.803	45.21	63.45	-	97.25	85.61	1.53	26.61
6	347	3.717	60.07	59.36	60.09	75.52	73.87	1.27	27.18
7	406	4.501	78.44	38.55	37.05	40.95	44.27	1.06	28.73
8	543	2.080	86.76	18.94	18.69	19.10	27.07	1.01	30.48
Esso 363	-	-	-	49.66	50.09	72.55	69.00(b)	1.46	27.39

Initial Amount of Polymer = 25 gms. Initial Volume = 2000 mls.

(a) 30.0 mls. T.H.F. added
(b) B. D. Kelly, M.A.SC. Thesis. (1969)

TABLE 1 - FRACTION ANALYSES.

solubility parameter "δ" as would be expected. The solubility parameters of mixed (non) solvents were calculated from the following formula[27]:

$$\delta = \frac{\phi_1\delta_1 + \phi_2\delta_2 + \ldots}{\phi_1 + \phi_2 + \phi_3 + \ldots} \qquad \ldots\ldots 24$$

The variation of the turbidity point with molecular weight and with the polydispersity index is shown in Figure 7. The samples used were PV-2 (Mn = 25,300, P.I. = 2.68), PV-4 (Mn = 54,00, P.I. = 2.45) and Esso 363 (Mn = 49,000, P.I. = 1.50). The samples with the larger polydispersity index reached the turbidity point over a wider range than those with the smaller polydispersity index as might be expected. It can be observed that the higher the average molecular weight of the sample, the lower the volume of non-solvent required to read turbidity, also, as would be expected, since the highest molecular weight polymer is invariably least soluble. Each point on the curve represents a "theta-solution" with incipient precipitation and consequently would be expected to exhibit the properties of a polymer in a theta-solvent.

B. Fractionation of Esso Grade 363 P.V.C.

The fractionation was carried out at an initial polymer concentration of 12.5 grams per litre with water being used as precipitant. Eight fractions were collected and analysed by osmometry, viscometry, light scattering and Gel Permeation Chromatography.

Solutions were prepared in 200 ml. portions and light-scattering analyses were the first to be carried out, followed by osmometry measurements. The higher molecular weight fractions did not prove more difficult to dissolve provided the dissolution was carried out in a beaker of T.H.F. agitated by a magnetic spin bar.

The results of fractionation are tabulated in Table 1, as well as a summary of the results of all molecular weight measurements.

The two molecular weight averages were calculated and these are:

$\bar{M}n = 49,850$ gm./gm. mole

$\bar{M}w$ (L-S) $= 81,720$ gm./gm. mole

$\bar{M}w$ (M-H) $= 79,160$ gm./gm. mole

Figure 8 shows three representative refractograms (G.P.C. recorder output) to illustrate the general shape of the distributions of the largest and smallest fractions as well as the shape of the whole sample. There are no points of inflection and as the refractogram shows, the original sample has a comparatively narrow distribution.

Because of the imperfections of the fractionating method, adjoining fractions overlap for a large portion of their breadth. Other difficulties that affect the accuracy of the calculated distribution are the size of the individual fractions and the loss of some

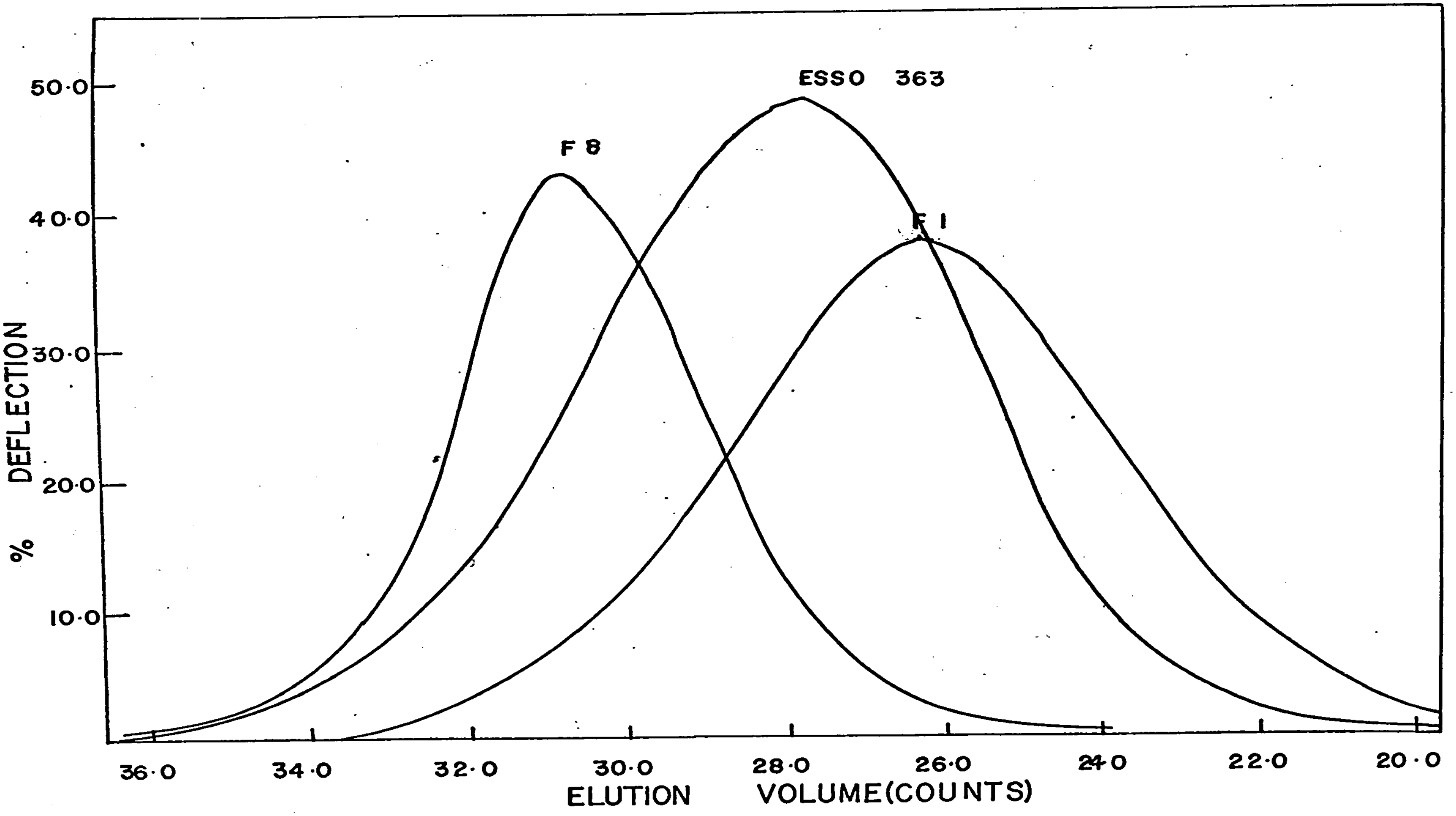


Figure 8 - Chromatograms of Fractions 1 and 8 and Esso 363.

of the sample amounting to approximately 13%, the molecular weight of which was unknown. The assumption was made however, that the amount lost for each fraction was proportional to its mass.

The molecular weights of each fraction and its mole fraction and weight were used to calculate the number and weight average molecular weights for the original polymer samples using the appropriate formulae. The calculated values are shown below with the measured values.

	Composite x 10^{-3}	Calculated from fractions x 10^{-3}
Mn	49.66	49.85
Mw(L-S)	72.55	81.72
Mw(visc.)	69.00	79.16

The $\overline{M}n$ values are in excellent agreement but those for $\overline{M}w$ do not agree. In view of the fact that a systematic error for all eight fractions in both light scattering and viscometry is highly unlikely, a small error in the measurements of the molecular weights of the whole sample, or one or more of the crucial fractions (for instance: fraction 4 where $w_4\overline{M}w_4$ is approximately 20% of $\Sigma w_i\overline{M}w_i$) is more than likely the cause of the error. This, combined with the aforementioned low molecular weight impurities which were not removed from the whole or composite sample, could be the cause of the discrepancy between the measured and the calculated values. The calculated values of $\overline{M}w$ are thought to be more representative.

The fractional precipitation method used, while basically satisfactory, does have disadvantages. The main one is the inability to correctly regulate the amount of polymer deposited. Ideally it would be necessary to do two fractionations, the first preliminary one to determine the deposition characteristics of the polymer-solvent-non-solvent system being investigated to ascertain at what non-solvent volume the fractions most representative of the averages are being precipitated. Once this is known, the method for control of a second fractionation should be more than adequate to control the amount of polymer deposited. Because of the relative size and molecular weights of fractions 7 and 8 obtained in this work, these fractions exerted the greatest effect on the distributions and hence any errors in the characterization of these two fractions were found to greatly affect the shape of the composite distribution.

The method of passing a polymer solution down the side of a heated rod proved unsuccessful. Sections of polymer coating the rod were analyzed by G.P.C. and showed little evidence of fractionation. In view of the time required for equilibrium in the other two-phase solubility methods. the probable cause was the comparatively fast evaporation of the solvent, not allowing sufficient time for equilibrium to be established between the two phases during deposition. There was no evidence of fractionation when strips of polymer taken at various positions along the rod were analyzed, in an attempt to investigate the fractionation. This fractionation method was subsequently abandoned in favour of the fractional precipitation method.

An attempt to reconstruct the original molecular weight distribution from the available information was made. The one assumption made was that the numbers of molecules within each fraction were normally distributed regardless of the extent of overlapping with other fractions. As has been shown with the refractograms, this is apparently a good assumption. The method of Blackley[31] was used, the treatment being similar to that used by Hayduk and Kelly[32].

The width of the normal distribution was considered to be a function of the number average molecular weight and of the polydispersity index. Therefore a separate distribution curve was constructed for each fraction making the area under that curve proportional to the mole fraction of polymer in the particular fraction. The cumulative number distribution for the original polymer sample could then be constructed by summing the individual contributions from all the fractions corresponding to particular molecular weights. The weight distribution was then calculated by multiplying the value of the number distribution function by the molecular weight to which it corresponded.

This procedure was followed using the weight average molecular weights from both viscometry and light scattering to calculate the distributions. For fraction 1, the value of 120,500 was used, instead of the more unlikely value of 126,200, which seemed to be more reasonable in view of the P.E.V. obtained from G.P.C. The distributions obtained are compared in Figures 9 and 10.

Figure 9 shows the normal distributions of fractions 6,7 and 8. Two peaks for fraction 8 are shown, the taller using weight average molecular weight determined by light scattering, the shallower is that obtained by using viscometry. Figure 10 shows the cumulative distributions using $\overline{M}w$ obtained with light scattering and viscometry.

The number and weight functions are plotted to show the effect of the change of weight average molecular weight on the distribution. The weight distribution function for the sample uses the normal distribution for fraction 8 calculated using $\overline{M}w$(viscometry) as there are no sharp peaks in the chromatogram, and consequently the value of 19,100 is thought to in error. The resulting distributions are generally in good agreement. The differences in the weight average molecular weights of the two most critical samples

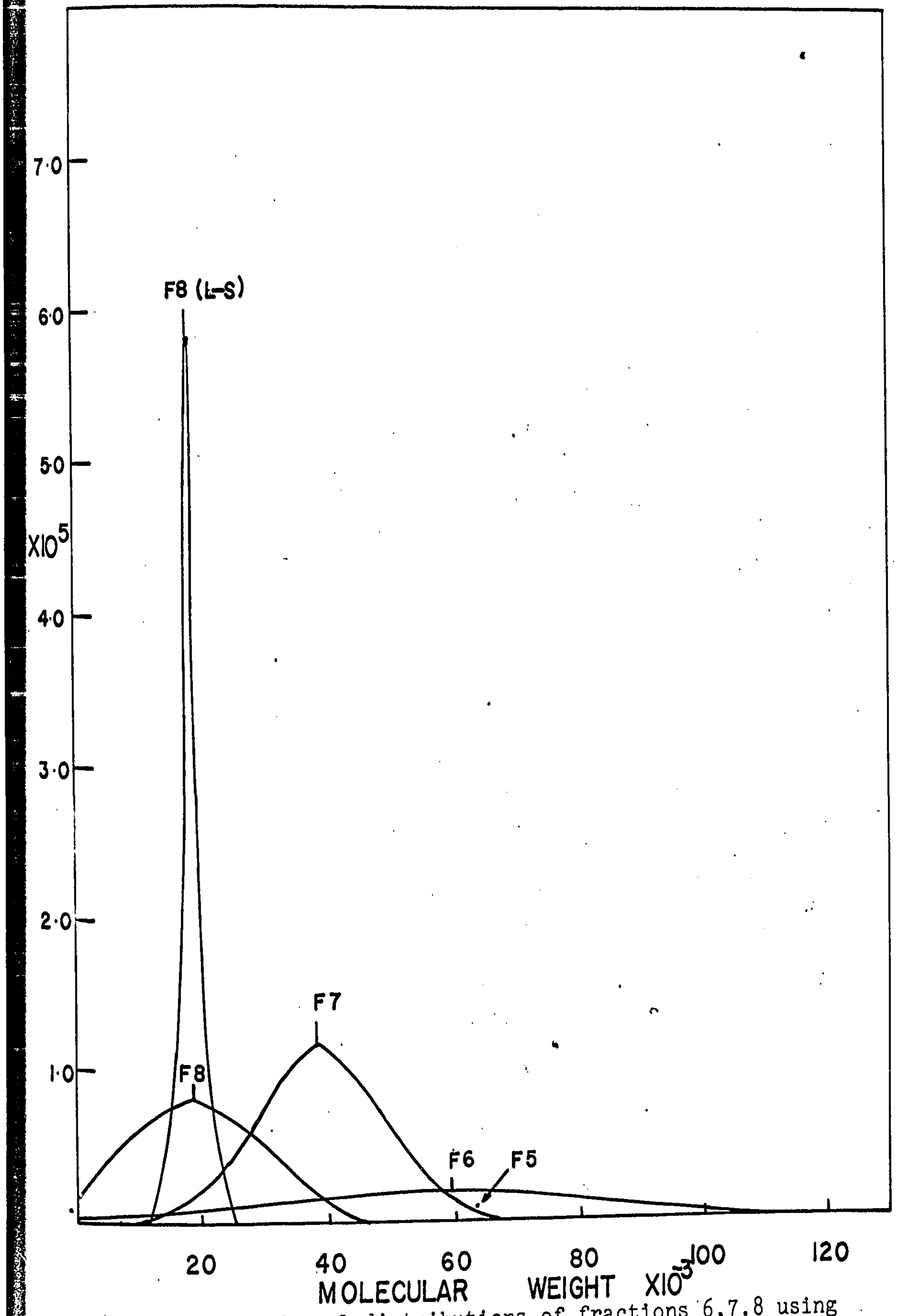


Figure 9 - Normal distributions of fractions 6,7.8 using $\overline{M}w$ (viscosity) and fraction 8 using $\overline{M}w$ (L-S)

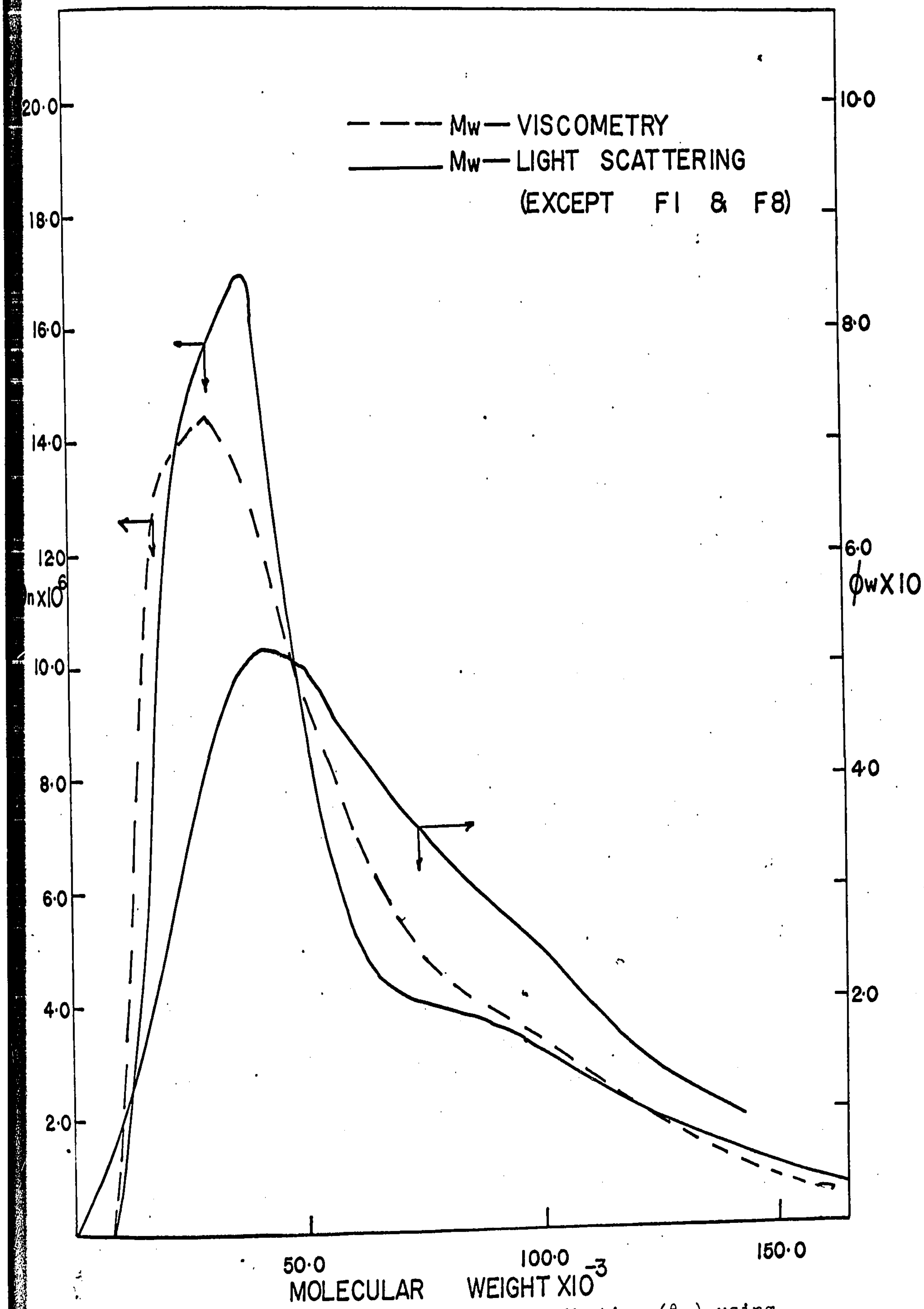


Figure 10 - Cumulative Normal Distribution (θ_n) using $\overline{M}w$ (viscosity) and $\overline{M}w$ (L-S, except fractions 1and 8) weight distribution using $\overline{M}w$ (viscosity)

is the cause of the variation between the two distributions.

C. One Point Osmometry.

The selection of suitable solvents for osmotic pressure measurements was restricted to those which would be compatible with the membranes used in the osmometer. Methanol was selected as being the most suitable since the membranes were normally conditioned initially to pure alcohol and subsequently to the solvent to be used.

A mixed solvent composition was selected at a point just below the turbidity curve and for the highest polymer concentration. Ideally a different "theta-solution" would be required for each polymer concentration as represented by the turbidity curve. Since it was difficult to change the solvent below the membrane, once the membrane was in place, only one composition was chosen. In the case of methanol the composition was0.72 mls./ml. solution and all osmotic pressure measurements were taken at this composition.

The results in Table 2 illustrate the effectiveness of the method in determining molecular weights. The slopes of the "Π/C" versus "C" lines are given to illustrate the large reduction in the second virial coefficient and Figure 11 shows the reduction of the

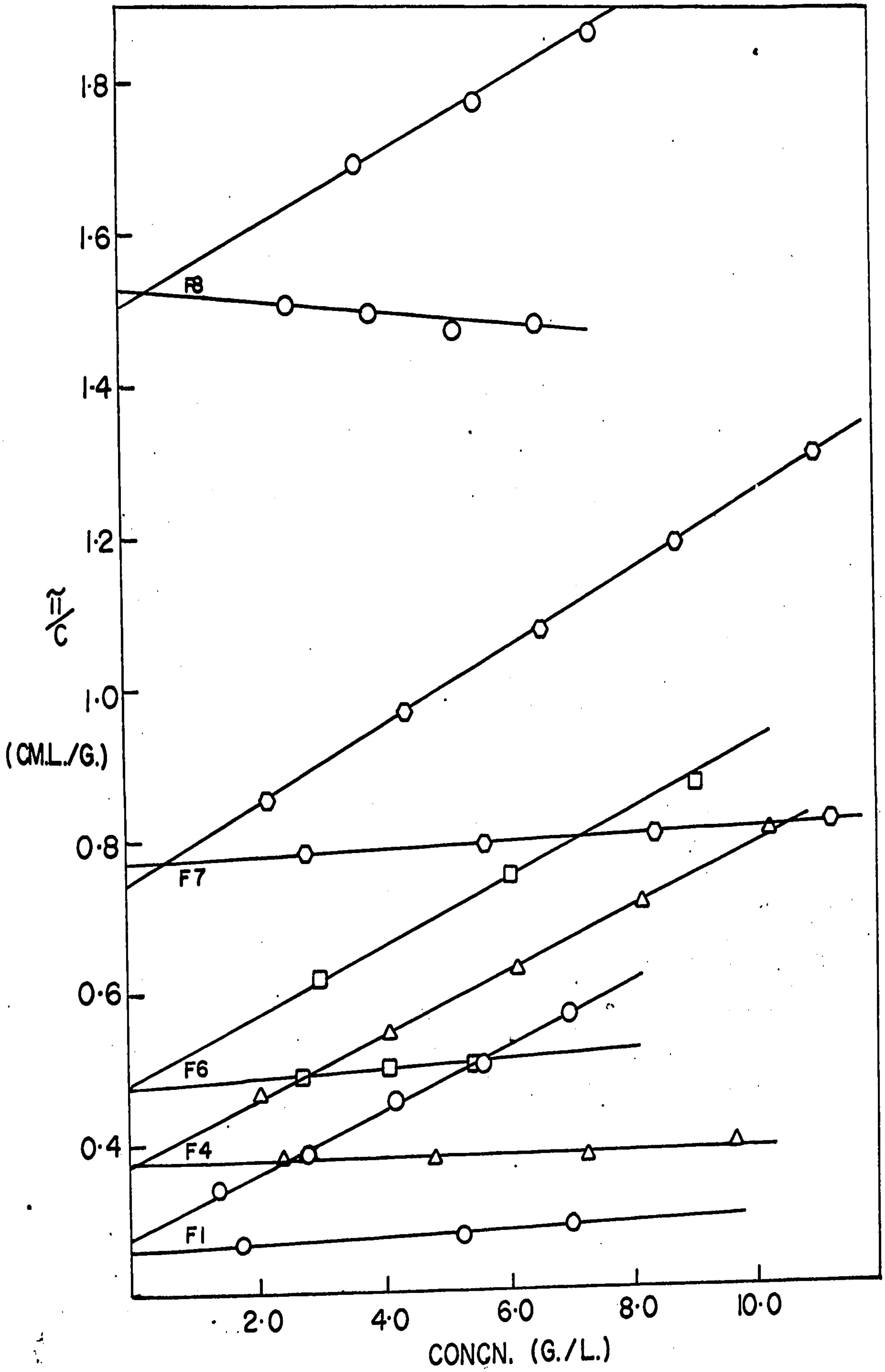


Figure 11 - Reduced osmotic pressures- comparison between regular and "theta solutions".

Polymer	Solvent Vol. Fraction Non-Solvent T.H.F.	Given(b) Mol. Wt. $\overline{M}n \times 10^{-3}$	Calc. Mol. Wt. (Int.) $\overline{M}n \times 10^{-3}$	'One Point' (Lowest Conc.) $\overline{M}n \times 10^{-3}$	Slope in θ-Solvent(c)	% Deviation
Fractions 1	42 CH_3OH	102.16	109.12	106.70	+0.0031	+6.8
2	"	97.45	98.74	95.27	+0.0035	+1.3
4	"	76.88	76.20	74.91	+0.0014	-0.9
6	"	59.36	60.09	58.26	+0.0061	+1.2
7	"	38.55	37.05	36.38	+0.0046	-3.9
8	"	18.94	18.69	18.92	-0.0084	-1.3
Esso 363	"	49.66	50.09	48.35	+0.0086	+0.8
363	.15 Meth, .05H_2O	40.63	38.12	-	+0.011	-6.2
PV-2	"	25.30	25.51	-	-0.0102	+0.8
PV-2	0.42 CH_3OH	25.30	26.56	-	-0.0143	+1.0
363	"	40.63	41.90	-	-0.0015	+3.1
Pv-4	"	54.00	53.03	-	-0.0059	-1.8
353(b)	0.43 N-C_7	35.10	50.80	-	+0.001	+44.7
363	"	40.63	66.85	-	-0.0011	+64.5
363	"	40.65	53.57	-	+0.0039	+31.8
363	0.35 N-C_7	40.63	45.86	-	+0.008	+12.9
373(b)	"	79.80	55.78	-	+0.0005	-30.1
PV-2	"	25.30	34.59	-	+0.0057	+36.7
PV-4	0.43 N-C_7	54.00	105.17	-	-0.0049	+94.8
PV-4	0.35 N-C_7	54.00	62.92	-	+0.0045	+16.5

TABLE 2 - ONE POINT OSMOMETRY

(a) The quoted weight is after removal of low molecular weight impurities.

(b) Molecular weights : 373, 363, 353 are from the M.A.Sc. Thesis of B. D. Kelly (1969). PV-2,4 supplied by manufacturer. Fractions calculated in this work

(c) Slope in T.H.F. varies from +0.045 to +0.055

slopes graphically in several fractions of Run R_2. The detailed osmotic pressure data are given in Appendix B-2.

Generally the use of a T.H.F.-methanol solvent solutions proved satisfactory in the determination of molecular weights. The dependence of the reduced osmotic pressure on concentration was greatly reduced. Consequently the use of one low concentration in T.H.F. of a polymer, suitably treated with methanol non-solvent should yield results which are satisfactory for quick characterization.

With heptane on the other hand, molecular weights were generally, greater than the known weights. By decreasing the heptane content of the solution from 43% to 35% it was possible to get somewhat closer to the correct values. It is considered that the turbidity curves themselves were in some error and that the point of incipient precipitation was being reached at an earlier point but was not easily visible.

D. Intrinsic Viscosity - Mw Relationship.

Intrinsic viscosities of the eight fractions recovered by fractionation of Esso 363 were measured in T.H.F. at 25°C. In most cases, portions of the same solutions as those used for the osmotic pressure measurements were used. Plots of reduced specific viscosity versus concentration were drawn, from which the intrinsic viscosity was calculated by the method of least squares. Table 1 shows a comparison between

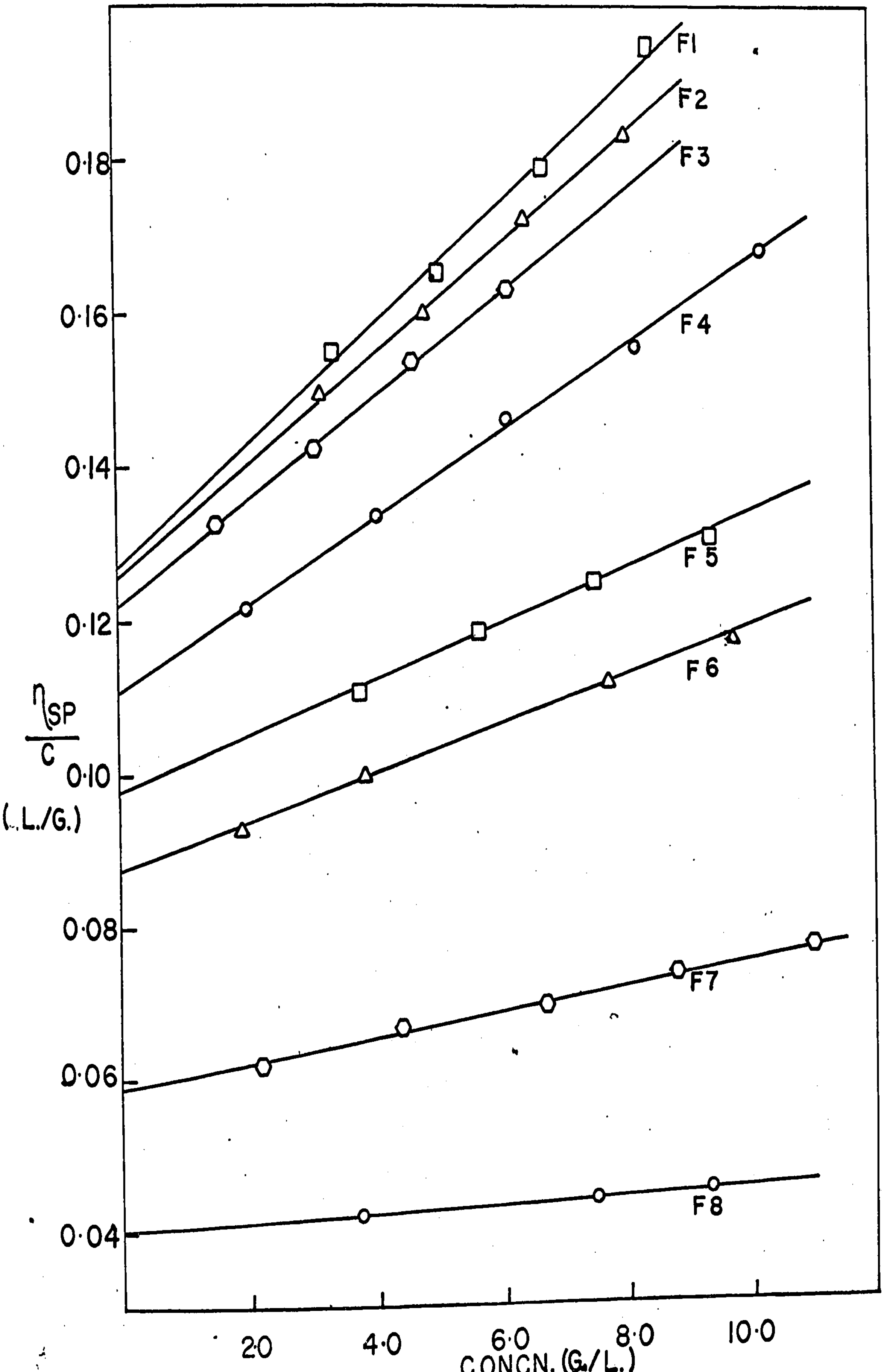


Figure 12- Reduced specific viscosity for all eight fractions.

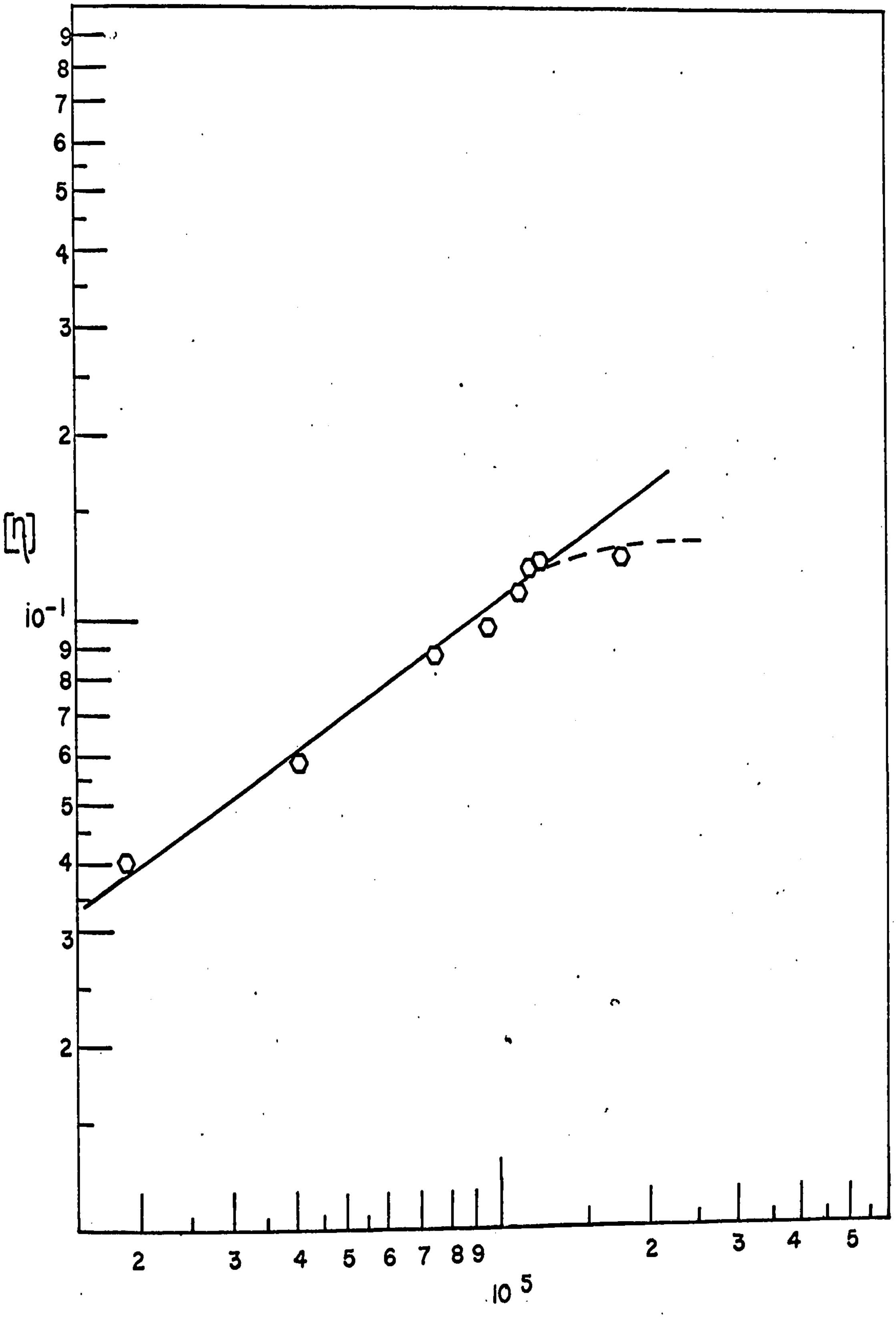


Figure 13 - Intrinsic viscosity versus molecular weight (M̄w).

the weight average molecular weights calculated from the intrinsic viscosity using equation 23 and that from light scattering measurements. Figure 12 is a plot of reduced specific viscosity for all eight fractions.

A log plot of intrinsic viscosity versus weight average molecular weight is shown in Figure 13 and from this, using the method of least mean squares, the constants for a Mark-Houwink type equation[25] were calculated:

$$(\eta) = K(Mw)^a \qquad .....25$$

-for all eight fractions: $K = 1.512$ $a = 0.566$

-for fractions 2 - 8 incl.: $K = 1.044$ $a = 0.601$

A plot of log Mw versus log (η)yielded some information. The evidence available in the literature suggests that the increase in the exponent from 0.566 to 0.601 with the removal of fraction 1 resulted from a decrease in the branching of the polymer samples as the exponent "a" decreases with increasing branching of samples. This supports the conclusion that F-1 is more highly branched than the other fractions.

E. Light Scattering Photometry.

Scattering ratios for different concentrations of the eight fractions were determined. The absolute turbidities of solutions and pure solvent were determined and from these the excess turbidities calculated. Plots of HC/τ versus concentration were made. Values of HC/τ at zero concentration were calculated by the method of least squares. Of the eight combinations of lights and neutral filters only the three were used. Which, in preliminary experiments with samples of known molecular weights, gave the most consistent results. The reported molecular weight of each fraction is the average of the three weights.

The three combinations are:

Light	Filter	Comb.
Green	1234	1
Green	234	2
Green	34	3

TABLE 3

Fraction	Filter Combinations		$Mw \times 10^{-3}$	Avg.
	1	2	3	$Mw \times 10^{-3}$
1	176.680	179.44	173.96	176.70
2	120.94	121.04	121.75	121.24
3	122.90	123.78	117.83	121.50
4	111.77	113.80	109.62	111.73
5	97.31	97.61	96.82	97.25
6	73.60	77.87	75.10	75.52
7	38.04	38.67	37.17	37.96
8	20.55	18.24	18.34	19.04
Esso 363	72.31	73.23	72.09	72.55

TABLE 4

LIGHT SCATTERING ANALYSES FOR 8 FRACTIONS AND ESSO 363

The molecular weights measured by light-scattering and estimated by viscometry were quite similar, the exception being for fraction 1. Other researchers have noted the "anomalous" behaviour of the first fraction (the heaviest fraction) and have attributed it to possible structural differences. However, agglomerates and microgels are known to form in polymer solutions and the amount of agglomeration increases with molecular weight; consequently solution turbidity would increase with the formation of agglomerates, giving even higher molecular weights.

With light scattering the refractive index difference was calculated by the use of a function with a positive intercept. This method (positive intercept) of calculation has not been reported in the literature. In preliminary experiments the refractive index differences of a large range of samples was measured by H. A. Laudie and the author, and it was found that there was a distinct tendency for the function not to pass through the origin. The function was determined by the method of least squares and for both blue and green light agreed very well. The occurrence of a positive intercept suggested that a material was absorbed or dissolved in all the polymer samples which, on solution, yielded a slight increase in the refractive index.

F. Gel-Permeation Chromatography.

The G.P.C. was calibrated for direct molecular weight ($\overline{M}w$) readings versus p.e.v. using polystyrene standards supplied by Waters Associates. A flow rate of 1.0 mls. per minute and a sample concentration of 0.1% by weight was used throughout the calibration and analytical runs.

For a given molecular weight polystyrene and poly(vinyl chloride) have different hydrodynamic volumes and, consequently, different p.e.vs. Therefore a polystyrene "calibration" curve has to be shifted or translated before it can be used to directly measure the molecular weights of P.V.C. samples. The procedure outlined by Coll and Prusinowski[29] was used, the constants being the ones used by Rudin and Benschop-Hendrychova[30]. The formulae are outlined in Appendix B-5 along with the appropriate constants and the p.e.vs. of the calibrating polystyrene samples.

Figure 14 shows the calibration curve in the molecular weight range of 10,000 to 150,000 which includes the molecular range of the fractions characterized. The weight average molecular weights of the eight fractions were read from the curve and tabulated in Table 5.

Figure 14 also shows a plot of log. Mw versus peak elution volume for all eight fractions characterized. Both concentrations are shown to illustrate the shift due to polymer concentration in solution. It is evident therefore, that reproducible results

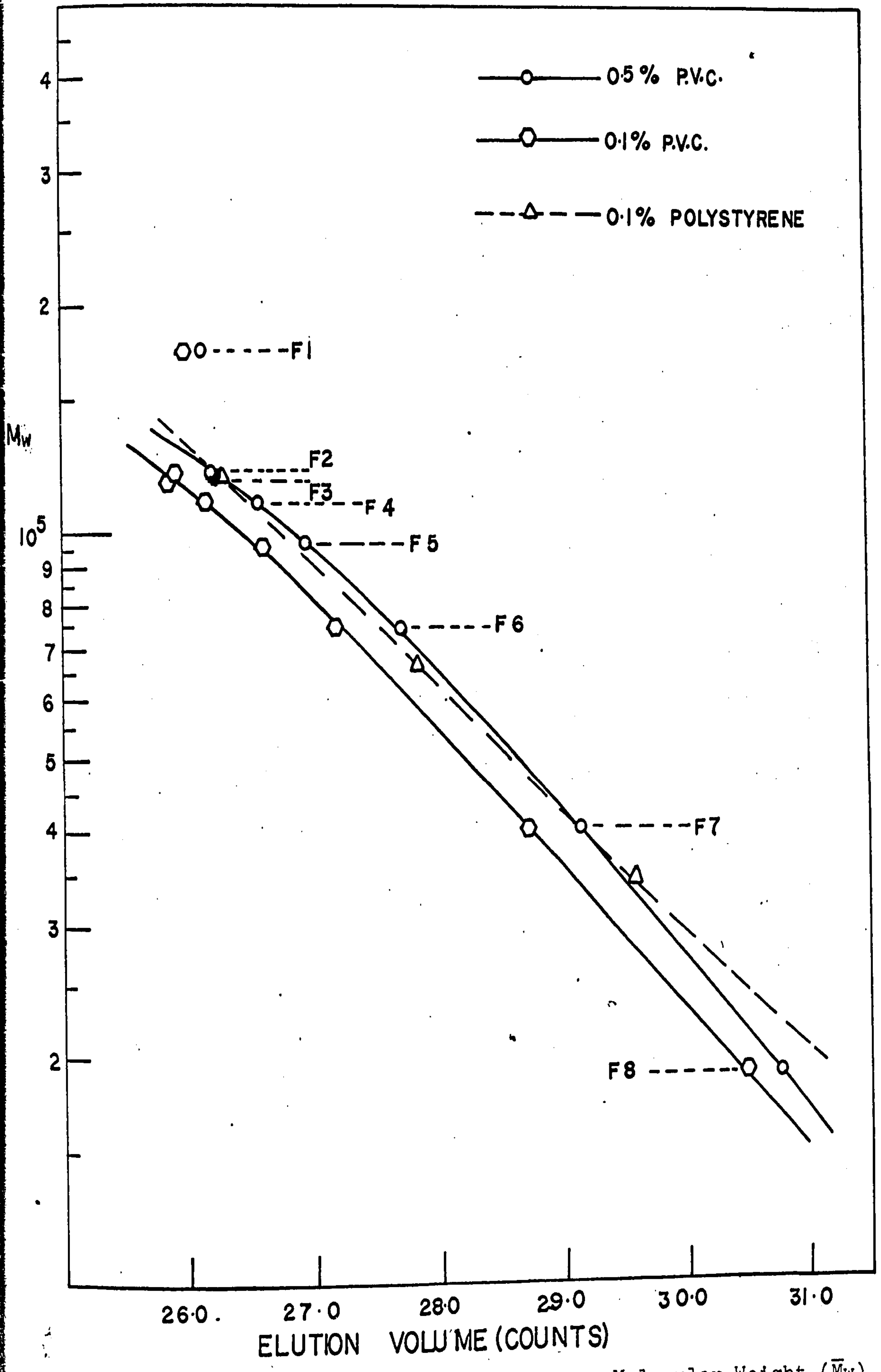


Figure 14 - Peak Elution Volume versus Molecular Weight ($\overline{M}w$) for eight fractions and polystyrene curve.

for Mw, based on p.e.vs., can only be obtained with polymer concentrations in solution identical to those used for calibration.

Fraction	P.E.V.		G.P.C.	L-S	Eqn. 23
	0.10%	0.50%	Mw x 10^{-3}	Mw x 10^{-3}	Mw x 10^{-3}
1	26.00	26.16	133.0	176.7	120.5
2	25.92	26.23	137.0	121.24	119.3
3	25.88	26.27	138.0	121.50	114.60
4	26.16	26.58	125.0	111.73	100.3
5	26.61	26.95	106.0	97.25	85.61
6	27.18	27.72	85.0	75.53	73.87
7	28.73	29.12	48.0	40.95	44.27
8	30.48	30.75	24.0	19.04	27.07

TABLE 5.

COMPARISON OF G.P.C., LIGHT SCATTERING AND VISCOMETRY VALUES OF Mw.

The calibration curve using the eight fractions is the most reliable in the chosen molecular weight range since the translated polystyrene curve is subject to inaccuracies. These occur not only in the constants used for the translation but also in the shapes of the calibrating samples. If a G.P.C. is to be used to measure the molecular weights of P.V.C. samples, the calibration should be by P.V.C. standards since the unknown samples will probably have a similar shape, for example, branching index, as those of the calibrating samples.

The weight average molecular weights measured by the G.P.C. were consistently higher than those measured by light scattering. This suggested a systematic deviation from the polystyrene curve. This was quite possible in view of the fact that the translation from polystyrene to poly(vinyl chloride) was accomplished by the use of Mark-Houwink constants which were themselves subject to error. It would be possible to change constants (Equation B-5.4) to give a calibration curve that would be closer to the results given by light scattering.

One point of the calibration curve is noticeably off the line in Figure 11. The p.e.v. of fraction 1 indicated a lower molecular weight (by G.P.C.) but this was based on the assumption that this particular sample had essentially the same molecular structure as the other calibrating samples. The previously mentioned "anomalous" behaviour of first fractions could be caused by differences in structure resulting from the longer reaction time necessary to form larger molecules and possibly, giving a higher degree of branching which in turn would result in a decrease in the hydrodynamic volume, giving lower apparent molecular weights as measured by both G.P.C. and viscometry.

CONCLUSIONS.

A commercial sample of P.V.C. was fractioned by a fractional precipitation method and the fractions characterized by osmometry, viscometry, light-scattering and G.P.C. The use of a high speed membrane osmometer allowed very rapid determinations of number average molecular weights. It was found possible to use a single "theta-solution" prepared for molecular weight determination which was in very good agreement with those determined in T.H.F. for a number of concentrations.

Light scattering and viscometry measurements were used to develop improved Mark-Houwink constants for P.V.C. in T.H.F. solutions. There was some evidence of anomalous behaviour of the first (highest molecular weight) fraction precipitated. The G.P.C. peak elution volumes were related to both light scattering and viscometry measurements. G.P.C. analyses with polystyrene were related to the molecular weights ($\overline{M}w$) for P.V.C.

It is considered that fractionation could be even more carefully controlled to produce a larger number of fractions at the critical molecular weight range.

REFERENCES.

1. Cantow, Manfred J. R., "Polymer Fractionation", Academic Press, New York, (1967).
2. Gibbs, J. W., "Thermodynamics", vol. 1 of "Collected Works", Longmans, Green, New York, (1931).
3. Flory, P. J., "Principles of Polymer Chemistry", Cornell Unversity Press, Ithaca, New York, (1953).
4. Flodin, P., Dissertation, University of Uppsala, Sweden, (1962). (Available from Pharmacia, Uppsala, Sweden).
5. Vink, H., Acta Chem. Scand., 18, 409. (1964).
6. Helfferich, "Ionenaustauscher", vol. 1 Weinheim, Bergstrasse, (1959), see "Ion Exchange" McGraw-Hill Series in Advanced Chemistry, (1962).
7. Porath, J., Pure Appl. Chem. 6, 223 (1963).
8. Laurent, T. C., and Killander, J., J. Chromatog. 14, 317, (1964).
9. Pannell, J., Polymer, 13, 277. (1972).
10. Dawkins, J. V., Maddock, J. W., and Coupe, D. J., Polym. Sci., (A-2), 8, 1803 (1970).
11. Cantow, M. J. R., Porter, R. S., and Johnson,J. F., Polymer Letters, 4, 707. (1966).
12. Rudin, A., J. Polym. Sci., (A-1), 9, 2587 (1971).
13. Little, J. M., Waters, J. L., Bombaugh, K. J., and Pauplis, W. J., J. Polym. Sci., (A-2), 7, 1775. (1969).
14. Goetze, K. P., Porter, R. S., and Johnson, J. F., J. Polym. Sci., (A-2), 9, 2255. (1971).
15. Yau, W. W., Suchan, H. L., and Malone, C. P., J. Polym. Sci., (A-2), 6, 1349 (1968).
16. Bagley, W. J. and Mark, H., "Osmometry and Viscosity of Polymer Solutions", in "High Molecular Weight Organic Compounds", edited by Burk, R. E., Interscience, New York, (1949).
17. Sarkar, D. K., and Palit, S. R., J. Polym. Sci., C, 30, 69 (1970).

18. Huggins, M. L., J. Am. Chem. Soc., 64, 2716 (1942).

19. Kraemer, E. O., Ind. Eng. Chem., 30 1200 (1938).

20. Staudinger, H., "Die hochmolebularen organischer Verbindungen", Springer, Berlin, (1932).

21. Flory, P. J., J. of Am. Chem. Soc., 65, 372 (1943).

22. Brandrup, J. and Immergent, E. H., "Polymer Handbook", John Wiley and sons, N. Y.,(1967)

23. Bohdanecky, M., Sole, K., Kratochvil, P., Kolinsky, M., Ryska, M., and Lim, D., J. of Polym. Sci., (A-2), 5, 343 (1967).

24. Debye, P., J. Appl. Phys., 15, 338 (1944).

25. Debye, P., J. Phys. Chem., 51, 18 (1947).

26. Pezzin, G., San Martin, G. and Zilio-Granai, F., J. of App. Polym. Sci., 11, 1539 (1967).

27. Hildebrand, Prausnitz and Scott, "Regular and Related Solutions", Van Nostrand Reinhold Co., (1970).

28. Freeman, M. and Manning, P. P., J. of Polymer Sci., 2, 2017 (1964).

29. Coll, H. and Prusinowski, J., J. Polym. Sci., B, 5, 1153 (1967).

30. Rudin, A. and Benschop-Hendrychova, I. J. App. Polym. Sci., 15, 2881 (1971).

31. Blackley, D. C., in "Addition Polymers: Formation and Characterization", D. A. Smith, Ed., Butterworth, London,(1968), p. 134.

32. Hayduk, W., and Kelly, B.D., App. Polym. Science, 14, 2279 (1970).

APPENDICES.

A - Light Scattering Equations and Constants.

The absolute turbidity, τ, is calculated as follows using any standard Brice-Phoenix Light Scattering Photometer:

$$\tau = \left(\frac{16\ TD}{3(1.049)L}\right)\left[N^2(Rw/Rc)\right]\left[bF(Gs/Gw)\right] \qquad .....A\text{-}1$$

For model number 2416 the above becomes:

$$\tau = 1.17\left[N^2(Rw/Rc)\right]\left[bF(Gs/Gw)\right] \qquad A\text{-}1a..\text{Blue Light}$$

$$\tau = 1.28\left[N^2(Rw/Rc)\right]\left[bF(Gs/Gw)\right] \qquad A\text{-}1b..\text{Green Light}$$

where:

-Rw/Rc is an experimentally determined correction for incomplete compensation for refraction efforts.

-F is the product of transmittances of the neutral filters used in determining the scattering ratio.

-b is a constant relating the working standard to the opal glass reference standard.

-Gs/Gw is the scattering ratio.

		BLUE	GREEN
b- working std. constant		0.0310	0.0445
Transmittance of	1	0.460	0.486
neutral	2	0.239	0.257
filters	3	0.108	0.129
	4	0.00374	0.0489

The absolute turbidity of each solution is calculated for each filter combination and the excess turbidity is calculated by subtracting the pure solvent turbidity from the absolute turbidity. This is then used in the calculation of Hc/τ.

The molecular weight is determined by plotting Hc/τ versus C, extrapolating to zero concentration and taking the reciprocal of the intercept.

From equation 22, we get:

$$H = 15.2 \times 10^{-5} N^2 (\Delta N)^2 / C^2 \qquad \text{A-2..Blue Light}$$

$$H = 6.18 \times 10^{-5} N^2 (\Delta N)^2 / C^2 \qquad \text{A-3..Green Light}$$

where ΔN is the difference in refractive index between polymer solutions and pure solvent. ΔN is calculated from the following functions:

$$\Delta N = (23.09 + 106.94C) \times 10^{-6} \qquad \text{A-4..Blue Light}$$

$$\Delta N = (23.33 + 106.804C) \times 10^{-6} \qquad \text{A-5..Green Light}$$

See tableA-1 for the data used to calculate the above two functions.

POLYMER	CONC. g/l	BLUE $\Delta N \times 10^{-6}$	GREEN $\Delta N \times 10^{-6}$
Esso 363	8.6818	980	979
	6.5113	725	731
	4.3409	491	503
	2.1704	242	259
	0.8682	104	105
PV-4	8.0539	844	825
	6.0404	661	656
	4.0269	463	455
	2.0135	251	223
PV-2	10.2225	1125	1110
	7.6669	830	825
	5.1112	562	559
	2.5556	299	297
	1.0222	120	120
	0.5111	72	40
PV-3	10.4082	1106	1116
	7.8062	858	844
	5.2041	502	516
	2.6021	325	319
PV-4	10.0023	1120	1108
	7.5017	854	854
	5.0011	600	590
	2.5005	319	347

TABLE A-1 REFRACTIVE INDEX DATA

B-1 Turbidity Data.

Polymer	Non-Solvent Sol. Parameter (cals./cc)$^{\frac{1}{2}}$	Conc. g/l	mls. Non-Solvent	N-Solvent Solution Ratio
Esso 363 δ = 9.7	Water δ = 23.4	22.562	1.30	0.13
		11.281	1.50	0.15
		5.641	1.50	0.15
		2.82	1.50	0.15
		1.41	3.10	0.155
		0.705	3.30	0.165
Esso 363	I-Methanol(a)	22.562	6.9	0.69
		11.281	14.8	0.74
		5.641	24.3	0.81
		2.82	17.05	0.85
Esso 363	Ethylene Glycol δ = 14.2	22.562	3.05	0.305
		11.281	3.15	0.315
		5.641	6.40	0.320
		2.82	6.90	0.345
Esso 363	Ethanol δ = 12.7	22.506	8.10	0.810
		11.252	9.50	0.950
		5.627	10.20	1.02
		2.813	23.75	1.188
Esso 363	s-Methanol(b) δ = 14.5	15.923	7.25	0.725
		7.961	7.80	0.780
		3.981	8.80	0.880
		1.990	17.80	0.890
Esso 363	N-Heptane	21.373	6.6	0.66
		17.099	6.9	0.69
		12.824	7.2	0.72
		8.549	7.5	0.75
		4.275	7.7	0.77
PV-4	s-Methanol δ = 14.5	14.055	6.80	0.680
		7.028	7.75	0.775
		3.514	8.10	0.810
		1.757	18.7	0.935
PV-2	s-Methanol	15.252	7.20	0.72
		7.626	16.6	0.83
		3.813	9.1	0.910
		1.907	19.55	0.978

(a) - minimum 95% Methanol
(b) - Spectro Methanol

Polymer	Non-Solvent Sol. Parameter $(cals./cc)^{\frac{1}{2}}$	Conc. g/l	mls. Non-Solvent	N-Solvent Solution Ratio
Esso 363	n-s-1(c)	22.506	3.20	0.320
	$\delta = 16.44$	11.253	2.95	0.295
		5.627	3.10	0.310
		2.813	6.40	0.320
Esso 363	n-s-2(d)	22.506	3.30	0.330
	$\delta = 16.73$	11.253	3.35	0.335
		5.627	3.50	0.350
		2.813	7.05	0.353
Esso 363	n-s-3(e)	22.506	2.30	0.46
	$\delta = 14.5$	11.253	4.70	0.47
		5.627	5.0	0.50
		2.813	10.6	0.53

(c) - 40% water, 40% Ethanol, 20% Acetone
(d) - 25% water, 75% s-Methanol
(e) - 17% water, 83% Ethanol

B - 2 One Point Osmometry Data.

Solvent legend:

1. 43% n - C_7 57% T.H.F. RT = 31,551
2. 35% n - C_7 65% T.H.F. RT = 30,955
3. 15% Methanol, 5% water, 80% T.H.F. RT = 28,780
4. 42% Methanol, 58% T.H.F. RT = 29,800

Membranes - s & s 08

Polymer	Solvent	Conc. g/1	Hydraulic Head cms. Solvent		Π/C
353	1	1.7204	1.07		0.6220
		3.4407	2.16		0.6278
		6.8815	4.31		0.6263
		8.6018	5.42		0.6301
				Int.* =	0.6210
				Mn =	50,807
363	1	2.696	1.29		0.4785
		5.392	2.44		0.4525
		10.784	4.97		0.4609
		13.480	6.16		0.4570
				Int. =	0.472
				Mn =	66,845
363	1	2.380	1.45		0.6090
		4.786	2.84		0.593
		7.180	4.41		0.614
		9.573	6.06		0.6330
				Int. =	0.589
				Mn =	53,567
373	2	1.9564	1.08		0.5520
		3.9129	2.17		0.5546
		5.8693	3.30		0.5622
		7.8257	4.42		0.5648
		9.7821	5.31		0.5531
				Int. =	0.5550
				Mn =	55,775
363	2	2.6315	1.83		0.6954
		5.2630	3.74		0.7106
		7.8944	5.84		0.7398
		10.5259	7.98		0.7581
		13.1574	10.59		0.8048
				Int. =	0.675
				Mn =	45,859

---

*Int. abbreviation for intercept.

Polymer	Solvent	Conc. g/l	Hydraulic Head cms. Solvent		Π/C
PV - 2	2	2.1549	1.96		0.9095
		4.4398	3.89		0.9026
		6.4647	6.03		0.9328
		8.6196	8.22		0.9536
		10.7745	10.50		0.9745
				Int. =	0.895
				Mn =	34,587
PV - 4	1	1.815	0.49		0.2783
		3.630	1.04		0.2865
		5.429	1.46		0.2690
		7.259	1.82		0.2510
		9.074	2.33		0.2568
				Int. =	0.300
				Mn =	105,170
PV - 4	2	2.074	1.06		0.511
		4.148	2.05		0.4942
		6.222	3.21		0.5159
		8.296	4.40		0.5304
		10.370	5.72		0.5516
				Int. =	0.492
				Mn =	62,916
363	3	1.923	1.490		0.775
		9.0346	7.77		0.8600
		11.2932	9.86		0.8731
				Int. =	0.755
				Mn =	38,119
PV - 2	3	1.984	2.25		1.134
		4.184	4.46		1.066
		8.385	8.71		1.051
		10.481	10.54		1.006
				Int. =	1.128
				Mn =	25,514
PV - 2	4	1.628	1.87		1.149
		3.351	3.44		1.027
		5.027	5.17		1.028
		6.877	6.91		1.005
		8.378	8.71		1.040
				Int. =	1.122
				Mn =	26,560

Polymer	Solvent	Conc. g/l	Hydraulic Head cms. Solvent		Π/C
363	4	1.852	1.30		0.702
		3.703	2.64		0.713
		5.555	3.94		0.709
		7.522	5.22		0.694
		9.258	6.46		0.698
				Int. =	0.7113
				Mn =	41,895
PV - 4	4	1.634	0.90		0.5508
		3.269	1.78		0.5450
		4.093	2.61		0.5323
		8.172	4.20		0.5140
				Int. =	0.562
				Mn =	53,025

The following is the "one-point" osmometry data for the fractions of the second fractionation. The Π/C reading equivalent to that in T.H.F. is given.

Fraction	Solvent	Conc. g/l	Hydraulic Hd. cms. Solvent	Π/C	Eq. Π/C in T.H.F.
F_1	4	1.7543	0.49	0.2793	0.2676
		5.2629	1.51	0.2869	0.2749
		7.0172	2.08	0.2964	0.2840
			Int. =	0.2731	0.2617
			Mn =	109,117	
F_2	4	2.4936	0.78	0.3128	0.2997
		4.9871	1.57	0.3148	0.3016
		7.4806	2.46	0.3289	0.3151
		9.9742	3.36	0.3369	0.3228
			Int. =	0.3018	0.2892
			Mn =	98,741	
F_4	4	2.4132	0.96	0.3978	0.3812
		4.8265	1.91	0.3957	0.3791
		7.2397	2.87	0.3964	0.3798
		9.6529	3.95	0.4092	0.3921
			Int. =	0.3911	0.3747
			Mn =	76,195	
F_6	4	2.7174	1.39	0.5115	0.4901
		4.0761	2.13	0.5226	0.5007
		5.4348	2.87	0.5281	0.5060
			Int. =	0.4959	0.4751
			Mn =	60,093	
F_7	4	2.808	2.30	0.8191	0.7848
		5.616	4.65	0.8280	0.7934
		8.424	7.10	0.8428	0.8075
		11.232	9.63	0.8574	0.8215
			Int. =	0.8044	0.7707
			Mn	37,046	
F_8	4	2.6214	4.13	1.5755	1.5096
		3.9322	6.14	1.5615	1.4962
		5.2429	8.08	1.541	1.4766
		6.5536	10.13	1.5457	1.4810
			Int. =	1.593	1.526
			Mn =	18,707	
Esso 363*	4	2.45	1.51	0.6163	0.5905
		4.90	3.52	0.6367	0.6100
		7.35	4.84	0.6585	0.6309
		9.80	6.66	0.6796	0.6512
			Int. =	0.5949	0.5700
			Mn =	50,093	

*After removal of low molecular weight impurities.

B - 3 Osmometry Data for Fractionation of Esso 363.

Measured in T.H.F. using s & s 08 RT = 28553

Fraction	Conc. g/l	Hydraulic Head cms. Solvent		Π/C
F_1	1.3988	0.48		0.3432
	2.7975	1.07		0.3825
	4.1963	1.91		0.4552
	5.5950	2.81		0.5022
	6.9938	3.97		0.5677
			Int. =	0.2795
			Mn =	102,157
F_2	2.9350	1.24		0.4225
	5.8701	3.23		0.5502
	8.8051	5.89		0.6689
	11.7402	9.29		0.7913
	14.6752	13.75		0.9370
			Int. =	0.2930
			Mn =	97,450
F_3	3.0958	1.55		0.5007
	4.6437	2.53		0.5448
	6.1916	3.93		0.6347
	7.7395	5.40		0.6977
			Int. =	0.3562
			Mn =	80,160
F_4	2.0477	0.95		0.4639
	4.0954	2.23		0.5445
	6.1431	3.86		0.6284
	8.1908	5.95		0.7142
	10.2384	8.35		0.8155
			Int. =	0.3714
			Mn =	76,880
F_5	1.8803	0.99		0.5265
	5.6408	3.88		0.6879
	7.5210	5.63		0.7486
	9.4013	7.90		0.8403
			Int. =	0.4500
			Mn =	63,451
F_6	3.0176	1.87		0.6197
	6.0353	4.53		0.7506
	9.0529	7.89		0.8715
	12.0706	12.41		1.0281
			Int. =	0.4810
			Mn =	59,362

Fraction	Conc. g/l	Hydraulic Head cms. Solvent		Π/C
F_7	2.2029	1.88		0.853
	4.4058	4.28		0.971
	6.6087	7.14		1.080
	8.8116	10.51		1.193
	11.0146	14.43		1.310
			Int. =	0.7406
			Mn =	38,554
F_8	3.7472	6.34		1.6919
	5.6208	9.97		1.7738
	7.4944	14.00		1.8681
	9.3680	18.54		1.9791
			Int. =	1.5078
			Mn =	18,937
whole 363(a)	3.3713	2.57		0.7623
	6.7426	6.25		0.9269
	10.1139	11.31		1.1183
	13.4852	17.55		1.3014
			Int. =	0.575
			Mn =	49,657

(a) After removal of low molecular weight impurities.

B - 4 Intrinsic Viscosity Data.

Tube no.	Tube constant
B-780	0.002407
D-489	0.004150
F-689	0.003978
M-523	0.01593

Viscometry constants [=] cs./sec.

Solvent density = .885 g./cc.

Solvent viscosity = 0.469 cp.

The flow time is the average of three or four runs.

Fraction	Conc. g/1	Tube	Time secs.	η_{sp}	η_{sp}/C 1./g.
F_1	3.3837	F-689	203.33	0.5246	0.1550
	5.0756	D-489	235.0	0.8382	0.1651
	6.7675	D-489	282.63	1.2108	0.1789
	8.4594	F-689	352.70	1.6445	0.1944
			Intrinsic	viscosity =	0.1271
				Mw =	120,500
F_2	3.2199	F-689	197.63	0.4818	0.1496
	4.8298	D-489	226.43	0.7712	0.1600
	6.4397	D-489	269.33	1.0168	0.1719
	8.0497	F-689	329.70	1.4721	0.1829
			Intrinsic	viscosity =	0.1262
				Ms =	119,300
F_3	1.5479	B-780	265.67	0.2053	0.1327
	3.0958	D-489	184.20	0.4408	0.1424
	4.6437	F-689	228.60	0.7141	0.1538
	6.1916	F.689	268.10	1.0102	0.1632
			Intrinsic	viscosity =	0.1223
				Mw =	114,600
F_4	2.0477	B-780	275.40	0.2495	0.1218
	4.0954	D-489	197.80	0.5471	0.1336
	6.1431	F-689	253.23	0.8987	0.1463
	8.1908	D-489	290-63	1.2734	0.1555
	10.2385	F-689	362.60	1.7188	0.1678
			Intrinsic	viscosity =	0.1108
				Mw =	100,700

Fraction	Conc. g/l	Tube	Time secs.	η_{sp}	η_{sp}/C l./g.
F_5	3.7605	F-689	188.80	0.4156	0.1105
	5.6408	D-489	213.30	0.6684	0.1185
	7.5210	F-689	258.53	0.9384	0.1248
	9.4013	M-523	74.17	1.2271	0.1305
				Intrinsic viscosity =	0.09785
				Mw =	85,610
F_6	1.9310	B-780	260.03	0.1797	0.0931
	3.8620	F-689	184.77	0.3855	0.09984
	7.7240	F-689	248.70	0.8647	0.1120
	9.6551	D-489	272.45	1.1311	0.1172
				Intrinsic viscosity =	0.0874
				Mw =	73,870
F_7	2.2029	B-780	250.5	0.1365	0.06196
	4.4058	F-689	172.67	0.2947	0.06688
	6.6087	D-489	186.43	0.4583	0.06935
	8.8116	D-489	210.57	0.6471	0.07344
	11.0146	F-689	246.00	0.8445	0.07667
				Intrinsic viscosity =	0.05903
				Mw =	44,270
F_8	3.7478	F-689	154.47	0.1582	0.04222
	7.4944	F-689	177.43	0.3303	0.04407
	9.3680	D-489	181.55	0.4200	0.04484
				Intrinsic viscosity =	0.0405
				Mw =	27.070

B - 5 Gel Permeation Chromatography Data.

The formulae used to translate a polystyrene calibration curve to a poly(vinyl chloride) curve are outlined below. If "A" represents polystyrene and "B" represents P.V.C., then:

$$\log M_B = \frac{1}{1+a_B} \log \frac{K_A \phi_B}{K_B \phi_B} + \frac{1+a_A}{1+a_B} \log M_A \qquad \text{.... B-5.1}$$

where "a" and "K" are the Mark-Houwink coefficients for each polymer in T.H.F. at the appropriate temperature. The "ϕ" terms are defined by:

$$\phi = \phi_o (1 - 2.6\varepsilon + 2.86\, \varepsilon^2) \qquad \text{....B-5.2}$$

$$\varepsilon = (2_a - 1)/3 \qquad \text{....B-5.3}$$

where "ϕ_o" is a constant which cancels out. The appropriate constants for use in the equations are:

$a_A = 0.682$, $K_A = 1.905 \times 10^{-2}$ dl./g. $\varepsilon_A = 0.1213$

$a_B = 0.6486$ $K_A = 5.012 \times 10^{-2}$ dl./g. $\varepsilon_B = 0.09973$

Equation B-1 reduces to:

$$\log M_B = -0.2697 + 1.02026 \log M_A \qquad \text{....B-5.4}$$

Table B-5.1 shows the molecular weights of the polystyrene standards and the translated P.V.C. curve.

Polystyrene Standard				Equiv. P.V.C. (Eqn. B-4)	
Peak Å	Mw	Mn	P.E.V.	Mw	Mn
48,000	2,145,000	1,780,000	20.74	1,549,000	1,280,000
20.200	867,000	773,000	22.32	614,600	545,700
9,800	402,000	392,000	23.87	280,600	273,500
4,160	173,000	164,000	26.29	118,700	112,400
2,360	98,200	96,200	27.84	66,600	65,200
1,220	51,000	49,000	29.54	34,100	32,800
480	19,850	19,650	32.04	13,000	12,900
244	10,300	9,700	33.38	6,700	6,300
117	5,000	4,600	35.09	3,200	3,000

TABLE B-5.1

Translation of Polystyrene curve into a poly(vinyl chloride) calibration curve.

B-6 Light-Scattering Photometry Data

LIGHT SCATTERING PHOTOMETER DATA FOR ESSO GRADE 363 FRACTIONS

ESSO 363

CONCN	DELTA N	GS 90	GS 0	T EXCESS	H	HC/T	COLOUR
THF	-	1.7600	1.6280	-	-	-	GREEN
THF	-	1.7600	3.3000	-	-	-	GREEN
THF	-	1.7600	13.0800	-	-	-	GREEN
2.1136	249.E-06	5.3300	1.5900	2.0184E-04	1.6907E-12	1.7705E-05	GREEN
2.1136	249.E-06	5.3300	3.2350	2.0376E-04	1.6907E-12	1.7538E-05	GREEN
2.1136	249.E-06	5.3300	12.8200	2.0008E-04	1.6907E-12	1.7860E-05	GREEN
4.2272	475.E-06	7.4000	1.5440	3.2986E-04	1.5382E-12	1.9712E-05	GREEN
4.2272	475.E-06	7.4000	3.1400	3.3343E-04	1.5382E-12	1.9501E-05	GREEN
4.2272	475.E-06	7.4000	12.4800	3.2616E-04	1.5382E-12	1.9935E-05	GREEN
8.4544	926.E-06	8.8500	1.4460	4.4785E-04	1.4614E-12	2.7589E-05	GREEN
8.4544	926.E-06	8.8500	2.9500	4.5106E-04	1.4614E-12	2.7392E-05	GREEN
8.4544	926.E-06	8.8500	11.7400	4.4064E-04	1.4614E-12	2.8040E-05	GREEN
10.5680	1152.E-06	9.2200	1.4700	4.6134E-04	1.4476E-12	3.3160E-05	GREEN
10.5680	1152.E-06	9.2200	2.9800	4.6825E-04	1.4476E-12	3.2671E-05	GREEN
10.5680	1152.E-06	9.2200	11.7800	4.6116E-04	1.4476E-12	3.3173E-05	GREEN

LIGHT SCATTERING PHOTOMETER DATA FOR ESSO GRADE 363 FRACTIONS

FRACTION #1

CONCN	DELTA N	GS 90	GS 0	T EXCESS	H	HC/T	COLOUR
THF	-	1.5700	1.4840	-	-	-	GREEN
THF	-	1.5700	3.0250	-	-	-	GREEN
THF	-	1.5700	12.0800	-	-	-	GREEN
1.3988	173.E-06	9.1500	1.8940	3.3379E-04	1.8634E-12	7.8089E-06	GREEN
1.3988	173.E-06	9.1500	3.8200	3.4153E-04	1.8634E-12	7.6318E-06	GREEN
1.3988	173.E-06	9.1500	15.3000	3.3152E-04	1.8634E-12	7.8622E-06	GREEN
2.7975	322.E-06	12.5000	1.9000	4.8841E-04	1.6140E-12	9.2443E-06	GREEN
2.7975	322.E-06	12.5000	3.8700	4.9347E-04	1.6140E-12	9.1497E-06	GREEN
2.7975	322.E-06	12.5000	15.4200	4.8210E-04	1.6140E-12	9.3654E-06	GREEN
4.1963	472.E-06	14.5400	1.9200	5.7635E-04	1.5413E-12	1.1222E-05	GREEN
4.1963	472.E-06	14.5400	3.8900	5.8590E-04	1.5413E-12	1.1039E-05	GREEN
4.1963	472.E-06	14.5400	15.5600	5.6979E-04	1.5413E-12	1.1351E-05	GREEN
5.5950	621.E-06	14.5000	1.7320	6.4702E-04	1.5007E-12	1.2977E-05	GREEN
5.5950	621.E-06	14.5000	3.4950	6.6072E-04	1.5007E-12	1.2708E-05	GREEN
5.5950	621.E-06	14.5000	13.9600	6.4362E-04	1.5007E-12	1.3046E-05	GREEN
6.9938	770.E-06	17.2000	1.9900	6.7103E-04	1.4767E-12	1.5390E-05	GREEN
6.9938	770.E-06	17.2000	4.0250	6.8338E-04	1.4767E-12	1.5112E-05	GREEN
6.9938	770.E-06	17.2000	16.0400	6.6744E-04	1.4767E-12	1.5473E-05	GREEN

LIGHT SCATTERING PHOTOMETER DATA FOR ESSO GRADE 363 FRACTIONS

FRACTION #2

CONCN	DELTA N	GS 90	GS 0	T EXCESS	H	HC/T	COLOUR
THF	-	4.8900	4.8000	-	-	-	GREEN
THF	-	4.8900	9.6000	-	-	-	GREEN
THF	-	4.8900	38.7000	-	-	-	GREEN
1.6099	195.E-06	20.4000	4.7500	2.9114E-04	1.7873E-12	9.8829E-06	GREEN
1.6099	195.E-06	20.4000	9.6400	2.9383E-04	1.7873E-12	9.7927E-06	GREEN
1.6099	195.E-06	20.4000	38.0000	2.9207E-04	1.7873E-12	9.8514E-06	GREEN
3.2199	367.E-06	29.3500	4.9000	4.4179E-04	1.5826E-12	1.1535E-05	GREEN
3.2199	367.E-06	29.3500	9.9500	4.4626E-04	1.5826E-12	1.1419E-05	GREEN
3.2199	367.E-06	29.3500	39.3500	4.4080E-04	1.5826E-12	1.1560E-05	GREEN
4.8298	533.E-06	30.0000	4.2100	5.4275E-04	1.4836E-12	1.3202E-05	GREEN
4.8298	533.E-06	30.0000	8.5800	5.4624E-04	1.4836E-12	1.3118E-05	GREEN
4.8298	533.E-06	30.0000	33.7500	5.4257E-04	1.4836E-12	1.3207E-05	GREEN
6.4397	711.E-06	42.3500	5.0300	6.5772E-04	1.4850E-12	1.4540E-05	GREEN
6.4397	711.E-06	42.3500	10.6000	6.3745E-04	1.4850E-12	1.5002E-05	GREEN
6.4397	711.E-06	42.3500	40.6000	6.5230E-04	1.4850E-12	1.4661E-05	GREEN
8.0497	883.E-06	47.0000	5.2200	7.0965E-04	1.4658E-12	1.6627E-05	GREEN
8.0497	883.E-06	47.0000	10.4400	7.3009E-04	1.4658E-12	1.6162E-05	GREEN
8.0497	883.E-06	47.0000	42.0000	7.0633E-04	1.4658E-12	1.6705E-05	GREEN

LIGHT SCATTERING PHOTOMETER DATA FOR ESSO GRADE 363 FRACTIONS

FRACTION #3

CONCN	DELTA N	GS 90	GS 0	T EXCESS	H	HC/T	COLOUR
THF	-	1.0600	0.9630	-	-	-	GREEN
THF	-	1.0600	1.9520	-	-	-	GREEN
THF	-	1.0600	7.9700	-	-	-	GREEN
1.7115	206.E-06	3.3800	0.9340	2.2277E-04	1.7648E-12	1.3559E-05	GREEN
1.7115	206.E-06	3.3800	1.8980	2.2531E-04	1.7648E-12	1.3406E-05	GREEN
1.7115	206.E-06	3.3800	7.7700	2.1390E-04	1.7648E-12	1.4121E-05	GREEN
3.4230	389.E-06	4.1600	0.9210	3.0221E-04	1.5733E-12	1.7820E-05	GREEN
3.4230	389.E-06	4.1600	1.8860	3.0265E-04	1.5733E-12	1.7794E-05	GREEN
3.4230	389.E-06	4.1600	7.7200	2.8746E-04	1.5733E-12	1.8734E-05	GREEN
6.8460	755.E-06	4.6000	0.8660	3.7253E-04	1.4816E-12	2.7228E-05	GREEN
6.8460	755.E-06	4.6000	1.7660	3.7529E-04	1.4816E-12	2.7028E-05	GREEN
6.8460	755.E-06	4.6000	7.2000	3.5831E-04	1.4816E-12	2.8309E-05	GREEN
8.5575	937.E-06	4.4100	0.8350	3.6985E-04	1.4605E-12	3.3794E-05	GREEN
8.5575	937.E-06	4.4100	1.7040	3.7224E-04	1.4605E-12	3.3576E-05	GREEN
8.5575	937.E-06	4.4100	6.9900	3.5265E-04	1.4605E-12	3.5441E-05	GREEN

LIGHT SCATTERING PHOTOMETER DATA FOR ESSO GRADE 363 FRACTIONS

FRACTION #4

CONCN	DELTA N	GS 90	GS 0	T EXCESS	H	HC/T	COLOUR
THF	-	4.0000	4.1750	-	-	-	GREEN
THF	-	4.0000	8.5100	-	-	-	GREEN
THF	-	4.0000	33.8500	-	-	-	GREEN
2.0477	242.E-06	15.5000	4.1400	2.4759E-04	1.7015E-12	1.4072E-05	GREEN
2.0477	242.E-06	15.5000	8.4200	2.5067E-04	1.7015E-12	1.3899E-05	GREEN
2.0477	242.E-06	15.5000	33.4500	2.4563E-04	1.7015E-12	1.4184E-05	GREEN
4.0954	461.E-06	20.4500	4.2900	3.3850E-04	1.5436E-12	1.8676E-05	GREEN
4.0954	461.E-06	20.4500	8.6900	3.4438E-04	1.5436E-12	1.8357E-05	GREEN
4.0954	461.E-06	20.4500	34.6500	3.3586E-04	1.5436E-12	1.8822E-05	GREEN
6.1431	679.E-06	23.0500	4.2600	3.9572E-04	1.4883E-12	2.3104E-05	GREEN
6.1431	679.E-06	23.0500	8.6700	4.0021E-04	1.4883E-12	2.2845E-05	GREEN
6.1431	679.E-06	23.0500	34.4000	3.9269E-04	1.4883E-12	2.3282E-05	GREEN
8.1908	898.E-06	24.5500	4.3250	4.1932E-04	1.4643E-12	2.8603E-05	GREEN
8.1908	898.E-06	24.5500	8.7900	4.2478E-04	1.4643E-12	2.8235E-05	GREEN
8.1908	898.E-06	24.5500	34.9000	4.1644E-04	1.4643E-12	2.8800E-05	GREEN
10.2385	1117.E-06	17.1400	2.8850	4.4285E-04	1.4500E-12	3.3523E-05	GREEN
10.2385	1117.E-06	17.1400	5.8700	4.4800E-04	1.4500E-12	3.3137E-05	GREEN
10.2385	1117.E-06	17.1400	23.1500	4.4273E-04	1.4500E-12	3.3532E-05	GREEN

LIGHT SCATTERING PHOTOMETER DATA FOR ESSO GRADE 363 FRACTIONS

FRACTION #5

CONCN	DELTA N	GS 90	GS 0	T EXCESS	H	HC/T	COLOUR
THF	-	4.0500	4.3200	-	-	-	GREEN
THF	-	4.0500	8.7000	-	-	-	GREEN
THF	-	4.0500	34.9500	-	-	-	GREEN
1.8803	224.E-06	17.6400	4.2850	2.8254E-04	1.7289E-12	1.1506E-05	GREEN
1.8803	224.E-06	17.6400	8.7700	2.8269E-04	1.7289E-12	1.1500E-05	GREEN
1.8803	224.E-06	17.6400	34.5500	2.8083E-04	1.7289E-12	1.1576E-05	GREEN
3.7605	425.E-06	27.2500	4.4800	4.5725E-04	1.5560E-12	1.2797E-05	GREEN
3.7605	425.E-06	27.2500	9.1000	4.6246E-04	1.5560E-12	1.2653E-05	GREEN
3.7605	425.E-06	27.2500	36.1500	4.5390E-04	1.5560E-12	1.2891E-05	GREEN
7.5210	827.E-06	41.1000	4.5950	7.1160E-04	1.4729E-12	1.5568E-05	GREEN
7.5210	827.E-06	41.1000	9.3000	7.2301E-04	1.4729E-12	1.5322E-05	GREEN
7.5210	827.E-06	41.1000	37.0500	7.0686E-04	1.4729E-12	1.5672E-05	GREEN
9.4013	1027.E-06	48.0000	4.6700	8.3014E-04	1.4537E-12	1.6464E-05	GREEN
9.4013	1027.E-06	48.0000	9.5300	8.3591E-04	1.4537E-12	1.6350E-05	GREEN
9.4013	1027.E-06	48.0000	37.7500	8.2228E-04	1.4537E-12	1.6621E-05	GREEN

LIGHT SCATTERING PHOTOMETER DATA FOR ESSO GRADE 363 FRACTIONS

FRACTION #6

CONCN	DELTA N	GS 90	GS 0	T EXCESS	H	HC/T	COLOUR
THF	-	5.3500	5.1500	-	-	-	GREEN
THF	-	5.3500	10.3400	-	-	-	GREEN
THF	-	5.3500	41.6000	-	-	-	GREEN
1.9310	230.E-06	15.2000	5.2300	1.6597E-04	1.7283E-12	2.0108E-05	GREEN
1.9310	230.E-06	15.2000	10.4200	1.7213E-04	1.7283E-12	1.9388E-05	GREEN
1.9310	230.E-06	15.2000	41.8000	1.6723E-04	1.7283E-12	1.9956E-05	GREEN
3.8620	436.E-06	23.2500	5.4500	2.8681E-04	1.5526E-12	2.0907E-05	GREEN
3.8620	436.E-06	23.2500	10.9000	2.9544E-04	1.5526E-12	2.0296E-05	GREEN
3.8620	436.E-06	23.2500	43.8000	2.8619E-04	1.5526E-12	2.0952E-05	GREEN
5.7930	642.E-06	21.6500	4.6350	3.2280E-04	1.4962E-12	2.6851E-05	GREEN
5.7930	642.E-06	21.6500	9.4300	3.2522E-04	1.4962E-12	2.6651E-05	GREEN
5.7930	642.E-06	21.6500	36.0000	3.3640E-04	1.4962E-12	2.5765E-05	GREEN
9.6551	1055.E-06	16.3000	3.1200	3.7198E-04	1.4545E-12	3.7753E-05	GREEN
9.6551	1055.E-06	16.3000	6.3400	3.7552E-04	1.4545E-12	3.7397E-05	GREEN
9.6551	1055.E-06	16.3000	25.0000	3.7241E-04	1.4545E-12	3.7709E-05	GREEN

LIGHT SCATTERING PHOTOMETER DATA FOR ESSO GRADE 363 FRACTIONS

FRACTION #7

CONCN	DELTA N	GS 90	GS 0	T EXCESS	H	HC/T	COLOUR
THF	-	4.6000	4.9800	-	-	-	GREEN
THF	-	4.6000	9.9600	-	-	-	GREEN
THF	-	4.6000	40.1500	-	-	-	GREEN
2.2029	259.E-06	11.5000	5.1000	1.1831E-04	1.6840E-12	3.1356E-05	GREEN
2.2029	259.E-06	11.5000	10.2200	1.2131E-04	1.6840E-12	3.0579E-05	GREEN
2.2029	259.E-06	11.5000	41.2000	1.1709E-04	1.6840E-12	3.1682E-05	GREEN
4.4056	494.E-06	16.7000	5.1400	2.0666E-04	1.5315E-12	3.2651E-05	GREEN
4.4058	494.E-06	16.7000	10.2800	2.1261E-04	1.5315E-12	3.1737E-05	GREEN
4.4058	494.E-06	16.7000	41.4500	2.0515E-04	1.5315E-12	3.2891E-05	GREEN
8.8116	964.E-06	21.7000	5.2300	2.8665E-04	1.4580E-12	4.4820E-05	GREEN
8.8116	964.E-06	21.7000	10.4800	2.9418E-04	1.4580E-12	4.3672E-05	GREEN
8.8116	964.E-06	21.7000	42.1500	2.8480E-04	1.4580E-12	4.5112E-05	GREEN
11.0146	1201.E-06	24.2000	5.4700	3.1109E-04	1.4483E-12	5.1281E-05	GREEN
11.0146	1201.E-06	24.2000	10.8600	3.2303E-04	1.4483E-12	4.9385E-05	GREEN
11.0146	1201.E-06	24.2000	43.7500	3.1206E-04	1.4483E-12	5.1122E-05	GREEN

```
              LIGHT SCATTERING PHOTOMETER DATA FOR ESSO GRADE 363 FRACTIONS

              FRACTION #8

 CONCN     DELTA N       GS 90      GS 0       T EXCESS          H           HC/T        COLOUR
 -----     ----- -       -- --      -- -       --------          -           ----        ------

  THF          -         4.7500     4.3850         -             -             -          GREEN
  THF          -         4.7500     8.9400         -             -             -          GREEN
  THF          -         4.7500    35.5000         -             -             -          GREEN

3.7472     424.E-06      9.9800     4.4550    1.0282E-04    1.5597E-12    5.6842E-05      GREEN
3.7472     424.E-06      9.9800     9.0900    1.0361E-04    1.5597E-12    5.6409E-05      GREEN
3.7472     424.E-06      9.9800    36.0000    1.0205E-04    1.5597E-12    5.7272E-05      GREEN

5.6208     624.E-06     12.4000     4.6250    1.4200E-04    1.5014E-12    5.9429E-05      GREEN
5.6208     624.E-06     12.4000     9.4300    1.4330E-04    1.5014E-12    5.8892E-05      GREEN
5.6208     624.E-06     12.4000    37.3500    1.4102E-04    1.5014E-12    5.9843E-05      GREEN

9.3680    1024.E-06     16.0800     4.8200    2.0022E-04    1.4556E-12    6.8105E-05      GREEN
9.3680    1024.E-06     16.0800     9.8300    2.0197E-04    1.4556E-12    6.7513E-05      GREEN
9.3680    1024.E-06     16.0800    38.8500    1.9930E-04    1.4556E-12    6.8418E-05      GREEN
```

B - 7 Molecular Weight Distribution Treatment and Data.

From the weight and number average molecular weight of each fraction, the standard deviation of a normal distribution about the number-average molecular weight for fraction "i" is defined as:

$$\sigma_{ni}^{2} = (\overline{M}_{ni})^{2}\left(\frac{M_{wi}}{M_{ni}} - 1\right) \qquad ....B\text{-}6.1$$

The molar distribution function is given as:

$$\theta_{n} = {}_{ni}/\left[(\sigma_{ni}\sqrt{2\Pi})\right] \text{ exp. } \left[-(M - \overline{M}_{ni})^{2}/2\sigma_{ni}^{2}\right] \qquad ....B\text{-}6.1$$

where "ni" = mole of fraction "i" in total sample.

The number distribution can be re-written as:

$$M_{ni} = \overline{M}_{ni} + Z\sigma_{ni} \qquad ....B\text{-}6.3$$

$$\theta_{A} = ({}_{ni}Y)/\sigma_{ni} \qquad ....B\text{-}6.4$$

$$\phi_{W} = \theta_{n}M \qquad ....B\text{-}6.5$$

where Z and Y are obtained from probability distribution tables and are tabulated below, and "ϕ_W" is the weight distribution function.

Z	-2.5	-2.0	-1.5	-1.0	-0.5	0
Y	0.0175	0.054	0.1295	0.242	0.3521	0.399
Z	0.5	1.0	1.5	2.0	2.5	
Y	0.3521	0.242	0.1295	0.054	0.0175	

The distribution data for the individual fractions are tabulated on the following pages.

```
                    MW MEASURED BY LIGHT-SCATTERING


          FRACTION #1                                      FRACTION #2


       MW=  0.1205000E 06GMS/GM MOLE                    MW=  0.1212400E 06GMS/GM MOLE
       MN=  0.1021600E 06GMS/GM MOLE                    MN=  0.9759000E 05GMS/GM MOLE
       WT=  0.1739850E 01GMS                            WT=  0.1685170E 01GMS
    MW/MN=  0.1179522E 01                            MW/MN=  0.1242340E 01
  STD DEV=  0.4328517E 05                          STD DEV=  0.4804165E 05
# GM MOLES=  0.1703063E-04                       # GM MOLES=  0.1726786E-04
 MOLE FRAC=  0.3913891E-01                        MOLE FRAC=  0.3968408E-01


      THE NUMBER DISTRIBUTION IS                  THE NUMBER DISTRIBUTION IS


          M                THETA N                    M                THETA N


    -0.6052875E 04     0.1582368E-07           -0.2251406E 05     0.1445560E-07
     0.1558969E 05     0.4882736E-07            0.1506750E 04     0.4460589E-07
     0.3723224E 05     0.1170952E-06            0.2552756E 05     0.1069715E-06
     0.5887483E 05     0.2188189E-06            0.4954835E 05     0.1999004E-06
     0.8051738E 05     0.3183724E-06            0.7356913E 05     0.2908469E-06
     0.1021600E 06     0.3607799E-06            0.9759000E 05     0.3295879E-06
     0.1238026E 06     0.3183724E-06            0.1216108E 06     0.2908469E-06
     0.1454451E 06     0.2188189E-06            0.1456316E 06     0.1999004E-06
     0.1670878E 06     0.1170952E-06            0.1696524E 06     0.1069715E-06
     0.1887303E 06     0.4882736E-07            0.1936733E 06     0.4460589E-07
     0.2103729E 06     0.1582368E-07            0.2176941E 06     0.1445560E-07
```

```
                    MW MEASURED BY LIGHT-SCATTERING


           FRACTION #3


      MW=  0.1215000E 06GMS/GM MOLE
      MN=  0.8016000E 05GMS/GM MOLE
      WT=  0.1624790E 01GMS
   MW/MN=  0.1515718E 01
 STD DEV=  0.5756573E 05
# GM MOLES=  0.2026933E-04
MOLE FRAC=  0.4658192E-01


       THE NUMBER DISTRIBUTION IS


          M                  THETA N


   -0.6375431E 05      0.1416091E-07
   -0.3497144E 05      0.4369655E-07
   -0.6188563E 04      0.1047907E-06
    0.2259427E 05      0.1958252E-06
    0.5137714E 05      0.2849177E-06
    0.8016000E 05      0.3228689E-06
    0.1089428E 06      0.2849177E-06
    0.1377257E 06      0.1958252E-06
    0.1665086E 06      0.1047907E-06
    0.1952914E 06      0.4369655E-07
    0.2240743E 06      0.1416091E-07
```

```
           FRACTION #4


      MW=  0.1117300E 06GMS/GM MOLE
      MN=  0.7688000E 05GMS/GM MOLE
      WT=  0.3448850E 01GMS
   MW/MN=  0.1453303E 01
 STD DEV=  0.5176160E 05
# GM MOLES=  0.4486016E-04
MOLE FRAC=  0.1030953E 00


       THE NUMBER DISTRIBUTION IS


          M                  THETA N


   -0.5252400E 05      0.3485532E-07
   -0.2664319E 05      0.1075535E-06
   -0.7623750E 03      0.2579293E-06
    0.2511840E 05      0.4819993E-06
    0.5099920E 05      0.7012891E-06
    0.7688000E 05      0.7947015E-06
    0.1027608E 06      0.7012891E-06
    0.1286416E 06      0.4819993E-06
    0.1545224E 06      0.2579293E-06
    0.1804032E 06      0.1075535E-06
    0.2062840E 06      0.3485532E-07
```

```
                    MW MEASURED BY LIGHT-SCATTERING
```

```
          FRACTION #5


       MW=  0.9725000E 05GMS/GM MOLE
       MN=  0.6345000E 05GMS/GM MOLE
       WT=  0.2802800E 01GMS
    MW/MN=  0.1532702E 01
  STD DEV=  0.4630991E 05
# GM MOLES=  0.4417336E-04
MOLE FRAC=  0.1015169E 00


     THE NUMBER DISTRIBUTION IS


       M                THETA N


 -0.5232475E 05      0.3836210E-07
 -0.2916981E 05      0.1183744E-06
 -0.6014813E 04      0.2838794E-06
  0.1714009E 05      0.5304930E-06
  0.4029505E 05      0.7718456E-06
  0.6345000E 05      0.8746560E-06
  0.8660494E 05      0.7718456E-06
  0.1097599E 06      0.5304930E-06
  0.1329148E 06      0.2838794E-06
  0.1560698E 06      0.1183744E-06
  0.1792248E 06      0.3836210E-07
```

```
          FRACTION #6


       MW=  0.7552000E 05GMS/GM MOLE
       MN=  0.5936000E 05GMS/GM MOLE
       WT=  0.3716850E 01GMS
    MW/MN=  0.1272237E 01
  STD DEV=  0.3097186E 05
# GM MOLES=  0.6261539E-04
MOLE FRAC=  0.1438994E 00


     THE NUMBER DISTRIBUTION IS


       M                THETA N


 -0.1806963E 05      0.8130729E-07
 -0.2583711E 04      0.2508911E-06
  0.1290222E 05      0.6016741E-06
  0.2838814E 05      0.1124364E-05
  0.4387407E 05      0.1635904E-05
  0.5936000E 05      0.1853807E-05
  0.7484588E 05      0.1635904E-05
  0.9033181E 05      0.1124364E-05
  0.1058178E 06      0.6016741E-06
  0.1213037E 06      0.2508911E-06
  0.1367896E 06      0.8130729E-07
```

```
                    MW MEASURED BY LIGHT-SCATTERING

          FRACTION #7

      MW=  0.4095000E 05GMS/GM MOLE
      MN=  0.3855000E 05GMS/GM MOLE
      WT=  0.4590810E 01GMS
   MW/MN=  0.1062256E 01
  STD DEV=  0.9618656E 04
# GM MOLES=  0.1190871E-03
 MOLE FRAC=  0.2736799E 00

   THE NUMBER DISTRIBUTION IS

       M                THETA N

  0.1450336E 05      0.4979275E-06
  0.1931269E 05      0.1536463E-05
  0.2412202E 05      0.3684665E-05
  0.2893134E 05      0.6885626E-05
  0.3374067E 05      0.1001831E-04
  0.3855000E 05      0.1135275E-04
  0.4335933E 05      0.1001831E-04
  0.4816866E 05      0.6885626E-05
  0.5297798E 05      0.3684665E-05
  0.5778731E 05      0.1536463E-05
  0.6259664E 05      0.4979275E-06
```

```
          FRACTION #8

      MW=  0.1910000E 05GMS/GM MOLE
      MN=  0.1894000E 05GMS/GM MOLE
      WT=  0.2080170E 01GMS
   MW/MN=  0.1008448E 01
  STD DEV=  0.1740796E 04
# GM MOLES=  0.1098294E-03
 MOLE FRAC=  0.2524043E 00

   THE NUMBER DISTRIBUTION IS

       M                THETA N

  0.1458801E 05      0.2537387E-05
  0.1545841E 05      0.7829653E-05
  0.1632880E 05      0.1877666E-04
  0.1719920E 05      0.3508845E-04
  0.1806960E 05      0.5105225E-04
  0.1894000E 05      0.5785242E-04
  0.1981039E 05      0.5105225E-04
  0.2068079E 05      0.3508845E-04
  0.2155119E 05      0.1877666E-04
  0.2242159E 05      0.7829653E-05
  0.2329199E 05      0.2537387E-05
```

```
          MW MEASURED BY LIGHT-SCATTERING


        THE CUMULATIVE DISTRIBUTIONS ARE


     THETA N                    M                   PHI W

0.0000000E 00          0.0000000E 00          0.0000000E 00
0.6665698E-07          0.1000000E 05          0.6665697E-03
0.5297127E-04          0.2000000E 05          0.1059425E 01
0.1038453E-04          0.3000000E 05          0.3115359E 00
0.1437798E-04          0.4000000E 05          0.5751191E 00
0.9555963E-05          0.5000000E 05          0.4777981E 00
0.5256318E-05          0.6000000E 05          0.3153790E 00
0.4176331E-05          0.7000000E 05          0.2923432E 00
0.3990130E-05          0.8000000E 05          0.3192103E 00
0.3583321E-05          0.9000000E 05          0.3224989E 00
0.3120472E-05          0.1000000E 06          0.3120471E 00
0.2611460E-05          0.1100000E 06          0.2872605E 00
0.2127031E-05          0.1200000E 06          0.2552437E 00
0.1709508E-05          0.1300000E 06          0.2222360E 00
0.1270617E-05          0.1400000E 06          0.1778864E 00
0.9962569E-06          0.1500000E 06          0.1494386E 00
0.7509946E-06          0.1600000E 06          0.1201591E 00
0.5495957E-06          0.1700000E 06          0.9343117E-01
0.3799224E-06          0.1800000E 06          0.6838602E-01
0.2365585E-06          0.1900000E 06          0.4494612E-01
0.1596781E-06          0.2000000E 06          0.3193563E-01
0.6910858E-07          0.2100000E 06          0.1451280E-01
0.1834179E-07          0.2200000E 06          0.4035193E-02
0.0000000E 00          0.2300000E 06          0.0000000E 00
0.0000000E 00          0.2400000E 06          0.0000000E 00
0.0000000E 00          0.2500000E 06          0.0000000E 00
0.0000000E 00          0.2600000E 06          0.0000000E 00
0.0000000E 00          0.2700000E 06          0.0000000E 00
0.0000000E 00          0.2800000E 06          0.0000000E 00
0.0000000E 00          0.2900000E 06          0.0000000E 00
0.0000000E 00          0.3000000E 06          0.0000000E 00
```

```
MW  MEASURED BY LIGHT-SCATTERING
(EXCEPT  FRACTIONS 1 & 8)
THE CUMULATIVE DISTRIBUTIONS ARE

     THETA N                 M                 PHI W

0.0000000E 00       0.0000000E 00       0.0000000E 00
0.6241166E-05       0.1000000E 05       0.6241166E-01
0.1135325E-04       0.2000000E 05       0.2270650E 00
0.1579382E-04       0.3000000E 05       0.4738149E 00
0.1640650E-04       0.4000000E 05       0.6562601E 00
0.9910305E-05       0.5000000E 05       0.4955152E 00
0.5256318E-05       0.6000000E 05       0.3153790E 00
0.4176331E-05       0.7000000E 05       0.2923432E 00
0.3990130E-05       0.8000000E 05       0.3192103E 00
0.3583321E-05       0.9000000E 05       0.3224989E 00
0.3120472E-05       0.1000000E 06       0.3120471E 00
0.2611460E-05       0.1100000E 06       0.2872605E 00
0.2127031E-05       0.1200000E 06       0.2552437E 00
0.1709508E-05       0.1300000E 06       0.2222360E 00
0.1270617E-05       0.1400000E 06       0.1778864E 00
0.9962569E-06       0.1500000E 06       0.1494386E 00
0.7509946E-06       0.1600000E 06       0.1201591E 00
0.5495957E-06       0.1700000E 06       0.9343117E-01
0.3799224E-06       0.1800000E 06       0.6838602E-01
0.2365585E-06       0.1900000E 06       0.4494612E-01
0.1596781E-06       0.2000000E 06       0.3193563E-01
0.6910858E-07       0.2100000E 06       0.1451280E-01
0.1834179E-07       0.2200000E 06       0.4035193E-02
0.0000000E 00       0.2300000E 06       0.0000000E 00
0.0000000E 00       0.2400000E 06       0.0000000E 00
0.0000000E 00       0.2500000E 06       0.0000000E 00
0.0000000E 00       0.2600000E 06       0.0000000E 00
0.0000000E 00       0.2700000E 06       0.0000000E 00
0.0000000E 00       0.2800000E 06       0.0000000E 00
0.0000000E 00       0.2900000E 06       0.0000000E 00
0.0000000E 00       0.3000000E 06       0.0000000E 00
```

```
                         MW MEASURED BY VISCOMETRY

          FRACTION #1                                   FRACTION #2


       MW=  0.1205000E 06GMS/GM MOLE            MW=  0.1193000E 06GMS/GM MOLE
       MN=  0.1021600E 06GMS/GM MOLE            MN=  0.9759000E 05GMS/GM MOLE
       WT=  0.1739850E 01GMS                    WT=  0.1685170E 01GMS
    MW/MN=  0.1179522E 01                    MW/MN=  0.1222461E 01
  STD DEV=  0.4328517E 05                  STD DEV=  0.4602904E 05
# GM MOLES=  0.1703063E-04               # GM MOLES=  0.1726786E-04
 MOLE FRAC=  0.3913891E-01                MOLE FRAC=  0.3968408E-01


   THE NUMBER DISTRIBUTION IS                 THE NUMBER DISTRIBUTION IS


         M               THETA N                  M               THETA N


 -0.6052875E 04     0.1582368E-07         -0.1748256E 05     0.1508767E-07
  0.1558969E 05     0.4882736E-07          0.5531938E 04     0.4655627E-07
  0.3723224E 05     0.1170952E-06          0.2854644E 05     0.1116488E-06
  0.5887483E 05     0.2188189E-06          0.5156096E 05     0.2086410E-06
  0.8051738E 05     0.3183724E-06          0.7457544E 05     0.3035640E-06
  0.1021600E 06     0.3607799E-06          0.9759000E 05     0.3439990E-06
  0.1238026E 06     0.3183724E-06          0.1206045E 06     0.3035640E-06
  0.1454451E 06     0.2188189E-06          0.1436190E 06     0.2086410E-06
  0.1670878E 06     0.1170952E-06          0.1666336E 06     0.1116488E-06
  0.1887303E 06     0.4882736E-07          0.1896481E 06     0.4655627E-07
  0.2103729E 06     0.1582368E-07          0.2126626E 06     0.1508767E-07
```

```
                         MW MEASURED BY VISCOMETRY


          FRACTION #3


        MW=  0.1146000E 06GMS/GM MOLE
        MN=  0.8016000E 05GMS/GM MOLE
        WT=  0.1624790E 01GMS
     MW/MN=  0.1429640E 01
   STD DEV=  0.5254240E 05
# GM MOLES=  0.2026933E-04
 MOLE FRAC=  0.4658192E-01


      THE NUMBER DISTRIBUTION IS


           M                  THETA N


    -0.5119594E 05      0.1551477E-07
    -0.2492475E 05      0.4787417E-07
     0.1346438E 04      0.1148093E-06
     0.2761760E 05      0.2145471E-06
     0.5388880E 05      0.3121573E-06
     0.8016000E 05      0.3537369E-06
     0.1064312E 06      0.3121573E-06
     0.1327024E 06      0.2145471E-06
     0.1589736E 06      0.1148093E-06
     0.1852448E 06      0.4787417E-07
     0.2115159E 06      0.1551477E-07
```

```
          FRACTION #4


        MW=  0.1003000E 06GMS/GM MOLE
        MN=  0.7688000E 05GMS/GM MOLE
        WT=  0.3448850E 01GMS
     MW/MN=  0.1304630E 01
   STD DEV=  0.4243261E 05
# GM MOLES=  0.4486016E-04
 MOLE FRAC=  0.1030953E 00


      THE NUMBER DISTRIBUTION IS


           M                  THETA N


    -0.2920150E 05      0.4251841E-07
    -0.7985188E 04      0.1311996E-06
     0.1323108E 05      0.3146362E-06
     0.3444739E 05      0.5879689E-06
     0.5566370E 05      0.8554705E-06
     0.7688000E 05      0.9694195E-06
     0.9809625E 05      0.8554705E-06
     0.1193126E 06      0.5879689E-06
     0.1405289E 06      0.3146362E-06
     0.1617452E 06      0.1311996E-06
     0.1829615E 06      0.4251841E-07
```

```
                              MW MEASURED BY VISCOMETRY


             FRACTION #5                                          FRACTION #6



      MW=  0.8561000E 05GMS/GM MOLE                     MW=  0.7387000E 05GMS/GM MOLE
      MN=  0.6345000E 05GMS/GM MOLE                     MN=  0.5936000E 05GMS/GM MOLE
      WT=  0.2802800E 01GMS                             WT=  0.3716850E 01GMS
   MW/MN=  0.1349251E 01                             MW/MN=  0.1244440E 01
 STD DEV=  0.3749732E 05                           STD DEV=  0.2934810E 05
# GM MOLES=  0.4417336E-04                      # GM MOLES=  0.6261539E-04
MOLE FRAC=  0.1015169E 00                        MOLE FRAC=  0.1438994E 00



   THE NUMBER DISTRIBUTION IS                        THE NUMBER DISTRIBUTION IS


        M              THETA N                            M              THETA N



  -0.3029325E 05     0.4737793E-07                 -0.1401025E 05     0.8580582E-07
  -0.1154463E 05     0.1461947E-06                  0.6637969E 03     0.2647723E-06
   0.7204016E 04     0.3505966E-06                  0.1533785E 05     0.6349632E-06
   0.2595268E 05     0.6551690E-06                  0.3001190E 05     0.1186572E-05
   0.4470134E 05     0.9532440E-06                  0.4468595E 05     0.1726414E-05
   0.6345000E 05     0.1080216E-05                  0.5936000E 05     0.1956373E-05
   0.8219863E 05     0.9532440E-06                  0.7403400E 05     0.1726414E-05
   0.1009473E 06     0.6551690E-06                  0.8870806E 05     0.1186572E-05
   0.1196959E 06     0.3505966E-06                  0.1033821E 06     0.6349632E-06
   0.1384446E 06     0.1461947E-06                  0.1180562E 06     0.2647723E-06
   0.1571933E 06     0.4737793E-07                  0.1327303E 06     0.8580582E-07
```

```
MW MEASURED BY VISCOMETRY
```

```
         FRACTION #7


     MW=  0.4427000E 05GMS/GM MOLE
     MN=  0.3855000E 05GMS/GM MOLE
     WT=  0.4590810E 01GMS
  MW/MN=  0.1148378E 01
STD DEV=  0.1484942E 05
# GM MOLES=  0.1190871E-03
MOLE FRAC=  0.2736799E 00


THE NUMBER DISTRIBUTION IS


     M                 THETA N


0.1426445E 04      0.3225306E-06
0.8851156E 04      0.9952373E-06
0.1627587E 05      0.2386728E-05
0.2370058E 05      0.4460137E-05
0.3112529E 05      0.6489319E-05
0.3855000E 05      0.7353701E-05
0.4597471E 05      0.6489319E-05
0.5339942E 05      0.4460137E-05
0.6082413E 05      0.2386728E-05
0.6824881E 05      0.9952373E-06
0.7567350E 05      0.3225306E-06
```

```
         FRACTION #8


     MW=  0.2707000E 05GMS/GM MOLE
     MN=  0.1894000E 05GMS/GM MOLE
     WT=  0.2080170E 01GMS
  MW/MN=  0.1429250E 01
STD DEV=  0.1240895E 05
# GM MOLES=  0.1098294E-03
MOLE FRAC=  0.2524043E 00


THE NUMBER DISTRIBUTION IS


     M                 THETA N


-0.1208236E 05      0.3559588E-06
-0.5877891E 04      0.1098387E-05
 0.3265820E 03      0.2634095E-05
 0.6531055E 04      0.4922403E-05
 0.1273553E 05      0.7161892E-05
 0.1894000E 05      0.8115860E-05
 0.2514447E 05      0.7161892E-05
 0.3134895E 05      0.4922403E-05
 0.3755342E 05      0.2634095E-05
 0.4375789E 05      0.1098387E-05
 0.4996236E 05      0.3559588E-06
```

```
                 MW  MEASURED BY VISCOMETRY


            THE CUMULATIVE DISTRIBUTIONS ARE


   THETA N                   M                     PHI W

0.0000000E 00        0.0000000E 00        0.0000000E 00
0.8488229E-05        0.1000000E 05        0.8488226E-01
0.1348597E-04        0.2000000E 05        0.2697192E 00
0.1446284E-04        0.3000000E 05        0.4338853E 00
0.1285449E-04        0.4000000E 05        0.5141796E 00
0.1000330E-04        0.5000000E 05        0.5001649E 00
0.7288100E-05        0.6000000E 05        0.4372860E 00
0.5486871E-05        0.7000000E 05        0.3840808E 00
0.4410296E-05        0.8000000E 05        0.3528237E 00
0.3871954E-05        0.9000000E 05        0.3484759E 00
0.3282444E-05        0.1000000E 06        0.3282444E 00
0.2648011E-05        0.1100000E 06        0.2912813E 00
0.2059651E-05        0.1200000E 06        0.2471581E 00
0.1586909E-05        0.1300000E 06        0.2062982E 00
0.1113722E-05        0.1400000E 06        0.1559210E 00
0.8460759E-06        0.1500000E 06        0.1269113E 00
0.5484965E-06        0.1600000E 06        0.8775938E-01
0.3934475E-06        0.1700000E 06        0.6688607E-01
0.2663439E-06        0.1800000E 06        0.4794190E-01
0.1349831E-06        0.1900000E 06        0.2564679E-01
0.9374281E-07        0.2000000E 06        0.1874857E-01
0.5250262E-07        0.2100000E 06        0.1102555E-01
0.0000000E 00        0.2200000E 06        0.0000000E 00
0.0000000E 00        0.2300000E 06        0.0000000E 00
0.0000000E 00        0.2400000E 06        0.0000000E 00
0.0000000E 00        0.2500000E 06        0.0000000E 00
0.0000000E 00        0.2600000E 06        0.0000000E 00
0.0000000E 00        0.2700000E 06        0.0000000E 00
0.0000000E 00        0.2800000E 06        0.0000000E 00
0.0000000E 00        0.2900000E 06        0.0000000E 00
0.0000000E 00        0.3000000E 06        0.0000000E 00
```